PHYSICAL CHEMISTRY

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

S. V. KARYAGIN

ON A POSSIBLE CAUSE OF THE ASYMMETRY OF THE COMPONENTS OF THE DOUBLEt IN THE MÖSSBAUER ABSORPTION SPECTRUM IN CERTAIN POWDERED TIN COMPOUNDS

(Presented by Academician V. N. Kondrat' ev, 26 VII 1962)

In recent works (^{1,2}) on the investigation of the Mössbauer effect in organotin compounds, the presence of asymmetry in the doublet splitting of the spectra was demonstrated. A possible interpretation of these observations is given below.

If one assumes that the components of the doublet of the Mössbauer spectrum are due to the splitting of the excited state ${}^3/{}_2{}^+$ in the inhomogeneous electric field of the crystal, then, in the case of axial symmetry of the field acting on the nucleus, the ratio of the intensities of the components for powders should have the form

$$\frac{i_\pi}{i_\sigma} = \frac{\displaystyle\int_0^\pi I_\pi(\vartheta)\, f'(\vartheta)\, \sin\vartheta\, d\vartheta}{\displaystyle\int_0^\pi I_\sigma(\vartheta)\, f'(\vartheta)\, \sin\vartheta\, d\vartheta}, \tag{1}$$

where i_π and i_σ are the intensities of the Mössbauer transitions

$$(\pm{}^3/{}_2,\ {}^3/{}_2{}^+) \rightarrow (\pm{}^1/{}_2,\ {}^1/{}_2{}^+) \quad \text{and} \quad (\pm{}^1/{}_2,\ {}^3/{}_2{}^+) \rightarrow (\pm{}^1/{}_2,\ {}^1/{}_2{}^+)$$

respectively (the numbers in parentheses correspond to the projections of the spin, the spin, and the parity of the nucleus); $I_\pi(\vartheta)$ and $I_\sigma(\vartheta)$ are the total intensities of the transitions (Mössbauer and non-Mössbauer) for γ-quanta incident at an angle ϑ to the crystal axis; $f'(\vartheta)$ is the factor determining the intensity of the Mössbauer line. Averaging over ϑ is carried out because the crystallites of the powder are oriented in an equiprobable manner.

The dependence $f'(\vartheta)$ can be calculated theoretically (^{3}). In addition, the dependence $f'(\vartheta)$ was found experimentally (^{4}) in the case of a single crystal of white tin. In work (^{3}), $f'(0°)/f'(90°) = 1.04$ was obtained at 0°K; in work (^{4}), $f'(0)/f'(90°) = 0.7$ at room temperature.

As follows from theory (^{3,5}), depending on the structure of the crystal cell, the elastic properties of the crystal lattice, and the temperature, the value of $f'(0)/f'(90°)$ can vary within wide limits.

In the case of axial symmetry of the crystalline field, using radiation theory (^{6,7}), it is easy to obtain

$$I_\pi(\vartheta) = \mathrm{const}\,(1 + \cos^2\vartheta) = \mathrm{const}'[2\sqrt{5}\,\overline{P}_0(\vartheta) + \overline{P}_2(\vartheta)], \tag{2}$$

$$I_\sigma(\vartheta) = \mathrm{const}\,({}^5/_3 - \cos^2\vartheta) = \mathrm{const}'[2\sqrt{5}\,\overline{P}_0(\vartheta) - \overline{P}_2(\vartheta)],$$

where $\overline{P}_0(\vartheta) = \sqrt{1/_2}$; $\overline{P}_2(\vartheta) = \frac{1}{2}\sqrt{5/_2}\,(3\cos^2\vartheta - 1)$ are normalized Legendre polynomials.

Let us expand $f'(\vartheta)$ in Legendre polynomials

$$f'(\vartheta) = \sum_k a_k \overline{P}_k(\vartheta). \tag{3}$$

Then, on substituting (2) and (3) into (1), we obtain

$$\frac{i_\pi}{i_c} = \frac{1 + \dfrac{1}{2\sqrt{5}}\dfrac{a_2}{a_0}}{1 - \dfrac{1}{2\sqrt{5}}\dfrac{a_2}{a_0}}. \tag{4}$$

In the case of lattices of tetragonal symmetry it is natural to assume that the axis of the crystalline field coincides with the c axis of the crystal; then $f'(\vartheta)$ takes the form (3)

$$f'(\vartheta) = \exp\{-T_1 + (T_3 - T_1)\cos^2\vartheta\}, \qquad T_1, T_3 > 0, \tag{5}$$

where T_3 and T_1—quantities characterized in (3)—are determined by the elastic properties of the crystal along the c axis and perpendicular to it, respectively, by the temperature, the structure of the crystal cell, and the recoil energy of the γ-quantum to the free nucleus.

