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A STUDY OF BROWNIAN MOTION BY MEANS OF THE MOSSBAUER EFFECT

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We discuss the resonance absorption of γ quanta in Sn^{119} in SnO_2 particles suspended in different liquids. We show that variation of the viscosity of a glycerine suspension by diluting the latter with water, at a constant temperature, increases the line width in accordance with the law formulated by Singwi and Sjolander.[1] The same happens to a suspension in a silicone oil whose viscosity is altered by changing the temperature. In suspensions, unlike ordinary liquids, the absorption occurs in crystallites, albeit small, to which the Debye-Waller formula for the solids applies. We discuss the mechanism of the absorption of the γ quanta in the suspension, on the basis of Frenkel's model for liquids, and take the settled lifetime of the colloidal particles into consideration.

THE connection between the resonance absorption of γ quanta and the dynamics of atomic motion in gases, liquids, and solids was considered theoretically by Singwi and Sjolander.[1] They found the dependence of the resonance-absorption cross section on the concrete type of correlation function, and showed, under the assumption that the ideal-gas molecules have a Maxwellian distribution, that the effective cross section for resonance-absorption is given by the expression

$$\sigma(E) = \sigma_0 \frac{2}{\pi^{1/2}} \int_{-\infty}^{+\infty} \frac{y^2 e^{-t^2}}{(x-t)^2 + y^2}\, dt = 2\pi^{1/2} \sigma_0\, y u(x, y),$$

$$x = \frac{1}{2}\left[\left(\frac{2M}{kT}\right)^{1/2} v - \left(\frac{R}{kT}\right)^{1/2}\right]; \qquad y = \frac{\Gamma_0}{2E_0} c \left(\frac{2M}{kT}\right)^{1/2};$$

$$R = E_0^2/2Mc^2; \qquad E = E_0(1 + v/c). \tag{1}$$

Here σ_0 is the resonance-absorption cross section when all the nuclei are absorbed without recoil, M is the nuclear mass, k Boltzmann's constant, T the absolute temperature, v the source velocity, R the recoil energy, Γ_0 the half-width of the resonance line, E_0 the transition energy, and c the speed of light. The function u(x, y) is used in spectroscopy and astrophysics for the theory of spectral-line broadening by the Doppler effect.[2]

If σ is maximal (σ_{max}) at $E = E_0$, the width of the resonance curve Γ is determined by the condition

$$\sigma(E_0 + {}^1/_2\Gamma) \equiv \sigma_{1/2} = {}^1/_2\sigma_{\max}$$

which is equivalent to

$$u(x_{1/2}, y) \,/\, u(x_0, y) = {}^1/_2. \tag{2}$$

Singwi and Sjolander considered a model of a solid, in which the atoms go from one crystal lattice site to another, staying an average time τ_0 at each site. The atoms can absorb only when they are at the lattice sites. In the case of a cubic lattice the maximum increase in the half-width will be

$$\Delta\Gamma = 2\hbar / \tau_0. \tag{3}$$

This expression is equivalent to the uncertainty relation.[3]

The character of motion of absorbing atoms in a liquid is far more obscure than in gases and solids. Using the Langevin function for Brownian motion, Singwi and Sjolander obtained

$$\sigma(E) = \frac{\sigma_0\Gamma}{4} - \frac{e^{-2W_a}(\Gamma + 2\hbar\varkappa^2 D)}{(E - E_0)^2 + {}^1/_4(\Gamma + \hbar\varkappa^2 D)^2}, \tag{4}$$

where W_a is a quantity analogous to the Debye-Waller factor for a solid and D is the diffusion coefficient. Then the line broadening is

$$\Delta\Gamma = E_0^2 D \,/\, \hbar c^2 \tag{5}$$

or, taking into account the expression for the diffusion coefficient[4]

$$\Delta\Gamma = \frac{E_0^2 k}{3\pi\hbar c^2 r} \frac{T}{\eta}. \tag{6}$$

Here r is the particle radius and η the viscosity coefficient of the liquid.

