PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Anisotropic Lattice-Dynamic Studies and Line Asymmetries in Mössbauer-Effect Doublet Spectra

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(Received 6 July 1967)

Asymmetries in the line intensities of component lines of electric-quadrupole doublets in Mössbauer spectra (the Karyagin effect) have been observed in linear chain-polycrystalline polymers over a wide range of temperatures. It was observed that the asymmetry increases at higher temperatures and almost disappears at low temperatures. No significant Karyagin effect has been observed for three-dimensional monomeric material.

ASYMMETRIES in the intensity of component lines of electric-quadrupole doublets in Mössbauer spectra of polycrystalline material have been interpreted by Karyagin[1-3] as being due to the lattice-dynamic anisotropy in the recoil-free fraction f_a in the absorber. It was analogously shown that such lattice anisotropy can influence the line intensities in Mössbauer spectra showing magnetic hyperfine interactions.[4] Alternatively, asymmetric-line intensities in polycrystalline samples can be attributed to spin-lattice and spin-spin relaxation effects.[5,6]

In a series of experiments with phenylchlorostannyl compounds, Goldanskii and co-workers[7] have attempted to show experimentally the existence of an asymmetry in the line intensity due to the Karyagin effect. This experimental work has, however, been challenged by others[8] on the grounds that impure substances were used by Goldanskii *et al.* and that differences in characteristic-quadrupole splitting and isomer shifts of the contaminants gave rise to the apparent Karyagin effect. We have undertaken this study to resolve the discrepancy in the reported experiments concerning the Karyagin effect and to offer direct experimental confirmation of such an effect.

The present experimental details have been described elsewhere.[9] All compounds were at least 98% pure and were obtained in fine powders, i.e., the absorbers were randomly oriented fine crystallites. The resultant Mössbauer spectra showed equal linewidths (full width at half maximum) Γ_{exp} for both doublet components at all temperatures. In addition, it was observed that $\lim_{f_a\to 0+}\Gamma_{\text{exptl}}\approx 2\Gamma$ at sufficiently high temperatures, and $\lim_{n\to 0+}\Gamma_{\text{exptl}}\approx 2\Gamma$, where n is the number of atoms capable of participating in resonance absorption and Γ is the total natural linewidth for the Sn^{119} $\frac{3}{2}+$ excited state. The temperature dependence of the line-intensity ratio (I_2/I_1) for trimethyltinhydroxide, trimethyltinfluoride, and triphenyltinchloride is shown in Fig. 1. I_1 and I_2 refer, respectively, to the line component associated with the γ-ray resonance energy $E_0-\delta$ and $E_0+\delta$, where E_0 is the γ-ray energy at the centroid of the spectrum.

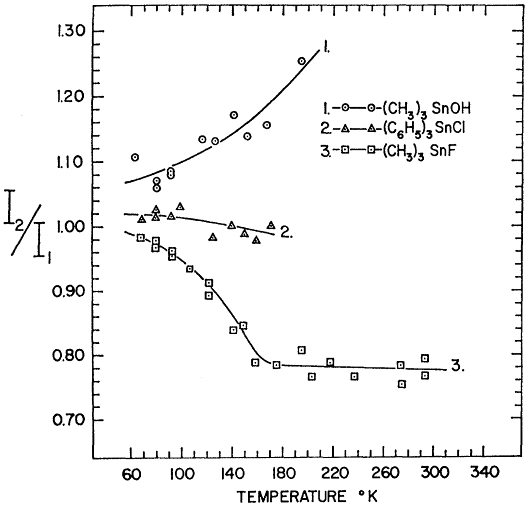

FIG. 1. The temperature dependence of the line-intensity ratio (I_2/I_1) for $[(CH_3)_3SnOH]_n$, $[(CH_3)_3SnF]_n$, and $(C_0H_5)_3SnCl$. The temperature is in °K.

The pertinent radiative transition in Sn^{119} is the $(\frac{3}{2}+)\rightarrow(\frac{1}{2}+)$ transition of each degenerate $E(2)$ sublevel to the unsplit degenerate ground-state level and

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[7] V. I. Goldanskii, E. F. Makarov, and V. V. Khrapov, Zh. Eksperim. i Teor. Fiz. **44**, 752 (1963) [English transl.: Soviet Phys.—JETP **17**, 508 (1963)]; Phys. Letters **3**, 344 (1963).

[8] V. S. Shpinel, A. Yu. Aleksandrov, G. K. Ryasnyi, and O. Yu. Okhlobystin, Zh. Eksperim. i Teor. Fiz. **48**, 69 (1965) [English transl.: Soviet Phys.—JETP **21**, 47 (1965)].

