Investigation of phase transitions in certain organic compounds by means of Rayleigh scattering of Mössbauer radiation

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The mean-square vibration amplitude and the diffusion mobility have been investigated in cyclohexane and cis-decalin by means of a specially developed technique of Rayleigh scattering of Mössbauer radiation (RSMR). The investigations carried out on these materials indicated that the RSMR technique is a promising method of investigating the dynamical effects in substances not containing Mössbauer atoms, in particular, in organic substances. A comparison with the other methods shows that the RSMR technique allows the determination and characterization of phase transitions in previously uninvestigated complex systems, e.g., in biological objects. Moreover, the RSMR method allows one to obtain for organic materials the Debye-Waller factors and the mean-square amplitudes, $<x^2>$, of the atomic and molecular-group vibrations, i.e., quantities whose determination by other methods turns out to be a much more complex problem.

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Recently, a number of papers have been published which have initiated a new direction in Mössbauer spectroscopy. The topic of discussion is the use of the so-called Rayleigh scattering of Mössbauer radiation (RSMR) for the study of phase transitions and molecular mobility in solids in the course of a phase transition and in the various phases of a substance. The RSMR technique is based on the use of a combination of a Mössbauer source and an absorber with a scatterer, which is the experimental material and which does not contain Mössbauer nuclei. On the face of it, it seems that in this case the scattering of the γ radiation occurs in much the same way as the diffraction of x rays or thermal neutrons, and that it will not be possible to obtain here any information that is inaccessible to these methods. However, using the exceptional energy resolution of Mössbauer detectors, which is determined by the nuclear-resonance width ($\sim 10^{-8}$ eV for Fe^{57}), we can easily separate in Mössbauer diffractometers the elastic and diffuse scattering in the region of a diffraction maximum,[1–3] something which cannot be attained by means of the x-ray method. Furthermore, the RSMR technique, by not imposing so strict beam-collimation requirements as does diffractometry, allows us to measure the absolute values of the fraction of elastic scattering of the γ quanta.[4] This in turn allows us to determine the Debye-Waller factor of the experimental material with a high degree of accuracy, and thus obtain data on the dynamics of the atomic and molecular motion in that material.

Further, the characteristic scattering time for Mössbauer γ quanta of wavelength $\lambda \sim 1$ Å, which corresponds to the lifetime, $t \sim 10^{-7}$ sec, of the resonance level, is much longer than the characteristic time, $t \sim 10^{-13}$ sec, of the resonance interaction of thermal neutrons of the same wavelength, i.e., with $\lambda \sim 1$ Å. Consequently, the RSMR technique corresponds to slower atomic motions, and allows the measurement of a completely different range of diffusion coefficients than can be measured by means of neutron scattering.

Thus, the main things that can be accomplished with the aid of the RSMR technique are the measurement of the Debye-Waller factor and, consequently, the mean-square amplitude of the vibrations of any, including the non-Mössbauer, atoms and the measurement of the diffusion coefficients.

For the performance of RSMR experiments one usually uses 14.4-keV γ quanta from a Co^{57} source, which are scattered on the object under investigation at an angle of 2θ and then pass through a Mössbauer absorber to the detector. By investigating the RSMR, we can obtain data on the fraction, f_R, of elastically scattered γ quanta and on the Mössbauer-line broadening ΔE.

It is well known[5,6] that the intensity of γ quanta elastically Rayleigh-scattered on an ensemble of N identical atoms is equal to

$$I_{el}(Q)=Nf^2(\theta)e^{-2W}S_{el}(Q), \tag{1}$$

where $Q=(2\pi\sin\theta)/\lambda$ is the scattering factor, $f(\theta)$ is the atomic form factor, e^{-2W} is the Debye-Waller factor, and $S_{el}(Q)$ characterizes the so-called scattering law, which is determined by only the structure of the scatterer.

If we neglect the diffraction effects,[7] i.e., if we set $S(Q)\equiv 1$, then the fraction of elastically scattered quanta[8]

$$f_R=\gamma\exp(-Q^2\langle x^2\rangle). \tag{2}$$

Here γ is the ratio of the Rayleigh-scattering intensity to the total Rayleigh- and Compton-scattering intensity; $\langle x^2\rangle$ is the mean-square amplitude of the atomic displacement along the direction of $\mathbf{Q}$. In the framework of the Debye model in the high-temperature approximation, $\langle x^2\rangle \sim T$, and then[8]

$$\ln f_R = \ln \gamma - 3\hbar^2 Q^2 T / k_B M \Theta_D^2, \tag{3}$$

where M is the effective mass of the scatterer and Θ_D is the Debye temperature. From the temperature dependence (3) we can determine the quantity $\langle x^2 \rangle$.