According to Frenkel's theory[5] the motion of the molecules in a liquid is similar to the diffusion of atoms in a solid. The liquid molecule vibrates about an equilibrium position during a time τ, after which it overcomes a potential barrier with energy w and goes into another position. This new position is located at a distance of the order of the molecule radius δ. The duration of the equilibrium position is given by

$$\tau = \tau_0 e^{w/kT}. \qquad (7)$$

According to this theory, the viscosity coefficient of the liquid is connected with τ by

$$\eta = \frac{kT\tau e^{-v_0\alpha\beta/k}}{\pi r\delta^2}, \qquad (8)$$

where v_0 is the volume per molecule under normal conditions, α the thermal expansion coefficient, and β a coefficient that shows the change in energy due to the volume expansion.

From (6) and (8) we obtain

$$\Delta\Gamma = \text{const}\cdot\tau^{-1}, \qquad (9)$$

which obviously is analogous to (3).

We would expect expressions (1) and (4) to coincide, at least for a liquid in which the molecules have random orientation[6] and the distribution is Maxwellian.[7] However, it follows from (2) and (6) that in gases the half-width of the line depends only on the temperature, whereas in liquids it depends also on the viscosity. In our opinion this is connected with the fact that in gases the molecules do not oscillate at all. This difference becomes obvious when the half-life $t_{1/2}$ is much smaller than the average time $\bar{t}_c$ between gas-molecule collisions. In the case when $t_{1/2} \geq \bar{t}_c$ the velocity and direction of the absorbing particles changes within a time $\bar{t}_c$, a fact not considered in the derivation of (1).

Boyle et al.[8] investigated the broadening of the resonance line near the melting point of metallic tin and reached the conclusion that the resonance absorption is best described by a diffusion model.

A check on the equations of Singwi and Sjolander for liquids was made by Craig and Sutin,[9] who investigated the diffusion broadening of the resonance line of Fe^{57}, using for this purpose glycerin solutions of $Co^{57}Cl_2$, porphyrin, and hemoglobin, which contained Co^{57} in place of iron. The absorber was solid. They investigated the dependence of $\Delta\Gamma$ on T/η. It is interesting to note that Craig and Sutin obtained very good agreement between experiment and theory, in spite of the fact that they operated with a liquid which is far from the ideal liquid for which the equations have been derived. The lower alcohols behave in other cases, too, like liquids with random molecule orientation, in spite of the presence in them of a hydrogen bond.[6]

The cited papers do not consider the question of resonance absorption in suspensions. It is known that the laws of particle diffusion in suspensions are the same as the laws of molecule diffusion in liquids. However, the tremendous dimensions of the suspension particles, even compared with high-molecular compounds such as hemoglobin, affect the resonance absorption of the γ quanta.

Recoilless absorption of the γ quantum by a particle has a certain probability, given by the Debye-Waller factor and dependent on the phonon spectrum of the suspension particles. This spectrum can differ noticeably from the final spectrum of a macrocrystal of the same substance.[10] This raises the question: how does diffusion influence the recoilless absorption in the lattice of the suspension particle? If we consider the Frenkel mechanism of molecular motion, then such an absorption should be influenced by two factors, the particle velocity and the equilibrium time τ. Unfortunately, however, there is apparently no mention in the literature whether Frenkel's theory is applicable to suspension particles.

If we assume that the particles have a Maxwellian velocity distribution and that it is meaningless to introduce the equilibrium time, then we obtain for the resonance absorption an expression similar to (1). But in this case the recoil energy R of the particle is practically zero, and σ_0 is replaced by the cross section for resonance absorption in a crystal, which depends on the Debye-Waller factor. For a sufficiently thin absorber this expression is obtained by multiplying the probability that the particle has a definite velocity (in the γ-quantum propagation direction) by the probability of resonance absorption at this velocity and by integrating from $-\infty$ to $+\infty$. Our calculations for a suspension of SnO_2 with particles containing 10^9–10^{11} molecules each, in the temperature interval from -40 to $+40°$ C, have shown that under these conditions u(x, y)(1) changes by less than 10%. If we neglect this change, then we find in accordance with the tables of [2] that $x_{1/2} \approx 1$, and consequently

$$\Delta\Gamma = E_0\left(\frac{2kT}{Mc^2}\right)^{1/2} = R^{1/2}(2kT)^{1/2} = \frac{(\bar{v}^2)^{1/2}}{c}E_0. \qquad (10)$$

Here $(\overline{v^2})^{1/2}$ is the component of the rms velocity in the γ-quantum propagation direction.

