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Метод комбинационного рассеяния впервые применен для исследования гетерогенного катализа

Методы колебательной спектроскопии являются мощным средством исследования гетерогенного катализа. До недавнего времени каталиматические превращения адсорбированных на катализаторах молекул изучались в основном методами ИК-спектроскопии (методами ИК отражения-поглощения, диффузного отражения и т.д.). Были достигнуты значительные успехи при исследовании ИК-спектров молекул, адсорбированных на материалах с сильно развитой поверхностью ($\alpha_{2}$) и на пленках металлов, нанесенных на такие материалы.

Однако исследование ИК спектров молекул, адсорбированных на металлических (или содержащих металлы) непрозрачных в ИК области катализаторах в условиях реального катализа (высокие температуры, давления, агрессивные среды) вызывает затруднения. Это обусловлено необходимостью изготовления окошек кювет из прозрачных в ИК области материалов (Al, Mg и т.д.), не отличающихся высокой прочностью и химической стойкостью.


Усиление KR поверхностью металлов проявляется в самых разнообразных условиях. Уже в первых работах, начатых в Институте спектроскопии АН СССР, по изучению спектров KR молекул, адсорбированных в вакууме на напыленных металлических пленках, были отмечены химические превращения адсорбированных молекул [2,3]. Так, в спектре этилена, адсорбированного на пленках Ag и Ni при Т~ 80 К, проявлялись линии ~1380 и ~1460 cm$^{-1}$, характерные для этаноподобных структур (фиг.1).

В связи с этим представляло интерес применить метод KR для исследования гетерогенного катализа in situ в реальных условиях, что до сих пор не делалось.

С этой целью была сконструирована обогреваемая кювета высокого дав-
Фиг. 1. Спектр КР этилена, адсорбированного на пленке Ni при Т ~ 60 К.

Линия на нержавеющей стали с кварцевыми окнами, позволяющая регистрировать спектры КР в ходе реакции от поверхности катализатора при давлениях до 10 МПа и температурах до ~700 К в вариантах "закрытого" и "открытого" (с прокачкой реакционной смеси) реактора.

Спектры возбуждались линией λ = 488,0 нм аргон-криптонового лазера мощностью ~ 100 мВт и регистрировались на спектрометре ДФС-24 при спектральной ширине щелей 12 см⁻¹.

Мы применили метод КР для изучения и активации водородом H₂ промышленного плавленного катализатора (промotor — 5 % V₂O₅) и реакции газофазного гидрирования на нем ацетофенола (АЦФ).

Фиг. 2. Спектры КР, полученные in situ от поверхности железного плавленного катализатора, активированного при T=460 К и р = 0,2 МПа: а) протием, б)дейтерием.

На фиг.2а приведен спектр КР, полученный in situ от поверхности катализатора, предварительно восстановленного H₂ при P=5 МПа и T = 700 К, а на фиг.2б — спектр того же участка катализатора через 60 мин. после замены H₂ на D₂. Видно уменьшение интенсивности линий ~ 980 см⁻¹ и появление линий ~650 - 850 см⁻¹. По-видимому, H₂ связывается с катализатором, образуя гидридоподобные структуры.

На фиг.3а приведен спектр КР, полученный in situ от того же участка при гидрировании АЦФ. При гидрировании в спектре появляются линии ~1624,937 и ~ 884 см⁻¹. Спектр существенно отличается от спектров исход-
Фиг. 3. Спектры KP: а) поверхности железного плавленного катализатора при гидрировании АЦФН₂ (T = 450 К, PАЦФ = 10³ Па); б) АЦФ; в) метилкарбилола; г) этилбензола.

Таким образом, впервые полученные спектры KP от поверхности железного плавленного катализатора при активации его Н₂ и гидрировании на нем АЦФ свидетельствуют о новых возможностях, которые открывает метод KP для исследования гетерогенно каталитических реакций. Он позволяет прослеживать за каталитическими превращениями молекул на поверхности катализатора в реальных условиях практического катализа.

Литература

DEPENDENCES OF CORRELATION CORRECTIONS FOR 4f SHELL LEVELS ENERGY ON ITS OCCUPATION NUMBER

G. LŽUKAUSKAS, P. O. BOGDANOVICH
Institute of Physics of the Academy of Sciences of the Lithuanian SSR
232600 Vilnius, USSR

The expressions of the averaged correlation corrections for the energy of tv configurations, while considering several types of virtual configurations \( n_3 \ell_3^{\nu_3+1} n_2 \ell_2^{\nu_2+1} n_1 \ell_1^{\nu_1+2} \), \( n_2 \ell_2^{\nu_2-1} n_1 \ell_1^{\nu_1-2} \), and \( n_3 \ell_3^{\nu_3+1} n_1 \ell_1^{\nu_1-1} n_2 \ell_2^{\nu_2-1} \), are obtained. The effective influence of these configurations for isionic sequence of triply ionized elements of La (4f\(^n\)) group is investigated.

The contemporary methods, such as many-body perturbation theory, multiconfigurational approach etc., which allow one to take into account the correlation corrections, are frequently applied only for fairly light atoms and ions. While applying these modern and powerful methods for the complex spectra calculations, such as heavy ions, rare earth elements, one is confronted not only with technical problems. Nevertheless, general regularities of the correlation correction influence in the spectra of many-electron atoms and ions can be investigated by the simplified methods.

One of such methods, proposed by Rajnak and Wybourne [1], allowed to interpret the semipirical parameters \( \alpha \), \( \beta \), \( \gamma \) etc. They suggested to substitute the energy difference in the expression of the correlation correction in the second order

\[
\Delta \mathcal{E}_{\mathcal{K}L'S} = \sum_{T'} \frac{|\langle \mathcal{K}L'S | H | \mathcal{K}'(T') L'S \rangle|^2}{E(\mathcal{K}L'S) - E(\mathcal{K}'(T') L'S)}
\]

by the energy, averaged by terms L'S. In this case the summation in Eq. (1) over the intermediate moments of the virtual configuration \( \mathcal{K}' \) may be carried out analytically. \( \mathcal{K} \) denotes the configuration under investigation. The best convergence of this method over the number of virtual configurations, which must be taken into account, may be achieved by the use of the solutions of multiconfigurational Hartree-Fock-Jucys (HFJ) equations [2]. However, the solution of these equations is difficult and not valid when the simplified method is used. Therefore, new transformed orbitals have been proposed [3, 4]. These orbitals, obtained from

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the Hartree-Fock functions of the configuration under investigation while using simple transformations

\[ P(n', l' | r) = N^{-1} r^{\Delta l} P(n, l | r), \quad \Delta l = l' - l; \]

\[ P(n', l' | r) = N^{-1} (A - r^2) P(n, l | r), \quad l' = l, \]

(2)

are similar to HFJ orbitals and ensure the convergence of the method. The expressions of the correlation corrections for the \( n_1 l_1^N, n_2 l_2^N \) configuration under investigation are published in [3,4]. The analysis of \( p, d \) and \( f \) electron energy spectra [3-6] enables one to maintain that the method allows to take into account about 90-95\% of correlation effects in comparison with a strong multiconfigurational approach. In the same way the method developed can be applied for the electron transition characteristic calculations [7], particularly for the so called "forbidden" E2 and M1 transitions.

This method allows one to investigate general regularities of correlation effects, to choose the configurations of great importance and then mix them in the strong multiconfigurational approach.

We have tried to investigate for this purpose the averaged correlation corrections of several types of configurations for the energy of configurations under investigation with one open shell \( n_1 l_1^N \). The analytical expressions of such averaged corrections have been obtained by summing up Eq. (1) over quantum numbers \( L_3 \), by using some results of paper [8]. When the virtual configurations of the types \( n_3 l_3^4 l_3^k l_3^{-k} n_2 l_2^{-k} n_1 l_1^N \) or \( n_3 l_3^4 l_3^k l_3^{-k} n_2 l_2^{-k} n_1 l_1^N \) are taken into account the averaged correction has the following form:

\[ \overline{\Delta E}_{K,K'} = - M \left[ \sum_k \left( \frac{2}{2k+1} - \sum \left( \frac{l_1^k k^2 l_3^k}{l_1^k k^3} \right) \right) \right] \times \]

\[ \times P(k, k, l_1 l_2 l_3) - \sum_{k \neq k'} \left( \sum \left( \frac{l_1^k k^2 l_3^k}{l_1^k k^3} \right) \right) P(k, k, l_1 l_2 l_3), \]

(3)

where

\[ M = \begin{cases} N_1 (N_1 - 1) / (2 l_1 + 1)(4 l_4 + 1), \quad K = n_1 l_1^N, n_2 l_2 n_3 l_3; \\
(4 l_1 + 2 - N_1)(4 l_4 + 1 - N_4) / (2 l_1 + 1)(4 l_4 + 1), \quad K' = n_3 l_3^4 l_3^k + n_2 l_2^{-k} n_1 l_1^N. \end{cases} \]

(4)
Fig. 1. Dependence of averaged correlation correction \( \Delta \mathcal{E}_{x,x'} \) for the energy of \( 4f^N \) configuration on the occupation number \( N \) of 4f shell.

Respectively, for the configuration \( n_3 \ell_3 \ell_1^{\ell_1+1} n_4 \ell_4^{N_4} n_2 \ell_2 \) we obtain

\[
\overline{\Delta \mathcal{E}}_{x,x'} = -\frac{N_1 (4 \ell_1 + 2 - N_1)}{(2 \ell_1 + 1)(4 \ell_1 + 1)} \left[ \sum_k \frac{P(k k, \ell_1 \ell_2 \ell_3)}{2 k + 1} + \sum_k \frac{P(k k, \ell_1 \ell_2 \ell_3)}{2 k + 1} - \sum_{k,k'} \left\{ \frac{\ell_2 \ell_3 k}{l_1 l_2 l_3} \right\} Q(k k', \ell_1 \ell_2 \ell_3) \right],
\]

(5)
where the following notation is used:

\[
P(k k', l_1 l_2 l_3) = R_k (n_1 l_1 n_2 l_2, n_1 l_1 n_2 l_2) \left( \ell_1 \parallel C \parallel \ell_2 \right) \left( \ell_1 \parallel C \parallel \ell_3 \right) \times \nabla \Delta E (\kappa, \kappa')
\]

\[
Q(k k', l_1 l_2 l_3) = R_k (n_1 l_1 n_2 l_2, n_1 l_1 n_2 l_2) \left( \ell_1 \parallel C \parallel \ell_2 \right) \left( \ell_1 \parallel C \parallel \ell_3 \right) \times R_{k'} (n_1 l_1 n_2 l_2, n_1 l_1 n_2 l_2) \left( \ell_1 \parallel C \parallel \ell_2 \right) \left( \ell_1 \parallel C \parallel \ell_3 \right) \nabla \Delta E (\kappa, \kappa').
\]

\(R_k\) and \((\ell \parallel C \parallel \ell')\) are generalized Slater integrals and submatrix elements of the spherical function operator, respectively [9]. Figure 1 illustrates the dependence of averaged correlation correction on the number of electrons in the 4f shell for the case of triply ionized isionic sequence of La group. As follows from the Figure 1 the role of different configurations, which have been taken into account, changes strongly when the number of 4f electrons increases. These dependences are parabolic, the terms in squared brackets of Eqs (3) and (5) change in magnitude only about few per cents along the sequence. Of course, when the transformed orbitals (2) are used in the correlation calculations, several types of excited configurations of the same symmetry must be taken into account, nevertheless the character of the dependences does not change. In the isoelectronic study the influence of correlation effects increases when the ionization increases, but more moderately than the spectral widths, and therefore, the relative role of correlation effects decreases.

References


* English translation: Soviet Physics Collection

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STUDY OF THE COLLISIONAL BROADENING OF THE BISMUTH LINE 648 nm HYPERFINE COMPONENTS BY FARADAY ROTATION SPECTROSCOPY

Yu.V. BOGDANOV, S.I. KANORSKII
P.N. Lebedev Physical Institute
Moscow, USSR

The spectral profiles of the Faraday effect for the hyperfine multiplet $^3S_{3/2} - ^3D_{5/2}$ at 648 nm in atomic bismuth have been measured accurately using the tunable dye-laser and computer controlled experimental apparatus. The collisional line broadening and shift rate constants are determined for perturbation by helium, nitrogen, argon and xenon. The more accurate value is obtained for the ratio of the electric quadrupole and the magnetic dipole amplitudes for this transition.

Introduction

The resonance Faraday effect in atomic gases can be used in a number of spectroscopic problems, e.g. for measurements of the atomic transition probabilities, for detection of small amount of atoms and for the study of the spectral line broadening.

In present work we made rather accurate measurements (the error does not exceed 0.3 per cent) of the Faraday rotation profiles for a number of hyperfine components of 648 nm atomic bismuth line (the transition $^3S_{3/2} - ^3D_{5/2}$). These measurements provided the accurate values of collisional linewidth and shift produced by various buffer gases and the more accurate value of the ratio of electric quadrupole $E_2$ and magnetic dipole $M_1$ amplitudes $\chi = E_2/M_1$ for this transition.

The method of measurement and experimental technique

For an isolated line the spectral profile of the Faraday rotation is proportional to the frequency derivative of the refraction index $\partial n/\partial \gamma$ and has two zero-points. The frequency separation between zero-points may be expressed as $\Delta v_0 \approx 1.8483 \Delta v_D + 0.4937 \gamma$, when $\gamma \ll \Delta v_D$ and $\Delta v_0 \approx \gamma$, when $\gamma \gg \Delta v_D$. Here $\gamma$ is the Lorenzian FWHM and $\Delta v_D = (2kT/Mc^2)^{1/2}$ is the Doppler half width at the level $e^{-1}$ of the maximum.

Measuring this separation with high precision (in the present study the error does not exceed 5 MHz when $\Delta v_0 \approx 800 \pm 1500$ MHz), and using then the plots like Stern – Vollmer plot one can deduce a small enough impact width and shift against rather large Doppler broadening. When a spectral line has a hyperfine structure the spectral profile of the Faraday effect has more complicated shape, nevertheless the position of zero-points are very sensitive to the collisional (Lorenzian) linewidth.

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The Faraday rotation profiles were measured using the same polarimeter that was previously used for the PNC experiment [1]. It was supplemented with a new computer-based system for laser frequency control, data acquisition, storage and processing. (Fig. 1)

![Block diagram of the apparatus](image)

Fig. 1. Block diagram of the apparatus: PhD-photodiodes; IQ - interrupt register; 1,2 - high voltage amplifiers for piezo-translator of the "thick" etalon and laser resonator; 3 - locking system for the "thick" etalon; 4 - confocal scanning interferometer with FSR=625 MHz; 5 - locking of laser frequency to the interferometer 4; 6 - stabilized confocal interferometer with FSR=74.354 MHz; 7 - monitoring of the interferometer 6 transmission peaks; 8 - computer terminal; 9 - external floppy-disk memory; 10 - color TV display; 11 - single-mode optical fiber; 12 - high voltage amplifier for tuning the etalon 4.

Laser frequency is stabilised by its locking to the transmission peak of the external confocal interferometer with FSR=625 MHz and finesse F=20, that has typical frequency drift about 1±2 MHz/min. The whole apparatus operates under the control of a micro-computer "Electronica NM 11100,1". The frequency marks are provided by the temperature and Pressure Stabilised confocal 1.007 m interferometer. These marks divided the whole spectral range into a number of spectral channels each 74,354 MHz wide. The Faraday rotation signal averaged over 74,354 MHz for every channel was measured. A series of tests showed that this technique enables to measure the Faraday rotation with precision $1\pm2\cdot10^{-7}$ radian and spectral

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resolution better than 5MHz when the total measurement time equals to 10 seconds for each channel.

The bismuth vapor partial pressure was sustained at sufficiently low level so that selfbroadening did not exceed the experimental error. The magnitude of the magnetic field strength was varied in the range 3+10 Gs to provide linearity and sufficiently high signal-to-noise ratio (200+500). The Faraday rotation profiles were measured at several values of the buffer gas pressure. Pressure intervals were chosen in such a way that the high frequency zero-point of the Faraday profile did not move more than one half of the channel width, i.e. < 3 MHz. That enabled subsequent determination of the line shift.

Experimental results

The spectrum of the transition is split in 6 groups of lines that correspond to different values of the total angular momentum of the excited state \( F = 2, 3, 4, 5, 6, 7 \) (the nuclear spin \( I = \frac{9}{2} \)). Faraday profiles for group 7 were measured with helium, argon, xenon and nitrogen buffer gases and for groups 6 and 5 with helium. Fig. 2 shows the measured profile, for the group 6.

![Experimental data points and the computed curve for the group with \( F=7 \) at 1112.2 Pa of xenon. The size of experimental points is equal approximately to two standard deviations. The solid line is computed curve with \( \chi = 0.637, \omega_B = 456 \text{ MHz}, \chi = 0.37 \text{ MHz}. \) Small difference between theoretical curve and experimental points may be attributed to small molecular rotation in bismuth vapor.](image)

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The following values of the broadening and shift rate constants ($\gamma/p$ and $\Delta/p$) were determined using experimental spectral positions of the Faraday profiles zero-points: $\gamma/p = 2.07 \times 10^{-2}$ MHz/Pa, $\Delta/p = -1.72 \times 10^{-3}$ MHz/Pa (for He); $1.75 \times 10^{-2}$, $-3.88 \times 10^{-3}$ (for N$_2$); $1.40 \times 10^{-2}$, $-4.33 \times 10^{-3}$ (for Ar) and $1.33 \times 10^{-2}$, $-4.63 \times 10^{-3}$ (for Xe); Temperature was about 1100K.

In all cases experimental error was $4 \times 10^{-4}$ MHz/Pa.

The value $-0.637 \pm 0.010$ was obtained for the ratio $\chi$.

References
A HIGH TEMPERATURE MICROPINCH PLASMA AS A SPECTRAL SOURCE OF MULTIPLY CHARGED IONS IN THE REGION \( \lambda < 0.1 \) \( \text{nm} \)

E.Ya.GOL'TS, L.A.DOROKHIN, K.N.KOSHELEV, A.A.KRAMIDA, A.A.PALICK and Yu.V.SIDNEIKOV

Institute for Spectroscopy, USSR Acad.Sci., 142092 Troitsk, Moscow region, USSR

The experiments on the "MP-100" device (linear Z-pinch with a gas-puff at currents \( \sim 1 \) MA) show the possibility of realisation of the micropinching process in the 1 MA linear Z-pinch plasma column aiming at registration of spectra of multiply charged ions. Spectra of He-like ions Kr XXXV and Xe LXIII were recorded.

Introduction

A "radiative collapse" model interprets micropinch (MP) as the result of the development of an \( m=0 \) instability subject to severe radiative energy losses and plasma escape from the plasma necking [1,2]. This model predicts that for pinch currents \( I \sim 1 \) MA the micropinching process may lead to creation of a plasma with temperature \( T \sim 10 \) keV sufficient for generation of spectra of H- and He-like ions of heavy elements \((Z_n \sim 50)\).

In the recent paper [3] we reported that MP plasmas in krypton were observed in the "MP-100" device \((E_{\text{max}} = 100 \) kJ). Herein we report also about our attempts to register spectra of K-ions (H- and He-like) of heavier gas xenon \((Z_n = 54)\).

Experiments

The "MP-100" device (Institute for Spectroscopy, USSR Acad.Sci.) is a linear Z-pinch with the following parameters: \( C = 96 \) \( \mu \)F, \( U = 15-50 \) kV, \( T/4 = 2.8 \) \( \mu \)s, \( I = 0.8-2.5 \) MA. The gas was injected into the discharge gap 1.4 cm between plane electrodes by a fast opening valve and "stored" for 100 s. The necessary linear density of the gas at the moment of initiating the discharge \((10^{19} - 10^{21} \) \( \text{cm}^{-1} \)) was provided by varying the gas pressure in the plenum \((0.1-20), 10^5 \) Pa). The control of the plasma radial compression time was accomplished by varying the time delay between the beginning of the gas injection and applying voltage to the electrodes. Radial compression time was indicated by a position of discontinuity on the trace of the current waveform registered by the Rogowski loop. The formation of MP plasma regions in the plasma column was detected with an X-ray "square pinhole camera", which is a square aperture with polished edges directed parallel and perpendicular to the discharge chamber axis. From the penumbras of the edges of the aperture image projected onto a screen (photofilm) by a point radiative source, one can estimate two dimensions of this source. Images from MPs in krypton plasma for \( I = 1 \) MA had penumbras of both.


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edges & 5 m corresponding to the Fresnel diffraction limit for used geometry (distance source-aperture 25 cm, distance aperture-photofilm 25 cm). MP plasmas in krypton produced radiation with effective energy ~10 keV as estimated using X-ray filters.

MP radiation spectra were studied using a Cauchois quartz crystal spectrograph (2d = 0.236 and 0.274 nm) with resolution Δλ/λ = 5.10^{-4}. In order to obtain spectra in a single discharge an electrooptical intensifier with a ZnS converting screen was used. The MP plasma formations were observed simultaneously with the registration of the resonance transitions in the He-like ion Kr XXXV and their satellites in the region 0.08-0.1 nm. (Fig. 1a).

Fig.1.a. Spectrum of krypton obtained from one discharge on the "MP-100" device. Cauchois quartz crystal spectrograph, 2d = 0.236 nm. b. Spectrum of xenon obtained from one discharge on the "MP-100" device. Cauchois quartz crystal spectrograph, 2d = 0.236 nm. The dropdown in the region 0.039-0.04 nm is due to mark placed onto an entrance screen of electrooptical image intensifier. The features between the mark and the krypton Kα -line are not identified.

In the experiments with injection of xenon into the discharge gap (U = 25 kV, I = 1.3 mA) the "square pinhole" images differed from those with krypton. As in the case of krypton, on the spectrograms corresponding to the images with dimensions 50-100 μm there was no hint of spectral lines of He-like ions Xe LXIII. Nevertheless, the spectral features coinciding with calculated position of the resonant line of Xe LXIII were recorded on some spectrograms (see Fig. 1b), but no sharp images were observed in the 2 square pinhole camera in these cases. We believe that this fact is due to the steep decrease of the sensitivity of used photofilm IF-3 from λ = 0.092 nm to λ = 0.04 nm. Because of that, MP images produced presumably by the radiation with λ = 0.04 nm were not recorded on the photofilm. The formations with dimensions 50-100 μm seem to correspond to the preliminary stage of compression. They emit mainly in the region λ ~ 0.3 nm as estimated using X-ray filters.

References

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INFRARED STUDY OF HYDROGEN CHEMISORBED ON W\(\text{100}\) BY SURFACE ELECTROMAGNETIC WAVE SPECTROSCOPY

G.N. ZHIZHIN, M.A. MOSKALOVA, P.A. SHAFRANOVSKII and B.R. SHUB
Institute of Spectroscopy, Academy of Science USSR
142092 Troitzk, Moscow Region, USSR

The inhibition of the structure \(c(2x2)\)H or \(c(2x2)\)D reconstruction in the case of H or D chemisorption on the surface W\(\text{100}\) is observed by surface electromagnetic wave spectroscopy. The strong band at 960 cm\(^{-1}\) is referred to overtone of wagging mode.

Infrared absorption spectra of adsorbates on metal surfaces are usually recorded by means of pellet technique [1]. The pellets are prepared by pressing the highly-dispersive silica powder on which the metal is chemically reduced (so-called spectroscopy of a well developed surface). The success in the development of infrared spectroscopic methods made now available the spectroscopy of weakly-developed surfaces. The new methods are: reflection-absorption spectroscopy with Fourier-transform spectrometers [2] and spectroscopy of surface electromagnetic waves (SEW) [3,4]. In this work we are using the laser SEW spectroscopy for investigation of the reconstruction of a clean W\(\text{100}\) surface and the influence of chemisorbed hydrogen and deuterium on its reconstruction.

The clean (100) face of a single W crystal with body-centered cubic lattice has a \(p(1x1)\) surface structure (\(a=0.316\) nm). It exists at \(T=350\)K, while the temperature is decreasing the reconstruction of the surface layer occurs, consisting in the shifting of surface metal atoms in 11 direction. At \(T=280\)K the \(c(2x2)R45^\circ\) structure exists on the W\(\text{100}\) surface [5].

In the case of dissociative hydrogen chemisorption on the W\(\text{100}\) face at low coverages the reconstruction of the surface layer also takes place. In this case metal atoms are shifted in the 10 direction forming the \(c2(2x2)R45^\circ\) structure [6]. An atom of hydrogen occupies a bridge site. When the W\(\text{100}\) surface is saturated with H, to each atom of W correspond two H atoms. With respect to symmetry only symmetric stretch vibration of W-H-W [7] and the first overtone of the wagging mode [8] can be active in the SEW absorption spectra.

For studying the surface reconstruction of W\(\text{100}\) by means of SEW spectroscopy technique which does not limit a pressure the vacuum chamber with working pressure \(2.7\times10^{-4}\) Pa was made. It was placed into a laser SEW spectrometer as an optical unit (Fig.1). In this chamber (10) a single crystal W was fit on a copper holder. Over the crystal W surface two blades were hanging separated one from the other by \(R=5\) mm. Thus the aperture couplers of the SEW was realized which previously well recommended themsel-
ves for the broadband SEW spectroscopy [9]. The entrance gap height was 50 μm and the output blade was located just above the edge of the crystal, the gap height being 120 μm. These conditions of the SEW coupling provided the lowest diffraction obstacles. The sample cleaning procedure consisted of 20 hours heating at 660 K with and periodic backing in 1.3PaXh.

![Diagram](image.png)

**Fig.1.** Laser SEW spectrometer. 1: CO₂ tunable laser; 2: diffraction lattice; 3: angle reflector; 4,5,6: additional mirrors; 7: abrupter; 8: light divider; 9: spheric mirror; 10: vacuum chamber; 11: adjusting screws; 12: KBr windows; D: detectors of IR radiation

To record the SEW absorption spectra for each CO₂-tunable laser generation line it is necessary to rate the main signal Iₚ (D₁, Fig.1) on the reference signal Iᵣ (D₂, Fig.1) because the lines have various intensities.

To obtain the SEW absorption spectra of the chemisorbed H and the SEW absorption spectra on clean W(100) at different temperatures (the background spectra) were measured first and then it was subtracted from the spectrum on the W+H and W+D surfaces obtained at the same temperatures. The SEW absorption spectra thus obtained of chemisorbed H on W(100) surface at three temperatures are shown in Fig.2. At 390K one can see the absorption band at 1045 cm⁻¹. With temperatures decreasing the peak intensity decreases and a new band at 960 cm⁻¹ appears. It is impossible to find the exact maximum of this band as there are no laser generation lines in this spectral region. At room temperature one can see only the absorption band at 960 cm⁻¹.

The chemisorbed D on W(100) in this spectral range has no absorption bands but the band 960 cm⁻¹ was really observed at room temperature which did not disappear at temperature rise up to 370-390 K only its intensity was decreasing. This band was shown to be attributed to residual hydrogen in deuterium (evidenced to be present in 10% in hydrogen).

The temperature dependence of the SEW absorption intensity at non-resonant frequencies (942 and 1072 cm⁻¹) was also studied. The curve N1 in the Fig.3 shows these measurements for a clean W surface. The shape of the curve is independent of temperature variation. Curve N2 (Fig.3) refers to

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Fig. 2. The SEW absorption spectra of hydrogen chemisorbed on W(100) at several temperatures.

The results of crystal heating in the presence of chemisorbed H and the curve N3 - to chemisorbed D. If H or D chemisorption occurred in a temperature interval 360 - 440 K and the sample was cooled down after the temperature dependence of SEW absorption in the non-resonant range coincides with the curve N1 for clean W surface.

Fig. 3. The dependence of SEW intensity on temperature: 1 - a clean surface of W(100) and some cases of cooling, when H or D on the surface are chemisorbed; 2 - heating W(100) with chemisorbed H and 3 - the same with D.

The results shown in Fig. 3 indicate that the SEW absorption is very sensitive to the reconstruction of W surface. The clean surface reconstruction is reversible and occurs in the temperature interval 270 - 370 K.
presence of H or D on the surface with p(1x1) structure doesn't prevent the reconstruction into c(2x2)H structure, i.e. it occurs just as in the case of a clean surface, if H or D are chemisorbed on W(100) with c(2x2)H structure, then with the increase of the temperature this structure is fixed and the p(1x1) structure appears simultaneously with desorption of H (460 K) or D (500 K).

The analogous inhibition of the reconstruction is observed at all frequencies. Fig. 1 shows H-spectra during the cooling. If the crystal with H is heated above 300 K the absorption band at 1045 cm⁻¹ is not observed. It justifies the fact that the CEW absorption band at 1045 cm⁻¹ is due to the p(1x1)H structure and the band at 960 cm⁻¹ to the c(2x2)H structure.

It is known that the band at 1045 cm⁻¹ is related with symmetric stretch W-H-W vibration [4], while the absorption band at 960 cm⁻¹ of the c(2x2)H structure is observed for the first time. We refer it to the first overtone of the wagging HW₂ vibration (480 cm⁻¹ 10) according to infrared selective rules. In the case of low coverage the asymmetric stretch vibration (967 cm⁻¹ 6) can exist. Its dipole transition is parallel to the metal surface and such vibrations are forbidden in IR spectra. The overtone of the wagging vibration of the p(1x1)H structure was observed by reflection-absorption spectroscopy [2]. The absorption band of the overtone has a big intensity on both structures of W(100) surface. Probably it is due to the resonance with the surface metal levels, these levels do not shift during reconstruction [11].

The fact that the SEW propagation length increases about 20 - 25% during the reconstruction of the W surface atoms seems to be rather strange and cannot be explained by existing theories.

References
MODERN ASPECTS OF MEASUREMENT TECHNIQUE FOR EXCITED STATE SPECTROSCOPY

W. BECKER, E. KLOSE, D. LEUPOLO, H. STIEL
Central Institute of Optics and Spectroscopy, Acad. of Sci. of the GDR
1199 Berlin, GDR

The paper deals with some special kinds of measurement technique useful for the determination of molecular parameters in higher excited energy states. This technique was developed for special purposes of spectroscopy but is very convenient to solve many other problems connected with ultra-fast phenomena in physics and technology.

The selective population of higher excited electron states is of common interest in photochemistry, photophysics as well as photobiology. This definite population makes applicable the great variety of new reaction courses of molecules to new material properties and chemical process courses. A very impressive work in this connection was published by V. S. Letokhov and coworkers: In different excited states (\(T_1\), \(T_2\), \(S_n\)) the same molecule of maleic acid undergoes different reaction courses to different products (isomerization, dimerization, reaction with water, forming a saturated oxyacid).

To use excited levels some problems must be solved: To define the level the molecule was excited to; to define the condition for the effective population of a given energy level; to determine the parameters for the energy transfer within the molecule. To analyse this situation one needs: i) an extensive knowledge of the energy level diagram for the given molecule including all excitation and desactivation channels. ii) the mathematical treatment of the light-matter-interaction under the given condition.

To solve this problem we improved existing ideas creating a new method to overcome the difficulty connected with the manifold of involved levels at the light absorption in the case of organic molecules. Furthermore, we installed a numeric program to combine the theoretical results with measured data. Finally, we developed new experimental apparatus to get the needed information about systems under investigation with high accuracy and high time resolution.

A physicomathematical program package was developed based on the measurement of nonlinear absorption or nonlinear emission of light. This program is the basis for a quantitative spectroscopy of excited states of organic molecules, especially of molecules with \(\pi\)-electron systems. This package contains: i) The creation of a start model for the molecular term scheme, which comes close to the real level scheme. This first part includes also the measured data. ii) The second part turns the implicit
information about the molecule parameters into explicit data, e. g. the minimum number and the structure of the level scheme being involved as well as limits for the unknown parameters of the energy transfer like cross section, relaxation time and population density. This part is like a set of information based on an analytical treatment of the rate equations for phonons and population density of the molecular levels \([\Sigma]\). iii) This knowledge is the basis for the numeric calculation with a definite number of levels and a limited range of parameter values.

This code (PISA) calculates the expected measurement data and compares them with the experimental data. A procedure for minimization fits the curves. With the optimized parameters the population density of all levels involved will be calculated as a function of incoming intensity and time \([5]\).

Measurement of the nonlinear absorption behaviour of organic molecules is carried out with the set-up TRANS-1. This equipment is a microcomputer based nonlinear absorption spectrometer for quantitative spectroscopy of excited molecular states \([6]\). It's main characteristics are given in Table I.

**Table I**

Trans-1: Microcomputer based nonlinear absorption spectrometer

<table>
<thead>
<tr>
<th>Determination of the nonlinear absorption behaviour of liquid samples, solid samples, dye solution, biological objects, semiconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical parameters</td>
</tr>
<tr>
<td>Excitation: 337 nm; (400 ... 800) nm; (\Delta \lambda \leq 0.1) nm</td>
</tr>
<tr>
<td>Photon flux: ((10^{21} \ldots 10^{27})) photons cm(^{-2}) s(^{-1})</td>
</tr>
<tr>
<td>Pulse duration: 0.6 ns; 2.5 ns</td>
</tr>
<tr>
<td>Dynamic range: 6 orders of magnitude</td>
</tr>
<tr>
<td>Mode of operation: 2 channel energy measurement</td>
</tr>
<tr>
<td>Accuracy of transmission measurement: better than 1 %</td>
</tr>
</tbody>
</table>

At the beginning of our work the system for signal processing was the boxcar integrator BCI-280, product of CSI, Ac. Sc. GDR. How we developed the new system MFA-105, a microprocessor controlled signal analyzer. The main characteristics are given in Table II.

This apparatus was used to determine the relaxation rate constant \(k_{31}\) from the \(S_3\)-state to the \(S_1\)-state of chlorophyll-a in dioxane \([7]\ Leupold, Thesis\).

Because of the complicated level structure of chlorophyll-a with the manifold of transitions at a given wavelength, the procedure is rather complex. Firstly, the nonlinear absorption measurement of chl-a in dioxane led to the result that there is a two-step absorption at 670 nm to a \(S_x\)-state followed by a nonradiative relaxation \(S_x - S_1\) with a rate of \(7.7 \times 10^{10} \text{s}^{-1}\).
Table II
Boxcar-System MFA-105 - A microprocessor controlled signal analyzer
(x)

Main Characteristics
- Recording of signals by sampling technique (improvement of SNR; 150 ps
time resolution; 4 signal channels; 2 decay units)
- Computer controlled, programmable (internal Z-80 microcomputer, incorpora-
ted graphic display, manual, interface to printer and plotter)
- Extensive software for signal analysis

(x) A joint project of CIOS and CSI of Ac. of Sci. of GDR

Now the question arises what the $S_x$-state is and whether the two-step ab-
sorption comes via the $S_{10}$-state or is interrupted by a $S_{1v}$ to $S_{10}$ relaxa-
tion. By variation of the solvent and the pulse duration of the exciting
light it becomes clear that there is no $S_{1v}$ to $S_{10}$ relaxation at 670 nm.

In the next step the method of the nonlinear double resonance was used.
Two wavelengths (670 nm and 435 nm) are interacting with the sample and the
results we get from the 670 nm interaction are used. With help of the non-
linear program package all unknown parameters are determined and we get for
the transition $S_3-S_1$ the rate constant $k_{31} = 1.6 \times 10^9 \text{ s}^{-1}$, and $T_{31} = 600 \text{ ps}$.
This is a rather unexpected value, hence up to now one believes that the re-
relaxation time of higher excited electron states is shorter than 100 ps, most-
lly in the order of 1 ps. Therefore photochemistry from higher excited states
was believed to be highly ineffective.

The presented method gives us more insight in the processes connected with
higher excited energy states in complex molecules. Further work in this
field is going on.

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RAMAN SPECTRA OF SILICATES

W. PILZ
Central Institute of Physical Chemistry, Academy of Sciences of the GDR
1199 Berlin, GDR

Raman spectroscopic investigations of silicates show a number of
different spectra in dependence of the condensation of SiO₄ tetrahedrons.
Adsorbed substances are easily detectable because of the weak Raman spec-
tra of silicates. A few optical arrangements are presented which were
applied successfully.

Assignments and intensities

Silicates and aluminosilicates consist of SiO₄ and AlO₄ tetrahedrons
(in general TO₄) which are more or less connected by their O-edges. Ortho
silicates contain isolated SiO₄ units with symmetry T₄. For this structure
four different vibrational modes exist which are all Raman active with
the symmetries A₂, E, and 2 F₂. The spectrum I in Fig.1 shows an example
with the symmetric and antisymmetric bending (δ₄ and δ₅) and stretching
(V₄ and V₅) vibrations.

In disilicates (e.g. rankinite, spectrum II) an additional band ap-
ppears at 670 cm⁻¹. It is assigned to the SiO₃ bridge vibration. The
stretching modes have a higher frequency compared with those of ortho si-
licates. This trend is continued by passing to ring and chain silicates
(α- and β-wollastonite, spectra III and IV).

By double chains (see spectrum V, xenotlite) one can distinguish be-
tween the two types of oxygen bridges in this rope-ladder like structure
due to the two strong bands in the SiO₃ region 600...700 cm⁻¹.

In the spectra of sheet and framework aluminosilicates muscovite and
nafrolite (spectra VI and VII) the Raman intensity of the stretching mo-
des near 1000 cm⁻¹ decreases rapidly. For these structures the most inten-
sive bands belong to the bending vibrations. Our investigations of nearly
50 similar minerals (mica, quartz, harmotome, felspar...) secure this fact
as a general law. The reason for that behaviour may be a hindered symme-
tric stretching Raman active vibration because of the rigidly connected
TO₄ tetrahedrons. On the other hand, the less condensed chain silicates
are sufficient movable for a symmetric stretching TO vibration (balance
motion of the chain links). Furthermore it seems to be a general fact that
for growing condensation the frequencies of the vibrations arise and for
the same structure depend on the Si/Al ratio. If a prepared single crys-
tal is present, one can get 6 independent Raman spectra by careful orien-
tation of the laser beam to the crystal axis. In this way the measured Raman bands can be assigned to the possible vibrations of the crystal lattice with good security.

Fig. 1. Typical Raman spectra of silicates
I : Orthosilicate (garnet)
II : Disilicate (rankinite)
III : Ring (α-wollastonite)
IV : Chain (β-wollastonite)
V : Double chain (xonotlite)
VI : Sheet (muscovite)
VII : Framework (natrolite)
Practical experiences

Our applications of silicates are related to adsorption and catalysis. Fig 2 shows a simple heating cell up to 700 K for an in-situ observation of sorption processes. The temperature is regulated by voltage variation. Another in-situ Raman cell for investigations of zeolite crystallization is shown in Fig. 3. During the synthesis both the liquid and the crystalline phases could be observed.

By the investigation of powders it is necessary to reduce the strong stray light of the exciting laser line after the scattering process. Commonly filters or triple monochromators are used. Unfortunately the filter absorption curves are not steep enough and on the other hand the users of a double monochromator cannot extend their instrument to a triple one without great expense. Fig. 4 shows a simple plane grating premonochromator which we apply in the region below 500 cm⁻¹. After a spectral dispersion the light point of the laser line is blocked by the slit aperture.

Advantages of the Raman spectroscopy in comparison with infrared investigations are:

- complete spectrum without break (10...5000 cm⁻¹)
- use of micro samples (less than 0.1 mg)
- no sample preparation and destruction
- good lateral resolution (better than 50 μm).

Fig. 2. Heating Raman cell

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Fig. 3. In-situ cell for zeolite synthesis

Fig. 4. Premonochromator

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ИНФРАКРАСНАЯ СПЕКТРОСКОПИЯ ЦЕОЛИТОВ

КР. ПОЙКЕР
Центральный институт физической химии Академии наук ГДР
II99 Берлин, ГДР

На примере цеолитов показываются возможности применения ИК-спектроскопии для изучения синтеза, изменений структуры при термической обработке, адсорбционных центров и адсорбированных молекул. При этом обращается внимание на применение помимо метода пропускания, метода диффузного отражения и на включение длинноволновой области спектра.

Введение

Инфракрасная спектроскопия играет важную роль при исследовании таких неорганических соединений как катализаторы, алюмосиликаты, стекла. При этом в основном используют метод пропускания. Применение Фурье-спектрометров позволяет не только расширить спектральную область до ниже 200 см⁻¹, но и даёт возможность использовать эмиссионную и технику диффузного отражения.

В случае цеолитов измерения длинноволновых спектров позволяют в первую очередь сделать заключения о взаимодействии катионов с адсорбированными молекулами.

По сравнению с методом пропускания применение метода диффузного отражения обладает рядом преимуществ. Спектры катализаторов в области валентных колебаний ОН и адсорбированных молекул могут быть измерены без предварительной обработки образцов. Тем самым катализаторы могут быть изучены в таком виде, в котором их применяют в промышленности.

Синтез

Цеолиты типа ZSM-5 обладают катализитическим свойством превращения метанола в ароматы.

За образованием кристаллов ZSM-5 можно следить по интенсивности ИК-полосы около 550 см⁻¹ (рис.1). В большинстве случаев синтез проводится при помощи органических катионов. При этом методы ИК-спектроскопии и спектроскопии комбинационного рассеяния дополняют друг друга [1]. В то время как в ИК-спектре появляется главным образом спектр цеолита, в спектре комбинационного рассеяния наблюдаются из-за малоинтенсивного спектра цеолита почти исключительно полосы спектра органического катиона. Только полоса при 385 см⁻¹ в спектре комбинационного рассеяния (рис.1) относится к ZSM-5.

Температурная обработка

Цеолиты являются метастабильными алюмосиликатами, вследствие чего
они подлежат фазовым превращениям при термической обработке. ИК-спектры цеолита типа А, как в средней спектральной области, так и в длинноволновой, позволяют следить за фазовым превращением в нефелин [2].

**Адсорбционные центры**

В случае цеолитов с высоким соотношением Si/Al, например цеолиты типа Y — катализаторы крекинга — и ZSM-5 катализатически активными центрами являются в первую очередь OH-группы. Их количество и кислотность можно определить по интенсивности и волновому числу полос валентных колебаний OH-групп. Уменьшение количества OH-групп в зависимости от температурной обработки коррелирует с катализатическими свойствами соответствующих катализаторов [3].

В случае катионсодержащих цеолитов, например цеолиты типа A и X, ад-
сorptionными центрами являются в первую очередь катионы. С катионами связаны ИК полосы в длинноволновой области [4]. Тем самым длинноволновые спектры позволяют изучать взаимодействие адсорбированных молекул с катионами (рис. 2).

Для измерения спектров пропускания в средней и в длинноволновой ИК-области используется стеклянная вакуумная кювета с припаянными кремниевыми окошками [5]. Низкотемпературная и высокотемпературная установки позволяют измерения при температурах от 80 до 670 К.

Кроме ИК-метода пропускания для изучения цеолитов в области валентных колебаний ОН и адсорбированных молекул может быть использован метод диффузного отражения. Для измерения спектров диффузного отражения применяется аппаратура, при которой излучение источника фокусируется на образце находящемся в одном фокусе эллиптического зеркала. Во втором фокусе находящемс сорбционными центрами являются в первую очередь катионы. С катионами связаны ИК полосы в длинноволновой области [4]. Тем самым длинноволновые спектры позволяют изучать взаимодействие адсорбированных молекул с катионами (рис. 2).

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дятся приёмник, при помощи которого измеряется диффузное отражение [6].

**Адсорбированные молекулы**

Сравнение ИК-спектроскопических данных адсорбции NH₃ и H₂O в Na-ZSM-5 и в H-ZSM-5 позволяет сделать выводы о состоянии адсорбированных молекул и характеризовать кислотность разных ОН-групп. Для этого применялся метод пропускания и метод диффузного отражения (рис. 3), причём результаты этих двух методов в области валентных колебаний ОН-групп и адсорбированных молекул совпадают [7].

Рис. 3. Спектры диффузного отражения H-ZSM-5:
1 - исходная форма; 2 - 5 часов при 670 К; 3 - после адсорбции NH₃; 4 - после одной недели; 5 - как 3, 1 час при 470 К; 6 - как 3, 1 час при 670 К

**Литература**


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INVESTIGATION OF MOLECULES BY THE METHODS OF RESONANCE COHERENT LIGHT SCATTERING

P.A. APANASEVICH
Institute of Physics, BSSR Academy of Sciences, Minsk, 220602, USSR

The main peculiarities of resonance coherent Raman scattering (RCRS) are considered and some results of application of RCRS methods to investigation of Ni-, Zn- and Cu-octaethylporphyrins (OEP) in tetrahydrofuran, toluol and piridine are presented and discussed. In particular, it is shown that at intermediate intensities of resonant excited light, the Ni-OEP and Cu-OEP-in-tetrahydrofuran spectra consist of lines observed at low intensities (main lines belonged to molecules in ground electronic state) and of additional lines caused by RCRS on molecules in triplet state or on complex of Cu-OEP with solvent molecules.

In the recent years, the methods of coherent Raman scattering (CRS) have been widely used to investigate the structure of molecules, intra- and inter-molecule interactions, different processes in substances [1]. The application of resonance CRS for studying molecules seems especially attractive, because it permits investigation of molecular vibrations in the ground and excited electronic states, redistribution of molecules over the levels in the field of high-power laser radiation, channels and times of relaxation of excited states [2-4].

In the present work some peculiarities are considered of the methods of resonance coherent Raman scattering (RCRS) and the results are presented of investigating by these methods molecules of Ni-, Cu-, Zn-octaethylporphyrins (OEP) in tetrahydrofuran (THF), toluol, and piridine.

The CRS methods rely on frequency \( \omega_3 \) light scattering by molecular vibrations of frequency \( \Omega_2 \) excited by two light waves with the frequency difference \( \omega_1 - \omega_2 \) close to \( \Omega_2 \). The scattering intensity is determined by the nonlinear cubic susceptibility \( \chi^{(3)} = \chi^{NR} + \chi^R \) at frequency \( \omega = \omega_3 + \omega_1 - \omega_2 \) and the product of intensities of the light beams used. In the degenerate case the role of the wave \( \omega_3 \) is played by the wave \( \omega_1 \). Modelling a molecule by a four-level system (see Fig. 1) and assuming that all the molecules are at the lower level, the dependence of the resonance susceptibility \( \chi^R \) on the frequencies \( \omega_A \) may be described by the expression

\[
\chi^R(\omega_A) \sim \sum_{\xi, k} \frac{P^A_{\xi \xi} P^3_{\xi} P^2_{\eta k} P^1_{\eta N_A}}{(\omega_3 - \omega_1 + \omega_2)(\omega_3 - \omega_1 + \omega_2)} +
\]
in the case of anti-Stokes scattering (RCARS, $\omega_1 > \omega_2$, $\omega_A = \omega$) and

$$\chi^R(\omega_5) \sim \sum_{\ell, k} \frac{P_{bl}^2 P_{la} P_{ak}^2 P_{kb}^4 Na}{(\omega_{ab} - \omega_1 + \omega_2)(\omega_{kb} - \omega_5)(\omega_{ak} + \omega_2)} + \ldots$$

in the case of Stokes scattering (RCSRS, $\omega_1 < \omega_2$, $\omega_5 = \omega$). Here $\overline{\omega}_{nm} = = \omega_{nm} - i \gamma_{nm}$, Na is the density of molecules at the level $\alpha$, $P_{\alpha \in m}^{\infty}$ is the projection of the transition $n \leftrightarrow m$ dipole moment on the polarization vector of the wave $\alpha$. Relations (1) and (2) are applicable to any pair of electronic states if the population of the higher state may be neglected.

Fig. 1. Scheme of levels and resonances in RCARS (a) and RCSRS (b). Absorption Q-bands of metalloporphyrins (c)

The first terms in expressions (1) and (2) contribute to the susceptibility due to RCRS at the vibrational transition $a \leftrightarrow b$ of the molecule.

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in the lower electronic state. The second terms make a contribution due to RCRS at the vibrational transition $c \leftrightarrow d$ of the excited electronic state. The latter is usually termed extra-resonance caused by states dephasing [5]. Its intensity is proportional to the population $N_a$ of the lower electronic state and the value of $\gamma_{cd} - \gamma_{ad} - \gamma_{ca} = \Delta_{cd} - \Delta_{ad} - \Delta_{ca}$ where $\Delta_{nm}$ is a portion of the $n \leftrightarrow m$ transition spectral width due to the state dephasing (fluctuations of energies $E_n - E_m = \hbar \nu_{nm}$). The investigation of this signal makes it possible to obtain information about the vibrations $\omega_{cd} = \omega_{cd} - i \gamma_{cd}$ of the excited state without populating it (which is particularly important in the case of short-lived electronic states), as well as about dephasing perturbations of molecules. The most favourable condition of observing extra-resonances is simultaneous realization of four resonances, which is easily achieved at $\omega_3 = \omega_2$ (but $\mathbf{k}_3 \neq \mathbf{k}_2$, $\mathbf{k}_3$ is the wave vector of the wave $\varphi$).

In RCRS experiments, the molecules under study may go, under the action of resonance radiation, to excited states and accumulate there if the lifetime of these states is not very short. RCRS by these molecules may also occur leading to the appearance of additional lines in the observed spectra. To describe them, one can use expressions (1) and (2) where $N_a$ is the density of molecules in such an excited state.

In our experiments at measuring RCRS spectra of metalloporphyrins, the frequency $\omega_1$ was tuned to the $Q_{0,0}$-absorption band and the frequency difference $\omega_1 - \omega_2$ was varied by tuning the frequency $\omega_2$. The measurements were made with polarization suppression (by $10^3$ times) of the non-resonance background caused by the solvent (signal due to $\gamma^{NR}$). We studied changes of spectra depending on the resonance radiation intensity $I_1 = I(\omega_1)$, excitation profiles of different lines in the RCRS spectrum (dependence of their intensities on $\omega_3$ at $\omega_1$ and $\omega_2$ constant or on $\omega_1$ at $\omega_3$ and $\omega_1 - \omega_2$ constant), scattering tensor invariants characterizing the molecular vibrations symmetry. The results of these investigations may be briefly presented as follows.

At light intensities smaller than $10^6 \text{ W/cm}^2$ in the RCARS and RGSRS spectra of all the samples only the lines of scattering by vibrations of the ground state are present. With increasing $I_1$ different samples behave much differently. In spectra of Ni-OEP in THF and toluol in low-frequency regions from the main lines observed at low $I_1$ additional lines appear whose intensity increases with increasing $I_1$, the regular lines intensity decreasing. At $I_1 \approx 10^8 \text{ W/cm}^2$ the RGS spectra consist only of additional lines. It has been found that additional lines are formed by light scattering from molecular vibrations in a relatively long-lived triplet $T_d$-state with an excited d-shell of the Ni atom.

In the case of Zn-OEP in THF the scattering completely disappears as $I_1$ is increased. This is attributed to the transition of molecules to

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the long-lived triplet state $T_1$ the scattering from which is of low efficiency because of the absence of one-photon resonances. The spectra of Cu-OEP in toluene behave similarly. Cu-OEP spectra in pyridine are generally independent of $I^*$, which is explained by the formation of a complex of these molecules in the $T_1$-state with pyridine molecules leading to fast decay of this state. In Cu-OEP spectra in THF the main lines do not completely disappear as $I^*$ is increased, and at large $I^*$ their intensity remains comparable to the intensity of the additional lines. In this case the additional lines belong to the relatively stable complex of Cu-OEP molecules and the solvent which, however, decays under light.

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НАУЧНЫЙ ПРИБОРНЫЙ КОМПЛЕКС ДЛЯ ИССЛЕДОВАНИЯ СВЕРХБЫСТРЫХ ЯВЛЕНИЙ В ОПТИЧЕСКОЙ СПЕКТРОСКОПИИ

Н. КЕМПЕ, Х. ЭНДЕРТ
Центр Научного приборостроения АН ГДР
1199 Берлин, ГДР

Представляется разрабатываемая в ЦНП АН ГДР модульная система узлов и приборов, позволяющая компоновать разнообразные измерительные комплексы для исследования процессов в пикосекундном временнм диапазоне.

Введение

Большое разнообразие задач и возможностей применения перестраиваемых пико- и субпикосекундных лазерных импульсов с одной стороны, и довольно высокая сложность соответствующих установок, требующих, как правило, специалистов-физиков для работы с ними, с другой стороны, побудили нас к созданию приборного комплекса, позволяющего компоновку измерительных установок в зависимости от задач и с высокой степенью автоконтроля и автоматизации проведения эксперимента, включая обработку данных, средствами современной микроэлектроники. Разрабатываемая в ЦНП пикосекундная модульная система (ПМС) позволяет создание контролируемых последовательностей лазерных импульсов в диапазоне 0,7 - 15 пс, перестраиваемых в области 380 - 900 нм (а также вторую гармонику от них до 240 нм) с энергией от пДж до мДж в импульсе и с частотами повторений, как в областях десятков Гц, так и сотен МГц. Кроме того, система ПМС включает в себя элементы манипуляции луча (селекторы, линии задержки и т.д.), а также целый ряд контрольных и измерительных приемных устройств для работы с быстрыми оптическими сигналами. Одной из существенных и качественно новых особенностей системы является широкое применение современной "интеллектуальной" микроэлектроники как для управления отдельными блоками и узлами, так и всем компонуемым измерительным комплексом в целом.

Источник импульсов

ПМС предлагает разные конфигурации. Рассмотрим более подробно два базовых варианта.

Аutomатизированный источник на основе струйного лазера на красителях

Этот представленный на рис. 1 комплекс для получения пикосекундных лазерных импульсов в диапазоне 540 - 750 нм (4 красителя) использует струйный лазер FSL 101 с системой прокачки красителя LVE 100, накачиваемый аргоновым лазером ILA 120 (Карл Цейс), который в свою очередь модулируется акусто-оптическим модулятором AOM 100, запускаемым электрическим кварцевым генератором ЕАОМ 100. Импульсы накачки контролируются специальным узлом МКЕ 100, а получаемые пикосекундные импульсы - сканирующим коррелятором KRL 100. Основные параметры отдельных узлов следующие:

ILA 120: выходная мощность по всем линиям - не менее 4 Вт, селективно 514,5 нм более 1,2 Вт, 488 нм более 1,3 Вт, длина резонатора 1200 мм.

FSL 101: коэффициент преобразования лучше 20% в максимуме при Rh 6 к и накачке на 514 нм не менее 1 Вт (непрерывный режим), ширина линии не более 0,25 нм, поляризация Е горизонтальная, диаметр луча 1,3 мм, дивергенция лучше 1,5 мрад, режим работы: непрерывный. импульсный (пассивная или активная синхронизация мод), длина резонатора 600+2 мм.
LVE 100: давление в системе 100 - 300 кПа, средняя скорость в струе 4 - 10 м/сек, объем жидкости (краситель в растворе) около 1 л, охлаждение водяное.

AOM 100: оптические потери менее 5%, длительность импульсов менее 150 пс, частота повторения 125 МГц.

EAOM 100: электрическая выходная мощность на 50 Ом не менее 5 Вт, стабильность частоты: 10 мин $10^{-7}$, 10 час $10^{-6}$.

KRL 101: диапазон сканирования 30 пс, разрешение 30 фс, линейность по оси времени 2%, частота сканирования 20 Гц.

Рис. 1 Автоматизированный источник пикосекундных импульсов на базе струйного лазера

На примере прибора FSL 101 (рис. 2) рассмотрим принцип построения мультимикропроцессорной системы. При его разработке были поставлены следующие задачи:
- лазерный тандем не должен требовать специальной квалификации в управлении,
- лазерная система должна гарантировать как непрерывный режим с высоким коэффициентом полезного действия для различейших применений, в том числе, и для спектроскопии высокого разрешения, так и непрерывно-импульсный режим с пассивной синхронизацией мод или с синхронной накачкой от модулированного лазера,
- максимально возможная пригодность для спектроскопии, т.е. стабильность выходных параметров (направление луча, выбранная длина волны, энергия и длительность импульсов),

Нижеописываемая система полностью решает эти задачи. Выбрана классическая резонаторная система Когельнера. При этом фокусирующее и поворотное зеркала жестко закреплены в головке. Их юстировка производится в процессе монтажа с помощью специальных юстировочных прецизионных колец. Сопло имеет три степени свободы и может быть установлено оптимально без дюстровоки резонатора. Выходное зеркало и призма завода можно накачки могут очень точно перемещаться без качаний и независимо поворачиваться вокруг двух взаимно перпендикулярных осей. Зеркало имеет три, а призма две степени свободы. Используемые здесь пьезотрансляторы позволяют перемещения на несколько нанометров (100 В на 1 нм). Два полупроводниковых сенсора $S_1$ и $S_2$ контролируют мощность излучения накачки и лазера на красителях. Соответственно две замкнутые петли регулировки в цикле системы реального времени (200 мкс) поддерживают лазер на максимум излучения, при этом контролируется также качество струи с помощью сенсора-линейки с переносом заряда $S_3$, управляемого собственным однокристальным микропроцессором, и температура активной среды сенсором $S_4$. Перестройка по длине волны производится одно- или двухступенчатым фильтром $L$, привод которого осуществляется электромотором. Специальный полупроводниковый сенсор $S_5$ контролирует длину волны. Поддержание ее с точностью долей ангст-
Аргоновый лазер

Полуфокусное зеркало

Падающее излучение

Фокусирующее зеркало

STR-электроника управления лазером (ЭВМ нижнего уровня)

$s_1$ - сенсор контроля излучения аргонового лазера
$s_2$ - сенсор контроля эффективности лазера на красителях
$s_3$ - сенсор контроля качества струи
$s_4$ - сенсор контроля температуры активной сферы
$s_5$ - сенсор контроля длины волны излучения

Схема лазера на красителях FSL-100 с микропроцессорным блоком управления STR и ЭВМ верхнего уровня (системная ЭВМ)

Рис. 2 Блок-схема лазера на красителях FSL-100 с микропроцессорным блоком управления STR и ЭВМ верхнего уровня (системная ЭВМ)
режим также осуществляется в замкнутой петле регулировки. Все регулировочные петли цифровые, через микропроцессор. При этом вся управляющая микрэлектроника встроена в корпус лазера, так что наружу выводится лишь сетевой шнур и два штеккера последовательного стандартного интерфейса, один для соединения с системой ЭВМ верхнего уровня, другой - для возможного подключения какого-либо прибора ПМС.

По той же самой схеме разрабатываются и другие узлы и приборы ПМС, например, приёмные устройства, измерительные корреляторы и т.д. При этом они компонуются в систему для эксперимента, управляемую любой современной мини-ЭВМ потребителя, имеющей набор стандартных последовательных интерфейсов. Строго иерархический принцип соединения микропроцессоров и ЭВМ по принципу "ведомый-ведущий" позволяет четкое разделение обязанностей: ЭВМ верхнего уровня управляет комплексом в целом, осуществляет диалог с потребителем и обрабатывает данные, микропроцессорные блоки в отдельных узлах контролируют порученные им приборы, причем вызов и командование ими возможно лишь через управляющую ЭВМ. Тем самым достигается большая гибкость всей системы. Благодаря этому, а также потому, что во всех микропроцессорных блоках используется единая модульная операционная система реального времени, в ПМС подготовлены условия для создания совместно со специалистами-потребителями экспертных систем.

Автоматизированный источник на основе РОС-лазера

Потребителям, желающим иметь более мощные импульсы и более широкий диапазон (380-900 нс) предлагается такой вариант (рис. 3).

Здесь импульсы формируются в разработанном совместно с Институтом физики АН БССР лазером АМЕТИСТ, накачиваемым нашим трансверсальным азотным лазером IGT-250 с параметрами: ширина импульса короче 500 пс, мощность более 250 кВт, частота повторения до 60 Гц. На выходе системы получается импульсы в несколько десятков пс в широком диапазоне (10 красителей) длительности волн и высоким коэффициентом преобразования.

Заключение

В ЦНП идут дальнейшие разработки блоков и узлов системы ПМС. Так для усиления пикосекундных импульсов предлагается мощный отпаянный азотный лазер NIL-1000 с особо тщательной помехозащитой, имеющий мощность в импульсе не менее 600 кВт, длину их 10 нс и частоту повторения 25 Гц. Ведутся работы по введению в систему ИАГ-лазеров, как для накачки, так и для усиления пикосекундных импульсов. Настоящие разработки велись в тесном контакте с группой проф. Б.Вильгельми (Университет им. Фридриха Шиллера в Йене).

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The electronic and vibrational spectra of some diazines were investigated in a wide acidity region from strong alkaline solution to strong acidic one. Electronic spectra were applied to the determination of the acidic ionization constants. Besides, ionization constants were calculated quantumchemically, too. Measured and calculated ones are correlated. A theory was developed for the application of ionization constants to multicomponent analysis of ampholytes. Vibrational spectra were measured at pH (H₀) values where the ion in question is the bulk. A special IR cell was elaborated for these measurements. Force constants and fundamental frequencies were calculated at CNDO level by the extension of the force method to soluted molecules (FORSOL programme). Geometric parameters of some ions were optimized by ab initio calculations.

Introduction

The investigation of heterocyclic compounds in aqueous solution has increasing importance since they are models of biologically active compounds and biological processes proceed in aqueous media.

The acidity of the solution has a strong effect on the compound. The gain or loss of proton changes the ionic state of the molecule and in this way changes in the geometric parameters will occur, too. In our work the pH (H₀) dependence of electronic and vibrational spectra was investigated.

Electronic spectra

The investigation of the pH dependence of the electronic spectra is an adequate method for the determination of the (acidic) ionization constants [1]. The spectra were measured mostly in the -10.00<pH (H₀)<14.30 region.

The spectra of some pyridazines, pyrimidines and pyrazines were recorded. Table I contains some spectral data of investigated pyrazines (PZ) at pH (H₀) values where the ions in question are the bulk species [2]. The substituent effect of the acidic ionization constant (as pKₐ) is demonstrated on pyrazines in Table II [2]. Both spectra and ionization constant (0/+1) of 2-carboxypyrazine make the out-of-place position of the carboxy group probable.

Ionization constants were calculated by the CNDO/2 method from the binding energies of the isolated molecules (ions) supposing the approximate equality of the differences of binding energies to the change in free energy.
For this purpose electronic energies were calculated for all possible con-
formers of all tautomeric ions descending from the molecule in question. The
configuration with minimal electronic energy was accepted for the calcula-
tions.

Table I
Electronic spectral data of some investigated pyrazines $\lambda(\text{nm})/\log \alpha$

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Ionic state</th>
<th>$-2$</th>
<th>$-1$</th>
<th>$0$</th>
<th>$+1$</th>
<th>$+2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>261(3.76)</td>
<td>268(3.90)</td>
<td>284(4.29)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-COOH</td>
<td></td>
<td>267(3.82)</td>
<td>209(3.83)</td>
<td>209(3.87)</td>
<td>209(3.87)</td>
<td></td>
</tr>
<tr>
<td>2-COONH$_2$</td>
<td></td>
<td>314(2.81)</td>
<td>270(3.90)</td>
<td>278(3.91)</td>
<td>293(3.90)</td>
<td></td>
</tr>
<tr>
<td>2,3-(COOH)$_2$</td>
<td></td>
<td>282(3.81)</td>
<td>278(3.77)</td>
<td>213(3.76)</td>
<td>215(3.78)</td>
<td>215(3.81)</td>
</tr>
<tr>
<td>2,3-(CONH$_2$)$_2$</td>
<td></td>
<td>269(3.81)</td>
<td>268(3.78)</td>
<td>278(3.82)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II
Some measured ionization constants of pyrazines as $pK_a$'s

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Lower/higher ionic state</th>
<th>$-2/-1$</th>
<th>$-1/0$</th>
<th>$0/+1$</th>
<th>$+1/+2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td>0.60</td>
<td>-6.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-COOH</td>
<td></td>
<td>5.55</td>
<td>0.90</td>
<td>-7.81</td>
<td></td>
</tr>
<tr>
<td>2-COONH$_2$</td>
<td></td>
<td>-0.29</td>
<td>-5.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-(COOH)$_2$</td>
<td></td>
<td>4.20</td>
<td>2.26</td>
<td>-3.39</td>
<td>-7.13</td>
</tr>
<tr>
<td>2,3-(CONH$_2$)$_2$</td>
<td></td>
<td>-2.15</td>
<td>-7.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-NH$_2$-3-COOH</td>
<td></td>
<td>7.60</td>
<td>-2.66</td>
<td>-5.88</td>
<td></td>
</tr>
<tr>
<td>2-NH$_2$-3-COOC$_3$</td>
<td></td>
<td>2.58</td>
<td>-5.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-NH$_2$-3-COOC$_3$-5-Cl</td>
<td></td>
<td>-0.74</td>
<td>-8.64</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Linear regression was used to correlate measured and calculated ioniz-
ation constants. Taking 21 equilibria, the equation of the regressional
line has the form

$$pK_a,\text{meas} = 0.0459 pK_a,\text{calc} + 1.256$$

with a correlation 0.801.

Ionization constants of diazines were also determined in deuterated (D)
media. For the first proton gain we found for pyridazine $pK_a = 2.26$ and $pK_{a,D} = 2.32$, for pyrimidine $pK_a = 1.37$ and $pK_{a,D} = 1.31$, for pyrazine $pK_a = 0.60$ and $pK_{a,D} = 1.09$. The difference of the two pyrazine $pK_a$ values is reproducible.

The determined ionization constants are applicable in the analysis of multicomponent ampholyte systems by potenciometry. A theory was developed for this purpose which gave the possibility of on-line control and data acquisition in potenciometry which can be followed by the data processing [3].

Vibrational spectra

Vibrational spectra were measured at pH ($H_0$) values where the ion in question was the bulk species. In this way spectra of the ions were recorded.

There arose difficulties with the recording of IR spectra. The high absorbance of the water and the sulfuric acid requires small cell length. This cell length, however, is commensurable with the wavelength of the IR light and interference will occur. Besides, the solvents are very corrosive. Therefore a special cell was constructed [4] for our purpose with germanium windows having a thickness $\approx 1 \mu m$.

Based on the assigned spectra of the parent compounds in solid, liquid and gas states the spectra of some pyridazines and pyrazines were approximately assigned in alkaline and acidic solution. In this way we get vibrational fundamentals of some protonated diazine ions [5].

For a better interpretation of the vibrational spectra a new quantum-chemical computational method was elaborated. The CNDO/force method [6] was extended to soluted molecules. The method named FORSOL is based on the theory of Miertuš and Kysel [7] which is the extension of CNDO/2 to soluted molecules [8]. Some additional approximations were introduced: solvaton-solvaton interactions were omitted (solvaton is an image charge in the solvent), solvaton-atomic charge ($Z$) interaction were symmetrized, atom-own solvaton distances ($r$) can be scaled, solvatons were positioned. The forces ($F$) were derived analytically:

$$F (s, \alpha) = F_0 (s, \alpha) - \frac{\epsilon}{2\epsilon_0} \sum_{i=1}^{N} P_{kk} (Z_s - P_{ss}) \frac{\partial \rho_s}{\partial \theta_s} \frac{\partial \theta_s}{\partial \theta_s},$$

where $\alpha = x, y, z$, $\epsilon$ is the relative dielectric constant, $P$ is the density matrix, $\rho$ is the exchanging integral, the force of the isolated species is labelled by index zero. Table III contains some measured and calculated frequencies for pyrazine in solution. In the calculations the scaling factors $r_{CH}^* = 0.33$, $r_{CC}^* = 0.42$, $r_{CH}^* = 0.44$, $\beta_{ring} = 1.05$, $\beta_{CH} = 0.83$ were used.

Ab initio calculations were carried out (STO-3G) for the determination of the geometric parameters of pyrazine and its protonated ions [9] to supply their force constant calculations which are now in progress. Table IV shows the calculated geometric parameters.

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Table III
Measured and calculated (FORSOL) fundamental frequencies \( \text{[cm}^{-1} \text{]} \) of the \( \text{B}_3\text{u} \) species of pyrazine

<table>
<thead>
<tr>
<th>Fundamental</th>
<th>( \varepsilon = 1 )</th>
<th>( \varepsilon = 78 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc.</td>
<td>meas.</td>
</tr>
<tr>
<td>12b ( \nu_{CH} )</td>
<td>3046</td>
<td>3066</td>
</tr>
<tr>
<td>13b ( \nu_{CN} )</td>
<td>1456</td>
<td>1418</td>
</tr>
<tr>
<td>9 ( \beta_{CH}^{+} )</td>
<td>1146</td>
<td>1145</td>
</tr>
<tr>
<td>10 ( \beta_{ring}^{+} )</td>
<td>1016</td>
<td>1056</td>
</tr>
</tbody>
</table>

Table IV
Optimized (STO-3G) geometries of the isolated pyrazine and its protonated ions (distances in pm, angles in degrees)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PZ</th>
<th>( \text{PZH}^+ )</th>
<th>( \text{PZH}_2^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&quot;N&quot; side</td>
<td>&quot;NH&quot; side</td>
<td>&quot;NH&quot; side</td>
</tr>
<tr>
<td>( r_{CN} )</td>
<td>135.5</td>
<td>136.1</td>
<td>136.3</td>
</tr>
<tr>
<td>( r_{CC} )</td>
<td>139.0</td>
<td>138.8</td>
<td>138.8</td>
</tr>
<tr>
<td>( r_{CH} )</td>
<td>108.6</td>
<td>108.9</td>
<td>110.0</td>
</tr>
<tr>
<td>( r_{NH} )</td>
<td>-</td>
<td>-</td>
<td>103.6</td>
</tr>
<tr>
<td>( \Psi_{NCC} )</td>
<td>123.0</td>
<td>122.6</td>
<td>118.3</td>
</tr>
<tr>
<td>( \Psi_{CNN} )</td>
<td>114.1</td>
<td>117.0</td>
<td>121.3</td>
</tr>
<tr>
<td>( \Psi_{NCH} )</td>
<td>116.8</td>
<td>117.4</td>
<td>117.7</td>
</tr>
<tr>
<td>( \Psi_{CNH} )</td>
<td>-</td>
<td>-</td>
<td>119.4</td>
</tr>
</tbody>
</table>

References


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CONTACT TRANSFORMATIONS IN THE MIXED MATRIX-OPERATOR FORM: EFFECTIVE ROTATIONAL HAMILTONIANS FOR THE EXCITED VIBRATIONAL STATES OF SYMMETRIC TOP MOLECULES

S. URBAN, M. GARCÍA HERNÁNDEZ* and D. PAPOUŠEK
The J. Heyrovský Institute of Physical Chemistry and Electrochemistry
Czechoslovak Academy of Sciences, 160 00 Prague 6, Flemingovo n. 2,
Czechoslovakia

The effective rotational Hamiltonian for \( C_3v \) or \( D_3 \) molecules written in the basis of the vibrational wavefunctions \( |\Omega^2\rangle \) and \( |\zeta^2\rangle \) has been transformed by a rotational contact transformation such that the operators of the \( \hat{A} \)-type interactions and of the \( \Delta \alpha^2 \Delta k \) \( \neq 0 \) interactions are eliminated from the first order terms of the expansion of the Hamiltonian in terms of the smallness parameter \( \lambda \).

Introduction

The expanded vibrational-rotational Hamiltonian \( H_{\text{vr}} \) can be written in the following form \([1-3]\):

\[
H_{\text{vr}} = \sum_{m,n} H_{mn} , \tag{1}
\]

where the first subscript in each \( H_{mn} \) term is the degree in the vibrational operators (coordinates \( q \) and momenta \( p \)) while the second subscript is the degree in the components of the total angular momentum operator.

Suppose that by successive vibrational contact transformations, the vibrational operators have been eliminated from the expanded form of \( H_{\text{vr}} \) to such extent that for a nondegenerate vibronic state, the effective rotational Hamiltonian can be written in the following well-known form \([1-3]\):

\[
\tilde{H}_{\text{rot}} = \tilde{H}_{02} + \lambda \tilde{H}_{04} + \lambda^2 \tilde{H}_{06} + \ldots \tag{2}
\]

where \( \lambda \) is a formal "smallness" parameter.

Furthermore, if there are terms in \( H_{\text{rot}} \) which are completely off-diagonal in the rotational quantum number \( k \), they can be eliminated by rotational contact transformations and \( H_{\text{rot}} \) can be reduced into a form containing fewer independent parameters.

For example, in semirigid molecules belonging to the \( C_{3v} \) or \( D_3 \) groups, the quartic term of the so-called \( \Delta k = \pm 3 \) interaction \([1,4]\) can be written as

\[+ \text{Permanent address: Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, 28006, Madrid, Serrano 119, Spain}\]
\[ H^{(1)}_{S} = \alpha [J_{x}^{3} + J_{y}^{3}] J_{z} + \alpha \alpha [J_{z}^{3} + J_{x}^{3} J_{y}^{3}] \]  

where \( J_{x}^{\pm} = J_{x} \pm iJ_{y} \) and \( H^{(1)}_{S} \in H_{04} \).

If we apply a rotational contact transformation to \( H^{(1)}_{rot} \),

\[ H^{(1)}_{rot} = \exp(i\lambda S) H_{rot} \exp(-i\lambda S) = (1 + i\lambda S - \frac{1}{2} \lambda^{2} S^{2} + \ldots) \tilde{H}_{02}^{(1)} + \ldots \]  

with the transformation function \( S \) defined as (see, e.g., [1],[4])

\[ S = z \frac{\alpha}{B_{z} - B_{x}} \]  

then \( H^{(1)}_{rot} \) can be written in the form

\[ H^{(1)}_{rot} = \tilde{H}_{02}^{(1)} + \ldots \]  

in which \( H^{(1)}_{S} \) has been removed from \( H_{04} \) to higher order terms [1,4].

The situation is not so simple if we consider the excited vibrational states pertaining to the doubly degenerate vibrational modes. This is because there are certain terms in the expanded form of \( H_{vr} \) [Eq.(1)] which cannot be eliminated by a standard contact transformation.

For example, the Coriolis operator for the rotation around the \( z \)-axis pertaining to the doubly degenerate mode \( q_{\pm} = q_{a} - iq_{b} \) is

\[ H_{Cor}^{(z)} = -\frac{1}{2} B_{z} y^{2} t a b J_{z}(q_{+} p_{-} - p_{-} q_{+} + p_{q_{+}} - q_{q_{+}}) + \text{higher order terms}; \]  

\( H_{Cor}^{(z)} \) is diagonal in the rotational quantum numbers \( J, k \) as well as in the vibrational quantum numbers \( v_{t} \) and \( \ell_{t} \).

Furthermore, there are two types of the \( \ell \)-type interactions in symmetric top molecules which are diagonal in \( v_{t} \) but off diagonal in \( \ell_{t} \) as well as in \( k \). The so-called "2,2" interaction is present in all symmetric top molecules [2]; it is described by the operator

\[ H^{("2,2")\ell} = \omega(q_{+}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2}) + \omega(J) J^{2}(q_{+}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2}) + \omega(K)(q_{+}^{2} J_{z}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2} J_{z}^{2}). \]  

In molecules with an odd principal axis of symmetry \( C_{n} \) but without a \( S_{h} \) plane of symmetry (\( C_{3v}, C_{5v} \) etc. point groups), we have in addition the "2,1" \( \ell \)-type interaction described by the operator

\[ H^{("2,1")\ell} = \delta(q_{+}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2}) + \delta(J) J^{2}(q_{+}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2}) \]  

\[ + q_{+}^{2} J_{z}^{2} (J_{z} + 1/2) J_{z}^{2} + q_{-}^{2} J_{z}^{2} (J_{z} + 1/2) J_{z}^{2}. \]  

In a previous paper [6], we have used the mixed matrix-operator scheme of the contact transformations (see, e.g. [4,5]) to eliminate \( H^{(1)}_{S} \) [Eq.(3)] and the operators

\[ H^{(1)}_{\ell}("2,2") = \omega(q_{+}^{2} J_{z}^{2} + q_{-}^{2} J_{z}^{2}) \]  

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CONTACT TRANSFORMATIONS IN THE MIXED MATRIX-OPERATOR FORM

\[ H_{0}^{(1)}(\text{"2,-1"}) = \delta_{2}^{2} J_{z} + 1/2 J_{+} + q_{2}^{2} J_{-} (J_{z} + 1/2) \]  

(11)

from the effective rotational Hamiltonian for the doubly degenerate fundamental level of symmetric top molecules.

In this paper, we will extend this approach to the first overtone level \((v_{t}^{E} = 2,-2,2)\) of \(C_{3v}\) or \(D_{3}\) molecules.

First overtone \((v_{t} = 2)\)

In this case, the effective rotational Hamiltonian is written in the basis of the vibrational wavefunctions \(|2^2\rangle\) (E species) and \(|2^0\rangle\) (A species):

\[
\begin{bmatrix}
|2^2\rangle & |2^0\rangle & |2^2\rangle & |2^0\rangle & |2^2\rangle & |2^0\rangle & |2^2\rangle & |2^0\rangle
\end{bmatrix}
\]

(12)

where

\[ \tilde{H}_{rot}(0) = B_{x}' J_2 + (B_{z} - B_{x}') J_z^2 + 48 \gamma_{z} y_{t}^{2} + E_{v}(v), \]

(13)

\[ \tilde{H}_{rot}(0) = B_{x}' J_2 + (B_{z} - B_{x}') J_z^2 + E_{v}(v), \]

(14)

\[ \tilde{H}_{rot}(0) = -D_{y} J_2 - D_{y} J_z^2 z - D_{y} J_z^2 + 2 \gamma_{y} J_2 J_z + 2 \gamma_{z} J_z^2 + \alpha' [J_3 + J_3 J_{z}^2] + , \]

(15)

\[ \tilde{H}_{rot}(0) = -D_{y} J_2 - D_{y} J_z^2 z - D_{y} J_z^2 + \alpha' [J_3 + J_3 J_{z}^2] + , \]

(16)

\[ \tilde{H}_{rot}(0) = H_{x}(1) = 2 \sqrt{\omega} J_2^2 + 2 \gamma (J_{z} + 1/2) J_{+} ; \]

(17)

\[ \tilde{H}_{rot}(0) = H_{x}(2) = \alpha J_2 [J_{+} + J_{-} J_{z}] + \alpha K_{z} [J_{+} + J_{-} J_{z}] + + h_{3} (J_{+} + J_{-}) + + H_{y} J_6 + H_{y} J_{4} J_{z} + H_{y} J_{4} J_{z}^2 + H_{y} J_{6} + \]

(18)

\((\tilde{H}_{rot}^{0},0)\) contains the same functions of the rotational operators as \(\tilde{H}(2)\) but we will use the primed symbols \(\alpha', \alpha', \omega, \gamma' \) etc. for \(\tilde{H}(2)\).

Now \(\tilde{H}_{rot}\) is subjected to a rotational contact transformation such that terms with \(\omega', \alpha', \omega, \gamma' \) are eliminated from the right-hand sides of Eqs. (15) - (17):

\[ \tilde{H}_{rot} = \exp \{i \lambda [S] \} \tilde{H}_{rot} \exp \{-i \lambda [S] \}, \]

(19)

where

\[
[S] = \begin{bmatrix}
S_{2} & S_{+} & 0 \\
S_{+} & S_{0} & S_{-} \\
0 & S_{-} & S_{2}
\end{bmatrix}
\]

(20)
In Eq. (20),

\[ S_\pm = \frac{\omega_x}{2} \left\{ J_\pm^2 (2J_z - 3) \left[ (2J_z - 3)(B_z - B_x) \mp 4B_z J_z^2 \right]^{-1} - \left[ (2J_z - 3)(B_z - B_x) \mp 4B_z J_z^2 \right]^{-1} \times (2J_z - 3)J_\pm^2 \right\} \]  

(21)

eliminates the last term on the right-hand side of Eq. (15); \( S_0 \) is identical, with \( S \) in Eq. (5) but \( \alpha', B_z, \) and \( B_x \) have to be replaced by \( \alpha', B_z', \) and \( B_x' \).

Furthermore, \( S_\pm \) in Eq. (20) can be written in the following condensed form:

\[ S_\pm = \left( \frac{\omega_x}{2} \right) J_z^2 \left\{ \left( E_0 (v) - E_2 (v) \right) \mp 4B_z J_z^2 \right\} \left\{ \left( B_z - B_x \right) (2J_z - 1) \right\}^{-1} + i \left( \frac{\omega_x}{2} \right) J_z \left( 2J_z - 1 \right) \times \left\{ \left( E_0 (v) - E_2 (v) \right) \mp 2B_z J_z^2 \right\} \left( B_z - B_x \right) (2J_z - 1) \]  

(22)

where \( B_z, B_x \) should be \( B_z, B_x \) for \( S_+ \) and \( B_z', B_x' \) for \( S_- \).

Conclusions

After carrying out the corresponding algebra, we obtain the transformed form of the effective rotational Hamiltonian from which we can make the following conclusions concerning the correlation between the parameters of the various vibrational-rotational interactions.

For the first overtone \( (v_2 = 2) \), the parameters of the "2,2" and "2,-1" interactions can be in principle determined separately but certain relations must be satisfied as for the difference between the \( A \) and \( E \) vibrational levels. The \( \alpha' \)-parameter (the \( A \) vibrational state) is correlated completely with other interaction parameters while the \( \alpha \)-parameter (\( E \) state) can be in principle determined separately.

Full details of the treatment will be described elsewhere [6,7].

References


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Absorption, emission and laser fluorescence spectra of GdO, EuF, and UO were studied. The character of the ground states and the nature of the low-lying states were established. Term energies and rotational constants were determined for each state. The vibrational constants were derived for GdO and EuF.

The knowledge of the electronic structure and molecular constants of the molecules with partly filled d and f shells are important for many applications, particularly for calculations of reliable thermodynamic properties of these substances [1]. The first attempts to study high resolution spectra of such diatomic molecules were started about 20 years ago [2,3] and were continued in several laboratories [4-7]. Still, due to extremely complex nature of these spectra relatively full information on low-lying electronic states was obtained only for 3 molecules: CeO [6], PrO [4] and TbO [8].

In our laboratory the high resolution electronic spectra of PrO, NdO, SmO, GdO, TbO, DyO, HoO, ErO, UO, and EuF were studied and partially analyzed. Emission and absorption spectra were obtained using small vacuum furnace [3]. The spectra were photographed in the spectrograph with real resolving power up to 5·10⁶. The laser excitation and fluorescence spectra were studied using the same furnace, the Ar⁺ laser CR-8 and the dye laser CR-490. The selectively detected fluorescence techniques were similar to those used in [9]. The main results were reviewed in [7].

This paper reports only the results of analyses of some transitions in the spectra of GdO, EuF, and UO carried out during the last year.

Fig. 1 gives the diagram of the electronic transitions which were analyzed in the spectra of the isoelectronic GdO and EuF molecules. Emission, absorption and fluorescence spectra were investigated. The rotational structure of transitions involving terms of high multiplicity such as ²Σ and ⁷Σ is very complicated. That is why the emission bands are rarely available for a rotational analysis.

The 568 nm band of GdO, denoted in Fig. 1 as ²Π - ²Σ transition, consists theoretically of 27 branches; from them 17 were identified with certainty. The type of lower state was proved to be ²Σ on the basis of very satisfactory agreement between the observed and the calculated lines at N<10. The analysis provided the rotational and spin splitting constants for the ²Σ (v = 0) state.

The analyses of the ²Σ - ²Σ (0 - 0) and ⁷Σ - ⁷Σ (0 - 0) bands are very cumbersome. It was not difficult to pick out all the P branches but not R branches. The latter form multiplet heads at N≈30 and heavily overlap one another. The data are not
The accurate values of rotational constants for the \( X^9\Sigma \) and \( a^7\Sigma \) states were derived from the analysis of fluorescence spectra excited at the \( \text{Ar}^+ \) laser lines which situated in the region of the \( 9\Sigma - X^9\Sigma \) and \( 7\Sigma - a^7\Sigma \) systems. The spectra were photographed on a high resolution spectrograph. The spectra contain 8 resonance series of the single \( R_i \) and \( P_i \) lines. Five of them are connected with \( X^9\Sigma \) state (\( v = 0 - 8 \)) and three - with the \( a^7\Sigma \) (\( v = 0 - 3 \)) state. In addition the fragments of the same \( R_i \) and \( P_i \) branches were observed near the strong fluorescence lines due to rotational relaxation induced by buffer gas. All the data were used for calculation of constants given in Table I. The energy of the \( a^7\Sigma \) state was obtained from two series which do not include the laser line and correspond to the intercombination transitions.

The rotational structure of the \( \text{EuF} \) bands (550 - 760 nm) is practically unresolved because of the overlapping of bands of two isotopic molecules and the broadening of lines due to hyperfine structure \( (I = 5/2) \). Regular and more or less sharp lines were detected at 597 nm. The analysis of the fluorescence spectra excited by the dye laser tuned to the wavenumbers of these lines revealed 7 bands: \( \Omega_1 - X^9\Sigma \) \((v'' = 0, 1)\), \( \Omega_2, \Omega_3 - X^9\Sigma \) \((v'' = 0)\), \( \Omega_4, \Omega_5, \Omega_6, \Omega_7 - a^7\Sigma \) \((v'' = 0)\) each upper state is presented by one component of \( \Omega \)-doubling. The transitions terminating at the \( X^9\Sigma \) state consist of branches with \( J' - N'' = \pm 5, \pm 3, \pm 1 \), those terminating at the \( a^7\Sigma \) state consist of branches with \( J' - N'' = \pm 3, \pm 1 \). Measurements of lines over a wide range of \( N \) permitted to calculate accurate values of constants for the \( X^9\Sigma \) and \( a^7\Sigma \) states (see Table I) and the energy of the \( a^7\Sigma \) state. The upper states are perturbed.

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Table I

Molecular constants of GdO and EuF (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>State</th>
<th>(T_0)</th>
<th>(\omega_e)</th>
<th>(\omega_e \chi_e)</th>
<th>(B_0)</th>
<th>(D_0 \cdot 10^7)</th>
<th>(A \cdot 10^3)</th>
<th>(r_o (nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdO</td>
<td>1837.6(2)</td>
<td>837.11(6)</td>
<td>2.62(2)</td>
<td>0.3557(4)</td>
<td>2.57(2)</td>
<td>1.47(2)</td>
<td>0.1806</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EuF</td>
<td>1421.7(1)</td>
<td>493.1(1)</td>
<td></td>
<td>0.2300(2)</td>
<td>1.3(4)</td>
<td>0.2083</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a) \beta = -2(1) \cdot 10^{-9}\)
\(b) \lambda = -0.099(6), \ \eta = 5(3) \cdot 10^{-4}\)
\(c) \beta = -8(2) \cdot 10^{-10}\)
\(d) \Delta \delta_{1/2}\)

Emission and absorption spectra of UO were obtained when a slightly oxidized uranium metal was heated to temperature around 2400-2600 K. About 500 bands were measured in the 400-900 nm region. Rotational analysis of 4 well-resolved bands in the photographic infrared with common upper state revealed 4 low-lying electronic states [10]. The rotational constants and the relative energies of the combining states were determined. Simultaneously M.Heaven and al [11] investigated the laser excitation spectrum of UO at very low temperatures and observed transitions only from the ground \(v = 0\) state. Comparison of our and their data implied that the lowest state in our analysis is the ground state.

![Diagram of the electronic transitions of UO](See Fig. 1 for denotations)
The spectrum of UO near 600 nm is extremely complex. The very strong 593.4 nm band was recorded by laser excitation spectroscopy with selective fluorescence detection. The band consists of R, Q, and P branches which were identified from the lowest J'' = 4 value up to J' = 55. The upper state is heavily perturbed. The fluorescence spectra obtained through excitation of selected rotational lines in the 593.4 nm band have established energies, rotational constants, and Ω-values of 5 low-lying states. The comparison has shown that the fluorescence and emission bands analyzed have 3 levels in common. The diagram of the transitions of UO investigated up to now is presented in Fig.2. Molecular constants are given in Table II.

### Table II

Molecular constants of UO (in cm⁻¹)

<table>
<thead>
<tr>
<th>Assignment, ν</th>
<th>Ω</th>
<th>T₀</th>
<th>B₀</th>
<th>r₀ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1573.89(9)</td>
<td>0.3286(5)</td>
<td>0.1850</td>
<td></td>
</tr>
<tr>
<td>4(ν=1 ?)</td>
<td>1184.42(9)</td>
<td>0.3460(3)</td>
<td>0.1803</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1043.00(3)</td>
<td>0.3297(2)</td>
<td>0.1847</td>
<td></td>
</tr>
<tr>
<td>4(ν=1 ?)</td>
<td>882.28(1)</td>
<td>0.3298(1)</td>
<td>0.1847</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>651.12(2)</td>
<td>0.3276(1)</td>
<td>0.1853</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>294.07(5)</td>
<td>0.3459(2)</td>
<td>0.1803</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.3330(1)</td>
<td>0.1838</td>
<td></td>
</tr>
</tbody>
</table>

The data obtained imply that the low-lying states of UO arise at least from 2 superconfigurations. There are some reasons to assign the 882 cm⁻¹ state as the v = 1 level of the ground state. But in this case the Δν = 1/2 value differs significantly from that derived from matrix isolation study [12]. A more complete understanding of the matter calls for further study.

### References

Reconstruction problem of a pulsed NMR spectrometer is discussed. The development work extends on the architecture of applied computer system, programmable pulse and gradient generator, flux stabilizer, magnetic field stabilizer and its modulator.

Introduction

The development of NMR accessories in our institute looks back on a history of more than thirty years. Solid state NMR investigations started with a home-built spectrometer. Since then many items of equipment have become available on the market, but the special position of our country vis-à-vis the market and the financial situation of our institute makes the development of some instruments inevitable.

In the present paper we report on some equipment which has recently been developed in our institute, which might arouse the interest of our colleagues.