The presence of diffusive motion in the present procedure is determined from the RSMR-line broadening.[8,9] In this case the diffusive motion connected with the hopping of an atom from one localized position to another can be characterized by the localization time τ determined from the expression

$$\Delta E = 2\hbar/\tau. \tag{4}$$

In its turn, the diffusion coefficient is connected with τ, for example, by the expression $D = l^2/\tau$, where l is the distance between the positions of the atom before and after the jump.

In the present work we carried out, using the RSMR technique, an investigation of the phase transitions and the molecular mobility of two organic materials: cyclohexane and cis-decalin.

EXPERIMENTAL PROCEDURE

As the source of γ quanta (see Fig. 1), we used Co^{57} in Cr, with an activity of ~ 50 mCi and a diameter of the active spot ~ 8 mm. The source and the detector were fitted with a lead collimator for the purpose of preventing the γ quanta from directly hitting the detector. The optimal scattering geometry was chosen such that the scattering angle of 2θ differed little from the value of the principal Bragg angle of the material under investigation, and the distance from the source to the detector was made as small as possible so as to increase the luminosity. In our experiments we normally chose the conditions: $2\theta = 12°$ (for cyclohexane we also chose $2\theta = 20°$), the angle of reception (determined by the collimator) $\varphi = \pm 3°$, and the distance from the source to the detector ~ 21 cm.

The cuvettes for the samples were prepared in the form of Dural washers with a wall thickness of ~ 2 mm and an internal diameter of ~ 10 mm. The washer was sealed up on both sides with Mylar films of thickness 10 μ by means of epoxy resin. The thickness of the layer of material under investigation in the cuvette was chosen to be equal to the mean free path of 14.4-keV quanta in order to secure the combination of a scattering maximum with a minimum of the photoelectric absorption. For cyclohexane and cis-decalin the computed mean free paths are respectively equal to ~ 17 and ~ 16 mm. The sample under investigation was placed in a nitrogen foam-plastic cryostat with a 150-W heater. As in the case of the cuvette, the double windows of the cryostat were made of mylar of thickness ~ 10 μ in order to reduce undesirable scattering. The temperature of the sample was fixed and automatically maintained with the aid of a simple precision proportional temperature regulator,[10] which ensured an accuracy of control ~ 0.04 deg in the 80–300-K temperature range. The cryostat with the sample was placed on a special stand, with the aid of which we could set any scattering angle from 0 up to 35° and change the distance from the sample to the detector.

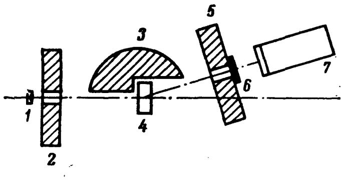

FIG. 1. Schematic diagram of the apparatus: 1) source; 2), 3), 5) lead collimators; 4) experimental material (scatterer); 6) "black absorber" or potassium ferrocyanide; 7) photomultiplier.

As the radiation detector, we used a photomultiplier with a NaI(Tl) crystal of thickness ~ 0.1 mm, the signal from which was fed into the input section of a multichannel analyzer, which was used in two regimes: a regime of constant, and one of variable, speed. To determine the elastic scattering fraction f_R, we used the so-called black absorber $Li_3FeF_6 + (NH_4F)_3(FeF_3)_2$, containing 7.0 mg/cm² of Fe^{57}, and having an almost rectangular absorption spectrum. The experimental line width at half-height is equal to 2.23 ± 0.03 mm/sec. The experimental value of f_R was found in the following manner[8,9]:

$$f_R = \frac{F}{F'} = \frac{N_\infty - N_0}{N_\infty} \frac{N_\infty'}{N_\infty' - N_0'}, \tag{5}$$

where F is the relative contribution of the RSMR effect when the black absorber is placed between the scatterer and detector and F' is the relative contribution of the RSMR effect when the black absorber is placed between the source and the scatterer. The quantity F' remains constant for a given scatterer, and does not depend on temperature, and therefore it is sufficient to measure it once; N_∞ and N_0, N_∞' and N_0' are respectively the counting rates in the cases of moving and stationary sources. Such a procedure for finding f_R makes it independent of the probability for the absence of recoil in the source and in the resonant absorber, as well as of the undesirable background of back-scattering, which is not necessarily connected with the 14.4-keV radiation.

The RSMR spectra were analyzed with the aid of a standard potassium ferrocyanide $(K_4Fe(CN)_6 \cdot 3H_2O)$ absorber having an experimental line width of 0.51 ± 0.03 mm/sec.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Cyclohexane C_6H_{12}

Cyclohexane was chosen as an object of investigation because of the occurrence in it of a strongly pronounced first-order phase transition[11] and the existence of several modifications. Cyclohexane is a well-known globular compound, so called because of the almost spherical shape of its molecule. At a temperature of 186 K the crystal structure of cyclohexane transforms from the low-temperature monoclinic phase (denoted in Fig. 2 by the numeral II) into the high-temperature face-centered plastic phase I.