Comparison of (5) and (3) gives

$$\frac{1}{2\sqrt{5}}\frac{a_2}{a_0} = \frac{1}{8}\left\{\frac{3}{\alpha^2} - 2 - \frac{6e^{-\alpha^2}}{\sqrt{\pi}\alpha\ \mathrm{erf}\,\alpha}\right\} \qquad \text{for } T_3 > T_1, \tag{6}$$

$$\frac{1}{2\sqrt{5}}\frac{a_2}{a_0}=\frac{1}{8}\left\{-\frac{3}{\alpha^2}-2+\frac{3e^{\alpha^2}}{\alpha F(\alpha)}\right\} \qquad \text{for } T_3<T_1. \tag{7}$$

Here

$$\alpha=\sqrt{|T_3-T_1|}, \qquad F(\alpha)=\int_0^\alpha e^{t^2}\,dt. \tag{8}$$

For $T_3-T_1\gtrsim 5$,

$$\frac{1}{2\sqrt{5}}\frac{a_2}{a_0}\simeq -0.25+\frac{0.38}{\alpha^2}, \qquad \frac{i_\pi}{i_\sigma}\simeq 0.6+\frac{0.48}{\alpha^2}. \tag{9}$$

Thus, the intensity ratio for $1/\alpha^2\ll 1$ turns out to be the same as when observing Mössbauer absorption on a single crystal whose c axis is oriented perpendicular to the direction of the incident γ-quanta.

For $T_1-T_3\gtrsim 5$ we find

$$\frac{1}{2\sqrt{5}}\frac{a_2}{a_0}\simeq +\frac{1}{2}-\frac{0.38}{\alpha^2}, \qquad \frac{i_\pi}{i_\sigma}\simeq\frac{1+0.5}{1-0.5}=3-\frac{3.2}{\alpha^2}. \tag{10}$$

In this case the effect is the same as when observing absorption on a single crystal whose c axis is parallel to the direction of the absorbed γ-quanta.

The foregoing makes it possible to find $f'(\vartheta)$ without measurements on a single crystal, if one identifies the σ-component of the doublet, for example by passing from the spectrum of an isotropic powder to the spectrum of a powder with an excess longitudinal (transverse) orientation of the c axis, as a result of which the ratio i_π/i_σ increases (decreases);

a comparison of the spectra will concomitantly give the sign of the quadrupole splitting in (8); the latter is determined without taking into account the possible anisotropy of f'.

In those cases where the crystal field of the single crystals has no axial symmetry, the excited state $3/2^+$ is split into two sublevels which are no longer characterized by the spin-projection quantum numbers $\pm 3/2$ and $\pm 1/2$. The spin wave functions of these two sublevels, as calculation shows (the matrix elements* for the quadrupole interaction used in the calculation were obtained by Pound (9)), have the form

$$G_\pm=N_\pm(\chi_{1/2}+\lambda_\pm\chi_{-3/2}), \qquad G'_\pm=N_\pm(\chi_{-1/2}+\lambda_\pm\chi_{3/2}), \tag{11}$$

where $N_\pm=(1+\lambda_\pm^2)^{-1/2}$; $\lambda_\pm=\dfrac{\pm\varepsilon+a}{b}$; $\varepsilon=\sqrt{a^2+b^2}$; $a=\dfrac{3}{2}Aeq$; $b=$

$$= \frac{\sqrt{3}}{2} Aeq\,\eta; \qquad A = \frac{eQ}{2I(2I-1)}; \qquad I = \frac{3}{2} \text{ for } \mathrm{Sn}^{119*}; \qquad eq = \frac{\partial E_z}{\partial z}; \qquad \eta =$$

$$= \frac{\partial E_x/\partial x - \partial E_y/\partial y}{\partial E_z/\partial z}; \qquad eQ = \left(II \middle| \sum_i e_i r_i^2 (3\cos^2\vartheta_i - 1) \middle| II \right)$$

is the quadrupole moment of the nucleus; $\hbar\omega_0 \pm \varepsilon$ is the frequency of the resonant γ-quantum corresponding to excitation to the "plus"or "minus"level, respectively; ω_0 is the frequency of the γ-transition in the absence of the quadrupole field. The principal axes of the tensor of the field-gradient strength of the crystal field are chosen as the x, y, and z axes.