First of all we discuss a computer used to control a spectrometer. A 16 channel pulse generator as a special intelligent slave computer provides the required pulse sequences. A magnetic field gradient generator is attached to the pulse generator. A Transient-Digistore instrument is used to store the fast signal and transfer it to the main computer (see Fig. 1).

In order to provide necessary stability of the magnetic field we use a current stabilizing power supply, an NMR stabilizer and a flux stabilizer, providing precise and sufficiently fast stabilization (Fig. 2). The required value of the stabilized magnetic field can be changed, or even swept.

The computer

After a long trial we chose a Janus computer with a Q-BUS system, built in our institute. This is a 16-bit data bus system with available hardware and software.

Pulse generator

The pulse generator is able to produce pulses at 16 independent output channels with run accuracy in width and position. The pulses and inter-pulse distances cannot be shorter than 300 ns. The changes are simultaneous on all 16 channels. The time between the pulses can be increased up to 100 seconds, with 0.01%, but not less than 10 ns accuracy.

The information concerning the pulse sequence is stored in the memory of the generator, and a given trigger initiates the pulse generating process. There is a possibility to provide loops in the memory for cyclic pulse sequences. The number of runs in the cycle can be adjusted, and two loops can be generated simultaneously, one within the other.
Fig. 1. Pulse generating and signal receiving system

The generator has a HALT instruction to terminate the pulse sequence. There is a status register which informs the Q-BUS whether the pulse sequence is running or not. In addition, there is a possibility that on the output after the last change with 60 ns distance and 20 ns increase, every output channel is grounded.

**Gradient generator**

In order to study diffusion processes by the spin-echo technique [1-3] we must create a gradient of amplitude of magnetic field strength. This can be achieved by the use of a Helmholtz double coil with opposite current directions in the two coils. Another possibility is to use cylindric quadrupole coils for generating the gradient [4]. A quadrupole coil gives a gradient with constant components over a large volume and has around 10 times smaller inductance than that of a Helmholtz coil with the same gradient [5].

Our generator can produce gradients up to 120 G/cm over 3 cm³ (cylindrical shape) with independent adjusting of position and width of each gradient pulse (max 15 ms) in a spin echo diffusion measurement sequence. For measurement of diffusion coefficients in the presence of a background magnetic field gradient, we developed a generator which can produce alternating pulses of magnetic field gradient (see e.g. [6]).

**Flux stabilizer**

For measurement in NMR - especially in the case of a phase detected spin echo signal - the short time stability of \( H_0 \) must be as good as possible.

The large time constant of the electromagnet does not allow the regulator of the system to follow a correction signal, so fast fluctuations cannot be eliminated even with a NMR field stabilizer.

Fast changes of field can be detected by a coil with a great number of windings. Amplifying the signal of measured changes of flux and applying this signal to the next correction coil by current of opposite phase enables changes of the flux to be greatly reduced. In the realized equipment the short time field stability is better than 2.5 mG/h, for the case of sweep; swept linearity is of the order of \( 10^{-4} \).
For approximate stabilization of the magnetic field during the NMR experiment we use detection of dispersive resonance signal of NMR stabilizer [7,8] with a conventional phase detection-lock to the magnetic field.

By means of a flux stabilizer and shimming coils we can achieve long-term stability better than 20 Hz/24 h, and one coil of the probe can cover a range of nearly 10 MHz.

Better stability can be achieved by a frequency field lock, where free induction decay signal behaves as a voltage controlled oscillation, but in this case the basic requirement is excellent homogeneity of magnetic field in the volume overlapping spectrometer probe and stabilizer probe, which is easily obtainable by superconduction magnets. In this case the stability can be 0.1 Hz/h.

Modulator of NMR field stabilizer

For measurement of parameters of wide line NMR signals we have developed a frequency source with user defined frequencies, and a possibility to change at a given value by incrementation [9] (manually or via the computer) over the range of 300 kHz in 10 Hz steps, 10 MHz internal oscillator (short and long-term stability better than $10^{-8}$), or 10 MHz external oscillator.

In our case the used frequencies are: 10, 20, 30, 40 and 50 MHz.

References


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A novel spectroscopic technique - picosecond spectrochronography - a tool for measuring secondary radiation transient spectra with combined high spectral and temporal resolutions limited by uncertainty relation $\Delta \omega \cdot \tau \leq 1$, is described. The results of determining hot luminescence and exciton-polariton radiation of some systems, are summarized.

**Introduction**

When one studies secondary radiation of crystals, for more complete describing of physical processes of transformation by an object of primary energy flux into secondary one, besides its spectral features the temporal characteristics of the emitted light packet are of serious interest. From the experimental point of view the improvement of spectral instruments and low temperature techniques towards higher spectral resolution is needed as well as the development of temporal measurement methods of transient spectra - the temporal reaction of an object on pulse excitation - of higher speed, accuracy and sensitivity. The principally new trends have appeared after the introduction of lasers. It can be mentioned that the development of (sub)picosecond lasers has caused a new attitude towards the measurement of time-dependent spectra - one must keep in mind the statement that, when simultaneously determined, the limiting spectral and temporal resolutions are ruled by uncertainty relation $\Delta \omega \cdot \tau \leq 1$. Accounting of this fundamental law and its extensions leads us to necessity to term an appropriate secondary radiation measuring technique as (picosecond) spectrochronography [1]. This technique allows one, for example, to monitor various vibrational relaxation processes in condensed media, radiation from upper excited states, transfer, migration and transformation of energy in complex molecules etc.

**Experimental setup**

In practice the achievement of combined high spectral and temporal resolutions simultaneously with high sensitivity of registration is a serious problem. In solving it a number of unexplored technical difficulties have been overcome. Our picosecond spectrochronograph is an unique experimental setup [1,2], consisting of a synchronously mode locked CW dye laser providing a train (82 MHz) of tunable picosecond pulses, an emission-analyzing double monochromator in the subtractive dispersion mount and a synchroscan streak camera, followed by vidicon camera and optical multichannel analyzer connected to a data processing computer (see Fig.1). Here are the
Fig. 1. Experimental setup

Main numeric characteristics of the setup:
1) excitation band 345-420, 470-520, 685-850 nm;
2) average excitation power 200 mW (main frequency), 1 mW (second harmonics);
3) length of the transform-limited excitation pulses varied from 1 to 10 ps;
4) detection band 350-1100 nm;
5) energetic resolution (halfwidth of the spectral response function) 7 cm⁻¹;
6) typical temporal resolution (halfwidth of the time response function) 6-10 ps;
7) the best combined resolution ΔωΔτ≥3;
8) typical sensitivity 100 photons/s per the resolution element;
9) dynamical range 3·10³.

One of the main advantages of our system compared with setups, using single powerful picopulses, is a low peak power of the pulses from the CW train - only 1 kW at the main frequency and 10 W at second harmonics, that enables to excite only exclusively linear phenomena in the objects under in-
vestigation. This circumstance is essential in reliable study of the dynamics of the processes, for example, in photosynthetic units [3].

Results

Up to now we have applied our picosecond spectrochronograph to a number of various objects and problems. Herewith we discuss two of them.

Hot luminescence spectrochronography

We have a certain experience of vibrational relaxation study of aromatic polycyclic impurity molecules by measuring the relative intensities of hot luminescence (HL) lines under stationary excitation of secondary radiation [4]. Using picosecond technique it was possible in a straightforward way to measure appropriate spectrochronograms of guest perylene (see Fig.2) and

Fig. 2. Two views of the 3-dimensional spectrochronogram of secondary radiation of perylene in n-heptane at 4.2 K. Excitation at 395 nm, half-width of the excitation band 5 cm⁻¹, spectral width of the medium slit of spectrochronograph 31 cm⁻¹.
anthracene molecules in low temperature matrix of n-heptane. Here the picosecond decay times (15-30 ps) of HL lines express the vibrational relaxation of vibronic modes in excited electronic state [5]. The results coincide well enough with the data from steady state paper [4]. The thermal bath of matrix modes allows the excited molecules to lose its energy exceeding the thermal quantity by exchange using the phonons of n-paraffin.

In the case of F-centres in alkali halide crystals with strong electron-phonon coupling, the lack of structured HL in appropriate spectrochronogram manifests the relaxation of such excited states taking place in time domain of order 100 fs [6].

**Electron-polariton radiation spectrochronography**

Anthracene is a model organic crystal that exhibits a number of prominent effects of formation of secondary radiation of pure crystal. We have measured the resonance secondary radiation spectrochronograms of anthracene in the range of the bottom of exciton band [7] and have determined the polariton dispersion curve near the resonance using the method of time-of-flight of light picopulses through a thin crystal [8]. It has been cleared up, when exciting deeply into exciton band, three stages of relaxation of polaritons with different time scale <1 ps, 10-100 ps and 1 ns can be distinguished. First, by scattering at optical phonons a comparatively broad energetic distribution of polaritons near the "bottleneck" of the dispersion curve is formed; second, a sharp (4-5 cm⁻¹) distribution of polaritons near the resonance appears; third stage results in polaritons going down through the "bottleneck". The last process is roughly speaking similar to the radiative decay of free molecules.

**References**

ROTATIONAL CONTRIBUTION TO THE VIBRATIONAL BANDSHAPE OF ORDERED SYSTEMS

N. KIROV¹, I. DOZOV¹, M.P. FONTANA² and B. ROSI²

¹ Institute of Solid State Physics 72 Blvd. Lenin, Sofia 1784, Bulgaria
² Department of Physics 85 M. d'Azeglio, Parma 43100, Italy

Fourier analysis of IR and Raman bands is used to obtain the reorientational correlation functions of aligned anisotropic fluids. New equations for evaluation of the rotational contribution to the total bandshape of IR and Raman bands are suggested.

Introduction

One important and principal problem in the vibrational spectroscopy is the separation of the rotational relaxation from the vibrational part which usually encompasses all non-orientational contributions to the correlation functions. It is generally assumed that the rotational broadening mechanism predominates for small molecules in pure liquids or dissolved in inert solvents while the vibrational effects are preponderant in the case of heavy polyatomic and associated species. However, the quantitative evaluations of rotational contribution to the total vibrational bandshape are scarce and usually discuss small molecules in isotropic media [1].

In the present paper we report new expressions for the rotational relaxation contribution to IR and Raman bands in terms of the rotational diffusion coefficients $D^T_{||}$ and $D^T_{\perp}$ (which are in turn connected with the reorientational relaxation times $\tau^T_{||}$ and $\tau^T_{\perp}$) and the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ - the two lowest order coefficients in the molecular orientational distribution function [2] in anisotropic aligned fluids composed of rod-shaped molecules.

Correlation functions and rotational relaxation contribution to the bandshape

The molecular dynamics in ordered systems is governed by two main factors: i) the rotational diffusion tensor which for uniaxially aligned species reduces to a good approximation to the spinning ($D^T_{||}$) and tumbling ($D^T_{\perp}$) diffusion coefficients and, ii) the statistical orientation described by the order parameters [2].

IR absorption

In this case we calculate the Fourier transforms of suitable bands in both polarization geometries of the incident light - parallel and perpendicular to the axis $z$ of the uniaxial alignment. The order parameter $\langle P_2 \rangle$ is determined independently from the dichroic ratio of a strongly longitudinally polarized absorption band. Within a decoupling approximation of the vibrational and rotational contribution to the total bandshape, by taking the ratio $a_z(t)/a_x(t)$ or equivalently the difference in their natural loga-
rithms, we automatically exclude the vibrational relaxation \([3]\). For cylindrically symmetric molecular potential in the short-time-limit approximation the rotational contribution \(\delta^\tau\) to the halfwidth is:

\[
\delta^\tau = \delta_x - \delta_z = \frac{\langle P_2 \rangle}{\Pi c} \left( \frac{D^\tau_{||} - D^\tau_{\perp}}{D^\tau_{||}} \right) = \frac{\langle P_2 \rangle}{\Pi c} \left( \frac{D^\tau_{||} - D^\tau_{\perp}}{D^\tau_{||}} \right)
\]

for bands with \(R \gg 1\) \((1a)\)

\[
\delta^\tau = \delta_x - \delta_z = \frac{9 \langle P_2 \rangle}{\Pi c(1-\langle P_2 \rangle)(1+2\langle P_2 \rangle)} \cdot D^\tau_{\perp}
\]

for bands with \(R \gg 1\) \((1b)\)

\[
\delta^\tau = \delta_x - \delta_z = \frac{9 \langle P_2 \rangle}{\Pi c(1-\langle P_2 \rangle)(2+\langle P_2 \rangle)} \cdot D^\tau_{\perp}
\]

for bands with \(R \ll 1\) \((1c)\)

where \(R\) is the dichroic ratio of the band.

In the framework of biaxial molecular potential, i.e. \(C_{2v}\) effective molecular symmetry (more details are available in \([4]\) ), Eq. \((1a)\) remains the same, as it is expected. For weakly polarized bands the rotational contribution is:

\[
\delta^\tau = \frac{18yD^\tau_{\perp} + (10y + \langle P_2 \rangle)(D^\tau_{||} - D^\tau_{\perp})}{\Pi c(1-2y)(1+4y)}
\]

\((2b)\)

where \(y = \cos 2\Phi \langle D^2_{02} \rangle / \Pi c\), \(\langle D^2_{02} \rangle\) being the biaxial order parameter.

Considering that \(y \ll \langle P_2 \rangle\) the corrections are small. For strongly transversally polarized modes there is a drastic qualitative correction:

\[
\delta^\tau = \frac{-9D^\tau_{||}(\langle P_2 \rangle - 6y) + 36(D^\tau_{||} - D^\tau_{\perp})y}{\Pi c(1-\langle P_2 \rangle + 6y)(2+\langle P_2 \rangle - 6y)}
\]

\((2c)\)

since the new term depending on \(D^\tau_{||} - D^\tau_{\perp}\) can be rather large because \(D^\tau_{||} \gg D^\tau_{\perp}\).

For weakly polarized bands \((0.6 < R < 2)\) whose transition dipole moment vector can move with molecular rotation around the long molecular axis (spinning motion) the rotational halfwidth at the beginning of the ordered phase (where \(\langle P_2 \rangle\) is highest, typically 0.6-0.7) is 1.5 - 3 cm\(^{-1}\), the \(x\) component being larger. For strongly transversally polarized modes \((R < 0.4)\) the rotational contribution is also between 2 and 4 cm\(^{-1}\), the \(z\) component being larger. The strongly parallel bands \((R > 5)\) are modulated by the hindered rotation around the short axes (tumbling motion). The reorientational part of the halfwidth of these modes is small - 0.2-0.4 cm\(^{-1}\). In general the rotational contribution to the total bandshape decreases with increasing molecular weight.

**Raman scattering**

In Raman scattering we record the intensities \(I_{ik}\) of the investigated bands at three scattering geometries, where \(i,k\) are the polarizations of the incident and scattered light respectively (for more details the reader is referred to \([5]\)). We then take their Fourier transforms and the total polarizability correlation functions contain both the vibrational and rota-

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tional contribution to the total bands shape. In the Raman case, however, the connection between vibrational modes and the specific correlation functions is not so simple as in the IR absorption, where the rod-shaped molecules feature well defined parallel or perpendicular bands. The equations for the halfwidth of Raman lines are complex since both the polarizability tensor components and the angle between the vibrational transition moment and the main molecular axis should be known. In the most general case the molecular differential polarizability tensor could be diagonalized:

$$\mathbf{\lambda} = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1-a-b \end{pmatrix},$$

where its main component concludes an angle $\theta$ with the long molecular axis. The most interesting from the point of view of molecular reorientation are tensors with $a$ and $b$ much smaller than 1 since in this case the rotational contribution to the total bands shape is largest and highly anisotropic. For the case of non-uniaxial polarizability tensor ($a \neq b \neq 0$) concluding an arbitrary angle $\theta$ with the long molecular axis the equations connecting the halfwidth with the orientational order parameters and rotational diffusion coefficients are very complex (much more complex than the corresponding expressions in the IR case) and we will not report them here. We shall present here the more simple case of highly anisotropic tensor ($a \equiv b \equiv 0$) with arbitrary $\theta$. In the framework of the cylindrically symmetric molecular potential we have:

\begin{align}
\delta_{xx} &= \delta_y + \frac{4}{9} \left[ (Dz' - Dz) (14(1-P_e^2)(1+\langle P_2 \rangle/2) -3(\langle P_2 \rangle^2 - \langle P_4 \rangle)(\langle P_2 \rangle + 3\langle P_4 \rangle)/7) + \\
&+ \left. 6Dz' (7-5\langle P_2 \rangle/2 - 9\langle P_4 \rangle/2) \right] / \left[ \Pi c(7-10\langle P_2 \rangle + 3\langle P_4 \rangle) \right] \tag{3a} \\
\delta_{xy} &= \delta_y + \left[ (Dz' - Dz) (14(1-P_e^2)(1+\langle P_2 \rangle) - 72(\langle P_2 \rangle^2 - \langle P_4 \rangle)(\langle P_2 \rangle + 3\langle P_4 \rangle)/7) + \\
&+ \left. 6Dz' (7-5\langle P_2 \rangle - 2\langle P_4 \rangle) \right] / \left[ \Pi c(7-10\langle P_2 \rangle + 3\langle P_4 \rangle) \right] \tag{3b} \\
\delta_{xz} &= \delta_y + \left[ (Dz' - Dz) (14(1-P_e^2)(1-\langle P_2 \rangle/2) + 36(\langle P_2 \rangle^2 - \langle P_4 \rangle)(\langle P_2 \rangle + 4\langle P_4 \rangle)/7) + \\
&+ \left. 6Dz' (7+5\langle P_2 \rangle/2 + 8\langle P_4 \rangle) \right] / \left[ \Pi c(7+5\langle P_2 \rangle - 12\langle P_4 \rangle) \right] \tag{3c} \\
\delta_{zz} &= \delta_y + \frac{4}{9} \left[ (Dz' - Dz) (14(1-P_e^2)(1-\langle P_2 \rangle^2) + 72(\langle P_2 \rangle^2 - \langle P_4 \rangle^2)(\langle P_2 \rangle - \langle P_4 \rangle)/7) + \\
&+ \left. 6Dz' (7+5\langle P_2 \rangle - 12\langle P_4 \rangle) \right] / \left[ \Pi c(7+20\langle P_2 \rangle + 8\langle P_4 \rangle) \right] \tag{3d} \\
\end{align}

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where \( P_n^\Theta = P_n(\cos \Theta) \) are the Legendre polynomials. Eqs (3a) - (3d) contain both vibrational and rotational relaxation contribution but since the vibrational part \( \delta_v \) is equal for all four equations it can be easily accounted for. In contrast to the IR case the reorientational part of the Raman bands depends not only on \( \langle P_2 \rangle \) but also on \( \langle P_4 \rangle \). In the simplest case \( \Theta = 0 \) the expressions (3a) - (3d) reduce to the more simple equations already reported in [5].

The anisotropic contribution to the Raman modes associated with tensor with large \( \Theta \) is \( 2 - 4 \) cm\(^{-1}\). Such vibrations are all benzene ring out-of-plane deformations, aromatic part - substituent bendings, alkyl chain rocking, various torsional modes and many other vibrations below 800 cm\(^{-1}\). The anisotropic contribution to the halfwidths of these lines is usually bigger than the reorientational part of the corresponding IR modes. The rotational influence on the Raman bands with \( \Theta = 0 \), e.g. all triple and double bond valence vibrations, benzene ring stretch and in-plane deformations and other modes in the spectral range 1000-2500 cm\(^{-1}\) is, like in the IR case, very small - 0.2-0.4 cm\(^{-1}\).

In the framework of biaxial molecular orientational potential significant differences between the IR absorption and Raman scattering appear. The spinning rotational contribution to the IR halfwidth is compensated for \( \Theta = 90^\circ \) if an uniaxial potential is adopted (Eq. (1c)). In the biaxial case this compensation does not play almost any role and therefore Eq. (2c) differs completely from Eq. (1c). In the Raman scattering there is no such compensation and the corrections due to the molecular biaxiality lead only to small quantitative effects on the rotational contribution to the Raman halfwidths.

**Conclusion**

In this paper we have shown the applicability of the Fourier bandshape analysis to the calculation of reorientational dipole and polarizability correlation functions from the IR and Raman spectra of aligned systems. The proposed equations, applicable for all types of ordered systems with rotational degree of freedom, solve one very important spectroscopical problem - to evaluate or even to predict the rotational contribution to the total bandshape of IR and Raman bands.

**References**

СОВРЕМЕННОЕ СОСТОЯНИЕ МИКРОВОЛНОВОЙ СПЕКТРОСКОПИИ

Б.С. ДУМЕШ
Институт спектроскопии АН СССР
Московская обл., г. Троицк, СССР

Современное развитие техники микроволновой (МВ) спектроскопии характеризуется в основном доведением до высоких эксплуатационных параметров разработок 70-х годов. В данной работе будет рассмотрен современный статус универсальных МВ спектрометров на разные диапазоны длин волн, а именно: импульсных МВ спектрометров, спектрометров с радиоакустическим детектированием (РАД) и спектрометров двойного МВ-МВ резонанса.

СВЧ диапазон

В этом диапазоне наиболее высоких характеристик достигнули импульсные МВ спектрометры. Хотя первый такой спектрометр был построен в 1986 [1], большое развитие эти установки получили в последние годы в связи с работами группы Флайгера [2], разработавшей высокочувствительные импульсные МВ спектрометры с Фурье преобразованием сигнала (ФС). Этим спектрометрам принадлежит современный "рекорд" чувствительности для одночастотных МВ спектрометров - измеренные линии поглощения в метане с коэффициентом поглощения $\gamma = 2.5 \times 10^{-12}$ см$^{-1}$ [3].

Принцип импульсной МВ спектроскопии состоит в регистрации переходного излучения молекулярного перехода, возбужденного коротким резонансным СВЧ импульсом. Это излучение, аналогичное свободной индукции в случае ЯМР и ЭПР, называется сверхизлучением или когерентным спонтанным излучением [1]. По сравнению со стационарными методами МВ спектроскопии импульсные схемы позволяют в единичном измерении сравнительно широкий спектральный интервал $\Delta f = \tau^{-1}$, где $\tau$ - длительность возбуждающих импульсов, позволяют упростить СВЧ тракт и не нуждаются в модуляции. Недостатком этих схем является необходимость супергетеродинного приема сигнала и усложнение периферийных частей МВ спектрометра.

Принципиальным новшеством схемы Флайгера являлось создание импульсного МВ спектрометра, базирующегося на когерентной последовательности возбуждающих СВЧ импульсов. Использование такой последовательности позволяет с помощью процедуры синхронного детектирования сузить полосу приема, и тем самым увеличить чувствительность спектрометра в фактор $(T_2/\tau)^{1/2}$ [2] $(T_2$ - время релаксации) по сравнению с непрерывными и некогерентными импульсными спектрометрами. Кроме того, хорошая привязка СВЧ импульсов по частоте позволяет с высокой точностью производить процедуру Фурье преобразования временных зависимостей переходного излучения и получать высокое спектральное разрешение $\Delta f << \tau^{-1}$.

Ф.С. [2] строится по классической схеме с раздельными возбуждающими генераторами и гетеродином, связанными между собой системой фазовой автоподстройки частоты. Когерентная последовательность возбуждающих импульсов создается внешней модуляцией излучения непрерывного СВЧ генератора с помощью системы...
ключей на pin-диодах. Требования к ключам довольно высоки, так как уровень просачивающегося между импульсами излучения должен составлять 100 дБ от величины импульсов. Диапазон таких ФС составляет 4-40 ГГц. Одно из наиболее успешных направлений их использования - сочетание с импульсной молекулярной стреу для изучения молекулярных комплексов [4].

Недавно появилась оригинальная модификация импульсного ФС, позволяющая расширить его частотный диапазон до 150 ГГц [5]. В данном случае когерентная последовательность возбуждающих импульсов создается когерентным смешиванием второй гармоники мощного задающего генератора с излучением радиочастотного генератора.

Субмиллиметровый диапазон

Этот диапазон привлекателен большими величинами коэффициентов поглощения $\gamma \propto z^3$ (соответственно, большой чувствительностью по количеству молекул) и большой величиной центробежных эффектов. На этот диапазон разработан оригинальный вариант импульсного МВ спектрометра [6], в котором также как и в схеме [1,5] роль возбуждающего и гетеродинного генератора выполняет один СВЧ источник (ЛОВ). Однако здесь перенос частоты от возбуждающих импульсов к гетеродинным производится электронным управлением частоты генератора. Такой метод позволяет более эффективно использовать мощность СВЧ генератора, и тем самым продвинуться в субмиллиметровый диапазон.

В настоящее время чувствительность спектрометра [6] составляет $\gamma_m = 10^{-7}$ см$^{-1}$, что еще достаточно далеко от теоретического предела. Однако следует отметить, что в силу некогерентного характера возбуждающих СВЧ импульсов, в данном случае нельзя организовать синхронное детектирование сигнала по промежуточной частоте и теоретическая чувствительность спектрометра [6] в фактор $(T_2/\tau)^{1/2}$ хуже, чем для ФС.

Другим перспективным спектрометром этого диапазона является спектрометр с акустическим детектированием (РАД) [7]. В этой установке детектирование поглощения осуществляется аналогично известному приемнику ИК излучения - ячейке Голея [8], но в данном случае поглощающим элементом является исследуемый газ. При этом поглощение СВЧ поля и излучение акустических колебаний происходит только на его линиях поглощения. Основным преимуществом такого метода детектирования является слабая чувствительность к неоднородностям частотных характеристик источника и СВЧ тракта. Недостатком - низкое ($\delta f > 10$ МГц) разрешение, связанное с повышенным ($p \geq 133$ Па) рабочим давлением исследуемого газа.

Размер поглощающей ячейки РАД ограничен необходимостью согласования акустических импедансов газа и мембраны детектора и составляет 10 см. Поэтому чувствительность спектрометра с однопроходной поглощающей ячейкой в силу малости ее "оптической" длины невелика и составляет $\gamma_m = 10^{-7} \cdot 10^{-8}$ см$^{-1}$. Недавно авторы РАД создали многопроходную поглощающую ячейку в виде открытого резонатора (типа Фабри-Перо) с добротностью $10^4$, и тем самым увеличили...
эффективную длину ячейки до 10 м. В результате чувствительность спектрометра РАД выросла до 10^{-10} см^{-1} [9].

Дециметровый диапазон длин волн

Преимуществом этого диапазона является очень высокое абсолютное разрешение даже в случае обычных газовых поглощающих ячеек (6f ≈ 1 кГц), сравнимое с разрешением установок, использующих хорошо коллимуируемые молекулярные пучки, однако вследствие малости коэффициентов поглощения молекулярных переходов для работы в этом диапазоне требуется очень высокая чувствительность. При этом чувствительность стандартных для этого диапазона ЯКР спектрометров недостаточна для решения широкого круга задач.

Основные способы повышения чувствительности — использование высокодобротных поглощающих ячеек и методики двойного резонанса, которая позволяет увеличить интенсивность сигнала приблизительно в фактор f_p/2f_s, где f_p, f_s — частоты накачиваемого и сигнального перехода соответственно. Если накачиваемый переход лежит в СВЧ диапазоне, где мощность источников излучения достаточно для насыщения перехода, фактор усиления может составлять 10 \approx 50.

Спектрометр двойного MB-РЧ резонанса с высокодобротной поглощающей ячейкой построен Б.Д.Осиповым и успешно эксплуатируется в ИСАЯ СССР [10]. В последние годы на нем проведены широкие исследования сверхтонкой структуры вращательных спектров в молекулах типа симметричного волчка с разрешением 1 кГц. Наиболее слабые линии, зарегистрированные в этих экспериментах, имеют \gamma \approx 2 \times 3 \times 10^{-12} см^{-1} [11]. В отличие от спектрометров, использующих молекулярные пучки, данная установка позволяет измерять спектры с большими значениями вращательного квантового числа.

Таким образом в последние годы разработаны MB спектрометры универсального применения с повышенными параметрами по чувствительности и, отчасти, по разрешению, перекрывающие весь микроволновый диапазон длин волн. На данном этапе, как представляется, задача состоит в более широком применении этих установок в спектроскопической практике.

Литература

FT-IR SPECTROSCOPY IN CATALYSIS

J. MINK
Institute of Isotopes of the Hungarian Academy of Sciences
1525 Budapest, Hungary

Supported metal catalysts are opaque to infrared rotation generally below 1200 cm$^{-1}$ thereby preventing all the very important vibrations involving surface-adsorbate or "metal-ligand" motions from being observed by the conventional transmission technique. The possible methods which do not suffer from these limitations are summarized in this paper.

Introduction

The usefulness of vibrational spectroscopy in identifying surface species, determining adsorbate structures and studying surface reactions has been widely demonstrated. Relatively fast progress became possible with the development of the FT-IR technique in the 1970's. Most of the infrared work on surface species is currently performed using the transmission technique with very thin pressed discs of supported metal catalysts.

Although hundreds of papers are published annually on this topic, nearly all are restricted to a narrow range of the infrared spectrum. Support materials (silica, alumina, zeolites, etc.) do not transmit infrared radiation in the low frequency region (below about 1200 cm$^{-1}$). Above this only a few vibrational features are observable in most cases. All vibrations involving the surface-adsorbate linkage or simply the metal-"ligand" motions are inaccessible. Consequently there is only a small amount of vibrational information on adsorbed molecules pertaining to the low frequency region. Alternative methods which do not suffer from this limitation are diffuse reflectance (DR), photoacoustic spectroscopy (PAS) and infrared emission or Raman spectroscopy.

Diffuse reflectance and photoacoustic spectroscopy

For many years diffuse reflectance and photoacoustic techniques have been used in the UV and visible regions by virtue of the availability of highly sensitive detectors and high power sources. Recently these spectroscopic techniques have been extended into the infrared region because of the development and fast progress in FT-IR instrumentation.

A cell and an optical configuration for measuring diffuse reflectance Fourier transform infrared spectra of adsorbed species at high sensitivity were described by Griffiths et al [1]. The heatable and evacuable cell permits the activation and treatment of catalysts and adsorbents in situ. The optical design allowed for the collection of over half of the diffusely reflected radiation from the sample. DR/FT-IR spectra of CO on 1% and 5% Rh/Al$_2$O$_3$ have been studied. Two strong bands around 2010 and 1850 cm$^{-1}$ were...
detected due to the linearly bonded and bridged CO, respectively. Based on these data it was concluded that adsorbed CO present at about $10^{-4}$ monolayers may be observed using the cell and optics described [1].

DR/FT-IR spectroscopy has been used to study surface groups on activated carbon during oxidative treatment in situ in an evacuable IR cell [2]. Several allyl carbonyls and surface carboxylate ions were detected after treatment in oxygen at a number of different temperatures.

Both of the teams ([1] and [2]) recorded the spectra down to 600 cm$^{-1}$, but for studying lower wavenumbers a helium-cooled germanium bolometer could be used. Up to now there are no reported spectroscopic results in the far-infrared region.

Photoacoustic spectroscopy has become popular comparatively recently in FT-IR spectroscopy [3]. The process at solid surfaces can be measured by this technique. The main difficulty in studying adsorbed species on supported catalysts is that the sample has to be enclosed in an evacuable cell. Kinney and Staley [4] have described a photoacoustic cell designed for temperature (-60°C - 100°C) and atmosphere control in chemical studies. The spectrum of CO on alumina-supported platinum showed a strong peak at 2060 cm$^{-1}$ and a weaker, broad peak at about 1820 cm$^{-1}$ which correspond to the CO stretching mode of "linearly" and "bridge" bonded CO molecules, respectively. High sensitivity is observed with relatively little sample preparation. Data collection times are short and the potential for observing in situ reactions is certainly interesting. The PAS spectra were recorded in the range of 4000-500 cm$^{-1}$. Despite the strong absorbance by the support, which makes conventional transmission techniques impractical, the low frequency region (below 1000 cm$^{-1}$) can also be studied. No report is available on such experimental results.

It is clear that the properties of PAS make it a potentially valuable tool for studying surface species. This capability has been demonstrated in other papers as well [5-8].

Emission spectroscopy

In contrast to DR and PAS the emission infrared spectroscopic technique has been fairly well-known for a considerable time but to avoid sample decomposition or desorption the heating should not be much higher than room temperature. In view of this, the radiation energy is very low and therefore highly sensitive IR spectrometers are required. Since the pioneering work by Eischens and Pliskin [9] in 1956, only a few attempts have been made to carry out emission studies of adsorbed species [10-12]. Here we report our results of infrared emission measurements of the CO molecules adsorbed on Pt/Al$_2$O$_3$ catalysts (partly published under ref. [13]).

The impregnated (1% wt. metal) Al$_2$O$_3$ (Degussa) sample was treated at 470 K under H$_2$ for two hours, then cooled to 420 K. After evacuation of the cell 70 Pa CO was added, and infrared emission spectra were recorded using a Digilab FTS-20C spectrometer with a room temperature TGS detector. The single
beam spectra were rationed against the spectra of the initial supported metal catalysts. Table I summarizes the results of double beam emission spectra of chemisorbed CO on Pt/Al₂O₃. A very strong band at 2043 cm⁻¹ is assigned to the stretching mode of CO linearly bonded to Pt°, and a weak band at 2115 cm⁻¹ is assigned to the same species bonded to an oxidized surface Pt⁺ atom. This means that the reduction of platinum under H₂ was not perfectly carried out. The broad band near 1800 cm⁻¹ refers to the CO stretching of bridged or multicentered carbon monoxide. The weak bands at 1650, 1450 and 1230 cm⁻¹ assigned to surface carbonate groups.

Low frequency very weak bands at 457 and 437 cm⁻¹ can reasonably be assigned to stretching vibrations of Pt°-C and Pt⁺-C, respectively. The difference between emission and transmission measurements in CO frequencies can be attributed either to different coverage or to a difference in support. From PtC stretching force constants it could be concluded that CO is more tightly bound to Pt/SiO₂ than to Pt/Al₂O₃ or Pt/NaY.

For comparison purposes Table I contains some spectroscopic data of [Pt(CO)Cl₃]⁻ anion.

Table I

| Stretching frequencies (cm⁻¹) and calculated force constants (Ncm⁻¹) for adsorbed CO on supported Pt and [Pt(CO)Cl₃]⁻ anion |
|---|---|---|---|---|---|
| Stretching vibrations and force constants | Pt/Al₂O₃ | Pt/SiO₂ | Pt/NaY | [Pt(CO)Cl₃]⁻ solution |
| | emission (420 K) | transmission (300 K) | emission (383 K) | (ref 14) |
| Pt⁺ CO str (a) | 2125 w | 2043 vs | 2098 vs | 2070 s |
| Pt⁺ CO str (b) | - | 1800 m,b | 1850 w,b | 1850 w,b |
| PtC str (a) | 437 vw | 457 w,b | 475 (475) | 465 m |
| PtC str (b) | - | 523 vw(?) (569) | 580 w(?) | 504 sh |
| K(CO) (a) | 18.2 | 16.9 | 16.5 | 17.3 |
| K(CO) (b) | - | 13.1 | 12.6 | 13.8 |
| K(PtC) (a) | 2.92 | 3.53 | 3.72 | 3.34 |
| K(PtC) (b) | - | 5.25 | 5.34 | 4.85 |

Remarks: Calculated frequencies are shown in brackets, (a) linearly bonded CO, (b) bridged or multicentered CO group, (c) experimental data taken from ref.[15], (d) experimental data taken from ref.[11].

The charge and the oxidation state of the metal in the anion are very different from those on metal surfaces; nevertheless, there are marked similarities between the spectroscopic data for the two cases. Comparison between the CO stretching band intensities from the emission and transmission techniques shows that the emission bands are considerably

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weaker at the same coverage. This indicates that the detectable emission signal originating from that part of the catalyst's surface that was facing the interferometer, and the emission from deeper in the sample was either being readsorbed or scattered. This limitation, however, does suggest that it should be possible to measure the emission from species chemisorbed onto metal single crystal surfaces or on evaporated metal films. Modifications such as the development of more efficient light-collecting optics would enhance the usefulness of emission measurements for studying adsorbed species.

Conclusions

One of the main advantages of these three measurement methods is that no or nearly no sample preparation is needed. All three techniques are able to cover the full mid-IR range (4000-400 cm\(^{-1}\)), and catalysts can be studied in situ near to reaction conditions. Opaque samples can also be studied but for DR the sample must have a good scattering surface or it must be possible to pulverize it. However, DR spectroscopy has an important advantage over PAS in that the sensitivity for pulverized samples is much better. Emission spectroscopy is a true surface technique and can be adapted to samples of widely different shape. Even at the present stage of development, IR emission spectroscopy is useful for studying real catalysts in the presence of adsorbates and at reasonably high catalytic temperatures. A wider knowledge of the low frequency part of the spectrum, which includes all molecule-substrate vibrations, should permit a deeper understanding of the structure and bonding of the surface species. Many further developments of all three techniques are expected in the future.

References


Acta Physica Hungarica 61, 1987
PICOSECOND STUDIES OF RELAXATION PROCESSES IN SEMICONDUCTORS

H. BERGNER, V. BRUCKNER, L. LEINE and M. SUPIANEK
Friedrich-Schiller-Universität Jena, Department of Physics
DDR 6900 Jena, Max-Wien-Platz 1, GDR

We studied relaxation processes in high excited silicon by transient reflectivity and transmission. Changing the excitation wavelength it is possible to separate the influence of different relaxation processes as surface and bulk recombination and diffusion on the measured carrier dynamics.

The used well-known excite and probe technique is based on the generation of free carriers by a laser pulse and the test of the photoinduced optical properties by a time delayed probe pulse. The transient reflectivity and absorption changes are caused by the temporal and spatial behaviour of the generated non-equilibrium charge carriers. Reflectivity and transmission contain different information about the relaxation, so reflectivity is more sensitive to surface processes, transmission integrates over the bulk and surface processes.

![Fig.1. Experimental setup](image)

Our experimental setup was chosen in such a way, that both the changes in reflectivity as well as in the absorption coefficient are proportional to the induced carrier concentration. We have measured simultaneously time-resolved reflectivity and transmission in n-doped silicon (100) wafers of d = 200 μm thickness using a ps Nd-YAG laser equipment with a tuning range from 400 nm to 1600 nm.
In the first experiment a homogeneous carrier distribution was generated in the whole bulk because of the weak absorption (\(\alpha = 10 \text{ cm}^{-1}\)) of the used excitation wavelength \(\lambda_{\text{ex}} = 1064 \text{ nm}\). The induced absorption measured at \(\lambda_p = 1500 \text{ nm}\) is constant in the investigated time range corresponding to the known bulk recombination time of some \(\mu\text{s}\) (Fig. 2a). Another behaviour was found exciting the sample by pulses of \(\lambda_{\text{ex}} = 532 \text{ nm}\). In this case only a small layer near to the surface was excited because of strong absorption (\(\alpha = 8 \cdot 10^3 \text{ cm}^{-1}\)).

That means the measured relaxation of the induced transmission changes is due to surface recombination (crosses in Fig. 2b). The simultaneously measured reflectivity changes show a faster relaxation (Fig. 2b - circles). The reflectivity detects only the carriers near to the surface. The strong absorption of the excitation radiation generates a carrier concentration profile with respect to the direction perpendicular to the surface. This gives rise to a diffusion process into the bulk diminishing the carrier concentration at the surface within a diffusion time \(t_D = 0.59/D\alpha^2\) [\(\alpha\)], where \(D\) is the ambipolar diffusion constant. This diffusion process determines the temporal behaviour of the reflectivity additional to the surface recombination, whereas the transmitted pulse cannot check this process.

In a second experiment we have proved the influence of the induced carrier profile on the time behaviour of the reflectivity changes by changing the excitation wavelength. In the case of infrared excitation...
generated and no diffusion takes place. The temporal behaviour is due to surface recombination (Fig. 3a). Changing the excitation wavelength \( \lambda_{ex} = 532 \text{ nm}, \alpha = 8 \cdot 10^3 \text{ cm}^{-1} \) the induced carrier profile gives rise to an additional diffusion process and the measured relaxation became faster (Fig. 3b). In the case of a steeper profile \( \lambda_{ex} = 450 \text{ nm}, \alpha = 2 \cdot 10^4 \text{ cm}^{-1} \) the diffusion time has to become smaller as can be seen in Fig. 3c.

To obtain characteristic parameters of the semiconductor processes (surface and bulk recombination and diffusion constant) we solved the inhomogeneous differential equation describing the temporal and spatial behaviour of the photoexcited carrier concentration \( N(x, t) \) numerically

\[
\frac{\partial N(x, t)}{\partial t} - \frac{D}{\partial x^2} N(x, t) + \frac{N(x, t)}{\tau} = G(x, t).
\]  

(1)

\( D \) is the ambipolar diffusion constant, \( \tau \) is the carrier lifetime, is the direction into the depth, and \( G(x, t) \) describes the generation by the laser pulse. The boundary conditions are

\[
\frac{\partial N(x, t)}{\partial x} \bigg|_{x=0} = \frac{E}{D} N(0, t)
\]

(2)

\[ N(d, t) = 0. \]

(3)
Eq. (2) describes the influence of the surface recombination velocity \( s \). To fit the results of reflectivity measurements the calculated value \( N(x=0, t) \) was used because the reflected beam probes only a small layer near to the surface. To fit the transmittance experiments we have to take into account all generated carriers in the whole bulk because

\[
\ln \frac{T}{T_0} = C \int_0^d N(x, t) \, dx
\]

is valid, where \( T \) and \( T_0 \) are the transmission of the probe pulse with and without excitation, respectively, and \( C \) is a constant.

From the fitting process we find in both experiments a bulk recombination time greater than our maximum delay time corresponding to the known bulk recombination time in monocrystalline silicon of some \( \mu \)s.

The best fit of the diffusion process was obtained at \( D = 18 \text{ cm}^2/\text{s} \) which is the value of the ambipolar diffusion constant in silicon in the non-degenerated semiconductor. The surface recombination velocity was \( s = 5 \times 10^4 \text{ cm/s} \) (Fig. 2) and \( s = 2 \times 10^5 \text{ cm/s} \) (Fig. 3), respectively. The numerically calculated temporal behaviour of reflectivity and transmission changes using the parameters mentioned above are depicted in Fig. 2 and 3 as solid lines.

References
APPLICATION OF ATOMIC SPECTROSCOPY TO TRACE ANALYSIS

K. DITTRICH, B. HANISCH and H.-J. STÄRK
Kar1-Marx-Universität Leipzig, Sektion Chemie, WB Analytik, DDR-7010 Leipzig, Talstr. 35, G.D.R.

The formation of stable diatomic molecules in graphite tube furnaces is described. Systematic studies of the application of atoms and diatomic molecules (MX-type) for trace analysis of metals and non-metals (X) were carried out. Results are given for molecular absorption with electrothermal evaporation (MAS-ETE). Principles of "over-excitation" for improvement of detection limits of metals and non-metals are applied. The application of the non-thermal FANES excitation leads to the development of the new method MONES-ETE (molecular non-thermal excitation spectrometry with electrothermal evaporation). The application of the principle of laser excited fluorescence leads to the new method LAMOFS-ETE (laser excited molecular fluorescence with electrothermal evaporation) (similar to LAFS-ETA).

Introduction

The development of atomic absorption spectrometry (AAS) with electrothermal atomization (ETA) was initiated by the studies of L'vov [1] and continued by Massmann [2]. Due to the extraordinary good absolute detection limits (pg range) and the possibility using microsamples, this technique has become over the last decade the leading technique for determination of individual elements - mainly metals.

Because of the initially great success, systematic studies of interferences etc. were hardly carried out over the first few years. It became apparent very soon, however, that both the signals and the background were strongly affected by the matrix and by the parameters of vapour generation. This leads to a poor accuracy.

Of particular importance is the fact that there are only temperatures up to 3,300 K in the tubes and negative temperature gradients between the sample holder and the vapour. Chemical matrix interference causes the change of free atom concentration of the analyte by incomplete or accelerated evaporation, molecule formation and dissociation. The background is influenced by stray light, continuous emission of incompletely vaporized particles and light emission and absorption by incompletely dissociated small - mainly diatomic - molecules. This all leads to problems in the accuracy. Another disadvantage of the AAS-ETA lies in the fact, that nonmetals can not be determined successfully. In this publication we will deal with new possibilities for analytical determination of metals and nonmetals using non-thermal excitation.

Quantitative determination of nonmetals by molecular absorption spectrometry (MAS) in electrothermal generated vapours in graphite furnaces

General aspects

Parallel and independent studies on the use of electrothermally heated graphite tube furnaces for the determination of nonmetals by MAS using diatomic molecules were undertaken in Acta Physica Hungarica 61 (1), pp. 79—82, 1987
Akadémiai Kiadó, Budapest
our laboratory [3-6] and in those of Haraguchi and Fuwa [7-13]. By analogy with the abbreviation of AAS-ETA the abbreviation MAS-ETE was introduced by us [14].

**Procedure**

The method is extremely simple. The sample solution containing the anion (X) to be determined is mixed with an added substance (M) with which this anion forms stable diatomic molecules (MX). Microvolumes of these solutions are introduced into the graphite furnace. After dosage the thermal program ensues: drying - ashing - evaporation (here better than atomization in AAS). The molecules are generated in last phase and the MA may be measured.

**Analytical results of pure solutions**

In Table I our results for determination of halides and sulphur are shown. The results show that AlX molecules gave the best analytical values for halogens. Because the basicity of $\text{Al}^{3+}$ is weak, addition of $\text{Ba(OH)}_2$ as matrix modifier is useful to avoid X losses by thermal hydrolysis. Optimal conditions: 1 μg Al, 30 μg Ba/10 μl; pH=12; T_{evap} = 2,600–3,000°C.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dissociation energy in eV</th>
<th>Wavelength in nm</th>
<th>Detection limit of X in ng</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF</td>
<td>6.8</td>
<td>227.5</td>
<td>0.3</td>
</tr>
<tr>
<td>GaF</td>
<td>6.0</td>
<td>211.4</td>
<td>0.8</td>
</tr>
<tr>
<td>InF</td>
<td>7.5</td>
<td>233.9</td>
<td>1.1</td>
</tr>
<tr>
<td>MgF</td>
<td>4.8</td>
<td>258.2</td>
<td>2.4</td>
</tr>
<tr>
<td>AlCl</td>
<td>5.1</td>
<td>261.4</td>
<td>1.6</td>
</tr>
<tr>
<td>GaCl</td>
<td>4.9</td>
<td>248.2</td>
<td>9.0</td>
</tr>
<tr>
<td>InCl</td>
<td>4.5</td>
<td>267.2</td>
<td>3.0</td>
</tr>
<tr>
<td>MgCl</td>
<td>3.3</td>
<td>376.2</td>
<td>5.8</td>
</tr>
<tr>
<td>AlBr</td>
<td>4.1</td>
<td>279.0</td>
<td>18</td>
</tr>
<tr>
<td>InBr</td>
<td>4.2</td>
<td>284.5</td>
<td>130</td>
</tr>
<tr>
<td>TlBr</td>
<td>3.4</td>
<td>266.8</td>
<td>50</td>
</tr>
<tr>
<td>TlI</td>
<td>2.9</td>
<td>202</td>
<td>80</td>
</tr>
<tr>
<td>GeS</td>
<td>5.7</td>
<td>215.2</td>
<td>50</td>
</tr>
</tbody>
</table>

From the results we can conclude that trace element determinations can be carried out for nonmetals.

**Table II**

FANES and LAFS results in comparison to AAS

<table>
<thead>
<tr>
<th>Element</th>
<th>Method</th>
<th>Wavelength in nm</th>
<th>Detection limit in pg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>FANES</td>
<td>396.2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>AAS/ETA</td>
<td>308.2</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>LAFS/ETA</td>
<td>308.2/308.2</td>
<td>4</td>
</tr>
<tr>
<td>Ga</td>
<td>FANES</td>
<td>417.2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>AAS/ETA</td>
<td>294.4</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>LAFS/ETA</td>
<td>287.4/294.4</td>
<td>10</td>
</tr>
<tr>
<td>In</td>
<td>FANES</td>
<td>451.1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>AAS/ETA</td>
<td>303.9</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>LAFS/ETA</td>
<td>303.9/325.6</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Quantitative determination of metals by FANES (furnace nonthermal excitation spectrometry) and of nonmetals by MONES (molecular nonthermal excitation spectrometry) in graphite furnace

A thermal excitation technique was developed in recent years by Falk [15,16] for determination of free atoms at low pressures. They used a graphite furnace as in AAS, but after the drying and the ashing phase the system was evacuated and than filled with Ar at low pressure. An electrical glow discharge (the graphite tube acts as a hollow cathode) excited the atoms which were formed in the atomization phase. The technique is called FANES. We investigated the possibility of such a system for determination of nonmetals using diatomic molecules generated in the FANES atomizer and developed the new technique MONES-ETE (molecular nonthermal excitation spectrometry with electrothermal evaporation).

**Procedure**

The procedure is generally the same as described above. The sample solution (for FANES without, for MONES with M addition) is introduced into the graphite tube. The controlled
programme ensues: drying and ashing at normal pressure, evacuation (13 Pa) Ar (or He) filling (up to 26 kPa) generation and stabilization of discharge (20-60 mA, 3-5 s), atomization /evaporation for MONES) at low pressure into discharge. The duration of the whole cycle is similar to that of AAS-ETA (about 1-2 min).

Analytical results of FANES and MONES-ETE

The analytical results of FANES measurements for some metals are shown in Table II. All detection limits are better than in AAS-ETA and additionally the method has multielemental character.

At first the existence of diatomic molecules in the FANES-System was indirectly proved by FANES measurements of Ga and In in presence of halides. In all cases we found signal depression, which - as we assumed - is caused by molecule formation. After this the molecular emission of InX molecules in the FANES source was found. The characterization of the transitions tested and the analytical results of InX MONES-ETE obtained are shown in Table III. In comparison to MAS-ETE (see Table I) better detection limits were obtained. Also the MONES-ETE has multielemental character.

Table III

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Transition</th>
<th>Wave length [nm]</th>
<th>Excitation energy [eV]</th>
<th>Detection limit of X⁻ [pg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InF</td>
<td>C²⁺n — X¹⁺</td>
<td>233.9</td>
<td>5.3</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>B²⁺n — X¹⁺</td>
<td>328.1</td>
<td>3.8</td>
<td>300</td>
</tr>
<tr>
<td>InCl</td>
<td>C²⁺n — X¹⁺</td>
<td>267.2</td>
<td>4.6</td>
<td>weak</td>
</tr>
<tr>
<td></td>
<td>A²⁺n — X¹⁺</td>
<td>359.9</td>
<td>3.4</td>
<td>500</td>
</tr>
<tr>
<td>InBr</td>
<td>B²⁺n — X¹⁺</td>
<td>365.1</td>
<td>3.4</td>
<td>6,000</td>
</tr>
</tbody>
</table>

Quantitative determination of metals by laser excited atomic fluorescence spectrometry (LAFS-ETA) and of nonmetals by laser excited molecular fluorescence spectrometry (LAMOFS-ETE) in graphite furnaces

The improvement of detection limits by "over-excitation" in the glow discharge with FANES/MONES relatively to AAS/MAS shows that this way is a possibility for improvement of trace analysis. Therefore we tried to find also other more intense excitation sources.

As known from "pure atomic spectroscopy" the excitation of atomic fluorescence by strong light sources - especially pulsed dye lasers - lead to the best absolute detection limits of atomic spectroscopy for some metals [17]. To date, this technique has not been used for determination of nonmetals, because the wave length needed lie in VUV range and are not optimal for atomic fluorescence. We tried to develop a new sensitive technique for determination of nonmetals by laser excited molecular fluorescence of diatomic molecules generated in electrothermal atomizers. In analogy to the abbreviation LAFS-ETA we propose the abbreviation LAMOFS-ETE (laser-excited molecular fluorescence spectrometry with electrothermal evaporation).

Procedure

The procedure is the same as described for AAS/ETA and FANES (metals) and MAS/ETE and MONES (nonmetals).
Analytical results of LAFS-ETA and LAMOFS-ETA

In Tables II and IV the results of LAFS and LAMOFS measurements are shown. The detection limits were better than by the other methods.

Table IV

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Wave lengths of X [nm]</th>
<th>Detection limits of X [pg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF</td>
<td>268.94 - 274</td>
<td>11</td>
</tr>
<tr>
<td>InCl</td>
<td>267.21 - 272</td>
<td>15</td>
</tr>
<tr>
<td>AlBr</td>
<td>276.91 - 284</td>
<td>70</td>
</tr>
</tbody>
</table>

Conclusions

1. MAS-ETE, MONES-ETE, and LAMOFS-ETE can be used for determination of nonmetal traces.
2. The detection limits are the best for LAMOFS-ETE. MAS-ETE is most simple and MONES-ETE offers the best way to simultaneous multielement analysis.
3. The detection limits lie in the ng - pg range.
4. The comparison between AAS-ETE, FANES, and LAFS-ETA shows a similar situation: AAS-ETE is most simple, FANES gives better detection limits and has multielemental character, LAFS-ETA gives the best detection limits and offers a way to extreme trace analysis.
5. The detection limits lie in the pg - fg range.

References


Acta Physica Hungarica 61, 1987
APPLICATION OF SPECTROSCOPIC METHODS IN THE POLYMER INDUSTRY 
(RESULTS AND PROBLEMS)

W. KIMMER
Kombinat VEB Chemische Werke Buna
4212 Schkopau, GDR

Characterization and analytics of polymers have a special place in the wide ranging field concerning the analysis of thermoplastics and elastics for various reasons (developing highly refined polymers, attaining special properties, product substitution, customer service, plant disturbances, environmental protection etc.). A special way of characterization of polymers by means of spectroscopic methods (IR, NMR, UV) is described. The top method is the IR spectroscopy.

Spectroscopic methods have proved a success for some decades, also in the research and factory-own laboratories of chemical industry; they are indispensable for the development of new chemical products and processes and in the solution of application-related and environmental problems. The most important spectroscopic methods are the IR, NMR (**H, **C, **F) and UV spectroscopy and, for special problems, the Atomic Emission Spectrometry (AES), the Atomic Absorption Spectrophotometry (AAS), the Electron Spin Resonance (ESR), the Raman-Spectroscopy (Laser induced), and the X-ray Fluorescence Analysis (RFA).

In the field of polymer industry extensive analytical and structural investigations are carried out on the large range of commercially synthesized plastics, elastomers and additives, based on spectroscopic methods:

Qualitative analysis (identification) of starting materials, intermediate and final products as well as auxiliary materials (characterization of research products, product control and supervision of production process, investigation of averages, substitution of products formerly imported, comparison with the world standard, service, reclamations, environmental protection)

Quantitative analysis of polymers and additives from the research, production and application engineering departments

  e.g.  - analysis of composition of copolymers, graft polymers and compounds;
  - determination of monomers and additives in commercial polymers;
  - determination of chain irregularities and terminal groups.

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Structure analysis

e.g. Determination of
- chain structure (sequence length, tacticities, distribution of isomers
- state of order
- orientation.

Kinetics

e.g. - Cross-linking mechanisms for hardenable systems
- Interactions in polymer systems (e.g. PVC plasticizers)
- Mechanism and kinetics of degradation (stabilization).

Owing to continuous exploration of new applications for plastics and elastomers (e.g. microelectronics, medicine), the number of components contained in the commercially synthesized copolymers and compounds has rapidly increased in the recent years; this has resulted simultaneously in a development of numerous new additives for polymers. Therefore, the polymer spectroscopist is faced with an increasing complexity and with an increasing complicated composition and structure of polymer systems. In our days an exact and efficient investigation of analytical and technical problems is not possible without a purposeful optimization of polymer-analytical processes.

What has been achieved in this area in the recent years and what must be still done from the industrial point of view, but also in respect to the general interest in the analytical application of spectroscopic methods (IR, UV, NMR methods)?

1. By a critical analysis of procedure of polymer-spectroscopic and general polymer-analytical steps of operation based on the existing methods, data and experience, method- and substance-oriented analysis algorithms have been developed which permit the above-mentioned analytical problems to be settled largely in a systematic manner. Being the most expressive and universal spectroscopic method in the range of polymer spectroscopy, the infrared spectroscopy assumes a key position because it is frequently used for initial measurements.

2. For extending the information obtained in spectroscopic analysis using methods already introduced, the vibration spectroscopy and the HF spectroscopy have been combined considering their strong methodological points to develop an off-line problem-oriented method:

\[ \text{IR} - ^1\text{H} \]
(polyester, polyacrylates, polyethylene, identifications)
APPLICATION OF SPECTROSCOPIC METHODS IN THE POLYMER INDUSTRY

IR - $^1\text{H} - \text{UV}$
(identification incl. quantitative analysis of additives)

IR - Laser-Raman spectroscopy
(synthetic rubber, natural rubber, carboxylic rubber, prepolymers)

IR - $^1\text{H} - ^{13}\text{C}$
(Detailed determination of microstructure of plastics and elastomers)

$^1\text{H} - ^{13}\text{C}$
(surfactants, polyacrylates, general microstructure studies)

$^1\text{H} - ^{19}\text{F}$
(epoxides, prepolymers, oxo alcohols, surfactants)

$^1\text{H} - ^{13}\text{C} - ^{19}\text{F} - \text{IR}$
(determination of functionality, terminated polymers).

3. For rationalization and improvement of spectroscopic recording and evaluating technique and for application of new measuring principles, the following new and improved instruments and procedures have been transferred to industrial use and rendered efficient for practice:

- the microcomputer controlled UV/VIS spectrometry (C.Z. M 40),
- the microcomputer controlled infrared spectroscopy (C.Z. M 80)

which permit new, analytically useful operations, such as spectrum accumulation, addition, subtraction, multiplication; normalization, smoothing and deriving of spectra.

From the basic operations

Preparation - Measurement - Evaluation

which are decisive for the analytical procedure, hitherto, the first step was the time-determining factor, in spite of highly efficient spectrometers. The methods coupled include mainly:

- the LC - FT - IR coupling (liquid chromatography - FT - IR spectroscopy)

and

- the GC - FT - IR coupling (gas chromatography - FT - IR spectroscopy).

Using these methods the following effects can be achieved:

- Shortening the time required for the total analysis by eliminating the manual separating operations and by computer-aided evaluation
- Essentially increasing the information and results in the analysis of complex systems of substance and of by-products and traces
- Lowering the amounts of substance required.
The computerization of spectrometers results, apart from the instrument control, in the development of data banks specific for methods and substances which permits the analytical information processing to be improved qualitatively and quantitatively to a large extent.

So far as known, in the CMEA region IR Fourier spectrometers are not manufactured; therefore, numerous analytical and scientifically important problems, also in the field of methodological coupling of IR spectroscopy and chromatography as well as data acquisition and processing incl. the establishment of spectroscopic data banks, cannot be settled in conformity with the requirements and with the international level of science and technology.

References
AUTOMATED STABILIZED TUNABLE CO₂ LASER SPECTROMETER DESIGNED TO STUDY MOLECULE PARAMETERS

L.N. ORLOV, V.V. NEVDAKH
Institute of Physics, BSSR Academy of Sciences, Minsk 220602, USSR

A frequency-stabilized, tunable CO₂ laser has been employed to measure absorption coefficients and saturation parameters on the lines of several molecules. The results are used for determining the Einstein coefficients of CO₂, CH₂OH and CD₃OD molecules, frequency detunings and saturation intensities for CH₂OH and CD₃OD.

At the Institute of Physics of the BSSR Academy of Sciences an automated laser spectrometer has been developed. It is designed to determine optico-physical parameters of molecules in the IR mid-band. The principle component of the spectrometer is a stabilized tunable CO₂ laser based on sealed-off active elements produced in series. The laser geometry, details of its design, and the description of the automatic frequency control circuit are given in [1, 2]. The tuning range of the laser is 9.19 to 10.94 μm. The lasing power in individual lines reaches 8 W. The prolonged relative instability of the lasing frequency is less than 10⁻⁶ and that of the power is less than 1%. The recording system permits measurement of laser radiation intensity ratios in several channels and their absolute values. The control unit based on a micro-computer of the "Elektronika-60" type chooses the mode of operation of the instrument, carries out automatic tuning of the CO₂ laser spectrum according to a given program, controls the probing radiation intensity, and processes measurement data.

Consider a few examples of using the spectrometer to investigate gas molecules at low pressures.

We have determined the Einstein coefficients and collisional line-widths for the transitions [00°1- 10°0, 02°0] I,II and [00°2- 10°1, 02°1] I,II of the CO₂ molecule. The method of determining the probabilities of spontaneous radiation Aₘₙ and collisional widths 2Δνₑ consisted in comparing absorption coefficients at the centres of different lines of transitions of CO₂ molecules at greatly varying pressures corresponding to truly Lorentz and Poigt line broadening (usually 133 and 6.5 hPa) [3]. The employment of the double-beam method for measuring absorption coefficients on the line centres of the P- and R-branches of transitions in the CO₂ molecule in the 9 and 10 μm regions with rotational quantum numbers from 6 to 34 has made it possible to reduce the measurement error to less than 1%. The probabilities Aₘₙ for all the lines of the 00°1-02°0 transition are higher than for corresponding lines of the transition 00°1-10°0, while the value 2Δνₑ is larger for...
the 00$^0_1$-10$^0_0$ transition. In Table I analytical expressions are tabulated which describe dependences of $A_{mn}$ on the rotational quantum number $j$ and $2\Delta V_L(j)$ which are approximations of experimental results by the least-squares technique.

Table I

<table>
<thead>
<tr>
<th>Transition Branch</th>
<th>$A_{mn}(j) \left[ s^{-1} \right]$</th>
<th>$2\Delta V_L(j) \left[ MHz/hPa \right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>00$^0_1$-10$^0_0$ P</td>
<td>0.1902 - 8.875$\cdot 10^{-4}$j</td>
<td>12.191 - 0.0975j</td>
</tr>
<tr>
<td>00$^0_1$-10$^0_0$ R</td>
<td>0.1542 + 1.125$\cdot 10^{-3}$j</td>
<td>11.636 - 0.075j</td>
</tr>
<tr>
<td>00$^0_1$-02$^0_0$ P</td>
<td>0.203 - 9.50$\cdot 10^{-4}$j</td>
<td>12.109 - 0.104j</td>
</tr>
<tr>
<td>00$^0_1$-02$^0_0$ R</td>
<td>0.157 + 1.41$\cdot 10^{-3}$j</td>
<td>10.885 - 0.064j</td>
</tr>
<tr>
<td>00$^0_2$-10$^0_1$ P</td>
<td>0.402 - 1.805$\cdot 10^{-3}$j</td>
<td></td>
</tr>
<tr>
<td>00$^0_2$-10$^0_1$ R</td>
<td>0.319 + 2.439$\cdot 10^{-3}$j</td>
<td></td>
</tr>
<tr>
<td>00$^0_2$-02$^0_1$ P</td>
<td>0.378 - 1.656$\cdot 10^{-3}$j</td>
<td></td>
</tr>
<tr>
<td>00$^0_2$-02$^0_1$ R</td>
<td>0.291 + 2.152$\cdot 10^{-3}$j</td>
<td></td>
</tr>
</tbody>
</table>

Knowing the values of $A_{mn}$ and $2\Delta V_L$ for the lines of the regular band and comparing the gains on these lines and on the lines of the sequence band [00$^0_2$ - 10$^0_1$, 02$^0_1$] I,II we have determined probabilities of spontaneous transitions in the sequence band [4]. The results are tabulated in Table I. The dependence $A_{mn}(j)$ is practically linear too, but, unlike the regular band, the values of $A_{mn}$ are in this case larger for the lines in the 10.6 $\mu$m region.

The results obtained have made it possible to calculate the values of squares of matrix elements of transitions in a CO$_2$ molecule. A detailed comparison of their dependence on $j$ with the calculation and measurement data of other authors shows that in calculating probabilities of spontaneous transitions in a CO$_2$ molecule it is necessary to take into account higher-order terms in dipole moment expansion in normal coordinates.

Similar investigations have been made for a variety of spirits, methane haloid-substituted and deuterium derivatives [5]. As an example, Table II gives values of $A_{mn}$ for methanol and CD$_3$OD at several CO$_2$ laser frequencies.

The values $\delta \nu$ of probe frequency detuning from the absorption line centres were estimated for isolated absorption lines by comparing calculated and experimental pressure dependences of the spectral absorption coefficient. The measured values $\delta \nu$ are tabulated in Table II. Note that the high accuracy to which absolute values of stabilized CO$_2$ laser frequencies are known has made it possible to redetermine, in a number of cases, the values of vibrational and rotational constants of molecules.
The same equipment was used to measure parameters of absorption line saturation of CH$_3$OH type molecules. The values of saturating intensities $I_s$ for a number of absorption lines at minimum gas pressures mentioned above are tabulated in Table II. The data obtained play an important part in interpreting IR-laser photochemistry experiments, as well as in calculating parameters of FIR lasers at rotational transitions of molecules under resonance optical pumping.

An anomalous decrease in the $I_s$ intensity value with pressure (Fig. 1) in the region of small concentrations of molecules optimal for the CW regime of FIR lasers has been observed. It is shown that in this region the commonly used extrapolation by $I_s$ values measured at high gas pressures is not valid. The nonmonotonic character of the dependence $I_s(P)$ makes it possible to estimate the deactivation rates of radiationless processes of excited states of molecules. Using the known values of diffusion rates and $A_{21}$ measured by us, we have managed to estimate the number of collisions % rot between molecules that leads to the establishment of an equilibrium between rotational sublevels. For example, for CH$_3$OH molecules in normal conditions this value is close to 11, weakly depends on $j$ and strongly on the gas temperature. The spectrometer permits also investigation of parameters of absorption lines and gains for different substances in the gas and condensed phase. The results obtained may be used in theoretical photochemistry, astrophysics, as well as in

<table>
<thead>
<tr>
<th>CO$_2$ laser wavelength [µm]</th>
<th>$\delta \nu$ [MHz]</th>
<th>$A_{21}$ [s$^{-1}$]</th>
<th>$B_{21} \cdot 10^{-15}$ [erg s cm$^{-3}$]</th>
<th>$I_s$ [kW cm$^{-2}$]</th>
<th>$p$ [Pa]</th>
</tr>
</thead>
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<tr>
<td>9.282444</td>
<td>3</td>
<td>2.3565</td>
<td>11.3281</td>
<td>0.363</td>
<td>66.7</td>
</tr>
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<td>9.329370</td>
<td>7</td>
<td>0.0111</td>
<td>0.0544</td>
<td>0.422</td>
<td>133.3</td>
</tr>
<tr>
<td>9.488355</td>
<td>30</td>
<td>0.2558</td>
<td>1.3136</td>
<td>0.619</td>
<td>66.7</td>
</tr>
<tr>
<td>9.519808</td>
<td>40</td>
<td>0.7299</td>
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<td>26.7</td>
</tr>
<tr>
<td>9.675971</td>
<td>25</td>
<td>1.1774</td>
<td>6.4109</td>
<td>0.473</td>
<td>26.7</td>
</tr>
<tr>
<td>10.094676</td>
<td>14</td>
<td>0.0051</td>
<td>0.0287</td>
<td>0.501</td>
<td>200.0</td>
</tr>
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<td>2.2559</td>
<td>14.1210</td>
<td>0.806</td>
<td>26.7</td>
</tr>
<tr>
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<td>1.0786</td>
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<td>0.0371</td>
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<td>1.259</td>
<td>133.3</td>
</tr>
</tbody>
</table>

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developing and optimizing molecular lasers of various types.

Fig. 1. Dependence of CH$_2$OH absorption lines saturation intensities on gas pressure for two CO$_2$-laser lines

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СЕЛЕКТИВНАЯ СПЕКТРОСКОПИЯ ПИГМЕНТОВ БАКТЕРИИ В ТВЕРДОТЕЛЬНЫХ МАТРИЦАХ

И.В. РЕНГЕ, К.Х. МАУРИНГ, Р.А. АВАРМАА
Институт физики АН ЭССР, 202400 г. Тарту, ул. Рийа 142, ЭССР, СССР

В замороженных растворах бактериохлорофилла а (БХл) и бактериофеофитина при 5 К измерены спектры флуоресценции при селективном возбуждении в вибронной и 0-0 областях поглощения и спектры возбуждения флуоресценции при узкополосной регистрации. Определены частоты колебательных мод, активных в $S_0$ и $S_1$ состояниях. В пределах 0-0 полосы БХл с квантовым выходом $\times 10^{-4}$ выжжены узкие ($\leq 0.9 \text{ см}^{-1}$) провалы глубиной до 20% от первоначального поглощения.

Введение

Оптическим спектрам многих сложных органических молекул, введенных в качестве примесных центров в матрицы из замороженных растворителей, свойственны бесфоновые электронно-колебательные переходы [1]. Однако, выявление бесфоновых переходов большинства фотосинтетических пигментов типа хлорофиллов путем подбора матрицы Шпольского затруднено, ибо спектры останутся широкополосными вследствие неоднородного уширения. Лишь спектральное выделение группы центров с заданной энергией $S_1 - S_0$ перехода посредством узкополосного (как правило, лазерного) возбуждения позволяет частично устранить влияние неоднородностей матрицы [2].

В последние годы начаты исследования пигментов непосредственно в растениях [3-5] и в реакционных центрах бактерий [6-8], применяя методы монохроматического возбуждения и выжигания провалов.

В настоящей работе были изучены бактериальные пигменты - бактериохлорофилл а (БХл) и его безмагниевая форма - бактериофеофитин (БФео) с целью:
- оценить силу электронно-фононного взаимодействия в различных матрицах;
- измерить спектры флуоресценции и возбуждения, определить частоты и относительные интенсивности нормальных колебаний в $S_0$ и $S_1$ состояниях;
- выжечь провал в неоднородной 0-0 полосе БХл и оценить его ширину, глубину и квантовый выход образования.

Методика эксперимента

Возбуждение проводилось лазером на красителе оксазин 1 (область перестройки 690-780 нм, ширина линии генерации 0,03 нм), накачиваемым криптоновым лазером CR-2000 фирмы Coherent. Флуоресценцию регистрировали на монохроматоре ДФС-24 (ширина щелей 0,05 нм), снабженным ФЭУ, который обладает высокой чувствительностью в ближней ИК области и работает в режиме счета фотонов. Спектры записывали в многоканальном анализаторе Nokia 4900В. Растворы пигментов ($10^{-6}-10^{-5}$ М) охлаждали в парах гелия до 5 К.

Обсуждение результатов

Максимумы флуоресценции пигментов лежат в районе 750-780 нм. При возбуждении в вибронной области $S_1 - S_0$ перехода на фоне основной полосы появляется...
смя ряд острых пиков (рис. 1), на первый взгляд напоминающих мультиплет Шпольского (рис. 2). В отличие от последнего максимумы пиков сдвигаются вместе с линией возбуждения и представляют собой бесфононные линии центров, возбуждаемых через дискретные колебательные подуровни [1].

В разных растворителях контраст линий по отношению к фону сильно варьирует. Так, в снегообразных протонных средах (трет-бутанол) линии практически отсутствуют. Особенно отчетливо колебательное разрешение получено в неполярных стеклющихся матрицах. Чувствительность к состоянию матрицы наблюдалась раньше также для хлорофилла a, но не для более жестких плоских молекул порфиринов [9]. Можно предположить, что в стеклообразной среде примесный центр более плотно окружен молекулами растворителя, так что в значительной степени будут подавлены низкочастотные торсионные колебания макроцикла пигмента, способные внести вклад в фононную полосу.

Для обоих пигментов из спектров флуоресценции (рис. 3) и возбуждения оп-
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Рис. 2. Спектр флуоресценции БФео в матрице Школьского н-октана при белом возбуждении (400-600 нм). Отмечены компоненты мультиплета (в см⁻¹)

Решенные порядка 30 колебательных частот как в основном (ω₁) так и в S₁ состояниях (ωₑ). Проверена применимость правила зеркальной симметрии для значений ω₁ и ωₑ, которое для БФео выполняется практически идеально. Замена двух атомов водорода в БФео на атом Mg в БХл приводит к заметным изменениям наборов частот, в особенности ωₑ.

Центра́льный атом магния в БХл может координироваться посредством донорно-акцепторной связи с одной (в триэтиламине, ТЭА) или двумя (в пиридине, н-спиртах) лигандными молекулами. Установлено, что в дисольватах ряд высокочастотных мод ωₑ в области 1470-1620 см⁻¹ претерпевает сдвиг на 10-15 см⁻¹ в сторону более низких частот.

При облучении образца БХл в ди-изоамиловом эфире (ДИАЭ) монохроматическим светом в области 0–0 полосы в ней образуется провал. Формирование провала происходит с квантовым выходом около 10⁻⁴ в результате фотопревращений, заключ.

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Рис. 3. Спектр флуоресценции БХл в стекле ТЭА, возбуждение в области 767,1-770,8 нм при медленном сканировании лазера (во избежание выжигания линий). Отмечены частоты колебаний в $S_0$ состоянии (в см$^{-1}$).

чающихся, по-видимому, в переориентации подвижных атомных групп в примесном центре и/или молекул растворителя вокруг него. Максимальная глубина провала составляет $\sim 20\%$, что одновременно дает оценку вклада бесфононных линий в суммарную полосу поглощения, т.е. эффективного фактора Дебая-Валлера. Ширина выжженного контура ($\sim 0,9$ см$^{-1}$) определяется в настоящем эксперименте шириной лазерной линии.

Таким образом, для бактериальных пигментов, внедренных в матрицы ряда органических растворителей, доказано существование бесфононных линий. Определены частоты нормальных колебаний и осуществлен их предварительный анализ. Данные этой работы могут служить основой для понимания некоторых спектральных особенностей фотосинтезирующих бактерий и их фрагментов.

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Изучены спектры аннигиляционной замедленной флуоресценции (Ф) коронена и фенантрена в стеклообразных растворах при 4.2 К с применением селективного лазерного возбуждения. В этих условиях в спектрах Ф выявлена тонкая структура. Установлен степенной закон затухания Ф с показателем степени $\alpha = 0.8 - 0.9$, отражающий специфику взаимодействия близких пар молекул.

**Введение**

Замедленная флуоресценция (Ф) твердых растворов, возникающая при аннигилиации триплетных возбуждений в паре близких молекул, может служить чувствительным индикатором межмOLEкулярных взаимодействий. До последнего времени обычно исследовались широкополосные спектры Ф, идентичные широкополосным спектрам обычной флуоресценции (ОФ). Между тем в случае твердых растворов, в принципе, указанные парные взаимодействия могут приводить к тонким различиям в спектрах Ф и ОФ. При этом из-за локализации возбуждений в кинетике Ф на начальных этапах должны проявляться особенности (неконвективность), несушие информацию о законе взаимодействия и статистике распределения близких пар [1]. Для детальных исследований указанных проблем весьма перспективными могли бы быть тонкоструктурные спектры Ф. Развитые в последние десятилетия методы тонкоструктурной селективной спектроскопии твердых растворов [2] (позволяющие устранять неоднородное уширение в низкотемпературных спектрах излучения и поглощения и повышать реальное спектральное разрешение в $10^3 + 10^4$ раз) использовались до сих пор лишь для исследования изолированных молекул.

В настоящей работе была поставлена задача выяснения возможности исследования Ф и ее кинетики с помощью методов селективной лазерной спектроскопии. Некоторые предварительные данные были приведены ранее в кратком сообщении [3].

**Тонкая структура спектров Ф**

Прежде всего представляло интерес получить спектры Ф при селективном возбуждении для систем, спектры Ф которых характеризуются значительным неоднородным уширением. При монохроматическом возбуждении Ф таких систем неоднородное уширение устраняется и в спектре проявляется тонкая структура. Вопрос о том, какой характер будет носить спектр Ф в этих условиях, не является очевидным. Действительно, в Ф вносят вклад только пары близкораспо-
ложенных молекул, в то время как при не очень высоких концентрациях твердого раствора вклад таких пар в ОФ мал. Поэтому, в принципе, спектры ОФ и ЗФ могут различаться. Для близких пар могут быть эффективны процессы S-S и T-T – миграции энергии, которые в силу неоднородности системы могут приводить к потере селективности, достигаемой при монохроматическом S1-S2–возбуждении.

Для исследования были выбраны ароматические углеводороды: коронен и фенантрен, обладающие высоким выходом интерконверсии. В качестве основных растворителей использовались смесь бензола с толуолом (1:1) и этиловый спирт, образующие при 4.2 К прозрачное стекло. Концентрации растворов менялись от 10⁻⁵ М до 10⁻² М. Для возбуждения использовался импульсный азотный лазер (W ≈ 2 мДж, τ имп. ≈ 7 нс) и накачиваемый им лазер на красителях (Δν ≈ 1 см⁻¹, W ≈ 100 мДж). Частота импульсов изменялась в пределах от 0.3 Гц до 20 Гц. Спектры регистрировались с разрешением 1 ± 3 см⁻¹ (СДЛ-1, ДФС-24) в течение стробимпульса длительностью от 20 мкс до 20 мс с задержкой относительно лазерного импульса в диапазоне 300 мкс – 3 с. При измерении спектров и кинетики ЗФ проводилось длительное накопление сигнала.

Результаты проведенных исследований показали, что при невысоких концентрациях растворов переход от обычных способов возбуждения ЗФ к монохроматическому лазерному возбуждению приводит к резкому изменению характера спектра и появлению в нем узких бесфононных линий (БФЛ). В качестве примера на рис. I приведены спектры ЗФ коронена. Таким образом, упомянутые выше возможные причины потери селективности при наблюдении ЗФ в данном случае не являются принципиальным препятствием для выявления тонкой структуры.

Рис. I. Спектры ЗФ коронена в смеси бензол–толуол при 4.2 К (c=10⁻³ М): (a) при широкополосном возбуждении (λНа = 365 нм), (b) при селективном лазерном возбуждении (λ лаз. = 4259 нм).

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СПЕКТРЫ И КИНЕТИКА ЗАМЕДЛЕННОЙ ФЛУОРЕСЦЕНЦИИ

В качестве другого примера на рис. 2 приведен участок спектра ЗФ фенантрена при селективном возбуждении, но при разных концентрациях. Из него видно, что повышение концентрации (начиная с 10^{-2}М) приводит к росту крыва с длинноволновой стороны от узких БФЛ. Аналогичная концентрационная зависимость наблюдается и в спектрах ОФ. Такое концентрационное поведение спектров свидетельствует о развитии процессов S→S-миграции (а возможно также и T→T-миграции) энергии, приводящей при высоких концентрациях к потере селективности. Поэтому для получения наиболее структурных спектров ЗФ необходимо работать при умеренных концентрациях растворов. Сопоставление ширины БФЛ в спектрах ЗФ и ОФ, полученных при селективном возбуждении с разрешением 1 см^{-1} в каких-либо различий в них не обнаружено. Однако это не означает, что такие различия отсутствуют. Теоретический анализ показывает, что, например, диполь-дипольное взаимодействие в близких (r=20-30 нм) парах молекул может приводить к спектральным сдвигам ≤ 0,1 см^{-1}, для наблюдения которых необходимо на порядок повысить спектральное разрешение.

Кинетика ЗФ

В случае твердых растворов, где возбуждения локализованы, характер затухания ЗФ определяется зависимостью вероятности аннигиляции \( \lambda (r) \) от расстояния \( r \) между молекулами. В теоретической работе [4] анализировалась кинетика аннигилиационного тушения в зависимости от вида \( \lambda (r) \). Из результатов работы следует, что при импульсном возбуждении и мультипольном механизме аннигиляции \( \lambda (r) = \frac{1}{r^3} (R_F^2)^n \), где \( R_F \) - фёрстеровский радиус аннигиляции, а \( n \) зависит от "мультипольности" взаимодействия) интенсивность ЗФ \( \frac{I(3)}{I_{3f}} \sim t^{-\alpha} \), \( \alpha = \frac{2-3}{n} \). Например, в случае диполь-дипольного взаимодействия (n = 6) интенсивность ЗФ убывает по степенному закону с \( \alpha = 0.5 \). В общем случае кинети-
ка ЗФ может быть весьма сложной.

Измерения кинетики ЗФ твердых растворов коронена и фенантрена при интенсивном импульсном возбуждении выявили ее специфический характер. На начальных этапах затухания кинетика существенно неэкспоненциальна (рис.3(a)). Далее, для обоих исследованных соединений в различных растворителях затухание происходит по степенному закону с $\alpha = 0.8 - 0.9$. Один из примеров, иллюстрирующих сказанное, приведен на рис.3(b). Проведенный теоретический анализ показывает, что наблюдаемая кинетика может быть понята на основе рассмотрения обменного взаимодействия. При этом наряду с Т-Т-аннигиляцией необходим также учет $S-S$ и $S-T$-аннигиляции, а также, по-видимому, и влияния на эти процессы взаимной ориентации молекул в паре.

Таким образом, все приведенные выше данные демонстрируют возможность получения с помощью селективных методов тонкоструктурных спектров ЗФ. Дальнейшее развитие этих исследований с применением высокого спектрального и временного разрешения, а также применение поляризационных измерений представляются весьма перспективными.

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SPECTRAL DEPENDENCE OF LIGHT-INDUCED CHANGE IN DYE SOLUTION REFRACTIVE INDEX

V.V.KABANOV, A.S.RUBANOV
Institute of Physics, BSSR Academy of Sciences, 220602 Minsk, USSR

Results are reported of a theoretical analysis of peculiarities of the spectral behaviour of the dye solution phase response under excitation, which are due to the Stokes shift of absorption and luminescence bands. Analytical relations have been obtained for dyes modelled by two-, three-, and four-level schemes. The contribution has been analyzed of transitions between excited states, as well as of the thermal nonlinearity to the value of the light-induced change in the refractive index.

Introduction

Until recently, there have been no papers devoted to the investigation of light-induced change in the refractive index of solutions of complex organic compounds, although the amplitude response of such media is clearly understood in considering the generation characteristics of dye lasers. At the same time, the regularities of the phase response of dye solutions are of interest in studying diffraction characteristics of dynamic holograms, efficiency of four-wave wavefront conjugation, peculiarities of the line profile formation in resonance stimulated Raman scattering, as well as in analyzing the operation of DFB-lasers, amplifiers and phototrope shutters, and other problems of interaction of radiation with bleachable organic compounds.

Below results are presented of a theoretical analysis of the peculiarities of the spectral behaviour of light-induced change in the refractive index of dye solutions modelled by two-, three-, and four-level schemes. The contribution is estimated of transitions between excited states, as well as radiant energy thermalization to the phase response of organic compound solutions.

Refractive index of unexcited dye

In studying the spectral characteristics of a substance (spectral profiles and corresponding dispersions of the refractive index), the problem arises of their analytical representation in a form convenient for analysis and adequately describing observed values. The absorption and luminescence spectra of dyes have a complicated asymmetric shape and depend on many parameters. To describe them, expansion into an Edgeworth series in terms of Gaussian distribution derivatives (\( f^{(d)}(\lambda) = \sum_{n=0}^{\infty} \frac{d^n(\exp(-\lambda^2))}{n!} H_n(\lambda) \)) is used successfully.
\[ \mathcal{A}_0(\gamma) = \frac{m_e}{\pi^2/\sigma} \left[ f(\gamma) - \frac{\kappa_1}{3!} f^{(3)}(\gamma) + \frac{\kappa_2}{4!} f^{(4)}(\gamma) + \frac{10 \kappa_4}{6!} f^{(6)}(\gamma) + \ldots \right], \]

where

\[ \kappa_1 = \left( \frac{\gamma}{\omega} \right)^2 \left( \frac{\gamma}{\omega} - 1 \right), \]

\[ \kappa_2 = \left( 2 \pi / \omega \right)^2 \left( \frac{\gamma}{\omega} \right)^3 - 3 \left( \frac{\gamma}{\omega} \right)^5, \]

\[ \kappa_4 = \frac{1}{2} \left( \frac{\gamma}{\omega} \right)^4 \left( \frac{\gamma}{\omega} - 1 \right)^2, \]

are the initial and central moments of the spectral band under study. Using Kramers-Kronig dispersion transforms for the refractive index corresponding to the extinction coefficient of Eq. (1), we obtain the following series [2]:

\[ n_0(\gamma) = -\frac{m_e}{\pi^2/\sigma} \left[ \mathcal{G}(\gamma) - \frac{\kappa_1}{3!} \mathcal{G}^{(3)}(\gamma) + \frac{\kappa_2}{4!} \mathcal{G}^{(4)}(\gamma) + \frac{10 \kappa_4}{6!} \mathcal{G}^{(6)}(\gamma) + \ldots \right], \]

where \( \mathcal{G}^{(k)}(\gamma) = \frac{1}{2\pi}\int_0^\infty d\kappa \frac{e^{-\kappa^2} \kappa^k}{\sqrt{\kappa}} \) is the Hermite function of the second type. The expansion terms of Eq. (2), beginning with the second one, determine the deviation \( n_0(\gamma) \) from the Gaussian shape. The calculation of the refractive index for typical dye spectra shows that in the region of the absorption band marked dispersion transformation as compared to that calculated as a Gaussian approximation is observed, which may be written as

\[ n_0(\gamma) = -2 \pi^{-1/2} \mathcal{A}_0^m \exp \left( -\gamma^2 \right) F_1 \left( \frac{1}{2}, \frac{3}{2}; \gamma^2 \right), \]

where \( F_1 \left( \frac{1}{2}, \frac{3}{2}; \gamma^2 \right) \) is the degenerate hypergeometric function, \( \mathcal{A}_0^m = \mathcal{A}_0(\omega = \tilde{\omega}) \). At the same time the asymptotic behaviour \( n_0(\omega) \) of Eq. (2) coincides with the approximation of the refractive index of Eq. (3): \( n_0(\gamma) \approx -\pi^{-1/2} \mathcal{A}_0^m \gamma^{-1} \).

**Light-induced phase response of dye solutions**

In the steady-state regime of interaction the complex refractive index of a dye modelled by the three- or four-level scheme may be written as

\[ \hat{n}(\omega, I) = \hat{n}_0(\omega) + \mathcal{A}_0(\omega, \gamma) \left[ \mathcal{L}(\omega) I + \mathbf{\hat{p}}(\omega) I^2 \right] / \left[ 1 + \mathcal{J}(\omega) I + \beta(\omega) I^2 \right], \]

where \( \hat{n}_0 = n_0 + i \mathcal{A}_0, I \) is the exciting radiation intensity at frequency \( \omega_p \). The parameters \( \mathcal{J}, \mathcal{L}, \mathbf{\hat{p}} \) are determined by the following expressions:

\[ \mathcal{J} = (\beta_{12} + \beta_{21})/\sqrt{p_{21} + p_{32} / \gamma p_{22}}, \]

\[ \mathcal{L} = \alpha + i \mathcal{L} = (\beta_{12} + \beta_{21} - \beta_{23}) / \sqrt{p_{21}}, \]

\[ \beta = \beta + i \beta = [b_{22}(\beta_{12} + \beta_{32}) + b_{32}(\beta_{21} + \beta_{21} - \beta_{23})] / \sqrt{p_{21}p_{32}} \]

for the three-level system and

\[ \mathcal{J} = [\beta_{12}(1 + p_{23} / p_{31}) + \beta_{21}] / \sqrt{(p_{21} + p_{32}) + \beta_{43} / \gamma p_{43}}, \]

\[ \mathcal{L} = [\beta_{12}(1 + p_{23} / p_{31}) + \beta_{21}] / \sqrt{(p_{21} + p_{32})}, \]

for the four-level system.

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\[
\hat{\beta} = \left[ (\hat{\beta}_{34}(\hat{\beta}_{43} + \hat{\beta}_{34}) + \hat{\beta}_{43}(\hat{\beta}_{43} - \hat{\beta}_{34})) \right] \hat{\beta}_{23} / \hat{\beta}_{21} + \hat{\beta}_{43}(\hat{\beta}_{43} + \hat{\beta}_{21})] / \nu^2 \hat{\beta}_{23}(\hat{\beta}_{21} + \hat{\beta}_{23})
\]

for the four-level system. Here \( \rho_{ij} \) are probabilities of spontaneous and nonradiative transitions in the channel \( i \rightarrow j \), \( \nu \) is the velocity of light in the medium, \( \hat{\beta}_{ij} = \hat{\beta}_{ij} + i \delta_{ij} \), \( \hat{\beta}_{ij} \) are coupled by dispersion relations with the Einstein coefficients \( \delta_{ij} \).

The spectral behaviour of the light-induced change in the refractive index \( \Delta n = n(\omega, I) - n_0(\omega) \) of an excited dye is very dependent on the relative positions of the absorption (luminescence) bands of the main and the excited channel. It should be noted that the contribution of each channel to the total change \( \Delta n \) may vary over a wide range assuming both positive and negative values, depending on the exciting radiation intensity and the probe beam frequency.

Let us exemplify the influence of the Stokes shift of absorption and emission bands on the spectral dependence of the dye phase response by a two-level model for which we have from Eqs (4) - (5) at \( \hat{\beta}_{23} = \hat{\beta}_{32} = 0 \)

\[
\Delta n = - G(\omega_p, I) a(\gamma) ; \quad a(\gamma) = \left[ \hat{\beta}_{21}(\gamma) + \hat{\beta}_{21}(\gamma - \delta) \right] / \nu^2 \hat{\beta}_{21},
\]

\[
G(\omega_p, I) = \mathcal{R}(\omega_p) I / [1 + \mathcal{R}(\omega_p) I], \quad \delta = (\omega_{21} - \omega_1) / \sigma.
\]

It is seen from the spectral dependence of the refractive index change of Eq. (7) (Fig. 1) calculated as an approximation of the mirror-symmetric

![Fig. 1. Spectral dependence of the dye phase nonlinear response at \( \delta = -1.2 \)](image)
Gaussian shape of the absorption and luminescence bands profiles (see Eq. (3)) that the resonance phase response of the dye solution vanishes at the frequency of the electronic transition $\omega = (\omega_e^2 + \omega_r^2)^{1/2}$ assumes positive values for $\omega > \omega_e$ and negative ones for $\omega < \omega_e$ [4]. The ratio of the refractive index change to the change of the extinction coefficient $\Delta n/\Delta \alpha = \alpha/\Delta \alpha$ in the $\omega_e$ region is practically linearly dependent on the frequency (for dyes with a relatively small Stokes shift $\delta$ of the absorption and luminescence bands). At $|\delta| > 2$ in the $\omega_e$ region a second anomalous bend $\Delta n$ appears (see Fig.1a). The abovementioned regularities of the phase response of dyes modelled by the two-level scheme are in good agreement with experimental data [5].