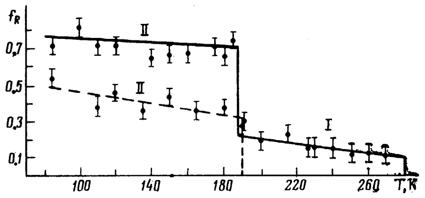

FIG. 2. Temperature dependence of the fraction, $f_R(T)$, of Rayleigh scattering. The solid curve is for $2\theta = 12°$; the dashed curve, for $2\theta = 20°$. I) temperature range 185–273 K; II) temperature range 85–185 K.

For the experiments we took chemically pure cyclohexane. A chromatographic analysis indicated the presence of not more than 0.1% impurities. The investigations were carried out in the temperature range 85–300 K. The crystal structure of the sample changes in the course of the phase transformation, as a result of which the scattering law $S(Q)$ in the expression (1) also changes. Therefore, in choosing the scattering geometry, we should bear in mind that the angle of reception should encompass the corresponding diffraction maxima in both phases. As is well known,[5] the principal Bragg maximum is determined by the intermolecular distance, and its position changes little in the course of the phase transition.

Debye-Waller diagrams for the two cyclohexane phases, obtained in Ref. 12, indicate that the principal Bragg maximum is located near 10°, and its position almost does not change during the phase transition. Therefore, we chose a scattering angle of $2\theta = 12°$ (at smaller angles it is inexpedient to perform the experiment with weak sources, since the beam-collimation requirements in this case become stricter, and the intensity of the scattered radiation decreases sharply).

The results of the measurement of the temperature dependence of the fraction, f_R, of elastic scattering without recoil are shown in Fig. 2. A sharp phase transition is observed at $T = 190$ K, but the effect does not vanish completely upon further increase of the temperature, contrary to what was observed by Champeney and Sedgwick.[13] For the purpose of comparison with their data,[13] we also carried out investigations, using an analogous scattering geometry, i.e., with $2\theta = 20°$. (The results are represented in Fig. 2 by the dashed line.) In this geometry the effect indeed vanished at 190 K—in accord with Champeney and Sedgwick's data.[13] Such a disappearance of the effect can be connected with the fact that in the plastic phase I almost the entire intensity of the scattered beams falls within the interval between 10 and 12°. Therefore, when the scattering angle is equal to $2\theta = 20°$, the angle of reception does not quite encompass the diffraction lines, and the sensitivity of the present technique turns out to be no longer sufficient for the observation of the effect.

Furthermore, if we analyze the various experimental data presented in Table I with respect to the mean-square amplitude of the atomic vibrations in the plastic phase, and take into account the angular dependence of the Debye-Waller factor, then it turns out that the effect observable at $2\theta = 20°$ should be $f_R < 0.01$, which already falls outside the limits of sensitivity of the apparatus.

In Table I we give the values, obtained from the experiments with the use of the expression (3), of the Debye temperature and the contribution of the Rayleigh scattering for both cyclohexane phases. For comparison we give experimental data obtained for cyclohexane from the experimental results of other authors.[11,13] It should be noted that the mean-square vibration amplitude values obtained for the phase II in our experiment are in quite good agreement with de Graaf's neutron-diffraction data.[11] In the present work we also succeeded in determining the mean-square displacement amplitude for the plastic phase of cyclohexane. Notice also that the quantity γ can be computed, using the procedure proposed by Champeney and Dean.[7] It turned out that, for $2\theta = 12°$, the computed value, $\gamma \sim 0.8$, is in fairly good agreement with the experimental value.

To investigate the cause of so sharp a change in the value of f_R, we measured the RSMR spectra for both phases, as well as in the phase-transition region at a temperature of 185 K. It turned out that the line width everywhere remains constant within the limits of experimental error. The existence of rotational-jump diffusion in the plastic phase I is usually assumed. It is known that in this phase the cyclohexane molecule has 144 different orientations.[11] Estimates based on the fact that no line broadening was observed in the plastic phase allow us to establish the fact that the time between two consecutive jumps in this phase $\tau > 4 \times 10^{-7}$ sec.

2. Cis-decalin $C_{10}H_{18}$

Cis-decalin is a molecular crystal that undergoes a first-order phase transition at 100 K from one polymorphic modification II into another I. A vitreous form of the compound is formed when the crystal is subjected to shock freezing. In this case[14] devitrification of the sample occurs in the temperature range 145–148 K upon heating, and there is formed a phase whose viscosity corresponds to a quasi-liquid. However, this state is unstable, crystallizing within 10 minutes into the phase II.