APPARATUS AND EXPERIMENTAL PROCEDURE

The resonance absorption spectra were obtained with a Mossbauer spectrometer with moving source of velocity ranging from 0 to 30 mm/sec. The velocity could be determined within 0.5% of its absolute value. In each cycle of source motion, there are two periods in which the velocity has the same absolute magnitude but opposite signs.

The source, $Sn^{119m}O_2$, was at room temperature. The absorber temperature changed from −196 to +250 °C. The absorber was prepared in a grinder by grinding for several days in water, glycerin, silicone oil, and paraffin. The viscosity was measured by the Hepler method.

RESULTS AND DISCUSSION

Figure 1 shows the half-width of the resonance line obtained in measurements of SnO_2 suspensions in glycerin as a function of T/η. The viscosity was varied by dilution with water at a constant temperature, +9.8 °C. We see from the figure that the variation is the same as given by expression (6) in accord with the Singwi and Sjolander theory.

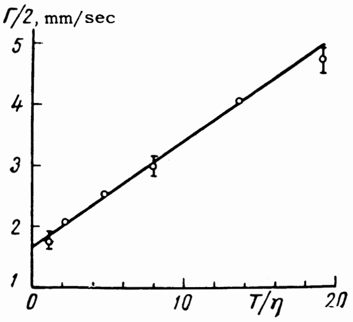

FIG. 1. Plot of $\Gamma/2$ against T/η for a glycerin solution diluted with water at a constant temperature 9.8°C.

As already noted, the particle-velocity distribution should be Maxwellian and must not depend on the dilution of the suspension if the temperature is constant, since a Maxwellian distribution does not depend on the viscosity. Consequently, the change in the resonance line width with changing viscosity cannot be explained by assuming that the γ quantum is absorbed "instantaneously." Nor can this be explained by assuming that the γ quantum is absorbed within a certain time interval within the order of the half-life of the nuclear level.[3] Since the system of particles in the suspension is governed by the ergodic principle, the dependence of the γ-quantum absorption probability on the particle velocity distribution will be the same in both cases. The physical picture of the process that leads to the line broadening can be deduced by assuming that the suspension particles stay in equilibrium during some time. The absorption of the γ quantum then depends not only on the instantaneous particle velocity, but also on the time interval between the jumpwise changes in velocity.

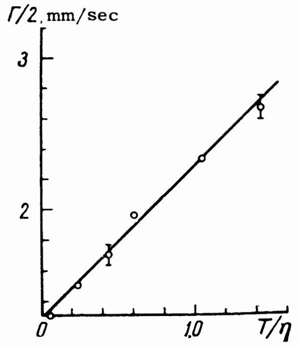

FIG. 2. Plot of $\Gamma/2$ against T/η for a suspension in silicone oil.

The line broadening with change in temperature, for a suspension in silicone oil, has a similar variation (Figure 2). It is interesting, however, that when the temperature of a glycerin suspension is changed, the half-width varies in accord with (10) and not (6) (see Figs. 3 and 4). We are unable to explain this phenomenon at present. It may be connected with the fact that some of the SnO_2 settles, and this may lead to an accidental agreement between the experimental data and (10).

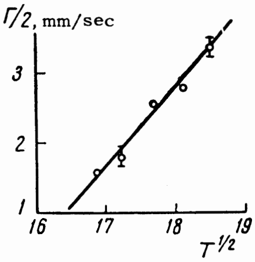

FIG. 3. Plot of $\Gamma/2$ against $T^{1/2}$, according to (10) for a suspension in glycerin.

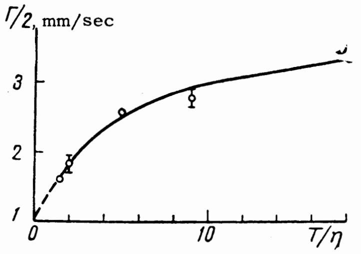

FIG. 4. Plot of $\Gamma/2$ against T/η according to (6) for a suspension in glycerin at variable temperature.

The line half-width obtained following freezing to liquid-nitrogen temperature or settling of the glycerin or silicon suspension is practically always the same. This means that the dimensions of the suspension particles are very large and there is no noticeable change in the phonon spectrum compared with the SnO_2 macrocrystal. It is interesting, however, that these values are approximately 30% lower than those obtained for these samples by extrapolating the straight lines in Figs. 1–3 to $\eta \to \infty$, when both should coincide.