The change in the refractive index caused by adiabatic heating of the dye solution is described by the equation

$$\Delta n_T = \frac{\chi_0 Q (\alpha_r I + \beta_r I^2)}{(1 + \beta I + \beta I^2)},$$

where $Q = 2(\omega n/d\tau)/C_p$, $\alpha_r = 1 - \mu_{21}$, $\beta_r = B_32(1-\mu_{21})/\omega^2_32 + B_33(1-\mu_{21})/\omega^2_33$, for the three-level model and $\beta_r = B_33(1-\mu_{21})/\omega^2_33 + B_36(1-\mu_{21})/\sigma$. $\mu_{31}$ for the four-level model, $dn/d\tau$ is the thermocoefficient, $C_p$ is the heat capacity per unit volume, $\mu_{ij}$ is the luminescence quantum yield in the channel $i\rightarrow j$, $t$ is the time. For typical dye solutions the absolute value of thermal change in the refractive index reaches that of the resonance change (as a two-level approximation) at interaction lengths $10^{-3}$ to $10^{-5}$s for $\mu_{21} = 10^{-1}$ to 0.99.

**Conclusion**

The light-induced change in the dye solution refractive index of dye solutions has a number of peculiarities associated with the Stokes shift of absorption and luminescence spectra, the contribution to the integrated phase response of transitions between excited singlet and triplet states, as well as with radiant energy thermalization. At the same time, it should be noted that in certain situations even a relatively small phase response of the dye may significantly influence the process of nonlinear interaction of radiation with the solution [5]. Therefore, the regularities of light-induced change in the refractive index of dye solutions may prove useful in investigating many phenomena of quantum electronics, nonlinear optics and spectroscopy.

**References**

INVESTIGATIONS OF SURFACE POLARITONS IN THE Ag-GaAs SYSTEM

L.V. BELYAKOV, D.N. GORYACHEV, O.M. SRESELI, I.D. YAROSHETSKII
A.F. Ioffe Physico-Technical Institute, USSR Academy of Sciences
194021 Leningrad, USSR

We have studied surface polariton (SP) excitation in the air-metal-semiconductor system with diffraction grating (DG) at the interface and its influence on semiconductor photoresponse. It was shown that photoresponse enhanced greatly due to SP excitation. The SP dispersion was studied as a function of DG modulation height, metal thickness and semiconductor permittivity.

It is well known that a metal diffraction grating (DG) may lead to resonant coupling of an incident photon to surface polaritons (SP) at certain angles of incidence or light frequencies.\[1\]. A pronounced dip in the reflectivity of the grating characterizes SP excitation. Recently some photovoltaic effects in MOM-tunnel junctions have been associated with SP excitation\[2\].

In the present paper SP excitation in the air-metal-semiconductor system and its influence on Schottky diode photoresponse has been investigated. It was shown \[3\] that a resonance peak on the spectral dependence of photoresponse appears when a corrugated surface of the metal-semiconductor structure is illuminated with collimated TM-polarized light. This peak is absent at TE-polarization (Fig. 1, curves 1,4, respectively). The peak shifts with variations of the tilt angle. A similar peak is observed at the photoresponse angular dependence during monochromatic illumination, its position coinciding with that of a reflectivity dip. This allows to unambiguously relate the observed photoresponse resonance enhancement to SP excitation in the metal film at corrugated surface of a semiconductor. The position and width of the photoresponse peak are defined by the SP dispersion relation in the air-metal-semiconductor system and by the DG parameters at the interface. Photoresponse enhancement is explained by SP re-emission into the volume light wave at the metal-semiconductor interface when the penetrating depth of the SP field exceeds metal thickness and semiconductor dielectric constant $\varepsilon_3$ is larger than $(k\lambda/2\pi)^2$ where $K$ is the SP wave vector.

Investigations were carried out on Schottky barriers formed on semiconductors of n-type – GaAs and GaP, with electron concentration $10^{17}$–$10^{18}$ cm$^{-3}$. A relief sinusoidal diffraction grating was fabricated on a semiconductor surface using the laser photochemical etching technique \[4\] with a period of 0.33–1.0 um and a peak-to-peak modulation height of 10–60nm, and then was covered with an evaporated metal (Ag or Au) film of various thicknesses.
An ohmic indium back contact was melted. Photoresponse (photovoltage or photocurrent) between metal film and back contact was measured at TM-polarized light illumination whose electric vector was perpendicular to DG grooves (see insert, Fig. 1). The SP wave vector $\mathbf{K}$ was determined by the relation

$$K = \frac{2\pi}{\lambda} \sin \theta \pm \varphi,$$

(1)

where $\lambda$ is light wavelength, $\theta$ the tilt incident angle of TM-polarized light responsible for the resonance peak, $\varphi$ the DG vector with a period $\alpha$. In this case $G=2\pi/\alpha=1.0-1.3\times10^5$ cm$^{-1}$. The dispersion relation was obtained from angular dependences of photoresponse and reflectivity at various wavelengths and from spectral dependences of photoresponse. The SP dispersion was studied as a function of DG modulation height, metal thickness and semiconductor permittivity.

DG modulation height has a pronounced effect on the position and width of the polariton peak. Peak magnitude and width grow with increasing height, a position of peak shifts to greater SP wave vectors. SP wave vector increasing at the corrugated (as opposed to smooth) metal-air interface is known and theoretically calculated for sinusoidal profile [5]. These experimental data exceed several times the calculated ones due to

*Fig. 1. Photoresponse spectra of the Ag-GaAs structure with DG at the interface for TM- (1,2,3) and TE- (4) polarization. Angles of incidence: 1 - 0°, 2 - 3°, 3 - 6°*
SP reemission at the metal-semiconductor corrugated interface.

Position of the dispersion curve is considerably influenced by the metal film thickness. Modification of the SP dispersion relation caused by the second boundary influence was theoretically calculated by Kretschmann\textsuperscript{[6]}, on the assumption that $d \gg \frac{\lambda}{2} \frac{1}{\sqrt{|\varepsilon_2|} - 1}$ the relative wave vector correction is

$$\frac{\Delta \kappa}{\kappa} = \frac{2 |\varepsilon_2|}{(|\varepsilon_2| + 1)(|\varepsilon_2| - 1)} \exp\left(-\frac{4\pi d |\varepsilon_2|}{\lambda \sqrt{|\varepsilon_2| - 1}}\right) \frac{\varepsilon_2^2 - \varepsilon_3^2}{\varepsilon_2^2 + \varepsilon_3^2},$$

where $\Delta \kappa = |\varepsilon_2|(|\varepsilon_3| - 1) - \varepsilon_3$. One can see from the equation that SP wave vector can both increase or decrease according to the relationship between the parameters. In other words, interaction of SP wave with the second boundary may both slow down or accelerate SP propagation. The change of sign $\Delta \kappa$ occurs when the following condition is fulfilled:

$$\left|\varepsilon_2\right| = \frac{\varepsilon_3 (\varepsilon_3 + 1)}{\varepsilon_3 - 1}.$$

Correction for the SP wave vector in case of $\varepsilon_3 = 14-17$ (GaAs) obtained from Eq. (2) is negative when photon energy $\hbar \omega$ exceeds 2 eV and positive at lower energies. As $\varepsilon_3$ decreases, the sign of $\Delta \kappa$ changes at greater $\hbar \omega$ and for dielectrics with $\varepsilon = 1.5-2.5$, usually applied in SP spectroscopy, $\Delta \kappa$ is positive throughout the whole visible wavelength region.

We have experimentally investigated the displacement of dispersion curves in air-metal-semiconductor structures versus metal thickness and semiconductor permittivity. In the range of 2.3 - 2.6 eV expe-
rimental dispersion curves for Ag-GaAs structure shifts to the left with Ag layer thinning (Fig. 2, curves 1, 2), i.e. \( \Delta K \) negative. At about 2 eV the shift is practically absent. For Ag-GaP structures (\( \varepsilon_3 = 11-13 \)) correction in the same quantum energy range is lower as is evident from Eq. (2). For comparison, Fig. 2 shows also dispersion characteristics of a Ag-dielectric structure (\( \varepsilon_3 = 4 \)) with a similar DG (curves 3, 4). The correction is positive within the whole range of 1.9 to 2.6 eV (see e.g. [6]). We observed also satisfactory quantitative agreement with the calculated \( \Delta K \).

The nature of the correction sign reversal is related to peculiarities of SP wave interaction with the second metal boundary. In addition to SP conversion into the radiative volume electromagnetic wave, the SF wave partly reflects from this boundary. Thus the spatial distribution of SP field intensity between the media changes and SP propagation velocity changes, too, resulting in dispersion curve shift. It should be emphasized that when condition (3) is fulfilled, \( \Delta K = 0 \), and influence of the second boundary manifests itself only in SP group velocity variation (\( v_g = \frac{d\omega}{dk} \)).

Spectral photoresponse plots of the given structures allow investigating interaction of surface polaritons, propagating in the opposite directions, and some features of dispersion characteristics caused by this interaction. Fig. 1 demonstrates the photoresponse of the Ag-GaAs structure with DG wave vector \( G = 0.984 \times 10^5 \text{ cm}^{-1} \) at different tilt angles. One can see two resonant peaks corresponding to wave vectors \( K_1 = \frac{2\pi}{\lambda_i} \cdot \sin \theta + G \) and \( K_2 = \frac{2\pi}{\lambda_2} \cdot \sin \theta - G \) at a fixed angle (curves 2, 3). The peaks move apart as the angle \( \theta \) increases. Note that only one peak is excited at normal incidence. The resonance wavelength obeys the condition \( K = G \). Investigations of the peak fine structure allow to get information concerning dispersion curve splitting (mini-gaps).

The phenomena under study are of interest for practical applications. The metal-semiconductor structure with the regularly corrugated interface is a selective photodetector with SP resonance enhanced photoresponse. Various DG wave vectors permit to have selective photodetectors for a given wavelength and crossed gratings - to use unpolarized light.

References

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LUMINESCENCE OF EXCITONIC SURFACE POLARITONS IN CdS CRYSTAL

V.J. TRAVNIKOV

A.F. Ioffe Physico-Technical Institute of the USSR Academy of Sciences

I94021 Leningrad, USSR

Two new luminescence lines are found in emission spectra of n=1A exciton state of CdS crystal. It is supposed that one of the lines arises as a result of surface polaritons scattering on surface roughness and the other one as a result of surface polariton scattering on impurities and acoustic phonons.

In the case of ideal plane surface and in the absence of any scattering processes surface polaritons (SP) cannot transform into observable emission [1]. SP can contribute to external emission only after some scattering process. It has been shown theoretically [2] that scattering processes on acoustic phonons and roughness can lead to appearance in luminescence two lines between the energies $E_L$ and $E_T$, which correspond to the bottoms of longitudinal and transverse excitonic bands. The results of [2] are presented in the right upper corner of Fig.1. The shortwave line near energy $E_3$ appears due to acoustic phonon scattering. The energy $E_3$ in the case of vacuum-crystal boundary and in the absence of spatial dispersion is determined by the equation $E(E_3) = -I$ ($E(E)$ - dielectric function). The roughness scattering processes must give the line from the high energy side of the $E_T$. Earlier possible display of SP in photoluminescence (PL) spectra have been reported in papers [3] (ZnTe) and [4] (Xe). The only argument in favour of such interpretation was the energy position of observable features. In this work we have managed not only to find two lines in the longitudinal-transverse range (LT range) of excitonic state but to fulfill a number of experiments to substantiate their SP origin.

We have investigated the PL spectra of excitonic state n = IA of CdS crystal at T = 2K. Essential points for detection of SP displaying in PL have appeared to be using clean surfaces (CS), which were obtained by cleavage of samples in liquid helium and registration of emission in "forbidden" geometry $\vec{E}||C$ $\vec{k}||C$ ($\vec{E}$ and $\vec{k}$ - vector of polarization and wave vector of luminescence emission, $C$ - optical axis of crystal). Cleavage has been made along C axis. Earlier for "forbidden" geometry of excitonic state in question it has been reported only about lines $A_L$ and $A_F$ corresponding to luminescence of longitudinal excitons and "forbidden" ortho-excitons. In this work between lines $A_L$ and $A_F$ we have found two new lines B and C in spectra of clean surfaces immediately after cleavage (Fig.2
Energy position of B and C lines is in good agreement with the predictions of [2]. Therefore it is naturally to suppose that line B corresponds to emission originating due to SP scattering on phonons and line C due to SP scattering on roughness.

Fig. 1. Simplified scheme of dispersion curves for excitonic state n = 1A of CdS crystal. Curves T, L, F, SP correspond to dispersion of transverse polaritons (EiC), longitudinal excitons, orthoexcitons and surface polaritons. In the right upper corner the results of [2] are presented, they have been obtained without taking into account spatial dispersion and anisotropy (a - density of SP states, b and c - probabilities of SP scattering on acoustic phonons and roughness).

The spectrum 2 (Fig. 2) has been obtained from the same surface as spectrum 1 and also immediately after cleavage but at the excitation intensity (Iex), which is approximately one order smaller than Iex for spectrum 1. The relative intensity of line B increases with rising of Iex as one can see from Fig. 2. In principle, such increasing in the frame of supposed interpretation may be explained by the increasing of the number of nonequilibrium acoustic phonons arising in surface range as a result of energy relaxation of photogenerated electronic excitations. However, contribution to the B line formation may be given also by elastic SP scattering on imperfections of crystal (impurities or defects). With the increasing of Iex the probability of such processes rises owing to the fact
that after filling up by carriers centres of exciton capture turn into centres of elastic exciton scattering [5]. We believe that elastic scattering gives the main contribution to the B line formation since the change of occupation phonon number is hardly essential in $I_{ex}$ range used by us.

Spectrum 3 (Fig.2) has been obtained at the same excitation and registration conditions and from the same surface as for spectrum 1 but after exposure of crystal on air at the room temperature. Oxidation reduces noticeably the intensity of line B, the line C disappears out of the spectrum. Oxidation is accompanied by appearing of space charge region (SCR). Electric field of SCR reaches a large value at the boundary [6]. Apparently, it leads to decreasing of SP amplitude on the boundary and as a consequence to diminishing of C line intensity. Line B originating as a result of imperfection scattering is formed by all range of SP existence (by depth of the order of SP wave length). It is naturally to consider
that oxidation must not influence its intensity as C line intensity.

Decrease of registration solid angle of observable emission allows to display the spectral form of line B (Fig. 3). It is a consequence of decrease of relative intensity of $A_L$ line which is proportional to $\cos^2 \alpha$ ($\alpha$ - angle between axis C and wavevector of "practically" longitudinal exciton [7]). The halfwidth of line B is essentially larger than the halfwidth of forbidden lines $A_L$ and $A_F$, the shortwave tail covering the range above the energy $E_g$. Taking into account that the SP dispersion curve has continuous character and covers the energy range above $E_g$ in case of spatial dispersion [1] the observable line B form also agrees with supposed interpretation.

In conclusion, all revealed properties of B and C lines - energy position and spectroscopic form, oxidation influence on absolute intensity, relative intensity dependence on $E_x$ - are in agreement with the supposition that line B appears in spectra as a result of SP scattering on imperfections and phonons and line C due to SP scattering on roughness. The fact that the energy structure of n = 1A excitonic state in CdS is well known and in the range in question there are not any other spectral features also speaks in favour of the supposed interpretation. For making more definite the mechanism of SP transforming into observable luminescence in our case it is necessary to do the analysis by taking into account spatial dispersion and anisotropy.

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APPLICATION OF THE METHOD OF IRREDUCIBLE TENSORIAL OPERATORS TO STUDY THE EXPANSION OF STATIONARY PERTURBATION THEORY

G.A. GAIGALAS, G.V. MERKELIS
Institute of Physics of the Academy of Sciences of the Lithuanian SSR
232600 Vilnius, USSR

In this paper a graphical method is presented to calculate spin-angular parts of matrix elements of the effective operators of stationary perturbation theory which are expressed in irreducible tensor form in the second quantization.

The task to apply graphical methods of angular momentum theory when studying the perturbation theory expansion of various quantities in many-electron atoms and ions is of great interest for many years (see [1]). Nowadays the main attention is paid to the representation of separate terms of the expansion which are summed up over one-electron magnetic quantum numbers. This allows one to develop a more effective method to analyze and calculate spin-angular parts of the interaction under investigation. To our mind the best perspective is the application of the method of the second quantization.

The diagrams $A_4$ and $A_5$ represent the tensorial operators of electron creation $\alpha^{x}_{m_x}$ and annihilation $\bar{\alpha}^{y}_{m_y}$, where $(y) = (l, s)$ in the case of $L, S$ coupling and $(y) = (j)$ in the case of $j, j$ coupling [2].

The contraction can be graphically expressed as a connection of two lines in the direction of an arrow (see diagram $A_5$). For creation and annihilation operators both the contraction and the term, appearing in the commutation of operators and having a Kronecker symbol $\delta(i, j)$, have the same algebraic expression, therefore we represent the commutation relation

$$[ \tilde{\alpha}^{(1)}_{x} \alpha^{(2)}_{x}]_{M_r} = (-1)^{x_1+x_2} \delta_{(1)_{M_r}}^{(1)_{M_r}} \alpha^{(1)}_{x} \alpha^{(2)}_{x} + \sqrt{\delta_{(1)_{M_r}}^{(1)_{M_r}}} \delta(1, 0) \delta(j_1, j_2)$$

by the diagrams $A_3, A_4, A_5$. $A_3$ represents an irreducible tensorial product in the left part of (1), and $A_4$ - an irreducible tensorial product obtained after the interchange of $\alpha^{(1)}_{x} \alpha^{(2)}_{x}$ and $\alpha^{(1)}_{x} \alpha^{(2)}_{x}$ in $[ \tilde{\alpha}^{(1)}_{x} \alpha^{(2)}_{x}]_{M_r}$. It is necessary to add to the common [3] graphical representation of a complex product of the second quantization operators the rule, which determines the correspondence between the order of operators in a algebraic expression and the order of free lines, representing the second quantization operators in the diagram. In the present paper the beginning of an arrow
Fig. 1

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near the free line in the block (see the diagram $A_8$) means that it represents the very left operator in the algebraic expression, and the free lines in the direction of an arrow represent operators on the right side. In the second quantization representation the wave function of the shell of equivalent electrons $|n_j^N\alpha\Gamma M_r>$ is expressed as $\tilde{\varphi}(n_j^N\alpha)^{(r)}_{M_r}$ [4], where $\tilde{\varphi}(n_j^N\alpha)^{(r)}_{M_r}$ is an irreducible tensor (cf. diagram $A_6$), made of creation operators $A_6^{(r)}$. Therefore, a complex wave function which has shell structure is graphically represented as a product of diagrams $A_8$ and $A_9$. $A_9$ represents vacuum state $|0>$ Analogically the bra function $\langle n_j^N\alpha\Gamma M_r|$ is represented by the expression $\langle 0|\tilde{\varphi}(n_j^N\alpha)^{(r)}_{M_r}$, where $\tilde{\varphi}(n_j^N\alpha)^{(r)}_{M_r}$ is irreducible tensor (see diagram $A_7$), obtained from $\varphi(n_j^N\alpha)^{(r)}_{M_r}$ simply changing $A_7$ to $A_8$ [4]. Then the bra function with $k$ shells will be represented by a product of diagrams $A_{10}$ and $A_{11}$, where $A_{10}$ is a vacuum state $\langle 0|$. While constructing the diagram of a submatrix element of the tensorial operator $T^{(k)}$ we employ the relation [4]

$$
\langle \Gamma|T^{(k)}|\Gamma'\rangle = (-A)^{k-1} \left[ T^{(k)} \right]^{(0)}^{(r)} = 0,
$$

where $\beta$ is a phase, which depends on the number of electrons in the shells of bra function. Let us take as an example a diagram $A_{12}$, which represents the scalar product in the right side of (2) when the operator $T^{(k)} = [A_{12}^{(k)}]^{(k)}$ acts on the first and the second shell of equivalent electrons. The following scheme is possible to rearrange the tensorial product under investigation: 1) to collect all the operators corresponding to one shell (with the same $n_j^N$) so, that they would be side by side (see diagram $A_{13}$); then the factor $(-A)^{N_j^N}$ corresponds to each crossing of free lines $i_{ij}$, representing the second quantization operators and having $N_j^N$ operators $A_9$ and $A_8$. 2) after this procedure the obtained diagram is cut through free lines corresponding to operators with the same $n_j^N$ and covered with such generalized Clebsch-Gordan coefficient, that diagrams $A_{15}$ and $A_{16}$ represent scalar products in the right side of (2). As a result we have a product of transformation matrix $A_{14}$ and two scalar products $A_{15}$ and $A_{16}$ which correspond to the submatrix elements $(n_j^N\alpha\|A_9^{(k)}\|n_j^N\alpha)$ and $(n_j^N\alpha\|A_8^{(k)}\|n_j^N\alpha)$. The sum of Feynman diagram $A_{17}$ over $n_j^N$ can be represented (see Fig. 2) by the irreducible tensor $A_{18}$, one of the ways of such representation is discussed in paper [5]. Then the calculation of submatrix
elements of effective Hamiltonian of atom, expressed as an expansion of perturbation theory, each term of which is represented by Feynman diagram, can be performed in a given model space by the above described graphical method, which, we think, can be easily algorithmized.

References


* English translation: Soviet Physics Collection
SOME RESULTS OF ANALYTICAL ATOMIC SPECTROSCOPY FROM THE GDR

H. PALK
Central Institute for Optics and Spectroscopy (ZOS), Academy of Sciences of the GDR
Berlin 1199, GDR

Research activities of the GDR in the field of analytical atomic spectroscopy are considered. Special attention is paid to techniques using electrothermal atomization such as graphite furnace emission (PANES) and laser excited fluorescence spectrometries.

1. Introductory remarks

There is an interaction between spectroscopic research and manufacturing of spectroscopic instruments. On the one hand new scientific instruments are developed as a part of the research process. On the other hand a modern instrumentation is a prerequisite for successful and efficient basic and applied research. Therefore, a prompt reaction of the instrument manufacturers on the advent of new principles and methods may help both fundamental research and practical application.

Analytical atomic spectrometry is used in various fields: metallurgy, medicine, biology, agriculture, electronics industry, protection of environment etc. A broad application of spectroscopic methods needs detection capabilities in the ppt (10^{-12}) range and even lower.

2. Electrothermal atomizers

Electrothermal atomization in a graphite tube provides atomization efficiencies near to the theoretical limit in favorable cases [1]. A prerequisite for high and reproducible efficiencies of electrothermal atomizers is their temperature program. Heating rates of 2 Ks^{-1} should be accomplished in the temperature range from ambient to 3000 K. This has been realized by the atomic absorption spectrometer AAS 3/EA 3 from Jenoptik [2]. Using these high temperature ramp rates starting from ambient provides a prolonged isothermal zone of the atomizer tube during the atomization stage [3].

3. Furnace nonthermal excitation spectrometry (PANES)

The aim of using the very efficient electrothermal atomizer for atomic emission purposes led to the PANES system. A schematic cross-section of a PANES source is shown in Fig. 1.

Here, the graphite tube is not only an atomizer but also a hollow cathode while using it in a low pressure rare gas atmosphere. The plasma is essentially restricted to the inside of the graphite tube. The high electron temperature of the PANES plasma provides an efficient excitation.

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of the sample vapour inside the tube. Therefore, PANES accomplishes multielement capability when coupled with a polychromator. Some selected detection limits achieved with PANES are compared with those of other methods in Table I. As can be seen from Table I the detection limits of PANES are typically comparable or better than the GPAAS values but orders of magnitude lower than the ICP values.

The PANES method has been successfully applied to the determination of impurities in super pure substances by the Institute for Physical Chemistry/AdW d. DDR in cooperation with ZOS. The extension of the PANES method to the excitation of molecules has been carried out at the Karl-Marx-University, Leipzig [5].

4. Laser excited atomic fluorescence (LAPS)

With the help of tunable dye lasers (pulsed) a radiance across the absorption profile of an atomic line of the order of 10 kW cm\(^{-2}\) can be achieved. Such intensity is sufficient to saturate atomic transitions which means that about one half of the atoms within the volume irradiated populates the excited level. Then, the fluorescence intensity becomes maximum and the influence of intensity fluctuations of the laser may be decreased considerably.

A block diagram of the LAPS set-up developed in ZOS is shown in Fig. 2 [6]. In this case an open cup electrothermal atomizer has been used to meet the necessity for irradiation and observation of the atom cloud with low background radiation from the incandescent cup.

The limit of detection for volatile elements was in many cases

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### Table I

Detection limits (pg) of PANES, GPAAS and ICP

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP$^+$</th>
<th>GPAAS$^\dagger$</th>
<th>PANES$^{11}$</th>
<th>PANES [nm]</th>
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<tr>
<td>K</td>
<td>60000</td>
<td>1</td>
<td>0.03</td>
<td>766.5</td>
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<tr>
<td>Li</td>
<td>3000</td>
<td>30</td>
<td>0.02</td>
<td>670.8</td>
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<tr>
<td>Mo</td>
<td>4000</td>
<td>2</td>
<td>400.00$^+$</td>
<td>379.8</td>
</tr>
<tr>
<td>Na</td>
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<td>1</td>
<td>0.04</td>
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</tr>
<tr>
<td>Ni</td>
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<td>5</td>
<td>1.7</td>
<td>341.5</td>
</tr>
<tr>
<td>Pb</td>
<td>300000</td>
<td>2</td>
<td>3</td>
<td>405.8</td>
</tr>
<tr>
<td>Rb</td>
<td>300000</td>
<td>20</td>
<td>1.2</td>
<td>780.0</td>
</tr>
<tr>
<td>Ti</td>
<td>2000</td>
<td>100</td>
<td>800</td>
<td>364.3</td>
</tr>
<tr>
<td>V</td>
<td>4000</td>
<td>1</td>
<td>6</td>
<td>318.4</td>
</tr>
<tr>
<td>Zn</td>
<td>2000</td>
<td>0.5</td>
<td>2.7$^x$</td>
<td>213.9</td>
</tr>
<tr>
<td>Ag</td>
<td>3000</td>
<td>0.4</td>
<td>0.4$^x$</td>
<td>328.1</td>
</tr>
<tr>
<td>Au</td>
<td>10000</td>
<td>10</td>
<td>3</td>
<td>242.8</td>
</tr>
<tr>
<td>B</td>
<td>2000</td>
<td>500</td>
<td>1.2</td>
<td>249.7</td>
</tr>
<tr>
<td>Ca</td>
<td>50</td>
<td>1</td>
<td>0.07</td>
<td>422.7</td>
</tr>
<tr>
<td>Cd</td>
<td>2000</td>
<td>0.3</td>
<td>1.1$^x$</td>
<td>228.8</td>
</tr>
<tr>
<td>Cu</td>
<td>3000</td>
<td>2</td>
<td>1.2</td>
<td>324.7</td>
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<tr>
<td>Cl</td>
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<td>-</td>
<td>80</td>
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</tr>
<tr>
<td>Tl</td>
<td>400000</td>
<td></td>
<td>0.2</td>
<td>535.1</td>
</tr>
</tbody>
</table>

Spectrometer: 2m-Ebert (Jenoptik, Jena), 2-channel  
$x$ 0.75-m Echelle-grating (Spectraspan III), 1-channel; $+$ 1.5-m Rowland, 10-channel; $+$ ARL 34000, ICP; ARL brochure (1982); HGA 500, Perkin-Elmer brochure (1981); 11 sample amount: 50 $\mu l$

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**Fig. 2. Block diagram of the LAPS set-up**

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better than those reported from GPAAS. Because of the strong temperature gradient above the cup the detection capability decreased for involatile elements. An improvement of the detection capability for these elements may be achieved by using a tube atomizer in connection with LAPS as has been done at Karl-Marx-University, Leipzig [7].

![Pulse shapes of LAPS signals](image)

The high sensitivity of LAPS may be used successfully to determine trace components in solid samples without dissolution. This could be shown by analysing photographic materials [6]. Matrix influences may be efficiently suppressed by making use of the fractionated vaporization of the sample. An example is shown in Fig. 3. It can be seen from this figure that the stray light peak caused by NaCl particles may be discriminated by using an adequate time interval for the registration of the signal.

References


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ЛАЗЕРНЫЙ АТОМНО-ФЛУОРЕСЦЕНТНЫЙ АНАЛИЗ С ВАКУУМНОЙ ЭЛЕКТРОТЕРМИЧЕСКОЙ АТОМИЗАЦИЕЙ

М.А. БОЛЬШОВ, А.В. ЗЯБИН, В.Г. КОЛОЩУКОВ, И.И. СЫРИЕНКИНА
Институт спектроскопии АН СССР 142092, г. Троицк, Московской обл., СССР

Лазерный атомно-флуоресцентный метод с вакуумной электротермической атомизацией применен для анализа олова на содержание кобальта и анализа образцов, полученных из руды в результате просеянного концентрирования, на содержание рутения. Показано, что использование вакуумной атомизации устраняет влияние матрицы и позволяет вести эталонирование по водным растворам. Достигнутые пределы обнаружения составляют 5·10^{-8} % для Co и 10^{-7} % для Ru.

Введение

В настоящее время проблема борьбы с матричным эффектом является одной из основных в спектральном анализе. Применение лазерных методов детектирования свободных атомов не снимает, естественно, влияния матрицы, которое, как правило, возникает на стадии атомизации. Однако, благодаря запасу чувствительности, обеспечиваемому лазерными методами, в ряде случаев удается существенно уменьшить влияние матрицы, частично пожертвовав этим запасом. Одна из таких возможностей обсуждалась нами в [1] и связана с разбавлением матрицы.

Другая, по-видимому, более универсальная возможность связана с электротермической атомизацией в вакууме (БЭТА). По сравнению с атомизацией в атмосфере буферного газа вакуумная атомизация значительно проигрывает в эффективности использования атомов, поскольку тепловые скорости атомов в вакууме на 3-4 порядка превышают скорость конвекционных потоков в газе и, соответственно, концентрация свободных атомов в аналитическом объеме оказывается на 3-4 порядка меньшей. Поэтому вакуумная атомизация не привлекала ранее внимания аналитиков.

Ситуация, однако, существенно изменилась с развитием высокочувствительных лазерных методов детектирования свободных атомов. На перспективность применения БЭТА было указано в работах, посвященных методу лазерной ступенчатой фотоионизации атомов с детектированием образовавшихся ионов при помощи вторичных электронных умножителей (ВЭУ) [2]. Для работы ВЭУ необходимо высокий вакуум (не хуже 1·10^{-3} Па), поэтому в этом методе атомизация в буферном газе невозможна и используется вакуумная электротермическая атомизация. При этом выявилось чрезвычайно важное свойство БЭТА: для широкого круга объектов, включая такие сложные для анализа матрицы, как кровь и морская вода, БЭТА обеспечивает степень атомизации близкую к 100% и практически полное отсутствие матричного эффекта.

Несмотря на то, что лишь малая часть (≤ 1%) испарившихся атомов попадает в аналитический объем и только 10^{-5} из них пролетает через аналитический
объем в момент действия лазерных импульсов, благодаря высокой эффективности детектирования ионов, провзаимодействовавших с лазерным излучением, метод позволяет измерять концентрации примесей до $10^{-9}$.

Отметим, однако, что метод фотоионизации технически достаточно сложен. Для его реализации необходимы, в общем случае, три перестраиваемых лазера на красителях с достаточно узкой линией. Кроме того, необходимость высокого вакуума $10^{-3}$ - $10^{-4}$ Па для работы ВЭУ снижает экспрессность метода. В то же время есть основания предполагать, что достоинства ВЭТА реализуются уже при вакууме 1 - 10 Па. В связи с этим представляет интерес применение лазерной флуоресцентной методики детектирования в сочетании с ВЭТА. По чувствительности детектирования свободных атомов в аналитическом объеме ВЭТА может оказаться в 2-3 порядка эффективнее фотоионизационной. Однако, во флуоресцентной методике примерно во столько же раз выше эффективность использования атомов, поскольку нет необходимости формировать атомный пучок и аналитический объем можно расположить на расстоянии 3-5 мм от тигля, в котором происходит испарение. При этом практически все атомы, испарившиеся из тигля, пролетают через аналитический объем. Кроме того, более низкие требования к интенсивности излучения накачки позволяют использовать лазеры с большей частотой повторения для возбуждения флуоресценции и, соответственно, увеличить чувствительность. Исследованию возможностей лазерного атомно-флуоресцентного анализа с вакуумной электротермической атомизацией (ЛАФС-ВЭТА) и посвящена настоящая работа.

**Экспериментальная часть**

Для исследования были выбраны две задачи, представляющие практический интерес: (1) определение содержания кобальта в чистом олове, (2) определение содержания рутения в геологических образцах. Исследования проводились на атомно-флуоресцентном спектрометре, включающем в себя импульсный лазер на красителях, атомизатор и систему регистрации.

**Лазер на красителях**

Для возбуждения флуоресценции использовалось излучение второй гармоники импульсного лазера на красителях (ИЛК). ИЛК возбуждается излучением второй гармоники лазера на основе $Nd:YAG$. В качестве селективных элементов в резонаторе ИЛК использовались три призмы и интерферометр Фабри-Перо с толщиной воздушного зазора 2 мм. Перестройка длины волны излучения ИЛК осуществлялась за счет поворота призм интерферометра. Частота излучения ИЛК удваивалась в кристалле КДР длиной 4 см. Спектральная ширина излучения второй гармоники составляла 3-10$^{-3}$ нм, длительность импульса 7 нс, мощность в импульсе 1 кВт, частота повторения импульсов 25 гц. Точная настройка на резонансную линию нужного элемента осуществлялась по максимуму сигнала флуоресценции, возбуждаемого лазерным излучением в разряде лампы с полым катодом.

**Атомизатор**

Атомизация образцов проводилась в откачиваемой камере со съемной верхней крышкой и с кварцевыми окнами для ввода лазерного излучения и вывода из-
лучения флуоресценции. Образец загружался в графитовый стаканчик, с внешним диаметром 6 мм, внутренним диаметром 4 мм и глубиной 7 мм. Стаканчик закрывался между графитовыми электродами, закрепленными в массивных медных держателях, охлаждаемых водой. Нагрев стаканчика осуществлялся электрическим током. Максимальная температура стаканчика — до 3000°С. Лазерный луч проходил над стаканчиком на высоте 5 мм. Поперечное сечение луча над стаканчиком формировалось линзой и диафрагмами и представляло собой квадрат, размером 6 х 6 мм².

Система регистрации
Излучение флуоресценции собирали линзой на входную щель монохроматора МДР-2 с относительным отверстием 1:2,5. За выходной щелью монохроматора располагался фотоумножитель ФЭУ-130, сигнал которого усиливался и регистрировался с помощью стробинтегратора с длительностью строба 100 нс. Стробинтегратор измерял амплитуду каждого импульса флуоресценции и суммировал амплитуду всех импульсов за время атомизации пробы (пополный аналитический сигнал). Кроме того, амплитуда импульсов выводилась на аналоговый выход интегратора для регистрации динамики атомизации с помощью самописца.

Методика и результаты
Анализ олова проводился без какой-либо предварительной подготовки образца. Кусочек олова весом 50 мг вносили в стаканчик атомизатора, камера атомизатора откачивалась до давления 1,3 Па и стаканчик нагревался до температуры 1600°С. Цикл испарения длился до 120 с, причем выяснилось, что испарение примеси Со происходит лишь после полного испарения кусочка олова. Работа проводилась с синтетическими эталонами, приготовленными в ИПРМГТе. Аналитическая кривая оказывалась линейной в диапазоне концентраций 10^{-2} - 10^{-7}%.

Предел обнаружения Со в олове составил 5·10^{-8}%, а Со в воде 1·10^{-8}%. Аналитический сигнал в водных эталонах и в эталонах из олова с одинаковым содержанием Со совпал в пределах ошибок.

Анализ руд на содержание Ru проводился с предварительным пробирным концентрированием в свинцовый или медный король по обычной методике с последующим анализом королька. Предел обнаружения Ru в свинцовых и медных корольках составил 1·10^{-7}% и в водных растворах 1·10^{-5}%.

Динамика испарения Ru из водных растворов и из корольков существенно различаются, однако полный аналитический сигнал от одинаковых количеств Ru в обоих случаях совпадает в пределах ошибок, т.е. в этом случае влияние матрицы на аналитический сигнал практически снимается и можно вести прямой анализ с эталонированием по водным растворам.

Литература

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Design problems of a nanosecond decay time spectrometer are discussed and suggestions are made as to the most appropriate components for building up a sensitive, single pulse and relatively inexpensive instrument.

Introduction

Research work in molecular physics, chemistry and biology requires, to a continuously increasing extent, excitation lifetime data for investigating the intra- and extramolecular mechanisms of energy transfer. With modern instruments excitation lifetimes can be measured in the wide time range from fs to 10 s. In the present work we deal with the determination of lifetimes longer than ns because the shorter lifetimes require highly sophisticated instrumentation.

The primary excited state of a single molecule can be populated by light absorption in about $10^{-18}$ s. The spontaneous emission time of single molecules is the same as the absorption time. The macroscopic excited state lifetime is a molecular statistical event and the experimental decay curve $D(t)$ can be described as usual by the sum of exponentials

$$D(t) = \sum A_i \exp (-t/\tau_i),$$

where $A_i$'s are the emission intensities in $t=0$ and $\tau_i$'s are the experimental average lifetimes. The physical meaning of eq. (1) is not completely clear. It is probably only a mathematical description of a non-exponential time evolution.

Eq. (1) will be more complicated when $\tau_i$'s and the halfbandwidth of the exciting pulses are commensurable. In this case the experimental decay curve $B(t)$ is a convolution integral of the exciting function $k(t)$ and the sum of exponentials

$$B(t) = \int k(t) \cdot D(t-t') \, dt.$$  

The experimental task is to measure $B(t)$ (or $D(t)$) as precisely as possible. Evaluation of the measurement, i.e. the determination of the $A_i$ and $\tau_i$ parameters, is computational work using any type of deconvolution procedure [1].

Functional block diagram of a decay time spectrometer

The technique of decay time measurements has improved considerably together with the general instrumentation level. However, here, we have no wish to analyse the route of this development, our aim is now to select the components for building up the most suitable instrument based on our evaluation. Basically, two types of decay time instruments are known:

1. Single Pulse Spectrometers
2. Composite Pulse Spectrometers
a) Phase and/or amplitude modulation decay time meters are commercially available [2]. They are suitable for precise and relatively fast measurements because of the extreme frequency selectivity attainable by the state-of-the-art electronics. The disadvantages of these instruments are:
- A high intensity light source (450 W Xenon lamp) is required and this may cause significant photochemical damage;
- The parameters of only a single exponential can be determined.

b) Pulsed light instruments are also highly advanced and commercially available. They are suitable for determining the complete decay curves without any supposition. Because of the minimum illumination intensity any photochemical damage can be neglected.

These are the reasons that hereafter we shall deal only with pulsed light methods.

In Fig. 1 the functional block diagram of a pulsed light decay time spectrometer is outlined. Spectrometers in this category differ from each other only with regard to the light source and the measuring electronics.

![Functional block diagram](image)

**Fig. 1**

**Requirements for the modules**

The specification of the spectrometer components can be defined as follows:

For the exciting light: (i) Continuously variable in the full range of the UV/VIS region (from 220 to 750 nm). (ii) The monochromaticity is better than the half-bandwidth of the vibronic transitions in the vapour state (~5 cm⁻¹). (iii) The light intensity is high enough to have emission light from samples with low quantum efficiency or low concentration.

For the sample chamber: (iv) Variable (wide temperature range cryostat, high precision thermostat, application of polarization adapters, etc.).

For the emission monochromator: (v) Interchangeable (high resolution measurements require 1 m or longer collimator focal length, for applied spectroscopic works 0.25 m of that is enough).

For trigger detectors: (vi) The rise time must be less than 200 ps to eliminate time jitter.

For the measuring detector (now in most cases PMT-s): (vii) Low time spread to decrease the convolution effect of the instrument. (viii) Wide spectral sensitivity (from 180 to 750 nm). (ix) High quantum efficiency. (x) Low noise. (xi) Good magnetic and radio-

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frequency shielding. (xii) Low dark current. (xiii) High gain (up to $10^{-8}$). (xiv) High loadability.

For the electronic measuring system: (xv) The decay curve must be measured with higher precision than 1 per cent. (xvi) Wide time range (from ns to 10 s). (xvii) Utilization - if possible - of the full decay curve in each pulse.

**Built-up systems and experience**

The most important types of pulsed light decay time instruments have been built-up in our laboratory. All parts of the equipments except the detectors, electronic components and oscilloscopes were developed in our own laboratory or other departments of our institute.

A summarized description of the measuring set-ups and the experience gained is as follows:

a) A time correlated single photon counting system was built-up from two constant fraction discriminators, a time-to-amplitude converter, ICA-70 multichannel analyser, controller, gated nanosecond flashlamp with 50 kHz repetition rate, and two monochromators with 25 cm focal length [4].

b) The original high speed storage oscilloscope method [5] was reproduced by using a TEKTRONIX Mod. 7633 oscilloscope with 7A26 dual trace amplifier and 7A22 differential amplifier plug-ins. The fastest calibrated sweep rate is 5 ns/div, the highest sensitivity of the vertical deflection is 5 mV/div with plug-in 7A26. The same values for plug-in 7A22: 1 μs/div(hor) and 10 μV/div(vert).

A 400 kW $\text{N}_2$ laser was used as a light source (made by Institute for Experimental Physics, JATE Szeged) with a repetition rate of 25 pulses/s. The other components are the same as described for the time correlated single photon counting system.

For recording the analog results a photographic procedure was applied and for the computerized evaluation the digital data were prepared manually.

The required light intensity in this case must be high enough to produce a good measurable pulse shape at the detector output. This means that the required light intensity is 2 or 3 orders of magnitude higher than in the case of time correlated single photon counting.

c) For the sampling oscilloscope technique [6] a sampling unit was developed with 200 ps sampling time. (The most advanced version of this type of instruments is the Mod. 400 Signal processing System by EG&G PARC. The price of this instrument is very high, and we have not experience in its use.) The other version of the sampling instruments - the so called transient recorders - and the conventional multichannel analyser (e.g. ICA-70) were also used. The conversion times are in these cases 100 ns/point and 100 μs/point, respectively.

d) Digital oscilloscope forms the last step in this field. Information represented by the time evolution of the emitted light is stored in an analog manner which is converted automatically to digital form and stored in the built-in random access memory. Data processing takes place by an on-line microcomputer.

**The optimum system and its evaluation**

On the basis of our experience the most suitable measuring system consists of the following components: High pressure $\text{N}_2$-laser light source with 400 kW power combined with dye laser and frequency doubler the pulse-width in this case is less than 500 ps. Variable
sample chamber and interchangeable emission monochromators are as defined in (iv) and (v).

Trigger detector: vacuum photodiode with -120 ps risetime. Interchangeable measuring photomultipliers: Philips XP-2020, and 56-TVP, RCA 8850, 8852 and C31024. Measuring system: IWATSU TS-8123 digital oscilloscope and ICA-70 multichannel analyser. On-line microcomputer with Z-80 microprocessor was used to collect the measured data.

Evaluating the optimum system we can state: (i) The intensity of the light source is high enough to excite the samples in the spectrum range from 230 to 750 nm. (ii) High intensity signals can be achieved by selection of the measuring detectors. (iii) The computerized IWATSU oscilloscope together with the ICA-70 multichannel analyser provide for automated high precision and highly sensitive measurements in the full time range. (iv) The pulsed light source and the streaming sample minimize photochemical damage. (v) The time jitter (less than 0.2 ns), the noise (in general less than 5 per cent in the ns range as a slowly waving signal is superimposed on the measurements), and the reproducibility of the pulse shape (maximum deviation is 3 percent) can be reduced by averaging repeated measurements. In our experience the agreement between two consecutive (averaged) measurements is better than 1 per cent summing 25 repeated decay curves. (vi) The evaluation software based on the Meiron non-linear least squares procedure [7] gives a numerical precision in the decay time better than 0.1 per cent. The program is written for a Z-80 based and IBM XT microcomputers in compiler BASIC and the most time consuming procedures in machine language. The evaluation time in general is less than 5 to 10 minutes [8] depending on the type of computer employed.

Acknowledgements

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APPLICATION OF THE NEW METHOD FOR ENDO STUDIES OF DISORDERED SYSTEMS. 14N ENDO STUDY OF POWDERED SAMPLE OF BIS(8-MERCAPTOQUINOLINE)OXOVA NADIUM(IV) MAGNETICALLY DILUTED IN THE CORRESPONDING IN(III) HOST LATTICE

N. D. YORKANOVA and M. ZORAUKOVA
Institute of Kinetics and Catalysis, Bulgarian Academy of Sciences
1113 Sofia, Bulgaria

The recently developed new method for ENDO studies of disordered systems is described and applied for 14N ENDO study of the title compound.

Introduction

The method of Electron Nuclear Double Resonance (ENDOR) is a relatively new spectroscopic tool for study of some weak and very weak interactions of the unpaired electron with the magnetic nuclei in paramagnetic species. Usually these interactions are in the region of 0.5 - 10 MHz and very often are not detectable by the EPR spectroscopy. The information obtained by ENDO study of these interactions is very important at least in two aspects - to study the distribution of the spin density on its own molecule and to find some interactions between it and neighbouring nuclei from lattice molecules. The studies are carried out both in ordered (single crystal) and disordered (powders or solid solutions) systems, the latter being much more common. The experimental methods available [1-3] for studying disordered systems by the method of ENDO spectroscopy are strongly limited. Until recently only one method (called method of "turning points") was available [4] showing some disadvantages [5]. In view of this a new improved method for ENDO study of disordered systems was developed recently [5] the results of which give the real magnitudes of the hyperfine (hf) interaction tensor and polar angle between the direction of the symmetry axis of the paramagnetic species and the direction of the corresponding nucleus. Thus in the frame of polar coordinate system it is possible to calculate some important structural data for the paramagnetic molecule and to obtain information about its environment [5,6].

Principle of the new method for ENDO study of disordered systems

Let's consider a powdered sample consisting paramagnetic molecules with axial symmetry and to assume that hf interactions of the unpaired electron are too weak to be resolved by the method of EPR spectroscopy. The EPR spectrum which will be recorded in integral form (absorption curve) is shown on Fig. 1a assuming that the lines have finite widths. However, every such EPR spectrum is consisting of discrete "spin packets" for every one of which the resonant magnetic field \( H(\theta) \) is

\[
H(\theta) = h\nu_o/\alpha_o g(\theta) = h\nu_o/\alpha_o (g_h^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta)^{1/2},
\]
Fig. 1. a. Hypothetical EPR spectrum of powdered sample; b. Theoretical angular dependence of hf constants versus B and as a function of $\alpha$.

where $B$ is the angle $(g_{||}; H)$. Now if we select some of the "spin packets" by setting the magnetic field (EPR observer) at some position between $H(g_{||}) = H(0^\circ) \leq H(B) \leq H(90^\circ) = H(g_{||})$ and assume that $T_{xx} < T_{1e}$ we will record ENDOR transitions corresponding only to them. Consecutively setting the EPR observer in the above region we will record several ENDOR spectra for every one of which the hf splitting constant will be described by the following equation

$$A(B) = A_{\text{aniso}} (3\cos^2(\alpha_0 - \alpha) + A_{\text{iso}})$$

where $\alpha$ represents the polar angle between $g_{||}$ and the position of the appropriate nucleus.

Plotting the values of $A(B)$ thus found versus $B$, which may be calculated by the equation

$$Q_2 = \cos^{-1} \left[ \left( \frac{\hbar \gamma_0/\gamma_e}{g_{||} + g_{\perp}} \right) - g_{||} \right]^{-1/2}$$

or by the theoretical EPR spectrum, we will find several curves depending on the value of $\alpha$—Fig.1.b. It is clear from the figure that the method of "turning points" (in our case $g_{||}$ and $g_{\perp}$) gives real results only when $\alpha = 0$ or $90^\circ$. In all other cases some error is introduced depending on the deviation of the magnitude of $\alpha$ from 0 or $90^\circ$ [5].

Application to the study of $^{14}N$ ENDOR transitions in powdered sample of $V(O_{\text{tox}})_{2}$ magnetically diluted in $In(O_{\text{tox}})_{3}$ host lattice

The powdered EPR spectrum of $V(O_{\text{tox}})_{2}$ magnetically diluted in $In(O_{\text{tox}})_{3}$ host lattice (tox = 8 mercaptoquinoline anion -$C_{9}H_{6}NS^{-}$)—Fig.2 suggests approximately axial symmetry of the complex. Due to the presence of quadrupole moment ($Q$) in $^{14}N$ nucleus each ENDOR resonance line must satisfy $\nu_{\text{ENDOR}} = A/2 \pm \nu_{N} \pm 3Q/2$ where $\nu_{N}$ is the free $^{14}N$ nuclear resonance frequency and $A$
Fig. 2. EPR spectrum of VO(tox)$_2$ magnetically diluted in In(tox)$_3$ host lattice. The region in which the EPR observer was setted is shown.

is the hf coupling constant. Usually such spectra are complicated because not all of the lines are resolved when the method of "turning points" is applied [7]. On Fig. 3 are shown some representative $^{14}$N ENDOR spectra recorded at different polar angles $\theta$.

Fig. 3. Some representative $^{14}$N ENDOR spectra of VO(tox)$_2$ taken at different polar angles $\theta$.

different polar angles $\theta$, and on Fig. 4 the angular dependence of all resonance transitions (A) versus $\theta$. It follows from fig. 4 that the nuclei $^{14}$N are equivalent in the frame of the experimental error and are situated in the plane xy of the complex ($\alpha = 0^\circ$). No X-ray structural data for VO(tox)$_2$
Fig. 4. Angular dependence of $^{14}\text{N ENDOR}$ transitions of VO(tox)$_2$ magnetically diluted in In(tox)$_3$ host lattice versus $\theta$.

are available at the moment but the above data have shown that the complex is planar with a V=O bond perpendicular to the plane. The $^{14}\text{N ENDOR}$ parameters evaluated from Fig. 4 in the frame of the VO complex coordinate system are:

$A_{zz} = 7.4$, $A_{xx} = 7.52$, $A_{yy} = 8.18$ MHz and $Q_{zz} = \pm 0.66$, $Q_{xx} = \pm 0.84$, $Q_{yy} = \pm 0.17$ MHz.

The data give $A_{iso} = 7.7$ MHz and in the frame of $^{14}\text{N}$ local coordinate system the $^{14}\text{N}$ anisotropic hf tensor is $^{14}\text{N}T = [-0.18, -0.3, 0.48]$. Since the unpaired electron of VO moiety is assumed to be located mainly on $d_{xy}$ orbital [8], the presence of isotropic hf coupling suggests a mixing of $d_{xy}$ and $d_{x^2-y^2}$ orbitals of vanadium in the studied complex.

References

STUDY OF TRIPLET EXCITON INTERACTION IN MOLECULAR CRYSTALS

A.A. DELYUKOV, G.V. Klimusheva, A.V. Turchin
Institute of Physics, Academy of Sciences of the Ukrainian SSR
252650 GSP Kiev, USSR

This research continues the study of interaction and relaxation of triplet excitations and is devoted to the magnetic field effect on spin-lattice relaxation (SLR) of triplet excitons and to the triplet-triplet annihilation properties at high density of excitons.

Introduction

Triplet excitons have some advantages over singlet ones when studying interaction between excitons in molecular crystals. A comparatively long life of triplet excitons facilitates production of their high concentrations. The triplet excitons are characterized by narrow bands (~1 cm⁻¹), which promotes manifestation of even weak static interaction between them. Triplet excitons in the benzophenone crystals possess a supplementary property due to the static dipole moment of about 1 Debye. It is a result of the dipole moment variation in the benzophenone molecule with its transfer from the basic state S₀ to the triplet one T₁.

Effect of the magnetic field on the SLR of triplet excitons

Rapid SLR (10⁻⁵ - 10⁻⁸ s) is typical of triplet excitons as a result of excitation migration on translation-nonequivalent molecules /1/. The theory prognosticates suppression of this mechanism under the effect of the external magnetic field /2/, providing the mentioned effect to be observed both with a coherent mode of exciton movement and with an incoherent (diffuse) one.

The study of the dependence of the exciton SLR rate in the benzophenone crystals on the magnetic field was based on the known phenomenon of the spin memory in the triplet exciton capture by a trap /3/. With this aim a deuterobenzophenone-d₁₀ crystal with 0.2% benzophenone-h₁₀ impurity was taken. The latter served to form triplet traps with the depth about 30 cm⁻¹. Pulse excitation of the host crystal to the singlet state S₁ and rapid intercombination conversion were followed by formation of triplet excitons. Then excitons might either relax or be trapped by impurities. The calculated capture period amounted to about 300 ns. The pumping density was chosen low to neglect annihilation for the capture period.

The experiment has shown that the trap phosphorescence intensity after

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cessation of the exciton capture depends on the magnetic field. As the exciton capture period does not depend on the field and localized triplet excitations in the magnetic field \( B < 10 \text{T} \) relax slowly, the found effect depends on the competition between the SLR of excitons and their capture. The competition result is "stored" by traps.

At the stage of capture the population of spin sublevels of excitons \( N_{0,1} \) and traps \( N_{0,1} \pm 1 \) are described by six differential equations which may take no account of the phosphorescence of excitons and traps of the relaxation of the latter:

\[
\begin{align*}
\dot{N}_1 &= -K N_1 - W_1(N_1 - \varepsilon N_0) - W_2(N_1 - \varepsilon^2 N_{-1}), \\
\dot{N}_0 &= -K N_0 - W_1(N_0 - \varepsilon N_1) - W_1(\varepsilon N_0 - N_1), \\
\dot{N}_{-1} &= -K N_{-1} - W_1(\varepsilon N_{-1} - N_0) - W_2(\varepsilon^2 N_{-1} - N_{-1}), \\
\dot{n}_1 &= K n_1, \\
\dot{n}_0 &= K n_0, \\
\dot{n}_{-1} &= K n_{-1},
\end{align*}
\]

where \( \varepsilon = \exp \left( \frac{\varepsilon B}{kT} \right) \). Initial conditions are as \( N_i(0) = N_i^0; n_i(0) = 0 \), \( i = 0, \pm 1 \).

After integration of the system (1) by \( t \) within the limits from 0 to \( \tilde{t} \), where \( \tilde{t} \) is the complete capture period, \( \tilde{t} \gg K^{-1}, \tilde{t} < (k_0 + k_1 + k_{-1})^{-1} \), we obtain a system of algebraic equations which binds rates of SLR of excitons \( W_1 \) and \( W_2 \) with finite populations of spin sublevels of traps \( n_i \):

\[
\begin{align*}
N_1^0 &= \tilde{n}_1 + W_1 K^{-1}(\tilde{n}_1 - \varepsilon \tilde{n}_0) + W_2 K^{-1}(\tilde{n}_1 - \varepsilon^2 \tilde{n}_{-1}), \\
N_0^0 &= \tilde{n}_0 + W_1 K^{-1}(\tilde{n}_0 - \varepsilon \tilde{n}_{-1}) + W_1 K^{-1}(\varepsilon \tilde{n}_0 - \tilde{n}_1), \\
N_{-1}^0 &= \tilde{n}_{-1} + W_1 K^{-1}(\varepsilon \tilde{n}_{-1} - \tilde{n}_0) + W_2 K^{-1}(\varepsilon^2 \tilde{n}_{-1} - \tilde{n}_{-1}).
\end{align*}
\]

The magnetic field-dependent relation between values of \( \tilde{n}_1 \) was found from the \( \frac{J_B}{J_{B=0}} \) dependence on \( B \). Initial populations of exciton sublevels \( N_1^0 \) were calculated from data on the triplet state of the isolated benzophenone molecule.

The system (2) does not permit finding both relaxation rates \( W_1 \) and \( W_2 \). The value of \( W_1 \) which depends on \( W_2 \) as on the parameter has been found from this system. The obtained dependence of rate \( W_1 \) on the magnetic field is shown in Fig. 1. The dashed part responds to all possible values \( W_2 \). A triangle shows the value \( W_1^{-1} \) obtained in the paper [2].

Thus, the experiment has confirmed suppression of the exciton mechanism of spin relaxation by the magnetic field prognosticated by the theory. The \( W_1(B) \) dependence demonstrated in Fig. 1 is similar to the theoretical one expected during incoherent motion of excitons \( W \sim B^{-2} \) [2].

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Self-suppression of exciton-exciton annihilation at high density of triplet excitons

Measurements of the quenching kinetics of exciton phosphorescence of benzophenone crystals after pulse excitation by the nitrogen laser have shown that the exciton-exciton annihilation is the main channel of departure of the triplet excitons, if their initial rate $N_0 > 10^{17}$ cm$^{-3}$. Fig. 2 shows quenching of the exciton phosphorescence at $T = 4.2$ K, $N_0 \approx 3 \times 10^{17}$ cm$^{-3}$ (curve 1). The respective kinetics is well described by an ordinary equation

$$\frac{dN}{dt} = -\gamma N^2,$$

where $\gamma = 5 \times 10^{-13}$ cm$^2$/s is an exciton-exciton annihilation constant.

In this case the specimen excitation inhomogeneity due to the absorption of the exciting light is taken into account.

At the same time in case of more intensive pumping when $N_0 \approx 10^{20}$ cm$^{-3}$ the observed quenching rate (curve 2, Fig. 2) proves to be considerably less than the calculated one (curve 3).

It is natural to relate an essential decrease in the efficiency of the exciton-exciton annihilation with high density of excitons to retardation of the exciton diffusion, as annihilation of triplet excitations

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proceeds, as a rule, the contact way. The cause of the excitons migration retardation is, probably, their interaction. Estimates show that the dipole-dipole part of energy of interaction between two triplet excitons may vary within the ranges from 25 to 30 cm$^{-1}$ depending on their mutual arrangement. Already at N $\sim 10^{19}$ cm$^{-3}$ the dipole-dipole interaction of neighbouring excitons exceeds the resonance one which is less than 1 cm$^{-1}$. Thus, excitons prove to play the role of movable lattice defects. The defective structure formed (probably it contains exciton clusters) is to weaken exciton diffusion and annihilation resulted from it. The fact that the crystal temperature elevation by several degrees accelerates the annihilation adds to this interpretation.

**Main conclusions**

It is found that the triplet exciton SLR rate in the magnetic field decreases as a result of the orienting action of the field on the triplet spins.

At high density of triplet excitons their migration and annihilation related to it are retarded. This fact is, probably, a result of static interexciton interaction.

**References**

NEW MEASUREMENTS OF SUB-MILLIMETRE-WAVE ROTATIONAL TRANSITIONS FOR THE KETENE (H₂CO) MOLECULE

L. NEMES¹, J. DEMAISON² and G. WLODARCZAK²

¹Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budapest, Hungary
²Laboratoire de Spectroscopie Hertzienne, U.E.R. de Physique Fondamentale Université des Sciences et Techniques de Lille, Villeneuve d'Ascq, France

Using the superheterodyne sub-millimetre spectrometer at the Microwave Laboratory of the University of Lille I, France some hitherto unavailable pure rotational transitions have been measured for the ketene molecule (CH₂CO). The measurements were extended up to almost 800 GHz and contained a-type ΔKₐ=0 transitions. These new data were then used in conjunction with cm- and mm-wave transitions reported in the literature, plus various ground-state combination differences recalculated from an earlier high-resolution infrared study of ketene. This data set was used to re-derive ground state rotational constants for ketene both in the A and S reduction scheme of Watson.

Introduction

Ketene is a fairly abundant molecule in interstellar space [1]. Since the available millimetre-wave data for this molecule is restricted to relatively low frequencies [2], i.e. only up to 200 GHz, it has been considered worthwhile to extend the measurements into the high-frequency sub-millimetre-wave spectral range. Another motivation for these studies has been to cast the rotational and centrifugal distortion constants into the recent notation due to Watson [3].

Experimental

Ketene gas was generated from liquid diketene (CH₂CO)₂ in a flow system containing a quartz tube heated to about 600°C. Diketene was first frozen out in a liquid N₂ trap while the spectrometer was pumped down. Then the sample was allowed to warm up in order to distil at a needle-valve controlled rate into the waveguide, wherefrom it was pumped away. Pure ketene could be produced in this way in sufficient quantities.

The sub-millimetre spectrometer used in these studies was described by Burie et al [4]. To find the high-frequency rotational transitions their position was predicted using previously reported ground state constants (see: Johns et al [2]). For this purpose a computer programme written by Dr. Koichi Yamada was used. This procedure facilitated greatly the search for the right ketene line. In the case of the Lille spectrometer this was particularly important since the super-heterodyne detection system applied resulted in very high sensitivity. Once the transition was located its line parameters were measured by the sophisticated data-processing software.
developed at the Laboratoire de Spectroscopie Hertzienne in Lille.

Analysis of the spectra

The input data for the least-squares calculation of molecular constants consisted of three subsets: i. cm- and mm-wave lines given in ref. [2], ii. the presently reported measurements of sub-mm-wave lines, and iii. combination differences recalculated from the b-type ν7 infrared band frequencies in ref. [2]. The distribution of data among the three subsets is as follows: i.: 52, ii.: 82 and iii.: 278.

The least-squares determination of the ground state rotational constant set was made partly in Lille and partly in Giessen, Justus-Liebig-University, West Germany. In Lille we have used a computer programme written by Dr. V. Turke, adapted to the local DPS8 computer. The Giessen calculations were carried out by another programme originally written by Dr. K. Yamada and later modified by Dr. Brenda Winnewisser for the local computer at the University of Giessen. In this paper only the Giessen calculations shall be reported as they were made on the original Lille data set, but were carried out in both the A- (asymmetric top), and S- (symmetric top) reduction schemes of Watson [3].

Ground state rotational constants of H₂CCO

A-reduction

The following rotational Hamiltonian was used in the data fitting procedure:

$$\hat{H}^{(A)}_{\text{rot}} = \mathcal{A} z^2 + \mathcal{B} x^2 + \mathcal{C} y^2 - \Delta_{J} \hat{J}^2 - \Delta_{JK} \hat{J}^2 + \Delta_{JL} \hat{J}^2 -$$

$$- \Delta_{KL} \hat{J}^2 - \Delta_{KL} \hat{J}^2 - (1/2) \left[ \mathcal{D}_{J} + \mathcal{D}_{K} \right] + \left( \mathcal{E} + \mathcal{F} \right) \hat{J}^2$$

$$+ \mathcal{G} z^2 + \mathcal{H} x^2 + \mathcal{I} y^2$$

S-reduction

In the S-reduction scheme the Hamiltonian is of the following form:

$$\hat{H}^{(S)}_{\text{rot}} = \left( \mathcal{A} - (\mathcal{B} + \mathcal{C} )/2 \right) \hat{J}^2 + \left( \mathcal{B} + \mathcal{C} /2 \right) \hat{J}^2 - \mathcal{D} z^2 -$$

$$- \mathcal{D}_{JK} \hat{J}^2 - \mathcal{D} z^2 + \mathcal{H}_2 \hat{J}^2 + \mathcal{H}_{JK} \hat{J}^2 + \mathcal{H}_{JL} \hat{J}^2 + \mathcal{H}_{KL} \hat{J}^2$$

$$+ \mathcal{H}_2 \hat{J}^2 + \left( \mathcal{H}_2 /4 + \mathcal{D} \hat{J}^2 + \mathcal{H}_2 \hat{J}^2 \right) \hat{J}^2 +$$

$$+ \left( \mathcal{D} + \mathcal{H}_2 \hat{J}^2 \right) \hat{J}^2 + \mathcal{H}_2 \hat{J}^2$$

It is possible to relate the rotational constants in the A- and S-reduction forms (see: Table 8.16 in ref. [5]). Such a comparison was performed among the least-squares determined A-reduction constants and those calculated from S-reduction constants using the relationships in ref. [5].

In addition to this the least-squares errors were checked by error propagation. It was found that the data in Table I and II satisfy such relations.

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within the calculated error limits. The only exception is $\Phi_{JK}$ that is significantly different from $H_{JK}$ although these constants are expected to be identical in the present constraint: $h_2 = h_3 = 0$.

Table I

Results of the A-reduction fit for $H_2CCO$

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>$\tilde{A}$</td>
<td>282198.0(71.3) MHz</td>
<td></td>
</tr>
<tr>
<td>$\tilde{B}$</td>
<td>10293.913(19) MHz</td>
<td></td>
</tr>
<tr>
<td>$\tilde{C}$</td>
<td>9915.245(19) MHz</td>
<td></td>
</tr>
<tr>
<td>$\Delta J$</td>
<td>3.3876(52) kHz</td>
<td></td>
</tr>
<tr>
<td>$\Delta J K$</td>
<td>468.73(27) kHz</td>
<td></td>
</tr>
<tr>
<td>$\Delta K$</td>
<td>30.1(4.6) MHz</td>
<td></td>
</tr>
<tr>
<td>$\xi J$</td>
<td>0.1463(38) kHz</td>
<td></td>
</tr>
<tr>
<td>$\xi K$</td>
<td>313.2(9.4) kHz</td>
<td></td>
</tr>
<tr>
<td>$\Phi_{JK}$</td>
<td>3.73(21) Hz</td>
<td></td>
</tr>
<tr>
<td>$\Phi_{KJ}$</td>
<td>-0.9009(46) kHz</td>
<td></td>
</tr>
</tbody>
</table>

Table II

Results of the S-reduction fit for $H_2CCO$

<p>| | | |</p>
<table>
<thead>
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</thead>
<tbody>
<tr>
<td>$(\tilde{A}-(\tilde{B}+\tilde{C})/2$</td>
<td>272093.0(71.3) MHz</td>
<td></td>
</tr>
<tr>
<td>$(\tilde{B}+\tilde{C})/2$</td>
<td>10104.5791(33) MHz</td>
<td></td>
</tr>
<tr>
<td>$(\tilde{B}-\tilde{C})$</td>
<td>377.4150(27) MHz</td>
<td></td>
</tr>
<tr>
<td>$D_J$</td>
<td>3.2790(42) kHz</td>
<td></td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>469.38(27) kHz</td>
<td></td>
</tr>
<tr>
<td>$D_K$</td>
<td>300.7(4.6) MHz</td>
<td></td>
</tr>
<tr>
<td>$H_{JK}$</td>
<td>3.26(21) Hz</td>
<td></td>
</tr>
<tr>
<td>$H_{KJ}$</td>
<td>-0.8994(46) kHz</td>
<td></td>
</tr>
<tr>
<td>$d_1$</td>
<td>-0.1463(38) kHz</td>
<td></td>
</tr>
<tr>
<td>$d_2$</td>
<td>-54.3(1.6) Hz</td>
<td></td>
</tr>
</tbody>
</table>

The correlations among the A-reduction parameters and those for the S-reduction parameters are significantly different. In the asymmetric top reduction the strongest correlations ($>0.9$) are between members of pairs: $(\tilde{A}, \Delta_{JK})$; $(\tilde{A}, \xi_K)$; $(\tilde{A}, \Phi_{KJ})$ and $(\xi_K, \Phi_{KJ})$ whereas in the symmetric top reduction 

Although a direct comparison to the results of Johns et al. [2] is not possible due to the different notations, it is interesting to note that in the present S-reduction $D_K$ is significantly larger, whereas $H_{JK}$ is significantly smaller than in ref.[2].

Further work is in progress for the more accurate determination of the
ground state rotational constants. Dr. J.W.C. Johns and one of the present authors (L.N.) have recorded Doppler-limited resolution spectra of ketene in the spectral range 1100-350 cm\(^{-1}\) using the BOMEM DA3.002 FTIR spectrometer at the Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa. New, highly dependable ground state combination differences have already been derived from the rotational structure of the \(\nu_8\) fundamental and these have been used to extend the scope of the present work significantly [6].

Acknowledgements

This work was carried out mainly at the Lille University during the tenure of visiting professorship awarded to L.N. The computations done at the Justus-Liebig University, Giessen, West Germany were made possible by the support from the Alexander von Humboldt Foundation, Bonn, West Germany. L.N. is grateful to Dr. Jean Demaison, Prof. Manfred Winnewisser and Dr. Brenda P. Winnewisser for the extensive help given to this work.

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WITH INTERNATIONAL PARTICIPATION

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22–25 July, 1986

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The final manuscript was received by the Editorial Office on 20 October 1986.
It was one hundred years ago, in 1887, that Zoltán Gyulai, late Professor of the Technical University of Budapest, Member of the Hungarian Academy of Sciences, President of the Roland Eötvös Physical Society, Kossuth- and State-Prize winner, holder of numerous other Hungarian and foreign orders, was born.

The Editorial Board of our periodical considers it a debt of honour to commemorate the excellent scholar of experimental physics, the renowned scientist, the master, the respected colleague who was always ready to help, the warm-hearted and noble-minded friend.

Zoltán Gyulai was one of the first prominent scholars of modern solid state physics. His first results were connected with his fellowship in Göttingen in the early twenties. There, he worked under the guidance of R.W. Pohl with whom he later developed a close friendship. In this period he established the quantum nature of photoconductivity using alkali halide crystals coloured with X-rays, which at that time - in the developmental period of quantum physics - was a problem still to be clarified. He was the first to observe and describe the changes in the absorption and photoconductivity spectra of additively coloured crystals which are now called F-F' and F'-F transformations, respectively.

After his return to Hungary his interest turned from colour centres, i.e. artificial crystal imperfections, to the problem of natural crystal defects. For example, his investigations - carried out in collaboration with D. Hartly in 1928 - into the change of electric conductivity of NaCl monocrystals under pressure have remained fundamental. This work was the first deliberate experiment to reveal the existence of natural crystal defects.

The second half of the thirties again brought a change of topics in Gyulai's life: he began to study the mechanism of crystal growth; he was especially interested in Kossel's theory of crystal growth. He was one of the first with his colleagues to observe and describe the appearance and movement of layers of microscopic thickness that were connected with the growth of ionic crystals; he found that the rules following from the theory are in agreement with the observable mechanism of growth, although the theory operates with single ions whereas the microscopic observation refers to layers of several thousand Å. Thus the agreement is formal, and there is a fact behind it which is neglected by the theory. To surmount this difficulty Gyulai assumed the existence of a semi-ordered boundary layer in the lipid phase close to the crystal surface. His view was that in reality precrystalline formations rather than single ions take part in the growth in a way similar to that suggested by Kossel.

He was among the first to produce whiskers and to observe their physical features. His activities had an important role in arousing interest the world over in the fifties and sixties in whiskers both from theoretical and practical aspects.
In the sixties he observed the interesting forms of appearance of crystallites in super-saturated aqueous solutions of alkali halides. The fundamental phenomenon is that upon mechanical effects an avalanche-like process of crystallization consisting of several phases well separated in time, starts spreading throughout the whole volume of the solution. The crystal forms are determined by the degree of supersaturation, temperature, impurities, etc.

Gyulai had always searched for the simple manifestations of principles comprising a wide range of phenomena. He liked to work with simple methods and attempted to follow the processes by expressive descriptions. He was an excellent representative maybe one of the last, of classical experimental physics. He was the type who planned and assembled his experimental equipment himself and already in this gave something new and original, something better than did his predecessors or contemporaries. He carried out his observations himself, so to say feeling the phenomena.

Zoltán Gyulai not only bequeathed his professional results, the progressive thoughts of an investigative researcher, he also educated his students to the love of science, to the admiration of the new, to high scientific morals. The first part of his bequest is an experience for everybody in Hungary or abroad who came into contact with the fields initiated or cultivated by him, the latter part only for those who had the chance to know him or work with him; nevertheless, his example should be followed by everybody who is involved with science.

Imre Tarján

Acta Physica Hungarica 61, 1987
CONTACT RESISTANCE PROFILING OF LPE GROWN GaAs(GaAl)As MULTILAYER STRUCTURES

L. CSONTOS and Gy. HOFFMANN
Research Institute for Technical Physics of the HAS
1325 Budapest, Hungary

Contact resistance profiling (C.R.P.) is also applied for investigation of LPE grown GaAs(GaAl)As layer structures in our laboratory. It is known that the C.R.P. measurement, compared to the numerous layer profiling methods (electron beam microanalysis, SIMS, C(V) measurement, photoluminescence, electrochemical depth profiling, etc.) is relatively quick, cheap and less precise. The C.R.P. technique was developed by Goodfellow and his co-workers [1].

Measuring apparatus

The scheme of the C.R.P. apparatus is shown in Fig. 1 [1,2]. The multilayer sample is angle lapped and is provided two fixed contacts using silver paste. The top contact being on the bevelled side, is a stripe of silver paste and a gold wire dipped in it. The back side of the substrate is connected - also by silver paste - to the output of the voltage monitor, and fixed to the moving holder.

The stripe contact maintains a constant potential \(U_{ps}\) above earth potential using the stabilized reference voltage and the voltage monitor. The current, maintained by the voltage between the tungsten carbide (WC) probe and the stripe, is monitored by (virtual earth) logarithmic amplifier, the output of which is displayed on a chart recorder. Thus the probe is practically at earth potential.

Preparation of sample

The samples were angle lapped applying 4 \(\mu\)m and 0.3 \(\mu\)m Al\(_2\)O\(_3\) powder, on pellon plate, shaping on them a bevel of 1.5°.

Angle lapped samples and bulk reference GaAs crystals of known impurity concentration pasted onto an iron holder plate are shown in Fig. 3.

Measuring method

The C.R.P. of a sample is measured as follows (Fig. 1). The tip of the probe traced along the sample's surface, parallel to the stripe contact as the holder was moved by the mechanism. At the same time the output voltage \(U_{o}\) of the logarithmic current amplifier is...
displayed by the chart recorder as a function of time, that is the layer thickness $d(U/d)$. This is the contact resistance profiling record (C.R.P.R.).

**Evaluation of C.R.P.R.**

The electric equivalent scheme of C.R.P. apparatus is shown in Fig. 4. Here $R$ is the resistance between the probe and the stripe, $R_f$ is the resistance between the stripe and bottom contact of the sample (feed-back resistance). The value of contact (layer) resistance $R$ is given by

$$U_o \quad R = \frac{P_S}{I},$$

where $U_o$ is the fixed voltage between the probe and the stripe, $I$ is the current flowing between the stripe and the probe.

Calibrating the logarithmic current amplifier for input current $I$ and output voltage $U_o$, the following formula is obtained

$$I = a \cdot 10^b U_o,$$

where $a=1.95 \cdot 10^{-12}$, $b=0.889$.

The position of p-n junction is determined by using C.R.P.R. on the basis of characters of current - voltage curves ($I(U_{ps})$) of GaAs and (GaAl)As [1,2]. The $I(U_o)$ curve of n-type GaAs monocrystal is shown in Fig. 5 and that of a p-type one is shown in Fig. 6. To determine the position of p-n junction it is necessary to measure the C.R.P.R. of layer structure at both positive and at negative $U_{ps}$ voltages [3]. Then values of $U_o$ in C.R.P.R. have moved in opposite direction in the p and n regions. Experimental C.R.P.R.-s measured at positive $U_{ps}$ and at negative $U_{ps'}$, are designated by + and - signs, respectively.

**Experimental C.R.P. records**

C.R.P.R.-s of model layer and laser structures grown by LPE in pumping graphite boats at different experimental conditions are shown in Figs 7-9.

**Acknowledgements**

The authors express their thanks to J. Pfeifer, H. Borody, F. Koltai and I. Szabados F.Abrasits for their useful contribution to this work.

*Acta Physica Hungarica 61, 1987*
Fig. 7. C.R.P.R. of n-n-p GaAs structure and sketch of its angle lapped layers. The 1st GaAs layer was grown from undersaturated melt; the 2nd was grown from oversaturated melt. $U_p = 1.5$ V.

References

Acta Physica Hungarica 61, 1987
Two undoped melts were used for active layer growth. $U_{ps} = 1.2$ V

The active layer was grown using two melts. The first was undoped, the second was Ge-doped. $U_{ps} = 1.5$ V

Acta Physica Hungarica 61, 1987
GaAs/GaAlAs MULTILAYER STRUCTURES GROWN BY LPE METHOD

T. GÖRÖG, E. LENDVAY and V. RAKOVICS
Research Institute for Technical Physics of the HAS
1325 Budapest, Hungary

Multilayer LPE of GaAs and GaAlAs using a vertical system with rotary graphite crucible has been developed. Using this equipment superlattice structures in the GaAs-GaAlAs system were grown. The layer thicknesses were varied from 20 to 500 nm. Structures up to 100 layers were deposited using constant cooling rate and step-cooling LPE methods; the growth times varied for an individual layer in the range of 1 to 50 s. It was observed that calculating the respective growth rates and layer thicknesses the experimental values differed to a great extent from the calculated data showing the insufficiency of the diffusion limited growth rate theories in our case. The doping of the multilayer structures with Si, Ge and Sn was also studied. Anomalous growth rates depending on the dopant quality were observed.

Introduction

In the last few years a great number of new GaAs-GaAlAs multilayer structures, with a characteristic layer thickness shorter than the charge carrier mean free path, have been prepared. These systems are called "superlattices" [1]. Superlattices have already been applied in laser diodes (e.g. [2]), in high electron mobility transistors [3] and as laser reflectors and modulators [4]. To prepare these structures usually MO-CVD and MBE techniques have been applied. LPE is considered as an unsuitable method, some authors, however, demonstrated the feasibility of the LPE for superlattice growth. The growth of single LPE GaAs and GaAlAs layers as thin as 40-80 nm have already been published [5]. Multilayer GaAs/GaAlAs structures were also prepared by LPE method [6] and in an earlier work the growth of InP/InGaAsP superlattice with layer thicknesses less than 50 nm was also described [7]. Recently InP/InGaAsP superlattices, as well as doped GaAs and GaInAs superlattices were grown by the LPE method [8,9].

In this work a new GaAs/GaAlAs multilayer and superlattice growth by the LPE method is described.

Experimental

For superlattice growth the vertical rotation LPE system described earlier [10, 11] was used. A multihole graphite crucible was applied, where the successive holes contained a sequence of Ga melts containing GaAs or GaAlAs. The melt chambers were cut into two parts by a 350 μm thick slit, where the substrate crystal could be rotated. The rotating substrate separated the melts into free-standing and confined melts in each chamber.

The sources were prepared by adding the GaAlAs and the dopants to the oxide-free Ga and preheating the system 20-40 °C above starting temperature T_s for 2-4 hours. The (100) GaAs substrate was fixed in a graphite sample holder. To avoid the thermal decomposition of the substrate the GaAs was kept near to room temperature in a cool zone in elevated position. The growth was performed by microprocessor controlled and programmed linear cooling and stepping program. Different, slow cooling rates were used from 0.1 °Cmin⁻¹ up to 2 °Cmin⁻¹. The successive layers were grown either by rotation or by a forward and backward movement of
the substrate between two wells. After the last growth step was finished, the substrate was moved out of the hot zone of the reactor.

The multilayer structures were developed by chemical etching, and were studied by scanning electron microscopy. The cleaved surfaces usually were etched by $\text{NH}_4\text{OH}$-$\text{H}_2\text{O}_2$ etchant to make the individual layers visible.

**Results and discussion**

Semiconductor device production requires mirror smooth surfaces and structurally perfect interfaces. This problem is even more important in optoelectronics, where DH layer structures are built on exactly oriented (100) substrates to avoid the so-called terrace growth [12]. In multilayer growth two types of orientation change appear: depression formation and island growth. The LPE growth of superlattices is rather sensitive to the presence of foreign ions, heat conduction differences and to the surface inhomogeneities. Depressions and voids occasionally appear in layers. The depressions usually extend from the epitaxial surface into the layers but during the successive growth steps the holes are filled with material and a structural inhomogeneity is formed [12]. The development of such voids sets in at the newly formed interface during nucleation in the very first period of the LPE growth. Void formation was also observed in LPE superlattice growth, but no depression generation on them was detected. In Fig. 1 a cleaved cross section of a multilayer wafer is shown, where at the buffer/substrate interface triangular voids can be seen. This voids are flat-bottomed and they are probably caused by local undersaturation (melt-etch), as the apex of the triangular voids tends toward the substrate. In these systems depressions are also formed but independently of the voids. The growth process reinforces the surface irregularities and in the superlattice region depressions and voids are formed. In Fig. 2 two characteristic samples can be seen. On the left side (Fig. 2.a) the role of the substrate surface irregularity is illustrated, where the melt-back effect produces a waving interface between the GaAs buffer and the SL region. Owing to the local misorientation after some successive growth steps, a depression and a void formed in the SL region. The continuous deposition of solid in the depression eliminates the fault and to visualize the effect the wafer has to be cleaved and etched. The dopant segregation usually differs at different orientations [13], so the doping level of the material inside the filled fault differs from that of the multilayers in the adjacent regions. As a consequence, these local spots act as conducting channels. The voids, occasionally appearing in SL regions, are filled with semiconductor.

The misorientation effect illustrated in Fig. 2.b is very strong. In this case a slight melt-back produces a local misorientation in the SL region itself. This irregularity was amplified during the next few growth steps giving a macroscopic depression which was eliminated only in the last but one growth step. The growth around the irregularity usually proceeds without any perturbation. In etched cross sections only the curvature in the layer trajectories and some change in the curved area in layer distances can be detected. This means that in case of multilayer growth the formation of depressions and voids is caused by local misorientations, most probably by curved surface elements (with high crystallographic indices).

Analysing the multilayer structures the assumption that the formation of depressions and voids was controlled mainly by melt-back effects was demonstrated. It was also observed that a slight initial supercooling prevents melt-back effects and eliminates the faults.
Fig. 1. GaAs/GaAlAs multilayer structures grown by LPE method. The arrows denote small, triangular voids formed at the buffer/substrate interface.

Fig. 2. Structural irregularities formed in GaAs/GaAlAs multilayer structures
   a. / Formation of depression and void on a wavy GaAs surface
   b. / Formation of depression in a slight meltbacked layer

Fig. 3. GaAs/GaAlAs DH structure separated from the substrate by a superlattice region

Usually the GaAs/GaAlAs superlattice (SL) was grown by the rotational LPE system with \( \Delta T \approx 1-4 ^\circ \text{C} \). The entire SL region was 0.8 \( \mu \text{m} \) thick, it was embedded between two cladding GaAlAs layers. Within the SL region there were 20-26 individual layers, each having a layer thickness of 40-60 nm. (Owing to the small change in supersaturation, the layer thickness slightly decreases according to [9].) The layers were highly uniform and evenly spaced. Heterostructural multilayers made of GaAs and GaAlAs, separating a normal DH structure from...
the substrate were also deposited. A characteristic structure of this type is shown in Fig.3, where the cross section of a laser structure is presented. The DH region has a thickness of about 6 μm with a 0.3 μm thick active layer, whereas the SL region, consisting of 12 layers, is 1 μm thick.

Si, Ge and Sn were used as dopants in a wide range of concentration. Silicon has been known to be an amphoteric impurity in GaAs and GaAlAs, the conversion in electrical conduction from the n-type to the p-type is about 800-900 °C depending on the amounts of Si in the melts [14,15]. Using this dopant the multilayers were grown at elevated temperatures \(10^{-4} < X_{Si} < 5.10^{-3}\), the growth was started well above 850 °C and it was terminated at about 700 °C. The multilayer structures grown were described in [10,11].

Although the roles of Ge and Sn in GaAs conduction have been thoroughly investigated, very little work has been done on their behaviour in superlattice systems. The multilayers and superlattices containing a p-n junction were grown from melts prepared using Sn \(10^{-5} < X_{Sn} < 10^{-3}\) and Ge \(10^{-4} < X_{Ge} < 10^{-3}\) dopants in relatively low concentrations. In these structures two distinct series of layers can be distinguished, the periods in them are different. In the n-side the growth rate was remarkably lower than that of the Ge-doped part. The SL growth was performed from 750 °C to 745 °C, at similar temperatures, the growth time was the same for each layer (30 s). It is noticeable that in the n-side the layer thickness \(d\) is quite reproducible, while in the p-side there is a continuous decrease in layer thickness corresponding to the previously described supersaturation effect [9]. The growth rates are different. In the case of Sn-doping \(X_{Sn} = 10^{-4}\) 50 nm thick layers were deposited, and the thickness of the Ge-doped layers \(X_{Ge} = 10^{-4}\) varied from 150 nm to 30 nm. This means that the growth rate is significantly changed depending on the dopant quality and shows a strong supersaturation effect in Ge-containing melts. In principle, during the experiments the observed layer thicknesses have to agree either with the equilibrium cooling, or with the supercooling model but none of them suits for the real measured values. The strong orientation dependence, as well as the supercooling (dopant) sensitivity of the growth rate and the alteration of the theoretically predicted growth rate (layer thickness) values indicate that the governing mechanism in LPE thin multilayer growth is not the diffusion of the components.

References


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OPTIMIZATION OF FLUX COMPOSITION FOR THICK YIG LAYERS

B. KÉSZÉI1, J. VANDLIK1, P. GÖRNERT2, R. HERGT2, M. WENDT2, K. FISCHER2 and E. SINN2

1Central Research Institute for Physics, 1525 Budapest, Hungary
2Institute for Phys. and Technics of Acad. of Sci. of GDR, Jena GDR

Thick, nominally pure (only lead substituted) Y3Fe5O12 (YIG) films have been grown on gadolinium gallium garnet (GGG) substrates 2 inches in diameter by isothermal dipping method of liquid phase epitaxy from lead-borate melt. If the liquidus temperature of the melt and the supercooling are varied over a wide range, 1151-1319 K and 10-48 K, respectively, and one examines the supercoolability of the melt, the lattice parameter, Pb content, FMR line-width and the surface quality of the prepared layer it can be stated that nominally pure YIG layer on GGG substrate 50 mm in diameter can be grown by only one dipping step up to about 80 μm in thickness without surface defects.

Introduction

LPE garnet films with thicknesses of 1.5-5 μm are used as media for storage (magnetic bubbles) [1] and in magnetooptical printers [2]. Thick, 20-100 μm garnet layers are needed for microwave devices [3] and 100-300 μm layers in thickness for optical isolators and switches in 1.2-1.7 μm wavelength fiber optics communication systems [4]. It is known that morphological instabilities can easily occur due to atomically rough {111} garnet faces [5]. The surface quality of {111} thick Gd:YIG LPE layers was studied by Hibiya [6]. In an earlier paper Glass [7] mentioned the growth of a single crystal 115 μm-thick pure YIG film on GGG substrate.

In the present paper the relationship between the quality of thick LPE YIG films and the growth conditions, such as melt composition (liquidus temperature) and supercooling are discussed.

Experimental

Thick, nominally pure (only lead substituted) Y3Fe5O12 (YIG) films have been grown isothermally on <111> GGG substrates (50 mm in diameter) from PbO-B2O3 based melt using a horizontal dipping technique. The total weight of the melt was 2000 g contained in a cylindrical Pt crucible. The melt compositions used in the experiments are compiled in Table I. The liquidus temperature was controlled between 1151 and 1319 K by changing the melt composition which can be characterized with the help of R1, R2 and R4 molar ratios defined by Blank and Nielsen [8]. The supercooling used was changed between 10 and 48 K and growth rates were varied between 0.3 and 4.4 μm/min. The substrates were rotated by 80 rpm in every case.

The layer thickness was measured by sectioning films and then observing them edgewise through an optical microscope. The relative lattice misfit measurements were carried out by double crystal diffractometry using Cu-K radiation and the (444) garnet reflex, with the experimental error of ± 5%. Pb and Pt contents of the layers were analysed by the EPMA.


Akadémiai Kiadó, Budapest
technique. The systematic error of $C_{Pb}$ is less than ± 10 wt% and that of $C_{Pt}$ is less than ± 0.1 wt%.

<table>
<thead>
<tr>
<th>Melt composition</th>
<th>$T_L$ (K)</th>
<th>Supercoolability</th>
<th>Melt depletion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt &quot;A&quot;</td>
<td>1238</td>
<td>90 min. at $T=30$ K</td>
<td>1.0</td>
</tr>
<tr>
<td>Melt &quot;B&quot;</td>
<td>1151</td>
<td>120 min. at $T=38$ K</td>
<td>1.5</td>
</tr>
<tr>
<td>Melt &quot;C&quot;</td>
<td>1265</td>
<td>30 min. at $T=36$ K</td>
<td>1.1</td>
</tr>
<tr>
<td>Melt &quot;D&quot;</td>
<td>1179</td>
<td>90 min. at $T=34$ K</td>
<td>0.5</td>
</tr>
<tr>
<td>Melt &quot;E&quot;</td>
<td>1214</td>
<td>90 min. at $T=28$ K</td>
<td></td>
</tr>
<tr>
<td>Melt &quot;F&quot;</td>
<td>1319</td>
<td>20 min. at $T=30$ K</td>
<td></td>
</tr>
</tbody>
</table>

1Molar concentration ratios among the oxides in the melt
$R_1=Fe_{2}O_3/Y_2O_3$; $R_3=PbO/B_2O_3$; $R_4=(Fe_{2}O_3+Y_2O_3)/(PbO+B_2O_3+Y_2O_3+Fe_{2}O_3)$

2Liquidus temperature

3Period and supercooling at which spontaneous nucleation starts (during layer growth!)