Applying the theory of radiation (6, 7), we obtain for the total probabilities of transitions (Mössbauer and non-Mössbauer taken together) to the "plus" and "minus" levels the expression

$$I_\pm(\vartheta,\varphi) = \text{const} \cdot N_\pm^2 \left\{ \frac{5}{6} + \frac{\lambda_\pm^2}{2} + \left(-\frac{1}{2} + \frac{\lambda_\pm^2}{2} \right) \cos^2\vartheta \pm \lambda_\pm \sqrt{\frac{1}{3}} \sin^2\vartheta \cos^2\varphi \right\} \tag{12}$$

Here ϑ, φ are spherical angles defining the direction of the absorbed γ-quanta in the system of the principal axes of the tensor of the field-gradient strength of the crystal field.

For $\eta \to 0$ the "plus" level tends to the level ($\pm 3/2$, $3/2^+$), the "minus" level to ($\pm 1/2$, $3/2^+$), the magnitude of the splitting is $2a$, and formulas (12) go over into (2).

Averaging (12) with the factor $f'(\vartheta, \varphi)$ over directions, we obtain the intensities of the Mössbauer lines for powders:

$$i_\pm = \text{const} \cdot N_\pm^2 \{ \overline{A} \lambda_\pm^2 + \overline{B} - \overline{C} \lambda_\pm \}, \tag{13}$$

where $\overline{A}$, $\overline{B}$, and $\overline{C}$ are the corresponding quantities averaged with the factor $f'(\vartheta, \varphi)$ over directions:

$$A = \frac{1}{2}(1 + \cos^2\vartheta), \qquad B = \frac{1}{6}(5 - 3\cos^2\vartheta), \qquad C = \frac{\cos 2\varphi}{\sqrt{3}}(1 - \cos^2\vartheta). \tag{14}$$

It is easy to verify that when $f'(\vartheta, \varphi) = \text{const}$, then $i_+ = i_-$, and the doublet will be symmetric. Therefore, from the point of view under consideration, an asymmetry of the crystal field alone is insufficient for the appearance of asymmetry of the Mössbauer doublet of powders: a necessary and sufficient condition for asymmetry of the doublet is anisotropy of the Mössbauer effect in the single crystals of the powder.

---

* For the components $(\Delta E)_{\pm 2}$ of the irreducible tensor of the field-gradient strength, an error in the factor was made in (9). The indicated components should have the form

$$\nabla E_{\pm 2} = -\left(\frac{6^{1/2}}{12}\right)\left[\left(\frac{\partial E_x}{\partial x}\right) - \left(\frac{\partial E_y}{\partial y}\right) \pm 2i\left(\frac{\partial E_x}{\partial y}\right)\right].$$

The ratio i_+/i_- depends on the parameter η; therefore, when the local values of the field-gradient tensor are spread, the components of the doublet may differ not only in intensity but also in shape. It should be emphasized that the asymmetry of the doublet must depend on temperature, since $f'(\vartheta, \varphi)$ is some function of temperature (1,2).

The author expresses his gratitude to V. I. Goldanskii and N. D. Sokolov for valuable discussions.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
20 VII 1962

References

[1] V. A. Bryukhanov, V. I. Goldanskii et al., ZhETF, **43**, No. 2 (8) (1962).
[2] V. I. Goldanskii, G. M. Gorodinskii et al., DAN, **147**, No. 1 (1962).
[3] Yu. Kagan, DAN, **140**, 794 (1961).
[4] N. A. Alekseevskii, F. M. Zuykov et al., Anisotropy of the Mössbauer Effect in a Single Crystal of β-Sn, report at a working conference on the Mössbauer effect, Moscow, 1962.
[5] Yu. Kagan, ZhETF, **40**, No. 1, 312 (1961).
[6] A. I. Akhiezer, V. B. Berestetskii, *Quantum Electrodynamics*, Moscow, 1953.
[7] A. M. Baldin, V. I. Goldanskii, I. A. Rozental, *Kinematics of Nuclear Reactions*, Moscow, 1959.
[8] A. J. F. Boyle, D. St. Bunbury, C. Edwards, Proc. Phys. Soc., **79**, 416 (1962).
[9] R. V. Pound, Phys. Rev., **79**, 685 (1950).

Note: Figure translations are in progress. See original paper for figures.