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the transition energy $\Delta E_Q=\frac{1}{2}e^2qQ(1+\eta^2/3)^{1/2}$. For $(CH_3)_3SnF$, $\Delta E_Q=3.87\pm0.09$ mm/sec, and for $(CH_3)_3SnOH$, $\Delta E_Q=2.97\pm0.09$ mm/sec. The isomer shift for $(CH_3)_3SnF$ and $(CH_3)_3SnOH$ is 1.27 ± 0.09 mm/sec and 1.14 ± 0.09 mm/sec, with respect to SnO_2, respectively. The quantities eq and η are the usual components of the symmetric second-rank electric-field-gradient tensor $\boldsymbol{\nabla}\mathbf{E}$ which is diagonalized by a transformation to a set of principal axes x', y', and z' where $eq=(\delta E_{z'}/\delta z')$ and

$$eq\eta=(\delta E_{x'}/\delta x')-(\delta E_{y'}/\delta y').^{10,11}$$

Letting β and γ be the spherical angles of the direction of the γ-ray relative to the principal axes of the local field, the functional dependence of the total radiative transition probabilities on the angles β and γ is[3]

$$I_\pm(\beta,\gamma)=cN_\pm^2[\tfrac{1}{2}\lambda_\pm^2(1+\cos^2\beta)+\tfrac{1}{6}(5-3\cos^2\beta)$$
$$+(\lambda_\pm/\sqrt{3})\cos 2\gamma(1-\cos^2\beta)], \qquad (1)$$

where

$$\lambda_\pm=[(3)^{1/2}\pm(3+\eta)^{1/2}]/\eta$$

and

$$N_\pm^2=(1+\lambda_\pm^2)^{-1}.$$

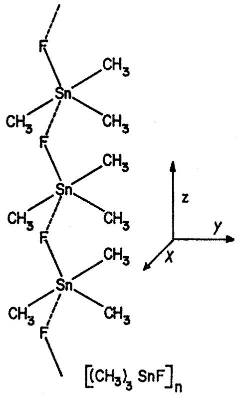

FIG. 2. The crystal structure of the linear-polymeric material $[(CH_3)_3SnF]_n$.

The recoiless fraction f_a is functionally dependent on the γ-ray momentum $\mathbf{p}$, i.e., the wave vector $\mathbf{k}=\mathbf{p}/\hbar$, and the instantaneous displacement $\mathbf{u}_r$ of the rth absorbing nucleus from its mean position such that $f_a=\exp-\langle[\mathbf{k}\cdot\mathbf{u}_r]^2\rangle$. The instantaneous mean-square vibrational amplitude $\langle u_r^2\rangle$ in the direction of the unit vector $\mathbf{l}$ can be represented by the symmetric 3×3 anisotropic mean-square displacement tensor $\mathbf{U}^r$ so that[12–15]

$$\langle u_r^2\rangle=\sum_{i,j=1}^{3}U_{ij}^r l_i l_j+\langle u_r^2\rangle_d, \qquad (2)$$

where $\langle u_r^2\rangle_d$ corresponds to nonrigid-body distortional vibrations which are neglected in the present discussion. $\mathbf{U}^r$ is composed of rigid-body vibrations and is represented by two symmetric 3×3 tensors, $\mathbf{T}$ the anisotropic translational vibrations of the mass center and $\mathbf{L}$ the anisotropic angular vibrations about the axes through the center of the molecule. It is assumed that the present molecules are centrosymmetric, where the origin of the inertial axes coincide with the origin of the principal axes of $\boldsymbol{\nabla}\mathbf{E}$. In general, however, molecules are noncentrosymmetric and an additional unsymmetric tensor $\mathbf{S}$ is needed to correlate $\mathbf{T}$ and $\mathbf{L}$, which results in helical molecular motion[16]; in such a case the origin of the inertial axes do not always coincide with those of $\boldsymbol{\nabla}\mathbf{E}$.[17] The $\langle u_r^2\rangle$ in a direction $\mathbf{l}$ at a point $\mathbf{r}$ of the rth Sn^{119} atom is

$$\langle u_r^2\rangle=\sum_{i,j=1}^{3}U_{ij}^r l_i l_j=\sum_{i,j=1}^{3}[T_{ij}l_i l_j+L_{ij}(\mathbf{l}\times\mathbf{r})_i(\mathbf{l}\times\mathbf{r})_j], \qquad (3)$$

where x, y, z is the rectangular coordinate system of $\mathbf{U}^r$, which is now a vibrational ellipsoid whose semiaxes are $\langle u_r^2\rangle_x$, $\langle u_r^2\rangle_y$, and $\langle u_r^2\rangle_z$. Letting θ and ϕ be the spherical angles of the direction of $\mathbf{k}$ relative to $\langle u_r^2\rangle$, the angular dependence of $f_a(\theta,\phi;g(T))$ in terms of the principal axes of $\boldsymbol{\nabla}\mathbf{E}$ is $f_a(\beta,\gamma;g(T))$ by the transformation

$$U_{k,l}{}^r(x')=\sum_{i,j}U_{i,j}{}^r(x)\frac{\partial x_k'}{\partial x_i}\frac{\partial x_l'}{\partial x_j}, \qquad (4)$$

where $g(T)$ is a temperature-dependent scalar amplitude function. $I_\pm(\beta,\gamma)$ will generally contain a temperature-dependent function $h(T)$ implicit in the temperature-dependent behavior of $\lambda_\pm$ (i.e., of eq and η) in the crystalline state.[17] The total relative intensities of the transition is

$$\left(\frac{I_2}{I_1}\right)=\int_0^{2\pi}\int_0^{\pi}I_+(\beta,\gamma;h(T))f_a(\beta,\gamma;g(T))\sin\beta d\beta d\gamma\Bigg/\int_0^{2\pi}\int_0^{\pi}I_-(\beta,\gamma;h(T))f_a(\beta,\gamma;g(T))\sin\beta d\beta d\gamma. \qquad (5)$$