4Liquidus temperature decrease resulting from the preparation of one layer with thickness of 1 μm and 50 mm diameter

Results and discussion

On <111> oriented GGG substrates 50 mm in diameter, the preparation of high quality YIG layers more than 30 μm in thickness is rather difficult. The melt composition and the supercooling used during the layer growth have to be optimized in order to ensure suitable growth rate (reasonable growth time, spontaneous nucleation!) and the suitable Pb content of the YIG film (to fit the substrate and layer lattice parameter) simultaneously.

Fig. 1 shows the growth rate versus the supercooling at different melt compositions (at different $T_L$). As is demonstrated by this figure, melt F would be the best composition for growing thick layers because it has the fastest growth kinetics. But the melt composition and supercooling have to be optimized against the spontaneous nucleation, too. Namely, the growth time of the layer preparation cannot take an unreasonably long time as the higher the supercooling and the liquidus temperature of the melt during the layer growth, i.e. the higher the growth rate, the shorter the period at which the spontaneous nucleation starts (Table I). The surface defects of layer caused by crystallites increase the FMR linewidth of the YIG layer. The maximum layer thickness which can be grown without spontaneous nucleation can be calculated by using supercoolability data (Table I). These values are 140, 35, 70, 105 and 60 μm for A, B, C, D, E and F melts, respectively.
In order to be able to ensure the narrow FMR linewidth, the most important thing is to control the Pb content of the YIG films, that is the control of the substrate/film lattice misfit. If the relative misfit is not adequate the layer will crack. The critical layer thickness belonging to a given relative lattice misfit can be calculated from the surface energy of the crack, the Young’s modulus and from the Poisson’s ratio for YIG [9], provided that the lattice parameter of substrate is larger than that of the film, e.g. the critical layer thicknesses belonging to $5.6 \times 10^{-4}$, $4.0 \times 10^{-4}$ and $2.8 \times 10^{-4}$ relative lattice misfit are 50, 100 and 200 μm, respectively. This means for instance at the relative misfit of $4.0 \times 10^{-4}$, that one can grow a layer without any cracks when its thickness is less than 100 μm.

The Pb content of the layer and thus the relative lattice misfit can be adjusted both by varying the melt composition and changing the supercooling at a given composition (as shown in Figs 2 and 3). In Fig. 3, the critical misfit belonging to the 100 μm thickness

![Fig. 1. Dependence of the growth rate on supercooling at various $T_L$](image)

![Fig. 2. Pb content of the YIG layers interpolated to supercooling temp. of 30, 20 and 10 K versus the growth rate](image)

![Fig. 3. Relative lattice misfit interpolated to supercooling temp. of 30, 20 and 10 K versus the growth rate](image)

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is indicated too. It is obvious from this figure that a 100 μm layer can be grown without cracks from the melt marked by B, D, E and melt A at a very high supercooling. At the same time melts B and D cannot be used to grow 100 μm layers because of their supercoolability and the very small growth rate - as was mentioned above.

The detected Pb contents were larger than Pt contents for all the samples. When the layers were grown at high temperature no Pt was detected. This suggests (assuming that divalent lead ions occupy the dodecahedral Y³⁺ sites in the garnet lattice), that besides Pb⁴⁺ ions and oxygen vacancies the existence of Pb⁴⁺ ions must be supposed too as charged compensator ions in the garnet layers. This existence is supported by Figs 2 and 3. While the lead content versus growth temperature curves monotonously decrease the relative misfit-growth temperature curves show a maximum. Another indication of the existence of Pb⁴⁺ is that our samples have systematically larger Pb contents than the published [5,7] data at the same relative lattice misfit. (The ion radius of Pb⁴⁺ is smaller than that of Pb²⁺.)

Conclusion

It is impossible to grow pure, about 80-100 μm thick or thicker YIG layers on GGG substrates of 50 mm diameter by one dipping step without surface defects (cracks, or spontaneous crystallites). The preparation of the YIG layer of such a thickness requires that the substrate lattice parameter be decreased.

References


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The Hot Wall Epitaxy (HWE) technique has been employed for the first time to grow thin epitaxial films of cadmium phosphide (Cd$_3$P$_2$) on mica substrates at different substrate temperatures in the range 150 – 300°C. The films were characterised by X-ray diffraction and SEM. The lattice constants calculated from the Bragg reflection are in close agreement with those reported in ASTM data. The grain size of the films is observed to increase from 1 - 2 µm as the substrate temperature is increased from 150°C to 300°C. The resistivity of the as-grown sample is around 10 Ohm cm. Thermal probe method has indicated the films to be n-type. Optical absorption measurements yielded a bandgap value of 0.58 eV.

Introduction

Cadmium phosphide (Cd$_3$P$_2$), a II-V compound semiconductor with a direct band-gap value around 0.58 eV, is gaining importance recently owing to the possibility of using it in conjunction with zinc phosphide for photovoltaic applications. Single crystals of Cd$_3$P$_2$ have been prepared by vapor transport using the polycrystalline material synthesized from the elements, transport and optical properties have also been reported [1,2]. Photoluminescence and stimulated emission have been reported by Bishop et al [3]. Energy band structure and optical properties have also been reported by Sobolev et al [4]. To our knowledge there are no reports on the preparation and properties of films. In this paper some of the preliminary results on the growth and properties of Cd$_3$P$_2$ films by Hot Wall Epitaxy (HWE) technique are reported and discussed.

Experimental methods

Cadmium phosphide was prepared by the reaction between the elements Cd and P. For this purpose stoichiometric quantities of Cd and P were sealed in a quartz ampoule and kept at a uniform temperature of about 500°C. At this temperature the reaction starts and Cd$_3$P$_2$ forms a layer on the Cd surface preventing further reaction of phosphorous with Cadmium. To overcome this, the ampoule was moved into another portion of the furnace kept at 700°C for a short while and then brought back to the zone at 500°C permitting the Cd$_3$P$_2$ to sublime from the molten cadmium and provide a complete reaction between the two elements. Three or four zone passes were sufficient to obtain homogeneous polycrystalline Cd$_3$P$_2$ powder. The material obtained above
was powdered to a uniform grain size of 75 \( \mu m \) and used in the experiments. The X-ray diffractogram of the powder exhibited only the sharp lines assignable to single phase \( \text{Cd}_3\text{P}_2 \). Epitaxial layers of \( \text{Cd}_3\text{P}_2 \) have been prepared using a relatively new evaporation method called Hot Wall Epitaxy (HWE). The main characteristic of this technique is its simplicity and the possibility to grow epitaxial layers under conditions closer to thermodynamic equilibrium than most other evaporation methods. The system used in the present work consists of a bell jar in which a base pressure of 267 \( \mu \text{Pa} \) could be achieved prior to growth. The source material was loaded into the quartz tube and freshly cleaved mica was used as substrate. Three furnace windings served to heat the source, wall and substrate independently. The substrate was preheated to around 450°C for degassing of the absorbed gases and moisture for about 30 min. This temperature was then brought down to the growth temperature. The films were grown at various substrate temperatures ranging from 150 - 300°C keeping the source and wall temperatures at 450°C. An epitaxial growth rate of 6 \( \mu \text{m/h} \) at a substrate temperature of 300°C was obtained.

Results and discussion

The grown films were tested for single crystallinity using X-ray techniques. The Bragg diffraction patterns of \( \text{Cd}_3\text{P}_2 \) films grown on freshly cleaved mica substrates placed at different substrate temperatures are shown in Fig. 1. The lattice constants of \( \text{Cd}_3\text{P}_2 \) calculated from this were found to be in close agreement with the values reported in ASTM data. It is observed from the X-ray diffraction that various orientations were present in the case of films prepared on mica substrates kept at temperatures below 200°C. As the substrate temperature increases above 200°C the peak corresponding to \( (202) \) plane increases in intensity and the other planes of orientation were very small. At a substrate temperature of 300°C only the peak corresponding to \( (202) \) plane was present. This appears to be the preferential orientation for these films.

The grain size of the films measured by SEM increases from 1 - 2 \( \mu \text{m} \) as the substrate temperature increases from 150 - 300°C. The resistivity of the film also increases as the substrate temperature is increased. The resistivity of the as grown epitaxial \( \text{Cd}_3\text{P}_2 \) film is around 10 Ohm cm at room temperature and they exhibited photoconductive behaviour when illuminated with a lamp. Thermal probe measurements indicated the films to be n-type.

Optical absorption measurements were made using a Varian 2300 spectrophotometer at room temperature using unpolarised light. The optical density of the films was recorded as a function of wavelength in the range 0.3 - 0.6 eV. Substrate absorption, if any, was corrected for by introducing an uncoated glass substrate into the reference beam. The optical density O.D. was converted to the transmittance \( T \) using the relations,

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\[
\text{O.D.} = \log_{10} \left( \frac{I_o}{I} \right),
\]

\[
T = \frac{I}{I_o},
\]

where \( I_o \) is the intensity of light incident on the film and \( I \) is that of the transmitted beam. From \( T \) the absorption coefficient \( \alpha \) was determined. In

- \( T_s = 300 \, ^\circ C \)
- \( T_s = 225 \, ^\circ C \)
- \( T_s = 150 \, ^\circ C \)

Fig. 1. X-ray diffractograms of \( \text{Cd}_3\text{P}_2 \) films grown on mica substrates at different temperatures.

Fig. 2. Dependence of \( \alpha \) on the photon energy \( h\nu \) of epitaxial \( \text{Cd}_3\text{P}_2 \) films.

Fig. 2. the spectral dependence of the absorption coefficient \( \alpha \) for \( \text{Cd}_3\text{P}_2 \) epitaxial films is shown. The spectrum satisfies a relation of the form

\[
\alpha = \frac{A}{h\nu} (h\nu - E_g)^{1/2}
\]

with a direct bandgap value \( E_g = 0.58 \) eV. Further work on the growth of thicker films and measurement of their transport parameters is in progress.

References


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COMPUTER AIDED MODELLING OF VPE GROWTH PROCESS OF GaAs

I. MÉSZÁROS, I. GYŐRÖ and K. SOMOGYI
Research Institute for Technical Physics of the HAS
1325 Budapest, Hungary

The understanding of the main processes in a VPE system is necessary to grow epitaxial structures with wanted parameters and also to control the growth process. On the basis of Shaw's adsorption model [1], Korec and Heyen [5] have extended these studies and given a complete description of growth kinetics of VPE GaAs including all steps: diffusion in the gas phase, adsorption, chemical reactions and surface diffusion. They applied their model to growth on the (100) surface. Since for the device application, especially for microwave devices, this process and this orientation are used in our case, too, an attempt was made for computer assisted modelling of the growth rate. Computed results are compared with experimental data and a good agreement is obtained.

Introduction

In our Institute a vapour phase epitaxial apparatus (based on the chloride transport) [1] is used to grow GaAs epitaxial layer structures for microwave devices. The experimental results on this system [2,3] show great similarity to the results published in the literature [4], but clearly indicate also the peculiarities of this system (connected mainly with the reactor geometry). On this basis conclusions can be made on the validity of the different models and their explanations - published earlier - in our circumstances. In addition, some useful information is provided showing directions, in which more detailed study and further experiments are needed.

General

During this work a computer aided modelling of the growth process was started. The aim of this work is:
- further comparison of our system to those published elsewhere;
- better understanding of the nature of the growth processes;
- due to the better understanding of the different technological steps to shorten the time and lessen the number of runs during the period of setting before the growth of active structures for different device purposes.

The model based on the method presented by Korec and Heyen [5] discusses the processes in the deposition zone. The main assumptions of the described model:
- The reactor used for epitaxial growth operates under quasi-steady state conditions and forced convection;
- the components of the gas phase are fully mixed in the main stream region;
- a stagnant gas layer exists directly above the substrate;
- chemical reactions do not occur in the gas phase in the deposition zone;
- chemical reactions over the Ga source go on with nearly 100 % efficiency.

The deposition process can be described with the following steps (Fig. 1):
- diffusion of GaCl and As through the stagnant gas layer from the main stream to the substrate surface (1);
- the adsorption of GaCl and As molecules (2);
- chemical reactions on the surface (3);
- desorption of HCl (4);
- diffusion of HCl through the stagnant layer to the main stream (5).
The overall chemical reaction of the growth process is
\[
\text{GaCl} + \frac{1}{4} \text{As}_4 + \frac{1}{2} \text{H}_2 = \text{GaAs(s)} + \text{HCl}
\]  
(1)

**Diffusion in the gas phase**

The first step is the diffusion of the different species from the main gas stream towards the surface. (It is assumed that only \( \text{H}_2, \text{HCl}, \text{GaCl}, \text{H}, \text{As}_4 \) are present in the system.) The mass balance equations for different species are:

\[
K_d,\text{HCl}(P^0_{\text{HCl}} - P_{\text{HCl}}) + K_d,\text{GaCl}(P^0_{\text{GaCl}} - P_{\text{GaCl}}) = 0
\]  
(2)

\[
4K_d,\text{As}_4(P^0_{\text{As}_4} - P_{\text{As}_4}) = r
\]  
(3)

\[
K_d,\text{GaCl}(P^0_{\text{GaCl}} - P_{\text{GaCl}}) = r
\]  
(4)

- \( K_{d,i} \) - the mass transfer coefficient for the reagent \( i \)
- \( r \) - growth rate
- \( P^0_i \) - the partial pressure of the gas component \( i \) in the main stream region
- \( P_i \) - the partial pressure of the gas component \( i \) near the substrate surface

**Adsorption processes**

The description of the adsorption process was based on the assumption, that \( \text{As}, \text{GaCl} \) and \( \text{AsGaCl} \) molecules are adsorbed on the surface, and the \( \text{As} \) and \( \text{AsGaCl} \) molecules occupy the same type of sites.

The following equilibria are taken into account:

\[
\frac{1}{4}\text{As}_4 \rightleftharpoons \frac{1}{2}\text{As}_2
\]  
(5)

\[
\frac{1}{2}\text{As}_2 \rightleftharpoons \text{As(ad)} \text{ for the adsorption of As}
\]  
(6)

\[
\text{GaCl} + \text{V} \rightleftharpoons \text{GaCl(ad)} \text{ for the adsorption of GaCl}
\]  
(7)

\[
\text{As(ad)} + \text{GaCl} \rightleftharpoons \text{AsGaCl(ad)} \text{ or}
\]  
(8)

\[
\text{As(ad)} + \text{GaCl(ad)} \rightleftharpoons \text{AsGaCl(ad)} + \text{V}
\]  
(9)

\[
\text{AsGaCl(ad)} + \text{H}_2 \rightleftharpoons \text{GaAs(ad)} + \text{HCl} + \text{H}
\]  
(10)

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where v is a vacancy for the formation of AsGaCl complexes.

Surface reactions

We assumed that the GaAs is produced by the reaction of absorbed AsGaCl complexes with H (10).

From the processes above one can get the equations describing the growth rates r:

\[ r = C \left( \frac{P_{\text{HCl}}^{1/2}}{P_{\text{H}_{2}}^{1/2}/K} \right) (a-1) \theta_v \]  
(11)

\[ P_{\text{HCl}} = P_{\text{HCl}}^0 + \frac{r}{K_{d,HCl}} \]  
(12)

\[ P_{\text{As}_4} = P_{\text{As}_4}^0 - \frac{r}{(4K_{d,HCl}^b As_4)} \]  
(13)

\[ P_{\text{GaCl}} = P_{\text{GaCl}}^0 - \frac{r}{K_{d,HCl}^b \text{GaCl}} \]  
(14)

\[ \theta_v = \frac{[1 + K_{b,\text{GaCl}} P_{\text{GaCl}}^{1/4} (1 + K_{b,\text{GaCl}} + K_{b,\text{GaCl}})]^{-1}}{1 + K_{b,\text{GaCl}} P_{\text{GaCl}}^{1/4} (1 + K_{b,\text{GaCl}} + K_{b,\text{GaCl}})} \]  
(15)

\[ b_1 = \left( \frac{D_{\text{GaCl}}}{D_{\text{As}_4}} \right)^{2/3} \]  
(16)

\[ C = 5 K_a (kT/hz) \lambda^0_{\text{GaCl}} \lambda_{\text{As}_2}^0 \lambda_{H_2}^0 V_1^{0.5} \]  
(17)

\( \theta_v \) - the surface coverage factor

a - the activity of the deposited material

\( \delta \) - thickness of the adsorbed layer

\( \lambda_i \) - absolute activity of the reagent i

\( \lambda_i^0 \) - activity of the reagent i in standard state

\( \Omega \) - molecular volume of the solid phase

To take into account the source process, the \( P_{\text{GaCl}}^0 \) was calculated from \( P_{\text{AsCl}_3}^0 \) which is one of the most important technological parameters:

\[ P_{\text{GaCl}}^0 = 3 P_{\text{AsCl}_3}^0 \left( B \frac{1/4P_{\text{AsCl}_3}^0}{1/4P_{\text{AsCl}_3}^0} \right)^{-1/4} \]  
(18)

\[ \ln B = (15.85 - 0.15) - (17900 - 150)/T \text{ source} \]  
(19)

To solve this set of equations the Newton-Raphson iteration method was used. For the variable of iteration only one parameter, a, - activity of the deposited material - was chosen. The function F(a) which approaches zero during the iteration process was built up from equations

\[ F(a) = C_0 \left[ P_{\text{HCl}}^{1/2}/K \right] (a-1) - K_{d,HCl}^b \text{GaCl} \left[ P_{\text{GaCl}}^0 - (P_{\text{HCl}}^{1/2}/P_{\text{H}_{2}}^{1/2}/P_{\text{As}_4}) a \right] \]  
(20)

The algorithm of the calculation procedure is shown in Fig. 2.

The calculated and measured results are shown in Fig. 3. The greatest difference between the calculated and the measured curve is about 4 %.

Conclusions

Having an experimental basis and experience in the growing of GaAs epitaxial layers using chloride VPE system, the model proposed by Korec and Heyen was slightly modified toward more convenient input parameters. This model i.e. this set of equations was successfully treated with computer using Newton-Raphson type iteration. Experimental results were obtained and compared with the theoretical ones and a good agreement was found.

The successful application of this model produced some experience in the deeper understanding

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Fig. 2. The algorithm of the calculation procedure of the growth process. Since it was supposed as a first step, it has to be continued taking into account also the other parts of the VPE system.

References

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GaAs VPE LAYERS FOR MICROWAVE SCHOTTKY TUNING VARACTORS

I.GYURÓ and Zs.J.HORVÁTH
Research Institute for Technical Physics of the HAS
1325 Budapest, Hungary

The GaAs Schottky microwave tuning varactors require active VPE layers with rather complicated accurate dopant profiles and an abrupt transition to the buffer layer. Moreover the thickness of the buffer layer is desirable to be the smallest and the concentration in it the highest possible. These requirements originate difficulties in the epitaxial growth. The character of the required dopant profiles and the solution of the above difficulties in a horizontal VPE reactor are treated.

Introduction

As it was reported already, at the Research Institute for Technical Physics of the Hungarian Academy of Sciences different types of GaAs-CrAu Schottky tuning varactors have been developed for RF and microwave applications [1-2]. This development created special requirements to the epitaxial growth technique. In this paper these requirements and the ways of their satisfaction are presented.

Requirements to the active epitaxial layers

The varactor is a device with voltage controled capacitance value. The capacitance-voltage (C-V) characteristics of the varactors are usually given by

\[ C = C_0 (1 + V/\phi)^{-\gamma} \]

where \( C_0 \) is the capacitance at zero bias voltage, \( \phi \) a coefficient, and \( \gamma \) the power of the exponent.

This expression may be rewritten in a form more convenient for the application:

\[ C = C_{\text{max}} < 1 + (V - V_{\text{min}})/(V_{\text{max}} - V_{\text{min}}) [(C_{\text{max}}/C_{\text{min}})^{1/\gamma} - 1] >^{-\gamma} \]

Here \( V_{\text{min}} \) and \( V_{\text{max}} \) are the minimum and maximum control voltages (according to their absolute values) and \( C_{\text{max}} \) and \( C_{\text{min}} \) are the corresponding maximum and minimum capacitances, respectively. If \( V_{\text{min}} = 0 \), then \( C_{\text{max}} = C_0 \) [3-4].

These C-V characteristics may be realised by the following dopant profiles:

\[ N(x) = N(w_{\text{min}})(x/w_{\text{min}})^{-\beta} \text{ with } w_{\text{min}} < x < w_{\text{max}} \]

where \( w_{\text{min}} \) and \( w_{\text{max}} \) are the minimum and maximum depletion depths corresponding to \( C_{\text{max}} \) and \( C_{\text{min}} \), respectively, and

\[ \beta = 2 - 1/\gamma \]

\( N(w_{\text{min}}) \) and \( w_{\text{min}} \) may be determined from the actual C-V characteristic and known the GaAs breakdown electric field, they may be optimized for the
minimum series resistance [1-5]. The characters of these profiles for different beta (gamma) values are shown in Fig. 1.

The dopant profile in the region of $x < w_{\text{min}}$ must set $C_{\text{max}}$ to $V_{\text{min}}$. For the minimum series resistance the dopant concentration must increase above $w_{\text{max}}$ as abrupt as possible, and the buffer layer thickness must be the smallest and the concentration in it the highest possible. Moreover the active epitaxial layer must have minimum crystal defects, because they decrease the GaAs breakdown electric field and the electron mobility, increasing the series resistance.

Of course the grown dopant profiles must be very close to the designed ones, in the opposite case the parameters of the prepared devices will differ from the designed parameters. Two actual designed dopant profiles are shown in Fig. 2.

**Epitaxial growth**

From the point of view of the epitaxial growth the problems connected with the above requirements may be divided into two groups: a. the optimization of the buffer layer and its transition to the active layer, b. accurate realization of the designed dopant profile.

**Buffer layer optimization**

In GaAs epitaxial structures a buffer layer is usually grown between the substrate and the active layer. It gives the possibility of a good isolation of the active layer from the non-desired effects of the substrate (outdiffusion from the substrate, autodoping during the epitaxial growth, defects at the substrate-epilayer interface), and it makes possible to create an abrupt dopant concentration transition to the active layer.

Investigating the effect of the dopant concentration in the buffer layer we have found that the less the concentration the more abrupt the transition, as it is seen in Fig. 3. The less abrupt transition at higher concentrations is due to the high level of doping material in the gas phase, which can decrease only slowly after the reduction of the doping gas entering the chamber. Therefore the transition may be made more abrupt by the stopping of the growth process introducing HCl gas before the growth of the active layer for a few minutes, giving the doping material enough time to leave. Such a transition is also shown in Fig. 3. For the minimum series resistance the optimal dopant concentration of the buffer layer is about $7 \times 10^{17}$ cm$^{-3}$. The least possible buffer layer thickness necessary for the isolation from the non-desired effects of the substrate is not clear yet.
Fig. 1: Normalized dopant profiles for varactors with different constant beta (gamma) values

Fig. 2: Two designed dopant profiles for microwave tuning varactors

Fig. 3: The transition to the active layer for different conditions:
1 - without buffer layer; 2,3 - with buffer layer concentrations of $2 \times 10^{18}$ and $6 \times 10^{17}$ cm$^{-3}$; 4 - with buffer layer concentration of $6 \times 10^{17}$ cm$^{-3}$ by growth stopping technique

Fig. 4: One of the designed varactor profiles (1) and the grown ones measured at the different edges of the slice (2,3)

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Dopant profile realization

Our epitaxial reactor is capable of automatic growth, but it controls gas lines with fixed flow velocities [6]. If continuous changing of the doping gas is needed, as for varactor dopant profiles, it may be realized manually by needle valves only. Because of the backlash clearance of the needle valves, inertia of the measuring system and the reaction time of the operator successful growth requires great care and training [1-2]. Moreover the arrangement of the epitaxial growth on the basis of the dopant concentration and growth rate calibration curves is very exhausting.

Despite of the above difficulties rather accurate dopant profiles have been grown, as it may be seen in Fig. 4, and different types of varactors have been prepared [1-2,5,7-8].

To improve the reproducibility of the epitaxial growth and to simplify its arrangement the microcomputer controlling of our epitaxial reactor is being planned.

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HALL MOBILITY LOWERING IN GaAs EPITAXIAL LAYERS

K. SOMOGYI
Research Institute for Technical Physics of the HAS
1047 Budapest, Hungary

As Heyen and Balk [1] have shown, the free electron mobility measured on VPE layers occurs lower, in general, than the theoretically calculated mobility values. This fact, seemingly, cannot be explained simply supposing elevated compensation ratios or a worse crystal quality. In the present work it is shown that one of the most important reasons, or possibly the most important one, is due to the depth inhomogeneity of the layer. This is the result of the conditions of growth and can be avoided in many cases. Some concentration profiles and their interpretation are discussed.

When growing epitaxial layers, the process of primary importance is the characterization of the layer or the layered structure. The characterization includes first of all the electrophysical properties of the material, among others the mobility of the free carriers. For the measurement of the mobility the most important and the most frequently used method is based on the Hall effect, and is technically performed by van der Pauw’s method.

Very often the electron mobility values obtained in such a way are smaller than the theoretically predicted ones for many possible reasons (e.g. compensation, defects etc.). This paper deals with this question in GaAs, but concerning the inhomogeneity of the layer.

Measurement of Hall mobility

Experimental mobility data on GaAs epitaxial layers were collected by Heyen and Balk[1]. Fig. 1 shows this mobility vs concentration distribution at 77 K, the theoretical maximum mobilities (K=0, K is the compensation ratio) and, also, some of our own results. From Fig. 1 one could conclude that the smaller mobility values are regular and this is an inherent feature of the epitaxial layers [1].

The Hall mobility can be measured in the way described above only if the epitaxial structure has only one layer (the layer under question) on a semi-insulating substrate. In MESFET type structures the mobility in the active layer can be measured directly. In the case of devices requiring heavily doped substrates, like Gunn diodes, the mobility cannot be measured directly in the active layer but one has to grow a special one-layer structure on a semi-insulating substrate, supposing that the measured mobility in this wafer will be identical (or nearly identical) to the mobility in the active layer of the real device structure. This special structure for mobility measurements can be grown mainly in a special run with semi-insulating substrate and reproducing only one layer, the active layer, when also buffer and contact layers are desired for devices.

Because of the requirements for van der Pauw measurements, the measured and calculated mobility value is an integrated value, i.e. the mobility inhomogeneity along the wafer and also in depth is included. In this paper, however, only the question of the inhomogeneity of electrical properties in depth is dealt with, since it is supposed that this is the main reason for the lowered mobility in the epitaxial layer and all the other possible reasons might be excluded or neglected.

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Fig. 1. Carrier concentration dependence of the electron mobility in GaAs at 300 K and 77 K. Continuous line is a summarized mobility for GaAs VPE layers in [1], dotted line is the highest theoretical mobility, dots are our VPE layers.

**Experimental**

Epitaxial structures of GaAs were prepared by the chloride VPE system [2] under the usual technological conditions in the diffusion limited regime [3]. For mobility measurements one epitaxial layer was obtained on either a Cr doped or a nondoped semi-insulating substrate. These structures were prepared in similar technological conditions, except the presence of another substrate. In this sense there are two types of structures, viz: type B: in the same deposition zone of the reactor there is a heavily doped, n type substrate, too, and the semi-insulating substrate is placed behind the conducting substrate, along the gas flow direction; type W: there is only one semi-insulating substrate in the deposition zone, without a conducting substrate.

The integrated mobility values were obtained as above, by DC technics. Some mobility data are shown Fig. 1.

Also the carrier concentration depth profiles were measured by electrochemical etching, using a Post Office Profile Plotter system.

**Layer thickness**

If one considers Fig. 1, it can be seen that the "lowered" mobility is a relative notion; the mobility is lower relative to the carrier concentration. The same mobility would be relatively higher at a higher concentration value, respectively. So the first question is the layer thickness since for the determination of the carrier concentration the exact value of the layer thickness is necessary. In possession of bulk samples the thickness obviously can be measured but this is not true for epilayers [4].

Figure 2 shows two concentration profiles: the active layer is grown (i.) on a highly doped substrate (curve 1) and (ii.) on a semi-insulating substrate (curve 2).

Let us suppose that the carrier concentration in the depth of the layer is homogeneous (as shown in Fig.2). Curve 1 of this figure clearly shows that there is no absolutely abrupt junction between the heavily and lightly doped regions. In view of this, the question arises as to how we can define the layer thickness. Because of the continuously decreasing concentration, it is not evident. But it has to be the same situation for the semi-insulating substrates, with opposite sign concentration gradient. On MESFET type structures the concentration profile shows this phenomenon more clearly.

With the usual decoration technique (angle lapped or cleaved structures) the thickness values obtained by us agree with the metallurgical interface and these are in the region.
Fig. 2. Two carrier concentration vs depth profiles, showing the discrepancy between the crystallographic and electrically active layer thickness (see text).

indicated by "b" in Fig. 2 for the structures with semiconducting substrates.

For the structures with a semi-insulating substrate the concentration profile shows a smaller depth value—smaller than that estimated from the growth rate and indicated by "a" in Fig. 2. This discrepancy suggests that the thickness values used for the determination of the carrier concentration are smaller than the real ones and, since \( n = \frac{1}{t} \) (where \( n \) is the carrier concentration, \( t \) is the layer thickness), it is possible to suppose that the mobility data in Fig. 1 are shifted left, in the direction of smaller concentrations, which may result in an apparent mobility "lowering".

Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness at 0.4x( n^a ) ( t_1 ) [( \mu m )]</th>
<th>Concentration determined using ( t_1 ) [( \text{cm}^{-3} )]</th>
<th>Carrier concentration by POPP [( \text{cm}^{-3} )]</th>
<th>Corrected thickness ( t_2 ) [( \mu m )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>2.2x10^{15}</td>
<td>3.0x10^{15}</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>2.6x10^{15}</td>
<td>4.5x10^{15}</td>
<td>4.1</td>
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<td>7</td>
<td>3.1x10^{15}</td>
<td>4.5x10^{15}</td>
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</tr>
<tr>
<td>4</td>
<td>7</td>
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<td>5.0x10^{16}</td>
<td>9.9</td>
</tr>
<tr>
<td>5</td>
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<td>3.6x10^{16}</td>
<td>7.0x10^{16}</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
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<td>5.0x10^{16}</td>
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<td>0.16</td>
</tr>
<tr>
<td>7</td>
<td>0.28</td>
<td>5.9x10^{16}</td>
<td>1.0x10^{10}</td>
<td>0.17</td>
</tr>
</tbody>
</table>

For more precise analysis we suggest that one measures the carrier concentration at the surface by the C-V method and then on the basis of the Hall voltage to fit the thickness. The starting value of the thickness, \( t_1' \), is determined from the concentration profile, having the depth value at 0.4x\( n_a \), where \( n_a \) is the concentration value in the homogeneous (or active) concentration region (first column). The second column shows concentration values determined using \( t_1' \). The third column shows the \( n_a \) values determined by POPP and the fourth shows the thickness values \( t_2 \) fitted from Hall data with \( n_a \). The differences both in the concentration and depth values are more remarkable in the case of thin (MESFET type) layers.

Inhomogeneous layers

Curve 2 in Fig. 2 shows a concentration distribution that we called homogeneous (W type). At the same time one can find some other distribution with a clear inhomogeneity in depth—as in Fig. 3 and 4. Figure 3 shows an occasional disturbance in the system. Fig. 4 shows a

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In our experience this type of inhomogeneity always occurs in В type samples. Evidently, it is the influence of the heavily doped substrate; consequently, the obtaining of structures for Hall measurement in this way should be avoided. As for the W type samples, sometimes we have seen the same type of inhomogeneity, using some types of substrates. In view of this, it is assumed to be connected with the behaviour of the substrate material. Usually, in such cases if the technological conditions are changed or special technological steps are followed this type of inhomogeneity can be eliminated.

One more remark: the formula used for the integrated Hall constant or for the integrated mobility in inhomogeneous samples [5] is based on the supposition, that the Hall voltage, Дд, does not depend on the thickness coordinates. In fact, this is not so since with the concentration inhomogeneity a mobility inhomogeneity also occurs. The Hall voltage, at the same time, in a sublayer, Дд, will be proportional only to Дμ, in the same layer. And while Дμ changes with coordinates, Дд will not be constant, and will be averaged due to an excess current through the sample.

Conclusions

The measured lowering of the electron mobility in GaAs epitaxial layers can be the result of (i) a false thickness value or (ii) a concentration and mobility inhomogeneity in the layer. For this reason, for a better understanding of the Hall measurements it seems to be necessary to have a concentration depth profile of the same sample, and to compare them. Some inhomogeneities can be avoided in the technological process.

References


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THE NPM MODEL AS A PRACTICAL GUIDE TO STUDY THE INCORPORATION OF DOPANTS INTO SINGLE CRYSTALS GROWN BY THE CZOCHRALSKI TECHNIQUE

K. RAKSANYI, S. ERDEI, I. CRAVERO, B. VAJNA, A. MECSEKI

Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences
Budapest 1502, p. b. 132, Hungary

The concentration distribution of dopants or impurities in crystals grown from melts with Pr ≥ 1 is studied by a simple model called the Neglect of Parallel Motion (NPM) one. A brief derivation of the model is given and an attempt is made to adjust some model parameters to measured concentration distributions.

Introduction

Literature data on bulk segregation coefficients for impurities in oxide crystals grown by the Czochralski technique are relatively rare[1], and the papers dealing with the determination of effective segregation coefficients (ESC) pay less attention to the thermotechnological conditions during crystal growth and the choice of dopants often does not encompass the "critical" ones exerting a detrimental effect on crystal properties already at a reduced concentration level[2-4]. The knowledge of these is important not only with respect to crystal properties, but with respect to the rationale of starting material purification work.

Method

We now give the derivation of the NPM model. We rely strictly on the results of Kobayashi[5] who solved the dimensionless momentum and energy transfer partial differential equation system coupled by buoyancy and convective terms for the stationary case giving the dimensionless temperature gradients on the crystallization interface for a wide range of parameters, such as Re, Pr, l, r∞, and first of all Gr, some of which may depend on x via the changes in geometry parameters and in the case of Gr via the measured ΔT(x) function as well. The Gr(x) function for our apparatus is displayed in Fig. 1. The temperature layer width can be calculated very simply. Now borrowing the relation suggested by Rosenberger[6] the concentration layer width can be obtained from the temperature layer width as follows:

\[ 6c(x) = \left( \frac{D}{k} \right) \frac{\Delta T(x)}{6r(x)} \]  

(1)

At this stage we reduce the diffusion equation to the one dimensional case. For this end we omit the following terms from the equation:

\[ \nabla \cdot (a \nabla c) \quad \frac{D}{r^2} (a \frac{\partial c}{\partial r}) \]  

(2)

For the first term it follows directly from similarity considerations that it will have the order of magnitude \((6c/r^2)\). In the case of the second term, however, the reduction factor is only of the order of \(6c/r\), but in virtue of the relatively high value of the Prandtl number for oxides, \(\delta_c\).
will exceed $\sigma_z$ considerably, and thus within the domain delimited by the interface and $\sigma_z(r)$ the flow can be considered as radially stagnant. Now we are in position to use any analytical or numerical solution of a one-dimensional impurity mass transfer equation supplied with advective terms accounting for the process of crystallization within the above domain if the necessary boundary conditions are given on the $\sigma_z$ surface. For example in the Burton-Prim-Slichter (BPS) case [8] from the solutions $c_e(x,z,r)$, we get

$$k_{BPS} = k_0 / (k_0 + (1-k_0) \exp(-v_0 \sigma_z(x,r)/D))$$

but more sophisticated cases taking into account electrostatic potentials and impurity adsorption on the liquid-solid boundary, as e.g. that of Tiller [9] can be employed as well. Note, that in these solutions $k_{BPS}$ becomes a function of $r$ and $x$.

In the case of unstable growth, the criterion given by Hurle [10] was cast into a slightly modified form

$$m(x,r) = -\frac{T(x)D k_0}{v(x)c_e(x)k_{BPS}(x,r)c_e(x,r)(1-k_0)},$$

where $m$ stands for the minimum initial slope or critical slope of the phase diagram liquidus curve, which yet permits a normal growth. The maps of $m$ are very useful for predicting the location of inhomogeneity boundaries in the crystal, which may correspond to the isoclinic curves $m(x,r) = m$. It is expected that in regions where the actual $m$ value of a substance is greater than the critical slope, the conditions for cellular growth are fulfilled, and the effective segregation coefficient tends to unity. To tackle such situations we developed a phenomenological equation for the effective segregation coefficient

$$k_{eff} = k_{BPS} + (1-k_{BPS}) \exp(-m(x,r)/m_0).$$

This formula has a correct asymptotic behaviour, namely if $m_0$ is equal to zero, the BPS coefficient is restored, and if $m$ is equal to zero, $k_{eff} = 1$. The exponential accounts for the critical event, and for the fact that if $m_0$ is about but less m. "latent" critical effects can be expected.

The model was implemented to a program package "IMPUR" in FORTRAN. Subroutines were written to calculate experimental effective segregation coefficients from impurity concentration measurements and to adjust phase diagram and temperature field characteristics to experimental data using a conjugate gradient minimalization procedure. Spline interpolations were used to obtain the $\sigma_z(x,r)$ function.

Results and discussion

Fig. 2 presents ESC curves (radial averages) with fixed $k_0$, $c_0$, and $m$, varying $Gr$. It can be seen that these are not affected considerably, but there is a rise in the minima at medium values of $Gr$, with the appearance of plateaus. Much more expressed variations can be observed if the dimensionless radius is divided into an inner part $(0 < R < 0.5)$ and an outer part $(0.5 < R < 1)$, and the respective averages are calculated. The inner averages run over the former curves, the plateaus grow into retroflections, whereas the outer averages are insensitive to this parameter. We present in this con-
text an experimental ESC curve based on analytical concentration measurements performed on a LiNbO₃ crystal doped with 1 mmoleSi(SiCfe)/moleNb. (Fig.3). The simultaneous fitting of three parameters, kₐ, logGr, and m, led to the following results: kₐ=0, logGr=4.65, mₐ=925, and the calculated curve agrees well with the experimental one. The most pronounced deviations can be found in the vicinity of minimum and in the bottom part of the crystal. The first, along with the illusoric zero value for kₐ, is due to an overemphasized "latent" constitutional supercooling, whereas the second can be ascribed to the onset of a new incorporation mechanism. The
3. and $k_m=0.16$, but the fitting turns out to be very poor. We obtained analogous segregation curves for Al and P in LiNbO$_3$ [3,4]. The variation of $Gr$ leads to drastic changes in the isoclinal curves in a relatively narrow interval (5.1 < log$Gr_x$ < 5.4). This is due to the switch from centrifugal flow to centripetal one. This again emphasizes the experimentally well known fact that the inhomogeneous regions can be used as indicators for temperature fields [2]. The effect of the variation of $Gr_x$ on the ESC and isoclinal curves implies an upward displacement in the ESC curve and a general decrease of the transparent regions. Decreasing the value of $m_0$ results in an overall broadening of the ESC curves. Fig. 4 shows the effect of variation of $k_m$.

Note that the convexity of ESC curves turns to concavity if the value of unity is exceeded. The inhomogeneity contours show a significant broadening of the transparent region for $k_m$ values approaching unity. These findings correlate well with observed results obtained on LiNbO$_3$ crystals doped with Mg, having a $k_m$ value exceeding unity. It is borne out as well that in this case the outer regions are richer in impurities [11]. These results show that whereas the thermal regime has an impact on the radial distribution of the impurities and on the shape and extension of the visible inhomogeneity regions, the main characteristics of the radially averaged ESC curves is governed mainly by material constants, e.g. by $m_0$ and $k_m$.

Nomenclature

- $C_a/C_i$: actual/initial impurity concentration in the melt
- $C_m$: impurity concentration in the solid
- $D$: impurity diffusivity in the melt
- $6_c/6_r/6_z$: concentration/thermal/velocity layerwidth
- $Gr/Gr_x$: actual/at $\Delta T=5; l=1$, value of the Grashof number
- $l/l_0$: actual/initial melt height
- $*$: thermal diffusivity
- $k_{meff}/k_{BP}$: effective/BPS effective segregation coefficient
- $Pr$: Prandtl number
- $r_0/r$: ingot radius/radial coordinate
- $R$: dimensionless radial coordinate ($r/r_0$)
- $Re$: Reynolds number
- $T/T_m/T_e$: temperature: actual/of melting/of crucible
- $\Delta T$: $T_m - T_e$
- $v/v_0$: advective/radial flux velocities
- $x$: crystal/batch mass fraction ($0 < x < 1$)
- $z$: axial coordinate ($0 < z < 1$)

References


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SIMULATION OF CZOCHRALSKI BULK FLOW UNDER VERTICAL MAGNETIC FIELD

GY. SZABÓ, Z. JUHÁSZ, J. PAITZ and J. PÖLTL
Central Research Institute for Physics
H-1525 Budapest, P.O.B.49, Hungary

An experimental model of magnetic Czochralski growth was constructed to investigate the hydrodynamic behaviour of the melt. The time dependence of temperature in molten gallium was measured and analysed as a function of heating, rotation and magnetic field. The temperature fluctuations were damped when the magnetic field exceeded a threshold value dependent on heating temperature and rotation rate.

Introduction

The application of an external magnetic field in the Czochralski growth of semiconductors has become a very useful technique for improving the crystal quality [1-7]. Hurle [8] and Chedzey and Hurle [9] applied first a magnetic field to suppress the temperature fluctuations in molten gallium. The first experiments on magnetic Czochralski growth were reported by Witt et al [10]. During the past few years the effect of vertical [1-3], horizontal [4,5] and rotating [6,7] magnetic field on crystal quality was extensively investigated. Replacing the rotating crystal with three thermocouples Hirata and Inoue [11] studied the effect of a vertical magnetic field on the temperature distribution and oscillation in silicon melt. Numerical simulations [12-16] of the Czochralski bulk flow have proved the smoothing effect of the magnetic field on the flow and the temperature fluctuations.

Unfortunately, the analytical treatments [17-19] are limited with simplifications. Chandrashekar [17] studied the Rayleigh-Bernard instability between two horizontal planes heated from below. In agreement with the experimental results he found that $R_{c}$, the critical value of the Rayleigh number characterizing the onset of convective flow, was increased by the vertical component of the magnetic field. Using different simplifications Hurle and Series [18] and Kobayashi [19] have investigated the effect of crystal rotation on the melt flow.

In this paper we describe an experimental model of magnetic Czochralski growth constructed to study the temperature oscillations in the melt at room temperature. In the earlier model experiments [20-22] transparent working fluids were used for visualizing the flow pattern. Using molten gallium as the conductive working fluid we studied the effect of vertical magnetic field on temperature oscillation at different rotation rates and heating temperatures.

Experimental

An experimental apparatus was constructed to model the magnetic Czochralski growth. The inner dimensions of the double-walled glass crucible were: diameter 8 cm, depth 10 cm. The rotating crystal was a copper cylinder.
of 4 cm diameter with a flat bottom. The temperature of both the crucible and the crystal was stabilized by circulating water. We could vary the vertical magnetic field produced by a water cooled solenoid up to 480 A/cm. The molten gallium of 8 cm depth was covered with a 5 mm layer of silicon oil to minimize oxidation of gallium.

The temperature of the working fluid was measured by a copper-constantan thermocouple inserted into the melt between the crystal and the crucible wall. Using a computer controlled system the temperature was sampled 4096 times at a rate of 2 Hz, and from these data the average temperature and the standard deviation, $\sigma_T$ were calculated. The standard deviation was taken to be a measure of the amplitude of fluctuations.

To model the hydrodynamic behaviour of semiconductor melt the used molten gallium is advantageous because the hydrodynamic and thermal properties of molten metals and semiconductors are similar [23]. At the same time, due to the higher electrical conductivity of molten gallium a lower magnetic field is required to produce the same damping effect.

Results and discussion

It is well known that the magnetic field can suppress the temperature fluctuations in the melt. In the present work we concentrate on this magnetic damping effect analysing $\sigma_T$ measured at different values of the magnetic field ($H$), the rotation rate and the temperature difference ($\Delta T$) between the crucible wall and the crystal. We study the competition between the magnetic damping effect and the buoyance or rotation driven convection.

The buoyancy driven flow is generated by the temperature difference $\Delta T$ and usually characterized by the Rayleigh number defined as

$$Ra = \frac{\Delta T g R^3}{\kappa \nu},$$

where $g$ is the acceleration of gravity, $R$ is the crucible radius and $\alpha, \kappa, \nu$ are the thermal expansion coefficient, the thermal diffusivity and the kinematic viscosity of the melt. The damping effect of a magnetic field is conventionally characterized by a $Q$ number [17],

$$Q = \frac{\sigma B^2 R^2}{\rho \nu},$$

where $B = \mu_0 H$ is the magnetic flux density, $\sigma, \rho$ are the electrical conductivity and the density of the melt.

The magnetic damping effect is illustrated in Fig. 1 where $\sigma_T$ is plotted against $Q$ (or $H$) for two different $\Delta T$ while the rotation rate is fixed at 20 rpm. As it is expected, at higher $\Delta T$, a higher magnetic field is required to damp the temperature oscillation.

Fig. 1 shows that the temperature fluctuations are completely suppressed when $Q$ exceeds a threshold value $Q_{th}$ which is dependent on $\Delta T$ and rotation rate. For practical reasons in our experiment $Q_{th}$ is determined by the value of magnetic field where $\sigma_T$ becomes less than 0.2 C. The data denoted by triangles in Fig. 2 were measured at a rotation rate of 30 rpm. In this figure the dashed line separates two different types of hydrodynamic behaviour, the steady and the periodic states. Similar behaviour was observed by hydrody-
The effect of crystal rotation on temperature oscillation was studied by measuring $\sigma_T$ as a function of rotation rate for different values of the magnetic field (see Fig. 3). Due to the stirring effect of the rotating crystal, the temperature oscillation disappears at sufficiently high rotation rates even in the absence of magnetic field. In the presence of a magnetic field, the stirring effect of the conductive crystal on the melt flow becomes more efficient because the magnetic field increases the thickness of the viscous boundary layer [18]. Fig. 3 shows that in higher magnetic field the temperature oscillation was suppressed by this stirring effect at lower rotation rates.

The effect of magnetic field is not clear when the rotation rate is less than 10 rpm. In this case the aperiodic temperature oscillation, which is characteristic to the turbulent flow, is easily suppressed by applying a low magnetic field, but in a higher magnetic field a periodic oscillation with high amplitude was observed. Nevertheless, this kind of time dependence was also suppressed by the increase of the magnetic field.

**Summary**

The described experimental apparatus proved to be a useful tool for investigating the onset and the suppression of the thermal instabilities appearing during the magnetic Czochralski growth. We found that the temperature oscillations were completely suppressed when the magnetic field exceeded a...
threshold value which is strongly dependent on the temperature difference and the rotation rate. This kind of experimental investigations provides good conditions for better understanding the magnetic damping effect as well as for testing the results of numerical simulations.

We are grateful to A. Süveges for his critical reading of the manuscript.

References

The transport behaviour of the Ti- and Mo-silicides was studied with halogens (Cl₂, I₂, HCl) as transport agent. The experimental behaviour agrees well with the calculated results. Monocrystals of Ti-silicides were obtained.

Introduction

The chemical transport of some transition metal silicides is possible with halogens as transport agent according to the literature [1 - 5]. In the case of the transport with I₂ as transport agent the transport direction is dependence on pressure [1]. Moreover the silicides can be formed during isothermal transport reactions, in which either the metal (M) is transported to Si (M = Ti, V, Cr, U) or the Si to the metal (Ta, W, Mo) [2].

In the binary system Ti-Si the following compounds exist: Ti₅Si₁, Ti₃Si and Ti₃Si₂. The phase Ti₅Si₁ has a homogeneity range: 37.5 - 40 at% Si. Two further phases have been discussed in the literature: the phase Ti₃Si, forming by peritectic reaction at 1170 °C after 2Ti + Ti₅Si₁ = Ti₃Si [6, 7] and the phase Ti₃Si₂ [6]. In the phase diagram Mo-Si three binary compounds exist: Mo₃Si, Mo₈Si₃ and Mo₈Si₂. It was to investigate the conditions of the crystal growth of Mo- and Ti-silicides by chemical transport with halogens as transport agent.

Thermodynamic analysis

The chemical transport in the system Ti-Si-X can be described by an improved Schäfer model [8, 9]. It could be assumed, that both in the source and in the crystallization zone the gas and the solid phase are in equilibrium. From the knowledge of the gas phase composition in one zone it is possible to establish the gas phase composition in the other one via a connecting flow relation. Consequently the transport direction, transport rate and the composition of transported phases can be predicted even in the...
case of a subsequential transport which is typical in systems with several coexisting phases. For numerical calculations the data were taken from the tables [10, 11], corrected for consistency between the Ti-silicides and Si.

Results of Ti-silicides

Ti-Si-Cl system

The calculated gas phase composition above the deposited solid TiSi$_x$ at 1173 K shows, that the gaseous species TiCl$_4$, TiCl$_3$, TiCl$_2$, Ti$_2$Cl$_3$, SiCl$_4$, SiCl$_3$ and SiCl$_2$ are transport-effective species ($p_i > 1$ Pa). With increasing the gross composition value $X = Si/Ti$ the Si-containing species become dominating. On the other hand over Ti$_5$Si$_3$ in equilibrium with Ti the gas phase does not contain any species with silicon with a remarkable concentration. It may be concluded that in this case a transport of the silicides is not expected. The partial pressure of the PTiCl$_4$ and PTi$_2$Cl$_6$ decrease with increasing temperature, at the same time the partial pressure of the other species increases.

In conformity with the calculated transport direction the transport of the Ti-silicides takes place from hot to cold. The transport rates are between 0.4 and 4 mg/h, and agree well with the calculated ones.

Table I shows the transport sequence of the Ti-silicides when starting with a two-phase solid.

Table I

Transport sequence in the Ti-Si-Cl system

<table>
<thead>
<tr>
<th>Starting composition</th>
<th>Transported phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti + Ti$_5$Si$_3$</td>
<td>Ti$_5$Si$_3$ Si-richer phase</td>
</tr>
<tr>
<td>Ti$_5$Si$_3$ + TiSi</td>
<td>TiSi  Si-richer phase</td>
</tr>
<tr>
<td>TiSi$_2$ + Si</td>
<td>TiSi$_2$ Si-poorer phase</td>
</tr>
</tbody>
</table>

Monocrystals of Ti$_5$Si$_3$, TiSi and TiSi$_2$ were obtained at temperatures $T_{hot} = 1273$ K and $T_{cold} = 1173$ K. Under the applied transport conditions, preferential isometric and needle-like crystals grow in the case of Ti$_5$Si$_3$ and TiSi, respectively. The TiSi-needles are up to 20 mm long and the faces show striations along the longitudinal direction. TiSi$_2$-crystals are isometric, needle-like and flat-like, respectively, having mirror-smooth surfaces (Fig. 1).

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Fig. 1. Single crystals of TiSi$_2$ grown from the vapor using Cl$_2$ as transport agent

**Ti-Si-I system**

The calculated gas phase composition over solid Ti-silicides depends on total pressure, as well as on the temperature. At $p_{\text{tot}} \approx 0.5 \times 10^5$ Pa the partial pressures increase for all species apart from TiI$_4$. The species TiI$_4$ decomposes to TiI$_3$ and further to TiI$_2$. At $p_{\text{tot}} \approx 0.1 \times 10^5$ Pa the partial pressures of TiI$_4$ and SiI$_4$ decrease with increasing temperature, on the other hand the partial pressure curves of TiI$_3$, TiI$_2$, I$_2$ and SiI$_2$ pass through a maximum. According to this thermodynamic behaviour a reversal of the transport direction is observed in the case of iodine transport with Ti-silicides. For higher pressure ($p_{\text{tot}} \approx 1 \times 10^5$ Pa) the transport direction is from hot to cold. When starting with a two-phase solid the Si-richer phase is transported. The transport rates are between 0.3 and 0.5 mg/h. For lower pressure ($p_{\text{tot}} < 5 \times 10^4$ Pa) the transport direction is from cold to hot and a Ti-enrichment is observed.

Starting from mixtures of gross compositions between Ti and Ti$_5$Si$_3$ or between Ti$_5$Si$_3$ and TiSi neither crystals of Ti$_3$Si nor such of Ti$_5$Si$_4$ could be obtained, indicating that Ti$_3$Si and Ti$_5$Si$_4$ are not equilibrium phases at least if SiO$_2$ (from the tube) is present.
Remarks to the Mo-Si-Cl system

The thermodynamic analysis shows that a very high difference between the heat of formation of the gaseous Mo- and Ti-halogenides exists (Table II).

![Table II](image)

The heat of formation of the gaseous Mo- and Ti-halogenides

<table>
<thead>
<tr>
<th>Me</th>
<th>$\Delta H^\circ_\text{f}(298, \text{g})$/KJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCl$_4$</td>
<td>Ti: -763.5, Mo: -389.3</td>
</tr>
<tr>
<td>MeBr$_4$</td>
<td>Ti: -552.0, Mo: -117.2</td>
</tr>
<tr>
<td>MeI$_4$</td>
<td>Ti: -288.4, Mo: -232.7</td>
</tr>
</tbody>
</table>

On the other hand the heat of formation of the Mo- and Ti-silicides do not differ remarkably. It follows that the Mo-silicides cannot be transported like the Ti-compounds, according to a formal reaction, e. g.:

$$\text{TiSi}_2 + 6 \text{Cl}_2 = \text{TiCl}_4 + 2 \text{SiCl}_4$$

because of the partial decomposition reaction is the main reaction in the system Mo-silicide + Chlorine:

$$5 \text{MoSi}_2 + 14 \text{Cl}_2 = \text{Mo}_5\text{Si}_3 + 7 \text{SiCl}_4$$

Therefore single crystals of the Mo-silicides cannot be produced by chemical transport with the applied transport conditions.

References


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EFFECT OF ULTRASOUND ON CRYSTAL GROWTH FROM MELT AND SOLUTION

V.S. ARAKELYAN
The Institute of Radiophysics and Electronics
Armenian Academy of Sciences, 378410, Ashtarak-2, USSR

The effect of ultrasonic waves on the process of crystal growth from melt and solutions was studied. A certain periodicity forms during the growth of crystals from melts and solutions in a standing ultrasonic wave field.

Introduction

The interest in the research into the effect of ultrasonic waves on the growth of crystals from melts and solutions is explained by the effectivity of this exposure [1,2]. At the same time, the available data in the literature about the effect of ultrasound on the growth process are contradictory because the instrumentation for measuring the growth rate is not sufficiently accurate. In view of this, interference rate meter investigations were performed to examine the effect of ultrasonic waves on the growth rate of KNT crystals.

Effect of ultrasound on crystallization rate

The effect of ultrasound on the rate of crystallization depends on supersaturation. In the case of low supersaturation (when the crystallization rate is $10^{-8}$ cm/s) the effect of ultrasound doubles the growth rate, whereas in the case of higher rate of growth ($10^{-5}$ cm/s) the ultrasound will not (with accuracy of 2%) cause any change in the growth rate. Such a characteristic of the effect can be explained by the small gradient of concentration in the case of low supersaturation; that is why the flow of construction material to the crystal is small, too. When ultrasound is applied the acoustic flow takes place, and gives rise to the agitation of the solution close to the crystal and, correspondingly, increases the feed of construction material to the crystal. In the case of high supersaturation the gradient of concentration is high, too. An intensive flow of construction material to the crystal is available, so the acoustic effect does not lead to any change in the crystal’s growth rate. Thus, at high supersaturation the acoustic effect is negligible.

Effect of pressure and absorption of ultrasound on crystal growth

The pressure and absorption of ultrasound may have an effect on supersaturation in the case of growth from solution and also in the case of growth from the melt.

The difference of chemical potential of melt and crystal is equal to [3]

$$\mu_m - \mu_c = \frac{q(T_o - T_C)}{T_o}.$$  \hspace{1cm} (1)

Here $T_o$ is the equilibrium temperature, $T_C$ is the crystallization temperature, $q$ is the melting heat.

Absorption of ultrasound energy in the melt leads to an increase in temperature and a reduction in the rate of crystal growth. In the regime of an ultrasonic standing wave the heat sources will be localized in an area of maximal shift and they will be periodically distributed along the axis of the ultrasound resonator. If the ultrasound amplitude is small, then...
where \( k \) is the wave number of the ultrasound, \( \Delta T_Y \) is the temperature increase caused by absorption of ultrasound energy, and \( x \) is the coordinate directed along the resonator's axis.

\[
\gamma \nu^2 (q - 1/q) \frac{\Delta T_Y}{16 \pi^2 t^2}
\]

Here \( \gamma \) is the absorption factor, \( \nu \) is the speed of ultrasound, \( w \) is the acoustic power density, \( Q \) is the \( Q \) factor of ultrasound resonator, \( f \) is the ultrasound frequency, \( \eta \) is the thermal conductivity [4]. In the ultrasonic standing wave regime the difference of chemical potential of melt and crystal is equal to

\[
\mu_m - \mu_c = q\left( T - \frac{T + \Delta T_Y \sin^2 kx}{T_0} \right)
\]

In accordance with Eq. 4 the crystal growth rate will be modulated, too. The crystal growth rate modulation leads to a change of the dopant's segregation condition at the crystallization interface. The growth condition's space dependence leads to the same dopant's entry's dependence and to the creation of a periodic structure in the crystal.

When the crystal grows from solution then

\[
\mu_m - \mu_c = kT(C - C_o)/C_o.
\]

The change in supersaturation by absorption of ultrasound energy is

\[
\Delta C = \frac{\Delta T_Y}{RT}
\]

The time averaging of ultrasound pressure is equal to zero. However, if second order effects are taken into account, the time averaging of ultrasound pressure is not equal to zero [5], in which case

\[
P = \frac{1}{4} P_o 2G,
\]

where \( P_o \) is the amplitude of the pressure of ultrasound

\[
G = \frac{1}{\rho_o c_o^2} \left( 1 + \frac{1}{2} \frac{\partial^2}{\partial p^2} \right)
\]

The change in supersaturation due to pressure [4] is

\[
\Delta C_p = \frac{C_o V_p}{RT},
\]

where \( C_o \) is the equilibrium concentration of the crystallizing material, \( \Delta V \) is the crystallizing material's change in volume at the phase transition, \( R \) is the gas constant, and \( T \) is the temperature of solution. The estimations for a KNT solution at \( I = 1 \) W/cm², and \( \gamma = 2 \) cm⁻¹ give \( \Delta C_p/\Delta C_p\sim 10^2 \). So the basic deposit in the periodic structure formation gives the absorption of ultrasound energy. Then the difference between the chemical potential of the solution and that of the crystal is

\[
\mu_m - \mu_c = kT(C - C_o + \Delta C_p \sin^2 kx)/C_o.
\]

The difference between the chemical potential of solution and that of the crystal modulated in space leads to space modulation of the rate of crystallization and to different conditions of the dopant's entry into the crystal. The periodic distribution of the dopant in the crystal has a space period equal to half of the wavelength of the ultrasound.

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In our experiment a CuSO₄ solution was used as the dopant with a concentration of (0.5-5) g/l. The ultrasonic standing wave is in the region of 10-90 Mc with an intensity up to 2 W/cm². The rate of crystallization was 10⁻⁶-10⁻⁷ cm/s. The periodic distribution of dopant in the crystal was examined by light diffraction after crystal growth process was complete and the ultrasonic source was switched off. The space period of the structure is equal to half of the wavelength of the ultrasound. The diffraction efficiency was increased with the increase in the concentration and ultrasonic power; over a crystal length of 1 cm it reaches up to 25-30 %. Periodic structures possess high regularity of dopant distribution \( \Delta \lambda/\lambda \lesssim 10^{-3} \). KNT crystals grown from solution without a dopant in an ultrasonic standing wave field do not have a periodic structure. Crystals with a periodic structure possess high optical quality and very low scattering. When the crystallization rate increases up to \( 10^{-5} \) cm/s the periodic structure is created by the mother liquor. In this case, considerable light scattering takes place. The scattering centre period is equal to half ultrasound wavelength. The mother liquor entrance takes place in the ultrasound intensity interval \( 0.2 \text{ W/cm}^2 \leq J < 2 \text{ W/cm}^2 \). With an ultrasound intensity of less than 0.2 W/cm² scattering centre formation does not take place. At an ultrasound intensity higher than 2 W/cm² the crystal surface is damaged. Transition from the regime when the dopant is periodically distributed to the regime when the scattering centre distribution is periodic takes place in the crystallization rate interval \( 2.10^{-6} \text{ cm/s} \) to \( 7.10^{-6} \text{ cm/s} \), when the ultrasound intensity is 1.8 W/cm². Scattering centres obtain a periodic structure only with a rate that is higher than \( 7.10^{-6} \text{ cm/s} \) and an ultrasound intensity that is equal to 1.8 W/cm².

Ice crystal growth in an ultrasonic standing wave field was also investigated. Ice grown from degassed water was shown to have a periodic structure [6]. Our method of forming periodic structures is by means of ice grown from air saturated water. Air bubbles are extracted during the freezing process and they distribute in the standing wave field with a period equal to half the ultrasound wavelength [7]. The bubbles freeze in the ice and form the periodic structure. The experiment was carried out in the 10-50 Mc frequency interval at an ultrasound intensity of \( 0.5-1 \text{ W/cm}^2 \). Light diffraction with 50 % efficiency was observed after switching off the ultrasound source.

References
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ADMISSIBLE MANOEUVRES IN SOME CRYSTAL GROWTH TECHNIQUES

S. BALINT and Z. SCHLETT
Mathematics and Physics Department, University of Timișoara
Timișoara, Roumania

We study in what conditions a manoeuvre in the case of thin filament growth is or is not admissible.

It is known \[1, 2\] that the system of differential equations which describes the time evolution of the state parameter \( R \) and \( h \) in the case of thin filament growth in vacuum is:

\[
\begin{align*}
\frac{dR}{dt} &= -v \cdot \tan \left( a(R, h) - a_e \right), \\
\frac{dh}{dt} &= v - \frac{1}{\xi \cdot \rho} \left[ \lambda_1 G_1(R, h) - \lambda_2 G_2(R, h) \right],
\end{align*}
\]

where: \( R \) - crystal radius, \( h \) - meniscus heights,
\( v \) - pulling rate
\( a_e \) - growth angle
\( G_1,2 \) - temperature gradient (melt and crystal)
\( \xi \) - latent heat
\( \rho \) - density
\( \lambda_1,2 \) - thermal conductivity coefficient (melt and crystal)
\( a(R, h) \) function is the solution of the implicit equation

\[
h = R \cdot \sin \alpha . \ln \frac{R_0 + \sqrt{R_0^2 - R^2 \sin^2 \alpha}}{R(1 + \cos \alpha)} = 0 \quad \text{(2)}
\]

\( R_0 \) is the die radius.

During the growth the pulling rate \( v \) and melt temperature \( T_p \) can be manoeuvered. For this reason they can be called manoeuvre parameters.

It is known \[3\] that (1) system has two stationary solutions \( R_1^*(v, T_p) \); \( h_1^*(v, T_p) \) and \( R_2^*(v, T_p) \); \( h_2^*(v, T_p) \). The first is unstable, the second is asymptotically stable and they are obtained by resolving the system:
\[
\begin{align*}
\ln \left( \frac{R_0^2 - R^2 \sin^2 \alpha}{R(1 + \cos \alpha)} \right) &= 0 \\
R - R_0 \sin \alpha + V R_0^2 &- R^2 \sin^2 \alpha = 0
\end{align*}
\]

The stationary asymptotically stable solution \( R(t) = R^*_2(v, T_p) \), \( h(t) = h^*_2(v, T_p) \) has a region of attraction. This region contains those initial conditions \( R', h' \) for which the solution of the Cauchy problem

\[
\begin{align*}
\frac{dR}{dt} &= -v \tan \left[ \alpha(R, h) - \alpha_e \right] \\
\frac{dh}{dt} &= v - \frac{1}{\xi_p} \left[ \lambda_1 G_1(R, h) - \lambda_2 G_2(R, h) \right] \\
R(0) &= R' \quad h(0) = h'
\end{align*}
\]

tends to the stationary solution \( R(t) = R^*_2(v, T_p) \) \( h(t) = h^*_2(v, T_p) \) when \( t \) tends to \( +\infty \).

It is also known [4] and [5] that the region of attraction is open and connected in the plane of \( R, h \) variables and contains the point with the \( R_2^*(v, T_p) \), \( h_2^*(v, T_p) \) coordinates.

When the seed is brought into contact with the melt and we wait long enough, an \( R' h' \) state appears, which is the \( R_2^*(0, T_p) \), \( h_2^*(0, T_p) \) stationary state.

When the pulling begins, we are in the stationary state \( R_2^*(0, T_p) \), \( h_2^*(0, T_p) \) and we want to arrive in the stationary state \( R_2^*(v_0, T_p) \), \( h_2^*(v_0, T_p) \) if the pulling rate is constant.

The operation of changing the values of the manoeuvre parameter \( v \) from zero to \( v_0 \) is called admissible manoeuvre if in fact, from the state \( R_2^*(0, T_p) \), \( h_2^*(0, T_p) \), it arrives in the state \( R_2^*(v_0, T_p) \), \( h_2^*(v_0, T_p) \).

It results that the manoeuvre is admissible if and only if the stationary state \( R_2^*(0, T_p) \), \( h_2^*(0, T_p) \) is in the region of attraction of the \( R_2^*(v_0, T_p) \), \( h_2^*(v_0, T_p) \) stationary state.

This region of attraction coincides with the natural analytical domain of the Liapunov function \( V(R, h) \), which satisfies the equation:

\[
- v_0 \tan \left[ \alpha(R, h) - \alpha_e \right] \frac{\partial V}{\partial R} + \left[ v_0 - \frac{1}{\xi_p} \left( \lambda_1 G_1(R, h) - \lambda_2 G_2(R, h) \right) \right] \frac{\partial V}{\partial h} =
\]

\[
- \left[ R - R_2^*(v_0, T_p) \right]^2 - \left[ h - h_2^*(v_0, T_p) \right]^2
\]

and the condition:

\[\text{Acta Physica Hungarica 61, 1987}\]
The stationary state \( R^*_2(0,T_p) , h^*_2(0,T_p) \) belongs to the natural analytical domain of the function \( V(R,h) \) if and only if the point \( R, h \) which has the coordinates \( R^*_2(v_0',T_p) - R^*_2(0,T_p), h^*_2(v_0',T_p) - h^*_2(0,T_p) \) is in the domain of analyticity of the function \( U(R,h) \) which satisfies the equation:

\[
-v_0 \cdot \tan \left[ a(R + R^*_2(v_0',T_p), h + h^*_2(v_0',T_p)) - a_0 \right] \frac{\partial U}{\partial R} + \\
\left[ v_0 - \frac{1}{2} \lambda_1 \cdot G_1(R + R^*_2(v_0',T_p), h + h^*_2(v_0',T_p)) - \\
- \lambda_2 \cdot G_2(R + R^*_2(v_0',T_p), h + h^*_2(v_0',T_p)) \right] \frac{\partial U}{\partial h} = -(R^2 + h^2)
\]

and the condition

\[
V(R^*_2(v_0',T_p), h^*_2(v_0',T_p)) = 0
\]  

Thus, we can decide if the manoeuvre \( 0 \rightarrow v_0 \) is admissible or not by testing if the point with the coordinates \( R^*_2(v_0',T_p) - R^*_2(0,T_p), h^*_2(v_0',T_p) - h^*_2(0,T_p) \) belongs or not to the analytical domain of \( U(R,h) \).

In order to determine the \( U(R,h) \) function, which satisfies (7) and (8), we consider its development in origin

\[
U(R,h) = \sum_{m=2}^{\infty} \left( \sum_{j_1+j_2=m} A_{j_1j_2} R^{j_1} h^{j_2} \right)
\]

where the coefficients \( A_{j_1j_2} \) are undetermined [7].

By derivation and replacement in (7) we obtain the coefficients \( A_{j_1j_2} \) by identification.

If there exists a constant \( C \) such as \( |A_{j_1j_2} R^{j_1} h^{j_2}| \leq C \) where

\[
R = R^*_2(v_0',T_p) - R^*_2(0,T_p) \quad \text{and} \quad h = h^*_2(v_0',T_p) - h^*_2(0,T_p),
\]

then the manoeuvre

\[
0 \rightarrow v_0
\]

is admissible [8].

**Remarks**

1. The region of attraction presented by us and the stability domain considered in [9] are not the same.
2. If a manoeuvre \( 0 \rightarrow v_0 \) is not admissible, but the stability conditions are satisfied for any \( v \in [0, v_0] \), then by successive manoeuvres we arrive from the stationary state \( R^*_2(0,T_p), h^*_2(0,T_p) \) in the stationary state \( R^*_2(v_0',T_p), h^*_2(v_0',T_p) \) [6].
3. The system (3) can also be used for the determination of the die radius in order to grow a crystal of predicted diameter.

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BRIDGMAN GROWTH IN A SHAPED GRAPHITE FURNACE

I. NICOARĂ and D. NICOARĂ
Physics Department, University of Timișoara
1900 Timișoara, Roumania

An improved Bridgman-type crystal growth system is presented. By using these types of heaters, fluoride single crystals with diameter up to 50 mm and 150 mm length have been obtained. The dislocation density distribution has been examined in different growth conditions.

Introduction

Lately, significant experimental [1-3] and theoretical [4-6] works have been reported for the Bridgman-Stockbarger configuration providing thermal boundary conditions that lead to a meaningful thermal analysis. The results of heat transfer analyses have mainly been confirmed by experimental investigations. The purpose of theoretical investigations were: to provide basic criteria for the establishment of conditions which lead to improved chemical and crystalline perfection during conventional Bridgman growth; to establish the applicability of results obtained from theoretical heat transfer studies; to offer an experimental basis for the design of an improved Bridgman-type growth system.

The aim of the present paper is to describe a new type, variable shape graphite heater by means of which an optimized temperature profile for Bridgman crystal growth is obtained, a heater which eliminates the need of using two separate heating zones. We also report the optimum conditions for the growth of good quality CaF₂-type crystals by studying their dislocation etch pits distribution.

Description and characteristics of the heater

An important factor controlling the quality and perfection of any crystal grown from melt is the temperature gradient at growth interface. Taking into account the analysis of the equilibrium interface shape, a concave isotherm toward the liquid should be realized in order to eliminate the formation of facets and dendritic growth. As a consequence the crystallization of the melt must take place in a high temperature gradient zone. This condition is essential in order to obtain single crystals of large dimensions.

Fu and Wilcox [5] investigated a three-zone furnace in which the hot and cold zone were separated by a short adiabatic zone. It was shown that
the use of an adiabatic zone significantly reduces the curvature of the isothermes between the hot and cold zone and allows a much better control over the shape of the melt interface.

Taking into consideration the analysis of Jasinski [6] which recommends a certain proportion between the lengths of the three zones - hot, cold and gradient zone - referring to the diameter and the length of the crystal, several types of graphite heaters were designed [7,8], whose characteristics would satisfy the above mentioned demands.

In the present paper we propose a new type of graphite heater which eliminate the need of using two heating chambers, independently controls and with a intermediate diaphragm, recommended in Bridgman-technique; this heater can produce temperatures of up to 2200°C in vacuum of $10^{-2}$-$10^{-3}$ Pa.

The model contains an adiabatic zone and a booster heater zone that can be used to increase the thermal gradient near the solidification interface.

Figure 1 illustrates the longitudinal section of three types of heaters and the temperature distribution along them. Built of graphite, the heater produces an almost constant temperature zone (the hot zone-B-C) necessary for the melting of the substance and a high temperature gradient zone (D-E). The C zone (the booster heater) is conceived as a meander-type resistance by means of which an overheating is obtained in the lower level of the upper zone. The D zone is inserted for the improvement of heat transfer towards the upper part of the heater. The E zone, which appears like a wall thickening has the role of an adiabatic zone, leads to the high temperature gradient. The F zone is used as the lower cooling chamber (the cold zone). The electrical and thermal characteristics of the furnace are: for working temperature of 1400°C, the electrical power is 4.2 kW, with supply voltage 16 V; 50 Hz. Electronic regulation and automation assures the thermal stability of the system. In order to obtain small-diameter (up to 10 mm) crystals, the C zone can be eliminated, as the necessary temperature gradient can be obtained by means of heater wall thickness adjustment (Fig.1).

Results and discussion

By using these types of heaters, CaF$_2$, BaF$_2$, etc. single crystals up to 50 mm diameter and 150 mm length can be obtained, while by means of a special crucible, oriented single crystals can be produced (Fig. 2). Due to the remarkable optical properties of fluoride crystals, the problem of obtaining them in large quantities has often been raised. With a multiple type crucible [9] several up to 12 mm diameter crystals can be obtained during a single growth process.

The crystals are clear, colorless and have good cleavage planes. For cleaved 1 mm thick slides, the transmission coefficient is 98 % in visible and infrared up to 9 µm for CaF$_2$ and 10 µm for BaF$_2$. The quality of the crys-
tals was studied by examining their dislocation distribution. For this purpose, the crystals were cut into slices upon the cleavage surface (111) and their surfaces were etched to show up dislocation pits. Fresh cleavages were subjected to etching in aqueous solution using 2N HCl.

The formation, multiplication and high mobility of the dislocation in ionic crystals lead not only to high densities of individual dislocation, but also cause arrangement of dislocations into well developed grain subboundaries, which are stable and nearly immobile in contrast to individual dislocations. Subboundaries cannot be easily removed by annealing. The dislocation density along the sample and also for a given cross section in radial direction has been studied.

The studies of the etched cross section of the crystal taken at different levels, indicate the following: the density of pits and subboundaries is quite low and fairly uniform through the volume (Fig. 3.a.) in up to 12 mm diameter crystals which were grown in a III type heater with a 6 mm/h pulling rate and the temperature gradient of 7°C/cm. The dislocation density is about $10^3 - 10^4$ cm$^{-2}$. For a higher pulling rate, the dislocation density increases rapidly to a much higher value at the upper end of the ingot (Fig. 3.b.).

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Fig. 2. The multiple crucible, crystals obtained with this and oriented CaF₂ crystal

Fig. 3. The dislocation etch pits distribution

For obtaining crystals with diameter larger than 12 mm a meander type heater must be used in order to assure the necessary temperature gradient at the melt-solid interface; the temperature gradient is about 20 °C/cm and the pulling rate 4 mm/h.

By establishing the A-E heater zone dimensions and bearing in mind the thermal characteristics of both the crystal and the crucible, an improved Bridgman-type system can be realized in which the crucible lowering in the heater will not unfavorably modify the axial temperature gradient (Fig. 1, Ia) especially at the melt-solid interface, a system which produces good quality crystals.

References


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GROWTH OF POTASSIUMDIHYDROGENPHOSPHATE (KDP) SINGLE CRYSTALS BY MEANS OF THERMOELECTRIC COOLER

L. VANNAY
Department of Experimental Physics, Institute of Physics, Technical University of Budapest
1521 Budapest, Hungary

A new method of constant temperature has been developed for single crystal growth from solution. The principle of the method is the following: the amount of the solvent condensed on the lid of the crystallization vessel is regulated by means of controlled cooling of the lid, and the condensed liquid is returned to the solution through the powder of material to be grown. Thus a constant supersaturation is created in a solution of constant amount. The utilization of the method for growing KDP crystals is described.

KDP crystals have already been grown by several growth methods including the method based on temperature lowering [1], forced convection [2], concentration convection [3], and evaporation [4]. To grow crystals of good quality the methods of constant temperature are favourable, where the parameters of the growth depending on temperature remain constant. Therefore the growth by evaporation of the solvent at constant temperature was chosen.

In the following we summarize the conditions which are necessary for growing good quality KDP crystals, give a brief description of the apparatus used in our experiments, and describe how KDP single crystals were grown by means of the apparatus.

KDP crystals are grown at a pH of 4.5 or a little higher, at a growth rate of less than 1 mm/day from pure raw material (the amount of impurities is less than 100 ppm) on a Z-cut seed. Under such circumstances the growth rates along the x and y axes are negligible as compared to that along the z axis.

The scheme of the growth apparatus is shown in Fig.1. The operation area is placed in a glass cylinder (1) of 130 mm in diameter and 230 mm in height. The lid of the cylinder moulded into a conical shape (2) is made of aluminium. The side of the cone facing the operation area is covered with PTFE. On the other side of the cone two thermoelectric coolers (3) are mounted. The thermal insulation of the upper part of the lid is ensured by silicone rubber (4) and polystirene (5). The heat is conducted away from the warmer side of the cooler by means of copper blocks (6). The upper part of the lid and the thermoinsulator are separated from the thermostated water by a plexiglass cover (7).

The thermoconducting copper blocks and terminals needed for the correct operation protrude from this plexiglass box. The plexiglass tubes for the electric wires leading out of the vessel, for the shaft of the stirrers and for the recharge of raw material are sealed with silicone rubber. The plexiglass raw material holder (Fig. 1/b) is carried out and set under the lid so that the saturated condensate returning to the growth solution does not raise the growth of any parasite crystals, and does not bring any microcrystals of the raw material into the growth solution.

If the coolers on the lid operate, the lid is colder than the vapour above the solution, and the vapour condensates on the lid. The condensed fluid trickles down the
Fig. 1. Scheme of the growth apparatus (a) and the raw material holder (b)
cover, flows through the raw material and becoming saturated returns into the growth solution.

At a given temperature the supersaturation of the growth solution is determined by the rate of condensation, which can be regulated by the current of the thermoelectric coolers.

The operation characteristic of the apparatus is shown in Fig. 2, where the amount of the liquid condensed in one day versus the current of the thermoelectric coolers is depicted at two different temperatures (30 °C and 40 °C) of the thermostated water using one or two coolers. Knowing this characteristic, the solubility data and the surface area of the growing crystal, one can estimate the cooling current required for the desired growth rate.

In our experiments we used 30x30x6 mm Z-cut seeds, which were fixed to the bottom of the growing vessel with silicone rubber.

The growth apparatus was heated together with the mounted seed to 30 °C. The constant temperature of the thermostated water was kept by means of a controlling device operating with an electronic heater and a thermocouple sensor. The fluctuation of the temperature of the thermostated water was less than 0.05 °C.

The growth solution was prepared with the assumption that the solubility of KDP is 28 g/100 g water, and quartz bidistilled water was used. The water was heated to 40 °C under continuous mixing, and after solving the raw material the solution was filtered through a glass filter. Then it was cooled down to 35 °C and was charged into the crystallization vessel.

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The process of charging the solution was continued until the level of the solution in the vessel reached the raw material holder. After charging the solution the stirrer was started. The mixing was alternated \[5\] with an alternation period of 12 s. The speed of rotation of the stirrer was \(35 \text{ min}^{-1}\).

After filling the solution the raw material holder was charged with KDP powder or with smaller crystals. The raw material used was of Merck "Optipur" purity.

After charging the raw material the cooling current was increased until reaching a growth rate of approximately 1 mm/day. The raw material was recharged once or twice every week.

In consequence of recharging of the raw material the level of the solution increased a little during the growth. This is advantageous because it prevents the development of parasite crystals, which were not observed in our experiments. The experiment was continued until the growing crystal approached the stirrer within a distance of 5-10 mm.

The grown crystals did not contain any visible defects or stresses. They were used to make electrooptical devices.

References
GROWTH OF TRIGLYCINE SULPHATE (TGS) CRYSTALS AT CONSTANT GROWTH RATE

L. VANNAY and A. TÓTH

Department of Experimental Physics, Institute of Physics
Technical University of Budapest
H-1521 Budapest, Hungary

An automated method for growing TGS crystals from solution at constant growth rate by the evaporation technique is presented. The amount of solvent to be extracted is determined by a computer program taking into account the change of the area of growing crystal faces, and the extraction of the appropriate amount of the solvent is carried out by the aid of an electronically operated magnetic valve.

One of the most widely studied ferroelectric crystals is triglycine sulphate (TGS). The continuous interest in growing this crystal is partly due to its scientific importance in investigating ferroelectricity [1, 2], and partly due to its excellent pyroelectric properties, which make possible the utilization of this crystal for infrared detection and thermal imaging [2, 3, 4].

TGS is grown from aqueous solution, and in many cases, in order to improve the properties of the crystal important for applications, some doping is used. In these cases the possibly homogeneous incorporation of impurity into the crystal is of great importance, which requires stationary growth conditions. This requirement can particularly be satisfied by using isothermal growth method, e.g., growth by the evaporation of the solvent. In this method the supersaturation necessary for growth is ensured by the extraction of solvent from the solution. The extraction of the solvent may be carried out (a) by the aid of evaporation through bores made on the lid of crystallization vessel, (b) by ventilating the space above the solution by the aid of dry inert gas, (c) by condensation of evaporated solvent on the cooled lid of crystallization vessel, and its subsequent extraction from the system.

With method (a) crystallization can hardly be controlled, because the growth process is highly affected by the changes in the environment. The method denoted by (b) is much better in this respect, and the control of the process can easily be carried out, but here the appearance of unwanted parasite crystals is of considerable probability. The best results can be expected by using method (c), therefore this latter method was utilized in our experiments.

If the growth takes place at a temperature higher than the temperature of the environment, the lid of the crystallization vessel is cooler than the
solution, consequently the solvent begins to condensate here. With this method the lid is usually moulded into a conical shape. With this construction one attains the condensate trickling down the lid and being collected in a small pot. The solvent is then extracted from this pot. Since rather small amounts of solvent are to be extracted, continuously working pumps are usually of not much use, and the solvent extraction is better carried out with a syringe several times a day.

With this method the condensation is usually strong, if the crystal grows at an elevated temperature or in a cooler environment, when the solvent extracted from the collecting pot will be replaced pretty fast. This results in an increase of the supersaturation. When, on the other hand, the pot becomes filled the condensing and trickling solvent gets back into the solution decreasing its supersaturation. Thus without appropriate control of extraction of the solvent from the system these processes lead to fluctuations of the growth rate.

Growing TGS by this method another problem arises. It is well known that the area of growing faces of a TGS crystal changes during the growth, consequently the constant rate of extraction of the solvent results in changing supersaturation.

As a first step in avoiding these limiting conditions a special equipment was developed, which enables a quasi-continuous and automated solvent extraction. The main point of this method is that the extraction of the solvent from the collecting pot is realized by a syphon equipped with a magnetic valve. The scheme of the growing apparatus including magnetic valve and electronic controlling unit is shown in Fig. 1. The conveying of the solvent to be extracted from the system is carried out by a small diameter silicone rubber pipe. As the discharge hole of the pipe is at a lower level than the collecting pot, after sucking the pipe the condensate flows out of the collecting pot through the pipe. The magnetic valve is mounted on the end of the pipe, and extraction takes place only when it opens. The time during which the valve is open and the time interval between the openings of the valve can be adjusted electronically by a special timing unit [5] in a wide range, which enables us to regulate the extracted solvent quantities within broad limits. With the timing unit used in our experiments the time interval between the openings of the valve can be varied from 20 to 60 minutes in 11 identical steps, whilst the open time of the valve can be varied continuously from zero to 3 seconds.

Of course, the extracted fluid-quantity depends not only on the opening parameters of the electronics but also on the setting of the valve (the difference in level between the small pot within the growing vessel and the discharge hole) as well as on the hydrostatic resistance of the conveying system. If the hydrostatic resistance is constant, a linear relationship between the extracted fluid-quantity and the vertical position of the valve may be expected. The results of measurements carried out
with a 70 cm long silicone rubber pipe with a diameter of 1.0 mm are shown in Fig. 2. The diameter of the valve was 2.0 mm, every experimental run consisted of 50-50 valve openings. The level of the valve was measured from an arbitrarily selected zero-value. The measurements yielded, as expected, a linear relationship. With this calibration and knowing the data of the electronics one can set quite exactly the fluid-quantity to be extracted per day.

As is mentioned above, another problem of maintaining constant supersaturation is related to the fact that TGS crystal has considerable growth rates in all the three crystallographic directions. As a result, the area of growing faces increases during the growth process, consequently the maintenance of constant supersaturation requires increasing rate of extraction of the solvent. The rate of the amount of solvent to be extracted can be estimated by modelling the change of dimensions of the growing crystal. After reaching the equilibrium form TGS has a growth habit shown in Fig. 3.
Neglecting the faces of little area the growing crystal can be modelled by a parallelepipedon with dimensions changing in accordance with the known growth rates in different directions.

The calculation begins with measuring the starting dimensions of the crystal in the directions of axes b and c. Then choosing the desired growth rate in b-direction the necessary rate of change of mass of the crystal can be obtained. Knowing the change in mass and using solubility data one can calculate the actual rate of the amount of solvent to be extracted.

The calculations are carried out by a computer, and the actual operating parameters of the magnetic valve are set according to the data obtained from the computer. Thus the method described offers the possibility of a computer-aided growth at constant growth rate.

The results of investigation of some doped TGS crystals grown by this method will be presented in a forthcoming paper.

References
GROWTH OF SINGLE CRYSTALS BY MEANS OF MEMBRANES

M. VARGA and L. VANNAY
Department of Experimental Physics, Technical University of Budapest
1521 Budapest, Hungary

A method is described for growing AgI and Ag$_3$I(NO$_3$)$_2$ single crystals from solution. The method relies on slow dilution through a PTFE membrane. This new growth technique is specially applicable to crystals which can be precipitated from solution. The X-ray crystallographic data are given for the Ag$_3$I(NO$_3$)$_2$ single crystals.

Traditional crystal growth techniques cannot be applied at all to a great number of single crystals. In other cases the growth may be very slow and sometimes it is difficult to control the growth parameters. Such materials are for instance which are prone to decomposition below their melting point and which have no suitable, simple solvent.

Moreover, classical methods have the disadvantage that the rise of crystal seeds is rather casual and the chance to obtain large single crystals is small. Furthermore these methods are sensitive to environmental changes (temperature, vibration...) and in some cases require very complicated equipment. In the course of experimenting with various growth techniques to obtain good quality single crystals a membrane growth system has been developed. In this system the driving force of the growth consists of hydrostatic pressure and concentration gradients across some properly selected membrane filter.

The method can be used to grow crystals with a solvent pair one of which dissolves the substance to be grown easily, while in the other its solubility is rather poor (an approximately 100-200-fold solubility difference is required). An additional requirement is the unlimited solubility of the two solvents with regard to each other.

The advantage of the method may be summarized as follows: the supersaturation of the system can be easily regulated, and also homogenized by proper mixing. Further on, not only the spontaneously developed, uncontrollable nuclei act as seeds, but also only one properly selected nucleus placed in advance into the system can be used to induce a controlled growth. The system is relatively insensitive to environmental influences. It is possible to grow large, good quality single crystals of organic and inorganic compounds in a relatively short period of time.

Operating principle the growth apparatus

The water in the external glass cylinder is diluted slowly by the hydrostatic pressure and the concentration gradient across the membrane of the system of the second cylinder. In this way the required supersaturation is obtained and the crystals start growing either on the few spontaneously developed nuclei, or only one crystal grows on a single nucleus fastened at the end of the mixer (see Fig.1).

The supersaturation is regulated by adjusting the hydrostatic pressure (which is the difference in the levels of the two liquid columns), and by the correct selection of the active membrane diameter.

The membrane with an active surface of 314.16 mm$^2$ (20 mm diameter) was fitted into a
cylinder of 32 mm in diameter. The active area of the membrane has been adjusted with silicone rubber by leaving its centre free, while the rest was covered with the silicone concentrate, which also fastened the membrane to the cylinder. In order to eliminate the effect of the temperature fluctuations the equipment was placed in a thermostat.

Growing single crystals of $\beta$-AgI

Silver iodide has two modifications below 146 °C at atmospheric pressure [1], a cubic, sphalerite type $\gamma$ structure and a hexagonal, wurtzite $\beta$ structure. The $\gamma$ type crystals transform slowly to the $\beta$ structure at room temperature. Both the $\gamma$ and $\beta$ phases undergo phase transition to a cubic $\alpha$ structure at 146 °C. Consequently, it does not seem possible to grow single crystals from melt. The most obvious way is to grow the crystals from solution. Unfortunately, AgI has no one-component solvent suitable for solution growth. AgI is highly soluble in aqueous solutions of KI or HI and the solubility decreases with decreasing KI or HI concentrations. Slowly diluting the solutions, the AgI precipitates in the form of single crystals. Thus in order to obtain single crystals of good quality, one has to dilute the solution in a slow and controlled way. One of the methods used by crystal growers is diluting the solution through a layer of gel [2]. Dilution is also possible by the slow diffusion technique [1,3].

Another method makes use of the mass transfer process between the AgI dissolved in HI and pure water in a closed vessel [4]. In this case the evaporating water dilutes the solution and the HI vapour dissolves in the water. Both processes result in the precipitation of AgI.

One of the main problems with the AgI-KI-H$_2$O system is its sensitivity to temperature changes. To the rise of temperature the system can respond with an undesired AgI precipitation. In order to avoid this inconvenient phenomenon we chose, by using the solubility curve published by Mills [3], a KI/AgI concentration, where the change of temperature has no effect on the solubility. The optimum concentrations used in our experiments were 5.75 mol/l KI and 3.25 mol/l AgI. All of our chemicals were of pro analysi purity and the water quartz bidistillated.

The slow dilution was carried out by means of a membrane. After testing a number of membrane materials the Reichelt Chemie Technik’s 1–5 $\mu$m pore size hydrophobic PTFE membrane proved to be the best for our purpose. Crystals obtained after 2–3 weeks were transparent, pale yellow hexagonal prism or pyramids without inclusions and were 5 mm in diameter and 15–20 mm in length.