In Fig 3c we present data on the temperature dependence of the elastic RSMR contribution. A singularity

TABLE I.

Phase	Θ_D, K	$\langle x^2\rangle_T$, Å^2	γ
Neutron-scattering method[11]			
II	74	0.069; T=185 K	–
I	54–44	–	–
RSMR method according to Ref. 13			
II	56±6	0.105	0.66±0,06
I	Not found	0.59 *	–
RSMR method, $2\theta = 12°$			
II	76±6	0,065; T=185 K	0.78±0.1
I	25±5	0.64; T=230 K	0.64±0.1
RSMR method, $2\theta = 20°$			
II	69±5	0.079; T=140 K	0.55±0.1
I	Not found	–	–

*On theoretical grounds.

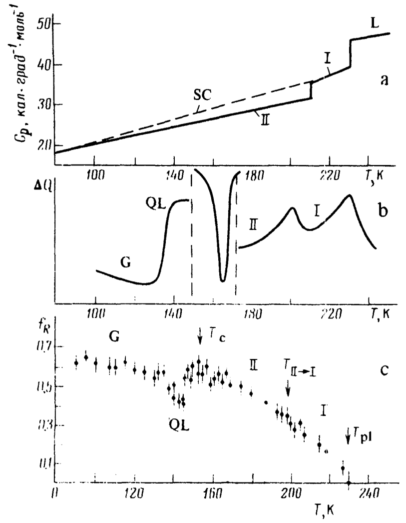

FIG. 3. Calorimetric and RSMR data on cis-decalin. a) Temperature dependence of specific heat at constant pressure (SC denotes supercooled crystal, L liquid); b) calorimetric data for shock-frozen cis-decalin (QL denotes quasi-liquid, G glass); c) temperature dependence of the fraction of Rayleigh scattering for shock-frozen cis-decalin.

is observed in the temperature behavior of f_R in the 145-K region. We have obtained the RSMR spectra in the phase-transition regions, as well as in the existence domains of the phases, but nowhere did we observe a line broadening. It is expedient to compare the RSMR data with the calorimetric data (Fig. 3, a and b). Indeed, it can be shown that in the high-temperature limit of the Debye model

$$C_P = C_V + A\langle x^2\rangle. \tag{6}$$

Thus, the specific-heat data can characterize the dynamics of the motion in one or the other phase. Here C_P and C_V are respectively the specific heats at constant pressure and constant volume and A is some constant. It follows from a comparison of the RSMR and calorimetric methods that the RSMR method has an advantage, since it characterizes the diffusion processes and yields direct experimental information about the magnitude of the mean-square displacements. Furthermore, for complex organic molecules, for which the Debye model and, consequently, the expression (6) are inapplicable, it is difficult to characterize the quantities $\langle x^2\rangle$ with the aid of the calorimetric methods.

Comparing the calorimetric data with the data obtained by means of the RSMR technique, we easily notice a correlation in the temperature dependence, but the RSMR does not vanish completely in the 145–148-K region (i.e., f_R does not decrease to zero), something which might have been expected from the calorimetric data. Such a discrepancy is connected with the characteristics of the RSMR technique, since about 10 minutes is required to obtain one value of f_R. Partial crystallization of the sample occurs during this time, and

TABLE II.

Phase	γ	Θ_D, K	$\langle x^2\rangle_T$, Å^2
Vitrified sample	0.67±0.1	50±5	0.042 (T=100 K)
Low-temperature phase II	0.67±0.1	31±2	0.17 (T=155 K)

the quantity f_R becomes different from zero. The absence of line broadening in the RSMR spectra shows that here, as in the case with cyclohexane, the molecule-localization time $\tau > 4\times10^{-7}$ sec. We could, in principle, have studied the crystallization kinetics during these 10 minutes if we had a stronger source.

The data about γ, Θ_D, and $\langle x^2\rangle$ for cis-decalin are presented in Table II.

Thus, the investigations carried out on cyclohexane and cis-decalin showed that the RSMR method of investigating the dynamical effects in substances not containing Mössbauer atoms, in particular, in organic materials, is a promising method. A comparison with the other methods shows that the RSMR technique allows the determination and characterization of the phase-transition regions in previously uninvestigated complex systems, as, for example, in biological objects. Moreover, the RSMR method enabled us to obtain for the organic substances the Debye-Waller factors and the mean-square amplitudes, $\langle x^2\rangle$, of the vibrations of the atoms and molecular groups, i.e., quantities whose determination by other methods turns out to be a much more complex problem.

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