Of course, the increase in the half-width leads to a decrease in the effect $\epsilon = (N_\infty - N_0)/N_\infty$. This is clearly seen from Fig. 5, which represents

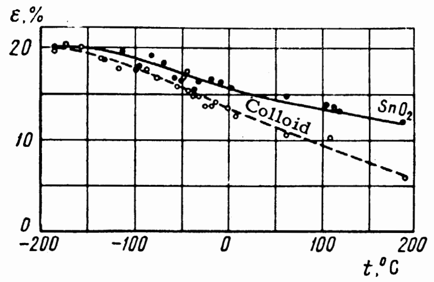

FIG. 5. Temperature dependence of the effect $\epsilon = (N_\infty - N_0)/N_\infty$ for solid SnO_2 and a suspension of SnO_2 in silicone oil.

the temperature dependence of ϵ for solid crystalline SnO_2 and for suspensions of the same substance in silicone oil. (It must be noted that these results were obtained with the source and absorber at the same temperature.) If, however, we define the effect as the area under this line, then it remains constant within the limits of errors. This is a natural consequence of the diffusion nature of the line broadening.

A very interesting result was obtained by investigating a suspension of SnO_2 near the freezing point. It is seen from Fig. 6 that in the temperature interval from 0 to +2.5 °C the half-width changes by a factor of four. (The measurement at 0 °C was made with the suspension not frozen. The sharp increase of Γ at 2.5 °C is a result of settling of the suspension.) The viscosity of the water in this interval changed by only 8%.[11] Consequently, the abrupt change in the half-width near 0 °C cannot be described by means of (10). It is obvious that this phenomenon should be connected with the special structure of water near the freezing point.

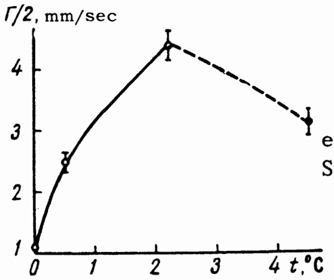

FIG. 6. Temperature dependence of $\Gamma/2$ for a suspension of SnO_2 in water.

Figure 7 shows the variation of the resonance-line half-width for a suspension of SnO_2 in paraffin. The strong change in the line half-width occurs at the instant of melting of the paraffin.

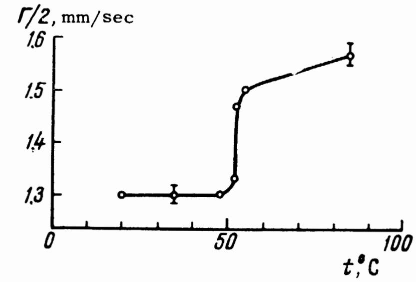

FIG. 7. Temperature dependence of $\Gamma/2$ for a suspension in solid paraffin.

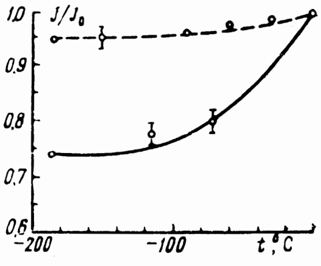

FIG. 8. Temperature dependence of the intensity of radiation from Sn^{119m} dispersed in silicone oil in the form of SnO_2. Stable Sn^{119m} in SnO_2 form was also dispersed in the silicone oil. The solid curve pertains to measurements made immediately after mixing the two suspensions, while the dashed curve pertains to measurements made 5 days later.

We have used also a different procedure. Figure 8 shows the intensity of resonance emission in the case of a mixture of two different SnO_2 suspensions in silicone oil. One suspension was obtained with Sn^{119m}, and the other with stable tin. The solid curve pertains to a freshly prepared mixture and the dashed to measurements made five days later. We see that the temperature dependence becomes weaker in the course of time. It seems to us that the change in the temperature dependence can be attributed to the linking of radioactive and nonradioactive particles, which reduces their average velocity.

The results of the work show that investigation of the Brownian motion by the Mossbauer effect uncovers interesting possibilities for the investigation of the structure of liquids and the γ-quantum absorption mechanism.

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