The growth of $\text{Ag}_3\text{I(NO}_3\text{)}_2$ single crystals

Silver iodide dissolves readily in aqueous solutions of silver nitrate and the solubility of this compound increases with increasing silver nitrate concentration. The dilution of the aqueous solution of AgNO$_3$ saturated with AgI leads to the precipitation of several microcrystalline compounds. This process depends upon the AgNO$_3$ concentration. Table 1 shows the concentration dependence of some resulting precipitates. The third item in the Table, $\text{Ag}_3\text{I(NO}_3\text{)}_2$ proved to be a self-consistent compound, since the 4.23 $\text{nm}$ band characteristic for AgI cannot be detected in its adsorption spectrum. Any attempt to grow single crystals from this compound with the usual methods presented various difficulties. The evaporation technique could not be employed because of the increasing solubility of AgI with the concentration increase of in AgNO$_3$. The method of temperature decrease resulted in AgNO$_3$ precipitation, since this substance crystallises more readily.
Fig. 1.
Scheme of the growth apparatus
1 - outside cylinder,
2 - internal cylinder,
3 - PTFE membrane,
4 - silicone rubber,
5 - stirrer,
6 - AgI-AgNO$_3$-H$_2$O system,
7 - bidistilled water

Fig. 2.
Line profile of (002) reflection of a single crystal of Ag$_3$I(NO$_3$)$_2$
Table I

<table>
<thead>
<tr>
<th>Concentration of AgNO₃ solution saturated with AgI mol/l</th>
<th>Precipitating compounds while diluting with water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0-0.6</td>
<td>AgI</td>
</tr>
<tr>
<td>0.6-2.0</td>
<td>Ag₂I(NO₃)</td>
</tr>
<tr>
<td>2.0-</td>
<td>Ag₃I(NO₃)₂</td>
</tr>
</tbody>
</table>

from the system H₂O-AgNO₃-AgI than Ag₃I(NO₃)₂. The gel growth was rather slow for our purpose, moreover this technique is extremely sensitive to environmental influences (e.g. vibration, temperature fluctuations, etc...). A further difficulty is presented by the fact that in the gel growth the nucleation cannot be properly regulated.

In order to avoid these difficulties another growth technique has been developed. An AgI-AgNO₃-H₂O system saturated for both AgI and AgNO₃ has been slowly diluted across a membrane. Pro analysi chemicals and quartz bidistilled H₂O were used. The membrane selected was a hydrophobic Chetra "Gore-Tex" PTFE filterlaminate of 1.0 μm pore diameter. Within 2-3 weeks 3 to 4 mm long good quality single crystals with an axial length of 10-13 mm were grown.

X-ray investigations

The orientation and the quality of the as grown crystals were investigated with a manually operated SECASI type PZ diffractometer developed for single crystal orientation. CuK radiation (λ=0.1542 mm) was used with a current of 13 mA at a voltage of 30 KV. The best developed surface of the crystal belonging to the P2₁₁₁ space group i.e. (002) plane was studied. The orientation as measured by the reflection of this plane according to Bond’s method [5] was \( \theta_{\text{orient}} = 10^\circ 34'42'' \) and by a line profile analysis of the same reflection \( \theta = 10^\circ 41'53'' \). The difference between the two methods amounts thus to 7'11" (an error of -0.56 %). From the line profile depicted in the Figure one may conclude that the crystals are of rather good quality. The half width line was 3'19"-0'10". Some small deviation on the right side of the profile curve (denoted by A and B, respectively) refer to some mosaic development tendency (Fig. 2).

Results

By the above method relatively large single crystals of good quality were obtained for application in analytical chemistry as solid state single crystal ionselective electrode membrane. In comparison with gel methods the advantage of the described system is the possibility to grow a seed crystal which is previously placed into the growth area and that by means of mixing the probability the formation of new nuclei is diminished.

References


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CORRELATION BETWEEN GROWTH MECHANISM AND MICROSEGREGATION STUDIED BY ELECTRON MICROSCOPY

H.P. STRUNK\textsuperscript{1}, A. KESSLER\textsuperscript{1}, Y.C. LI\textsuperscript{2,3} and E. BAUSER\textsuperscript{2}

\textsuperscript{1}Technische Universität Hamburg-Harburg
D-2100 Hamburg 90
\textsuperscript{2}Max-Planck-Institut für Festkörperforschung
D-7000 Stuttgart 80
\textsuperscript{3}Permanent address: Institute of Semiconductor Devices
Beijing, P.R.China

Based on an electron microscopic analysis, the molecular microsegregation mechanisms are derived that lead to the formation of an atomically thick plane of Ga in Si grown from Ga solution under conditions of dislocation-controlled facet growth. Terrace and valley traces are then interpreted in the light of this knowledge and shown to represent similar segregation effects on a larger scale.

Introduction

Homogeneity and compositional and structural perfection are prominent requirements in the crystal growth of technologically important bulk crystals. This holds particularly for semiconducting materials, because impurity or dopant inhomogeneities or extended defects degrade their electronic properties. In order to meet these requirements the crystal growth process must be carefully controlled, taking into account the operating mechanisms of growth and also of microsegregation.

In this paper direct observations by electron microscopy of dopant microsegregation in silicon layers grown by liquid phase epitaxy will be presented. The observations indicate a correlation between segregation effect and mechanism on a molecular scale. The results will be utilized to interpret larger scale nonuniformities called 'valley' and 'terrace' traces.

Experimental techniques

Silicon epitaxial layers grown from Ga solution on (111)-oriented Si-substrates were used for the electron microscope work. The analysis of the defect structure was performed in a high voltage transmission electron microscope which permits Si layers with a thickness of up to a few \( \mu \text{m} \) to be analysed. The specimens were, after optical inspection of the growth surface, prepared by thinning from the substrate side, until only the upper part of the epilayer remained.

The investigation of terrace and valley traces was performed by photo-etching of internal surfaces exposed by fracturing or cutting. The photo-etch-effect is very sensitive and delineates small concentration fluctuations that escape detection by other methods, especially by electron microscopy. The results rely on a variety of investigated crystals including Si, Ge, GaAs, either Cz- or solution-grown.

Growth induced microsegregation

Observations by electron microscopy

The investigations have been performed on layers grown at temperatures \( \leq 500 ^\circ \text{C} \). In this temperature range, shallow growth pyramids that develop on the (111) facets assume a triangular shape. The growth can be conducted in a way that the monomolecular steps forming the shallow pyramids can be optically resolved by Nomarski differential interference contrast (N-DIC). Fig. 1 shows an example. The typical defect structure present in the center of such pyramids is shown in Fig. 2. The electron micrograph reveals that one dislocation caused the formation of the pyramid. It has been shown earlier \cite{1} that in addition to dislocations according to Frank's growth model ('screw' dislocations) \cite{2} also 'edge' dislocations give rise to growth pyramids. (A corresponding nucleation model is discussed in \cite{3}).

The defects most interesting in the present context are indicated by the three sets of fringes that emanate from the dislocation in a star-like arrangement. Each set of fringes indicates, as in the case of a stacking fault, the presence of a planar defect in the silicon.
The spatial arrangement of the three planar defects with respect to the growth pyramid is depicted in Fig. 3. Each planar defect is extended between the dislocation and one of the \(<112>\) ridges of the pyramid, cf. Fig. 1. Information on the physical nature of the planar defects has been obtained by contrast analysis. Fig. 2 shows already that the sets of fringes cannot be caused by stacking faults, because they fade away within the specimen; this is not possible for a stacking fault, which can be terminated within the crystal by a partial dislocation only. A quantitative evaluation of the fringe contrasts was performed in comparison to the contrast of 'normal' stacking faults, which sometimes happened to grow nearby in the silicon layers. The planar defect is found to be of extrinsic type, i.e. it causes a dilatation essentially perpendicular to its plane. This extension amounts to ~20 \% [4].

Model of the planar defect

The formation and nature of the observed planar defects bases on the fact that any nonuniformity in the morphology of the growth interface may lead to a fluctuation in the concentration of impurity atoms.

Fig. 1 indicates that this nonuniformity is represented by the sharp bends in the monomolecular growth steps. The 'impurities' have to be identified with the solvent Ga atoms, which are substitutionally incorporated into the growing crystal in an overall concentration up to \(5 \times 10^{20} \text{ cm}^{-3}\) Ga atoms [5]. Since Ga atoms are 7 \% larger in diameter than Si atoms, it is conceivable that Ga atoms are incorporated at bends rather than at straight step segments, because of space reasons. The formation of the planar defects becomes obvious, if one assumes that Ga is exclusively incorporated at these bends. Due to the correlated motion of consecutive bends into a \(<112>\) direction (Fig. 1), one row of Ga atoms after the other is deposited in the wake of these bends. Thus a 'plate' of Ga is built up in the growing silicon crystal. A hard sphere model of such a plate is shown in Fig. 4. An estimate of the expected dilatation corroborates this plate model.

In the plate arrangement, the volume expansion due to the larger Ga atoms can be relaxed perpendicularly to the plate only. Thus the extension of 7 \% in each of the three dimensions adds up to 21 \% perpendicular to the plate, which is in excellent agreement with the value obtained by electron microscopy. The atomistic structure of the planar defect, i.e. whether the Ga atoms form precisely one atomic plane or whether they are distributed within several adjacent planes, could not be determined so far by electron microscopy. This distribution is determined by the localization of the bends in the growth steps. The bends may laterally slightly shift during step motion, they also may be rounded. Both effects would tend to distribute the incorporated Ga atoms over several atomic planes, i.e. the drastic local concentration fluctuation is broadened and reduced in amplitude. This effect becomes obvious at higher growth temperature (>500 °C), at which the triangular step pattern is rounded [5]. Therefore at these temperatures, the planar defect cannot be formed anymore [4,6].

Terrace and valley traces

Terrace traces are found after so-called terrace growth. This growth mode develops if the growth surface deviates by one or a few degrees from the low-index plane (e.g. [7]). The corresponding growth interface structure is depicted in Fig. 5 in a way which may also account for terrace and valley trace formation. In terrace growth the monomolecular surface steps are generally bunched and form risers of varied height. Crystal growth proceeds by attachment of molecules to these risers and to those monomolecular steps that cover the treads between each two risers. Due to this growth mechanism, the height of the risers is not constant, it merely is determined by the netto flux of monomolecular steps that results from steps arriving at the top and leaving at the base of a riser. A riser therefore may newly be formed by step bunching, grow in height and then reduce its height until it disappears. The lateral velocity of such a riser is the lower, the higher the riser is; this becomes evident if the arrival rate of molecules at the growth interface is to a first approximation assumed to be constant. Therefore, the trace of such a riser generally takes up a sigmoidal shape [8] (Fig. 5).

In many cases the growth interface is slightly wavy, which is shown in Fig. 5. Terraces with opposite slopes (model of a concave growth interface) move in opposite directions, or at
least have opposite components of motion, and form a valley, where they meet. Since, as outlined above, the heights of successive risers are generally different, the risers on meeting there do not annihilate completely and the remaining part of the higher riser moves further (indicated by arrow). In consequence the position of the valley is not stationary but moves laterally according to the height distribution of the arriving risers [9] (Fig. 5).

In the sense of the foregoing section one may identify risers and valleys as those nonuniformities at which impurity or solvent atoms may be incorporated preferentially (preferential refusion may also be possible, depending on conditions that shall not be discussed here). Thus incorporated dopant or impurity atoms delineate the path of terrace risers and valleys. Fig. 6 shows a photetched cross-section of a Cz-grown Ge-crystal. In the middle part, the zig-zag shaped trace of a valley is clearly seen. Inspection at glancing angle parallel to the horizontal margin indicates that each sharp turn of the valley trace is associated with a trace that runs slightly obliquely to the horizontal direction (best visible in the lower part of the micrograph, some are arrowed). These traces represent terrace traces, the terrace heights of which always were larger than the riser making up the opposite part of the valley. Thus the valley trace is always bent into the direction of the arriving terrace trace.

The interactions of terrace and valley traces lead to various types of trace patterns, some of which have been discussed elsewhere [9]. The present example already indicates that the interaction of these two trace types supports their identification; it would have been very difficult otherwise to discriminate the nearly horizontal terrace traces from other striations in Fig. 6 that run horizontally and mark the instantaneous growth interface.

Conclusions

The presented results show that the morphology of the growth interface and the growth kinetics determine the distribution of impurities or dopants in the bulk of a crystal. It has especially been shown that all types of nonuniformities may cause fluctuations in the concentration of incorporated dopant atoms. Special conditions of dislocation controlled facet growth made it possible to analyse unambiguously by electron microscopy a planar defect that forms due to segregation on a molecular scale. Comparable segregation effects occur at risers in terrace growth and at valleys. Conclusion from this evidence is that the growth kinetics has to be carefully controlled on a molecular scale if homogeneous crystals are to be grown, irrespective of the growth method.

References


Fig. 1. Optical micrograph (N-DIC) of a growth pyramid. The growth spiral (monomolecular steps of height 0.31 nm) assumes the threefold symmetry of the (111) growth surface

Fig. 2. Center of a growth pyramid as seen in a transmission electron microscope. Si grown from Ga solution. The dislocation extends from the apex of the pyramid (A) to the bottom of the specimen (B). Three sets of black-white fringes are attached to the dislocation and indicate the planar defects discussed in the text. These end within the specimen (compare with dislocation)

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Fig. 3. Schematic of the spatial arrangement of dislocation and planar defects in the growth pyramid (see Fig. 2).

Fig. 4. Hard sphere model of the planar defect. Direction of view is parallel to a ridge towards the center of the pyramid.

Fig. 5. Model of a concave growth interface in the terrace growth mode. Scale perpendicular to the growth surface is exaggerated. The valley is generally very shallow (less than 1°).

Fig. 6. Photoetched cross-section of a Cz-grown Ge crystal. PMG: Direction of macroscopic growth. Delineated are: a zig-zag shaped valley trace and terrace traces (prominent ones are arrowed). Superimposed to this striation pattern are narrowly spaced striations that delineate the horizontal instantaneous growth interface.

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THE DISTRIBUTION OF METAPHOSPHATE ION. A NEW CRITICAL IMPURITY IN LiNbO₃ SINGLE CRYSTALS GROWN BY THE CZOCHRALSKI TECHNIQUE

K. RAKSÁNYI, Á. PéTER, ZS. SZALLER, I. FORIZS, S. ERDEI
Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences
Budapest 1502, p.b. 132, Hungary

Laboratory for Geochemical Research of the Hungarian Academy of Sciences
Budapest 1502, p.b. 132, Hungary

LiNbO₃ single crystals doped with metaphosphates were subjected to chemical analysis and studied by EPM. The distribution of P found in the crystal can be described by the NPM model. The results indicate that the metaphosphates belong to the "critical" impurities for this substance.

Introduction

The incorporation of impurities into LiNbO₃ with segregation coefficients near unity has been extensively studied because of their strong influence on optical properties. Far less is known about impurities having lower segregation coefficients and causing structural breakdown during growth. The strangely detrimental effect of Si and Al on the habitus and properties of LiNbO₃ crystals was studied by us previously [1, 2]. This work discusses the role of metaphosphate ions in producing similar growth defects and correlates the conditions of defect formation with growth parameters and material constants making effective use of the NPM theory discussed elsewhere [3]. Throughout the paper the nomenclature of [3] is used.

Method

Two single crystals were grown from congruent melt containing 10⁻³ mole/mole(Nb) metaphosphate ion. The first one was doped by adding lithium metaphosphate prepared by heating monolithium orthophosphate at 400 °C for 5 hours to the powder mixture to be sintered. Monolithium orthophosphate was obtained from the reaction of lithium carbonate and phosphoric acid in an aqueous solution by setting the pH at 4.1. For the second crystal we used monopotassium orthoophosphate as dopant. In both crystals the inhomogeneity regions appeared at the same positions. This led us to conclude that the dehydration of orthophosphates can be performed simultaneously with the sintering process. All but one reagent used were of MERCK a.gr. quality. The Nb₂O₅ was of STARCK suprapure quality.

The growth apparatus with automatic diameter control was described elsewhere [4]. The growth parameters were given in [1], corresponding to Re = 57, Sc = 519 and Pr = 5.5. The Gr(x)(Grashof) function of the growth apparatus was given in [3].

A longitudinal slice of 2 mm width was cut along the growth axis of the first crystal (the crystallographic z axis) as it is shown in Fig. 6. From the slice 24 slabs of 2 mm width were cut perpendicularly to the
growth axis, which along with a broader plate taken from the bottom region of the slice and the crucible residue served as samples for chemical analysis. For EPM measurements four plates of 2 mm width were cut from the slice (Fig.6). The measurements were performed by a JEOL Superprobe-733 type electron microprobe equipped with facilities for EDAX analysis.

For the determination of traces of phosphorous in LiNbO₃ we developed a new spectrophotometric method based on the phosphomolybdic blue reaction. The samples were fused in teflon bombs in a mixture of 5M HF/11.75M H₂SO₄. The bulk Nb was removed from the system by a twofold extraction with dibuthyl ketone from a 9M HF/6M H₂SO₄ solution. After the removal of excessive HF and H₂SO₄ by boiling the mixture in a Pt crucible to about 1ml final volume, the solution was diluted to 1M H₂SO₄ concentration and was heated for two hours to complete the conversion. The development of colour was performed according to the procedure of Riley [5], at 0.3M H₂SO₄ concentration. The absorbance measurements were performed by a Perkin-Elmer 254 type UV-VIS spectrophotometer. The linearity holds up to 500 μmole/mole and the detection limit amounted to 6 μmole/mole.

The radially averaged concentration distribution along the growth axis was calculated by the computerized version of the Neglect of Parallel Motion (NPM) method, i.e. by the "IMPUR" program package [3].
Results and discussion

The crystals doped with metaphosphate showed up extended inhomogeneous regions very similar to those found in crystals doped with silica and alumina[1,2]. In Fig. 6 a photograph taken of the longitudinal slice is presented. The inhomogeneity boundaries are well separated from the rest of the crystal. In the region lying between the boundaries contours can be observed the shape of which correlates well with the isoclinal surfaces calculated by the NPM method corresponding to elevated values of critical steepness (m). These regions mark off "latent" constitutional supercooling (CSC) effects and are extremely sensitive to the features of Grashof function.

As the EPM images show, the inhomogeneous regions contain a disperse, frequently difform phase, the particles of which are of 10-50 μm size, with shapes varying from circular (rare) through oblong to string-like very elongated ones extending over several hundred μms with bulb-like endings (frequent, Fig. 4). In the majority of cases the particles are made up of P and form a separate, probably lithium metaphosphate phase. (Fig. 2, P distribution image) Si was detected very frequently, typically on inner or outer surfaces, at extremities, cracks or outgrowths of the particles (Fig. 3, Si distribution image of the same particle as in Fig. 2). The minor components in the sequence of their occurrence are Si, K, Ca, Cl, Al and Pt (Fig. 4).

Curve 1 in Fig. 5 presents the $K_{\rightarrow \infty}(x)$ function as calculated by "IMPUR" [3] from analytical data. The rise of the function in the x<0.1 region is linked with imperfections brought about in the crystal during neck formation and with the related memory effects. In the region between 0.1<x<0.3 a solid solution type incorporation mechanism dominates. Between x=0.3 and x=0.5 "latent" CSC effects dominate, which have a bearing on the outgrowths seen in Fig. 6, contributing probably to the sharp rise of P content in this region. The uptake of P slows down however at x=0.45, due to a substantial decrease in the concentration layer width if Gr goes through the critical region (5.3>logGr>5.1, see shoulder on curve 1). The continuous increase of impurity concentration in the melt eventually leads to the onset of unstable growth. Later as the impurity concentration in the melt or above all in the interface layer becomes substantial, the conditions for the growth with crystal facets are fulfilled as e.g. in flux growth. This results in a $K_{\rightarrow \infty}$ pushed down towards the equilibrium value, instead of approaching unity.

Curves 2 shows the result of an attempt to adjust curve 1 to that calculated by the NPM method using our formula for $K_{\rightarrow \infty}$, varying the values of $m_0$ and Gr (ΔT=5). The value of $K_0$ was taken as 0. This corresponds to the lowest observed values of $K_{\rightarrow \infty}$ derived from concentration measurements under detection limit. Curve 3 adjusts the same parameters using the Burton-Prim-Slichter (BPS) formula for $K_{\rightarrow \infty}$ in regions with $m_0<m$, and our formula if $m_0>m$, i.e. in the case of "true" CSC. The results are as follows:

- Curve 2: $m_0 = 2.4$, Gr(ΔT=5) = 5.5
- Curve 3: $m_0 = 3.08$, Gr(ΔT=5) = 5.13

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It can be seen that curve 2 reproduces well the shoulder on curve 1, and the subsequent increase of slope correlates well with the observed inhomogeneity boundary. Curve 3 runs closer to curve 1, but sets the onset of full CSC at an earlier stage. This discrepancy between the two curves is due probably to the oblique outgrowths on Fig.6. This could be explained by higher values of $\phi$ at r values near $r_0$. This might occur at lower Re values, but exact solutions for this case are missing. The curves show that our formula is far superior to the BPS one. It reproduces well the convexity of the observed curve, the position of which agrees well with the onset of inhomogeneity regions and the shoulder at $x=0.4$ appears too. The agreement is far worse at elevated $x$ values, and in the case of curve 2 at the minimum of curve 1. This originates from the fact that our model overemphasizes latent supercooling effects and disregards the facet growth.

These results show that the primary act responsible for the appearance of inhomogeneous regions with a new disperse phase is the elevated rate of impurity incorporation if the conditions for the onset of unstable growth are fulfilled. The increased concentration of impurity exceeds its solubility at a given temperature, and an exsolution takes place. Here the principal impurity may act as a collector for a defined set of other impurities present probably already in the basic material.

References

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ELECTROOPTIC INVESTIGATION OF LiNbO$_3$ MONOCRYSTALS

Cs. KUTI$^1$, J.L. PRESMANES$^2$ and K. POLGÁR$^3$

$^1$Department of Experimental Physics, Institute of Physics, Technical University of Budapest
1521 Budapest, Hungary

$^2$Department of Physics, Faculty of Electronics, Havana Technical University
Havana, Cuba

$^3$Laboratory for Crystal Physics of the HAS
1112 Budapest, Hungary

Electrooptic test of different aperture light modulators constructed with optic axis cut LiNbO$_3$ crystals has been performed. The experimental results are discussed considering applications and developments.

Introduction

LiNbO$_3$ has an exceptional combination of properties that are useful for electrooptic devices. Its large electrooptic coefficients make it very suitable for electrooptic modulation. LiNbO$_3$ is currently regarded as the primary material of choice for the fabrication of integrated optic waveguide modulators of low voltage. Preliminary results obtained in the electrooptic investigation of optical quality LiNbO$_3$ monocrystals recently grown at the Laboratory of Crystal Physics of HAS are reported.

Preparation of the LiNbO$_3$ crystal samples

LiNbO$_3$ single crystals were grown by a balance controlled Czochralski method from melt [1]. Raw materials were Starck specpure Nb$_2$O$_5$, Merck suprapure Li$_2$CO$_3$, reacted in solid phase. The pulling rate was 2 mm/h and rotation rate 12 rpm.

Rectangularly shaped Z-cut samples (of size $l_x \times l_y \times l_z$) sliced out of the X-ray oriented monocrystals were polished optically flat for light propagation along the optic axis. The Y-faces of the samples were electroded. Copper-plate electrodes slightly pressed to the crystal were used.

Measurement of the modulator parameters

Electrooptic investigations were completed on intensity modulators consisting of the LiNbO$_3$ samples placed between crossed polarizers (Fig. 1). Some samples were measured with parallel polarizers as well. The half wave voltages ($V_{1/2}$) obtained by measurement (practical value) are compared with the calculated ones (theoretical value) as shown in Table I. The contrast ratios obtained with crossed (unbiased) and parallel (biased) polarizers are listed as well. The measurements were performed with a collimated beam of 1 mm diameter of the He-Ne laser (0.63 $\mu$m) crossing the modulator crystals is the middle of the aperture except the investigation of the crystal № 1 where the laser beam was focussed into the modulator crystal because of its small electrode distance ($l_y$).
Table I
Modulator parameters

<table>
<thead>
<tr>
<th>Cryst. dimensions [mm]</th>
<th>Half wave voltage [V]</th>
<th>Contrast ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theoretical</td>
<td>practical</td>
</tr>
<tr>
<td>1</td>
<td>2.15</td>
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<tr>
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<td>2.00</td>
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<tr>
<td>3</td>
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<td>4.07</td>
</tr>
<tr>
<td>4</td>
<td>16.3</td>
<td>16.1</td>
</tr>
</tbody>
</table>

Remarks on applications and developments

The fairly good agreement between the calculated and measured value of half wave voltages can be considered as an evidence of the proper electrooptic behaviour of the LiNbO₃ crystals investigated.

The relatively large uncertainty of the half wave voltage of the modulator No. 2 constructed for range-finder applications in surface-surveying [2] is due to the zero-bias and hysteresis observed in the transmission-voltage characteristics. Inspite of this behaviour an appropriate analog modulation of the He-Ne laser beam was observed in the ten MHz frequency range.

The relatively low voltage of modulator No. 1 which was devoted by H.L. Presmanes to construct a short distance atmospheric link for digital data transmission, seems to be acceptable considering the capabilities of high speed electronics.

The contrast ratio of large aperture modulators No. 3 and 4 promises good full aperture contrast required for Q-switches of solid-state lasers. Application and development is in preparation.

References

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MICROSCOPIC OBSERVATIONS OF AS-GROWN DEFECTS IN LITHIUM NIOBATE SINGLE CRYSTALS

L. MALICKÓ
Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences
1502 Budapest, P.O.Box 132, Hungary

The microdefects connected with the visual imperfections of lithium niobate single crystals grown by the Czochralski technique were studied by using different optical and electron microscopical methods including electron beam microanalysis.

Introduction

Because of their excellent ferroelectric and optical behaviours lithium niobate (LiNbO₃; LN) single crystals are used in several fields of the microelectronics and laser technics [1]. The practical applications have required the intensive study of the as-grown quality of the crystals. The visually observable quality deteriorations of LN single crystals are yellow or reddish-brown colourations and random occurrences of opaque clouds, cracks and cavities [1,2]. They are thought to be caused by impurities and the constitutional supercooling connected with them [1,3,6].

The aim of the present paper is to study the connection between the visual deteriorations of LN crystals and the microdefects causing them.

Experimental

For the investigations colourless (CL), yellow (Y) and reddish-brown (RB) single crystals grown in <001> direction by the Czochralski technique in our laboratory [7] were used. Axial and cross sectional plates cut from the crystals and polished, furthermore cleavage plates were used for the macrooptical (MO) and optical microscopic (OM) investigations. Several plates were also etched in HP:H₂SO₄=1:1 mixed solutions at 100 °C. From perfectly transparent and more or less opaque regions of the plates samples were prepared for the scanning electron microscopic (SEM) and the energy dispersive X-ray spectrometric (EDX) investigations. Chosen regions were subsequently prepared by mechanical and chemical thinning into samples for the transmission electron microscopic (TEM) studies.

Results and discussion

According to the MO and OM investigations on the axial and cross section plates, the opaque clouds mainly appear in the mantle and the lower regions both of the colourless and the coloured LN crystals. These regions, though they seem to be transparent, can contain single defects and optical inhomogeneities caused by compositional changes, as shown in Fig.1.
The more or less opaque regions of crystals densely contain single defects. By the aid of OM and SEM three types of defects could be recognized and distinguished in agreement with the earlier observations [8]: spherical and elongated cavities, microcracks often forming three-fold symmetrical systems, and solid inclusions shaping often whiskers or dendrites (Fig. 2).

By EDS analyses carried out in the SEM, in the transparent regions of CL, Y and RB samples the matrix element Hb could only be detected in general. But in the opaque regions both of the colourless and the coloured crystals, and at the single defects mentioned above, the peaks of impurity elements also appear in the EDS spectra. They are listed in Table I. The highest peak intensities, that means, concentrations of impurity elements were registered at microdefects and their close surroundings. This fact directly verifies that the impurities found may be responsible for the formation of the microscopic defects and the opaque clouds. With the darkening of the colour of the crystals as well the number as the average peak intensities of the impurities increase. Consequently, these impurities can be assumed to contribute to the colourations of LN crystals beside the oxygen deficiencies [1,9].

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Table I
Elements and their occurrences (+), detected in CL, Y and RB crystals by EDS in the SEM

<table>
<thead>
<tr>
<th>Elements</th>
<th>Colour</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CL</td>
</tr>
<tr>
<td>Nb</td>
<td>+</td>
</tr>
<tr>
<td>Pt</td>
<td>+</td>
</tr>
<tr>
<td>Mg</td>
<td>+</td>
</tr>
<tr>
<td>Al</td>
<td>+</td>
</tr>
<tr>
<td>Si</td>
<td>+</td>
</tr>
<tr>
<td>K</td>
<td>+</td>
</tr>
<tr>
<td>Cl</td>
<td>+</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
</tr>
</tbody>
</table>

By etching the samples one can obtain a review about the dislocation distributions and densities in the different crystal regions, as demonstrated in Fig. 3. In the mantle regions, in particular at the growth ridges, a few tenth mm thick "skin" is observable in which the etch pit density is high (appr. \(10^5\) cm\(^{-2}\)) in comparison to that in the central areas (appr. \(10^3\) cm\(^{-2}\)). But, in the central parts small areas of high etch pit densities, sometimes around recognizable solid inclusions, also appear. In the opaque regions the etch pit densities were generally found to be higher than those in the transparent regions of the same crystals.

According to the TEM diffraction contrast investigations for the transparent regions both of the Cl and the Y crystals the presence of single defects possibly revealed also by etch pits is characteristic (Fig. 4a). For the opaque regions and RB crystals the local grouping of different lattice defects, as shown in Fig. 4b, seems to be typical e.g. the grouping of twins mentioned already in [10] rather than the presence of single defects. The grouping points to interactions among the defects of different types [11].

Summarizing it can be established as follows. For the growth of LN single crystals the impurities found may be the "dangerous" ones. Namely, they can accumulate at the growing front surfaces. Their distributions and incorporations probably contributing to the as-grown colourations of crystals are non-uniform along the actual front surfaces. It results then in the in-
Fig. 4. High-Voltage TEM micrographs showing:

- a single dislocation segment (S) sitting in an etch pit (EP), and
- a group of lattice defects, such as a grain boundary (G), planar defects (P), single dislocations (S and S₁), trapping a ferroelectric domain segment (D).

Homogeneous distribution of the grown-in microscopic and lattice defects randomly forming the opaque regions.

The author thanks the Direction of IFE der AdW der DDR (Halle) for enabling the SEM and HVEM investigations, furthermore Dr. Th. Krajewski, Mr. A. Hunold, Mrs. S. Kovács and Mrs. M. Kiss for their valuable help. This work was supported by the State Office for Technical Development (OMFB) and the Academic Research Foundation (AKA) in Hungary.

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CHARACTERIZATION OF LiNbO₃ CRYSTALS RESISTANT TO LASER DAMAGE

L. KOVÁCS, I. FÖLDVÁRI, K. POLGÁR
Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences, 1502 Budapest, POB 132, Hungary

Optical damage resistant LiNbO₃ crystals were grown from melts of different compositions doped with magnesium. The AC conductivity of the crystals was measured in the temperature range 600-750 K and compared to that of the pure or slightly doped samples. The high activation energy and the low value of the conductivity together with a narrow OH infrared absorption band peaking near 3540 cm⁻¹ can be interpreted as the formation of Mg-OH complexes in lithium niobate crystals heavily doped with magnesium.

Introduction
Laser applications of LiNbO₃ are limited by the photorefractive effect (optical damage). Recently a dramatic damage reduction was observed in crystals heavily doped by Mg [1], the reduction appearing above a threshold Mg level depending on the Li/Nb ratio [2]. Mg-doped crystals have been characterized by various methods [2,3].

In the present work a series of Mg-doped LiNbO₃ crystals grown from melts of different compositions were investigated by the AC conductivity method. IR and UV spectrophotometry were also used to monitor the OH⁻ vibrations and the UV absorption edge of the same crystals.

Experimental
Lithium niobate crystals were grown in air by a balance controlled Czochralski technique [4] along the hexagonal C-axis and subsequently poled applying an electric field.

Various melt compositions Li/Nb = 0.945 - 1.2 and dopant (Mg) concentrations 1-5.4 mol % were used.

The sample platelets were cut from identical parts of the middle region of the crystal boules, perpendicularly to the growth axis, paying attention to the distribution of Mg along the pulling axis [5]. 1 mm thick samples were used for electrical conductivity and UV measurements while 5 mm thick ones were cut from adjacent parts of the same boule for IR investigations. A Perkin-Elmer 554 UV-VIS and a Jasco DS-702G IR spectrophotometer and an R-571 alternate current bridge at 1 kHz frequency were used.

Results and discussion
According to Bryan et al [1], damage resistant LiNbO₃ crystals can be distinguished by monitoring the IR stretching vibration of OH⁻ ions: in these
crystals the absorption band appears at 2.83 μm in contrast to the well-known 2.87 μm line found in other crystals. Fig. 1 shows the OH band of our pure and Mg-doped crystals.

Fig. 1. Infrared absorption bands of OH vibrations in LiNbO₃

Instead of a broad band peaking at ~3485 cm⁻¹ (2.869 μm) in a congruent LiNbO₃, a damage resistant crystal has a narrow peak at ~3540 cm⁻¹ (2.825 μm) with a small shoulder near 3530 cm⁻¹. The details of the band profile will be discussed elsewhere [6]. The transition between the two OH bands occurs sharply above a threshold concentration of magnesium depending on the Li/Nb ratio of the melt (e.g. in crystals grown from the melt with Li/Nb = 1.1 and 3 mol % Mg practically only the 3485 cm⁻¹ band is present, while in crystals with Li/Nb = 1.1 and 3.5 mol % Mg only the 3540 cm⁻¹ band is found).

Fig. 2 shows the temperature dependence of the electrical conductivity of several magnesium doped LiNbO₃ crystals. In the temperature range between 340-470 °C the logarithm of the conductivity was found to be a linear function of the reciprocal temperature. The activation energies determined using the Arrhenius equation and the values of the conductivity measured at 400 °C are listed in Table I. Increasing the Mg concentration in the crystals with a given Li/Nb ratio the activation energy seems to increase. However, the activation energy of the damage resistant crystals is apparently higher than that of the other crystals even if their Mg concentration is definitely not the highest.

In LiNbO₃ and KTaO₃ crystals treated in water vapour at elevated temperatures the value of the electrical conductivity showed a linear dependence on the OH⁻ ion content of the crystals measured by infrared spectroscopy [7,8]. In both cases the concentration of OH⁻ ions was taken in terms of
Fig. 2. Temperature dependence of the electrical conductivity of LiNbO₃ crystals. --- Li/Nb = 1.1 + 2% Mg,
  Li/Nb = 1.1 + 3.5% Mg, . . .
  Li/Nb = 0.945 + 5.4% Mg

Fig. 3. Dependence of the conductivity on the OH⁻ ion content.
  O O O OH band at 3485 cm⁻¹
  . . . OH band at 3540 cm⁻¹

Table I. Electrical conductivity and UV absorption parameters

<table>
<thead>
<tr>
<th>Li/Nb ratio in the melt</th>
<th>Mg concentration [mol %]</th>
<th>Activation energy [eV]</th>
<th>$\sigma$ at 400 °C [10⁻⁶ Ω⁻¹ m⁻¹]</th>
<th>Absorption edge at $\alpha = 20$ cm⁻¹ [nm]</th>
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<tr>
<td>0.945</td>
<td>-</td>
<td>1.16±0.02</td>
<td>3.0</td>
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<td>1.10</td>
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<td>3.5 X</td>
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<td>1.1</td>
<td>306.8</td>
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</tr>
<tr>
<td>4 X</td>
<td>1.30</td>
<td>1.1</td>
<td>307.2</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>1.32</td>
<td>1.1</td>
<td></td>
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</tr>
</tbody>
</table>

Damage resistant crystals, x x x A detailed study can be found in [9]

xxx Variably varies strongly along the growth axis

the absorption coefficient $\alpha$. Since the width of the OH bands of the Mg-
doped LiNbO₃ was rather different we used the integrated absorption to

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evaluate the OH⁻ ion content of the samples as described in [9]. In our "as-grown" crystals (without any heat treatment) we found the values of the electrical conductivity measured at 400 °C to depend linearly on the integrated absorption (Fig.3). In spite of the fact that the measured points are fairly scattered the straight line fitted using the least square method almost passes through the origin. In two cases, however, the damage resistant LiNbO₃ crystals showed a much lower value of conductivity than expected from the OH⁻ ion content. This deviation cannot be explained by the inaccuracy of the measurements.

The UV absorption edge of LiNbO₃ depends on the stoichiometry and the Mg concentration [10]. The increase of the Li/Nb ratio as well as the Mg content up to a critical level shifts the absorption edge to shorter wavelengths [9]. Both effects can be observed cumulatively e.g. in the crystals with Li/Nb = 1.1 + 3.5% Mg (Table I). In the case of crystals grown from melt with Li/Nb = 1.1 the absorption edge seems to be shifted towards longer wavelengths above 3.5% Mg similarly to the crystals grown from congruent melts, where the critical Mg concentration is ~4.5% [9]. This phenomenon was assumed to be caused by the appearance of some kind of Mg aggregation [9].

### Conclusion

In addition to previous results listed in [2,3], we found the electrical conductivity to be sensitive to make a distinction between laser damage resistant and other LiNbO₃ crystals (relatively high activation energy of the damage resistant crystal). The low value of the conductivity measured at 400 °C and the narrow OH absorption band peaking near 3540 cm⁻¹ is interpreted as the formation of Mg-OH complexes in heavily Mg-doped LiNbO₃. At high concentrations of Mg some kind of aggregates may also be present.

IR measurements were performed by the authors at the Physics Department of the University of Parma. Special thanks for that are due to Prof. R. Capelletti. This work was supported by the State Office for Technical Development (OMFB) and the Academic Research Foundation (AKA) of Hungary.

### References

COMPLEX MICROSCOPIC INVESTIGATIONS ON THE AS-GROWN QUALITY OF BISMUTH GERMANATE SINGLE CRYSTALS

L. MALICSKÓ
Research Laboratory for Crystal Physics of the Hungarian Academy of Sciences
1502 Budapest, P.O.Box 132, Hungary

The microscopic defects causing the as-grown quality deteriorations in bismuth germanate single crystals grown by the Czochralski technique were investigated by using optical, scanning and transmission electron microscopic methods.

Introduction
Because of the advantageous intrinsic luminescence properties of the bismuth germanate (Bi\(_{4}\)Ge\(_{3}\)O\(_{12}\), BGO) single crystals, they are widely used as high energy photon detectors [1,2]. Yellow colourations and random occurrences of opaque clouds containing inclusions are mentioned as the most striking as-grown quality deteriorations of the Czochralski grown BGO crystals [3-6]. The colourations and the formations of inclusions, present in the cloudy regions of the crystals, can be caused by impurities and by changes in the host composition [4,6,7].

The aim of the present paper is to investigate systematically the reasons of the as-grown quality deteriorations of BGO single crystals by using different optical and electron microscopical methods including electron beam microanalysis as well.

Experimental
For the investigations colourless (CL) and yellow (Y) BGO single crystals grown in the \langle 100\rangle direction by the Czochralski technique in our laboratory [5,8], were used. From the crystals axial and cross section plates were cut and then mechanically polished for the macrooptical (MO) and optical microscopic (OM) investigations.

Typical, optically perfect and imperfect regions of the plates were then prepared by subsequent steps of polishing and mechanical and finally chemical thinning into samples for the study in a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) and finally in a transmission electron microscope (TEM) using selected area diffraction (SAD). By the aid of the EDS spectra and the SAD patterns different defects and defect-free areas were analysed and compared.
Results and discussion

Both in the CL and the Y crystals cylindrical (Fig. 1) or stripe-like (Fig. 2), more or less opaque clouds can randomly occur. In the cloudy crystal regions considerable stresses can be revealed, as shown in Fig 1b.

Fig. 1. Optical macrographs of the cross section of a BGO single crystal containing a cylindrical opaque cloud (the arrows) a - at unpolarized illumination, and b - between crossed nicols, showing a considerable stress field

Fig. 2. Optical dark field micrographs of a - spherical cavities arranged into stripes nearly perpendicular to the growth direction (arrow), and b - a stripe of cavities elongated nearly parallel to the growth direction

According to the OM and SEM observations the opaque clouds densely contain cavities and solid inclusions forming small platelets and whiskers, as demonstrated in Figs. 2-3. But single cavities and solid inclusions can occur in the transparent regions of crystals as well. The occurrence frequency of the solid inclusions was found to be the highest in the vicinity of cavities. These inclusions seem to be embedded with random orientations concerning the matrix, whereas the inclusions far away from any cavities are definitely oriented. It was generally found that with the darkening of the crystal colour the occurrence of the single cavities, solid inclusions and the opaque clouds becomes more frequent.

By the EDS microanalyses at the inclusions and cavities in the opaque regions of crystals the presence of the following impurity elements could be detected: Pt, Fe, Al, K, Si and Te. Among them the Al, Si and Te have taken place in the highest concentrations. But, almost everywhere in the cloudy regions the presence of Pt and Fe impurities could be indicated in-

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dependently of the colouration of crystals. Beside the impurity inclusions solid inclusions were also found at which considerable deviations in the Bi/Ge composition ratio could only be detected as compared to that of the stoichiometric matrix (Fig.4). Some Bi/Ge composition changes were also indicated in the surroundings of cavities.

Fig.3. Secondary electron image of small plate- and whisker-like solid inclusions (arrow) in the opaque region of a dark yellow BGO single crystal

Fig.4. Secondary electron images of small solid inclusions (arrow) (a, and b): the same area as in b, mapped by the BiM-line, showing only a smaller Bi content than that of the BGO matrix.

It should be mentioned that starting from the top parts towards the bottom parts of the BGO single crystals used, systematic decreases in the \( \text{Bi}_2\text{O}_3: \text{GeO}_2 \) ratios were found by macroscopic chemical analyses [9].

The conventional and high-voltage TEM observations fully verified the establishments made above concerning the distributions, the orientations and the arrangements of the solid inclusions and the cavities, as demonstrated in Fig.5. In the SAD patterns taken on crystal regions containing inclusions extra spots appear. In the SAD patterns from cavity-free areas the extra spots generally form definitely oriented spot systems related to the matrix one (Fig. 5c). Whereas, the SAD patterns from the close vicinity of cavities contain any amount of extra spots and rings (Fig.5b) and the concerning bright (or dark) field images show densely and randomly distributed and oriented foreign particles (Fig.5a). According to the fitting analyses of the SAD patterns the majority of the foreign extra spots could be assigned to the following foreign phases: \( \alpha- \) and \( \beta-\text{Bi}_2\text{O}_3, \text{Bi}_2\text{O}_3-x: \text{GeO}_2, \text{Bi}_{12}\text{GeO}_{20} \) and \( \text{Al}_2\text{O}_3 \). The question of inclusions from the oxyzdes of other metal impurities found is not cleared yet.

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Fig. 5. Bright field electron micrograph taken by a high-voltage TEM on a dark yellow crystal region containing solid inclusions randomly oriented in the surrounding of cavities (a). The concerning SAD pattern (b) shows foreign spots and rings. For comparison a SAD pattern from a cavity-free area at the same matrix orientation close to $\mathbf{B}=[133]$(c).

Summarizing, the present results demonstrate that for the as-grown quality deteriorations, especially the opacities, of the BGO single crystals complicated molecular processes taking place at the actual growth front, can be held responsible. These molecular processes belong to the macroscopic growth regime nearby or at the constitutional supercooling. They include, as seen, the material specific accumulation of interacting impurities and the inhomogeneous incorporation of the matrix and the foreign components, furthermore, the nucleation of foreign phases from the decomposed matrix components and the impurity elements found.

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THE GROWTH AND SOME PROPERTIES OF DOPED YALO₃ SINGLE CRYSTALS

B. PERNER, JIŘÍ KVAPIL, K. BLAŽEK, J. HORÁK, JOSEF KVAPIL and B. MÁNEK
Monokrystaly, 511 19 Turnov, ČSSR

The growth of perfect YAP crystals doped with Nd, Cr and Ce in resistance furnace, reductive conditions and high vacuum and Mo crucible are described. The growth conditions for decreasing decomposition of crystals, iron content and twinning are found. Distribution coefficients of dopants, some spectral and generation properties of the crystals were measured.

Introduction

YAP:Nd is a solid state laser material the properties of which seem to be similar to the widely used YAG: Nd. In practice YAP: Nd has shown lower performance than expected [1], which may be attributed to a detrimental role of Fe and OH ions. Fe content is 5–100 ppm in practically all crystals [2]. The main disadvantage of both Nd³⁺ doped yttrium aluminate is relatively low efficiency of radiation coupling from the pump source to the laser system, because of narrow absorption lines of Nd³⁺ [3, 4]. To increase the efficiency, one can utilize a second dopant, e.g. Cr³⁺, absorbing in broad bands in the visible region. Cr³⁺ → Nd³⁺ energy transfer in YAP [5], (on the contrary to YAG), seems to be only a little lower than in GSGG: Nd, Cr [6]. Cr was doped in the range of 0.05 – 0.1 at %. At higher Cr concentrations the crystals was of bad optical quality (second phase). As the lifetime of Cr³⁺ in YALO₃ is long, this dopant is potentially attractive for high-energy storage of Q-switch laser [7]. It was experimentally proved that b-oriented crystals are the best from the point of view of maximal gain and of growth properties too. The maximum of effectivity was reached for YAP: Nd, Cr in pulsed regime and it was 1.8 time higher than of YAG: Nd [8]. At present time only relatively small YAP: Nd rods (up to 75 mm in length) from the crystals grown in vacuum from Ir-crucibles are commercially available [9].

Experimental

YAP, YAP: Nd, YAP: Nd, Cr and YAP: Ce single crystals were grown by the Czochralski method employing resistance furnace and tungsten or molybdenum crucibles of the volume of 250–400 ml. The growth apparatus was described before [10].

The automatic weighing puller of own construction and analog controlling system was used. The sensitivity of the weighing cell is < 20 mg, maximum load 5 kg. Growth was performed under the mixture of Ar and He with H₂ (usually 2–10 vol %) or in vacuum. The pulling rate varied from 1.5 to 5 mm h⁻¹, rotation rate from 15 to 25 rpm. The temperature gradients measured by Ir-W thermocouple over the melt were: 0–3°C above the
melt: 7-10 °C/cm, 3-15 cm above the melt: 2-4 °C/cm. Analysis of stoichiometry of the melt and of dopants content in crystals and melt was made by X-ray spectrometer (Philips PW 1410/20). Trace analysis was made by NAA. Optical absorption between 200-1100 nm was taken on the polished plates, using Perkin-Elmer SP 500 spectrometer. Twinning was observed between crossed polaroids. Strain facets were detected by the polarized shadow projection. Laser characteristics were measured on the rods of 6 mm in diameter and 75 mm in length. The details of the measurements were described earlier [11,12].

Results and discussion

YAP melts at 1875 °C and it is thermodynamically unstable at 1835 °C. Decomposition to two other phases (Y2O3:Al2O3 - 3:5 and 2:1) takes place. This decomposition is starting on the structure defects on the crystal surface (stretches, intersections of dislocations with surface). Such decomposition sources may be deactivated by removing of the garnet phase - product of decomposition. It is possible by using of negatively charged afterheater (-25V) in an atmosphere rich in Ar (> 60 vol %) or by addition of 10^-2 vol% H2O to the growth atmosphere or by using of high vacuum (< 10^-3 Pa). The crystal has relatively smooth etched surface with limited and little areas of decomposition. The solid/liquid interface of YAP grown from non-stoichiometric melt with surplus of Y2O3 (Y:0,97Al:0,03) is very sharply conical in consequence of increasing of solidifying point of laminar layer.

In the case of Al2O3 surplus (Y:0,97Al:0,03) the interface is rather more blunt (decreasing of solidifying point). The core (facetted region) in the axial part of the b-oriented crystals is relatively small. The angle of conical interface and consequently the dimensions of facetted region is influenced also by the ratio of axial and radial temperature gradients in the melt and by rotation rate of crystal.

Twinning along (112) planes [13] or microtwinning along (110) planes [14] is often evident in YAlO3 crystals. Considerably higher twinning tendency is at c-oriented crystals. It is caused by the action of thermal gradients and by the anisotropy of thermal expansion coefficients. (Thermal expansion coefficients in a and c directions is 2 times higher than that in the b-direction [15]. The suppression of anomalous coloration which increases the temperature gradients in the crystal by suitable chemical conditions is the best way to decrease the twinning. It may be reached by the increasing of He:Ar ratio or H2O content in the protective atmosphere or by the growth in vacuum.

The effective distribution coefficients of all common dopants are relatively high and in consequence it enables the high rates of the growth (3-5 mm/h), without decreasing the optical quality of the crystals. We have measured these coefficients in our growth conditions with the following results: $K_{ef \text{Nd}} = 0.8$; $K_{ef \text{Cr}} = 1.1$; $K_{ef \text{Ge}} = 0.45$
There are some differences with other authors $K_{ef} ^{Nd} = 0.65 \ [14]$ and $K_{ef} ^{Cr} = 2.5 \ [7]$. Such a difference may be explained by a strongly reducing atmosphere used in our experiments which converts a substantial part of $Cr^{3+}$ to $Cr^{2+}$.

The crystals of good optical quality and free of Fe impurity ($<10^{-4}$ wt %) of 185 mm in length and of 35 mm in diameter were grown with 0.5-5 at % Nd and 5$ \times 10^{-4}$ - 1$ \times 10^{-1}$ at % Cr for laser measurement and with 0.5-1 wt % Ce for scintillation measurement.

The laser output of Nd-Cr doped YAP was, in the experiments, negatively influenced by the colour centre formation as is seen in Fig.1 and 2.

![Absorption of YAP: Nd, Cr (1 wt % Nd, 3$ \times 10^{-4}$ wt Cr) grown in Ar-H$_2$ atmosphere after an intense Xe-lamp flashing (without filter). The crystals were annealed before irradiation: 1 - in H$_2$, 2 - in O$_2$.](image1)

![Dependence of the pulsed output of 1 - YAG: Nd, 2 - YAG: Nd, Ce, Cr (1$ \times 10^{-2}$ wt % Ce, 3$ \times 10^{-2}$ wt % Cr), 4 - YAP: Nd, Cr (8$ \times 10^{-3}$ wt % Cr), and 5 - YAP: Nd, Ce, Cr (1$ \times 10^{-2}$ wt % Ce, 3$ \times 10^{-2}$ wt % Cr) on the shot number of pulsed laser. The crystal was annealed in H$_2$: 1, 2, 3a, 4, 5 (or O$_2$: 1, 3b). Input 100 J. Full line: the first application. Dashed line: following application.](image2)

The absorption in the range 280-500 nm is very high for crystals annealed in oxidizing conditions (curve 2, Fig.1). The crystal annealed in hydrogen (curve 1, Fig.1) is better but not perfect. This absorption eliminates partly the contribution of $Cr^{3+} \rightarrow Nd^{3+}$ energy transfer to the gain of the laser rod. In Fig.2, curve 5, one can see the influence of the formation of colour centre on the sharp drop of laser output after several first shots. It is obvious that before colour centre formation, the effectiveness of this YAP: Nd, Cr laser is 2.3 times higher than of YAG: Nd. The factors causing this undesirable colour centre formation are hitherto not known.
YAP:Ce grown in vacuum or reduction protective atmosphere gives a β -scintillator with outstanding properties:
- high luminescence efficiency for low energy β radiation;
- relative luminescence efficiency compared with plastic scintillator SPF 3 for 14C is 150 %;
- maximum emission: 370 nm;
- high chemical and mechanical stability.

Summary

The growth of perfect YAP single crystals 35 mm in diameter and 185 mm in length may be accomplished either using Ar-He-H₂ protective atmosphere with decreased Ar content or in high vacuum. The former enables one to grow the crystals doped with rare earth ions and chromium, the latter one enables the activation with rare earth ions only. The decomposition of the YAP phase may be effectively suppressed by the negatively charged electrode above the melt level or by controlling of water content in growth atmosphere. The twinning was suppressed by suitable chemical conditions which decrease the formation of growth colour centre. The higher distribution coefficients of important dopants (Nd, Cr) enable high growth rate and result in good concentration uniformity. It is shown that even if the colour centers are formed in YAP:Nd, Cr, this crystal is outstanding material especially for pulsed lasers and may be potentially better if the formation of colour centres would be decreased. YAP:Ce has high luminescence efficiency and is suitable detector for low energy electrons and β.

References

IR SPECTRA OF SOME RARE-EARTH IRON GALLIUM GARNETS

E. BEREGI and E. HILD
Research Institute for Telecommunications
1026 Budapest, Hungary

The infrared lattice spectra of over 20 various compositions of rare-earth iron gallium garnets have been recorded. All observed bands were assigned to the motion of the crystal lattice. The absorption band at ~480 cm⁻¹ can be assigned to the motion of octahedral polyhedron.

Introduction

N.T. McDevitt [1] showed that the frequency shift observed for the strongest absorption band in the 800-600 cm⁻¹ IR region of rare-earth Al, Ga and Fe garnets is directly associated with the unit-cell volume, and it was assigned to the motion of the oxygen anions bonded to the rare-earth cation.

This assignment was in disagreement with some data reported by Tartel [2] who assigned the high frequency band in YAG to the isolated AlO₄ tetrahedra. His interpretations were based on various compounds containing AlO₄ tetrahedra, these compounds, however, fall into a number of different space groups.

In our previous study of ScGaYG [3] the absorption band between 500-300 cm⁻¹ was assigned to the octahedral polyhedron because it seemed to be associated with the change in the concentration of the Sc ions preferring the octahedral sites.

The aim of this paper is to investigate how the gallium substitution influences the IR-spectra of the rare-earth iron garnets and to compare the experimental results with the observations reported by McDevitt and Tartel.

Experiments

The experiments were carried out on a large number of garnets R₃Fe₅₋ₓGaxO₁₂, where R = Lu, Yb, Er, Gd and Sm and 0 ≤ x ≤ 5.

The crystals were grown from high temperature flux, then they were chemically analysed and their lattice constants were determined by the X-ray powder method.

The crystal spheres of 0.8 mm diameter were dissolved in conc. H₃PO₄ at different temperatures between 100 and 330°C in order to determine the activation energies of the crystals.

The IR spectra of the crystals were recorded on a Perkin-Elmer 580
spectrophotometer at room temperature in the 800-300 cm\(^{-1}\) region from powder samples using the KBr pellets technique. Also reflection spectra of Y\(_3\)Fe\(_{5-2}\)Ga\(_2\)O\(_{12}\) crystals were recorded.

**Results and discussion**

**Lattice constant and activation energy**

The lattice constant increases with increasing diameter of the dodecahedral ion and also with increasing of Fe substitution in RGG.

The activation energy, however, decreased with increasing diameter of the dodecahedral ion and was smaller for the iron garnets. /Fig.1/.

![Graph showing activation energy (E) and lattice constant (a) versus diameter of the dodecahedral ion (D).]

**IR measurement**

Each spectrum consists of a set of two separate groups of bands (Fig. 2, 3, 4). The strongest band of the group was denoted by "A" and "B", respectively.

According to Tart [2] the wavenumber range of the "A" band corresponds to the range characteristic of the vibrations of the isolated tetrahedra and that of the "B" band to that of the isolated octahedra. The high intensity of both bands and the sharp transmittance maxima following both of them indicate that the bands correspond to fundamental lattice vibration modes which are accompanied by large dipole momentum changes.

The wavenumber of both bands decreases with increasing lattice constant (Fig. 5) but the slope is steeper for Ga-Fe substitution.

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than in the case when the lattice constant change was caused by replacing the dodecahedral ion.

At ~480 cm\(^{-1}\) there is a band characteristic of all rare-earth garnets which contain Ga at the octahedral sites \((z>3)\). The intensity of this band continuously increases with increasing Ga concentration (Fig. 2, 3, 4).

The rare-earth substitution influences the wavenumber of the "A" band stronger than that of the "B" band (Fig. 5).
Conclusions

The fact that the wavenumber of both the "A" and "B" bands is influenced more strongly by the Ga → Fe substitution than by the rare-earth ion substitution shows that those bands are more closely related to the vibrations of the tetrahedra and octahedra than to the vibrations of the dodecahedra.

Fig. 5. Variation of the wavenumber of the "A" and "B" bands versus lattice constant for different R-Fe-Ga-garnets. R = Yb, Y, Gd and Sm. The Ga content decreases from left to the right the dodecahedra.

The band characteristic of the Ga ion occupying an octahedral site and the earlier observed splitting in the "B" band [3] due to Sc-ions substituted in the octahedra, suggest the following: the "B" band might correspond to a vibration which involves the motion of the octahedral ion relatively to the surrounding oxygen. However, the tetrahedral ions move simultaneously with the oxygen ions connected to them.

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Sc-ION DISTRIBUTION AND DISSOLUTION FORMS OF ScGaYIG SINGLE CRYSTALS

E. BEREGI¹, E. HILD¹, E. HARTMANN² and J. LÁBÁR³

¹Research Institute for Telecommunications
H-1026 Budapest, Hungary
²Research Laboratory for Crystal Physics
H-1112 Budapest, Hungary
³Research Institute for Technical Physics
H-1047 Budapest, Hungary

Single crystal spheres of $\text{Y}_3\text{Fe}_{4.2-x}\text{Ga}_x\text{Sc}_x\text{O}_{12}$, where $0 \leq x \leq 1.45$, have been dissolved in acids and measured by Mössbauer and IR methods. It was observed that Sc-ions prefer the octahedral sites, and on dissolution in $\text{H}_3\text{PO}_4$ the combination of $\{720\}_D$ and $\{111\}_D$ faces changed into the combination of faces $\{310\}_D$ and $\{hhl\}_D$ with increasing Sc concentration. These changes were accompanied by alteration in the bands of IR spectra at 470 cm⁻¹ and 400 cm⁻¹.

Introduction

In the substituted yttrium iron garnet with general formula $\text{Y}_3\text{Fe}_{5-x-y}\text{Ga}_x\text{Sc}_y\text{O}_{12}$, the large yttrium cations occupy dodecahedral sites, the gallium cations can enter into both the tetrahedral and the octahedral sites, depending on their concentration, and Sc ions show an exclusive preference for octahedral sites [1, 2].

The aim of this paper is to investigate the dissolution forms of ScGaYIG single crystal spheres and to assign the results to Sc distribution using the data of Mössbauer and IR measurements.

Experiments

The experiments were carried out on single crystal spheres of $\text{Y}_3\text{Fe}_{4.2-x}\text{Sc}_x\text{O}_{12}$, where $x=0, 0.4, 0.7, 1.1$ and 1.45. The crystals were grown from high temperature solutions in the temperature range $1200$ to $1000^\circ\text{C}$ with a cooling rate of $0.5$ to $1^\circ\text{C}$.

The single crystals were chemically analysed and their lattice constants were determined by X-ray powder method. Energy dispersive X-ray spectra were measured to check the variation of the ratio of the metal components from sample to sample.

The Mössbauer spectra were measured in order to study the site preferences.

IR spectra of crystals were measured to obtain information about changes caused by increasing Sc concentration. For the IR measurement the KBr pellet technique was used and the spectra were recorded by a Perkin...
Elmer 580 spectrophotometer at room temperature.

Single crystal spheres of 0.8 mm diameter were dissolved either in concentrated $\text{H}_3\text{PO}_4$ at 150°C or in azeotropic HBr at 126°C. The dissolution forms were investigated by scanning electron microscope of type ISM-35. An optical goniometer was used for indexing the crystal faces. The preparation of spheres and the dissolution technique were the same as in [3].

**Results**

**Mössbauer measurement**

The Mössbauer spectra of ScGaYIG consisted of two doublets (Fig. 1a,b). The doublet of higher line separation belongs to iron ions in d-sites, Fe (d), and the doublet of lower line separation can be assigned to ions of a-sites, Fe (a) (see Table I). From the intensity ratio of the doublets the Sc(d)/Sc(a) can be obtained. It is known that Ga at the concentration of 0.8 formula unit enters into the tetrahedral sites [2]. So, it can be seen, according to the results of Mössbauer measurements that the Sc ions occupy octahedral sites.

![Mössbauer spectra](image)

**Fig. 1a.** Mössbauer spectra of $\text{Y}_3\text{Ga}_{0.8}\text{Fe}_{4.2-x}\text{Sc}_x\text{O}_{12}$ at temperature of liquid $\text{N}_2$, $x=0.4$, 0.7 and 1.1

**Fig. 1b.** Mössbauer spectra of $\text{Y}_3\text{Ga}_{0.8}\text{Fe}_{4.2-x}\text{Sc}_x\text{O}_{12}$ at room temperature, $x=0.4$, 0.7 and 1.1

**IR measurement**

In Fig 2, the spectra consist of two separate groups of bands. With increasing Sc concentration, the bands between 550 and 700 cm$^{-1}$ are nearly unchanged, the forms and the positions of bands are quite constant. At the same time the bands between 300 an 500 cm$^{-1}$ change. For $x=0.4$ "shoulders" appear at 470 cm$^{-1}$ and at 400 cm$^{-1}$ which develop for $x=0.7$, 1.1 and 1.45 into a new peak. With increasing Sc concentration the peak
at 470 cm\(^{-1}\) moves slightly to higher frequencies.

Reflection spectra of single crystals showed similar behaviour [4].

The group of bands at 700-550 cm\(^{-1}\) is believed to belong to the vibrations of the tetrahedra (d) and some of the lower-wave number bands, between 300 and 500 cm\(^{-1}\), to those of the octahedra (a). As Sc substitution happened into the octahedra, as now proved by the Mössbauer measurements, the distortion of the 410 cm\(^{-1}\) band ought to correspond to the alteration of the octahedra by the Sc substitution.

Dissolution of ScGaYIG in H\(_3\)PO\(_4\) at 150° C

After a few hours of dissolution \(\{111\}_D\) octahedron faces and \(\{720\}_D\) tetrakishexahedron faces appeared in Sc substitution range \(0 \leq x \leq 0.7\).

Dissolution of ScGaYIG in HBr

On the dissolution of ScGaYIG spheres in HBr both \(\{111\}_D\) and \(\{100\}_D\) faces were formed, (Fig. 4), for the crystals with \(0 \leq x \leq 1.1\). However, at the Sc concentration \(x=1.45\) this combination was reduced to \(\{111\}_D\). The surface of the crystals were rough and built up from terraces of (110) faces.

Measurement results concerning the lattice constants, a total Sc concentration, the ratio Fe(d)/Fe(a) calculated from Mössbauer measurement and the dissolution forms are collected in Table I.

It was observed that Sc-ions prefer the octahedral sites, and the Mössbauer measurements were supported by the IR measurements.

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Fig. 3. Triakisoctahedron \{553\}_D face on the dissolution form of ScGaYIG in H$_3$PO$_4$, x=1.1. Dissolution time: 5 h. Temperature: 150°C.

Table I

<table>
<thead>
<tr>
<th>X</th>
<th>Lattice const (nm)</th>
<th>Fe(d)/Fe(a)</th>
<th>Dissolution forms in H$_3$PO$_4$</th>
<th>Dissolution forms in HBr</th>
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<tr>
<td>0.00</td>
<td>1.2362</td>
<td>2.4/1.9</td>
<td>{720}_D + {111}_D</td>
<td>{100}_D + {111}_D</td>
</tr>
<tr>
<td>0.40</td>
<td>1.2386</td>
<td>2.4/1.4</td>
<td>{720}_D + {111}_D</td>
<td>{100}_D + {111}_D</td>
</tr>
<tr>
<td>0.70</td>
<td>1.2400</td>
<td>2.3/1.1</td>
<td>{720}_D + {111}_D</td>
<td>{100}_D + {111}_D</td>
</tr>
<tr>
<td>1.10</td>
<td>1.2413</td>
<td>2.4/0.6</td>
<td>{310}_D + {220}_D</td>
<td>{111}_D</td>
</tr>
<tr>
<td>1.45</td>
<td>1.2456</td>
<td>-</td>
<td>{553}_D + {221}_D</td>
<td>{111}_D</td>
</tr>
</tbody>
</table>

The substitution of iron in a-sites by scandium alters the dissolution forms of garnets. Intermediate dissolution forms of triakisoctahedron, \{553\}_D and \{221\}_D appeared instead of octahedron \{111\}_D with increasing of Sc concentration in a-sites.

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PECULIARITIES IN SHAPE OF FeBO₃ SINGLE CRYSTALS IN THE Fe₂O₃-B₂O₃-PbO-PbF₂ SYSTEM GROWN FROM THE FLUX

G.A. PETRAKOVSKII, V.V. RUDENKO, V.M. SOSNIN and G.N. STEPANOV

Institute of Physics
Krasnoyarsk 660036, USSR

The conditions of formation of FeBO₃ single crystals in the Fe₂O₃-B₂O₃-PbO-PbF₂ system are investigated. The solubility of FeBO₃ in the solvent 53.3B₂O₃-32.7PbO-14.0PbF₂ is 7.2 wt% at 854 °C which is the upper maximum temperature of the phase stability of FeBO₃. When measuring the growth rates V of FeBO₃ single crystal faces for that composition, upon melt supercooling ΔT indicates that V increases linearly along the [111] direction upon ΔT, while the dependence V upon ΔT in the plane (111) exhibits considerable nonlinearity. The growth rate of radial FeBO₃ single crystals in the (111) plane is 1.5 × 10⁻³ cm/h and in the plane along the [111] direction it is 4.10⁻⁴ cm/h on supercooling at 5 °C in dynamic conditions. The nature of the growth rate distribution of FeBO₃ single crystal faces upon ΔT suggests that massive specimens may be grown when supercooling at 3-7 °C. FeBO₃ crystals are grown by the temperature regime calculated on the basis of experimental data in controlled conditions. The dimensions of FeBO₃ crystals are 5x5x1.5 mm³; the linewidth of antiferromagnetic resonance absorption is 30-50 Oe.

1. Introduction

The compound FeBO₃ is antiferromagnetic with weak ferromagnetism having an unusual combination of magnetic and optical properties. In particular, FeBO₃ is transparent in a visible spectrum area and its Néel temperature is higher than room temperature. Such combinations of properties are of quite definite scientific interest and advantage in relation to the possible use of this material in practice [1-3].

The realization of the possibilities of this material is essentially determined by some success in synthesizing reasonably large and qualitative crystals. In particular, in order to utilize FeBO₃ in equipment, functional electronics systems are often necessary to grow massive crystals with a narrow linewidth of antiferromagnetic resonance absorption (AFMR).

The first instance of FeBO₃ single bulky crystals being synthesized was reported in ref. [4]. The authors of this paper obtained single crystals of 8x6x4 mm³ by vapour growth. However, the measurements show that the AFMR linewidth of FeBO₃ single crystals synthesized by this method is several times wider than that of specimens obtained by the flux technology.

Technological works connected with FeBO₃ single crystal growth by the flux method have been described in the literature by a number of authors [5-9]. The authors [5-7,9] utilized the law of linear temperature decrease in the region of ferric borate growth and therefore crystals were obtained in the form of thin (111) plates. In addition, in these works, the crystallization was realized at separate technological stages in conditions far from equilibrium that often led to a polyphase crystalline product and a melt flux. In [7] it is shown that it is impossible to achieve monophase crystalline product and a melt flux only by fulfilling the wellknown obligatory condition of choosing the corresponding composition in the phase diagram. Melt stirring is necessary to achieve the system at a state near to equilibrium and to obtain monophase crystalline and liquid products. This supplementary condition was realized in [8] where, besides using the law of nonlinear temperature decrease the authors obtained single large crystals with the dimensions 7x5x3.5 mm³ at the platinum stirrer, however the limited experimental data do not allow one to understand the causes leading to this result nor to reproduce the technology.

The investigations carried out here aim to elucidate the optimal, reproducible controlled conditions of FeBO₃ massive crystal growth with narrow line AFMR. For this purpose we use the solution composition selected by the authors of ref. [6] which is optimal from the viewpoint of crystal quality and differs from [8].

2. Experimental details

The solubility of FeBO₃ is investigated in the temperature region 740-860 °C in the fol-
Following way. The original special grade materials Fe$_2$O$_3$, B$_2$O$_3$, PbO, PbF$_2$ were weighed out to give compositions of 7.2 or 7.9 wt%. FeBO$_3$ of the pseudodouble system FeBO$_3$-(53.3B$_2$O$_3$-32.7PbO-14.0PbF$_2$) and were melted in a 50 cm$^3$ platinum crucible at 850-900 °C. The crucible was loaded into a furnace in which the temperature was increased to 1000 °C and complete charge solution was achieved. Then there was a rapid cooling to 800 °C and the crucible was kept at this temperature for one hour. After this the eventual experimental temperature $T_s$ was reached, which was maintained for 4 hours. At $T_s<800$ °C, intermediate exposure was not conducted at 800 °C. Such an intermediate exposure at 800 °C for $T_s>800$ °C was utilized for withdrawal of the system from the metastable condition. At the exposure the melt was stirred at 800 °C, 1000 °C, 1000 °C and $T_s$. The stirrer rotation rate is 60 revolutions/min. After exposure at $T_s$ the crucible was extracted from the furnace and tempered in air. The crystalline phases were separated from the hardened melt in a hot 20 % aqueous solution of nitric acid and were subjected to X-ray and gravimetric analyses. In the temperature range of 740-754 °C the crystalline product as well as the melt was monophase.

The calculation of FeBO$_3$ equilibrium concentration necessary for melt saturation at $T_s$ was made by taking into account the weight of the initial components and that of obtained product. The composition analytical grade Fe$_2$O$_3$-22.50, special grade B$_2$O$_3$-232.43, special grade PbO-136.57, special grade PbF$_2$-58.50 g was used to determine the growth rates of FeBO$_3$ single crystals faces, the parameters defined a crystal shape, and a number of nucleation centres. The reagent was melted into a 225 cm$^3$ platinum crucible. After full dissolution of the original materials at 1000 °C, the temperature was rapidly lowered and necessary supercooling $\Delta T$ of a melt was applied, based on the data of FeBO$_3$ solubility. At a definite $\Delta T$ the melt was allowed to stay for 24 h with continuous mixing. Crystallization was retarded only at the stirrer (of platinum), mainly because of the negative temperature gradient on the crucible axis in the growth zone which was -1.1 °C/cm. After exposing at definite $\Delta T$ the stirrer was removed and the experimental results were analysed. The number of centres of nucleation $N$ was calculated, and the diameter $d$ in the (111) crystal plane and the thickness along [111] direction $L$ were measured. Then an average parameter was constructed in all centres $\delta=(L/d)_\text{average}$ defining the shape of the average statistical crystal. The growth rates of faces were defined by utilizing the largest crystal grown at the stirrer. It was considered that the largest crystal was that which remained for 24 hours at a definite $\Delta T$. Since the number of centres arising at the stirrer is large, this is a good approach.

The estimation shows that the mass of precipitated crystals is relatively small and the saturation temperature $T_s$ practically does not change during the experimental procedure. In view of the fact that there is only a small amount of loss due to evaporation the same melt could be utilized repeatedly.

The measuring of the antiferromagnetic resonance absorption linewidth was made at temperatures of 100-200 and 300 K at frequencies 25 and 18 GHz, respectively.

3. Results and discussion

The curves of FeBO$_3$ solubility in the solvent 53.3B$_2$O$_3$-32.7PbO-14.0PbF$_2$ are given in Fig. 1 [10]. The solubility of FeBO$_3$ at the upper temperature limit (854 °C) of its phase stability fields is 7.2 wt%. At higher temperature and concentration of FeBO$_3$ both FeBO$_3$ and Fe$_3$BO$_6$ occur in the solvent.

The dependence of the FeBO$_3$ single crystals growth rates $V$ in the (111) plane and along direction [111] upon the supercooling of a melt $\Delta T$ are given in Fig. 2. It is seen from the figure that $V$ increased linearly on $\Delta T$ along the [111] direction, while in the (111) plane this dependence is considerably nonlinear. The radial growth velocity of FeBO$_3$ crystals in the (111) plane is $1.5\times10^{-3}$ cm/h, that in the [111] direction is $4.10^{-4}$ cm/h at the supercooling of 5 °C in the dynamic regime. The form of distribution of the growth rates of FeBO$_3$ faces on $\Delta T$ leads to the fact that massive samples can be grown at the supercooling of 3-7 °C.

This can clearly be seen from Fig. 3, which shows the dependence of the $\delta$ parameter defining the crystalline shape, and the number of crystallization centres $N$ arising at the stirrer, on the melt supercooling $\Delta T$. It is also seen from the Figure that $N$ sharply increases when supercooling below 7 °C.

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4. Synthesis of FeBO\textsubscript{3} single crystals

The charge for growing FeBO\textsubscript{3} crystals consists of (in grams): analytical grade Fe\textsubscript{2}O\textsubscript{3} - 22.50; special grade B\textsubscript{2}O\textsubscript{3} - 232.43; special grade PbO - 136.57; special grade PbF\textsubscript{2} - 58.50. The charge is melted separately in the 225 cm\textsuperscript{3} platinum crucible. The crucible is then placed in an electroresistance furnace and is kept at 1000 °C for 5 h with melt stirring. After this, temperature is quickly lowered and the supercooling of 6-10 °C about the saturation temperature T\textsubscript{s}=854 °C is maintained (the T\textsubscript{s} may deviate from other charge). At the given \Delta T the melt is stirred for 24 h. The reflector of platinum foil located above the stirrer blades considerably diminishes the number of crystallization centres N' at a given \Delta T. After 24 h the stirrer is removed from the melt, and the number of crystallization centres is counted in order to estimate \delta. From the data on \delta and Fig. 3, the real \Delta T and T\textsubscript{s} are estimated. If the number of centres N' is more than 20 or less than 10, then their dissolution is carried out at 1000 °C and another supercooling is set. This procedure is continued till the arising number of crystallization centres is within the limits 10 \leq N' \leq 20. In our experiments we find T\textsubscript{s}=852 °C and the necessary \Delta T=6 °C, here 13 nuclei with \delta=0.3 arise at the stirrer. After that the nuclei are dissolved at 1000 °C and the found supercooling \Delta T=6 °C is set again. At T=846 °C (\Delta T=6 °C) the system stays for 24 h with stirring the melt then the temperature is quickly increased to 849 °C (\Delta T=3 °C). At the last supercooling nucleation becomes less possible. Then the temperature decreases in the regime defined by the formula [11]

\[ T_t = T_s - \Delta T - \frac{m(1-C_o)G_1}{G_0 - G_1}, \]

where T\textsubscript{t} is the current temperature, T\textsubscript{s} is the saturation point 852 °C, \Delta T is the melt supercooling 3 °C, which we try to maintain as constant during the synthesis process. However, it is not an optimal variant. Because of the absence of additional experimental data we cannot vary it in time.

**m=\Delta T/\Delta C**, tangent of inclination of the solubility curve, 2.7.10\textsuperscript{3}.

**C** - FeBO\textsubscript{3} concentration at zero time, 0.072

**G\textsubscript{0}** - initial weight of melt, 450 g

**G\textsubscript{1}** - \textit{m}N\textsuperscript{\textsubscript{g}}V\textsubscript{111}V\textsubscript{111} - weight of solid phase, precipitating during the synthesis process, for disc-form crystals, \textit{g=4.28 g/cm\textsuperscript{3}}, N=10, V\textsubscript{111}=1.3.10\textsuperscript{-3} cm/h, 2V\textsubscript{111}=8.10\textsuperscript{-4} cm/h, t is the time (in hours) counting from the moment of T\textsubscript{s}=849 °C (\Delta T=3 °C) set. The number of nuclei arising after keeping at 846 °C (\Delta T=6 °C) is neglected here, and further one may consider in calculation that G\textsubscript{1} \ll G\textsubscript{0}.
Fig. 2. Dependence of FeBO$_3$ single crystal growth rates in the (111) plane and along the [111] direction on the supercooling $\Delta T$ of a melt.

Fig. 3. Dependence of $\delta$ parameter (defining crystal shape) $\delta = \frac{L}{d}$ average (L is the size of the crystal along the [111] direction, d is its diameter in the (111) plane and number of crystallization centres N appearing at a stirrer on supercooling of a melt $\Delta T$.

So the final expression for $T_t$ is

$$T_t = 849 - 1.6 \times 10^{-6} \cdot t^3 \, ^\circ C.$$  

In this regime the temperature decreases to 830 $^\circ$C. As the result of synthesis, 20-30 crystals are formed on the stirrer with a maximum size of 5x5x1.5 mm$^3$.

The AFMR linewidth is 30-50 Oe at room temperature at a frequency of 18 GHz. Notice that the quality of thin crystals, as a rule, is higher. The linewidth of single specimens is 4 Oe at temperatures of 100-200 K at a frequency of 25 GHz.

5. Conclusion

The performed investigations show the way to modify the shape of FeBO$_3$ crystals and to obtain massive specimens with a narrow linewidth of AFMR. The temperature regime given in this article was for trial purposes and will be modified as a result of new experimental data such as the temperature dependence of the $\delta$ parameter, the effective diffusion of the crystallized matter and the viscosity of the melt.

References


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Disturbing piezoelectric transients caused by impulse driving in KDP Pockels-cell electrooptical light modulators are reduced by orientation, shaping and sizing methods based on crystal-acoustic considerations.

Introduction

The piezoelectric influence of acoustic transients on the transmission of electrooptical light modulators limits their applications in light shutter operation [1]. Different methods - such as mechanical clamping, acoustic impedance-matched embedding, bias of the electrodes etc. - were developed earlier to reduce the piezoelectric disturbances. A new, simple, crystal-acoustic method based on an analysis of acoustic wave generation and propagation has been developed to get more effective suppression of the piezoelectric influences.

Reduction of the acoustic wave generation by orientation of the modulator crystal

The basic idea is to decrease the generation of the acoustic waves [2]. The sources of piezoelectrically induced sound are on the free faces of the modulator crystals. The analytical investigation has been made to obtain the optimum orientations characterized by weak acoustic wave generation on the faces of the modulator crystal.

According to the analysis performed on Z-cut KDP longitudinal modulator crystals 45°Z-cut used in longitudinal modulator arrangement seems to be optimum characterized by suppressed source distribution of acoustic waves. Generation of compression plane waves with moderate amplitudes is expected on the lateral faces oriented normal to the bisectors of the crystallographic XY-plane. The amplitude of the compression waves in 45°Z-cut sample is estimated to be about one 7th of that of the shear plane waves generated in conventionally used 0°Z-cut at the same driving voltage. The solution is plausible: by exchanging the 0°Z-cut modulator crystal by 45°Z-cut one a significant reduction of the piezoeptic influences can be expected.

Comparison of pulse response of KDP Z-cut modulator crystals

Experimental check of the calculations is performed by measurement of the pulse response of intensity modulators constructed with different Z-cut
modulator crystals. The pulse response is measured in the experimental arrangement shown by Fig. 1. The modulator crystals (KDP) placed between crossed polarizers (P, A) are driven by pulses of 12.4 kV amplitude and 500 ns halfwidth. The 1 mm diameter beam of the He-Ne laser crosses the modulator crystal in the middle of the aperture and incides into the photomultiplier (PM) across the interference filter (IF). The signal of the photomultiplier (PM), and the monitor of the high voltage pulse are displayed by the two channel oscilloscope (OSC). The 1st peak on the lower trace of the oscillogram represents the direct electrooptic opening of the modulators. The peaks following the electrooptic opening are induced by the piezooptic effect of the acoustic waves. In the case of $0^\circ Z$-cut modulator crystal - the oscillogram shown by Fig. 1 is taken with KDP $0^\circ Z$-cut - the first of the piezooptic openings is caused by the acoustic waves arrived at the laser beam directly from the lateral faces where they are generated. The following peaks on the pulse response are piezooptic openings caused by acoustic waves reflected repetitively.

The comparison of the pulse response of identically sized - 20 mm x 20 mm aperture and 25 mm long - $0^\circ Z$- and $45^\circ Z$-cut modulator crystals demonstrates a significant reduction of the piezooptic influences by substitution of the $0^\circ Z$-cut sample with the $45^\circ Z$-cut one, as it can be seen on Fig. 2. To illustrate the reduction by use of a cylindrical $Z$-cut KDP modulator crystal reported in [3] the pulse response of 11.6 mm diameter and 21.6 mm length KDP crystal is also demonstrated. Starting with Fig. 2 the time scale of the oscillograms is $1 \mu s/\text{div}$.

The reduction of the piezooptic influences obtained by $45^\circ Z$-cuts is considerable, more efficient that the one obtained by cylindrical-cut, but it is less than was expected according to the calculations. By careful inspection of the pulse response oscillogram of the $45^\circ Z$-cut modulator three piezooptic opening peaks can be distinguished. Considering the low sensitivity of the measurements performed on KDP crystals the experiments are re-
peated with ADP samples characterized by very strong piezoelectric properties to obtain better resolution, as it is shown by Fig.3.

Identification of the acoustic waves in 45°Z-cut crystals

Separation of the acoustic waves is possible on the basis of their travelling time - i.e. the time that acoustic waves need to reach the middle of the aperture. The 2nd peak on the pulse response of both 0°Z-cut and 45°Z-

Fig.2. Pulse response of KDP Z-cut modulator crystals

Fig.3. Pulse response of ADP Z-cut modulator crystals

Fig.4. Separation of the near-edge waves

cut ADP modulators are caused by the piezooptic effect of the plane acoustic waves described by the one dimension wave equations used for the analysis.

The actual problem emerges by the appearance of the 3rd and the 4th peaks in the pulse response of the modulator constructed with 45°Z-cut. Scanning

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the aperture of the modulator by the laser beam the peaks proved not to be the effect of plane waves. The peaks must be due to the piezooptic effect of acoustic waves generated in the edge-region of the lateral faces.

The acoustic waves generated in the edge-region of the 45°Z-cut modulator crystals can be identified on the basis of their travelling time compared to those calculated by the path and group velocity:
- the acoustic waves causing the 4th peak are pure transverse waves generated in a very narrow region of the lateral edges of the 45°Z samples,
- the acoustic waves inducing the 3rd strong piezooptic opening are generated in the near-edge regions of the lateral faces.

**Separation of the piezooptic influence of the edge waves**

According to the empirical model for the generation of the edge waves favourable distribution of the relatively strong piezooptic effect of the "near-edge waves" is possible. The pulse response – demonstrated by Fig.4 – of the ADP modulator constructed with a 15 mm x 25 mm rectangle aperture 45°Z-cut shows the splitting of the 3rd peak into two separated peaks of significantly smaller amplitude than observed with the square aperture 45°Z-cut crystal.

The total reduction including the orientation step and the separation of the near-edge waves exceeds one order of magnitude without substantial alteration of the processing technology of the modulator crystals.

By change of the rectangle aperture into rhomboid one further, more than half an order of magnitude reduction can be obtained. It results from the separation of the direct-edge waves and the additional distribution of the near-edge waves.

**Summary**

The 45°Z lateral faces of samples made of KDP type crystals are characterized with reduced acoustic wave generation as compared with 0°Z and cylindrical Z samples used conventionally to construct electrooptic Q-switches for control of high power, solid-state lasers. The relatively strong piezooptic influence caused by acoustic waves generated in the edge region of 45°Z-cut modulator crystals can be decreased by distribution of the effect of the edge waves based on shaping, sizing and additional orientation of the modulator crystals. By careful combination of the individual steps a reduction between one and two orders of magnitude can be obtained without essential change of the processing technology of the Q-switch modulators.

**References**


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GROWTH OF SINGLE-CRYSTALLINE SILICON FILMS ON INSULATING SUBSTRATES

W. SCHARFF and K. HOEPPNER
Technische Hochschule Karl-Marx-Stadt, Sektion Physik/Elektronische Bauelemente
9010 Karl-Marx-Stadt, GDR

The growth of device-worthy silicon crystal films on insulating substrates would offer a new type of semiconductor technology. The crystallization of continuous silicon layers on thermally oxidized silicon wafers was performed by a zone melting process. A number of material characterization techniques have been used to analyse the SOI-structures.

Introduction

The growth of single-crystalline silicon films or islands on insulating substrates (SOI-TECHNOLOGY) offers new interesting possibilities for the further development of electronic and optoelectronic devices. The incentive is to realize new concepts of micro- and optoelectronic devices such as high speed and high density integrated circuits, high voltage devices, optoelectronic memory devices and special sensors. In current research a large number of variants have emerged as promising techniques for obtaining oriented silicon films with perfect single crystalline regions on non-crystalline insulating substrates [1,2]. Here the results of material characterization of SOI-structures recrystallized by a movable light strip heater are presented. The fabrication and recrystallization of SOI-films were performed in co-operation with "VEB ZFTM Dresden", "Zfk Rossendorf der AdW der DDR" and "IHP Frankfurt/O der AdW der DDR".

Experimental procedure

For our recrystallization experiments polycrystalline silicon films deposited on thermally grown silicon dioxide and encapsulated with a combination of SiO₂ and Si₃N₄ layer were recrystallized by zone melting using the focused light of a rod like halogen lamp in an elliptical Al-mirror. The thermally insulated samples were preheated up to about 1500 K using a set of halogen lamps [3].

For TEM studies of recrystallized thin Si-islands the samples were evaporated with a thin film of carbon and subsequently immersed into a HF solution to separate them from the underlying substrate. The continuous recrystallized Si-films were directly immersed into a HF solution.

Results

Our results of optical and electron microscopy investigations are very similar to the one described by Vu et al [4].

After resolidification, 3 zones are clearly discernible:

(i): a narrow zone with statistical orientated Si-crystallites (this region has not been melted), (ii): a narrow transition region or "seed-region" with <100> texture (this zone has been partially melted). Giben that Si-crystallites with (100) planes parallel to the cap and substrate oxide have the lowest surface-energy contribution to their total energy, grains with <100> texture should dominate. Also, <100> textured crystallites, isolated by partial...
melting, will have a slightly higher melting temperature. (iii): a large zone with mono-
crystalline grains of several mm width by several cm in length with well-defined crystallo-
graphic orientations; the <001> axis is parallel to the surface normal and the <100> axis is
parallel to the scan direction (Fig. 1).

Fig. 1. TEM-micrograph of a recrystallized Si-film

Figs. 2a,b. TEM-micrograph of a secondary subgrain boundary from type 2 and schematic
illustration of the dislocation character

Within the large grains subgrain boundaries are observed. The subgrain boundaries have a
characteristic structure ("feather structure" - Fig. 1). They separate crystallites with a
0.5 up to 2 degree difference in orientation.

Three typical kinds of subgrain boundaries can be observed in a recrystallized layer:
(i): The primary subgrain boundaries are parallel to the <100> scan direction and separate
2 subgrains. The diffraction patterns taken on each side of the subgrain boundary have a
displacement of the Kikuchi lines indicating a tilting from 0.5 up to 2.5°. (ii): The se-
condary subgrain boundaries from type 1 (SSB 1) originated at the primary subgrain boundaries
are parallel to them and ending after a distance from several ten \( \mu m \) up to several hundred
\( \mu m \) in the subgrain [5,6]. (iii): The secondary subgrain boundaries from type 2 (SSB2) ori-
ginate along a primary subgrain boundary and are parallel to the <100> direction. They are
limited by a length of 10 \( \mu m \) up to 50 \( \mu m \) and consist of dislocations with poor edge
character. They are ending in the subgrain in form of dislocations (Fig. 2).
In continuous silicon films produced by the zone melting process the position of low-angle grain boundaries usually cannot be controlled. However, large area SOI-crystals will not always be necessary for circuits with high packing density, sensors and other microelectronic devices. The essential thing is how to fabricate SOI-crystals of excellent quality at desired positions. For entrainment of the subgrain boundaries it is necessary to control the position of the facet intersections [7]. Silicon films with grain boundary free areas can be produced by the recrystallization of long Si-stripes (Fig. 3). The critical width for

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a defect free stripe amounts to about 100 \( \mu m \). To describe the recrystallization process of continuous Si-films and long Si-strips on insulating substrates a simple mathematical model is given by Andrä [8]. The numerical calculation of the one- and two dimensional temperature profile is carried out by a difference method [8,9]. Fig. 4 shows the schematic illustration of the temperature distribution in the Si-stripes during the recrystallization process. For the fabrication of several types of microelectronic SOI-device applications (bipolar-devices, high voltage devices) it is necessary to use a several \( \mu m \) thick Si-layer on an insulating substrate.

In our experiments polycrystalline Si films 0.5 \( \mu m \) thick, deposited on 1 \( \mu m \) thick \( \text{SiO}_2 \) layers on Si-substrates were recrystallized by using a movable halogen lamp strip. Epitaxial layers about 2.4 \( \mu m \) thick were grown by CVD on the recrystallized Si-films. The epilayers grown on smooth recrystallized SOI-structures have distinct linear surface features (Fig. 5). These features are located above the subgrain boundaries in the recrystallized film.

Depending on the kind and the type of the grain boundary these features have typical dislocation network structure [5]. Optoelectronic sensor devices and memory devices have been successfully produced on the basis of this technology.

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INDIUM-SILICON CO-DOPING EFFECTS IN LEC - GROWN GALLIUM ARSENIDE CRYSTALS

V. RAKOVICS¹, R. FORNARI, C. PAORICI, L. ZANOTTI² and C. MUCCHINO³

¹Research Institute for Technical Physics of the HAS
1325 Budapest, Hungary

²MASPEC CNR
Parma, Italy

³Enichem Sintesi
Milan, Italy

In this paper we report the simultaneous (Si-In) doping in LEC grown GaAs crystals. The experimental results have shown that the double doping with Si (below 8x10¹⁷ electr./cm²) and In (around 4x10¹⁹/cm in the melt) makes it possible to grow GaAs ingots fully single and with a remarkable tendency to lower the etch-pits density down to about 5x10²-5x10³/cm² in large portions of the crystals.