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The x-ray diffraction crystal structures[18,19] of

$$[(CH_3)_3SnF]_n \qquad \text{and} \qquad [(CH_3)_3SnOH]_n$$

show that these compounds are one-dimensional linear-polymeric chains held together by weak van der Waals forces between methyl groups in neighboring chains, whereas $(C_6H_5)_3SnCl$ is a weakly bonded three-dimensional monomeric unit. The structure of $[(CH_3)_3SnF]_n$ is shown in Fig. 2, where a set of lattice-dynamic principal axes are indicated. In an intermediate temperature range T_2 such linear polymers have $(\langle u_r^2\rangle_x \approx \langle u_r^2\rangle_y) > (\langle u_r^2\rangle_z)$, the eccentricity of the vibrational ellipsoid being maximized.[20,21] At low and high temperatures T_1 and T_3 $\langle u_r^2\rangle_x \approx \langle u_r^2\rangle_y \approx \langle u_r^2\rangle_z$, the thermal motion being nearly a vibrational sphere. For a monomeric material, $\langle u_r^2\rangle_x \approx \langle u_r^2\rangle_y \approx \langle u_r^2\rangle_z$ at almost all temperatures. From Fig. 1, it is seen that the linear-chain compounds display a strong temperature-dependent Karyagin effect due to the significant anisotropic thermal behavior of the linear polymers in T_2. For $[(CH_3)_3SnF]_n$, $d(I_2/I_1)/dT<0$, whereas

$$d(I_2/I_1)/dT>0$$

for $[(CH_3)_3SnOH]_n$ in the range T_2. If $\lambda_\pm$ is constant in T_2 and $\eta \neq 1$, then a difference in the sign of $d(I_2/I_1)/dR$ indicates that $\delta E_{z'}/\delta z'$ in $(CH_3)_3SnOH$ and $(CH_3)_3SnF$ probably have opposite signs, and hence the $(\pm\frac{3}{2}, \frac{1}{2}+)$ and the $(\pm\frac{1}{2}, \frac{3}{2}+)$ levels are energetically reversed in these two compounds. At low temperatures, i.e., in the range R_1, $(I_2/I_1)\approx 1$ and $d(I_2/I_1)/dR \to 0$, and the Karyagin effect vanishes in these chain compounds. That $(I_2/I_1)\approx 1$ and $d(I_2/I_1)/dR \approx 0$ for $(C_6H_5)_3SnCl$ reflects the almost isotropic thermal behavior of the Sn^{119} atom in this compound and a negligible Karyagin effect is observed. This result is in agreement with the evidence found in Ref. 8 but substantially disagrees with that of Goldanskii *et al.*

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PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Stopping Cross Section in Carbon of 0.2–1.5-MeV Atoms with $21 \leq Z_1 \leq 39$

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(Received 29 August 1967)

The stopping cross section $S=dE/NdR$ in thin carbon foils has been measured for ions with $21 \leq Z_1 \leq 39$ and with energies from 200 to 1500 keV. The experimental data have been corrected numerically for nuclear stopping, and the electronic stopping obtained is compared with theory. At constant projectile velocity, the periodic dependence of the electronic stopping cross section on the atomic number Z_1 of the incoming ions, previously reported for $Z_1 \leq 20$, is seen also in the present extended Z_1 range. The data show that the amplitude of the successive oscillations is approximately constant over the whole Z_1 range. The relative amplitude, however, tends to decrease with increasing velocity. The relative accuracy of the results is about 3%.

INTRODUCTION

THE slowing-down of energetic atomic particles in matter is determined by two processes: electronic encounters and nuclear encounters. In the high-energy region, electronic stopping predominates, and the Bethe–Bloch formula describes the stopping cross section. However, in the low-energy region, i.e., for velocities below $v_0 Z_1^{2/3}$, where v_0 is the Bohr velocity, the electronic stopping cross section is proportional to the velocity of the incoming ion, and the nuclear stopping cross section becomes increasingly important when the velocity is reduced. For example, the energy at which the nuclear stopping becomes equal to the electronic stopping in carbon is 220 keV for Sc and 580 keV for Kr.

The theory of electronic stopping at low velocities has been given by Fermi and Teller[1] and by Lindhard[2] for an electron gas, and by Lindhard and Scharff[3] and by Firsov[4] for the atomic case.

The treatment by Lindhard and Scharff is based on the Thomas–Fermi statistical model for the atom, and they quote the following result for the electronic stopping cross section valid for ion velocities less than $v_0 Z_1^{2/3}$:

$$S_e = \xi_e 8\pi e^2 a_0 (Z_1 Z_2/Z)(v/v_0) \qquad (Z^{2/3} = Z_1^{2/3} + Z_2^{2/3}),$$

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