Introduction

One of the main problems limiting the development of LEC gallium arsenide technology is still represented by dislocations. Their relatively high density is due to various causes, whose effects overlap according to mechanisms which are not yet fully understood.

The experimental approaches for reducing the dislocation density are based: i, on the stoichiometry control, in an attempt to control (and hence reduce) the nucleation sources via control of point defects and their coalescence; ii, on reducing the thermal stress by appropriate thermal field adjustment during growth; iii, on suitable doping effects [1-6] which were observed either to increase the critical resolved shear stress or to reduce nucleation source density.

At the present stage of the heavy-doping procedures, some features need be clarified, among which we can consider whether i, n-type GaAs can be grown dislocation-free in the 1x10¹⁶-1x10¹⁸/cm³ free carrier concentration and ii, dopant-concentrations can be minimized (while still keeping dislocation density low) so that morphological instabilities can be reduced. Along these lines, the object of the present work was the study of the Si-In co-doping in LEC grown GaAs, in order to ascertain the possibility to grow n-type material with low dislocation density and low (1x10¹⁶-1x10¹⁸/cm³) free carrier concentration. In the same time, due to the simultaneous presence of silicon, dislocation reductions were expected to occur at lower indium concentrations, which would in turn have led to a reduction of morphological instability and possibility to the growth of entirely single-crystals ingots.

The authors report here on the results obtained with Si-In co-doped, In-doped, Si-doped and undoped crystals grown under the same growth conditions.

Experimental

The gallium arsenide crystals have been pulled from the melt by LEC procedure, making use of a ADL furnace (HPCZ model) in line with a temperature-ramp generating microprocessor for diameter control. The grown ingots (400-500 g in weight) were pulled through a 10 mm thick dry (H₂O content: 250 ppm ca) B₂O₃ layer (supplier: J. Mattey), counter pressured by...
nitrogen at 4-5 atm. Pulling rate, crucible and crystal counter rotations were, respectively: 12 mm/hr, 5 r.p.m. and 2 r.p.m. The pulling orientation was in any case (100) and use was always made of undoped seeds with EDP in the order of $1E4/cm^2$. Particular care was taken to start pulling the crystals from stoichiometric melts, whatever the content of dopants. As for the thermal conditions the thermal gradient in $B_2O_3$ layer was measured to be 115 °C/cm. In no case thermal shields and afterheater were used. The crystals grown under the above conditions and investigated in the present work are reported in Table I. The electrical characteristics (free-carrier density, mobility and resistivity) have been obtained by Hall measurements, with ohmic contacts made of Au-Ge (17:83) alloy. The EDP has been obtained by KOH etching, by keeping the samples for 7 minutes in molten KOH at about 400 °C. The In and Si concentrations in the crystal ingots have been detected by atomic absorption measurements in samples previously dissolved in acidic media.

Table I

<table>
<thead>
<tr>
<th>Samples</th>
<th>Dopants cm$^{-3}$</th>
<th>EPD cm$^{-2}$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In (melt)</td>
<td>Si (melt)</td>
<td>Si (crystals)*</td>
</tr>
<tr>
<td>33</td>
<td>-</td>
<td>-</td>
<td>10.000-30.000</td>
</tr>
<tr>
<td>ADL/7</td>
<td>4 $10^{19}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>93</td>
<td>1.5x10$^2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>-</td>
<td>6 x10$^{18}$</td>
<td>2- 5x10$^{17}$</td>
</tr>
<tr>
<td>LPA/4</td>
<td>-</td>
<td>1.5x10$^{19}$</td>
<td>1- 3x10$^{18}$</td>
</tr>
<tr>
<td>41</td>
<td>-</td>
<td>5 x10$^{19}$</td>
<td>2- 5x10$^{18}$</td>
</tr>
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<td>3 x10$^{18}$</td>
<td>1- 7x10$^{17}$</td>
</tr>
<tr>
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<td>6 x10$^{18}$</td>
<td>4-10x10$^{17}$</td>
</tr>
<tr>
<td>ADL/8</td>
<td>5 x10$^{19}$</td>
<td>1.2x10$^{19}$</td>
<td>2-25x10$^{18}$</td>
</tr>
</tbody>
</table>

*Axial free-carrier concentration  **Wafer core region

Results

Table I gives the average values of EDP, as they were measured in the central part of a wafer, and the corresponding dopant concentrations. The obtainement of twinned or single crystal per run is also indicated.

A typical In-concentration in In-doped crystals, as well as one of Si-concentration in Si-doped crystals are given in Fig. 1 for various locations in the crystals. From these data and taking into account Pfann’s relationship, [6] one gets for In and Si dopants the chemical distribution coefficients in GaAs for LEC process, (KLEC). We obtained KLEC values of 0.120-0.010 and 0.100-0.010 for In and Si respectively. One should here notice that the distribution coefficient of Si turns out to be greater than the electrical constant $Kn$(=0.035 see [3]) due to the amphoteric behaviour of Si impurities in GaAs. As reported by Fujii et al [7], the simultaneous presence of Si does not appreciably affect the value of the In distribution coefficient.

The main electrical characteristics for Si-In co-doped crystals are given in Fig. 2 and are compared with the same characteristics for In-doped and Si-doped crystals. It can be seen that the co-doping effects lowers the electron mobility.

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Fig. 1. In (■) and Si (△) concentration axial distribution in conventional single doped LEC crystal, as measured by AAS.

Fig. 2. Axial variation of carrier concentrations, resistivity and electron mobility in crystal with different doping, (see Table I) ■ = ADL5 ▲ = ADL7 • = ADL8 X = 24.
Comments and conclusions

If reference is made to LEC In-doped crystals, no dislocation reduction (with respect to udoped crystals) can be observed for In concentrations lower than $5 \times 10^{19}$ atoms/cm$^3$ in the melt. In the case of Si-doped crystals dislocation reduction is effective only for Si-concentrations in the $1 \times 10^{18}$ electrons/cm$^3$ (in the solid).

When Si-In co-doping is performed dislocation reductions (1000 EPD/cm$^2$) are observed down to Si and In concentrations of $1 \times 10^{17}$ electrons/cm$^3$ and about $1 \times 10^{18}$ atoms/cm$^3$ (in the solid), respectively. For these concentrations, entirely single crystals could be pulled.

As a prospect, it is expected that the EPD can be further decreased (even in larger size crystals) by reducing the thermal gradient while keeping the above Si and In concentration. A complete picture of co-doping performances needs further investigations, on the microdefects which can possibly be induced by the simultaneous presence of In and Si.

References

FERROELECTRIC OXIDES AND RELATED SUBSTANCES: GROWTH AND STUDY OF SINGLE CRYSTALS

Yu.N. VENETSEV
Karpov Institute of Physical Chemistry
Moscow, 107120, USSR

Known varieties of ferroelectrics have been characterized and their possible applications considered in particular as single crystals. Some materials-science aspects of the ferroelectric problem have been treated. Results of a search for ferroelectric oxides, including some results on growing and studying their single crystals, are described. Perspectives of further search and applications of ferroelectric organic and inorganic substances including ferroelectric metal oxides are discussed.

Introduction

Ferroelectrics (FE's) are electrical analogs of ferromagnets (see e.g. [1-4]). FE, piezo-, pyroelectrics and other related materials can fulfill many functions of semiconductors and ferrites. At the same time, the application of FE and related substances is more preferable in some cases. Now hydrolocation, optoelectronics, acoustoelectronics, microelectronics, robotics and other fields of technology are unthinkable without FE and other related materials. Promising applications are related to the joint use of FE’s, semiconductors, ferrites and other materials for the creation of new effective equipment.

FE's and antiferroelectrics (FE’s) were discovered many years ago [1-4]. At present some related substances are well known (ferroelastics [1, pp.23-24; 2, pp.92-94], FE’s-semiconductors [5], seignemagnets [6,7], FE’s-superconductors [1, pp.197-200; 8], FE’s-superionic conductors [9], FE’s-catalysts (for example, Bi₂WO₆ [1, c.244; 10] and layer structures of FE-Pt-catalyst type [11] and other related substances). The above-mentioned substances have valuable properties (dielectric, piezoelectric, pyroelectric, electro-optic, nonlinear-optic and others) for different applications. Due to this they have acquired considerable practical significance (see, e.g.[12,13]).

In the 65 years since the discovery of ferroelectricity, almost 800 FE and related substances have been found [14] of which more than 2/3 are metal oxides. However, science and technology interests dictate the necessity of a further search and creation of new similar substances.

Unfortunately many well known FE and related oxides have been synthesized and studied only as ceramics (or as powders). This hampered the investigation of their properties and the selection of new materials among them those with promising applications. Therefore an important task is the growth of single crystals (at the first stages even small ones), which are suitable for more detailed study and evaluation of their perspectives in practice.

The author with co-workers has been carrying out systematic investigations of FE and related substances for a long time, with the main aim of studying the nature of FE properties of metal oxides, and attempting to find and create new FE and related oxides. One of the results of these investigations is the finding of more than 280 similar oxides (see, e.g.[1,6,13-20]) which are included in the above-mentioned total number (800) of well-known FE and related substances. Moreover, considerable work has been done on growing and studying single crystals of these oxides [1,6,13-20].

This review contains some information about the properties and possible applications of well-known varieties of ferroelectrics and some of the results of the above-mentioned work. Finally this paper draws attention to the growing and studying of FE oxides of the most numerous FE families, many representatives of which have been synthesized and studied only as ceramic samples.

Ferroelectric varieties and their applications

Ferroelectrics and antiferroelectrics are described in many monographs, reviews and origi-
ginal papers (see, for instance, [1-4] and references therein). A real revolution in the investigation of FE's and in an extension of their applications was the discovery of the first oxide ferroelectric-barium titanate [13, pp.5-7], which became a progenitor of the group giving rise to the most numerous "oxygenoctahedron" ferroelectrics [14].

At present FE's and antiFE's of the barium titanate family are the most important and have the widest application as ceramics and films. Every year hundreds of milliards of capacitors and milliards of piezoelectric, pyroelectric and FE-semiconductor elements are produced throughout the world mostly from these FE's and antiFE's.

At the same time single crystals of FE oxides are used for manufacturing piezoelectric, pyroelectric, electro-optic and nonlinear optic elements and working bodies for holographic recording of information [12].

Ferroelectrics-semiconductors represent another FE variety of considerable scientific and technical significance [5,12,21,22]. These types of substances have also been studied for a long time and are already used quite widely as single crystals (SbSI and others) [21] and as ceramics mainly on a barium titanate base with semiconductor properties [22]. Such ceramics are highly suitable for producing pizzlyors and varystors [5,12,22].

Photoferroelectrics are another promising FE group. Some doped FE crystals (for example, LiNbO$_3$:Fe) are utilized as working bodies for recording and storing optical information [12,13].

Seignetomagnetics (SM's) are FE's with magnetic ordering. In the case of seignetomagnets, FE (or antiFE) properties can coexist with ferromagnetic (or antiferromagnetic) ones in a certain temperature interval [6,7]. This allows one to use SM's to create multifunctional radio-technical elements.

But the most important peculiarity of SM's is the interaction between their magnetic and dielectric properties. Due to this by applying an electric field to SM's it is possible to change their magnetic parameters and vice versa. This opens novel fields for SM applications.

At present, almost 70 SM compounds are known (most of them are metal oxides), and some SM solid solutions and composites are synthesized and studied [6,7,12]. Despite these achievements there still remains the very important task of searching and creating new SM's and growing SM single crystals.

Ferroelectrics-superionic conductors are substances with FE properties in a certain temperature interval above which these properties disappear and superionic conductivity appears. This variety of FE was found recently and the number of known representatives of this variety is comparatively small [25,26]. Superionic conductivity is manifested as a rule in one of the crystallographic directions and therefore the synthesis of single crystals of these substances is very desirable both for investigations and applications.

Ferroelastics differ from FE's in their transition parameter. In the case of FE's the transition parameter is a spontaneous polarization, whereas in the case of ferroelastics the transition parameter is a spontaneous deformation. Ferroelastics are investigated very intensively and their possible applications, chiefly as single crystals, are assessed. In the case of ferroelastics it is possible to control distances between domain boundaries with external mechanical stress and to create a number of effective instruments on this basis (see, e.g., [1, pp.23-24; 2, p.92-94]). Incidentally, a remarkable number of related compounds are known; these are classified as FE's-ferroelectrics.

Ferroelectrics-superconductors. It was found long ago that doped ferroelectric SrTiO$_3$ below T=0.3 K displays superconductive properties [27]. Superconductive properties were also found in solid solutions of the BaBiO$_3$-BaPbO$_3$ system and the maximum temperature of transition into the superconductive state appeared to be relatively high (almost 12 K) for metal oxides [28]. Complex studies of crystal structures and properties of single crystals and ceramic samples of these solid solutions were carried out [8]. They also showed the existence of a spontaneously-polarized state (SPS) in the solid solutions investigated. The data on SrTiO$_3$ and the solid solutions allowed us to conclude that the same metal oxide can have both FE and

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superconductive properties at least in different temperature intervals. Moreover it was concluded that the presence of SPS in a metal oxide favours its transition to a superconductor state. These results stimulate the further search for new superconductors (especially with high $T_c$) among FE and antiFE metal oxides with a high electric conductivity.

Ferroelectrics-catalysts. These FE's are the last to be considered in this paper. As is known $\text{Bi}_2\text{WO}_6$ oxide is FE with a Curie temperature of $T_c=935$ °C (see, e.g. [1,pp.244]). At the same time this oxide demonstrates catalytic properties in some chemical processes [10]. It is also known that $\text{BaTiO}_3$, $\text{SrTiO}_3$ and $\text{KTaO}_3$ are both FE's [13,14] and stable photoanodes (photolysis is possible without an external electrical field), see review [11]. At the same time these photoanodes have high efficiency (up to 20% for ultraviolet light in specially reduced $\text{SrTiO}_3$). A general disadvantage of these oxides is a wide forbidden zone ($\Delta E>3$ eV). Therefore they are sensitive merely to ultraviolet light and not suitable for transforming sunny light.

FE's can also effectively be used in catalysis in the case of the acretion of layer structures of the FE's-Pf-catalyst type [29]. Thus photocatalytic activity was studied on $\text{TiO}_2$ thin films deposited on the Pt intermediate conductive layer, which in its turn was deposited on a ferroelectric substrate of $\text{LiNbO}_3$ single crystals. Increased photocatalytic activity was observed with a maximum in the activity at the negative polarization of the surface of FE substrate. Some results on the growth and studying of single crystals of ferroelectrics and related oxides in connection with the continuously increasing and extending demands of techniques and the necessity for further studying the nature of ferroelectricity, the search and synthesis of new FE's continues to be a very important problem. In particular it is necessary to extend the working temperature interval of materials, to create cheaper and simultaneously more easier materials for technologists and to improve the technical parameters of devices on the basis of FE materials. Finally it is necessary to use less harmful reagents and FE materials from them. All these demands could be met more quickly if more FE and related substances were known so that they could be used to obtain new technical materials.

Some empirical criteria of ferroelectricity are known (see, e.g. [1, pp.126-127; 14,30,31]) They allow us the prognosis of FE or anti FE properties mostly in metal oxides more or less confidently. Usage of these criteria leads to the rapid increase of the number of FE and related substances. The importance of growth and investigations of single crystals should be also stressed.

Well known techniques (spontaneous crystallization from melts and melt solutions, Czochralski technique and others) are used for synthesizing FE single crystals.

Long ago large $\text{LiNbO}_3$ and $\text{LiTaO}_3$ single crystals were synthesized by the Czochralski technique [13,pp.118-133;32]. These crystals appeared very promising for manufacturing electro-optic, nonlinear-optic, piezoelectric and pyroelectric elements. Moreover, doped $\text{LiNbO}_3$ crystals can be used as working bodies for holographic recording of information [10].

Hydrothermal synthesis was used to grow FE single crystals of $\text{SbTaO}_4$ and $\text{SbNbO}_4$. This made possible a detailed study of their properties which enable us to conclude their high efficiency as pyroelectric detectors [20,33]. Similar single crystals of compositions $\text{Sb}_{11/2}\text{Sb}_4\text{O}_4$ and $\text{Bi}_{2}^3\text{B}_4\text{O}_7$, where $\text{B}=$$\text{Nb,Ta,Sn}$ and $\text{V}$, have been grown and studied [20].

Large scale investigations were carried out on attempting to make more accurate the phase equilibrium in the $\text{PbO-GeO}_2$ system, on the growth of crystals and the study of their structure, on the properties and phase transitions of many compounds in this system and their modifications [19]. It was found that besides the known FE phase $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ there are some other phases and their modifications ($\text{Pb}_5^\gamma\text{Ge}_3\text{O}_{11}$, $\text{Pb}_7\text{Ge}_3\text{O}_{11}$) with FE or related properties [19].

A very promising and numerous group of FE compounds is the group of FE's with a layer of perovskite - like structure of composition $\text{A}_2\text{B}_2\text{O}_7$ ($\text{Sr}_2\text{Nb}_2\text{O}_7$, $\text{La}_2\text{Ti}_2\text{O}_7$ and others with very high $T_c=1500$ °C) [14,18] and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ type ($\text{Bi}_2\text{ZnTiO}_5$ and others with high $T_c$) [14,16]. In [16] a crystal-chemical analysis of the necessary conditions for "designing" new similar Bi-containing compounds was carried out and a remarkable number of single crystals of similar compounds was synthesized and studied. FE's of this group are suitable as a basis for synthesizing different technical materials e.g. piezoelectric ceramics with a high working temperature.

The obtaining of texture ceramics is also of great interest. For example, it is important to obtain ceramics with needle-like crystalites oriented preferably in one direction. In this case piezoelectric, pyroelectric and other properties of ceramics approach the properties of single crystals [34], the latter are as a rule more expensive and often cannot be synthesized in necessary forms or sizes.

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Small crystals of non-isometric forms (for example, needle-like crystals) can also be used as fillings in polymers (composites) with a preferable crystal orientation. Certain technical parameters of composites are usually much better than those of inorganic FE fillings (they are some 100 times higher or more) [12]. Thus they can be applied in different fields of technique, particularly in robotics [35]. The problem of FE single crystal film synthesis is of special importance in science and technology [36].

Conclusion

The rate of investigations and applications of FE and related materials is higher than that of semiconductors and ferrites [14]. Many valuable technical materials have been designed and produced. But in the future there will be other important tasks on the search, creation, study, production and application of more efficient new FE and related materials, including single crystals.

According to statistics on results of structural data [37] almost 30 % of studied compounds appeared to be noncentrosymmetric ones (viz. FE's, pyroelectrics and piezoelectrics and related substances). Besides it should be noted that at present several millions of compounds are known [38]. At the same time there are almost 100 times more organic compounds than inorganic compounds. Therefore it is possible to expect the discovery of numerous FE organic compounds, including those that are valuable for applications. However FE and related inorganic materials have got certain advantages (high working temperature, radiation stability, etc.) [1, p. 228] and their considerable technical significance will remain.

In conclusion it should be noted that among perovskite-type oxides there is a big class of perovskites with "puckered" structures (more than 250 compounds) which were classified as antiFE's [1, pp. 117-120; 16]. However this big group has not been sufficiently studied as yet. Thus one important task is to look for the new proofs of existence of antiFE properties in these compounds. This task is of considerable scientific and practical interest.

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SEM INVESTIGATIONS OF MACROSCOPIC CRYSTAL DEFECTS IN GaAs VPE LAYERS

I. GYÚRÓI1, L. DOBOS1, Zs. J. HORVÁTH1, E. K. PÁL1
V. I. FINEBERG2, R. V. KONAKOVA2 and Yu. A. TKHORIK2

1Research Institute for Technical Physics,
Hungarian Academy of Sciences, 1325 Budapest, Hungary
2Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, 252650 Kiev, USSR

In GaAs vapour phase epitaxial layers macroscopic defects have been observed by scanning electron microscopy, namely pittings, stacking faults, hillocks, overgrown foreign particles and ring defects. In some cases their probable nuclei have also been found.

Introduction

Developing microwave tuning varactors [1-2] the breakdown properties of planar GaAs-CrAu Schottky contacts were recently studied as a function of the dopant concentration in the homogeneously doped active VPE layers, and it was found that the experimental breakdown voltage values were much lower than those following from the avalanche theory [1,3]. To understand the origin of the poor breakdown properties wide investigations were carried out [4] including structural defect studies by different experimental methods: scanning electron microscopy, X-ray diffraction [4], microplasma [5] and statistical breakdown [4] investigations. In the present paper results of the scanning electron microscope studies are presented.

Experiments

In GaAs layers grown by vapour phase epitaxy different defects may be present which affect the quality of the layers. These defects may be either microscopic (e.g. dislocations) or macroscopic. The scanning electron microscopy gives the possibility of the direct investigations of the macroscopic defects. In our VPE layers pittings, stacking faults, hillocks, overgrown foreign particles and ring defects have been observed.

Before the epitaxial growth the (100) GaAs substrates are submitted to in-situ vapour phase etch. The substrates have also been investigated after the vapour phase etch and for some defects their probable nuclei have also been found.

Pittings

One type of macroscopic defects are pittings. They arise in the case of three dimensional nuclei of crystallization, if the growth rate in direction normal to the surface is high relatively those in directions parallel with the surface. As a result the surface of the epitaxial layer will be matt.
Fig. 1: Stacking faults

Fig. 2: Different types of hillocks

Fig. 3: Two possible nuclei of hillocks: a chemically passive foreign particle (a) and probably a chemically active one or an inclusion (b)
Fig. 4: Overgrown foreign particle

Fig. 5: One of the probable nuclei of ring defects

Fig. 6: Two ring defects

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Because the growth rates are strongly affected by the gas phase composition and the temperature, this phenomenon may be completely avoided.

**Stacking faults**

Stacking faults are usually originated at the substrate-epitaxy interface as a trouble in the periodic structure of the crystal lattice. They may be caused by microscratches or foreign particles on the surface, by local segregation of the doping material in the substrate, etc. Their shape is always regular as shown in Fig. 1, and depends on the orientation of the surface. Their density may be influenced by the growth parameters and the preparation-cleaning process.

**Hillocks**

Fig. 2 gives different types of hillocks observed: mesa, hill and transitions between them. All of them are the same phenomenon but in different stages of its development. Investigations showed that the mesa is a twin originated in a Ga droplet, a foreign particle or a Ga\(_2\)O\(_3\) crystallite on the surface. During the growth process the twin is being covered by the epitaxial layer with matrix-orientation (100). This process results in a hill-type defect [7]. Two possible nuclei found after vapour phase etch are given in Fig. 3.

**Overgrown foreign particles**

As mentioned above the foreign particles can cause stacking faults and hillocks, but in some cases they may be overgrown with epitaxial layer which may be twin-orientated as well. An overgrown thread is seen in Fig. 4.

**Ring defects**

One of the probable nuclei of ring defects after vapour phase etch is shown in Fig. 5. It must be a spot remaind after a drop of cleaning reagents around a foreign particle or an inclusion with particles of sediment at the edge. These particles are the nuclei of twins yielding continuous ring shape mesa structure. Two examples of these ring defects are given in Fig. 6.

**References**

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BOOK REVIEWS

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PLANE SYMMETRIC COSMOLOGICAL SOLUTIONS
OF THE LYTTLETON–BONDI UNIVERSE

D. R. K. REDDY
Department of Applied Mathematics, Andhra University
Waltair, India

and
P. INNAIAH
College of Engineering
Gandhi Institute of Technology and Management
Waltair, India

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The exterior field of the plane symmetric metric in the Lyttleton–Bondi Universe is considered and exact solutions are obtained in some specific situations. Our solutions generalise the empty space-time solutions, with plane symmetry, previously obtained by Taub and Bera to the situation when Lyttleton–Bondi field is present. Various physical aspects of the solutions are discussed.

1. Introduction

Lyttleton and Bondi [1] have developed a cosmological model assuming that there is a continuous creation of matter due to a net imbalance of charge. This imbalance of charge may arise from the difference in magnitude of the charge of the proton and that of an electron, or from the difference in number of protons as compared to the number of electrons. To incorporate the idea of creation the Maxwell field equations are modified as

\[ F_{\mu\nu} = A_{\mu,\nu} - A_{\nu,\mu}, \]  
\[ F^\mu{}_{\nu} = J^\mu - \lambda A^\mu, \]  
\[ J^\mu_{\nu} = q, \]

where \( \lambda \) is a constant, \( A_\mu \) and \( J_\mu \) denote four-potential and current density four vector, respectively, \( F_{\mu\nu} \) denotes the antisymmetric electromagnetic field tensor and \( q \) the rate of creation of charge per unit proper volume. A semicolon, here, denotes covariant differentiation.

The energy momentum tensor of the field is

\[ T^\nu_\mu = (F^\mu_{\alpha}F^\nu_{\beta} + 1/4 g^\alpha_{\mu}F_{\beta\gamma}F^\gamma\beta) + \lambda (A^\mu A^\nu - 1/2 g^\alpha_{\mu}A_\alpha A^\nu). \]
When $F_{\mu \nu} = 0$ (with zero electromagnetic field) relation (2) becomes

$$J_{\mu} = \lambda A_{\mu}$$  \hspace{1cm} (5)

and the energy momentum tensor of the field becomes

$$T^{\nu}_{\mu} = \lambda (A_{\mu} A^{\nu} - 1/2 g_{\mu \nu} A_{\alpha} A^{\alpha}).$$  \hspace{1cm} (6)

Assuming that the charge created will not affect the dynamical characteristic of the metric and also the mechanical effect of such creation on the energy momentum tensor is nil, we can use the Einstein’s field equations

$$R^{\nu}_{\mu} - 1/2 g^{\nu}_{\lambda\mu} R = - K T^{\nu}_{\mu},$$  \hspace{1cm} (7)

where $K (= 8\pi G)$ is a constant, the velocity of light $c$ is taken to be unity and $T^{\nu}_{\mu}$ is given by (6).

Lyttleton and Bondi [1] have investigated the nature of the field in a Newtonian framework with zero electromagnetic field and nonzero potentials. The same assumptions have also been utilised by them to study the Desitter metric. Burman [2] has studied several aspects of the Lyttleton–Bondi field. One of his investigations pertains to the static spherically symmetric exterior solution. Rao and Panda [3] have formulated the analogous exterior problem in the case of the cylindrically symmetric Einstein–Rosen metric. Recently Reddy and Rao [4] have obtained exact solutions in the Lyttleton–Bondi universe with the aid of a static spherically symmetric conformally flat metric. The problem of Lyttleton–Bondi field has not been studied so far in the plane symmetric space-time of Taub [5] and Bera [6]. We have therefore taken up the investigation of the exterior field of the plane symmetric space-time in the Lyttleton–Bondi universe and have obtained exact static and non-static solutions which are observed to be similar to the plane symmetric solutions of the field equations corresponding to zero mass scalar fields obtained by Patel [7]. It is found that the empty space-times of general relativity discussed by Taub and Bera are obtained as special cases. Some physical aspects of the solutions are discussed.

2. A static plane symmetric solution

We consider a space-time whose geometry is described by the plane symmetric line element

$$ds^2 = e^{2\alpha} (dt^2 - dx^2) - e^{2\beta} (dy^2 + dz^2),$$  \hspace{1cm} (8)

where $\alpha$ and $\beta$ are functions of $x$ only. In a static plane symmetric situation, $A_{\mu}$ must have the form given by

$$A_{\mu} = (a, 0, 0, \phi).$$  \hspace{1cm} (9)
But since \( F_{\mu\nu} = 0 \), \( \varphi \) must be a constant. Now we have from (8) and (9)

\[
A^\mu = (-ae^{-2\varphi}, 0, 0, \varphi e^{-2\varphi}),
\]
so that

\[
A_\mu A^\mu = e^{-2\varphi}(\varphi^2 - a^2).
\]  

(10)

By considering the space-time (8) and using (6) and (10), the field equations (7) become

\[
\beta_1^2 + 2\alpha_1 \beta_1 = \frac{K\lambda}{2} (a^2 + \varphi^2),
\]

\[
\beta_{11} + \beta_1^2 + \alpha_{11} = \frac{K\lambda}{2} (\varphi^2 - a^2),
\]

\[
2\beta_{11} + 3\beta_1^2 - 2\alpha_1 \beta_1 = -\frac{K\lambda}{2} (a^2 + \varphi^2),
\]

(11)

\[
\lambda \alpha \varphi = 0,
\]

where subscript 1 denotes differentiation with respect to \( x \).

The field equations (11) yield a general exterior solution for the metric (8) given by

\[
ds^2 = (K_1x + K_2)^{2K_3/K_1}(dt^2 - dx^2) - (K_1x + K_2)(dy^2 + dz^2)
\]

with

\[
a = \pm (K_1x + K_2)^{-1} \left( \frac{K_1^2 + 4K_1K_3}{2K\lambda} \right)^{1/2},
\]

(12)

\[
\varphi = 0; \quad K_1 \neq 0,
\]

where \( K_1, K_2 \) and \( K_3 \) are constants of integration.

The static plane symmetric metric due to Taub [5] in Einstein’s theory is

\[
ds^2 = (K_1x + K_2)^{-1/2}(dt^2 - dx^2) - (K_1x + K_2)(dy^2 + dz^2),
\]

(13)

where \( K_1 \) and \( K_2 \) are constants. The corresponding metric in the Lyttleton–Bondi universe is given by (12). It can be seen that when \( K_3/K_1 = -1/4 \) the metric (12) reduces to Taub’s metric (13). Also, like the metric (13), the solution (12) has an intrinsic singularity (i.e. co-ordinate free singularity) at \( x = -K_2/K_1 \). Thus, we see that there is a one-to-one correspondence between the singularities of the Einstein vacuum solution and the exterior solution of the Lyttleton–Bondi universe. Also the solution (12) is formally similar to the static plane symmetric solution of the field equations for zero mass meson fields obtained by Patel [7].

The metric (12) can be transformed through a proper choice of the co-ordinates to the form (with \( K_1 = 1 \))

\[
ds^2 = X^{2K_3}(dT^2 - dX^2) - X(dY^2 + dZ^2).
\]

(14)
2.1 Some physical features

The potentials in the universe (14) are given by

\[ a = \pm X^{-1} \left( \frac{1+4K_3}{2K\lambda} \right)^{1/2} \]  

(15)

and

\[ \varphi = 0. \]

To avoid singularity in the potential we must have \( X > 0 \).

The motion of a test particle in the model is governed by the geodesics given by (since we have taken \( F_{\mu\nu} = 0 \))

\[ \frac{d^2x^i}{ds^2} + (j^i)k \frac{dx^j}{ds} \frac{dx^k}{ds} = 0, \]

which in this case integrate to

\[ e^{2\beta} \frac{dY}{ds} = A_1, \]

\[ e^{2\beta} \frac{dZ}{ds} = A_2, \]

\[ e^{2\beta} \frac{dT}{ds} = A_3 \]

(16)

and

\[ \left( \frac{dX}{ds} \right)^2 = A_3^2 e^{-4\alpha} - e^{-(2a + 2\beta)}(A_1^2 + A_2^2) - e^{-2\alpha}, \]

where \( A_i \)'s are constants of integration.

Using metric (14) and taking \( K_3 = 1/2 \) equations (16) reduce to

\[ \frac{dY}{dT} = L_1, \quad \frac{dZ}{dT} = L_2, \]

\[ \frac{dX}{dT} = 1 - L_1^2 - L_2^2 - L_3^2 X, \]

(17)

where \( L_1, L_2, L_3 \) are constants replacing \( A_1/A_3, A_2/A_3 \) and \( 1/A_3 \), respectively.

From equations (17) we obtain

\[ 1 - L_1^2 - L_2^2 - L_3^2 X = 1/4(L_3^2 T + L_3^2), \]

\[ \frac{d^2X}{dT^2} = -1/2L_3^2, \]

\[ V_X^2 = 1 - L_3^2 X - V_Y^2 - V_Z^2, \]

(18)
where $L_4$ is a constant and $V_x$, $V_y$ and $V_z$ represent the velocities along the $X$, $Y$ and $Z$ directions. From Eqs (18) we observe that the velocity along the $X$-direction is not constant but depends on $X$ and also that there exists a constant force acting on the test particle.

The track of a light pulse in the model (14) is obtained by setting

$$ds^2 = 0,$$

that is

$$\left( \frac{dX}{dT} \right)^2 + X^{-2} \left[ \left( \frac{dY}{dT} \right)^2 + \left( \frac{dZ}{dT} \right)^2 \right] = 1$$

and for the case when the velocity is along the $X$-axis it is a simple matter to show that no red shift is observed in this static model as in the case of Einstein Universe (Tolman, [8]).

3. A non-static plane symmetric model

We consider a Riemannian space-time described by the line element

$$ds^2 = e^{2h}(dt^2 - dr^2 - r^2d\theta^2 - S^2dZ^2),$$

where $r, \theta, Z$ are cylindrical polar co-ordinates and $h$ and $S$ are functions of time $t$ alone. It is well known that this line element is plane symmetric. Bera [6] and Carminati and McIntosh [9] discussed this type of non-static line element in general relativity.

In a non-static plane symmetric situation, we have

$$A^\mu = (-e^{-2h}a, 0, 0, \varphi e^{-2h}),$$

so that

$$A_\mu A^{\mu} = (\varphi^2 - a^2)e^{-2h},$$

(21)

where $a$ and $\varphi$ are functions of $t$ only. But since $F_{\mu\nu} = 0$, ‘$a$’ must be a constant.

Using (6) and (21) the field equations (7) for the metric (20), in this case, become

$$S_{44} + M = -\frac{K\lambda}{2}(a^2 - \varphi^2),$$

$$\frac{2S_{4}h_4}{S} - M = -\frac{K\lambda}{2}(a^2 - \varphi^2),$$

$$2(h_{44} - h_4^2) - M = -\frac{K\lambda}{2}(a^2 + \varphi^2),$$

(22)

where

$$\lambda\alpha\varphi = 0,$$

$$M = 2h_{44} + h_4^2 + \frac{2S_{4}h_4}{S},$$

and subscript 4 denotes differentiation with respect to $t$. 

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The field equations (16) yield an exact solution given by

\[ S = A \exp \left( \frac{C_1}{C_2} h \right), \]
\[ \exp \left[ (2 + C_1/C_2) h \right] = (2 + C_1/C_2) (C_2 A^{-1} t + C_3), \]
\[ (2 + C_1/C_2) \phi = \pm \left[ \frac{2C_2(C_2 + 2C_1)}{A^2 K} \right]^{1/2} (C_2 A^{-1} t + C_3)^{-1} \]

with

\[ a = 0, \quad C_2 \neq 0, \quad A \neq 0, \]

where \( C_i \)'s are constants of integration.

Bera [6] has discussed an interesting metric of the field equations in general relativity which is given by

\[ S = A \exp \left( -\frac{3h}{2} \right) \exp \left( h/2 \right) = 1/2 (C_2 A^{-1} t + C_3) \]

together with (20). It has been shown by him that this metric is Riemannian (non-flat) and satisfies Einstein field equations for empty space and hence is of great interest from the point of view of cosmology. The corresponding solution in the Lyttleton-Bondi universe is given by (23). It can be seen that when \( \phi = 0 \), in this particular case, we have from (23), \( 3C_2 + 2C_1 = 0 \) and consequently the solution (23) of this universe goes over to the Bera's solution given by (24). Also the solution (23) is formally similar to the non-static plane symmetric solution of the field equations for zero rest mass scalar fields obtained by Patel [7].

Using solution (23), the metric (20) can be transformed, through a proper choice of the co-ordinates and the constants (here we have set \( A = 1, C_1 = P, 2 + C_1 = Q \) and \( C_2 = 1 \)), to the form

\[ ds^2 = (QT)^{2/Q} \left[ dT^2 - dR^2 - R^2 d\theta^2 - (qT)^{2P/Q} dZ^2 \right], \]

where \( P \) and \( Q \) are positive constants.

3.1 Some physical features

The potentials in the model (25) are given by

\[ \phi = \left[ \frac{2(3 + P)}{K\lambda} \right]^{1/2} \frac{1}{QT} \]

and

\[ a = 0. \]

To avoid singularity in the potential we must have

\[ Q > 0, \quad T > 0. \]
The velocity field in the model is given by

\[ V^1 = V^2 = V^3 = V_4 = V_5 = 0, \]

\[ V^4 = (QT)^{-1/2}, \quad V_4 = (QT)^{1/2}, \]  \hspace{1cm} (27)

The flow vector \( V^i \) satisfies the equations of the geodesics \( V^i_j V^j = 0 \). Thus the lines of flow are geodesics.

The motion of a test particle in the model is governed by the geodesics given by

\[ \frac{d^2R}{ds^2} + \frac{2}{QT} \frac{sRdT}{ds} = 0, \]

\[ \frac{d^2\theta}{ds^2} + \frac{2}{R} \frac{dR}{ds} \frac{d\theta}{ds} + \frac{2}{QT} \frac{d\theta}{ds} \frac{dT}{ds} = 0, \]

\[ \frac{d^2Z}{ds^2} + (QT)^{2p/2} (1 + Q) \frac{dT}{ds} \frac{dZ}{ds} = 0, \]

\[ \frac{d^2T}{ds^2} + \frac{1}{QT} \left[ \left( \frac{dR}{ds} \right)^2 + \left( \frac{d\theta}{ds} \right)^2 + \left( \frac{dT}{ds} \right)^2 \right] + (QT)^{2p/2} (1 + Q) \left( \frac{dZ}{ds} \right)^2 = 0. \]  \hspace{1cm} (28)

If a particle is initially at rest, i.e. if

\[ \frac{dR}{ds} = \frac{d\theta}{ds} = \frac{dZ}{ds} = 0, \]  \hspace{1cm} (29)

we get

\[ \frac{dT}{ds} = (QT)^{-1/2}. \]

From the equations of the geodesics we conclude that for all such particles the components of spatial acceleration would vanish, namely

\[ \frac{d^2R}{ds^2} = \frac{d^2\theta}{ds^2} = \frac{d^2Z}{ds^2} = 0, \]

and the particle would remain permanently at rest.

The track of light pulse in the model (25) is obtained as

\[ \left( \frac{dR}{dT} \right)^2 + \left( R \frac{d\theta}{dT} \right)^2 + (QT)^{2p/2} \left( \frac{dZ}{dT} \right)^2 = 1 \]  \hspace{1cm} (30)

and for the case when the velocity is along the \( Z \) axis equation (30) gives

\[ \frac{dZ}{dT} = \pm (QT)^{-p/2} = \pm \psi(T). \]  \hspace{1cm} (31)
Hence the light pulse leaving a particle at \((0, 0, Z)\) at time \(T_1\), would arrive at the origin at a later time \(T_2\) given by

\[
\int_{T_1}^{T_2} \psi(T) dT = \int_0^Z dZ.
\]

Following the method outlined by Tolman [8] the redshift in this case is given by

\[
\frac{\epsilon + \delta \epsilon}{\epsilon} = \left( \frac{QT_1^{1/2}[(QT_1)^{-p/2} + U_Z]}{(QT_2^{1/2})^{p/2}[(QT_2)^{1/2} - U^2]} \right),
\]

where \(U\) is the velocity of the source at the time of emission and \(U_Z\), the \(Z\) component of the velocity.

By a straightforward calculation of the conformal curvature components for the model (25), it may be observed that the space-time given by (25) is in general not conformally flat. However, if \(P = 0\), it becomes conformal to flat space-time and reduces to a particular case of the Lemaitre Universe.

References

EXCITATION AND EMISSION SPECTRA OF UNDOPED POTASSIUM CHLORIDE PHOSPHORS

N. L. KEKAN and N. A. PATIL

Physics Department, Faculty of Science
M. S. University of Baroda, Baroda-2, India

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Pure potassium chloride, quenched rapidly from high temperatures, yields a pronounced excitation band at 274 nm which induces a prominent emission band at 348 nm. It is suggested that these bands are characteristic of the centres involving oxygen and ion vacancy interactions in the KCl lattice.

The present work concerns the investigation of the nature of the centres responsible for luminescence in heat-pretreated undoped potassium chloride. One specimen batch was annealed at 500 °C in evacuated and sealed tubes and quenched rapidly to room temperature (quenched in vacuo). Another specimen batch was quenched rapidly to room temperature in a porcelain crucible after annealing at 500 °C (quenched in air). In yet another pretreatment, KCl:Sr specimens prepared from aqueous solution with $10^{-4}$ m.f. Sr content were annealed in evacuated and sealed tubes and quenched rapidly to room temperature after annealing at 500 °C. All the specimens were annealed for a duration of 5 h. In all the cases the excitation and emission measurements were carried out with powder specimens on a Aminco-Bowman spectrophotofluorometer. Area of the sample exposed to the exciting radiation, geometry of the experimental arrangement, etc. remained unaltered throughout the course of the experiments. The luminescence output was recorded on Honeywell stripchart recorder.

The excitation and emission data presented in Figs 1 and 2 relate to the thermally treated undoped KCl powder specimens. It is obvious from these Figures that the excitation spectra consist of a single dominant band at 274 nm and the emission spectra induced by this excitation display a prominent band at 348 nm. It is worth noting that the excitation and emission bands are favoured if the heat treatment is carried out in air instead of an evacuated and sealed tube (compare Curves 1 and 2).

It is suggested that the heat–treated undoped KCl specimens acquire the property of becoming luminescent because the surface of a microcrystal (in the powder specimen) exposed to air becomes activated owing to adsorbed gases. Apparently the activating impurity, presumably $O_2^+$ molecule ions or $O_2$ neutral molecules, is
Curve 1: Undoped KCl powder annealed in an evacuated and sealed tube at 500 °C for 5 h and quenched rapidly to room temperature

Curve 2: Undoped KCl powder annealed in air at 500 °C for 5 h and quenched rapidly to room temperature

Curve 3: KCl: Sr powder specimen prepared from aqueous solution (Sr conc. $10^{-4}$ m.f.). Specimen annealed and quenched in an evacuated and sealed tube at 500 °C for 5 h and quenched rapidly to room temperature

incorporated in the surface of the microcrystal. At a given temperature the attack on the surface layers by oxygen molecules will naturally depend on the air pressure. This explains the difference in the luminescence intensity of the two specimens, one heated in vacuo and other in air (Curves 1 and 2) though both are annealed at 500 °C for the same duration. It is believed, therefore, that an oxygen molecule ion $O_2^+$ or a neutral molecule $O_2$ situated on a cation site is one of the components of the luminescence centre responsible for 274 nm excitation and 348 nm emission.

Comparison of the intensities of the excitation and emission bands displayed by an undoped KCl specimen, annealed and quenched from 500 °C in vacuo, with the intensities of the corresponding bands exhibited by a doped KCl specimen (Sr concentration $10^{-4}$ m.f.) also annealed and quenched from 500 °C in vacuo, clearly demonstrates that the introduction of a trace amount of strontium impurity suppresses the intensities of the luminescence bands by a factor two (compare curves 1 and 3). It is known that the major fraction of the divalent impurity ions incorporated in an alkali

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halide crystal becomes associated with positive ion vacancies forming impurity–vacancy dipole and their higher aggregates ([1–3]). It therefore seems plausible that the positive ion vacancies produced by quenching are used up in the generation of dipoles and this exhibits the formation of a 348 nm centre. It is not possible to specify the exact composition of the 348 nm centre. It may involve the O$_2$ molecule or the O$_2^+$ molecule ion in association with one or more positive ion vacancies.

**Fig. 2.** Emission spectra

Curve 1: Undoped KCl powder annealed in an evacuated and sealed tube at 500 °C for 5 h and quenched rapidly to room temperature

Curve 2: Undoped KCl powder annealed in air at 500 °C for 5 h and quenched rapidly to room temperature

Curve 3: KCl : Sr powder specimen prepared from aqueous solution (Sr conc. 10$^{-4}$ M). Specimen annealed and quenched in an evacuated and sealed tube at 500 °C for 5 h and quenched rapidly to room temperature

It may be mentioned that oxygen has been suggested as a common impurity of most of the ‘pure’ alkali halides, though of course, little definitive work has been done with this impurity ([5], [6]). Halperin et al [4] and Joshi et al ([7], [8]) attributed the thermoluminescence emission of undoped alkali halides to centres composed of oxygen impurity and ion vacancies.

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CHARACTERIZATION OF CHEMICALLY DEPOSITED Ag LAYER

A. K. ABASS, D. A. MUKHTAR and N. R. ADNAN

Department of Physics, College of Science
University of Basrah, Basrah, Iraq

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Thin layers of Ag were chemically deposited on borosilicate glass. The layers were characterized by X-ray diffraction and optical properties for photon energy range (1 eV—6 eV). Reflectance and transmittance data were used to investigate the plasma frequency ($\hbar \omega_p = 3.82$ eV) and optical constants. Bound electron absorption occurs at 3.85 eV, free electron absorption below 2.25 eV and interband transition at 3.8 eV.

Ag layers prepared by this novel method are identical to those prepared by high vacuum evaporation techniques.

Introduction

Ishiguro and Kuwabara [1] have shown that the value of extinction coefficient and refractive index of Ag film approaches a steady value at a thickness greater than 15 mm. Plasma absorption has been treated theoretically and experimentally by several workers [2–6]. Ferrell [7] has shown that in the case of metals films, a simple physical picture can be used to predict a peak in the transition radiation around the plasma frequency.

The optical properties of the metal depend on the response of bound electrons in the ultraviolet region and on that of free electrons at higher wavelengths. For metals, the plasma frequency lies in the ultraviolet region and the plasma energy is higher than the Fermi energy. The plasma oscillation is initiated by rigid displacements of the electrons in the film. The electron motion is described by

$$m \frac{d^2 x}{dt^2} + 4\pi Ne^2 x = 0,$$

where $m$, $N$, $e$ and $x$ are the electron mass, electron number per cm$^3$, electronic charge and the rigid displacement, respectively. The oscillation frequency of the film (plasma frequency):

$$\omega_p = \left( \frac{4\pi Ne^2}{m} \right)^{\frac{1}{2}}.$$

In the present work, we have carried out a detailed analysis of X-ray and optical data.
for chemically deposited Ag layers in the fundamental optical absorption region in order to identify plasma resonance, interband transition, bound and free electron absorption for film characterization.

**Film preparation**

Ag layers were prepared by spray pyrolysis. A suitable design of the spray nozzle is given in Fig. 1. The upper container 4 cm in diameter is connected to a capillary of 0.3 mm in diameter through a stopcock. The capillary tube was surrounded by a bubble tube through which compressed air at 2.5 kg/cm$^2$ was blown. A solution containing AgNO$_3$; glycerol; H$_2$O in the ratio of 0.2:0.24:0.56 respectively was prepared. This combination was found to give a good Ag-film without any observed yellowish colour which is due to incomplete reaction. The solution was sprayed on a preheated borosilicate glass slide as a substrate. The substrate was heated to 450 °C for 20 min before spraying the solution. Each spraying period (about 15 s) was followed by a 2 min stop to avoid excessive cooling of the hot substrate during spraying. To deposit a film with a uniform thickness, the distance between substrate and spray nozzle was kept 25 cm with a spraying rate 25 cm$^3$/min. The films were prepared in the thickness range 30–150 nm. The thicknesses were optically determined using the step method.

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Experimental results and discussion

X-ray diffraction patterns have been taken using the CuKα radiation from a Philips PM 1050/70 diffractometer with Ni filter. The measurements were repeated on ten samples of different thickness giving similar results. A typical diffraction curve is shown in Fig. 2. The values of interplanar spacing and intensity ratio are exactly the same as that given in the ASTM cards in a comparable range of diffraction angles. This confirms the chemical purity of films. The optical parameters, plasma frequency and other information regarding the electron band structure of Ag-films, were studied by recording the transmission, absorption and reflection of films of different thicknesses. This was achieved in the present investigation using a Pye–Unicam SP8–100 spectrophotometer. The measurements were repeated on 20 samples at a thickness above the minimum needed to provide bulk characteristics as mentioned in [1] and similar results were obtained. The transmittance (T) for films on transparent substrate has been given by Moss [8]. For low transmission we have:

\[ T = (1 - R_1)(1 - R_2)(1 - R_3) \left( 1 + \frac{K^2}{n^2} \right) e^{-\alpha d}, \]

where \( R_1, R_2 \) and \( R_3 \) are the reflection coefficients at air–film, film–substrate and substrate–air interfaces, respectively. The parameters \( n, K \) and \( d \) are the refractive index, extinction coefficient and thickness of the film, respectively, and \( \alpha \) is the absorption coefficient. Assuming that the change in reflection with thickness is

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negligible, the ratio of transmission of two films \( T_{1-2} \) of different thicknesses is given by:

\[
T_{1-2} = e^{-\alpha \Delta d}.
\]  

\( T_{1-2} \) is determined directly from the ratio-recording technique, \( \Delta d \) is the thickness difference of two films.

A typical curve of reflectivity is shown in Fig. 3. Reflectivity data of Ag films were taken for thick opaque samples (> 90 nm). It is important to state that reflectivity is a single surface reflectance when the sample is highly absorbing or thick enough so that no back reflection comes out from deeper interfaces. Therefore reflectivity data shown in Fig. 3 correspond to \( R_t \) and are determined by the equation

\[
R_t = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}, \quad K = \frac{\alpha \lambda}{4\pi},
\]

where \( \lambda \) is the wavelength.

Reflection is diffused due to sample roughness, polycrystallinity and translucence, therefore a primary information could be met regarding the films smoothness from reflectivity data. Since the present values of reflectivity are in good agreement with reported data by other investigators using high vacuum evaporated films \([10, 11]\), one can suggest that the new films roughness is comparable with those obtained from expensive techniques.

At the plasma frequency of the metal, one expects a strong interaction between the electromagnetic waves and plasma mode. This interaction manifests itself as total reflection at a frequency less than the plasma frequency (Fig. 3), while the sample is transparent around this frequency (Fig. 4). A critical wavelength at 324 nm corresponding to plasma frequency \( (\hbar \omega_p = 3.82 \text{ eV}) \) is noted. The value of the resonance frequency is in good agreement with the analysis of Mcalister and Stern \([9]\) on

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transmission of P and S-polarized light through Ag films as prepared by the thin film evaporation method.

The refractive index and extinction coefficient can be determined from Eqs (3) and (4). The spectral dependence of \( n \) and \( K \) are shown in Fig. 5. The absolute values of these parameters are well comparable with earlier workers results [10, 11]. Using \( n \) and \( K \) values obtained from Fig. 5 the real (\( \varepsilon_1 \)) and imaginary (\( \varepsilon_2 \)) parts of the dielectric constant were calculated via the relations \( \varepsilon_1 = n^2 - k^2 \) and \( \varepsilon_2 = 2nk \) (Fig. 6). \( \varepsilon_1 \) vs photon energy shows a peak at 3.85 eV. This peak is mainly due to bound electron absorption [10]. It shows also another structure at an energy below 2.55 eV which can be
attributed to free electron absorption. The sharp rise in $\varepsilon_2$ at 3.8 eV is identified with interband transmission from $d$-state to Fermi surface near $L_3 - L_2$ [11, 12]. The absolute values and structure behavior of $n$ and $K$ as well as $\varepsilon_1$ and $\varepsilon_2$ are mainly related to (i) surface morphology, (ii) the chemical identity of absorbed atomic and molecular species (including dissociation fragments), (iii) the structure arrangement of these species and (iv) charge distribution and energy level structure of the valence electrons. These factors therefore determine the unique chemical and physical properties of the interfacial state of matter.

Finally, it is concluded that a thin Ag film prepared by this simple and inexpensive method has the same characteristics as that prepared by the high vacuum evaporation method.

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References

THEORETICAL INVESTIGATION
OF FLUOROCARBONYLSULFENYL CHLORIDE
USING INFRARED AND RAMAN SPECTRA

A. NATARAJAN and P. KOLANDAIVEL
Department of Physics, Bharathidasan University
Tiruchirapalli 620023 Tamilnadu, India

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Normal coordinate analysis has been performed for the molecule FC(O)SCI on the basis of general valence force field. The force constants have been computed using Wilson's GF-matrix method. From the force constants other molecular constants such as mean square amplitudes of vibration, generalized mean square amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants have been calculated and reported. Using the vibrational frequencies and the structural parameters, the thermodynamic functions have also been calculated for several temperatures. The force constants and the mean amplitudes of vibration are compared with those of related molecules.

Introduction

Infrared studies of the FC(O)SCI molecule have been reported in the literature [1, 2]. Subsequently, there was no report on this molecule until 1983. Then, Della Vedova et al [3] reported the infrared spectra of this molecule in the solid and the gaseous states and the Raman spectrum in the liquid state. They have observed the existence of coplanar trans and cis conformers and suggested that the trans structure is more abundant at room temperature. Della Vedova et al [3] have assumed the geometry of the molecule from those of related molecules [4, 5]. They carried out a normal coordinate analysis for the trans conformer and derived the harmonic force field from their own infrared and Raman data. The present study was initiated for many reasons. First, up to now the structure of the FC(O)SCI molecule has not been determined experimentally. The results of our present study hence might be useful for the investigation of the structure of this molecule. Secondly, Della Vedova et al [3] have made only an approximate normal coordinate analysis using a few valence force constants transferred from related molecules without refinements. In this study, we started with Della Vedova's force field [3] as first approximation and refined it using Cyvin's W-matrix method [7]. Using the refined force constants so obtained, other molecular constants such as mean square amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants have been computed. In addition, some thermodynamic functions \([S, F, C_p\) and \(H\)] are reported for eleven temperatures.
The FC(O)SCl molecule belongs to the $C_s$ point group. The distribution of the normal vibrational frequencies among the two symmetry species is $7A'+2A''$. The geometrical parameters and the vibrational frequencies used in this investigation are taken from [3].

The molecular configuration, the numbering of atoms and the orientation of the Cartesian coordinate axes are shown in Fig. 1.

![Fig. 1. The molecular configuration, numbering of atoms and the orientation of the Cartesian coordinate axes of FC(O)SCl](image)

### Methods of calculation

The force constants, in principle, can be obtained from the solution of the inverse vibrational problem (i.e.) by solving the equation

$$GFL = L \wedge$$

for $F$ [6]. (The symbols have their usual meanings). For the solution, Cyvin's $W$-matrix method [7] provides a convenient practical computation. According to this method, the $G$-matrix can be factorized as $G = T \bar{T}$, where $T$ is a triangular matrix. The initial values of the elements of the force constant matrix $F$ were taken from related molecules and from the values of Della Vedova et al [3]. Then, the force constants were refined using the least square refinement procedure until the observed frequencies agree well with the calculated ones. For actual computation, Shimanouchi's [8] modified version of computer program was used.

The mean square amplitudes of vibration matrix [9] have been evaluated using the expression

$$\Sigma = L A \bar{L},$$

where $L$, consisting of the eigenvalues of matrix $GF$, and $A$ is the diagonal matrix with elements

$$A_i = \frac{h}{8\pi^2 C v_i} \text{coth} \left( \frac{hc v_i}{2KT} \right).$$
THEORETICAL INVESTIGATION OF FLUOROCARBONYLSULFENYL CHLORIDE

where $K$ is the Boltzmann constant, $h$ is the Planck's constant, $v_i$ is the $i$-th normal frequency and $T$ is the absolute temperature. The generalized mean square amplitudes of vibration viz., the parallel mean square amplitudes of vibration $\langle (\Delta Z)^2 \rangle$ and the perpendicular mean square amplitudes of vibration $\langle (\Delta Y)^2 \rangle$ and $\langle (\Delta X)^2 \rangle$ have been calculated using the relations of Morino and Hirota [10].

Applying Jahn's rule [11], the nonvanishing Coriolis coupling constants are evaluated using the relation

$$ \eta^2 = L^{-1} C^a L^{-1}, $$

where $C^a (a = x, y, z)$ is the skew symmetric matrix defined according to Meal and Polo [12].

The centrifugal distortion constants are calculated by the method suggested by Kivelson and Wilson [13] and by Cyvin et al [14].

Results and discussion

The internal force constants obtained by us are presented in Table I together with the values of Della Vedova et al [3]. Some of the interaction force constants ($f_{R\beta}$, $f_{R \delta}$, $f_{D \delta}$, $f_{D R}$, $f_{R \alpha}$) are fixed as given by Della Vedova et al [3]. These constants are mostly the stretch–stretch interaction force constants and these are not more sensitive in the change of the vibrational frequencies. The other force constants ($f_r$, $f_\delta$, $f_R$, $f_\alpha$, $f_\beta$, $f_\sigma$, and the number of stretch–bending interaction force constants) are refined until all

<table>
<thead>
<tr>
<th>Designation</th>
<th>Present investigation</th>
<th>Values from Ref. [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_r$</td>
<td>1295.0</td>
<td>1309.9</td>
</tr>
<tr>
<td>$f_{R\delta}$</td>
<td>46.7</td>
<td>28.2</td>
</tr>
<tr>
<td>$f_{R \alpha}$</td>
<td>50.8</td>
<td>50.8</td>
</tr>
<tr>
<td>$f_{R \beta}$</td>
<td>-19.9</td>
<td>-19.9</td>
</tr>
<tr>
<td>$f_{R \delta}$</td>
<td>18.5</td>
<td>18.5</td>
</tr>
<tr>
<td>$(f_{R \alpha} - f_{R \beta})$</td>
<td>-4.5</td>
<td>-18.9</td>
</tr>
<tr>
<td>$f_{S \alpha}$</td>
<td>-64.2</td>
<td>-06.5</td>
</tr>
<tr>
<td>$f_{S \beta}$</td>
<td>495.6</td>
<td>503.2</td>
</tr>
<tr>
<td>$f_{S \delta}$</td>
<td>55.0</td>
<td>55.0</td>
</tr>
<tr>
<td>$f_{S \delta}$</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>$f_{S \sigma}$</td>
<td>40.2</td>
<td>30.4</td>
</tr>
<tr>
<td>$(f_{S \beta} - f_{S \delta})$</td>
<td>1.7</td>
<td>25.7</td>
</tr>
<tr>
<td>$f_{S \alpha}$</td>
<td>20.3</td>
<td>14.8</td>
</tr>
<tr>
<td>$f_{S \beta}$</td>
<td>401.5</td>
<td>432.5</td>
</tr>
<tr>
<td>$f_{S \delta}$</td>
<td>-2.2</td>
<td>-2.2</td>
</tr>
<tr>
<td>$f_{S \sigma}$</td>
<td>-67.6</td>
<td>-53.1</td>
</tr>
</tbody>
</table>

Table I

The Internal Force constants (N/m) of FC(O)SCI molecule
the calculated frequencies agree fairly well with the observed values. The refined values of the stretching force constants of the C–F and C–S bonds are found to be 495.6 N/m and 401.5 N/m while the respective values of Della Vedova et al [3] are 503.0 N/m and 432.0 N/m, respectively. The stretching force constant for the S–Cl bond is 307.4 N/m. Our values agree well with the related molecules viz., SC12 and CF3SC1[16]. It is seen that except for some off-diagonal elements there is no considerable difference between our refined force constants and those of [3]. The observed and calculated frequencies along with the description of symmetry coordinates are listed in Table II. The potential energy distribution among the symmetry coordinates has been calculated by Della Vedova et al [3]. They found considerable mixing of $v_2$, $v_3$ and $v_5$ modes.

### Table II

<table>
<thead>
<tr>
<th>Species</th>
<th>Symmetry coordinates</th>
<th>Description</th>
<th>Observed frequencies</th>
<th>Calculated frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>$S_1 = \Delta r$</td>
<td>C = O stretch</td>
<td>1851</td>
<td>1848</td>
</tr>
<tr>
<td></td>
<td>$S_2 = \Delta d$</td>
<td>C–F stretch</td>
<td>1054</td>
<td>1051</td>
</tr>
<tr>
<td></td>
<td>$S_3 = \Delta R$</td>
<td>C–S stretch</td>
<td>748</td>
<td>746</td>
</tr>
<tr>
<td></td>
<td>$S_4 = \Delta D$</td>
<td>S–Cl stretch</td>
<td>572</td>
<td>573</td>
</tr>
<tr>
<td></td>
<td>$S_5 = \sqrt{\beta \Delta \phi}$</td>
<td>FCO deformation</td>
<td>499</td>
<td>498</td>
</tr>
<tr>
<td></td>
<td>$S_6 = \sqrt{\gamma d \Delta \phi}$</td>
<td>FCO rocking</td>
<td>351</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>$S_7 = \sqrt{\beta \Delta \phi}$</td>
<td>CSCI deformation</td>
<td>182</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>$S_8 = \sqrt{\beta \Delta \phi}$</td>
<td>Redundant coordinates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A''$</td>
<td>$S_9 = (rD)^{1/2} \Delta \theta$</td>
<td>C = O rocking</td>
<td>628</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td>$S_{10} = (rD)^{1/2} \Delta \tau$</td>
<td>FCSCl torsion</td>
<td>109</td>
<td>110</td>
</tr>
</tbody>
</table>

The mean square amplitudes of vibration are very helpful to improve the precision of a structure determined by electron diffraction and microwave studies. There are neither electron diffraction nor microwave studies reported on this molecule. Therefore, we have calculated the mean square amplitudes of vibration and presented them in Table III. The mean square amplitudes of vibration for the bonds C–F and S–Cl are found to be very close to each other. The force constant of the C = O bond is very high but for the same bond the mean square amplitudes of vibration are very low. The mean amplitudes of vibration for the related molecules are compared with the values of the present investigation and are given in Table IV. Our calculated values are found to be very reasonable.
Table III

Mean square amplitudes of vibration \((10^{-6} \times Nm^2)\) at 300 K of FC(O)SCl

<table>
<thead>
<tr>
<th>Designation</th>
<th>Values</th>
<th>Designation</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma_r)</td>
<td>13.992</td>
<td>((\sigma_{RD} - \sigma_{ds}))</td>
<td>0.785</td>
</tr>
<tr>
<td>(\sigma_d)</td>
<td>24.967</td>
<td>(\sigma_{ds})</td>
<td>-0.932</td>
</tr>
<tr>
<td>(\sigma_R)</td>
<td>30.257</td>
<td>(\sigma_{RD})</td>
<td>-2.688</td>
</tr>
<tr>
<td>(\sigma_D)</td>
<td>24.736</td>
<td>(\sigma_{Rd})</td>
<td>28.635</td>
</tr>
<tr>
<td>(\sigma_p)</td>
<td>116.998</td>
<td>((\sigma_{RD} - \sigma_{Dp}))</td>
<td>30.473</td>
</tr>
<tr>
<td>(\sigma_s)</td>
<td>118.154</td>
<td>(\sigma_{Rs})</td>
<td>-3.062</td>
</tr>
<tr>
<td>((\sigma_p + \sigma_v))</td>
<td>150.960</td>
<td>(\sigma_{Dp})</td>
<td>11.265</td>
</tr>
<tr>
<td>(\sigma_{rd})</td>
<td>-2.789</td>
<td>((\sigma_{RD} - \sigma_{Dv}))</td>
<td>-13.991</td>
</tr>
<tr>
<td>(\sigma_{rR})</td>
<td>-3.671</td>
<td>(\sigma_{DV})</td>
<td>-24.398</td>
</tr>
<tr>
<td>(\sigma_{RD})</td>
<td>-0.615</td>
<td>((\sigma_{Dp} - \sigma_{Dv}))</td>
<td>-33.875</td>
</tr>
<tr>
<td>(\sigma_{rp})</td>
<td>-5.206</td>
<td>(\sigma_{ao})</td>
<td>-10.820</td>
</tr>
<tr>
<td>((\sigma_{RD} - \sigma_{rs}))</td>
<td>-12.937</td>
<td>(\sigma_{a})</td>
<td>-11.095</td>
</tr>
<tr>
<td>(\sigma_{rs})</td>
<td>9.130</td>
<td>(\sigma_{s})</td>
<td>322.965</td>
</tr>
<tr>
<td>(\sigma_{rs})</td>
<td>-11.080</td>
<td>(\sigma_{t})</td>
<td>970.058</td>
</tr>
<tr>
<td>(\sigma_{rd})</td>
<td>0.203</td>
<td>(\sigma_{t})</td>
<td>324.161</td>
</tr>
<tr>
<td>(\sigma_{sp})</td>
<td>-18.185</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table IV

Mean amplitudes of vibration \((10^{-1} \times Nm)\) of FC(O)SCl and related molecules

| Molecules | \(l_{C-O}\) | \(l_{C-F}\) | \(l_{C-S}\) | \(l_{S-CI}\) | | |
|-----------|-------------|-------------|-------------|-------------| | | |
| FC(O)SCl  | 0.03741     | 0.04997     | 0.05501     | 0.04974     | Present investigation |
| SCl₂      | —           | —           | —           | 0.0487      | Ref [15] |
| CF₂O      | 0.0360      | 0.0439      | —           | —           | Ref [15] |
| CF₄        | —           | 0.0448      | —           | —           | Ref [15] |
| CS₂        | —           | —           | 0.0387      | —           | Ref [15] |

The generalized mean square amplitudes of vibration are presented in Table V. The parallel mean square amplitudes of vibration \(\langle (\Delta Z)^2 \rangle\) coincide very well with the mean square amplitude quantities \(\langle \sigma \rangle\).

The Coriolis coupling constants are useful to analyse the vibration–rotation spectra of polyatomic molecules. The constants \(\eta^x\) and \(\eta^y\) arise due to the coupling \(A' \times A''\) and their calculated values are listed in Table VI.

The centrifugal distortion constants are presented in Table VII. Due to the high moment of inertia \(I_c\), the \(D_{ij}\) and \(D_{JK}\) values are low. We could not compare our values with the experimental ones, since the experimental centrifugal distortion constants are not available in literature.

The thermodynamic functions such as enthalpy \((H)\), heat capacity \((C_p)\), free energy \((F)\) and entropy \((S)\) are listed in Table VIII. These functions are evaluated for

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Table V

Generalized mean square amplitudes of vibration \((10^{-6} \times \text{Nm}^2)\) of FC(O)SCI

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>Designation</th>
<th>FC(O)SCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C – S</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((30.257, 8.607, 59.013))</td>
</tr>
<tr>
<td>C – F</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((24.967, 119.273, 83.195))</td>
</tr>
<tr>
<td>C = O</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((13.996, 132.450, 29.857))</td>
</tr>
<tr>
<td>S – Cl</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((24.736, 111.741, 133.192))</td>
</tr>
<tr>
<td>Cl ... C</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((110.919, 80.609, 74.420))</td>
</tr>
<tr>
<td>F ... S</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((150.702, 62.279, 2.670))</td>
</tr>
<tr>
<td>O ... F</td>
<td>((\langle dZ \rangle^2, \langle dX \rangle^2, \langle dY \rangle^2))</td>
<td>((114.576, 8.672, 63.304))</td>
</tr>
</tbody>
</table>

several temperatures for one atmospheric pressure \((10^5 \text{Nm}^{-2})\) using the rigid rotor-harmonic oscillator approximation. The thermodynamic functions evaluated are the sum of translational, rotational and vibrational contributions.

Table VI

Coriolis coupling constants of FC(O)SCI

\(A \times A''\) coupling

<table>
<thead>
<tr>
<th>(\zeta_{ij}^x)</th>
<th>(\zeta_{ij}^y)</th>
<th>(\zeta_{ij}^z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\zeta_{18})</td>
<td>0.81749</td>
<td>0.46248</td>
</tr>
<tr>
<td>(\zeta_{19})</td>
<td>0.20708</td>
<td>0.08328</td>
</tr>
<tr>
<td>(\zeta_{28})</td>
<td>-0.49599</td>
<td>0.53730</td>
</tr>
<tr>
<td>(\zeta_{29})</td>
<td>-0.30540</td>
<td>0.11737</td>
</tr>
<tr>
<td>(\zeta_{38})</td>
<td>0.09928</td>
<td>-0.15561</td>
</tr>
<tr>
<td>(\zeta_{39})</td>
<td>-0.37506</td>
<td>0.03068</td>
</tr>
<tr>
<td>(\zeta_{48})</td>
<td>-0.05132</td>
<td>0.20932</td>
</tr>
<tr>
<td>(\zeta_{49})</td>
<td>0.29641</td>
<td>-0.04229</td>
</tr>
<tr>
<td>(\zeta_{58})</td>
<td>0.09257</td>
<td>-0.59523</td>
</tr>
<tr>
<td>(\zeta_{68})</td>
<td>-0.18922</td>
<td>0.20713</td>
</tr>
<tr>
<td>(\zeta_{69})</td>
<td>0.19303</td>
<td>0.13931</td>
</tr>
<tr>
<td>(\zeta_{78})</td>
<td>-0.17124</td>
<td>-0.07224</td>
</tr>
<tr>
<td>(\zeta_{79})</td>
<td>0.21679</td>
<td>-0.63448</td>
</tr>
</tbody>
</table>

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Table VII
Centrifugal distortion constants (kHz) of FC(O)SCI

<table>
<thead>
<tr>
<th>Designation</th>
<th>Computed values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_J$</td>
<td>19.219</td>
</tr>
<tr>
<td>$D_K$</td>
<td>17.399</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>-36.519</td>
</tr>
<tr>
<td>$R_5$</td>
<td>0.468</td>
</tr>
<tr>
<td>$R_6$</td>
<td>0.133</td>
</tr>
<tr>
<td>$\delta_J$</td>
<td>0.905</td>
</tr>
</tbody>
</table>

Table VIII
Thermodynamic functions of FC(O)SCI molecule (Joule·mol$^{-1}$K$^{-1}$)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$S$</th>
<th>$F$</th>
<th>$C_p$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>247.96105</td>
<td>209.17661</td>
<td>46.89268</td>
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</tr>
<tr>
<td>200</td>
<td>285.22557</td>
<td>238.46065</td>
<td>62.87627</td>
<td>46.76492</td>
</tr>
<tr>
<td>273.16</td>
<td>306.04589</td>
<td>253.87842</td>
<td>71.60534</td>
<td>52.16747</td>
</tr>
<tr>
<td>300</td>
<td>312.99714</td>
<td>258.93613</td>
<td>74.47482</td>
<td>54.06101</td>
</tr>
<tr>
<td>400</td>
<td>335.59541</td>
<td>275.33587</td>
<td>82.71751</td>
<td>60.25953</td>
</tr>
<tr>
<td>500</td>
<td>354.87464</td>
<td>289.44063</td>
<td>88.41830</td>
<td>65.43401</td>
</tr>
<tr>
<td>600</td>
<td>371.26923</td>
<td>301.67954</td>
<td>92.49781</td>
<td>69.58970</td>
</tr>
<tr>
<td>700</td>
<td>385.61705</td>
<td>312.57475</td>
<td>95.48918</td>
<td>73.04230</td>
</tr>
<tr>
<td>800</td>
<td>398.51089</td>
<td>322.52508</td>
<td>97.76125</td>
<td>75.98582</td>
</tr>
<tr>
<td>900</td>
<td>410.20849</td>
<td>331.67009</td>
<td>99.52708</td>
<td>78.53841</td>
</tr>
<tr>
<td>1000</td>
<td>420.94663</td>
<td>340.19397</td>
<td>108.89248</td>
<td>80.75257</td>
</tr>
</tbody>
</table>

Conclusions

In the present study a number of interaction force constants were refined and a reasonable set of force constants was obtained. The calculated mean amplitudes of vibration are found to be very reasonable, since they compare well with the related molecules. The centrifugal distortion constants would be useful for the future microwave studies of this molecule.

Acknowledgement

One of the authors, Dr. A. Natarajan, wishes to thank the University Grants Commission, Govt. of India, and the Hungarian Ministry of Culture and Education for having selected him to visit Hungary under the Indo–Hungarian Cultural Exchange programme. The authors gratefully acknowledge the valuable comments on the manuscript by Dr. P. Császár, Laboratory of Theoretical Chemistry, Eötvös Loránd University, Budapest, Hungary.

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PRESSURE DEPENDENT E.M.F. 
OF THERMOCOUPLES

A. HAAS

Central Research Institute for Measurement Techniques
Budapest, Hungary

(Received 2 April 1985)

The paper deals with the influence of the stationary pressure on the e.m.f. of a thermocouple, by using Onsager’s irreversible thermodynamic equations. The conductivities, the thermodynamic forces and fluxes are expressed by measurable physical constants, and the pressure dependent e.m.f. of a thermocouple is deduced by the phenomenological equations.

1. Introduction

Mechano-electrical phenomena constitute the most neglected part of theoretical physics. Although the very first observed electric phenomenon was triboelectricity, the theory of mechano-electrical phenomena has made very little progress even since the birth of irreversible thermodynamics. To this neglected group of phenomena belongs the pressure dependence of the e.m.f. of thermocouples.

Nowadays the measurement of temperatures by thermocouples is sometimes performed under extreme conditions. Such is the temperature measurement under high static pressures for which purpose the thermocouple is quite suitable in view of its small size and pressure resistance.

Since the measured thermo e.m.f. is pressure dependent, it is difficult to establish the temperature because of this second variable even if the pressure is precisely known. This is a good example of the often emphasized view against the usual reversible direct methods [1], [2], [3] that an axiomatic irreversible measurement theory based on thermodynamics is missing. If such a theory were available it might well furnish an overall comprehensive picture on the influencing quantities, and the information transport [10] and it would enable rigorous significance tests, in contrast to practices when the significance of variables is decided a priori on the ground of plausibility.

Instead of the quantitative evaluation of the conductivity matrix of Onsager [4], [5] which characterizes the direct and indirect interactions in all their respects, only one a priori chosen element or part of this matrix is considered by some reversible theory for a direct interaction, irrespective of the overlooked irreversibility and its neglected consequences. But measurement information or negentropy transport is typically an irreversible feature, which cannot be described by reversible methods.
The following phenomenologic treatment is restricted to static pressures and temperatures, i.e. to the stationary state of the thermocouples.

A successful treatment of thermoelectricity was given in 1854 by Kelvin, but even he himself emphasized that the used reversible thermodynamics does not necessarily explain the obtained agreement with the measurements. Therefore this treatment must be handled with care and must be regarded as a curious coincidence.

Despite this warning, Kelvin's reversible arguments were republished many times as a strict treatment of the thermoelectric phenomena, as was pointed out by Callen. The first strict irreversible theory of thermoelectric phenomena originates from Callen [6], [7]. Although his treatment covers the galvano and thermomagnetic phenomena of thermocouples too, he does not deal with the pressure dependence of the thermo e.m.f., though this aspect could be treated similarly to [7]. Despite this, the literature of thermoelectricity does not mention the theoretical treatment of this subject.

The pressure dependence of the thermo e.m.f. is an empirical fact [8], [9] and the authors emphasize the insufficiency of our present knowledge to give reliable theoretical statements on this subject.

Without negating this view, based on the Fermi statistics of electrochemical potential, I wish to point out that the phenomenological treatment of this complex problem was still not dealt with. However, in order to understand and define the basic quantities this first step cannot be bypassed if further more enlightening studies are envisaged.

The thermo e.m.f. is generated at every inhomogeneity also in a single wire of one material used as a thermocouple leg. Inhomogeneities are formed by local impurities or by local stresses such as the stress residues of forming, causing e.m.f. drifts.

In order that undesired drift effects could be accounted for, the idealized, i.e. homogeneous, case is to be treated first as a reference to define our expectations.

Similarly to the pressure independent case, here also crystal phase transitions disturb the better understanding of the underlying microphysical phenomena, however, the existence of such disturbing phenomena has not made unnecessary Kelvin's and Callen's basic theoretical endeavours. The application of thermocouples today would not be possible to the observed extent without a firm theoretical basis serving as a reference.

It is known from the literature [8], [9] that pressure dependence is significant only for the Kbar regions. For measurements of high accuracy, the order of the errors due to pressures at lower regions, may be of interest, too.

### 2. Strains and strain energies in a wire under static pressure

When compressing a substance, e.g. a measurement sensor, (besides the deformation) heat is generated, too, which is transferred to the environment until the substance reaches thermodynamic equilibrium and its temperature and pressure
becomes equal to that of its environment. When compressing a wire, e.g. a leg of a thermocouple, the same happens and stresses with accompanying strains are produced and the electrochemical potential also reaches a new equilibrium value due to the pressure dependence of the electrochemical potential of the electron gas whereas the number of molecules forming the wire remain unchanged.

The calibration of thermocouples is carried out in steady state of the measurand, therefore our investigations will be restricted to stationary, i.e. time independent, states. The compression of the molecular structure of the wire must remain below the elastic limit so that the material is not destroyed and remains suitable for measurements.

Since only the stationary state is examined, repeated dynamic pressures are excluded and so the heat developed by internal friction is transferred in due time to the environment. The elastic phenomenon may therefore be regarded as a reversible one and the irreversibility will be referred solely to the cross-effect of the compressed electron gas. The following treatment is therefore not applicable to quickly changing dynamic pressures causing accumulating, inner friction generated entropy-production and strains beyond the elastic limit.

The stress–strain relations are simply adopted from the usual reversible theory of elasticity.

Let us place into a closed space under pressure a loop of homogeneous wire, its parallel legs conducted through a seal. The loop may become axially freely deformed without any axial stresses.

More precisely, the axial stresses generated by the friction of the seal under pressure are neglected compared to the radial and tangential stresses in the wire under pressure. The same neglection would also be possible if instead of a loop a straight wire were to be conducted into the pressurized space, through two opposite seals, securing the free axial deformation of the wire [8], [9].

In order to obtain the strain energy of the wire, let us consider the principal strains produced by the principal stresses. From the differential equation of the

![Fig. 1. Wire cross-section with the principal stresses](image-url)
equilibrium of a radial volume-element of the wire under static external pressure (Figs 1 and 2), the principal stresses are: \( p_1 = 0, p_2 = p_3 = -p \) where \( p_1, p_2, p_3 \) are the axial, the radial and the tangential principal stresses, respectively. The sign (—) expresses compression.

As is known from the theory of elasticity, the principal strains in a compressed bar are:

\[
e_1 = (p_1/E) - \frac{p_2 + p_3}{mE} = 0 + \frac{2p}{mE} \text{ axial strain (exp.),}
\]

\[
e_2 = (p_2/E) - \frac{p_3 + p_1}{mE} = -(p/E)(1 - 1/m) \text{ radial strain (compr.),}
\]

\[
e_3 = (p_3/E) - \frac{p_1 + p_2}{mE} = -(p/E)(1 - 1/m) \text{ tangential strain (compr.).}
\]

where \( E \) is the Young's modulus and \( 1/m \) is the Poisson's ratio.

The strain energies for the principal strains are respectively:

\[
(1/2)p_1e_1 = 0; \quad (1/2)p_2e_2 = (1/2)p^2/E(1 - 1/m)
\]

and

\[
(1/2)p_3e_3 = (1/2)p^2/E(1 - 1/m).
\]

It may be inferred that for a compressed wire two equal volumetric works must be taken into account. Both of them are generated by a single scalar pressure \( p \). Therefore, the thermodynamic treatment may be carried out by scalar instead of tensorial calculus, similarly to the treatment of gases.

3. The fundamental equation

To obtain the fundamental equation of a wire under external pressure extensive parameters \( V_0e_1, V_0e_2, V_0e_3 \) are also to be regarded beyond the usual extensive parameters used for gases, where \( V_0 \) is the undeformed volume of the wire.
The internal energy change in the wire depends also on the volumetric deformation caused by the principal stresses:

\[ dU = TdS - \frac{p_1}{2}d(V_0e_1) - \frac{p_2}{2}d(V_0e_2) - \frac{p_3}{2}d(V_0e_3) + \mu dn. \]

The dimensions are in SI units, otherwise if the entropy were to be in Cal/K, \( AS \) would be supposed instead of \( S \) where \( A \) is the work-equivalent.

Substituting the values of principal stresses \( p_1, p_2, p_3 \) into the last equation:

\[ dU = TdS - pdV + \mu dn, \]

the fundamental equation is obtained, with volume \( V = (V_0e_2) = (V_0e_3) \).

The fundamental equation in entropy representation is therefore:

\[ dS = (1/T)dU + (p/T)dV - \mu/Tdn. \] (1)

The entropic intensive parameters are: \( 1/T, p/T, \mu/T \). The entropic thermodynamic forces are: \( V(1/T), V(p/T), V(\mu/T) \), where the \( V \) is the differential operator of the gradient. The mole number is composed from \( n = n_m + n_e \), the moles of the wire and of the electron gas within the wire. Since the mass of the wire is constant \( dn_m = 0 \) and \( dn = dn_e \), i.e. only the number of the electrons of the electron gas changes.

The chemical potential \( \mu \) consists of two parts \( \mu = \mu_m + \mu_e \), one for the molecules of the wire, the other for the electron gas.

The entropic intensive parameter is \( \mu/T = \mu_m/T + \mu_e/T \) and the work \( \mu/Tdn = \mu_m/Tdn_m + \mu_e/Tdn_e = \mu_e/Tdn_e \); that is, only the electrochemical part is effective. The time derivative of Eq. (1) is:

\[ J_s = (1/T)J_U + (p/T)J_V - (\mu/T)J_n. \] (2)

where \( J_s, J_U, J_V, J_n \) are the fluxes of entropy, internal energy, volume and electrons, respectively.

The entropy production is:

\[ \dot{S} = V(1/T) \cdot J_U + V(p/T) \cdot J_V - V(\mu/T) \cdot J_n. \] (3)

4. The dynamic equations

Onsager’s dynamic equations constitute linear relations between the generalized fluxes \( J_k \) and the generalized thermodynamic forces \( X_i \) by the generalized conductances \( L_{ik} : J_k = \Sigma L'_{ik}X_i \), where \( X_i = V(x_i/T) \) is for intensity \( x_i \). In the case of the wire under external pressure, Eq. (3) contains the required fluxes and forces by which the dynamic equations of the pressure dependent thermocouples are:

\[ -J_n = L'_{11}V(\mu/T) + L'_{12}V(p/T) + L'_{13}V(1/T), \]

\[ J_V = L'_{21}V(\mu/T) + L'_{22}V(p/T) + L'_{23}V(1/T), \]

\[ J_U = L'_{31}V(\mu/T) + L'_{32}V(p/T) + L'_{33}V(1/T). \] (4)
By the reciprocity relations $L_{12} = L_{21}, L_{13} = L_{31}, L_{23} = L_{32}$. The symmetric Eq. (4) will be transformed so that instead of the flux of the internal energy $J_U$ the flux of heat $J_Q$ should appear.

From Eq. (2):

$$J_Q = T J_S = J_U + p J_V - \mu J_n$$

(5)

and

$$\nabla \cdot J_Q = \nabla \cdot J_U + \nabla \cdot (P \cdot J_V) + p \nabla \cdot J_V - (\nabla \cdot \mu) J_n - \mu \nabla \cdot J_n.$$

(6)

In steady state:

$$\nabla \cdot J_U = \nabla \cdot J_V = \nabla \cdot J_n = 0.$$

(The continuity for a generalized $x_k$ extensive parameter is $\partial x_k/\partial t + \nabla \cdot J_k = 0$, at steady state $\partial x_k/\partial t = 0$, that is $\nabla \cdot J_k = 0$.)

From Eq (6):

$$\nabla \cdot J_Q = (P \mu) J_V - (P \mu) J_n.$$

The entropy production becomes, by Eqs (3) and (5)

$$\dot{S} = V(1/T) \cdot J_Q + V(P/T) \cdot J_V - V(\mu/T) \cdot J_n,$$

where $V(1/T) = -(V T/T^2)$.

With the new quantities, derived from the forces and fluxes $J_Q, J_V, -J_n$, the transformed dynamic equations are:

$$-J_n = L_{11} V \mu/T + L_{12} V P/T - L_{13} V T/T^2,$$

$$J_V = L_{21} V \mu/T + L_{22} V P/T - L_{23} V T/T^2,$$

$$J_Q = L_{31} V \mu/T + L_{32} V P/T - L_{33} V T/T^2,$$

(7)

where $L_{12} = L_{21}, L_{13} = L_{31}, L_{23} = L_{32}$.

The determinant of Eq. (7) is:

$$D = \begin{vmatrix}
L_{11} & L_{12} & -L_{13} \\
L_{12} & L_{22} & -L_{23} \\
L_{13} & L_{23} & -L_{33}
\end{vmatrix}.$$

5. Calculation of the thermodynamic forces

The quantities derived from the forces or affinities related to the $J_n, J_V, J_Q$ fluxes, from Eq. (7) are:

$$V \mu/T = D_1/D, \quad V P/T = D_2/D, \quad V T/T^2 = D_3/D,$$

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where:

\[
\begin{pmatrix}
-J_n & L_{12} & -L_{13} \\
J_v & L_{22} & -L_{23} \\
J_Q & L_{23} & -L_{33}
\end{pmatrix}
; \quad
\begin{pmatrix}
L_{11} & -J_n & -L_{13} \\
L_{12} & J_v & -L_{23} \\
L_{13} & J_Q & -L_{33}
\end{pmatrix}
; \quad
\begin{pmatrix}
L_{11} & L_{12} & -J_n \\
L_{12} & L_{22} & J_v \\
L_{13} & L_{23} & J_Q
\end{pmatrix}
\]

For the further calculations some special forms of the affinities are also required, when certain variables are kept constant.

a) If \( J_n = J_v = 0 \)

\[
(V\mu/T)_{n,v} = (J_Q/D)(L_{13}L_{22} - L_{12}L_{23}),
\]

\[
(VT/T^2)_{n,v} = (J_Q/D)(L_{11}L_{22} - L_{12}^2).
\]

From these:

\[
T(V\mu/V T)_{n,v} = -\frac{L_{12}L_{23} - L_{22}L_{13}}{L_{11}L_{22} - L_{12}^2}.
\]

b) If \( J_n = 0 \) and \( dp = 0 \). From the first Eq. of (7):

\[
(V\mu/V T)_{n,p} = (L_{13}/L_{11})(1/T).
\]

c) If \( J_n = J_v = 0 \) eliminating \((V\mu/T)_{n,v}\), from the first two equations of (7):

\[
(Vp/V T)_{n,v} = (1/T)\frac{L_{23}L_{11} - L_{12}L_{13}}{L_{22}L_{11} - L_{12}L_{12}}.
\]

d) If \( J_n = 0 \) and \( dT = 0 \), from the first equation of (7):

\[
(V\mu/V p)_{n,T} = -L_{12}/L_{11}.
\]

e) If \( J_n = 0 \) and \( dS = 0 \), from the first and third equations of (7) eliminating \((V\mu/T)_{n,S}\):

\[
(Vp/V T)_{n,S} = -(1/T)\frac{L_{33}L_{11} - L_{13}}{L_{12}L_{13} - L_{23}L_{11}}.
\]

6. Physical properties used to calculate the conductances

From the nine conductances \( L_{ik} \) three are symmetric. The remaining six unknown conductances are to be determined by using six relations for physical properties.
I) The electric conductivity at constant pressure and temperature:

\[ \sigma_{T,p} = - \frac{\text{electric current density}}{\text{gradient of electric potential}}. \]

The current density is: \( e(J_n)_{T,p} \).

The electric potential gradient is:

\[ (V \phi)_{T,p} = \left[ \frac{\partial (e \phi)}{\partial e} \right]_{T,p} = \frac{\partial (\mu/e)}{\partial T}. \]

\[ \sigma_{T,p} = - \left( \frac{e J_n}{V \phi} \right)_{T,p} = - e^2 (J_n/V \mu)_{T,p}. \]

II) The heat conductivity \( J_n = J_V = 0 \):

\[ (\kappa_h)_{n,V} = -(J Q/V T)_{n,V}. \]

III) The Seebeck coefficient \( J_n = 0 \) and \( dp = 0 \):

\[ (e_T)_{n,p} = (V \phi/V T)_{n,p} = (V \mu/e V T)_{n,p}. \]

IV) The pressure dependent thermoelectric coefficient \( J_n = 0 \) and \( dT = 0 \):

\[ (e_p)_{n,T} = (V \phi/V p)_{n,T} = (V \mu/e V p)_{n,T}. \]

The electrochemical potential \( \mu = f(t, p) \) is a function of two variables. Besides the Seebeck effect therefore, a second pressure-electric cross-effect does exist.

V) The isochor stress coefficient \( \beta, dV = dn = 0 \)

\[ \beta_{V,n} = (1/p) (V p/V T)_{V,n}. \]

Between this coefficient and the isobaric heat expansion coefficient \( \alpha_{p,n} \) and the isothermal compressibility \( \kappa_{T,n} \) there is a known relation:

\[ \frac{(V p/V T)_{V,n}}{(V p/V T)_{T,n}} = \frac{\alpha_{p,n}}{\kappa_{T,n}}, \]

where \( \alpha_{p,n} = (1/V) (V V/VT)_{p,n} \) and \( \kappa_{T,n} = -(1/V) (V V/V p)_{T,n} \).

VI) The adiabatic stress coefficient at \( dS = 0 \) and \( dn = 0 \) is:

\[ \beta_{S,n} = (1/p) (V p/V T)_{S,n}. \]

It is known that:

\[ \frac{(V p/V T)_{S,n}}{(V S/V T)_{p,n}} = \frac{(n/V) (c_p/T)}{\alpha_{p,n}}. \]

Namely \( c_{p,n} = (T/n) (V S/V T)_{p,n} \) is the specific heat at constant pressure, and in accordance with the Maxwell relations:

\[ V \alpha_{p,n} = -(V V/V T)_{p,n} = (V S/V p)_{T,n}. \]

By these six relations the unknown conductances \( L_{i,k} \) \( i, k = 1, 2, 3 \) are explicitly obtainable.

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7. Calculation of the \( L_{\text{ik}} \) conductances

By the six relations of para 6 six equations are obtained for the unknown quantities:

From I) of para 6:

\[
\sigma = -\varepsilon^2 (J_n/\mathcal{V}\mu)_{p,T}
\]

and from the first equation of (7):

\[
(-J_n)_{p,T} = L_{\text{i}1}(\mathcal{V}\mu/T)_{p,T} + 0 + 0,
\]

that is

\[
-(J_n/\mathcal{V}\mu)_{p,T} = L_{\text{i}1}/T = \sigma/\varepsilon^2.
\]

From II) of para 6:

\[
(\kappa_b)_{n,V} = -(J_q/\mathcal{V}T)_{n,V}.
\]

Substituting \( J_n = J_V = 0 \) into the first two equations of (7) and after the elimination of \( (\mathcal{V}\mu/T)_{n,V} \), the \( (\mathcal{V}p/T)_n,V \) quantity may be expressed by \( -(\mathcal{V}T/T^2)_{n,V} \).

By these from the third of equation of (7):

\[
T^2(\kappa_b)_{V,n} = \frac{(L_{\text{2}3}L_{\text{i}11} - L_{\text{i}12}L_{\text{i}3})^2}{L_{\text{i}11}(L_{\text{1}2}^2 - L_{11}L_{22})} + \frac{L_{33}L_{\text{i}11} - L_{3}^2}{L_{\text{i}11}}.
\]

From III) of para 6:

\[
(\varepsilon_T)_{p,n} = (1/\varepsilon)(L_{13}/L_{11})(1/T).
\]

From IV) of para 6:

\[
(\varepsilon_p)_{T,n} = -(1/\varepsilon)(L_{12}/L_{11}).
\]

From V) of para 6:

\[
(\mathcal{V}p/\mathcal{V}T)_{V,n} = \frac{L_{23}L_{\text{i}11} - L_{\text{i}12}L_{13}}{L_{\text{2}2}L_{\text{i}11} - L_{12}^2} (1/T) = \alpha_{p,n} / (\kappa_T)_{T,n}.
\]

From VI) of para 6:

\[
(\mathcal{V}p/\mathcal{V}T)_{S,n} = \frac{L_{33}L_{\text{i}11} - L_{3}^2}{L_{12}L_{13} - L_{23}L_{11}} (1/T) = (n\varepsilon_p)_{n}(TV\alpha_{p,n}).
\]
By solving the system of equations, the required $L_{ik}$ conductances are:

$$L_{11} = T\frac{\sigma}{e^2},$$

$$L_{12} = -(T\frac{\sigma}{e})(e_p)_{T, n},$$

$$L_{13} = (T^2\frac{\sigma}{e})(e_T)_{p, n},$$

$$L_{23} = -\frac{\kappa_h T^2}{\kappa_T n c_p} - T^2\frac{\sigma}{e} e_p,$$

$$L_{22} = \frac{T \frac{\sigma}{e} n c_p}{\kappa_T \alpha_p VT} - \frac{T \frac{\alpha}{e} e_p}{\kappa_T},$$

$$L_{33} = \frac{\kappa_h T^2}{\alpha_p VT} - \frac{T \frac{\alpha}{e} e_p}{\kappa_T} + T^3\frac{\sigma}{e^2}.$$

If the conductances are explicitly expressed by measurable quantities, the phenomenological equations of the pressure dependent thermoelectric phenomenon, i.e. the thermodynamic forces and fluxes, are also determined and may be used to calculate the e.m.f. of thermocouples.

8. Pressure dependent e.m.f. of thermocouples

Until now we have dealt with the thermoelectric potential of a single wire made of homogeneous material. The chemical potential like the electric potential is a one-valued function of the location.

Thermocouples are welded from two kinds of homogeneous wires. The scheme of a thermocouple under pressure is shown in Fig. 3.

Let us suppose that $T_2 > T_c = T_q > T_1$ and $p_2 \gg p_r = p_q = p_1$.

![Scheme of a thermocouple](image)

*Fig. 3. Scheme of a thermocouple with the characteristic parameters and pressure dependent e.m.f. $V_e$*

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From the first Eq. of (7) if $J_n = 0$:

$$V\mu = -(L_{12}/L_{11})Vp + (L_{13}/L_{11})(VT/T) = e(\varepsilon_T VT + \varepsilon_p VP),$$

or with other denominations:

$$d\mu = e(\varepsilon_T dT + \varepsilon_p dp) \quad \text{where} \quad \varepsilon_T = (\partial\mu/\partial T)_{n,p}$$

and

$$\varepsilon_p = (\partial\mu/\partial p)_{n,T}.$$ 

The line integral of the chemical potential in the closed loop is:

$$\oint d\mu = \oint A d\mu^A + \oint B d\mu^B = \mu_T - \mu_q \quad \text{since} \quad \mu^A = \mu^B_1 \quad \text{and} \quad \mu^A = \mu^B_2,$$

where

$$\oint A d\mu^A = \mu^A_2 - \mu^A_1 = e \oint \left[ (\varepsilon^A_T) dT + (\varepsilon^A_p) dp \right],$$

$$\oint B d\mu^B = \mu^B_2 - \mu^B_1 = e \oint \left[ (\varepsilon^B_T) dT + (\varepsilon^B_p) dp \right],$$

$$\oint q d\mu^Q = \mu^Q_2 - \mu^Q_1 = e \oint \left[ (\varepsilon^Q_T) dT + (\varepsilon^Q_p) dp \right].$$

Since $T_r = T_q$ and $p_r = p_q$, from these:

$$\mu_r - \mu_q = e \oint \left\{ (\varepsilon^A_T + \varepsilon^A_p(dp/dT)) - (\varepsilon^B_T + \varepsilon^B_p(dp/dT)) \right\} dT.$$ 

The thermo e.m.f. is:

$$V_e = (1/e)(\mu_r - \mu_q) \quad \text{and} \quad \partial V_e/\partial T_2 = \varepsilon^{AB} = \varepsilon^B - \varepsilon^A,$$

where $\varepsilon^{AB}$ is the pressure dependent thermoelectric coefficient of the thermocouple, with:

$$\varepsilon^B = -(\varepsilon^B_T + \varepsilon^B_p(dp/dT)),$$

$$\varepsilon^A = -(\varepsilon^A_T + \varepsilon^A_p(dp/dT)).$$

9. Summary

So far as we are aware, the literature contains no phenomenological equations dealing with the pressure dependent e.m.f. The present paper has attempted to fill this gap by extending the irreversible method of Callen to the pressure dependent case. The obtained relations may serve as a point of departure to further studies on the pressure dependence of thermoelectricity.
References

ON THE AMBIGUITY IN THE BETHE'S ANSATZ SOLUTION OF ONE-DIMENSIONAL MODELS WITH LINEAR DISPERSION

KAZUMASA ITAI

Central Research Institute for Physics
1525 Budapest, Hungary

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It is shown that one-dimensional models which are soluble by Bethe's Ansatz have in their solution a certain ambiguity. It is demonstrated that questions concerning the relations between physical quantities and coupling constants are meaningful only in the case of weak coupling.

In recent years Bethe's Ansatz has been successfully applied to many models. It is indisputable that the most remarkable one among them is the application to the Kondo problem [1]. In order to apply Bethe's Ansatz to this problem the original three-dimensional $s$--$d$ Hamiltonian is reduced to a one-dimensional one, and furthermore the energy spectrum of the conduction electrons is linearized. The latter process is not necessary but convenient for simplicity. When the dispersion is linear, the two kinds of variables, i.e. quasi wave numbers and quasi spin-wave numbers, are not coupled to each other in the Bethe Ansatz equations, and this property makes the calculations easier to be carried out to further extent than in coupled cases. The situation is the same in the one-dimensional electron gas model (Luttinger model), which was also solved by Bethe's Ansatz [2]. More specific statements are reached in this model than in other models of interacting electrons with non-linear dispersion, e.g. electron gas model with quadratic dispersion, the Hubbard model.

The linear dispersion, however, causes an undesirable property, that is, an ambiguity in the relation between physical quantities and coupling constants. This kind of ambiguity was shown first in the massless Thirring model a quarter of century ago [3].

This ambiguity can be demonstrated essentially even in a one-body problem with $\delta$-function potential. So first we will consider the Schrödinger equation for particles with linear dispersion:

$$-i\frac{\partial}{\partial x} \varphi(x) + g\delta(x)\varphi(x) = E\varphi(x). \quad (1)$$

The solution can be written in the form

$$\varphi(x) = \theta(x)C_+ e^{ikx} + \theta(-x)C_- e^{ikx}. \quad (2)$$
The problem is only to decide the relation between $C_+$ and $C_-$. By integrating Eq. (1) between $x = -\epsilon$ and $x = \epsilon$, where $\epsilon$ is infinitesimal, we get

$$C_+ = \frac{1 - ig/2}{1 + ig/2} C_-.$$  

(3)

It must be noted that here we have used

$$\int_{-\epsilon}^{\epsilon} \delta(x) \varphi(x) \, dx = \frac{1}{2} \{ \varphi(+0) + \varphi(-0) \}. \tag{4}$$

On the other hand, we can get a solution of Eq. (1) as a limit of that of some nonsingular equation which becomes Eq. (1) in the limit. In this way we obtain

$$\varphi(x) = \lim_{D(x) \to \delta(x)} \exp \left\{ -ig \int_{-\infty}^{x} D(x') \, dx' \right\} e^{ikx}, \tag{5}$$

from which the relation between $C_+$ and $C_-$ is now

$$C_+ = e^{-ig} C_-,$$  

(6)

which apparently does not agree with solution (3). The slight difference between the results of the Kondo problem by Wiegmann and Andrei originates from this ambiguity. Wiegmann uses (6) and Andrei (3).

This disagreement originates from the discontinuity of the wave function. When the wave function has a discontinuity, we are allowed to use instead of (4)

$$\int_{-\epsilon}^{\epsilon} \delta(x) \varphi(x) \, dx = \left( \frac{1}{2} + if \right) \varphi(+0) + \left( \frac{1}{2} - if \right) \varphi(-0), \tag{7}$$

where $f$ is an arbitrary real number. Now we have

$$C_+ = \frac{1 - gf - ig/2}{1 - gf + ig/2} C_-.$$  

(8)

If we choose $f = g^{-1} - f'$, (8) becomes

$$C_- = \frac{f' - i/2}{f' + i/2} C_-.$$  

(9)

This expression is a little bit surprising, for the original coupling constant, i.e. $g$, has disappeared. But one will soon notice that some restriction is naturally imposed on $f'$ as a consequence of the fact that when $g$ goes to zero the wave function must become continuous, that is, $f'$ must go to infinity when $g$ goes to zero. Now let us consider
Eq. (7) for small values of $g$. Using (9), Eq. (7) becomes

$$
\int_{-\epsilon}^{\epsilon} \delta(x) \varphi(x) \, dx = \left[ \left\{ \frac{1}{2} + i \left( \frac{1}{2} - f' \right) \right\} \frac{f' - i/2}{f' + i/2} + \left\{ \frac{1}{2} - \left( \frac{1}{g} - f' \right) \right\} \right] \varphi(-0)
$$

$$
= \frac{1}{g(f' + i/2)} \varphi(-0) \simeq \frac{1}{g f'} \varphi(-0).
$$

(10)

Since the left-hand side of (10) is equal to $\varphi(0)$ when $\varphi(x)$ is continuous, we have the further restriction on $f'$ that $gf'$ must go to unity as $g$ goes to zero. This leads to the condition that $f'$ must have the form

$$
f' = \frac{1}{\alpha(g)} + \beta(g),
$$

(11)

where $\alpha(g)$ and $\beta(g)$ are arbitrary functions of $g$ with such constraints that $\alpha(g) \to g$ and $g\beta(g) \to 0$ as $g \to 0$.

The disagreement between the two solutions (3) and (6) is understood as two different choices of $\alpha(g)$ and $\beta(g)$. If we take $\alpha(g) = 0$ and $\beta(g) = 0$, we get solution (3), and if we take $\alpha(g) = \tan g$, $\beta(g) = 0$, we get solution (6). The relation between $C_+$ and $C_-$ is written in the most general form as

$$
C_+ = \frac{1 - ig^2}{1 + ig^2} C_-, \quad \text{where} \quad \tilde{g} = \frac{\alpha(g)}{1 + \alpha(g) \beta(g)}.
$$

(12)

The situation is essentially the same in the $s$-$d$ model or the electron-gas model. In the following we are going to discuss the latter model, but the results can be translated also for the $s$-$d$ model, because the $s$-$d$ model can be obtained from the electron-gas model by slight modifications.

The Hamiltonian of the electron-gas model [2] is written in the form

$$
H = -i \int \psi_{aa}^{\dagger} \tau_x^z \frac{\partial}{\partial x} \psi_{aa} \, dx - \frac{1}{2} \int \psi_{ab}^{\dagger} \psi_{ab} \{ V \delta_{xx'} \delta_{\beta\beta'} + g_{ab} \sigma_{xx'}^{\dagger} \sigma_{\beta\beta'}^{\dagger} +
$$

$$
+ g_{\perp} (\sigma_{xx'}^{\dagger} \sigma_{\beta\beta'}^{\dagger} + \sigma_{xx'} \sigma_{\beta\beta'}) \} \{ \delta_{aa'} \delta_{bb'} + \tau_{\tilde{g}}^z \tau_{\tilde{g}}^z \} \psi_{b'b'} \psi_{a'a'} \, dx,
$$

(13)

where the $\tau^z$ operator $\left( \tau^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right)$ is used for brevity to point out right-going and left-going electrons. The wave function of $N$ particles satisfies the equation

$$
\sum_n \left( -i \tau_n^z \frac{\partial}{\partial x_n} \right) - \sum_{n < m} \{ \nabla + g_{ab} \sigma_{x}^{\dagger} \sigma_{y}^{\dagger} + g_{ab} (\sigma_{x}^{\dagger} \sigma_{y} + \sigma_{x} \sigma_{y}^{\dagger}) \} \{ (1 - \tau_n^z \tau_m^z) \} (x_n - x_m) \right] \varphi = E \varphi,
$$

and in the domain $Q: x_{Q_1} < x_{Q_2} < \ldots < x_{Q_N}$ it is expected to take the form

$$
\varphi^Q = \sum_{P} (-1)^{\pi_P} \Phi_{PQ} (\sigma_{Q_1} \sigma_{Q_2} \ldots \sigma_{Q_N}) u_1(\tau_{P_1}) u_2(\tau_{P_2}) \ldots u_N(\tau_{P_N}) \exp \left\{ i \sum_{j} k_j x_j \right\},
$$

(15)

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where \( P \) and \( Q \) are permutations of 1, 2, \ldots, \( N \). \( \Phi_{PQ}(\sigma_1, \ldots \sigma_N) \)'s correspond to \( C \) in (2), but now they contain the spin part of the wave function. \( u(\tau) \) is an eigenfunction of \( \tau^2 u(\pm 1) = \pm u(\pm 1) \), \( u(+1) \) and \( u(-1) \) correspond to right-going and left-going electrons, respectively.

The first step in the prescriptions of the Bethe Ansatz method is to decide the relation between \( \Phi \)'s of the neighbouring domains from the matching condition on the boundary. Integrating (14) in an infinitesimal interval around the boundary, we get

\[
\phi^Q(x_{Q+1}+0 = x_Q) - \phi^Q(x_{Q+1} = x_Q+0) +
\]

\[
i\left[V + g_{||}^Q \sigma_0^Q \sigma_{0,Q+1}^Q + g_\perp (\sigma_0^Q \sigma_{Q+1}^Q + \sigma_{0,Q+1}^Q \sigma_0^Q) \right] (1 - \tau_{PQ}^Q \tau_{PQ+1}^Q) \times
\]

\[
\left\{ \left( \frac{1}{2} + \imath \gamma \right) \phi^Q(x_{Q+1}+0 = x_Q) + \left( \frac{1}{2} - \imath \gamma \right) \phi^Q(x_{Q+1} = x_Q+0) \right\} = 0,
\]

where \( \gamma \) is an ambiguous quantity like \( f \) in (7), in the present case, however, spin operators can also be contained in it. When the coupling constants go to zero, the same kind of restrictions are imposed on \( \gamma \) as before, and we obtain the most general form of the relation between \( \Phi \)'s as follows

\[
\Phi_{PQ}(\sigma_1, \ldots \sigma_N) = S_{Q,Q+1}(\tau_{PQ} - \tau_{PQ+1}) \Phi_{PQ(i+1)}(\sigma_1, \ldots \sigma_{i+1}, \sigma_{i+1}, \ldots \sigma_N),
\]

where \((i,j)\) means permutation of \( i \) and \( j \), and

\[
a(\tau) = \frac{1}{2} - i \alpha_{11}(\tau)/2 + \frac{1}{4} \frac{1 - i \alpha_{10}(\tau)/2}{1 + i \alpha_{10}(\tau)/2} + \frac{1}{4} \frac{1 - i \alpha_{0}(\tau)/2}{1 + i \alpha_{0}(\tau)/2},
\]

\[
b(\tau) = \frac{1}{2} - i \alpha_{11}(\tau)/2 - \frac{1}{4} \frac{1 - i \alpha_{10}(\tau)/2}{1 + i \alpha_{10}(\tau)/2} - \frac{1}{4} \frac{1 - i \alpha_{0}(\tau)/2}{1 + i \alpha_{0}(\tau)/2},
\]

\[
c(\tau) = \frac{1}{4} \frac{1 - i \alpha_{10}(\tau)/2}{1 + i \alpha_{10}(\tau)/2} - \frac{1}{4} \frac{1 - i \alpha_{0}(\tau)/2}{1 + i \alpha_{0}(\tau)/2},
\]

\[
\alpha_{11}(\lambda_{11}) = \frac{1}{1 + \alpha_{1}(\lambda_{11}) \beta_{1}(\lambda_{11})}, \quad \lambda_{11} = \frac{1}{2} (V + g_{||}),
\]

\[
\alpha_{10}(\lambda_{10}) = \frac{1}{1 + \alpha_{2}(\lambda_{10}) \beta_{2}(\lambda_{10})}, \quad \lambda_{10} = \frac{1}{2} (V - g_{||} + 2g_\perp),
\]

\[
\alpha_{0}(\lambda_{0}) = \frac{1}{1 + \alpha_{3}(\lambda_{0}) \beta_{2}(\lambda_{0})}, \quad \lambda_{0} = \frac{1}{2} (V - g_{||} - 2g_\perp),
\]

where \( \alpha \)'s and \( \beta \)'s are the same kind of arbitrary functions as in (11).
Following the prescriptions of the Bethe Ansatz method, the energy eigenvalue of the system is obtained as

\[ E = \sum_{m=1}^{N} \tau_m k_m. \tag{21} \]

The quasi-momenta \( k_m \) in (21) are determined by the equation (the Bethe Ansatz equation)

\[ e^{ik_m L} = \prod_{\alpha=1}^{M} \left[ \frac{\sin \left\{ 2\xi + \frac{\mu}{2} (\nu_\alpha - \tau_m) \right\}}{\sin \frac{\mu}{2} (\nu_\alpha - \tau_m)} \right] \cdot \prod_{n=1}^{N} \frac{1 - i\lambda_{11} \frac{\tau_m - \tau_n}{2}}{1 + i\lambda_{11} \frac{\tau_m - \tau_n}{2}}, \tag{22} \]

where the quasi-spinwave numbers \( \nu_\alpha \) satisfy the equation (also the Bethe Ansatz equation)

\[ -\prod_{\beta=1}^{M} \left[ \frac{\sin \left\{ 2\xi + \frac{\mu}{2} (\nu_\beta - \nu_\alpha) \right\}}{\sin \left\{ 2\xi - \frac{\mu}{2} (\nu_\beta - \nu_\alpha) \right\}} \right] = \prod_{m=1}^{N} \left[ \frac{\sin \left\{ \frac{\mu}{2} (\nu_\alpha - \tau_m) \right\}}{\sin \left\{ 2\xi + \frac{\mu}{2} (\nu_\alpha - \tau_m) \right\}} \right]. \tag{23} \]

\( \xi \) and \( \mu \) in (22), (23) are related to \( \lambda \)'s in the following way:

\[ \cos \mu = \frac{\lambda'' + \lambda'}{\lambda'' - \lambda'}, \quad \cos 2\xi = \frac{\lambda'' \lambda' - 1}{\lambda'' \lambda' + 1}, \quad \sin 2\xi = -i\lambda \sin \mu, \tag{24} \]

where

\[ \lambda = \frac{\lambda_{11} - \lambda_0}{1 + \lambda_{11} \lambda_0}, \quad \lambda' = \frac{\lambda_{11} - \lambda_0}{1 + \lambda_{11} \lambda_0}, \quad \lambda'' = \frac{\lambda_{11} - \lambda_0}{1 + \lambda_{11} \lambda_0}. \tag{25} \]

Physical quantities are obtained from (21), (22) and (23), and those are expressed in terms of \( \xi \) and \( \mu \), which, in turn, are related to the coupling constants through (20), (24) and (25). Since the restriction on \( \alpha \)'s and \( \beta \)'s is not so strong, we have some freedom to choose these functions and thereby the relations between physical quantities and coupling constants. For example if \( \alpha(\lambda) = \tan \lambda \) and \( \beta(\lambda) = 0 \) are chosen, the physical quantities will show periodicity as a function of the bare couplings. So this show that the question concerning the relations between physical quantities and coupling constants is meaningless. Only in the case of weak coupling is it meaningful to discuss them, because the ambiguity happens only in higher order terms of the coupling constants. In the weak coupling limit we get

\[ \lambda \simeq \lambda_{10} - \lambda_0 = 2g_\perp, \quad \lambda' \simeq \lambda_{11} - \lambda_0 = g_\parallel + g_\perp, \quad \lambda'' \simeq \lambda_{11} - \lambda_{10} = g_\parallel - g_\perp. \tag{26} \]
For example let us consider the phase diagram of this model in the space of coupling constants. From (24) the phase boundaries are expected when \( \lambda' \) or \( \lambda'' \) is equal to zero. In the case of weak coupling, from (26) the phase boundary may be at \( g_{\|} = g_{\perp} \) and \( g_{\perp} = - g_{\|} \), and in fact we get three different excitation spectra for each region divided by the planes \( g_{\|} = g_{\perp} \) and \( g_{\|} = - g_{\perp} \) [2]. In the case of not weak coupling, a phase boundary can be introduced anywhere according to the choice of the functions \( x \) and \( y \), and of course this is meaningless. From Eq. (20) and (25), we see that \( \lambda' \) is a function of \( \lambda_{11} \) and \( \lambda_{0} \), and \( \lambda'' \) is a function of \( \lambda_{11} \) and \( \lambda_{10} \). So \( \lambda' \) or \( \lambda'' \) will be a function of small quantities when \( \lambda_{11} \) and \( \lambda_{0} \) or \( \lambda_{11} \) and \( \lambda_{10} \) are small, even when \( g_{\|} \), \( g_{\perp} \) and \( V \) themselves are not small. In this case, as well as in the case of weak coupling, the ambiguity happens only in higher order terms of these small quantities. When \( g_{\|} \simeq g_{\perp} \simeq - V \) (or \( g_{\|} \simeq - g_{\perp} \simeq - V \)), namely in the neighbouring region along the line of isotropic coupling, \( \lambda_{11} \) and \( \lambda_{10} \) (\( \lambda_{11} \) and \( \lambda_{0} \)) are small, and we get \( \lambda'' \simeq \lambda_{11} - \lambda_{10} = g_{\|} - g_{\perp} (\lambda' \simeq \lambda_{11} - \lambda_{0} = g_{\|} + g_{\perp}) \). The phase boundary is expected at \( g_{\|} = g_{\perp} (g_{\|} = - g_{\perp}) \), which is independent of the choice of \( x \)'s and \( y \)'s. Even in this region, however, \( \lambda_{0}(\lambda_{10}) \) is not small, so the physical properties of the domains divided by this phase boundary are decided according to the choice of \( x_3, y_3(x_2, y_2) \).

For another example, we will comment on the question how the Kondo effect is influenced by potential scattering. The \( s-d \) model is obtained from the Hamiltonian of the one-dimensional electron-gas model (13) by replacing \( \tau^z \) in the kinetic energy term by \( \frac{1}{2} (1 + \tau^z) \). Since the left-going electron has no kinetic energy now because of this factor, we can regard it as a localized spin. The couplings \( g_{\|} \) and \( g_{\perp} \) correspond to the \( s-d \) coupling constants \( J_{\|} \) and \( J_{\perp} \), and \( V \) corresponds to potential scattering by the impurity. The results of the electron-gas model, (21) to (25), are then valid for the \( s-d \) model, if we replace \( \tau_m \) by \( \frac{1}{2} (1 + \tau_m) \) and consider only one left-going electron and \( N \) right-going electrons. In the weak coupling limit we get like (26)

\[
\lambda \simeq 2 J_{\perp}, \quad \lambda' \simeq J_{\|} + J_{\perp}, \quad \lambda'' \simeq J_{\|} - J_{\perp}.
\]

The potential scattering \( V \) appears in higher order terms only. So what we can declare about the influence of the potential scattering on the Kondo effect is only that it has no influence in the weak coupling region, while for stronger couplings the model with linear dispersion leads to an ambiguous role of \( V \), depending on the choice of \( x \)'s and \( y \)'s.

In conclusion it is emphasized that, in these models discussed here, questions concerning the coupling constant are meaningful only in the case of weak coupling. It is also noted, however, that the relations among physical quantities themselves are decided definitely. So such quantity like e.g. Wilson’s number can be obtained without ambiguity.

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References

HYDRODYNAMICS IN CURVILINEAR COORDINATES

B. KÄMPFER

Central Institute for Nuclear Research Rossendorf
8051 Dresden, GDR

and

B. LUKÁCS

Central Research Institute for Physics
1525 Budapest, Hungary

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We consider the hydrodynamics in curvilinear comoving coordinates and present the equations governing the motion of a fluid with viscosity (and, in part, with heat conductivity). The underlying symmetry is spherical or planar. The Lagrangian form of the equations is suitable for numerically treating such problems as stellar collapse, neutron star dynamics, nuclear firecloud expansion, head-on heavy ion collision and pellet compression as well; for such purposes a difference scheme is given too here. Entropy production due to non-equilibrium phase transition, and a simple leak-out scheme (for drain terms) are involved.

1. Introduction

The hydrodynamic treatment of dynamic systems is very economical, reducing the full complexity of the system into a quite limited set of variables such as velocity, energy density and particle numbers, and thus such a formalism enables us to perform numerical calculations for the evolution of various systems. Ref. [1] contains a discussion of the hierarchy of approximations leading finally to hydrodynamics, so here it is not necessary to repeat the very details of the sufficient and necessary conditions of the applicability of such a treatment. For certain problems, as e.g. stellar dynamics, the possibility of a hydrodynamical formulation is obvious, being the mean free path small compared to the extension of the fluid. For other problems, like cosmology, the fluid approximation is a reasonable idealisation from the large scale viewpoint. There is a third class of problems, represented by e.g. heavy ion collisions, where the applicability of hydrodynamics is awkward since the mean free path is comparable to the size of the system. Nevertheless, even then it seems that the hydrodynamical treatment describes effects which in fact exist in the collision process [2], and it is edifying and useful to contrast the predictions of a model relying on full collectivity with those of another model starting from independent particle motion (the cascade model). Concerning heavy ion collisions we notice that:
1. a bombarding energy of about 10 GeV/nucleon seems to represent the upper limit for a simple hydrodynamic description, because of the nuclear transparency and the longitudinal growth [3];

2. for lower bombarding energies fluid models need sufficiently large particle number (so large nuclei) otherwise the statistical fluctuations are substantial;

3. for several hundred MeV/nucleon bombarding energies a hydrodynamical description of the whole collision is well established [4]; and

4. an improvement of the models can be achieved by multicomponent formalisms [5].

In addition we mention that the hydrodynamic picture is applied in the central rapidity region of ultrarelativistic heavy ion collisions or hadron–hadron collisions [6].

We do not want to discuss this problem further; in what follows we assume the applicability of a fluid description. Our aim here is to investigate hydrodynamics in curvilinear coordinates. The equation of motion possesses a suitable form to solve it in Lagrangian (comoving) coordinates. We present the hydrodynamic equations in a common form for such rather different problems as stellar collapse, neutron star dynamics, nuclear fireball expansion, head-on heavy ion collisions and pellet compression; such a common formulation is possible in curvilinear Lagrangian coordinates. For technical reasons here we restrict ourselves to spherical or plane-symmetric problems, depending only on two variables.

In Section 2 the basic notions are defined. The general evolution equations governing the system (such as e.g. conservation laws) are derived in Section 3. The case of phase transition with partial equilibration is treated in Section 4; Section 5 discusses the drain terms for a leak-out scheme. The dynamical equations as consequences of the Einstein equation are cast into a suitable form in Section 6, and the corresponding difference scheme is given in Section 7. The last Section contains some conclusions. In the Appendix we derive the form of the metric tensor used here and discuss the initial value problem.

2. Basic notions and relations

We start with the line element

\[ ds^2 = -e^{2\nu}dT^2 + e^{2\lambda}dY^2 + g_{RS}dx^Rdx^S, \]

\[ \phi = \phi(T, Y), \]

\[ \lambda = \lambda(T, Y), \]

\[ g_{IK} = g_{IK}(T, Y, x^I), \]

\[ I = 2, 3. \] (2.1)

Such a form can always be achieved when the situation is spherical or plane symmetric (then \( g_{IK} \) possesses some special form, too), some other symmetries may lead to similar
form, but here it is not necessary to discuss other symmetries. Now, assume that the
space is filled with particles, whose motions are so correlated that a unique velocity field
can be introduced. Assume, too, that the velocity field \( u' \) is of the form
\[
\begin{align*}
\mathbf{u}' &= (u^T, u^r, 0, 0), \\
g_{rs} u'^r u'^s &= -1.
\end{align*}
\]
This is true for strong spherical symmetry (i.e. when both the metric and the matter are
spherically symmetric; the Killing symmetry of the space–time does not necessarily
lead to the same symmetry of the matter, cf. [7]), and similarly for strong plane
symmetry. Then the motion of the particles can be described in a parametric way as
\[
\begin{align*}
T &= T(t, r), \\
Y &= Y(t, r), \\
x^A &= x^A_0,
\end{align*}
\]
where \( r \) and \( x^A_0 \) are some labels belonging to the particles, while \( t \) changes during the
evolution. By using \( t, r \) and \( x^A_0 \) as new coordinates, a Lagrangian or comoving
coordinate system is obtained, in which the velocity has only \( t \) component. By choosing
a proper \( t \) parameter the (2.1) structure can be kept:
\[
ds^2 = -e^{2\Phi} dt^2 + e^{2\Lambda} dr^2 + g_{RS} dx^R dx^S, \\
\Phi = \Phi(t, r), \\
\Lambda = \Lambda(t, r), \\
g_{1K} = g_{1K}(t, r, x^I), \\
\]
and, because of the unit length of the velocity,
\[
\mathbf{u}' = (e^{-\Phi}, 0, 0, 0).
\]
The existence of such a transformation is verified in the Appendix. The free trans­
formations preserving the form (2.4–5) are
\[
\begin{align*}
\tilde{t} &= t(t), \\
\tilde{r} &= \tilde{r}(r), \\
\tilde{x}^A &= \tilde{x}^A(x^B).
\end{align*}
\]
The metric tensor possesses a block structure. The metric is governed by the Einstein
equation [8]
\[
R_{ik} - \frac{1}{2} g_{ik} R = -8\pi \frac{G}{c^4} T_{ik}
\]
according to present knowledge, where \( R_{ik} \) is the Ricci tensor, \( R \) is its trace, \( G \) is the
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Cavendish constant, \(c\) is the velocity of light. \(T_{ik}\) is the energy-momentum tensor of the matter. As a consequence of the Einstein equation, one gets the contracted Bianchi identity, yielding local conservation laws for the energy and momentum as

\[
T^{ir};_r = 0, \tag{2.10}
\]

where the semicolon denotes covariant derivatives. For a slightly more general form of the field equation see [9]. In the coordinates (2.7) these equations determine simply some time derivatives, because of the block structure of the metric. The proper clock time \(\tau\) is related to the coordinate time \(t\) via

\[
d\tau = e^\phi dt. \tag{2.11}
\]

If the role of the gravity is negligible (e.g. for heavy ion collision), then the space-time is flat. Eq. (2.10) still holds as it can directly be seen by a limit going to flat space-time through any convenient set of space-times in which the equation holds, but the flatness of the space-time means stronger constraints for the metric than the Einstein equation (2.9): in a flat space-time the Riemann tensor vanishes [10]

\[
R_{iklm} = 0. \tag{2.12}
\]

Now, one has to choose the form for \(T_{ik}\). The energy-momentum tensor can be decomposed according to any timelike unit vector field \(u'\) as

\[
T'^{ik} = eu'u'^k + q'u'^k + u'q^k + t'^{ik}, \tag{2.13}
\]

for an observer moving with velocity \(u'\), \(e\) is the energy density, \(q'^{j}\) is a (heat) energy flux, and \(t'^{ik}\) is the stress tensor [11]. If there is a unique velocity field in the matter, which is now assumed (for some discussion cf. [9]), it is obvious to use this vector field for the decomposition. Then the velocities are small enough in this coordinate system, for \(e, q'^{j}\) and \(t'^{ik}\) one may take the classical hydrodynamic and thermodynamic formulae completed with terms guaranteeing the covariance [11, 12, 13].

Either in supernova explosions or in heavy ion collisions it is reasonable to assume that the matter is a fluid, i.e. its static response is isotropic. In first approximation, neglecting all the transport terms, one gets a perfect fluid

\[
(\rho)q^j = 0, \tag{2.14}
\]

\[
(\rho)t'^{ik} = pP'^{ik},
\]

where \(p\) is the pressure and \(P'^{ik}\) is a projection tensor into a 3-space orthogonal to \(u'

\[
P'^{ik} = g'^{ik} + u'u'^k. \tag{2.15}
\]

In a linear approximation the momentum transfer is described by an additive viscous term

\[
(\nu)t'^{ik} = -2\eta\sigma'^{ik} - \zeta\Theta P'^{ik}, \tag{2.16}
\]

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where $\eta$ and $\zeta$ are the coefficients of the shear and bulk viscosity, respectively, they are nonnegative according to the Second Law of Thermodynamics, and the shear velocity tensor $\sigma$ and expansion $\Theta$ possess the forms [11]

$$
\sigma^{ik} = \frac{1}{2} (u^i \cdot P^k + u^k \cdot P^i) - \frac{1}{3} \Theta P^{ik},
$$

$$
\Theta = u^r_{,r}.
$$

For the heat flux $q^i$ one may also assume linear transport law [11]. Eqs (2.10) determine the time evolution of the velocity and a thermal degree of freedom (e.g. energy density, entropy or temperature). Here we assume that it is sufficient to introduce one particle density $n$. For it, a source equation has to be specified [11]. If we identify $n$ with the baryon density, from baryon conservation

$$
(nu^r)_{,r} = 0
$$

yielding the time derivative of $n$. 

Now we have all the dynamical equations. In order to integrate them for a given system one needs initial and boundary conditions, and some equations of state, determining the relations among the thermodynamic quantities, and the coefficients of viscosity and heat conduction. Using $n$ and $T$ as independent variables the proper thermodynamic potential is the free energy density $f$ [14]. Here we want to use the energy per baryon $W$ and the pressure $p$ as functions of $n$ and $T$; they have to fulfil a compatibility condition

$$
ne^+ + Tp = e + p
$$

(cf. [15]). For later use we introduce the enthalpy $w$ (for which an alternative notation, more familiar in Thermodynamics, is $h$)

$$
w = (e + p)/n.
$$

The internal energy is defined as

$$
E = W/m_n - 1,
$$

where $m_n$ stands for the nucleon mass.

### 3. The conservation equations

Eq. (2.10) can be decomposed into directions parallel with and orthogonal to $u^i$. Contracting with $u^i$ and using Eq. (2.18) one gets

$$
dW - (p + Q) \frac{1}{n^2} dn + \frac{1}{n} (q^r_{,r} + q^r a_r - 2\eta \sigma^{rs} \sigma_{rs}) = 0.
$$

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Here we have used the particular form (2.16) of the momentum transfer terms, and have introduced the notations

\[ d = u^r \nabla_r, \]
\[ a^i = u^i u_{r,r} = d u^i, \]
\[ Q = -\zeta \Theta = \frac{1}{n} \zeta dn. \]

Now, consider the thermodynamic equation

\[ dW - \frac{1}{n^2} pdn - Tds = 0, \]

where \( T \) is the temperature and \( s \) is the specific entropy. This equation is an equivalent version of the differential form of the First Law; it is a direct consequence of the fact that the energy is a homogeneous function of first order of the extensive variables [11, 16]. Comparing this with Eq. (3.1) one can obtain the evolution equation for the specific entropy. Nevertheless, the Second Law must hold. It means that the four-divergence of the entropy current density has to be positive semidefinite. Now, the velocity field belongs to the particles, as it is shown by Eq. (2.18), so \( s^i \neq nsu^i \). Classical thermodynamics suggests

\[ s^i = nsu^i + \frac{1}{T} q^i. \]

Using this form a positive semidefinite entropy production can be obtained, thus this is, in fact, the correct form [11]. Namely then

\[ s^r_{,r} = \frac{1}{T} \zeta \Theta^2 + 2 \eta \sigma_{rs} \sigma_{rs} - \frac{1}{T} q^r \left( \frac{1}{T} T_{,r} + a_r \right). \]

The first two terms on the right hand side are automatically positive semidefinite if the viscosity coefficients \( \eta \) and \( \zeta \) are nonnegative, which is true for any known system. The third term can be made semidefinite, too, by accepting the heat conduction law

\[ q^i = -\kappa \Pi^r_{,r} (T_{,r} + T a_r), \]

where \( \kappa \geq 0 \) is the coefficient of heat conductivity; this law is familiar from classical thermodynamics, except for the acceleration term, which is required by the relativistic formalism, and negligible in everyday situations.

In the coordinate system (2.7) the heat current cannot possess timelike component. Because of the assumed plane or spherical symmetry the only nontrivial component is \( q_1 \). In an equilibrium state of a localized body heat currents must not flow. Calculating \( q_1 \) according to Eq. (3.8) one obtains

\[ q_1 = -\kappa (T_{,1} + T \Phi_{,1}). \]
Together with the stationarity of an equilibrium situation, this shows that then \( T^\phi \text{= const} \). This is a special case of the general theorem that \( u^i/T \) is a Killing vector in equilibrium \([11]\). For further interpretations of the consequences of Eq. (3.1) (as e.g. the inertia of the heat) see \([8]\).

The \( u \)-orthogonal components of Eq. (2.10) yield the Navier–Stokes equation. Namely, using the special linear viscous form of the momentum transfer terms, and projecting Eq. (2.10) by \( P_{ik} \) one obtains

\[
(e + p + Q)u^i,_{,i}u^i = -(p + Q),_{,i}P^i_{,i} - K^i,
\]

\[
K^i = \Theta q^i + u^i,_{,i}q^i + q_{r,s}u^i,_{,i}P^i_{,r} - 2\eta,_{,i}\sigma^i_{,i} - 2\eta^2,_{,i} \sigma^i_{,i}P^i_{,r}.
\]  

In contrast with the classical situation, this equation contains second order time derivative, too, for \( u^i \), since \( q^i \) contains the acceleration \([18]\). If and \( \eta \) vanish, Eq. (3.10) formally reduces to the Euler equation, but with a modified pressure. Since \( u^i \) is given by the scalar function \( \Phi \),

\[
u_{i,k} = v_{i,k} - \Gamma^r_{ik} \nu_r = - (\Phi_{ik} \delta^0 + \Gamma^0_{ik}) e^0,
\]

where \( \Gamma^1_{ik} \) stands for the Christoffel symbols \([10]\)

\[
\Gamma^m_{ik} = \frac{1}{2} g^{mr}(g_{rk,i} + g_{ri,k} - g_{ik,r}).
\]

4. Non-equilibrium phase transitions

Equation (3.7) shows that for perfect fluids there is no entropy production. Nevertheless, this result is a consequence of the assumption that the independent thermodynamic quantities are \( e \) and \( n \). This means that there is only one particle component, and the matter is in equilibrium. Now, the result remains valid for more than one components but the equilibrium condition is necessary.

If there is no unique velocity field (i.e. if the hydrodynamic equilibration is not full), the usual hydrodynamical treatment is not possible, which case is not a subject of this paper \([18]\). If the momentum distribution deviates from the equilibrium one, there is entropy production due to further equilibration, but then generally the usual set of thermodynamic parameters is not sufficient \([19]\). Nevertheless, there is a case when the hydrodynamic and thermodynamic treatment is possible but there is no full equilibrium. Namely, during a phase transition the two phases may possess different intensive parameters if the microscopic processes of the formation of the new phase are not sufficiently rapid. Then the set of independent thermodynamical characteristics has to contain at least the extensive densities of both phases and the relative weights. Since at the phase boundaries various equilibrating processes may take place, the situation is generally quite complicated. Nevertheless, in some cases the thermal and mechanical
equilibrations are more rapid than the chemical equilibration (cf. [20]), and such cases can be treated relatively simply.

Consider a phase mixture, with the particle numbers in the phases \( N_i \) and with phase volumes \( V_i \); the total particle number is \( N \), and the total volume is \( V \). Introduce the coefficients

\[
\alpha = \frac{N_1}{N}, \\
\beta = \frac{V_1}{V}.
\] (4.1)

If the individual phase regions are sufficiently small, then only volume averages appear in the hydrodynamic equations. These averaged quantities can be constructed as

\[
A = \alpha A_1 + (1 - \alpha) A_2, \\
a = \beta a_1 + (1 - \beta) a_2,
\] (4.2)

where \( A \) stands for any specific quantity and \( a \) for any density. Now, constructing the average particle number density \( n \) one gets

\[
\beta = \frac{n_2 - n}{n_2 - n_1},
\] (4.3)

while a combination of Eqs (4.1) yields

\[
\alpha = \frac{\beta n_1}{n}.
\] (4.4)

An obvious consequence is

\[
\frac{N_1}{N_2} = \frac{\alpha}{1 - \alpha} = \frac{n_1(n_2 - n)}{n_2(n - n_1)} = \frac{v_1 - v_2}{v_1 - v_2},
\] (4.5)

known as "Hebelregel" (\( v = 1/n \) is the specific volume). Now, the energy-momentum tensor of the mixture consists of densities, so it can be written as

\[
T^{ik} = \beta T^{ik}_{(1)} + (1 - \beta) T^{ik}_{(2)}.
\] (4.6)

Then again the entropy production can be calculated from the conservation equations (2.10), as in the previous Section for one phase. First it contains the same viscosity and heat conduction terms, but, for a perfect fluid, there remains an extra term [21]

\[
T(su^r)_{,r} = -\frac{\mu_1 - \mu_2}{(n_1 - n_2)^2} \left\{ (n_2 - n)n_2dn_1 + (n - n_1)n_1dn_2 + \frac{1}{n}(n_2 - n_1)n_1n_2dn \right\},
\] (4.7)

which, using Eqs (4.3–4), can be written into a more transparent form as

\[
ds = -(\mu_1 - \mu_2) \frac{1}{T} d\alpha.
\] (4.8)
This is the entropy production due to the non-equilibrium nature of the phase transition. Since Eq. (3.1) was obtained without any mention of thermodynamic variables, it holds again, and then, using Eq. (4.8), it can be rewritten as

$$\frac{dW}{n^2} p dn - T ds - (\mu_1 - \mu_2) da = 0 . \tag{4.9}$$

This nonequilibrium entropy production should always be taken into account if the time necessary for building up the new phase is comparable to (or longer than) the characteristic time of the change of the other thermodynamic quantities. Generally speaking, in such cases the relative weights of the phases differ from the values giving energy minimum. Then the equation of state depends on an additional variable, the so-called progress variable $\alpha$, determining the relative weights. In order to make the system of the evolution equations complete, one must get an evolution equation for $\alpha$ too. Since the microscopic theory of a phase transition is rather complicated, it is convenient and usual to use a linearized Ansatz for the conversion rate (cf. e.g. [22]):

$$d\alpha = -q(\alpha - \alpha_{eq}), \tag{4.10}$$

where $\alpha_{eq}$ is the equilibrium weight belonging to the minimal energy and $\mu_1 = \mu_2$; the driving force is the deviation from $\alpha_{eq}$. The constant $q$ determines the velocity of the transition; in order to get an idea on its value one may calculate the typical time scales of fluctuations and their time lag, droplet growth and evaporation as well as droplet coalescence [22].

5. Drain terms

In some stages of an expansion there may be direct particle emission from the system. Generally it is easier to simulate this effect by nonconservation terms than to calculate the diffusion or the heat current. The idea is as follows. The energy and momentum conservations (2.10) are consequences of the Einstein equation (or of the Noether theorem), and necessarily hold, if the energy-momentum tensor is complete, i.e. contains the contributions of all the parts and all the components of the system. On the other hand, Eq. (2.10) generally does not hold for a subsystem. Dividing $T_{ik}$ into two terms in any way, one gets

$$T_{i(r);r}^{(1)} = - T_{i(r);r}^{(2)} \tag{5.1}$$

which is, of course, a merely formal result. Now, consider a situation when some particles are scattered out of the fluid due to particle-particle collisions. Then the loss rate $q$ can be obtained by

$$q(r) = \frac{1}{n} \int f_1(u)f_2(u) e^{-d(u)/\lambda} |u_1 - u_2| d^3u_1 d^3u_2 d\Omega \tag{5.2}$$
where \( u \) is the three-velocity, \( f \) is the momentum distribution at the place \( r \), \( \sigma \) is the cross section, \( d(r) \) is the distance between the given point and the surface in the direction according to the actual value of \( \Omega = (\theta, \varphi) \), while \( \lambda \) is the mean free path. The indices 1, 2 stand for the scattering and scattered particles; if both kinds are nucleons the indices are unnecessary. For a general discussion of this problem see [23].

Now, consider the energy-momentum tensor of the fluid, without the particles scattered out. If a given volume belongs uniquely to the fluid, then Eq. (2.10) still holds. Nevertheless, the situation is more complicated, there are always particles just being scattered out; their number ratio is approx. \( \frac{\tau}{\tau} \), where \( \tau \) is some characteristic time for reaching the surface. According to the simplified model, these particles do not belong to the fluid. Then there is no particle conservation for the fluid, the continuity equation possesses a right hand term as

\[
(nu'),_r = nq. 
\]  

Equation (5.1) indicates that the energy and momentum balance equations possess source terms too:

\[
T^{ir},_r = Q^l. 
\]  

Now, the question is, how to calculate the source terms \( Q^l \). Of course, the energy-momentum tensor of the particles scattered out from the fluid can be determined if the differential cross section is known (in a slightly different context see [24]). However, then the decomposition of the energy-momentum tensor has not led to any simplification; if the correct equation (2.10) can be solved, it has to be solved. We are discussing such cases when one cannot handle the correct equations, and we are looking for decent approximations.

Such an approximation is that each departing particle carries away the average energy and momentum. Then, being Eq. (5.4) the energy-momentum balance, one gets

\[
Q^l \approx qP^l, 
\]  

where \( P^l \) is some average characteristic four-momentum density.

Obviously, \( P^l \) is a linear expression of \( T^{ik} \); being a vector, it has to contain a vector contracted with \( T^{ik} \); it may be the velocity vector \( u^l \) or some other given vector orthogonal to \( u^l \). Then one expects a form

\[
P^l = (\alpha \delta^l + \beta P^l) T^{rs}(\delta u_s + \epsilon x_s), 
\]  

Ignoring the shear viscosity and heat conduction in \( T_{ik} \), one gets

\[
P^a = \alpha \delta \left(- \frac{1}{\gamma} M^a + \gamma \tilde{p} u^a \right) - (\alpha + \beta) e \tilde{p} x^a, 
\]  

\[
P^0 = \alpha \delta \left(- \frac{1}{\gamma} \tilde{E} + \gamma \tilde{p} v^2 \right) + (\alpha + \beta) e \tilde{p} x^a v_\rho, 
\]  

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with the abbreviations
\[ \hat{E} = T^{00}, \]
\[ M^a = T^{0a}, \]
\[ u' = \gamma(1, v^a), \]
\[ \tilde{p} = p + Q. \]

Now, in the classical limit \( v \ll 1 P^a \) is obviously the three-momentum density and \( P^0 \) is the energy density of the fluid if \( \alpha\delta = -1 \), while the \( (\alpha + \beta)\epsilon \) terms do not reduce to anything reasonable, so disturbing the picture. This indicates that the correct choice is
\[ \alpha = -1, \]
\[ \beta = 0, \]
\[ \delta = +1, \]
\[ \epsilon = 0, \]
\[ P^i = - T^{ir}u_r. \]

Then the modified energy-momentum balance obtains the form
\[ T^{ir}_{,r} = - q T^{ir}u_r, \] (5.10)
where \( q \) is given by Eq. (5.1). In fact, this form leads to
\[ (\partial_t + (vF)) M = - M(\nabla v) - \nabla \tilde{p} + q(- M/\gamma + \tilde{p}v), \]
\[ (\partial_t + (vF)) \hat{E} = - \hat{E}(\nabla v) - \nabla (\tilde{p}v) + q(- \hat{E}/\gamma + \tilde{p}v^2), \] (5.11)

thus recovering the basic equations of [23]. Still ignoring the shear viscosity and the heat current, the decomposition of Eq. (5.10) leads to
\[ dW - pn^{-2}dn - e^0 q W dt = 0, \]
\[ u'^i, u'^r = -(e + \tilde{p})^{-1} \tilde{p}_r P^{ir}. \] (5.12)

By comparing this with the special \( (\eta = 0, q^i = 0) \) forms of Eqs (3.1) and (3.10), one sees that there is, of course, a loss term in the energy equation, nevertheless the equations of motion are unaffected.

This paper wants to use Lagrangian coordinates. So, strictly speaking, only non-baryonic losses could be treated in it in a natural way, because the space coordinates of the particles should be constant. Then, of course, the meaning of Eq. (5.3) is at least awkward. Attributing the constant space coordinates to mass elements, not to particles, Eq. (5.3) regains its meaning, and the leak-out scheme is applicable even to baryonic losses. Of course, there is no problem in Eulerian coordinates. For further discussion see [23].
Now we are in the position to calculate the evolution of the system. In general, the necessary equations are as follows:

a) the Einstein equation;

b) continuity equations (with or without sources) for the particle number densities; and

c) thermodynamical and continuum mechanical equations expressing the spatial stresses $t^{ik}$ and the (heat) energy flux $q^i$ by means of $P^{ik}$, $u^i$, the particle densities and a thermal variable, thus specifying the behaviour of the investigated matter [12, 13, 25].

It can be shown that this set of equations is sufficient indeed. Namely, because of item c), $T^{ik}$ can be expressed by means of, e.g. $g^{ik}$, $u^i$, $n_A$, $e$ and possibly of their derivatives. The Einstein equation yields the necessary evolution equations for the metric [8]. Its consequence is Eq. (2.10). In Section 3 it was shown that this equation gives the equation of motion for $u^i$, and the differential form of the First Law, which can be read as an evolution equation for $e$. Finally, item b) means that we have evolution equations for $n_A$, too.

The most practical form of the system of evolution equations may depend on the particularities of the system investigated. Here we restrict ourselves to a one component equilibrium fluid or gas, without heat conduction and shear viscosity, composed of conserved particles. Then, for $n$ we have Eq. (2.8):

$$(nu')_r = 0,$$

(6.1)

for $u'$ Eq. (3.10) with $K' = 0$, because of the block form of the metric the only nontrivial component of this equation reads

$$\Phi'_{\parallel} = -(p + e + Q)^{-1}(p + Q)'_{\parallel}.$$

(6.2)

Eq. (3.4) for $Q$:

$$Q = -\zeta(e, n)u'_r.$$

(6.3)

Finally, for the metric, we have the Einstein equation (2.9) (or, when the role of the gravitation is negligible, the flatness condition (2.12)), whose explicit form depends on the particular metric.

In this paper we want to investigate only spherical or plane symmetric problems. Thus $g^{ik}$ must possess one of these symmetries. Consider the spherical case; the other can be similarly handled. In Section 2 we showed that a metric of form (2.5) can be achieved in such a coordinate system that $u^i$ has only $^0$ component. Obviously, the form (2.5) is compatible with any coordinate transformation in the subspace $x^I = (x^2, x^3)$. Now, the metric has to be spherically symmetric, i.e. it has to possess three Killing vectors with SO(3) commutation and 2-dimensional transitivity; if the physical quantities do depend on $t$ and $r$, then the symmetry coordinates must be $x^I$, thus $g^{ik}$ must possess the well-known spherical form.

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Repeating this procedure, mutatis mutandis, for plane symmetry, in both cases one arrives at the same structure of the metric. Namely,
\begin{align}
    ds^2 &= -e^{2\Phi(t,r)}dt^2 + e^{2\Lambda(t,r)}dr^2 + Y^2(t,r)d\Omega^2, \\
    d\Omega^2 &= d\vartheta^2 + \Sigma^2(\vartheta)d\varphi^2,
\end{align}

where
\begin{align}
    \Sigma &= \begin{cases} 
        \sin \vartheta & \text{for } k = +1, \\
        \vartheta & \text{for } k = 0, \\
        \text{sh} \vartheta & \text{for } k = -1.
    \end{cases}
\end{align}

The $k = +1$ case is the spherical symmetry, $k = 0$ for plane symmetry. The third case can be called hyperbolic, it does not seem to occur in heavy ion collisions. In principle, such a symmetry may characterize some astrophysical process in curved space-time, nevertheless the physical meaning of such metrics is awkward [26, 27], so we ignore this case. For more discussion of the metric (6.4) see [28]. In the $k = 0$ case, if then the gravitation is negligible, the terms containing $Y^2$ must describe the $(\rho, \varphi)$ contribution to a cylindric line element
\[ dp^2 + \rho^2 d\varphi^2, \]
therefore then $Y$ is a constant which can be normalized to 1.

Now consider the particle conservation (2.18). Via Gauss' theorem [8, 28] a four-volume integral in a hypercylinder gives
\begin{equation}
    \int_{V_A}(nu')_rd^4x = \int_{\sigma_1} nu'd\sigma_1 + \int_{\sigma_2} nu'd\sigma_2 + \int_M nu'd\sigma_M = 0, \tag{6.6}
\end{equation}

where $\sigma_i$ denote the circular base and cover of the cylinder, while $M$ stands for the remaining part of the boundary. We are in Lagrangian coordinates, the space coordinates of any particle are constant, so if the axis is parallel with the time direction, then no particle crosses the mantle $M$, so an integral representing the total particle number $N$
\begin{equation}
    N = \int_{V_0} nu_0 \sqrt{-g}d^3x \tag{6.7}
\end{equation}
is conserved. The particular form of the integral can be taken from Eqs (6.4-5), thus
\begin{align}
    N(r) &= 4\pi \int_0^r e^4Y^2ndr \quad k = +1, \\
    N(r) &= F \int_0^r e^4Y^2ndr \quad k = 0. \tag{6.8}
\end{align}

In the second case $F$ is an arbitrary fixed volume on the infinite plane $(\vartheta, \varphi)$.

The form (6.4) does not fully fix the coordinate $r$; transformations of form $\bar{r} = \tilde{r}(r)$
are permitted. By means of them

\[ N(r) = N_0 r \]  \hspace{1cm} (6.9)

can be achieved, where \( N_0 \) is an arbitrary suitable constant, and then the coordinate \( r \) becomes fixed. By differentiating Eq. (6.8) \( n \) can be expressed by the components of the spatial part of the metric, \( e^A \) and \( Y^2 \):

\[ n = N_0 B e^{-A} Y^{-2}, \]  \hspace{1cm} (6.10)

\[ B = \begin{cases} 1/4\pi & \text{for } k = +1, \\ 1/F & \text{for } k = 0. \end{cases} \]

If the gravity is negligible, \( Y = 1 \) can be achieved for the \( k = 0 \) case (slab collision); we will use this coordinate system then.

Consider first the case \( k = +1 \). Introduce the quantities

\[ u = e^{-\Phi} \dot{Y} \quad \dot{r} = \partial_r, \]  \hspace{1cm} (6.11)

For these quantities the Einstein equation yields the following relations [8, 28]:

\[ e^{-\Phi} \dot{u} = -4\pi G Y^2 \frac{1}{\dot{w}} \dot{\rho} - \frac{G}{Y^2} (\dot{m} + 4\pi Y^3 \ddot{\rho}/c^2), \]  \hspace{1cm} (6.12)

\[ \Gamma = \left( 1 + (u/c)^2 - 2 \frac{G \dot{m}}{Yc^2} \right)^{1/2}, \]

where

\[ \dot{m} = \int_0^r \Gamma (1 + E) dr, \]  \hspace{1cm} (6.13)

\[ \dot{w} = \frac{1}{m_n n} (e + \ddot{\rho}), \]

and, combining Eqs (6.10-11):

\[ n = \frac{1}{4\pi} \frac{\Gamma N_0}{Y^2 Y'} \]  \hspace{1cm} (6.14)

Together with the thermodynamical relations for the functions \( W = W(n, T) \), \( p = p(n, T) \), with the defining equations (2.20) and (5.8), and with the balance equations (3.1) and (6.2), Eqs (6.11-13) determine the dynamics of a spherical mass distribution in its own gravity. For \( G = 0 \) the gravity is switched off, for \( c \to \infty \) the Newtonian limit is generally recovered (however, cf. [29]). For a static configuration Eq. (6.12) reduces to the Tolman–Oppenheimer–Volkov equation [30].

Here we note that by combining Eqs (6.10–11) with the balance equations (3.1) and (6.2), one gets

\[ u \Phi' e^\Phi = \dot{r} e^A. \]  \hspace{1cm} (6.15)

Now, consider \( k = 0 \), without gravity (since slab geometry is not expected in astrophysics). Then, as it was mentioned, \( Y = 1 \) can be used. In the symmetry

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coordinates the metric tensor (6.4) is cylindric; instead of it a flat form $dy^2 + dz^2$ can always be achieved by a proper coordinate transformation. For $Y=1$ the flatness condition (2.12) reduces to a single equation

$$(\Phi'' + \Phi'^2 - \Phi'\Lambda')e^{2(\Phi r^A)} - (\Lambda^2 - \Lambda \Phi) = 0. \quad (6.16)$$

Now, in this case the metric (2.4) has been obtained from a Minkowskian one ($\phi = \lambda = 0$ in Eq. (2.1)). Thus one can write

$$e^\Phi = u^{-1} \tilde{Y},$$
$$e^\Lambda = \Gamma^{-1} \tilde{Y}' ,$$
$$\Gamma = (1 + u^2)^{1/2},$$

where $\tilde{Y}$ is the $Y$ function of Eq. (2.3); here we use the tilde in order to prevent a confusion between it and the metric coefficient in Eq. (6.4). For the relations (6.17) see the Appendix.

Eq. (6.16) and the integrability condition for $\tilde{Y}$ yield two equations for $\Phi$, $\Lambda$ and $u$. These equations can be regrouped in such a way that one gets again Eq. (6.15), together with

$$u'e^\Phi = e^\Lambda \tilde{Y}.$$

This equation, by using Eqs (6.2) and (6.8), can be rewritten as

$$e^{-\Phi} u = F\tilde{w}^{-1} \tilde{p}' ,$$

while a combination of Eqs (6.8) and (6.16) yields

$$n = \frac{1}{F} \frac{N_0}{\tilde{Y}^r \Gamma} .$$

The system of dynamical equations, determining the evolution of the slab geometry, consists of the thermodynamic relations for $W$ and $p$, of Eqs (5.8) and (6.3) for $\tilde{p}$, of the defining equation of $\tilde{w}$ (6.13), of the balance equations (3.1) and (6.2), and of the Eqs (6.15), (6.18-20). The total energy of the matter is given again by

$$\tilde{m} = \int_0^r \Gamma (1 + E) dr .$$

Observe the great and unexpected structural similarity between the two discussed cases. The dynamical equations of a laboratory slab collision can be obtained from those of the general spherical case by the formal substitutions

$$G \rightarrow 0 ,$$
$$Y \rightarrow \tilde{Y} ,$$
$$4\pi \rightarrow F/\tilde{Y}^2 .$$

The initial value problem is discussed in the Appendix.
7. Difference equations

In Sections 2, 3 and 6 the full set of hydrodynamic equations for the motion of a fluid with bulk viscosity were derived, if the situation possesses either spherical or plane symmetry. However, even for such a high symmetry one cannot expect analytic solutions for realistic equations of state. (For $\tilde{p} = 0$ see [31]). For computer work the differential equations have to be translated into difference equations. In doing so one has to use proper weighting of the quantities. Here we follow [32] in weighting and notation:

1. The quantities $e, \tilde{p}, n$ and $\tilde{w}$ are calculated at full time steps (denoted by $n$ as upper index), and inside of cells, i.e. at half space steps (denoted by $j + 1/2$ as lower index).
2. The locations of the cell boundaries $R_j^n$ are calculated at full time steps and full space steps.
3. The velocities $u_j^{n+1/2}$ are calculated at half time steps and full space steps.
4. The coordinate time $t$ is synchronized with the proper time in the rest frame of a distant observer [32].
5. The first cell is fixed (symmetric collision), i.e. $R_1^n = 0, u_1^n = 0$.
6. For numerical calculation of shock spreading an artificial viscosity is generally used (cf. e.g. [33]), $Q = nm (\Delta u)^2$, where $u$ is defined in Eq. (6.12); $\Delta u$ is the velocity difference if the neighbouring cells move in the same direction, and $\Delta u = 0$ if they move oppositely.

Under these conditions the difference scheme reads as follows.

a) For spherical symmetry:

\[ S_j = 4\pi (R_j)^2, \]
\[ V = 4\pi /3, \]
\[ \frac{1}{3} \]

(7.1)

b) For laboratory slab geometry:

\[ S_j = F, \]
\[ V = F, \]
\[ \frac{1}{3} \]

(7.2)

with a suitable normalization surface $F$ (in principle the surface of the slab fronts is infinite).

c) For both geometries, in order to avoid cell crossing, the time steps must fulfil

\[ t < \min_{i,j} (R_j - R_{j-1}) / 2c. \]

(7.3)
The dynamical equations are:

\[
\tilde{w}_{j+1/2}^n = 1 + E/c^2 + \tilde{p}/nm|_{j+1/2,j=1...J-1},
\]

(7.4)

\[
\Phi^n_j = (1 - 2Gm/Rc^2)\left(1 + (u^n_{j-1/2})^2 - 2Gm/Rc^2\right)^{-1/2}|_j,
\]

(7.5)

\[
\Phi^n_{j-1} = -\Phi^n_j \exp \left\{ \left( p_{j-1/2} - p_{j-3/2} \right)/\left( c^2 m_n w_{j-1/2,n_{j-1/2}} \right) \right\}|_j,
\]

(7.6)

\[
e^{\Phi^n_j}|_{j-1} = e^{\Phi^n_j}|_j \exp \left\{ \left( \tilde{p}_{j+1/2} - \tilde{p}_{j-3/2} \right)/\left( 2c^2 m_n \tilde{w}_{j-1/2,n_{j-1/2}} \right) \right\}|_j,
\]

(7.7)

\[
\Phi^n_1 = e^{\Phi^n_1/2} \exp \left\{ \left( \tilde{p}_{3/2} - \tilde{p}_{1/2} \right)/\left( c^2 m_n \tilde{w}_{1/2,n_{1/2}} \right) \right\}|_1,
\]

(7.8)

\[
\tilde{m}_{j+1} = \tilde{m}_j + (1 + E_{j+1/2}/c^2)(\Gamma_j + \Gamma_{j+1})(r_{j+1} - r_j)/2|_{j=1...J-1},
\]

(7.9)

\[
u_{j+1/2}^n = \nu_{j-1/2}^n + \Delta t^n e^{\Phi^n_j}\left\{ 4S_j \Gamma_j \tilde{p}_{j-1/2}/[\tilde{w}_{j-1/2}(r_{j+1} - r_j)] - \right.
\]

\[
- G\tilde{m}_j/(R_j)^2 - (4\pi G/c^2)\tilde{p}_j_{1/2} R_j \right\}|_j,
\]

(7.10)

\[
u_{j+1/2}^n = \nu_{j-1/2}^n - \Delta t^n e^{\Phi^n_j}\left\{ 4S_j \Gamma_j (\tilde{p}_{j+1/2} - \tilde{p}_{j-1/2})/(\tilde{w}_{j+1/2} + \tilde{w}_{j-1/2})(r_{j+1} - r_j) \right\} + \tilde{m}_j/(R_j)^2 + (2\pi G/c^2)(\tilde{p}_{j-1/2} + \tilde{p}_{j+1/2})R_{j+1/2}|_{j=2...J-1},
\]

(7.11)

\[
R_{j+1}^n = R_j^n + \frac{1}{2}(\Delta t^n + \Delta t_{n+1}^n) e^{\Phi^n_j}|_{j=2...J-1},
\]

(7.12)

\[
\Gamma_j^{n+1} = \left\{ 1 + (u^{n+1/2}/c)^2 - 2Gm_n/(c^2 R_{n+1}^n) \right\}^{1/2}|_{j=2...J-1},
\]

(7.13)

\[
n_{j+1/2}^{n+1} = \frac{1}{2} V^{-1}(\Gamma_j + \Gamma_{j+1})(r_{j+1} - r_j)/[\left( (R_{j+1}^n)^d + (R_j^n)^d \right)]^{1/2}|_{j=1...J-1},
\]

(7.14)

\[
\Delta u_{j+1/2}^{n+1} = u_{j+1} - u_j^{n+1/2}|_{j=0...J-1},
\]

(7.15)

\[
Q_{j+1/2}^{n+1} = \frac{1}{2}(\Delta u_{j+1/2})^2 m_n n_{j+1/2}^{n+1} \Theta(-\Delta u_{j+1/2}) +
\]

(7.16)

\[
+ \zeta e^{-\Phi(n^{n+1} - n^n)/[(\Delta t^n + \Delta t_{n+1})n^{n+1}/2]}|_{j=1/2,j=0...J-1},
\]

\[
\tilde{p}_{j+1/2}^{n+1} = p + Q|_{j+1/2,j=0...J-1},
\]

(7.17)

\[
W_{j+1}^{n+1} - W^n + (\tilde{p}^{n+1} + \tilde{p}^{n+1}) (1/n^{n+1} - 1/n^n)/2|_{j=1/2,j=1...J-1} = 0,
\]

(7.18)

where the lower or upper index is not explicitly given, the quantity is to be taken at the step indicated on the extreme right end of the equation. Unfortunately, the sets of both the typographic symbols and the possible index locations are limited. Therefore some care is needed no to confuse the upper index \(n\) with the density. Similarly, \(\Phi\) is an upper index numbering the time steps, while \(d\) is an exponent.

Equations (7.16–18) have to be solved by iteration, using the thermodynamic equations \(W = W(n, T)\), \(p = p(n, T)\). In addition, \(\zeta = \zeta(n, T)\) must be given (cf. [2]) in order to determine \(T_j^{n+1}\). Since Eq. (7.15) is not well-centred, one has to choose sufficiently small time steps \(\Delta t^n = t^{n+1/2} - t^{n-1/2}\). The other dynamical equations are well-centred.
8. Conclusions

In this paper we have presented the differential equations and the corresponding difference scheme for calculating spherical or plane symmetric motion of a fluid with bulk viscosity. Non-equilibrium phase transitions and drain terms in a leak-out scheme are discussed. The equations are given in a curvilinear comoving coordinate system, where the structure of the equations of motion is simple, and we use the convenient notations of General Relativity.

The difference scheme is available as a Fortran code. It has been applied for stellar core collapse and neutron star dynamics (static problems are involved as special cases) [34] and for heavy ion reactions, namely, for
1. the collision process of nuclei in slab approximation [34, 35, 36];
2. the spherical expansion of a quark–gluon plasma [37];
3. the spherical expansion of weakly excited nuclear blobs [38];
4. a model of direct pion emission [39].

Finally, we mention that the Lagrangian method seems to be very useful for investigating pellet compression which is at present under consideration.

Acknowledgements

Many useful discussions with Drs H. W. Barz and L. P. Csernai are gratefully acknowledged.

Appendix A

The Lagrangian coordinates

Consider the class of metrics

\[ ds^2 = -e^{2\phi(T,Y)} dT^2 + e^{2\lambda(T,Y)} dY^2 + g_{RS}(T,Y,x^A) dx^R dx^S, \]  
\[ A = 2, 3. \]

The physical meaning of such line elements is not too important here; however, such a form can always be achieved for either spherical or plane symmetric situations [40]. Now, assume that the space is filled with a fluid of identifiable particles, and that the motion of the particles is sufficiently correlated to define a unique velocity field. Furthermore, assume that this velocity field possesses only \( T \) and \( Y \) components, which are independent of \( x^A \) (again, it is true for either spherical or plane symmetry). Then there are two dimensional shells containing particles of the same velocities. Introduce some continuous and monotonous numbering for the shells, denoted by \( r \); a particle on a specific shell can be labelled by \( r \) belonging to the shell, and by the coordinates \( x^A \). None of them changes during the evolution of the system. Then the
motion of a particle can be given in a parametric form

\[ T = T(t, r), \]
\[ Y = Y(t, r), \quad (A.2) \]
\[ x^A = x^A_t, \]

where \( t \) is some parameter describing the evolution. The other three parameters belong to the particles, so they are constant.

Now, it is obvious to introduce \( t, r \) and \( x^A_t \) as new coordinates; this will be a Lagrangian coordinate system. Henceforth we may forget about the coordinates \( x^A \); their roles are more or less trivial. Note that the pair \( (t, r) \) is not unique: \( r \) is simply a numbering of the shells, and \( t \) is a still undefined evolution parameter. Therefore a new pair

\[ \tilde{t} = \tilde{t}(r, t), \]
\[ \tilde{r} = \tilde{r}(r), \quad (A.3) \]

can also be used, if the matrix of the transformation is positive definite. Choosing a particular pair, in them the (two dimensional part of the) line element gets the form

\[ ds^2 = -(e^{2\phi} T_t^2 - e^{2\lambda} Y_t^2) \, dt^2 + 2(e^{2\phi} T_t T_r - e^{2\lambda} Y_t Y_r) \, dt \, dr + (e^{2\phi} Y_t^2 - e^{2\lambda} T_r^2) \, dr^2. \quad (A.4) \]

Now, by means of the transformation (A.3) the \( g_{tr} \) term can generally be removed. Namely,

\[ \tilde{g}^{rr} = \frac{d\tilde{r}}{dr} \left( \frac{\partial \tilde{t}}{\partial t} g^{rr} + \frac{\partial \tilde{t}}{\partial r} \tilde{g}^{rr} \right). \quad (A.5) \]

Ignore such special (and generally unphysical) cases when \( g^{rr} = 0 \). If \( g^{rr} \neq 0 \), by choosing a proper \( \tilde{t}(r, t) \) function, the bracketed term can be made 0. Then, the remaining transformation keeping the diagonal metric is

\[ \tilde{t} = \tilde{t}(t), \]
\[ \tilde{r} = \tilde{r}(r). \quad (A.6) \]

We write the resulting metric as

\[ ds^2 = -e^{2\Phi(t, r)} \, dt^2 + e^{2\Lambda(t, r)} \, dr^2 + g_{RS} \, dx^R \, dx^S. \quad (A.7) \]

In this system the velocity has only \( t \) component, since \( r \) is constant; and being normalized, it is

\[ u^t = (e^{-\Phi}, 0, 0, 0). \quad (A.8) \]

For spherical symmetry \( g_{IK} \) possesses a specific form [40], for further discussion.
see Section 6 or [28]. For plane symmetry the general line element reads as [41]

$$ds^2 = -e^{2\phi(T,Y)} dT^2 + e^{2\lambda(T,Y)} dY^2 + e^{2H(T,Y)}(dx^2 + dy^2).$$  \hspace{1cm} (A.9)

For our present purposes it is sufficient to investigate such plane symmetric situations when the gravity is negligible. But then $R_{iklm} = 0$. If the signature is physical, i.e. $(-+++)$, such metrics (at least in finite hypervolumes) can always be transformed into a Minkowskian form, when

$$\phi = \lambda = H = 0.$$ \hspace{1cm} (A.10)

Then, performing again the transformation thence into a Lagrangian system, one gets

$$ds^2 = -e^{2\phi} dt^2 + e^{2\lambda} dr^2 + dx^2 + dy^2,$$ \hspace{1cm} (A.11)

$$u' = (e^{-\phi}, 0, 0, 0).$$

Consider now the details of this transformation. Obviously

$$-e^{2\phi} dt^2 + e^{2\lambda} dr^2 = -dT^2 + dY^2.$$ \hspace{1cm} (A.12)

Since $u_r dx^r$ is a scalar,

$$-e^{\phi} dt = -\Gamma dT + u dY,$$ \hspace{1cm} (A.13)

$$\Gamma = \sqrt{1 + u^2},$$

where $\Gamma$ and $u$ are the velocity components in the Minkowskian coordinates. Hence

$$e^{2\phi} = T_i^2 - Y_i^2,$$

$$0 = T_i T_r - Y_i Y_r,$$

$$e^{2\lambda} = Y_r^2 - T_r^2,$$ \hspace{1cm} (A.14)

$$e^{\phi} = \Gamma T_i - u Y_i,$$

$$0 = \Gamma T_r - u Y_r.$$

From the second and fifth equations

$$T_r = v Y_r,$$

$$T_i = v^{-1} Y_i,$$ \hspace{1cm} (A.15)

$$v = \Gamma^{-1} u.$$

Substituting this into the remaining three equations, the solution is

$$e^{\phi} = \frac{1}{u} Y_i,$$ \hspace{1cm} (A.16)

$$e^{\lambda} = \frac{1}{\Gamma} Y_r.$$
The coordinate freedom (A.6) is still useful. Namely, consider a particular shell \( r = r_0 \). For it

\[
T = T(t, r_0) = T_0(t).
\]

But by means of the first of the transformations (A.6)

\[
T_0(t) = t
\]

can be achieved for one \( r_0 \) value. Now, choose the surface \( r_s \) for this specific shell. Outside there is no matter, therefore one may extend the velocity field into the vacuum in an arbitrary but continuous and convenient way, becoming purely time-directed in the CM system at the infinity. Nevertheless, one also may cut the metric at \( r = r_s \) and match it with the exterior metric [42], which is a Schwarzschild solution for the spherical case, possesses the form (A.9) for plane symmetry, but is Minkowskian if the gravity is negligible. The particles of the surface shell move in both metrics, and a comoving clock must measure a unique time, thus

\[
ds_1^2 = -e^{2\phi(t, r_s)} dt^2 = (- T_r^2(t, r_s) + Y_f^2(t, r_s)) dt^2 = ds_2^2
\]

being \( dr = 0 \) along a streamline. Since our choice has been

\[
T(t, r_s) = t,
\]

hence

\[
e^{\phi}|_{r_s} = e^\phi \sqrt{1 - e^{2\lambda - 2\phi} Y_f^2} |_{r_s}.
\]

For the Minkowskian case this equation gets a very simple form

\[
e^{\phi}|_{r_s} = \left. \frac{1}{\Gamma} \right|_{r_s}
\]

(cf. Eqs (A.13), (A.15) and (A.20)). Equation (7.5) has been obtained by this way, because for the spheric case

\[
e^{2\varphi} = e^{-2\lambda} \left. \left|_{r_s} = 1 - 2 \frac{G\dot{m}}{Y} \right|_{r_s} ,
\]

while \( u \) is defined in Eq. (6.11); without gravity Eq. (7.5) reduces to Eq. (A.22).

The other quantity, for which there is a gradient equation, thus a boundary condition is needed, is \( \dot{p} \). For \( p \) the boundary condition is [42]

\[
p(t, r_s) = 0
\]

for the \( Q \) term there is an iteration in Eqs. (7.16–18).
Appendix B
The initial conditions

The system of difference equations (7.4–18) explicitly shows that for some quantities (namely for \(u, R\) and \(W\)) initial conditions are needed. In general, the initial distribution of the matter has to be known, otherwise the physical situation is not fully defined. Now, the formalism presented here can be used for various situations, as it was mentioned in the conclusion, therefore various types of initial conditions are possible. For a wide class of problems (as e.g. stellar core collapse or spherical expansions) static initial configurations are relevant, and then the proper initial conditions are obvious. Nevertheless, for a heavy ion collision of slab geometry such conditions definitely cannot be used. So here we restrict our attention to this problem.

Consider a symmetric collision in the CM system. Because of the symmetry the centre of the collision will be at rest during the whole collision process, which has been explicitly built into the difference scheme (cf. Eqs (7.4–18)). Therefore one can simplify the problem to the collision of one nucleus of particle number \(N\) with a solid wall. The initial conditions are obviously determined by the history of this nucleus before the collision. Thus now we solve the “dynamical” problem for the free flight.

After the acceleration process but before the collision the nucleus moves rigidly, therefore [25]
\[
\mathcal{L}_\mu (g_{ik} + u_i u_k) = 0, \tag{B.1}
\]
where \(\mathcal{L}\) denotes the Lie derivative. Hence
\[
\dot{A} = 0. \tag{B.2}
\]
As a second consequence of the rigid motion [12, 25]
\[
Q = 0. \tag{B.3}
\]
The accelerated nucleus is in ground state, therefore
\[
n = n_0, \tag{B.4}
\]
\[
T = 0, \tag{B.5}
\]
so, as far as the fluid description is applicable, \(p = 0\), and from Eq. (B.3)
\[
\dot{P} = 0 \tag{B.6}
\]
and
\[
W = W_0, \tag{B.7}
\]
\(W_0\) being the energy/particle of the ground state. Then, from Eq. (6.2):
\[
\phi' = 0. \tag{B.8}
\]
Then, combining Eqs (6.15), (6.17) and (6.18), \( u \) and \( \Gamma \) are constant both in time and in space. But then, from (6.17):

\[
\dot{Y}' = 0,
\]

which equation can be integrated as

\[
Y(r, t) = \alpha(r) + \beta(t).
\]

According to Eqs (A.15):

\[
T(r, t) = T_0 + v_0 \alpha(r) + \frac{1}{v_0} \beta(t),
\]

\[
v_0 = \frac{u_0}{\Gamma_0}.
\]

One free function in the coordination has been fixed by Eq. (A.20), when

\[
Y = \alpha(r) - v_0^2 \alpha(r_s) - v_0 T_0 + v_0 t,
\]

\[
T = v_0 (\alpha(r) - \alpha(r_s)) + t,
\]

\[
e^\alpha = \frac{1}{\Gamma_0},
\]

\[
e^\beta = \frac{\alpha_r}{\Gamma_0}.
\]

A combination of Eqs (6.20) and (B.4) gives

\[
n_0 = \frac{\Gamma_0 N_0}{Fs_0}.
\]

Hence

\[
\alpha(r) = \frac{\Gamma_0 N_0}{Fn_0} r + A.
\]

So, finally,

\[
Y(r, t) = \frac{\Gamma_0 N_0}{Fn_0} (r - v_0^2 r_s) + (1 - v_0^2) A + v_0 (t - T_0),
\]

\[
T(r, t) = v_0 \frac{\Gamma_0 N_0}{Fn_0} (r - r_s) + t,
\]

\[
e^\alpha = \frac{1}{\Gamma_0},
\]

\[
e^\beta = \frac{N_0}{Fn_0}.
\]
The quantity $u_0$ is determined by the beam energy as

$$u_0 = \frac{\sqrt{E_{\text{beam}}}}{2N m_n},$$

(B.15)

which is the space-like component of the four-velocity in the CM system, therefore $v_0$ and $\Gamma_0$ are known, too; $n_0$ is the normal nuclear density. $N_0$ is an arbitrary parameter fixing the scale of $r$, and $F$ is an arbitrary normalization surface (cf. Section 6), the particular choices for them will not affect the final results. Eq. (6.9) yields

$$r_s = \frac{N}{N_0}.$$  

(B.16)

Now, choose the moment when the first cell is just arriving at the wall (i.e. when the two real nuclei become just touching) as the initial moment $t = 0$. Ignore first the first cell, which has been stopped; thence something similar to a shock wave is propagating [9, 18], but this does not influence the other cells in the initial moment. Therefore

$$u(r \neq 0, t = 0) = u_0,$$

$$W(r \neq 0, t = 0) = W_0.$$  

(B.17)

For the location $R$ observe that $R = Y(r, t)$; the condition that $Y(0, 0) = 0$ determines the constant $A$ in Eq. (B.14), and

$$Y(r, t = 0) = \frac{\Gamma_0 N_0}{F n_0} r = R(r, t = 0).$$

(B.18)

Now, we have obtained the initial conditions for all the cells except for the centre one. That cell has been stopped. Thus

$$R(0, 0) = 0,$$

$$u(0, 0) = 0.$$  

(B.19)

The specific energy of this cell can be calculated by taking the incoming energy and momentum into consideration (cf. e.g. [1], [9], [18], [20]).

References

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REINVESTIGATIONS ON THE ELECTRONIC TRANSITION MOMENT VARIATION IN \((A^2\Pi - X^2\Sigma^+)(A^2\Pi - X^2\Sigma^+)\) AND \((B^2\Sigma^+ - X^2\Sigma^+)(B^2\Sigma^+ - X^2\Sigma^+)\) BAND SYSTEMS OF BO MOLECULE

VEERAPPA M. MUMMIGATTI

Department of Physics
Jagadguru Shri Shivalingeshwar College, GOKAK, Karnataka, India

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The variation of electronic transition moment with internuclear distance in the case of \((A^2\Pi - X^2\Sigma^+)\) and \((B^2\Sigma^+ - X^2\Sigma^+)\) transitions of astrophysically significant BO molecule has been reinvestigated. On the basis of the results it is concluded that the conventional Morse potential is not appropriate to yield meaningful information about the electronic transition moments. The preferential superiority of the RKRV potential over Morse potential in such studies has been critically discussed.

1. Introduction

Using the intensity data of Elliott [1], Walvekar [2] has obtained decreasing and increasing expressions for the electronic transition moment functions respectively in the case of \((A^2\Pi - X^2\Sigma^+)(A^2\Pi - X^2\Sigma^+)\) and \((B^2\Sigma^+ - X^2\Sigma^+)\) transitions of astrophysically significant BO molecule. Because the intensity values due to Elliott were associated with 20% error, Robinson and Nicholls [3], using their own accurately measured intensity data on these band systems, have reported increasing electronic transition moment functions for both of these transitions. It must be pointed out here that, in the derivation of electronic transition moment functions, both Walvekar and, Robinson and Nicholls have used approximate Morse Franck-Condon (FC) factors and r-centroids. But recently, during their studies on RKRV FC factors and r-centroids on these band systems Mummigatti and Jyoti [4] have established the that there exists 20% to 40% error in the computed Morse FC factors. In accordance herewith it is thought worthwhile to reinvestigate the variation of electronic transition moment with internuclear distance taking into account the accurate intensity data in conjunction with FC-factors and r-centroids based on realistic potential models.
2. Derivation of electronic transition moments

Using the procedure already described by Mummigatti and Jyoti [5], the RKRV \( R_e(\tilde{r}_{v', v''}) \)-expressions are obtained on the band systems investigated here and the same are tabulated in Table I. The relative values of electronic transition moments, \( R_e(\tilde{r}_{v', v''}) \), are computed through

\[
R_e'(\tilde{r}_{v', v''}) = \frac{R_e(\tilde{r}_{v', v''})}{R_e(\tilde{r}_{0, 0})}
\]

and the same are tabulated in Table II. For the sake of comparison the relative \( R_e'(\tilde{r}_{v', v''}) \) values obtained by using the expressions (Table I) for electronic transition moment functions of Walvekar [2] and Robinson and Nicholls [3] are also presented in these Tables and the same are presented graphically in Figs 1 and 2. Here, the advantage of taking relative values of \( (R_e) \) lies in that it not only eliminates the arbitrary constant \( (k) \) from the \( R_e \)-expressions but also at the same time leads to a better comparison of various results obtained by other workers with the results of the present

<table>
<thead>
<tr>
<th>Transitions</th>
<th>( R(\tilde{r}) )-Expressions (RKRV)</th>
<th>Domain of ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( BO(A^2\Pi - X^2\Sigma^+) )</td>
<td>( R_e(r) = k(1-0.881r) )</td>
<td>1.270r &lt; 1.40</td>
</tr>
<tr>
<td>( BO(B^2\Sigma^+ - X^2\Sigma^+) )</td>
<td>( R_e(r) = k(1-0.852r) )</td>
<td>1.240r &lt; 1.424</td>
</tr>
</tbody>
</table>

"\( k \)" is a constant depending on the geometry of the scale chosen.

![Fig. 1](image-url)
REINVESTIGATIONS ON THE ELECTRONIC TRANSITION MOMENT VARIATION

1.30 r-centroids 1.36 1.40

Fig. 2

investigation, and, in turn enables one to test the preferential superiority of the results. In Table III the values of the differential, $\partial R^e_{r'} (\tilde{r}_{v',v''})/\partial \tilde{r}(v',v'')$, which represents the rate of variation of electronic transition moments with r-centroids, are displayed.

3. Discussion

A close survey of Tables II(a) and II(b) reveals that, in general, the values of the electronic transition moments obtained by using RKRV potential deviate considerably from the corresponding values due to Morse potential. Further, in the case of BO($A^{2}IIB - X^{2}\Sigma^{+}$) transition, as can be seen from Fig. 1, while the present investigation using RKRV potential and the Robinson and Nicholls investigation using Morse potential represent an increasing trend of $R^e_{r'} (\tilde{r}_{v',v''})$ values, the respective values decrease with increasing r-centroids when the same are investigated using values of Morse potential due to Walvekar. This discrepancy, as has been already pointed out [4], in the Walvekar results may naturally be due to the use of inaccurate band intensity data and FC factors and r-centroids computed using approximate Morse potential. Similar deviations, as can be seen from Table II(b) and Fig. 2, are also observed in the case of BO($B^{2}\Sigma^{+} - X^{2}\Sigma^{+}$) transition among $R^e_{r'} (\tilde{r}_{v',v''})$ values of RKRV and those of Morse due to both Walvekar and Robinson and Nicholls.

A word about the variation rates of electronic transition moments with r-centroids in both the band systems studied here will be in order; from Table III the following important observations are made:
Table II(a)

Relative values of electronic transition moments, $R'(v', v'')$, for the BO($4^3\Pi - X^2\Sigma^+$) transition expressed as $R'(v', v'') = R'(0,0) = 1$

<table>
<thead>
<tr>
<th>$v'$, $v''$</th>
<th>$r$-centroids</th>
<th></th>
<th>$r$-centroids</th>
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Table II(b)

Relative values of electronic transition moments, $R'(v', v'')$, for the BO($B^2\Sigma^+ - X^2\Sigma^+$) transition, expressed as $R'(v', v'') = R'(0,0) = 1$

<table>
<thead>
<tr>
<th>$v'$, $v''$</th>
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<th>$r$-centroids</th>
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<tr>
<td>2,7</td>
<td>1.423</td>
<td>–</td>
<td>1.445</td>
<td>1.7274</td>
<td>–</td>
</tr>
<tr>
<td>3,4</td>
<td>1.313</td>
<td>1.325</td>
<td>1.326</td>
<td>0.9650</td>
<td>0.9866</td>
</tr>
<tr>
<td>3,7</td>
<td>1.419</td>
<td>–</td>
<td>1.429</td>
<td>1.6997</td>
<td>–</td>
</tr>
<tr>
<td>3,8</td>
<td>1.435</td>
<td>–</td>
<td>1.465</td>
<td>1.8112</td>
<td>–</td>
</tr>
</tbody>
</table>

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Table III

Variation of electronic transition moments with r-centroids in the BO($A - X$) and BO($B - X$) transitions

<table>
<thead>
<tr>
<th>Electronic transitions</th>
<th>Potentials used</th>
<th>Average value of $\frac{\partial R_e(r)}{\partial r_{\nu',\nu''}}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO($A^2\Pi - X^2\Sigma^+$)</td>
<td>RKRV</td>
<td>+7.216</td>
<td>Increasing function of $R_e(r)$ variation</td>
</tr>
<tr>
<td></td>
<td>Morse (Walvekar)</td>
<td>-1.103</td>
<td>Decreasing function of $R_e(r)$ variation</td>
</tr>
<tr>
<td></td>
<td>Morse (Robinson and Nicholls)</td>
<td>+1.486</td>
<td>Increasing function of $R_e(r)$ variation</td>
</tr>
<tr>
<td>BO($B^2\Sigma^+ - X^2\Sigma^+$)</td>
<td>RKRV (present)</td>
<td>+6.943</td>
<td>Increasing function of $R_e(r)$ variation</td>
</tr>
<tr>
<td></td>
<td>Morse (Walvekar)</td>
<td>+7.7038</td>
<td>Increasing function of $R_e(r)$ variation</td>
</tr>
<tr>
<td></td>
<td>Morse (Robinson and Nicholls)</td>
<td>+1.582</td>
<td>Increasing function of $R_e(r)$ variation</td>
</tr>
</tbody>
</table>

*a. BO($A^2\Pi - X^2\Sigma^+$) transition*

The average rate of increase of RKRV electronic transition moments is greater than the corresponding $R'_e(\tilde{r}_{\nu',\nu''})$ values of Morse due to Robinson and Nicholls. For example, RKRV $R'_e(\tilde{r}_{\nu',\nu''})$ values increase at a rate of about 7.216 (Table III) while Morse $R'_e(\tilde{r}_{\nu',\nu''})$ values due to Robinson and Nicholls increase at a rate of about 1.486; however, the rate of decrease of Morse $R'_e(\tilde{r}_{\nu',\nu''})$ values due to Walvekar is about -1.103.

*b. BO($B^2\Sigma^+ - X^2\Sigma^+$) transition*

The average rate of increase of RKRV $R'_e(\tilde{r}_{\nu',\nu''})$ values is greater than the corresponding values [3] of Morse potential. For example (Table III), the RKRV $R'_e(\tilde{r}_{\nu',\nu''})$ values increase at a rate of about 6.943 whereas Morse $R'_e(\tilde{r}_{\nu',\nu''})$ values increase at a rate of about 1.582 and 7.704, respectively, for the values derived by Robinson and Nicholls, and Walvekar.

Bates [6] has suggested that a stronger variation of electronic transition moments persists in perpendicular band systems ($\Delta \Lambda = \pm 1$) than for parallel band systems ($\Delta \Lambda = 0$). Nicholls [7] has also presented some evidence in support of this observation of Bates. As can be seen from Table III, the results of the present investigation are also in accordance with the Bates observation, in that, the RKRV $R'_e(\tilde{r})$ values vary more strongly for BO($A^2\Pi - X^2\Sigma^+$) band system (perpendicular) than for BO($B^2\Sigma^+ - X^2\Sigma^+$) band system (parallel). The Morse values, either due to Walvekar or due to Robinson and Nicholls are unable to establish this point; it seems that the use of approximate Morse FC factors and $r$-centroids might be the reason for this discrepancy in their results.
Acknowledgements

The author wishes to thank Dr. B. G. Jyoti for valuable guidance during the present work and Dr. V. M. Korwar of the Karnataka University Physics Department for many useful suggestions. Thanks are also due to Professor N. Shreedhar Murthy of Mysore University for valuable correspondence during the present investigation.

References

The theoretical analysis and the experimental results show that the dependence of the laser output energy on the electron concentration mainly depends on the mechanism of the electron reduction in the main discharge.

The logarithmic increasing of the laser output energy with the increasing of the electron density (which was mentioned in the literature as a general formula), is found to be valid only when the reduction of the electrons is due to electron attachment, but it needs to be modified if the main reduction mechanism is recombination.

Introduction

Since the introduction of the CO₂ laser by Patel [1] in 1964, many advances have been made in the technology and understanding of electric discharge CO₂ lasers. Nighan [2] has shown that the optimum electric fields for pumping a CO₂ laser were below the fields required for a sustained discharge. Thus, the concept of separation of the ionization source from the discharge has led to the use of electron beams to sustain high pressure discharge for laser excitation.

The dependence of the laser output energy on the electron density in the CO₂ gas discharge was mentioned by Suzuki et al [3]. They have introduced a relationship defining the dependence of the laser output energy on the electron density in the discharge, to fit their experimental data.

In this paper we report on the validity of this relation to the e-beam pumped CO₂ lasers. A theoretical analysis and experimental measurements have been done using a cold-cathode glow-discharge e-beam gun pumped CO₂ laser.
Experimental work

The circuit diagram of the apparatus is shown in Fig. 1. The e-beam gun consists of a flat aluminum cathode and a multistage anode. The final anode is earthed. Helium at a pressure of about 10 Pa flows through the gun. A high voltage pulse is applied to the cathode and glow discharge forms in the gun volume. Ions formed in the discharge bombard the cathode and produce secondary electrons which are then accelerated through the multiple anode structure to form the e-beam.

![Circuit diagram of cold cathode-glow discharge e-beam gun pumped CO₂ laser](image)

The laser discharge chamber consists of a 2 cm thick perspex box of internal dimensions 23 cm × 13.4 cm × 8 cm. This box was screwed to the earthed anode of the e-beam gun. The laser anode is a Rogowski profile aluminium plate and the laser cathode consists of a stainless steel mesh. The anode to cathode spacing is adjustable, but for the results reported here, it was fixed to 3.2 cm. The active laser volume is probed by an optical resonator consisting of 3.5 cm diameter 20 meter radius of curvature copper gold coated mirror and 85% reflectivity dielectric coated germanium output window. CO₂, N₂ and He flowed through the laser gas chamber at atmospheric pressure.

The e-beam is passed into the laser through a 15 cm × 2.5 cm metal foil window. The window (12.5 μm Ti) is supported between two grids with geometrical transmission of about 80%. The transmitted e-beam current was collected by the laser anode 3.2 cm from the foil window with the laser box filled with the appropriate gas mixture at 1 atm, and it was detected by means of a Rogowski coil (English Electric MA 391, 20 A/V). The burning voltage of the high-voltage glow discharge was measured by means of a high voltage capacitor divider.

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Results and discussion

The measurement of the e-beam current variation in the laser gas chamber as a function of gas mixture ratio \( \gamma \left( = \frac{PCO_2}{P_{CO_2} + PN_2} \right) \) is shown in Fig. 2. Referring to this Figure the electron density decreases exponentially with \( \gamma \) in the range of \( \gamma \geq 0.4 \). This result is in good agreement with the results found by Ohwadano et al [4]. The

\[
- \frac{dn_e}{dt} = \alpha n_e^2, \tag{1}
\]

\[
- \frac{dn_e}{dt} = bN_0 n_e, \tag{2}
\]

where \( \alpha \) is the electron recombination coefficient, \( b \) is the electron attachment coefficient, \( n_e \) is the concentration of electrons produced by the injection of the e-beam in the laser cavity, and \( N_0 \) is the negative molecules concentration. It can be seen from the above relations (1) and (2) that the decreasing of the electron density due to electron attachment can explain the graph shown in Fig. 2.
It has been mentioned by Borisov et al [6] that the decay of the electron density in carbon dioxide and helium plasmas is due to attachment mechanism. Thus, the decreasing of the electron density due to electron attachment for \( \gamma \geq 0.4 \) is accepted, because in such mixtures the \( \text{CO}_2 \) and \( \text{He} \) gas molecules are dominant.

Since \( N_0 = K \gamma \), where \( K \) is a constant, Eq. (2) can be written as:

\[
- \frac{dn_e}{dt} = bk\gamma n_e
\]

and therefore:

\[
\ln n_e = - A\gamma \tau + \ln n_{e0},
\]

where \( \tau \) is the e-beam pulse duration, \( A \) is a constant, and \( n_{e0} \) is the electron concentration at the beginning of the e-beam pulse injected to the gas mixture \((t = 0)\).

The variation of the laser output \( E_{\text{out}} \) with the gas mixture ratio \( \gamma \) has been mentioned by many authors [7, 8] as well as in this work as shown in Fig. 3. In all these results the laser output energy increases with \( \gamma \) to a certain value and then decreases linearly as \( \gamma \) increases. The full explanation of this result was given elsewhere [9]. Thus for \( \gamma \geq 0.4 \) the dependence of the laser output energy \( E_{\text{out}} \) on the gas mixture ratio \( \gamma \) may approximately follow the relation

\[
E_{\text{out}} = C - G\gamma,
\]

where \( C \) and \( G \) are constants. From the relations (3) and (4) one can easily find that

\[
E_{\text{out}} = a \ln n_e + D,
\]

where \( a \) and \( D \) are constants, their values depending on the attachment coefficient, e-beam pulse duration and the concentration of the electrons at the beginning of the pulse. This relation is the same relation found experimentally by Suzuki et al [4]. In the region where the electron recombination is dominant \((a n_e^2 \gg bN_0 n_e)\) the work is carried

Fig. 3. Variation of the laser output energy with the gas mixture ratio \( \gamma \) of \( \text{P}_{10}(18) \)

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on to see the dependence of the laser output energy on the electron density. From the method of analysis this formula cannot be considered as a general relation for the CO\textsubscript{2} lasers, and it is valid only when the decay of the electron density is due to the attachment mechanism.

**Conclusion**

The relationship between the electron density in TEA CO\textsubscript{2} laser and the laser output energy has been clarified theoretically and experimentally. The theoretical analysis and the experimental measurements show that the CO\textsubscript{2} laser output increases logarithmically with increasing the electron density when the reduction of the electron concentration in the discharge is due to attachment mechanism, whereas this relation is not valid when the decreasing of the electron density in the gas discharge is due to recombination mechanism.

**References**


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CENTRES RESPONSIBLE FOR 340 AND 380 K GLOW PEAKS IN NaCl: Sr

R. V. JOSHI, N. L. KEKAN and N. A. PATIL

Physics Department, Faculty of Science
M. S. University of Baroda, Baroda – 2 India

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Thermal glow curves of NaCl: Sr phosphors were examined for emission in the ultraviolet and visible region using suitable filters. It is observed that the thermoluminescence emission for 340 K glow peak is mainly in the ultraviolet region whereas the emission for the 380 K glow peak is primarily in the visible region. It is suggested that the 340 K peak is associated with impurity–vacancy dipoles and the 380 K glow peak is related to isolated Sr⁺⁺ ions.

In the present experiment ultraviolet and visible components of the thermal glow curves of NaCl: Sr phosphors were recorded separately to examine the dependence of the glow peak intensities on the emission in the two regions. The results obtained clearly indicate that the centres responsible for the two glow peaks are different in nature. The base material used was analar grade sodium chloride in which strontium was introduced as an impurity. Single crystals of NaCl: Sr specimens were grown from melt. Specimens used were in the form of plates cleaved from the grown crystals. One lot of the specimen was annealed at 750 °C for two hours and subsequently quenched to room temperature (rate 100 °C/min). Another batch of the specimen was annealed and cooled slowly. The specimens were irradiated with ultraviolet light from an aluminium arc at room temperature. Glow curves were recorded after warming the specimen at the rate of 10 °C/min. The ultraviolet and visible components of the glow were separated by using Chance OX, and Corning OX₁₈ filters, respectively.

Results obtained for specimens with Sr concentration of the order of 10⁻² m.f. are presented for discussion. It is obvious from Fig. 1 that the thermoluminescence emission for an annealed and slowly cooled specimen is mainly in 340 K peak (Fig. 1(a)) whereas the quenched specimen exhibits a well-defined pronounced glow peak at 380 K (Fig. 1(b)). In the Figure curves 1 and 2, respectively, represent the glow curves for ultraviolet and visible emission. The data obtained clearly demonstrate that thermoluminescence at 340 K favours emission in the ultraviolet. As against this, the thermal glow at 380 K favour emission exclusively in the visible.

Since 340 K glow peak is observed in all the slowly cooled specimens, the occurrence of the peak may therefore be reasonably assumed to be related to the
crystallinity of the specimen. It is suggested that in the slowly cooled specimens, a large fraction of the divalent impurity ions in solid solution at annealing temperature forms precipitate and that a greater number of those retained in solid solution, of equilibrium concentration at room temperature, pairs off with positive ion vacancies to reduce the strain in the lattice. The 340 K glow peak is therefore suggested to be associated with the presence of dipoles (impurity–vacancy pairs) in the perfect region of the lattice.

When the specimen is annealed at elevated temperature and then cooled rapidly, there will be uniform distribution of the Sr$^{++}$ ions in the bulk of the specimen along with quenched-in anion and cation vacancies. A major fraction of the Sr$^{++}$ ions in solid solution will get associated with cation vacancies to form dipoles and thereby reduce the strain in the lattice. However, it is expected that few Sr$^{++}$ ions and positive ion vacancies will exist in the lattice independent of each other. The isolated Sr$^{++}$ ions are suggested to act as trapping centres for the electrons and thus get converted into Sr$^{+}$ ions. Such monovalent Sr$^{+}$ ions are presumed to be responsible for 380 K glow peak.

**Acknowledgement**

One of the authors (N.A.P.) is thankful to the Maharaja Sayajirao University of Baroda (India) for the award of a post-doctorate research scholarship.
VELOCITY OF MASS FLOW IN THE TEMPERATURE MAXIMUM IN A MAGNETICALLY DEFLECTED WALL-STABILIZED ELECTRIC ARC

J. Ramos-Barrado

Department of Physics, Faculty of Sciences, University of Málaga
29071 Málaga, Spain

(Received 27 September 1985)

The mass flow velocity in the temperature maximum of a magnetically deflected wall-stabilized electric arc is calculated based on the measures of the arc displacement and a characteristic time constant in the return process of the arc to axial position when the magnetic field is switched off.

1. Introduction

When an external transverse magnetic field is applied to a wall-stabilized electric arc burning in the axial direction in a tube with cylindrical cross section, the Lorentz forces disrupt the initial symmetry of the temperature distribution and set in motion a mass flow normal to the arc axis, so that the temperature maximum shifts in the direction of the magnetic forces.

Analysis for the rotational mass flow phenomena originated by the Lorentz forces is a basic problem of magnetofluidynamics; there have been theoretical attempts [1, 2, 3, 4] and a practical investigation by Rosenbauer [5] to resolve it using a low energy Ar arc in absence of gravity field disturbance. Sauter [6] also used an Ar arc but with greater arc current and stronger transverse magnetic fields.

This paper presents a very simple experimental method to determine the velocity of mass flow in the axis of a magnetically deflected wall-stabilized electric arc \( (V_M) \). According to Maecker [7] the arc velocity, \( V_A \), is the sum of the gas velocity in the temperature maximum, \( V_M \), and the arc velocity relative to that mass flow, \( V_{AM} \). The arc reaches a new equilibrium when the opposite velocities \( V_M \) and \( V_{AM} \) are the same at the point of maximum temperature. Consequently, \( V_M \) may be determined indirectly by measuring the velocity \( V_{AM} \) when the arc reaches its deflected stationary state.

2. Experimental method

When the magnetic field is switched off, the maximum isotherm returns to the axial position. During the return process there is only a passive movement of the maximum ionization point of the arc which shows then a tendency to recover its initial
temperature distribution symmetry. The relative displacement distance of the temperature maximum [8] is expressed as a function of time as follows:

\[ X_A(t) = RX_e \exp \left( -\frac{t}{t_c} \right) \]

where \( R \) is the radius of the cylindrical chamber, \( X_e \) is the initial relative displacement, \( t \) is time, and \( t_c \) denotes the time constant governing this phenomenon; its measurement at different arc current intensities is the key feature of the present method.

The velocity of an arc in the return process may now be evaluated from the derivative of Eq. (1) with respect to time:

\[ V_A = V_{AM} = -\frac{RX_e}{t_c} \exp \left( -\frac{t}{t_c} \right) \]

and the initial return velocity is given by:

\[ V_{AM0} = -\frac{RX_e}{t_c} \]

At the temperature maximum of a magnetically deflected arc in a non-equilibrium stationary position, the velocities \( V_M \) and \( V_{AM} \) have equal absolute value, consequently the velocity \( V_M \) has the same absolute value as the initial return velocity for that position. Thus, to determine \( V_M \) at the temperature maximum, it is only necessary in this method to measure the arc displacement caused by the transverse magnetic field and its characteristic return time \( (t_c) \) when the magnetic field is switched off.

### 3. Experimental results

The gas was argon of 99.996% purity. For the chamber we used a water-cooled quartz tube of \( 10^{-2} \) m radius. The magnetic field was produced by two coils on each side of the outer tube. The magnetic field was measured by a Gaussmeter with a precision of 1%. The time constant of the coil circuit was \( 2 \times 10^{-5} \) s.

The arc deviation was measured by photographing, in one exposure, both the initial axial position, and the magnetically deflected position. High contrast Kodak 9 din sensitivity film was used. The magnification was 1/2. Displacement measurements were made on the photogram using a Zeiss IV stereomicroscope.

To measure the time taken to return to axial position, we used a L.D.R. photocell signal. The L.D.R. was stimulated by emitted light, and the arc column halo was eliminated by a lens and diaphragm. The photocell was placed in the arc image position with an accuracy of 0.2 mm. The photoelectric cell signal was inverted and applied to one input of a “Y” gate. In addition to the inverted coil circuit comparator signal, clock pulses of \( 10^5 \) Hz were also applied to the gate. The “Y” gate was open to the clock pulses only when the inverted signal of L.D.R. (\( \bar{x} \)) and the inverted coil circuit signal (\( B \))
coincided. (Table I: Logic Diagram). Clock pulses were counted by a digital counter with a resolution of 50 ns.

The arc displacement, and the time for its return to the axial position, was measured for current intensity values of 1, 1.5, 2, 2.5 and 3 A, at pressures of 50.65, 101.3 and 202.6 KPa, and also for different magnetic field values between $0.5 \times 10^{-4}$ T and $8 \times 10^{-4}$ T. Displacement and time value measurement errors were less than 2%.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Logic diagram</td>
</tr>
<tr>
<td>( \bar{x} )</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

The influence of gas pressure on arc displacement was very small; the difference between the values of arc deviation, for the same intensity, the same magnetic field, and different pressures, were close to experimental error (0.01 mm). A factorial Yates analysis [9] of the influences of pressure, current intensity, and magnetic field on arc displacement shows that the influence of the pressure was $-0.01$ mm for each 101.3 KPa. This is insignificant, so the results are based on the variation of \( X_e \) with \( I \) and \( B \), at the standard pressure of 101.3 KPa. The arc current density for a canal model \((J_k)\) was calculated by the Maehcker and Stäblein method [10] and these results were fitted to the following by the Fletcher and Power method [11]:

\[
X_A(J_k, B) = \exp \left( -\frac{1}{B(a + b/J_k)} \right). \tag{4}
\]

The determination coefficient is larger than 0.99 and the fitting error is 0.01, so the expression (4) is:

\[
X_A(J_k, B) = \left( \exp \left( -\frac{B^{-0.570}}{0.815 + 0.818/J_k} \right) \right) \pm 0.01. \tag{5}
\]

On the other hand, based on the values of the time to return to axial position, we fitted the exponential function (1) to the experimental results by the least square method. In all cases the fitting error is smaller than $4 \times 10^{-3}$ s. The Student test gives characteristic time values \((t_c)\) whose probability difference is more than 95%. Fig. 1 shows the characteristic time vs the arc current intensity at pressures of 56.65, 101.3, and 202.6 KPa.

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The velocity $V_M$ at the maximum temperature of a magnetically deflected wall-stabilized electric arc at non-equilibrium stationary position may now be determined as follows:

$$V_A = 0,$$  \hspace{1cm} (6)

$$-V_{AM} = V_M = \frac{RX_e}{t_c}.$$  \hspace{1cm} (7)

Figure 2 shows the mass flow velocity $V_M$ vs the arc current intensity for the pressures of 56.65, 101.3 and 202.6 KPa, and a magnetic field strength of $8 \times 10^{-4}$ T. Fig. 3 displays the velocity $V_M$ plotted against the Lorentz force $(IB)$, for the above pressures.

4. Conclusion

In this method to evaluate the velocity $V_M$ it is only necessary to measure the arc displacement and the return time. A comparison of the velocities $V_M$ calculated by our method, and those of Rosenbauer and Sauter, is difficult because the diameters of the
chambers are different; however, the change of $V_M$ with $B$ and $I$ agrees well with the results of both Rosenbauer and Sauter. Fig. 4 compares the relative velocities $V_M/V_0$. Moreover, the present method reveals an interesting close relationship between thermal and dynamical phenomena in a magnetically deflected wall-stabilized electric arc.

The return phenomena are studied by analysing the variation of the characteristic return time $t_r$, and also the decrease observed when the arc intensity increases as the axis temperature rises. For this reason, the time characteristic should be a function of the initial arc displacement. However, the variation of the maximum temperature is very small, and we did not observe any perturbation of the experimental results. The increased thermal resistance to arc displacement must be compensated by an increase in the mass flow at the maximum temperature (Fig. 3). In a deflected arc, the asymmetrical temperature distribution may result from heating of the column side, near to the chamber wall by increased mass flow, while the other side cools. In other words, the asymmetrical heat conduction flux is balanced by the mass flow enthalpy transport.
The pressure increase signifies an increase of the power per unit volume of the arc column (Fig. 1) with the pressure for the same arc current intensity and magnetic field; in this way, the mass flow balances a larger asymmetrical heat flux. Thus, in the Elenbaas–Heller equation

$$V^2S - \frac{\rho C_p}{\chi} \nabla \cdot V S = -E \sigma(S),$$

where $\rho$ is the density; $\chi$ the thermal conductivity; $C_p$ the specific heat capacity at constant pressure; $E$ the electric field and $\sigma$ the electric conductivity: if we take gradients and apply them to the maximum temperature

$$\left( \frac{\partial}{\partial x} V^2S \right)_m = \left( \frac{\rho C_p}{\chi} \right)_m V_m \left( \frac{\partial^2 S}{\partial x^2} \right)_m,$$

that is to say that the asymmetric distribution of $S$ obtained for a given value of $S_A$ increases with the axial mass flow in the arc column. In addition, the following is obtained:

$$\left( \frac{\rho C_p}{\chi} \right)_m V_m = \frac{\left( \frac{\partial}{\partial x} V^2S \right)_m}{\left( \frac{\partial^2 S}{\partial x^2} \right)_m},$$

in such a way that $(\partial^2 S/\partial x^2)_m$ is the distribution curve of $S$ around its maximum potential, and that the reciprocal of this is a measure unit of the arc thickness, we may consider the term $(\rho C_p/\chi)V_m$ as being proportional to the asymmetry occurring in the heat flux divergence, expressed in units of arc thickness.

References

SHORT COMMUNICATIONS

A ROTATING MASS IN GÖDEL UNIVERSE WITH AN ELECTROMAGNETIC FIELD

L. K. Patel and Shardha S. Koppar

Department of Mathematics, Gujarat University
Ahmedabad, 380009 India

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The metric
\[ ds^2 = 2(du + g \sin \alpha d\beta) dx - \varepsilon(du + g \sin \alpha d\beta)^2 - R f (dx^2 + \sin^2 \alpha d\beta^2) \]  
with
\[ g = g(\alpha), \quad 2 f = g_\alpha + g \cot \alpha, \]
\[ g_\alpha = \frac{\partial g}{\partial \alpha}, \quad \varepsilon^2 = 1. \]

R is a constant and \( f(\alpha) \) satisfies
\[ \frac{1}{2} \left( \frac{f_\alpha}{f} \right)_\alpha + \frac{1}{2} \left( \frac{f_\alpha}{f} \right) \cot \alpha - 1 = -(1 + 3 \varepsilon) \frac{f}{R} \]

has been designated as Einstein–Gödel metric by Vaidya in [1]. When \( \varepsilon \) is put equal to +1, (1) represents Einstein Universe and when \( \varepsilon \) is put equal to −1 it represents a static rotating Gödel Universe. Patel and Vaidya [2] have discussed a solution of Einstein field equation which describes the gravitational field of a rotating mass embedded in Gödel Universe. The purpose of the present note is to introduce a source-free electromagnetic field in their solution.

For this purpose we take the metric in the form,
\[ ds^2 = 2(du + g \sin \alpha d\beta) dx - 2L(du + g \sin \alpha d\beta)^2 - R f (dx^2 + \sin^2 \alpha d\beta^2), \]
with \( L = L(\alpha), \quad g = g(\alpha), \quad 2 f = g_\alpha + g \cot \alpha \) and \( R \) is a constant.

By introducing the basic differential 1-forms
\[ \theta^{(1)} = du + g \sin \alpha d\beta, \]
\[ \theta^{(2)} = (R f)^{1/2} dx, \]
\[ \theta^{(3)} = (R f)^{1/2} \sin \alpha d\beta, \]
the metric (3) becomes
\[ ds^2 = 2\theta^{(1)}(\theta^{(4)})^2 - \theta^{(1)}{2} - \theta^{(3)}{2} = g_{(ab)}\theta^{(a)}\theta^{(b)}. \]

Here and in what follows a bracketed index implies the corresponding tetrad component. A metric more general than (3) has been investigated by Vaidya, Patel and Bhatt [3]. They have obtained the tetrad components \( R_{(ab)} \) of the Ricci tensor for their metric. Using their results the tetrad components \( R_{(ab)} \) for the metric (3) and the tetrad (4), they are given by
\[
R_{(23)} = R_{(24)} = R_{(34)} = R_{(12)} = R_{(13)} = 0,
R_{(44)} = \frac{-2}{R^2}, \quad R_{(11)} = L^2 R_{(44)},
\]
\[
R_{(14)} = L_{xx} + \frac{2L}{R^2},
R_{(22)} = R_{(33)} = \frac{Y}{R} + \frac{4L}{R^2},
\]
where \( L_{xx} = \frac{\partial^2 L}{\partial x^2} \) and \( Y \) stands for
\[
\frac{1}{2f} \left( \frac{f_x}{f} \right) + \frac{1}{2f} \left( \frac{f_x}{f} \right) \cot x - \frac{1}{f}.
\]

We shall use the following field equations
\[
R_{ik} - \frac{1}{2} g_{ik} R = -8\pi[(P + \rho)v_i v_k - P g_{ik}] - 8\pi E_{ik} - \Lambda g_{ik},
\]
with \( v_i v^i = 1 \).

Here \( E_{ik} \) is the energy tensor of the source free electromagnetic field given by
\[
E_{ik} = -g^{1m} F_{il} F_{km} + \frac{1}{4} g_{ik} F_{1m} F^{1m},
F_{ik} = A_{i,k} - A_{k,i},
F_{ik} = 0.
\]

A comma indicates ordinary derivative and a semicolon indicates a covariant derivative. The other symbols occurring in (7) have their usual meanings. One can now write down the field equations (7) in the following tetrad form
\[
R_{(ab)} = -8\pi \left[ (P + \rho)v_{(a)} v_{(b)} - \frac{1}{2} (\rho - P) g_{(ab)} \right] - 8\pi E_{(ab)} + \Lambda g_{(ab)}.
\]
For the metric (3) and the tetrad (4) we take

\[ v_{(a)} = \left( \frac{1}{2n}, 0, 0, n \right), \quad (9) \]

\[ n \text{ being a function of coordinates.} \]

The results (6), (8), and (9) imply

\[ E_{(22)} = E_{(33)}, \quad E_{(23)} = E_{(24)} = E_{(34)} = E_{(12)} = E_{(13)} = 0, \quad (10) \]

\[ R_{(11)} = - \frac{2\pi(P + \rho)}{n^2} - 8\pi E_{(11)}, \quad (11) \]

\[ R_{(22)} = - A - 4\pi(\rho - P) - 8\pi E_{(22)}, \quad (12) \]

\[ R_{(14)} = A - 8\pi P - 8\pi E_{(14)}, \quad (13) \]

\[ R_{(44)} = - 8\pi(P + \rho)n^2 - 8\pi E_{(44)}, \quad (14) \]

where \( R_{(ab)} \) are given by (6).

Vaidya and Patel [4] have shown that the source-free electromagnetic field satisfying (10) can be obtained from the 4-potential \( A_i \) given by

\[ A_i = (A(x), 0, g \sin \alpha A(x), 0), \]

where \( A_x^2 + \frac{4A^2}{R^2} = \text{constant} = b^2 \). They have also obtained the nonzero tetrad components \( E_{(ab)} \) of \( E_{ik} \). They are given by

\[ E_{(14)} = E_{(22)} = E_{(33)} = \frac{1}{2} b^2. \quad (15) \]

Substituting (15) in (11), (12), (13) and (14) it is painless to see that

\[ \frac{1}{n^2} = 1 - 2T, \quad (16) \]

\[ 8\pi P = A - 4\pi b^2 + \frac{1}{R^2} - \left( T_{xx} + \frac{2T}{R^2} \right), \quad (17) \]

\[ 8\pi(P + \rho) = \frac{2}{R^2} (1 - 2T), \quad (18) \]

\[ \frac{Y}{R} + 8\pi b^2 - \frac{2}{R^2} + \left( T_{xx} + \frac{4T}{R^2} \right) = 0, \quad (19) \]

where we have taken \( 2L = -1 + 2T(x) \).
As $Y$ is a function of $x$ only, the equation (19) will split into two equations

$$\frac{Y}{R} + 8\pi b^2 - \frac{2}{R^2} = 0 \tag{20}$$

and

$$T_{xx} + \frac{4T}{R^2} = 0. \tag{21}$$

Therefore, the pressure $P$ and the density $\rho$ are given by

$$8\pi P = \frac{1}{R^2} (1 + 2T) + \Lambda - 4\pi b^2, \tag{22}$$

$$8\pi \rho = \frac{1}{R^2} (1 - 6T) - \Lambda + 4\pi b^2. \tag{23}$$

It is possible to solve Eq. (20) for $f$. The solution is given by

$$\frac{f \sin \alpha}{g} = \frac{1}{R} e^{ky}, \quad g \sin \alpha = \frac{2}{kR} e^{ky}. \tag{24}$$

Here and in what follows the constant $k$ is given by $kR = 1 - 4\pi b^2 R^2$. The Eq. (21) is a linear differential equation whose solution can be easily obtained. Eg. $T = \left(\frac{a}{4}\right) R \sin \left(\frac{2x}{R}\right)$ is a solution of (21) where $a$ is a constant. Thus the metric (3) is completely determined.

We carry out the following transformation from

$$(u, \alpha, \beta, x) \rightarrow (t, x, y, z) \quad t = u + x, \quad dy = g \, dx,$$

$$\beta = z, \quad x = x.$$ The final form of the transformed metric is given by

$$ds^2 = dt^2 - dx^2 + \frac{4}{kR} e^{ky} \, dt \, dz - \frac{1}{2} kR \, dy^2 +$$

$$+ \frac{2(2-kR)}{k^2 R^2} e^{2ky} \, dz^2 - 2T \left( dt - dx + \frac{2}{kR} e^{ky} \, dz \right)^2. \tag{25}$$

When $b = 0$ the metric (25) reduces to

$$ds^2 = dt^2 - dx^2 + 4e^{y/R} \, dt \, dz - \frac{1}{2} dy^2 + 2e^{2y/R} \, dz^2 - 2T(dt - dx + 2e^{y/R} \, dz)^2. \tag{26}$$
The metric (26) represents the gravitational field of a rotating mass embedded in Gödel Universe.

When $T = 0$ in (25) we get a metric which represents Gödel Universe pervaded by a source-free electromagnetic field.

Thus metric (25) describes the gravitational field of a rotating mass embedded in Gödel Universe with an electromagnetic field.

References

ON THE CLASSIFICATION OF INFINITESIMAL INVARIANCE TRANSFORMATIONS

P. G. C. RIO-PRETO and J. D. M. VIANNA

Physics Department, Institute of Exact Sciences
University of Brasilia
70.910—Brasilia—DF—Brasil

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In recent years there has been an increasing interest [1–6] in the determination of the symmetry group and in the construction of invariants for the one-dimensional harmonic oscillator (OHO). The application of the Lie theory of extended groups to Newton's equation of motion and the use of Noether's theorem in the context of Lagrangian formulation are two methods found in the current literature to study such a system. As a consequence of these approaches there are differences in the results obtained. From the first method it is obtained that the symmetry group of the OHO is the eight-parameter Lie group SL (3, R). Considering Noether's theorem a certain five-parameter subgroup of SL (3, R) the members of which are called Noether symmetries (NS) [7] is found; furthermore in order to determine the additional three-parameter subgroup whose members are called non-Noether symmetries (nNS), the Euler-Lagrange equations are used. According to Lutzky [1, 7] although the full eight-parameter group SL (3,R) leaves the equation of motion invariant (solutions are transformed into solutions), only NS satisfy the condition of preserving the action-integral, i.e., only for NS it is verified that

\[ \delta L = L(q + \delta q, \dot{q} + \delta \dot{q}, t + \delta t) - L(q, \dot{q}, t) = e \frac{d}{dt} F(q, t) + O(\varepsilon^2), \]

where \( F \) is some function of \((q, t)\) and \( \varepsilon \) is such that \( 0 < \varepsilon \ll 1 \). We show in the present note that useful information on the matter can be obtained from an alternative procedure based on the standard methods of Lagrangian description without using the Lie theory of extended groups or Noether's theorem as a starting point. In the present approach the transformed action to first order in the parameter \( \varepsilon \), \( (0 < \varepsilon \ll 1) \), can be written as the untransformed action plus a term \( \varepsilon \int_{t_1}^{t_2} R(q, \dot{q}, t) dt \). Then we are able to clarify in a simple way the concept of Noether and non-Noether symmetries by imposing conditions on the quantity \( R(q, \dot{q}, t) \). In order to compare our results to the results of an OHO system

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we will only consider the case of one-degree of freedom, but the method outlined here can be generalized to $N$-dimensional dynamics system in a straightforward way.

Let a one-dimensional dynamical system be defined by a Lagrangian $L(q, \dot{q}, t)$ being the action

$$A[q] = \int_{t_1}^{t_2} L(q, \dot{q}, t) \, dt; \quad \dot{q} = dq/dt,$$

and correspondingly the Euler–Lagrange equation

$$[L] [q, \dot{q}, t] \equiv \frac{d}{dt} \frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = 0 . \quad (1)$$

Suppose that a near-identity transformation

$$q \rightarrow q' = q + \epsilon \eta(q, t), \quad (2)$$

$$t \rightarrow t' = t + \epsilon \theta(q, t), \quad (3)$$

is performed on $A[q]$; $\epsilon$ denotes an arbitrarily small expansion parameter: $0 < \epsilon < 1$; $\eta$ and $\theta$ are functions of $t$ and $q$.

Equations (2) and (3) determine that the transformation of $\dot{q}$ be

$$\dot{q} \rightarrow \dot{q}' = \dot{q} + \epsilon \left[ \frac{d \eta}{dt} - \dot{q} \frac{d \theta}{dt} \right], \quad (4)$$

where

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \dot{q} \frac{\partial}{\partial q}.$$

Thus the transformed action is

$$A[q'] = \int_{t_1}^{t_2} L(q', \dot{q}', t') \, dt'; \quad \dot{q}' = dq'/dt'.$$

(5)

Assume that there exists another Lagrangian $L'$ of the untransformed arguments, such that

$$L'(q, \dot{q}, t) = L(q', \dot{q}', t') \frac{dt'}{dt} \quad (6)$$

and define similarly an action $A'$ of the untransformed variables by

$$A'[q] = A[q'] . \quad (7)$$

It follows that the action $A'[q]$ can be written as

$$A'[q] = \int_{t_1}^{t_2} L'(q, \dot{q}, t) \, dt . \quad (8)$$
Using Eqs (2), (3), (4) and (6) in Eq. (8) and then expanding Eq. (8) to the first order in \( \varepsilon \) we find

\[
A'[q] = \int_{t_1}^{t_2} L(q, \dot{q}, t) dt + \varepsilon \int_{t_1}^{t_2} R(q, \dot{q}, t) dt + O(\varepsilon^2),
\]

(9)

where

\[
R(q, \dot{q}, t) = \eta \frac{\partial L}{\partial \dot{q}} + \left( \frac{d\eta}{dt} - \frac{\dot{\theta}}{\dot{q}} \right) \frac{\partial L}{\partial q} + \frac{d\theta}{dt} \frac{\partial L}{\partial \dot{q}}.
\]

(10)

in the present method, \( \eta \) and \( \theta \) are functions to be determined from imposing on \( R(q, \dot{q}, t) \) conditions (11), (12) or (13) below and using \([L][q, \dot{q}, t] = 0\).

Relation (9) is a particularly convenient form for examining the symmetry transformations. Actions \( A'[q] \) and \( A[q] \) are defined on the same variables \( q \), but in general \( A'[q] \) describes a system with different dynamics corresponding to a Lagrangian \( L'(q, \dot{q}, t) \). Retaining only first-order terms, \( A'[q] \) has two terms. The term of zeroth order in \( \varepsilon \) is \( A[q] \) and reproduces the original equation of motion \([L][q, \dot{q}, t] = 0\). Then in order that this be not altered (see the analysis below) by the term linear in \( \varepsilon \) we must have at least one of the following conditions on \( R(q, \dot{q}, t) \):

**Case 1:**

\[
[R][q, \dot{q}, t] \equiv \frac{d}{dt} \frac{\partial R}{\partial \dot{q}} - \frac{\partial R}{\partial q} = 0,
\]

(11)

**Case 2:**

\[
R(q, \dot{q}, t) \equiv \frac{d}{dt} F(q, t),
\]

(12)

where \( F \) is some function which depends only on \( q \) and \( t \), if so

**Case 3:**

\[
R(q, \dot{q}, t) \equiv 0.
\]

(13)

Dothan [8] has used identity (11) in the study of symmetry transformations in classical field theory. Identities (12) and (13) have not been previously noted in the context of the present method; they are associated directly with NS, as we will show.

Analysing each case we have:

**Case 1:** Identity (11) assures the invariance of the equation of motion \([L][q, \dot{q}, t] = 0\). In fact, from Eqs (5), (7) and (9) it follows that

\[
[L][q', \dot{q}', t'] = [L][q, \dot{q}, t] + \varepsilon [R][q, \dot{q}, t].
\]

(14)

Hence, \( q \) being a solution of \([L][q, \dot{q}, t] = 0\), if \( \eta \) and \( \theta \) can be chosen that \([R][q, \dot{q}, t] = 0\), the right-hand side of Eq. (14) vanishes and \( q' \) given by Eq. (2) will be a solution of

\[
[L][q', \dot{q}', t'] = 0.
\]

Therefore, identity (11) (see example below) is the differential equation for \( \eta \) and \( \theta \) to determine their dependence on \( q \) and \( t \) in such a form that any solution of \([L][q, \dot{q}, t] = 0\) be transformed into another solution of the same equation; identity (11) determines the symmetry transformations of the Euler–Lagrange equation (1), that is, the complete symmetry group of the system [1, 2].

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Case 2: Identity (12) appears naturally in the calculus of variations [9] as the most general modification of $L$ by an additive function which leaves the Euler–Lagrange equations invariant. This identity (12) is the equation obtained in the literature [1] by considering the generator of the first extended Lie group and the Noether theorem. In fact, together with Eqs (5), (7) and (9), identity (12) implies that

$$
\int_{t_1}^{t_2} L(q', \dot{q}', t') dt' = \int_{t_1}^{t_2} \left( L(q, \dot{q}, t) + \varepsilon \left( \frac{d}{dt} F(q, t) \right) \right) dt,
$$

which is the definition for invariance of the action integral adopted in [1]. Moreover, we can obtain from Eq. (10) and (12) a conserved quantity; computing $\frac{d}{dt} (L \theta), \frac{d}{dt} \left( \eta \frac{\partial L}{\partial q} \right)$ and $\frac{d}{dt} \left( \theta \frac{\partial L}{\partial q} \right)$ we are able to show from Eq. (10) and after some algebra that the quantity $R(q, \dot{q}, t)$ can be written as

$$
R(q, \dot{q}, t) = \frac{d}{dt} \left( L \theta + \eta \frac{\partial L}{\partial q} - \theta \frac{\partial L}{\partial q} \right) \left( \eta - \theta \frac{\partial L}{\partial q} - \frac{\partial L}{\partial q} \right).
$$

(16)

With condition (12) we have from Eq. (16)

$$
\frac{d}{dt} F(q, t) = \frac{d}{dt} \left( L \theta + \eta \frac{\partial L}{\partial q} - \theta \frac{\partial L}{\partial q} \right) \left( \eta - \theta \frac{\partial L}{\partial q} - \frac{\partial L}{\partial q} \right),
$$
or

$$
\frac{d}{dt} \left( \theta \frac{\partial L}{\partial q} - \eta \frac{\partial L}{\partial q} - L \theta + F(q, t) \right) = (\eta - \theta) \left( \frac{d}{dt} \frac{\partial L}{\partial q} - \frac{\partial L}{\partial q} \right).
$$

(17)

The right-hand side of Eq. (17) vanishes when the Euler–Lagrange equation $[L][q, \dot{q}, t] = 0$ is satisfied, and we get a conservation equation

$$
\frac{d}{dt} \left( \theta \frac{\partial L}{\partial q} - \eta \frac{\partial L}{\partial q} - L \theta + F(q, t) \right) = 0
$$
or, equivalently,

$$
\omega = \theta \frac{\partial L}{\partial q} - \eta \frac{\partial L}{\partial q} - L \theta + F(q, t)
$$

(18)

is a conserved quantity. The quantity (18) is exactly the result of Noether's theorem [12] and it is used in the literature [1] as the starting point to derive the differential equation for determining the Noether symmetries subgroup, i.e. our Eq. (12). Then, using $R(q, \dot{q}, t) = \frac{d}{dt} F(q, t)$ together with the equation $[L][q, \dot{q}, t] = 0$, it follows that if $F, \eta$ and $\theta$ can be chosen such that identity (12) is verified we have infinitesimal transformations which leave the action integral invariant in the sense of Eq. (15).

We remember the known result [10] that if a quantity $R(q, \dot{q}, t)$ is such that

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$R(q, \dot{q}, t) = \frac{d}{dt} F(q, t)$ then $[R] [q, \dot{q}, t] = 0$, though the reverse is not valid. Then there can occur two cases: i) any $\eta$ and $\theta$ obtained as solutions to identity (12) are also solutions to identity (11); ii) there may exist solutions $\eta$ and $\theta$ found from identity (11) for which there is not a function $F(q, t)$ such that $R(q, \dot{q}, t)$ can be written as its time derivative $\frac{d}{dt} F(q, t)$. As a consequence of these facts the solutions $\eta$ and $\theta$ to case i) leave the equation of motion and the action integral invariant and they are those called NS [7]; the solutions $\eta$ and $\theta$ to case ii) are said to preserve only the invariance of the equation of motion and they are denominated nNS [7, 11]. In the study of the OHO system, for instance, for the solutions $\eta = q$, $\theta = 0$; $\eta = q^2 \cos t$, $\theta = q \sin t$; $\eta = -q^2 \sin t$, $\theta = q \cos t$ there is not such a function $F(q, t)$ and then they determine nNS.

Case 3: With identity (13) the equation of motion $[L] [q, \dot{q}, t] = 0$ is invariant since from Eqs (5), (7) and (9), if $[L] [q, \dot{q}, t] = 0$ and using Eq. (13), it follows that $[L] [q', \dot{q}', t'] = 0$. The identity (13) also implies that

$$L(q', \dot{q}', t') = L(q, \dot{q}, t),$$

that is, the Lagrangian is invariant. Hence the action integral is also preserved. As a consequence, the solutions $\eta(q, t)$ and $\theta(q, t)$ obtained from identity (13) are also solutions of identity (12) with $F(q, t) = \text{constant}$ and are also solutions of identity (11).

In order to exemplify the method here presented we consider the OHO system. Choosing suitable values for the constants, we have

$$L(q, \dot{q}, t) = \dot{q}^2 - q^2,$$

$$[L] [q, \dot{q}, t] = \ddot{q} + q = 0.$$ (21)

From Eqs (10) and (20), we obtain

$$R(q, \dot{q}, t) = -(\dot{q}^2 + q^2) \frac{d\theta}{dt} - 2q\eta + 2\dot{q} \frac{d\eta}{dt},$$

and the identities (11), (12) and (13) become, with Eq. (21),

$$q^2 \frac{d^2 \theta}{dt^2} - 2q \frac{d\theta}{dt} - \frac{d^2 \eta}{dt^2} - \eta = 0,$$ (11a)

$$-(\dot{q}^2 + q^2) \frac{d\theta}{dt} - 2q\eta + 2\dot{q} \frac{d\eta}{dt} = \frac{d}{dt} F(q, t),$$ (12a)

$$-(\dot{q}^2 + q^2) \frac{d\theta}{dt} - 2q\eta + 2\dot{q} \frac{d\eta}{dt} = 0,$$ (13a)

respectively. Using $\theta(q, t) = h(q)g(t)$ and $\eta(q, t) = \alpha(q)\beta(t)$ we obtain from Eq. (11a) the particular solutions:
(a) \( \theta = \text{constant}, \eta = q; \)
(b) \( \theta = \text{constant}, \eta = \cos t; \)
(c) \( \theta = \text{constant}, \eta = \sin t; \)
(d) \( \theta = \sin 2t, \eta = q \cos 2t; \)
(e) \( \theta = q \cos t, \eta = -q^2 \sin t; \)
(f) \( \theta = \cos 2t, \eta = -q \sin 2t; \)
(g) \( \theta = q \sin t, \eta = q^2 \cos t; \)
(h) \( \theta = \text{constant}, \eta = \text{constant}. \)

It is observed from the eight particular solutions that: i) the solution (h) is also a solution of Eq. (13a) for \( \eta = 0 \) and a solution of Eq. (12a) for \( F(q, t) = \text{constant} \); it defines the one-parameter Infinitesimal Symmetry Transformation (IST) which preserves the Lagrangian according to definition (19), the action integral and the equation of motion; ii) the solutions (b), (c), (d), (f), (h) are also solutions of the Eq. (12a) for a function \( F(q, t) \) given by \( F_b = 2q \sin t, F_c = -2q \cos t, F_d = -2q \sin 2t, F_f = -2q^2 \cos 2t, F_h = \text{constant}, \) respectively; they determine the five-parameter IST called NS; iii) the solutions (a), (e), (g) are not solutions of (12a) or (13a) — there is no \( F(q, t) \) such that (12a) or (13a) is verified; they determine the three-parameter IST called nNS. The complete symmetry group is determined by considering the eight solutions (a) – (h).

In what concerns the study presented in this paper; the equation motion \([L][q, \dot{q}, t] = 0\) being satisfied, and defining the infinitesimal transformations by Eqs (2) and (3), we obtain that conditions (11), (12) and (13) on the quantity \( R(q, \dot{q}, t) \) given by Eq. (10) are differential equations to determine how \( \eta \) and \( \theta \) depend on \( t \) and on \( q \). Hence one can study in a simple and unified way different types of IST by considering Eqs (11), (12) and (13). To determine the IST that leave the Lagrangian, the action integral and the equation of motion invariant one must obtain some \( \eta \) and \( \theta \) solution of Eq. (13). The NS subgroup, that is, the IST which preserve the equations of motion and also the action integral according to relation (15) is obtained by determining \( \eta, \theta \) and \( F(q, t) \) satisfying Eq. (12). The complete symmetry group is derived from the solutions \( \eta \) and \( \theta \) of Eq. (11).

References


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NEUTRON STARS IN THE EARLY UNIVERSE

CALLEGARI GIMMI

Physics Institute, University of Ferrara, Ferrara, Italy
Sez. INFN Bologna, Italy

and

BREGOLA MAURO

Physics Institute, University of Ferrara, Ferrara, Italy
Sez. INFN Padova, Padova, Italy

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It is known that most part of neutron stars consist of supernovae remnants and that also a small part of them can be made from white dwarfs that, with suitable accretion conditions, overcame the Chandrashekar limit becoming neutron stars. In this paper we study a further possibility of neutron stars formation that could have taken place in the early stages of the universe. We show that at about $10^{-3}$ s after the Big-Bang conditions were such to allow for matter condensations of the size of a neutron star.

In the Standard Model at this time of $\approx 10^{-3}$ s, during the so-called leptonic era, the hot plasma temperature was $T \approx 10^{12}$ K and the plasma itself was made by $e^+, e^-$, neutrinos, antineutrinos, photons, neutrons and protons in thermal equilibrium [1].

At the temperature under consideration electrons, positrons, neutrinos and antineutrinos were able to induce very rapid transformations from neutrons to protons and vice versa [2]. After thermal equilibrium was reached, at a temperature $T \approx 10^{12}$ K the neutron density was about one half of the proton density. When, during the expansion, the temperature drops below $10^{10}$ K the neutrons begin to decay. We consider that the law of expansion of the very early universe is given by the law of expansion of the Friedmann Universe:

$$\rho = \frac{3}{32\pi G t} = \frac{4.5 \times 10^5}{t^2} \, \text{9/cm}^3,$$

where $\rho$ is the matter density, $G$ is the gravitational constant and $t$ is the cosmological time in seconds.

The temperature in terms of the cosmological time is:

$$T (\text{MeV}) = t^{-1/2} \chi^{-1/4} \times 1.3,$$

where $\chi$ is a dimensionless coefficient greater than one that accounts for the existence of many kinds of particles at thermal equilibrium.
The density of all types of particles is [1]:

\[ n = t^{-3/2} x^{1/4} \cdot 10^{31} \text{ cm}^{-3} \]

so for \( t \approx 10^{-3} \text{ s} \) we have a temperature \( T \approx 30 \text{ MeV} \) and a neutron density \( \rho_0 \approx 10^{12} \text{ g/cm}^3 \).

The modern theory of galaxy formation is based on the fact that small density perturbation in the early universe must have been transformed into the observed structure of inhomogeneities. The nature of perturbations may be considered to be of two kinds: Adiabatic and Entropic [1].

However, in both cases the evolution of the inhomogeneities is closely related to the initial spectrum of perturbations. The long-wave part of the spectrum is supported by astronomical observations made on stellar cluster, galaxies and cluster of galaxies but it is obvious that also the short-wave part of the spectrum of inhomogeneities is important in order to explain the evolution of the universe. Indeed, the existence of a density fluctuation on a small scale in the early universe may have been separated from the cosmological expansion forming, as we suppose, neutron stars. In the thermodynamical conditions considered above we have the Yeans length \( \lambda_J \approx 100 \text{ km} \) so we consider the condensation of a neutron system with a radius \( R \approx 100 \text{ km} \) and we study the dynamical evolution by means of the temperature dependent gravitational Thomas–Fermi equation [3].

We outline briefly the method: the gravitational temperature-dependent Thomas–Fermi equation is

\[
\Delta U(r) = \frac{\sqrt{32}}{\pi} \int_0^\infty d\epsilon \cdot \epsilon^{1/2} \left[ 1 + \exp \left( \frac{\epsilon + U(r) - \mu}{T} \right) \right]^{-1},
\]

where \( U(r) \) is the gravitational potential \( U(r) = -\int d^3r' \rho(r') |r - r'|^{-1} \)
which satisfies \( \Delta U(r) = 4\pi \rho(r) \);
\( \epsilon \) is the one-particle kinetic energy;
\( \mu \) is the chemical potential, which has to be determined by the total particle number of the system;
\( T \) is the temperature.

Here we assume that:

\( h = k = G = m_n = 1 \);

\( k \) is the Boltzmann constant;
\( G \) is the gravitational constant;
\( m_n \) is the neutron mass.

We assume further that our system is spherically symmetric and enclosed in a radius of
\( f(X) = \frac{\sqrt{32}}{\pi} \int_{0}^{\infty} d\epsilon \cdot \epsilon^{1/2} \left[ 1 + \exp \left( \frac{\epsilon + X}{T} \right) \right]^{-1} \)

with

\[ X(r) = U(r) - \mu, \]

and

\[ U(r) = U(0) - u(r). \]

We have to solve

\[ u''(r) + \frac{2}{r} u'(r) = f_{T}(\lambda + u(r)), \quad (2) \]

with

\[ \lambda = U(0) - \mu. \]

The initial conditions are:

\[ u(0) = u'(0) = 0. \]

By numerical computation of Eq. (2) for several values of the temperature with the initial thermodynamical conditions indicated above, we find a first order transition just below 6 MeV, from a homogeneous distribution to a structure formed by a core of radius \( \approx 10 \) km with \( \rho \approx 10^{14} \) g/cm\(^3\) and by a halo of \( \rho_0 \approx 10^{12} \) g/cm\(^3\).

From this result we speculate that the existence of neutron stars in the early universe is possible only via gravitational interaction.

References

BOOK REVIEWS

Common Problems in Low- and Medium-Energy Nuclear Physics
Edited by: B. Castel, B. Goulard and F. C. Khanna
Proceedings of a NATO Advanced Study Institute on Nuclear Theory, Banff, Canada, August 21–September 1, 1978.
Series B, Physics, Volume 45

Although it appeared several years ago, the problems treated in this comprehensive Volume are still in the focus of attention of low- and medium-energy nuclear physicists. It was a topical course emphasizing the role of the quark model applied in nuclear physics. The lectures and seminars forming the present Volume have been divided into four parts:

Part I deals with the weak interaction including the weak nuclear currents in nuclear processes, and some novel topics in pion and muon nuclear physics. Part II is devoted to the coloured quark model for hadrons, pion fields and quarks in nuclear matter, and baryon-antibaryon systems. The title of Part III is “Physics of electrons, protons and kaons”. Among others, it deals with the optical model for nucleons at negative, low and intermediate energies, giant resonances (both theoretically and experimentally), and strange nuclei. Part IV is a survey on pion physics including the pion absorption by nuclei, the pion–nucleus reaction, the pion–nucleus optical potential, and the NNπ system.

B. Apagyi

Quarks and Leptons, Cargèse 1979

The Cargèse Summer Institute is one of the oldest and most respectable series of summer schools, organized each year in Cargèse, Corsica. The 1979 Summer Institute has been devoted to high energy physics. The fifteen lectures presented are collected and published in this Volume.

The talks present a broad review of the status of high energy physics in 1979. While some of the more topical lectures are less important today, moreover the material presented in the talks on experimental results is much more complete today, the majority of lectures may still serve for the purpose of excellent introductory review. A few of these talks are on radiative corrections to electroweak theory (M. Veltman), on quantum electro-dynamics (D. R. Yennie, R. Gastmans), perturbative quantum chromodynamics (J. Ellis, C. T. Sachrajda) and grand unification (M. K. Gaillard, L. Maiani). The Volume closes with the famous talk “The future of elementary particle physics” by S. L. Glashow.

The volume can be recommended to graduate students as well as researchers in high energy physics.

F. Csikor

Structure and Approximation in Physical Theories
Edited by: A. Hartkämper and H. J. Schmidt

The material in this volume is from the: “Colloquium on Structure and Approximation in Physical Theories” held in Osnabrück (F.R.G.), in 1980. Fourteen contributions are presented.

The scope of the Colloquium and of this volume seems to have the effect of deepening the actually observable worldwide interest which manifests itself in the efforts to reconstruct the development of physical theories from the viewpoint of the philosophy of science, and to account for conceptualizing the moment of approximation.

Of the most effective approaches to the philosophy of science the volume offers considerable space to two: that of Sneed, Suppes and Stegmuller.
(the so-called “S-approach”) and that of Ludwig and co-workers (“L-approach”). The contributions mainly concentrate on the presentation, further elaboration, or even the criticism of the S- or the L-approach.

Taken as a whole, the papers discuss the different kinds of imprecision and its mathematical presentation by uniform structures, they give physical examples of the approximation either in classical (Kepler–Newton) or in modern (quantum) theory and they show the axiomatization in actual physical theories (geometry and the theory of grinding plates, special relativity and classical particle mechanics).

The reviewer is convinced that this work is an excellent state-of-the-art report: it helps the reader to appreciate the results of this branch of science as well as showing the intricate situations where these methods have hitherto not been able to penetrate.

I. Abonyi

**Physics and Contemporary Needs**


The Volume is the Proceedings of the Second International Summer College on Physics and Contemporary Needs, held from June 20–July 7, 1977 at Nathiagali, Pakistan. The lectures were divided into three more or less natural groups: 1) Physics and Technology, 2) Energy Resources and Earth Physics and 3) Physics and the Frontiers of Knowledge. The distribution clearly shows the threefold interest of present-day Society in science 1) problems of fundamental physics in today’s or tomorrow’s technology, 2) preparation of the assistance in science in the resolution of the major problems facing mankind, this being the program of the not so distant future, and 3) the struggle of an ever deeper understanding in physics.

Part One contains articles on semiconductor technology by E. H. Rhoderick; on semiconductor devices by L. Esaki; on sol-gel transitions by P. G. de Gennes; on Lasers by G. Leuchs and on applied systems theory by J. Casti.

Part Two concentrates on future energy resources: we find an article on magnetic fusion by B. McNamara, on solar energy conversion by I. F. Querica, on wind energy by P. Musgrove and on ocean waves by H. Charnock. A paper on seismology by P. L. Willmore ends this part of the Volume.

Part Three opens up to the more distant future. A. Salam writes on gauge unification of fundamental forces, J. Nuysts on monopoles and instantons, R. Ruffini and A. Qadir on cosmology, and finally, E. Peytremann introduces the reader to the scientific programmes of the ESA (European Space Agency).

The fourteen excellent specialists’ reviews offer a very good working horizon of the aspirations and capacities of our present-day science, in spite of the fact the number of blocks in the building of this Science is clearly not fourteen. We are convinced that the Volume does and will do a great service to its readers whether specialists in one of the subjects or not.

I. Abonyi

**Energy Storage and Redistribution in Molecules**


This is a book about an extremely interesting borderline territory between microscopic and macroscopic: the vibrational properties of moderately large molecules (not macromolecules), at high levels of vibrational excitation. The basic phenomenon is this: if much energy is pumped into an approximate normal vibrational mode, it is rapidly dissipated (as workers in this field say: “scrambled”) over the totality of nonlinearly coupled vibrations. The recent uprise of interest originates from a lucky coincidence between important experimental and theoretical developments. On the one hand, laser light sources stimulated the development of a number of spectroscopic techniques, ranging from the easy-to-do, hard-to-interpret multiphoton absorption to the more informative and accordingly more sophisticated techniques like double resonance, free induction decay, etc. On the other hand, the phenomena arising are very much in line with the enormous theoretical efforts recently devoted to the study of chaotic behaviour of nonlinear dynamical systems of few degrees of freedom. In this respect, the problem of highly excited molecular vibrations may prove quite stimulating for the most recent studies of quantum chaos, being systems of quasi-classical but not fully classical behaviour. The Volume contains experimental and theoretical papers on this exciting field, based on two related workshops held in Bielefeld, 1980. Well written, well edited, but now it is 1985, and one would be glad to see something more recent about an actively progressing field like this.

T. Geszti
Physics of Ion–Ion and Electron–Ion Collisions

Edited by: F. Brouillard and J. W. McGowan
Proceedings of a NATO Advanced Summer Institute, Baddeck, Nova Scotia, Canada, Sept. 13–16, 1981, NATO ASI Series

This book is devoted to the following lectures on current research fields:
1. Electron–Ion and Proton–Ion Collisions in Astrophysics (A. Dalgarno). The author describes some of the diverse variety of astrophysical phenomena in which collisions of electrons and protons with ions are significant.

2. The Role of Atomic Collisions in Fusion (D. E. Post) Atomic physics issues have played an important role in controlled fusion research. A general discussion of the present role of atomic processes in both magnetic and inertial controlled fusion work is presented.

3. Theory of Electron–Atom Collisions (Yong-Ki Kim). The theory of fast collisions is discussed, with emphasis on the systematics and relationships to other types of collisions, taking the relativistic and correlation effects in collision cross sections also into account.

4. Potential Energy Curves (Steven L. Guber-man). Different potential energy curves are given for dissociative recombination.


6. Electron-Impact Ionization of Ions (Erhard Salzborn). The characteristic features of electron-ionization processes with emphasis on recent experimental progress, are surveyed.


10. On the measurement of Ion(Atom)– Ion(Atom) Charge Exchange (F. Brouillard and W. Claeys). The authors derive some useful kinematic relations for the measurement of cross sections by means of intersecting beams.

11. Confinement of Ions for Collision Studies (J. B. Hasted). Confinement by electric and magnetic fields, the use of steady magnetic and electric fields in conjunction, and confinement in high frequency electromagnetic fields are discussed.

12. Studies of Ion–Ion Recombination using Flowing Afterglow Plasmas (David Smith and Nigel G. Adams) This paper presents the first reliable data obtained on pure binary ionic recombination coefficients.

The book contains very interesting lectures about ion–ion and electron–ion collisions. It is a very fundamental and up-to-date work and can be proposed for scientists in plasma physics, astrophysics, and atomic, molecular, and chemical physics.

B. Vasvári

Advances in Nuclear Physics

Edited by: J. W. Negele and E. Vogt, Volume 13

The three Chapters of Volume 13 of this series, started in 1968, contain the following three excellent reviews:

Chapter 1. A. W. Thomas: Chiral symmetry and the bag model: a new starting point for nuclear physics
This is a pedagogic article intended to make accessible to the nuclear physics community important new ideas from particle physics.

In the past decade, particle theorists' understanding of the structure of hadrons has undergone a revolution strikingly similar to that brought about in nuclear physics by the introduction of the nuclear shell model. Like the shell model, the bag model of hadrons phenomenologically specifies an interior region in which constituents are confined and described by single-particle wave functions that are only weakly perturbed by residual interactions. The phenomenological successes of the model are as dramatic as those of the shell model and the microscopic understanding of the transition between the bag interior, where quarks move freely, to the exterior region, from which quarks are excluded, is every bit as elusive as the microscopic origin of the single-particle potential in the early days of the shell model. Because the bag model of nucleons is the obvious starting point for considering the role of quark degrees of freedom in nuclear structure, the thorough and pedagogical review should be of significant value as the question of subnuclear degrees of freedom in nuclei continues to grow as a major focus of nuclear physics.

Chapter 2. A. Arima and F. Iachello: The interacting boson model

Acta Physica Hungarica 61, 1987
This is a review on a very interesting and controversial new approach to some of the central problems of nuclear spectroscopy.

In comparison with the contemporary topic of quarks in nuclei, a mature field like nuclear spectroscopy might appear an unlikely candidate for significant advances. However, due in large part to the interacting boson model, nucleon spectroscopy has experienced a striking renaissance. In contrast to standard collective or microscopic models, the interacting boson model provides a phenomenological framework which simultaneously addresses many bands of excited states in vibrational, rotational, and transitional nuclei throughout the periodic table. The primary aim of the review is presentation of the model and extensive comparison with experimental results. The success of the present phenomenology should be a stimulus both to further developments in experimental spectroscopy and to theorists in trying to understand its microscopic foundations.

Chapter 3. S. Nagamiya and M. Gyulassy: High energy nuclear collision

This paper, on relativistic heavy-ion physics, is a guide to the extensive literature on a new subject which has been full of great expectations, puzzling data, and speculative ideas.

Motivated by the possibility of uncovering dramatic new phenomena at the densities and temperatures arising in relativistic collisions between heavy nuclei, several high-energy heavy-ion accelerators have come into operation during the last decade. The first generation of experiments from these facilities has now been analyzed, and the authors have provided a thoughtful, comprehensive review of the salient results. Theoretical foundations, such as statistical, hydrodynamical, and intranuclear cascade models, and relevant aspects of the reaction mechanisms are reviewed. Fundamental physics questions addressed by these collisions include the equation of state and entropy of dense matter and possible novel states of matter, including the anomalon, superheavy nuclei, and multibaryonic excited states. This review should be useful both in introducing this growing field to the nonspecialist and in providing the background and perspective to understand the next generation of experiments.

Quantum Electrodynamics and Quantum Optics


Quantum optics is a rapidly developing field of coherent and cooperative optical phenomena that has grown out of laser physics. It can be regarded as applied quantum electrodynamics and, at the same time, it represents a test field for the newest ideas concerning the foundation of radiation theory.

The first part of the book is devoted to quantum electrodynamics. The basic tools are discussed: the Hamiltonian approach, the Green’s function methods, and some nonperturbative approaches with application to Lamb shift and anomalous magnetic moment.

The second main part deals with quantum optics with special emphasis on time-dependent and fluctuation phenomena and the decay of unstable states. The form of the interaction Hamiltonian (the $A_p$ versus $E_r$ controversy) and that of the gauge aspect in quantum optics are also discussed in detail.

The final part deals with the quantum theory of measurement. Various possibilities of testing Bell’s inequalities experimentally, especially by means of optical methods, are discussed and the relationship to the foundation of quantum theory is elaborated.

The contributors, all with considerable teaching experience, have been selected from among the prominent representatives of their own area, thus ensuring that the book is not only up to date but the material is presented in a tutorial way. In view of this the book can be recommended to a broad spectrum of readers ranging from students to specialists on the one hand and from field theorists to quantum opticians on the other.

J. Bergou
BOOK REVIEWS

Polarons and Excitons in Polar Semiconductors and Ionic Crystals

The Proceedings is a summary of the 1982 Antwerp Advance Study Institute held at Priorij Corsendonk, a monastery near Antwerp.

The Institute was the third major convention on understanding polarons and was held fifty years after the polaron concept had been introduced by Landau. The work of the Institute is summarized in twelve papers, which include recent developments.

The Editors mark some results as the major achievements: i) streaming motion and population inversion of polarons in silver halides, ii) plasmon LO phonon modes were observed in GaAs, iii) generalized quadratic trial actions were used in calculations, iv) the Feynman model was generalized to study the effect of static magnetic field, v) polaron concept fertilized the theory of ripplons in liquid helium, vi) experiments were made in InSb to show coupling of electrons to transverse phonons, vii) two dimensional magneto-optical spectra of polarons were achieved, viii) studies of the Boltzmann equation for polarons.

Most of these achievements are covered by the Volume, which is highly recommended to scientists not only directly in the field, but also others working in semiconductors and crystal physics.

J. Gyulai

Optical Bistability 2
Edited by: Charles M. Bowden, Hyatt M. Gibbs and Samuel L. McCall


Optical bistability is the property by which certain materials can be switched optically between two stable states. This phenomenon offers an intellectual challenge for those being interested in the basic properties of matter both from the theoretical and the experimental point of view. At the same time new fields of applications seem to become a reality. Advances in optical bistability in semiconductors relate closer to actual device applications. Using the biexciton resonance in CuCl picosecond switching times are expected. Strong optical nonlinearities to be used for optical bistability are also reported for InAs, GaAs and CdHgTe.

The latest advances in two level atoms, gases and polarization switching; optical chaos; instabilities; fluctuations; semiconductors; lasers, liquid crystals and dyes; and transverse effects and their connection with optical bistability are discussed by leading scientists.

The book gives a useful coverage for experimentalists and theoreticians working in the field of optics, laser physics and quantum electronics as well as optical engineering. It is, at the same time, a good source of information for any scientist interested in the state-of-the-art of this rapidly expanding field.

J. Gyulai

Acta Physica Hungarica 61, 1987
JOHN C. INKSON: Many-Body Theory of Solids
An Introduction

The modern theoretical study of the electrical, optical, thermal and magnetic properties of solids is based on the concepts and methods of quantum field theory. The aim of this book is to fill the gap which exists in the present literature on quantum mechanics and its application to solids.

The book consists of thirteen Chapters. In the first four Chapters the basic concepts of advanced quantum mechanics, such as the Green's functions, diagrams, representations etc., are presented starting always from simple illustrative examples. In Chapters 5 to 8 the Green's function self-energy techniques are developed on the basis of the equation of motion method. The last five Chapters deal with the application of the self-energy techniques to special examples, such as the jellium solids, thermal effects on the Green's function, boson particles, density functional method and superconductivity. At the end of each Chapter examples and a bibliography are given.

The book is an excellent introduction to quantum field theory and its application to solids and is recommended to everybody who has a basic knowledge of quantum mechanics and of solid state physics and wants to develop the ability to read the scientific literature of the subject.

I. Kovács

W. H. KING: Isotope Shifts in Atomic Spectra
“Physics of Atoms and Molecules” Series

Making use of the fast computers to evaluate the properties of many-electron atoms and laser spectroscopy this book has made it possible to measure—with a greater accuracy than before in both optical and X-ray transitions of muonic atoms—isotope shifts in the previously unmeasurable areas of very rare isotopes, short-lived radioactive isotopes, weak transition and transitions involving high-lying atomic level.

A short introduction reviews the essence of the isotope shift, then outlines its history. The reader is introduced to the theory of mass and field shifts in optical spectra as well as of the isotope shifts in X-ray spectra, and to the related techniques for the determination of nuclear structure and experimental techniques. The greatest and most interesting part is an element by element review about the isotope shifts and other relevant work. The last Chapter deals with applications and conclusions. The references include all important relevant papers until 1983, following the author, elements and subject index. This comprehensive and up-to-date review can be well used by experts in the field of atomic, molecular, chemical and nuclear physics.

Quantum Gravity

Edited by: M. A. Markov and P. C. West

The Moscow Quantum Gravity Seminars belong to the few memorable and recurrent pleasure periods the Reviewer has enjoyed most in the past few years. Every third year or so, a selection of relativists and astrophysicists are assembled in Moscow to review the state-of-the-art and to enjoy the hearty hospitality of Professor Markov's group in the Nuclear Physics Department of the Soviet Academy of Sciences.

The volume contains the material of the second in this series of Seminars, divided into five Sections. In the Quantum Gravity Section, introduced by Professor M. Markov, the loss of quantum coherence due to virtual black holes is highlighted by Stephen Hawking. This is followed by a lecture on asymptotic freedom in gravitation theories by E. Fradkin and A. Tseytlin, and an account by H. Terazawa of the concept of pregeometry, in a theory of primordial quantum fields.

Section II deals with quantum effects in cosmology, such as particle creation in the overall gravitational field of the Universe, or variations on the quantum history of the Big Bang, including a lecture on the new inflationary scenario by A. D. Linde. Section III is essentially devoted to the Hawking radiation around black holes, with contributions from W. Unruh, Ya. Zeldovich, V. Frolov, P. C. Davies and from other authors. Section IV contains the lectures about supersymmetry. P. C. West lectures on currents in the theory, the Dubna group expounds the \( N = 1 \) model, R. E. Kallosh discusses the counterterms in extended theories, and M. J. Duff and D. J. Toms investigate some features of Kaluza–Klein theories.

The final Section V is divided between gauge theories and twistors. A lecture by I. A. Batalin and G. A. Vilkovisky investigates under what conditions the generators of a (supersymmetric) gauge transformations form a closed algebra. I. V. Tyutin and B. L. Voronov take up the renormalization proper-

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ties of gauge theories, Z. Perjés gives a brief status report about twistor theory and M. B. Mensky elaborates on Mandelstam's path-dependent approach to gauge fields.

In summary, the Volume presents an enjoyable account of quantum gravitation theory, as of 1981. Although the Editors resorted to camera ready procedures, it took three more years for the English version to appear. This regrettable delay is probably due to translation work. But most certainly, readers of the Quantum Gravity Volume will look forward to the continuation of this successful endeavour.

Z. Perjés

Electron-Molecule Collisions
Edited by: I. Shimamura and K. Takayanagi

In this book the Editors have collected papers—written by a group of international experts—that consider a diverse range of phenomena occurring in electron-molecule collisions. Characteristics of the electron-molecule collisions distinguished from those of the electron-atom collisions are as follows:

a) The rotational and vibrational degrees of freedom can be excited by a small amount of energy supply as compared with electronic excitations.

b) The electron-molecule interaction is multi-centered and nonspherical.

c) Molecular targets can dissociate in collision with an electron (dissociative ionization, dissociative attachment).

The book is divided into seven main parts. The first Chapter explains the basic formulation for scattering problems and provides an overview of the electron-molecule collisions as an introduction to the subject. This Chapter gives a summary of important quantities and effects (cross section, long-range and short-range interaction, resonance effect, inelastic scattering process).

Rotational excitation of molecules by slow electrons is the main topic dealt with in Chapter 2. This part of the book emphasizes the basic physical concepts such as classical and quantum-mechanical angular momentum transfer, sudden-collision (or adiabatic-rotation) approximation, and division of the configuration space. The Chapter describes in brief the single center expansion of the interaction potential, the charge–dipole interaction, the charge quadrupole interaction and mult centered electrostatic field.

Chapter 3 whose title is "Vibrational excitation of molecules by slow electrons" concentrates on resonance phenomena and threshold structures. The Chapter discusses the various calculational methods, too (semiempirical calculation, ab initio calculation in the Born–Oppenheimer approximation, and "hybrid method").

Chapter 4 reviews the work on dissociative excitation, dissociative ionization and dissociative attachment.

Chapter 5 considers the use of electron–molecule collisions as a spectroscopic tool for studying the molecular electronic structures. (Resonance Spectroscopy of Molecules and Electron Energy-Loss Spectroscopy).

The final two Chapters review currently important experimental (Chapter 6) and computational (Chapter 7) techniques for the determination of cross sections.

The subject of Chapter 6 is electron collision phenomena which may be studied under single-collision conditions at low and intermediate electron-impact energies (from threshold to a few hundred eV) using gas phase molecular targets.

Chapter 7 emphasizes the various computational methods which have been adapted for performing electron–molecule cross section calculation. The aim of this Chapter is to discuss the numerical solution of the fixed nuclei equations.

Detailed references are cited in each Chapter. Numerous Figures and several Tables supplement the text. This book aims at introducing the reader to the problem of electron–molecule collisions, elucidating the physics behind the phenomena, and reviewing, to some extent, up-to-date important results. This book should be appropriate for graduate reading in physics and chemistry.

I. Nagy

Quarks, Leptons and Beyond
Series B, Physics, Volume 122

The book contains extensive discussions on the status of the standard model of the interactions of quarks and leptons, respectively. Several extensions of the standard model are also included into the Volume.

In his excellent contribution, C. Rubbia treats the physics results of the UA1 collaboration at the CERN pp-collider, that is the observation of jets,
BOOK REVIEWS

and the discoveries of the charged and neutral intermediate vector bosons (for which he was awarded a Nobel prize in 1984).

A very useful review of lattice Quantum Chromodynamics is given by P. Hasenfratz.

Among the extensions of the standard model various aspects of the supersymmetry are dealt with by a number of authors. In Particular, J. Ellis reviews supersymmetric grand unified theories and searches for supersymmetric particles.

A thorough discussion of the left-right symmetric models of weak interactions is given by R. N. Mohapatra.

The interplay of particle physics and modern cosmology is described in a remarkable contribution by M. S. Turner.

In addition to the above main lectures, brief reports have been contributed by excellent experts such as B. Stech, I. D. Stamatescu, P. Ramond, R. Barbieri, T. Yanagida, J. Wess, J. H. Schwarz, L. Girardello.

Clearly, the Volume is of great value, not only for those following with attention the newest developments but also for experts working in the corresponding field. It unifies standard and non-standard ideas into a whole: present-day particle physics on the usual high standard of the series.

G. Pócsik

H. Haken: Advanced Synergetics, Instability Hierarchies of Self-Organizing Systems and Devices

Synergetics is a field of interdisciplinary research, dealing with systems belonging to disciplines as diverse as physics, chemistry, biology, mechanical and electrical engineering, economy, ecology and sociology showing similarities in their behaviour when external conditions are changed. Systems may run through a hierarchy of instabilities in which more and more structured patterns evolve. This book continues the outline of methods presented by the author in his book “Synergetics. An Introduction”, Springer-Verlag 1977, published in English, Russian, Japanese, Chinese, Hungarian and German. Most part of the present book can be read independently of the previous one, but occasionally some knowledge of that book may be useful.

The book contains thirteen Chapters; an Introduction, Linear ordinary differential equations, both constant and quasiperiodic coefficients, Stochastic nonlinear differential equations, Coupled nonlinear oscillators, the Slaving principle, Spatial patterns, Discrete noisy maps, etc. In view of numerous links between synergetics and other fields, one might assume that synergetics employs a great number of quite different concepts and methods of different fundamental disciplines, and has not any new original concepts and principles which would be characteristic only of the new science of “synergetics”. The author's opinion is that this is not the case. However, we cannot find any original concepts or principles in the text which would be characteristic only of synergetics. On the other hand, the author is rather unfamiliar for example, with the field of modern nonequilibrium thermodynamics. He writes: "Thermodynamics acts at its full power only if it deals with systems in thermal equilibrium, and irreversible thermodynamics is confined to systems close to thermal equilibrium, Synergetic systems ... are driven far from thermal equilibrium and can exhibit new features such as oscillations." Indeed? Hic et nunc, we should like to mention only that several different but general and complete nonlinear theories of irreversible thermodynamics had been developed before synergetics was born. Nevertheless, the book can be recommended to physicists, chemists, biologists, etc., in the hope that the author will propagate his science in a more modest way in future.

I. Gyarmati

Thin Film and Depth Profile Analysis

The authors of this book were invited speakers at a high standard Seminar held at the “Physikzentrum” in Bad Honnef near Bonn. Therefore, the book does not outline systematically all aspects of thin film depth profiling analysis, but nevertheless it is an extremely interesting and useful book for all those applying modern surface analytical methods. One of the reasons for this is that it describes numerous practical application examples.

The book consists of 8 Chapters, 6 of them being of quite general interest. The first two Chapters (the Introduction by Oechsner, and The Application of Beam and Diffraction Techniques to Thin Film and Surface Micro-Analysis by Werner) give an extended comparison of different surface analytical possibilities, promoting the good choice among them. The 3rd, and 6th–9th Chapters (Depth

Acta Physica Hungarica 61, 1987
D. Marton

GEORGE H. DUFFEY: A Development of Quantum Mechanics, Based on Symmetry Considerations

Edited by: A. van der Merwe

Fundamental Theories of Physics, D. Reidel Publishing Company, Dordrecht, Boston, Lancaster 1984, pp. xiii + 342, US $60.00

There is a number of textbooks available for teaching quantum mechanics at various levels of audience. Dr. Duffey's book has recently appeared to join this "community". One is therefore tempted to search for the special features of this book to make certain that such an addition is needed. Let us start out by stating that this is a very useful, highly didactic text.

It contains ten chapters: Quantization of translatory motion; Quantization of rotatory motion; Quantization of vibratory motion; Radial motion in a Coulombic field; Quantum mechanical operators; Wavepackets, potentials and forces; Angular motion in a spherically symmetric field; Operators for angular momentum and spin; Propagation, spreading and scattering; Investigating multiparticle systems. Within each Chapter the author organizes the material to several subsections, discussion questions, problems, and references, while at the back of the book the Answers to Problems section contains the solutions.

The basic characteristics of the approach is to keep to the absolutely necessary mathematics, and within this limitation to give painstaking detail of the calculations and mathematical development. The treatment appears to be self-containing, although Dr. Duffey uses great many references for each of his chapters, frequently taken from renowned didactic journals, such as the American Journal of Physics and the Journal of Chemical Education. Due to this obvious aim to make details clear and understood, and to the explicit mathematics the Reviewer has no hesitation to recommend the book to those for whom the author has intended his work: to theoretically bent physicists and chemists. All the formulae used are carefully constructed to be easily perceived, all what is needed for a "hand on" learning process is pencil, paper and perhaps a programmable hand-held calculator with built in integration routine. The text is interspersed with fully solved numerical examples, placing stress on the appropriate use of (SI) units—another great didactic virtue. One should also mention the cautious exposition of advanced concepts, such as operator theory, propagation and scattering theory, the variation theorem and many-body effects.

A few critical comments appear, however, not to be out-of-place here. First and foremost, the book contains in its subtitle the hint to the rôle of symmetry in teaching quantum mechanics. Although symmetry is used throughout the text in its broad conceptual sense, the primary or perhaps sole apparatus of symmetry, group theory, is surprisingly avoided. There is a clear symptom for this attitude taken from the Name Index and also from the References sections to the Chapters: Wigner's name appears only sporadically, essentially only once in connection with the Wigner–Breit formula. Although the treatment proves to be quite successful without explicit recourse to group theory still this attitude is highly anachronistic. Another failure in
the references structure of the book reveals itself in
the second and third Chapters dealing with rota­
tional and vibrational motions of molecules. Almost
none of the well-known treatments on molecular
vibro-rotatory motions are included. While this is
apparent in Chapter 2, it is striking in Chapter 3.

The book is priced not much above the general
average level of US $50 of textbooks, and its physical
appearance is pleasing, well suited for class-room
use, it will hardly become “weather-beaten”.

L. Nemes

Advances in Liquid Crystal Research and
Applications
Edited by: L. Bata, Publishing House of the
Hungarian Academy of Sciences, Budapest and

The two volumes contain the Proceedings of
the Third Liquid Crystal Conference of the Socialist
Countries held in Budapest, 27-31 August 1979. The
first Conference of this series was held in Halle,
GDR, 1976, the second at Sunny Beach, Bulgaria
1977.

The material is presented in seven Chapters.
The first one contains 22 papers on phases and
structures. The second Chapter is devoted to
molecular dynamics and dynamical methods. The
21 contributions deal with molecular motions
determining the dielectric, magnetic, acoustical,
optical and other properties of liquid crystals. 25
talks devoted to continual properties are included in
the third Chapter. Amphiphilic substances and
mesomorphic polymers are studied by 9 and 8 works
in the fourth and fifth Chapters, respectively. In the
sixth Chapter, 13 papers describe the chemical
synthesis of mesogens. The 23 talks in the last
Chapter deal with a large variety of successes and
problems in the field of applications. Some papers
presented at the Thermography Session are not
given in the two volumes but are published together
with the associated colour plates in the Hungarian
Radiological Review.

The two volumes are concluded with a list of
the 266 authors, including many of high reputation.
The 121 papers are different in style but each of
them is concise and expedient. The multifariousness
of the questions raised and the answers found makes
the volumes valuable and interesting for the reader.

The Volumes can be recommended to special­
ists interested in the various problems of liquid
crystals.

J. Verhás

Statistical Physics and Dynamical Systems —
Rigorous Results
Edited by: J. Fritz, A. Jaffe, D. Szász
Second Colloquium and Workshop on Random
(Progress in Physics Vol. 10)

This volume contains the invited papers of the
Colloquium. This international conference assem­
bled a group of world-reknowned scientists in
mathematical physics. The lectures covered the
most recent results in statistical mechanics and in
the theory of dynamical systems. The papers in this
book include the following topics: theory of phase
transitions, renorm group methods, cluster expan­
sions, quantum probability, thermo-dynamical for­
malism in dynamical systems, maps of the interval,
vortex theory, hydrodynamical behaviour, diffu­
sion, the Boltzmann and random Schrödinger
equations.

K. Szlachányi

Diffraction Studies on Non-Crystalline Substances
Edited by: István Hargittai and W. J. Orville­
Thomas, Publishing House of the Hungarian Aca­
demy of Sciences, Budapest, 1981, pp. 894

The IXth Hungarian Diffraction Conference
organized by the Diffraction Group of the Roland
Eötvös Physical Society was held at Pécs, Hungary
between 14–19 August, 1978. The present Volume is
based on the lectures delivered at the International
School held on the same occasion. The contri­
butions are “quasi monographic” and the overall
aim was to provide a comprehensive treatment of
various diffraction studies. The non-crystalline states
discussed are then the gaseous phase, molecular
liquids, intermediary states between order and
disorder, polymeric substances and amorphous
solids. There are altogether twenty-one chapters in
the book.

As the Editors note in their Preface the
coverage is so broad that the nomenclature could
not be rendered uniform throughout. In addition of
course the concept of structure undergoes also a bit
of transformation upon passing from the gases to
amorphous metals. In molecular gases structure
means a precise knowledge of atomic arrangements
and even the dynamic fluctuations of the latter,
while in amorphous alloys one appears to be happy
to tell atomically ordered regions from unordered
ones. Herein lies the danger of merging various

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subdisciplines of the same field of a broader sense; although the physical effect is basically the same—diffraction of electromagnetic or material waves—the picture obtained therefrom can mean rather different things for the various phases.

Part I contains six Chapters on gas-phase diffraction of fast electrons with a typical energy of 40 keV. (Contributors: J. Karle, K. Kuchitsu, L. V. Vilkov, V. P. Spiridonov et al., and A. H. Lowrey.) The main topics of this part very homogeneous regarding the subject matter are molecular geometry, stereochemistry, harmonic vibrational potential functions and large amplitude motions.

Part II is devoted to the rather different methods of liquid structure elucidations, here aqueous electrolytes predominate. Contributors are M. D. Zeidler, G. Pálinkás, E. Kálmán and K. Heizinger. The knowledge about liquid structures derives mainly from X-ray and neutron diffraction with electron-diffraction used only relatively recently. The first Chapter is a very pleasing group-theoretical treatment of the pair-correlation function playing a central rôle in the structure of molecular liquids. Computer simulation of the dynamic structure of liquids is another interesting aspect of these studies, it shows the interpretative power of modern computer applications.

By the time the reader is through with Parts I and II half of the book has been read, the second half is composed of the remaining three parts, characterized by increasing molecular or atomic disorder. Part III is composed of three Chapters, the authors are A. Guinier, J. L. Finney, R. Hosemann and S. Steffen.

Part IV is aimed at polymers. The Chapter by G. Bodor is mostly an experimental treatment of elastomer-plastomer blends. In contrast P. W. Schmidt has written a purely mathematical text, admittedly published too fast. Then comes a short résumé on structural information on polymers by N. Kasai, and finally R. Lovell and A. H. Windle's brief text on conformational problems of some polymers.

Part V contains five contributions from W. Buckel, G. S. Cargill III, T. Mizoguchi and J. M. Cowley. This is the second longest part in this book. The subjects are liquid-like amorphous thin films, diffraction studies of amorphous metallic alloys and structural models for them, neutron diffraction studies of amorphous alloys and, finally, electron microdiffraction and microscopy of amorphous solids.

The book—due its coverage and monographic method—is very useful for diffractionists and perhaps also as recommended literature for students of molecular and material structure research. It is a coverage of a diverse field and as such it may prove to be thought stimulating.

The photographic printing technique applied has most certainly contributed to the feasibility of the publication of this sizeable book, but relegated the task of text composing to the individual authors. There are differences in this respect in the book, but the outlook is almost uniformly pleasing to the eye.

L. Nemes

Francis S. Wagner: Zoltán Bay, Atomic Physicist, Pioneer of Space Research
Publishing House of the Hungarian Academy of Sciences, Budapest, 1985, pp. 116

Zoltán Bay is one of the galaxy of Hungarian scientists who has achieved international success and recognition abroad. A member of a uniquely talented generation of physicists—among them several Nobel Prize winners—he regrettably, like the other stars of the galaxy, had to go abroad to find working conditions measured to his capabilities and ambition. But he never denied his Hungarian origin and close ties have always linked him with his native country.

His perhaps most sensational success Zoltán Bay scored in 1946 while still in Hungary, working in the laboratory of the Tungsram Factory: this truly sensational success was the observation of radar waves reflected by the moon. At the time of his elaboration of a method for measuring—to an accuracy of nine digits—he was in the United States of America, with the US National Bureau of Standards.

The major events of Bay’s scientific career are recounted by Francis S. Wagner in their essential features, as coordinates as it were of his achievements and their reception. The author, himself a Hungarian émigré, past member of the Library of Congress in Washington—after the publication of numerous works on historical subjects—embarked on science history, as an honourable amateur. His book is informative and handy, it gives us a means of orientating ourselves in the life of a very significant scholar. The book, 77 pages even with its interlined typography, is supplemented with a bibliography of Bay’s works and facsimiles of some of his more interesting letters and photographs.

After a brief introduction, without indicating the sources (the length and function of this introduction are questionable), Bay’s family, his childhood (born at Gyulavári in Békés County in 1900) and his schoolyears are described and reference is
also made to the four years spent in Berlin on a scholarship, where his attention turned towards particle counting.

Bay returned to Hungary in 1930. Between 1930 and 1936 he was Professor of Theoretical Physics at Szeged University. There, with his best students György Papp and Zoltán Szepesi—both were later to become his associates—he began to study the Compton effect based on a new measurement method.

The book covers here the stimulating atmosphere which prevailed at Szeged at the time and the influence on it of Albert Szent-Györgyi, Frigyes Riesz, Alfréd Harr, István Rusznyák, and others.

In 1936 Bay moved to Budapest to continue his activities in the then most outstanding experimental physics laboratory in Hungary, operated by Tungsram (the United Incandescent Lamp and Electrical Factory).

In 1938 the Technical University of Budapest set up a new chair for Bay, the Department of Nuclear Physics.

From the results of his work in the Tungsram laboratory Wagner mentions two: one being the new method of particle counting which Bay elaborated jointly with György Dallos in 1937, the other the detection of weak radar waves reflected from the moon. For the particle counting method, Bay and Dallos applied an electron multiplier which increased the rate of counting by three orders of magnitude. Wagner quotes Heisenberg’s appreciative letter written to Bay. The other achievement, the detection of weak radar waves reflected from the moon, Bay worked out with a team of 10 researchers and 30 technicians. The measurements, under extremely difficult conditions, on rather primitive technical equipment, were completed in 1946—a few weeks later than the investigations into the same field were finished in the USA. Wagner points out that, in addition to the great value of the findings, this experiment launched a new branch of science, Radar Astronomy.

The George Washington University had offered Bay a post and he accepted the offer and moved to the USA in 1948. He continued with his tests on coincidence, and demonstrated that in the Compton effect the electron and the secondary gamma quantum emission take place simultaneously. To our regret, however, the book does not go into any detail concerning the facts or events which motivated Bay to settle abroad. All the more interesting is the part on the cooperation between Bay and Szent-Györgyi in the USA: they so to speak resumed their work done in Szeged and published several books on their findings.

The book goes into rather more detail on the period after 1955 spent with the US National Bureau of Standards, and the years following his retirement in 1982. In the focus of attention were two main topics: the previously mentioned high accuracy measurement of the propagation of light and—equal in importance—Bay’s concept about the new unit of length. He made efforts to prove the advantage of introducing a combined space-time unit based on the velocity of light. Wagner introduces the reader to the lively debate on the proposal, extends it to the objections and Bay’s consistent repartees, but does not delve to greater depths into the discussions, arguments and counter-arguments.

The author finally outlines Bay’s philosophy, referring to four of his shorter theses. While the few pages devoted to this do not satisfy the reader’s interest they may well stimulate further analysis. At this point it might have been useful to reiterate an earlier statement in the book relating to the harmonious way in which Bay combined the theory, experiments in, and applications of, modern physics.

The book is of particular interest to the Hungarian reader because Wagner deals in extenso with the scientist’s contacts in his native country, his works published in Hungary, the lectures he delivered at home, and his close and friendly relationships with Hungarian professionals. These friendly ties are no doubt as important as they are useful for both parties.

The bibliography in the Appendix helps the reader to orientate himself in Bay’s oeuvre but the photographic material might have been more complete, more variable, and more personal.

We may sum up by saying that we are lucky to have the book but would have been happier if its author had gone more deeply into the interrelationships of scientific history and biography. Of course, to write a comprehensive biography of a living scientist is by no means easy since it lacks perspective and finality, both of which are important for objectivity. But the fact that the protagonist is in a position to make corrections to the book and thereby increase its value as a source of later works, adds considerably to its significance.

G. Palló

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