

It seems, therefore, that the existence of discrete x-ray Raman lines cannot be doubted anymore. However, the defocused condition for weakening of the Compton band is rather troublesome to obtain. No explanation can be offered for the negative results of Weiss, since his paper gives no information about the geom-

etry of his arrangement.

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### PSEUDOQUADRUPOLE SHIFT OF GAMMA RESONANCE SPECTRA\*

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In most recoilless gamma-ray resonance experiments the magnetic-dipole and electric-quadrupole hyperfine interaction do not cause any shift of the center of gravity of the velocity spectrum. This is usually related to the fact that the trace of the hyperfine-interaction Hamiltonian is zero. Nevertheless a large shift can be caused under proper conditions by a magnetic hyperfine interaction in second order, the so-called "pseudoquadrupole" interaction.<sup>1</sup> This paper reports the first observation of the pseudoquadrupole shift of gamma lines.<sup>2</sup>

In nondegenerate electronic states there is no first-order magnetic hyperfine interaction since the electronic states are invariant under time reversal. However, if the energy separation,  $k\theta$ , of the lowest two electronic states is quite small, comparable to the magnetic hyperfine energies, a large magnetic hyperfine interaction arises in second order. This pseudoquadrupole interaction can cause a shift of the center of gravity of the gamma-spectrum line positions when there is a difference in the thermal populations of the two electronic levels involved. We have observed pseudoquadrupole shifts of the 8.4-keV gamma transition of Tm<sup>169</sup> in TmCl<sub>3</sub>·6H<sub>2</sub>O and Tm<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O. The sites of the non-Kramers Tm<sup>3+</sup> ions in these salts have such a low symmetry ( $C_2$  for TmCl<sub>3</sub>·6H<sub>2</sub>O) that all of the 4*f* electronic levels are nondegenerate.<sup>3</sup> However, in both cases the separation  $k\theta$  of the lowest two levels is only of order 1 cm<sup>-1</sup>.<sup>4</sup> The pseudoquadrupole interaction then causes the electronic ground state |*G*⟩ and excited state |*E*⟩ to repel each other, as is illustrated in Fig. 1(a). In gamma resonance experiments at low temperatures one observes the superposition of the hyperfine spectra associated with only these two electron-

ic states, as illustrated in Fig. 1(b). At temperatures where both electronic states are equally populated, the center of gravity of the spectrum is not shifted by the influence of the pseudoquadrupole interaction. With decreasing temperature the intensities of lines *a*-*b*, *a*-*c* of Fig. 1(b) (which are associated with the excited electronic level) decrease, causing a shift of the center of gravity towards *E*<sub>0</sub> (*E*<sub>0</sub> < 0 for Tm<sup>169</sup>), which is the center of lines *d*-*e*, *d*-*f*. It is easy to show that the temperature dependence of the center of gravity *E*<sub>*c*</sub> is given by

$$E_c = E_0 \tanh(\theta/2T) \approx E_0 \theta/2T \text{ for } \theta \ll T. \quad (1)$$

The magnetic hyperfine interaction is given by<sup>5</sup>

$$H_M = 2\beta \langle r^{-3} \rangle \langle J \| N \| J \rangle g \beta_N \vec{I} \cdot \vec{J}, \quad (2)$$

where  $\beta$  and  $\beta_N$  are the Bohr and nuclear magnetons,  $\langle r^{-3} \rangle$  is a radial matrix element of the 4*f* electrons,  $\langle J \| N \| J \rangle$  is a reduced matrix element,<sup>6</sup>  $g$  is the nuclear  $g$  factor, and  $\vec{I}$  and  $\vec{J}$  are the nuclear and electronic angular-momentum operators. For nondegenerate electronic levels the matrix elements  $\langle G | \vec{J} | G \rangle$  and  $\langle E | \vec{J} | E \rangle$  vanish. It can be shown that the second-order magnetic interaction (the pseudoquadrupole interaction) produces a net shift of the spectrum lines given by

$$E_0 k\theta = \frac{1}{3} (\vec{H})^2 (\mu_g^2 - \mu_e^2),$$

$$\vec{H} = 3\beta \langle r^{-3} \rangle \langle J \| N \| J \rangle \langle G | \vec{J} | E \rangle,$$

$$\mu^2 = g^2 \beta_N^2 I(I+1), \quad (3)$$

where the subscripts  $g$  and  $e$  refer to the nuclear ground and excited states. In particular, it should be noticed that this shift is not affect-

ed by the ordinary electric quadrupole interaction. Simultaneous nuclear and electronic transitions such as  $a \rightarrow e$ , which occur with weak intensities at high velocities, have not been observed. Inclusion of these transitions in our analysis would merely change the definition of  $E_0$  (above) but not the temperature dependence given by Eq. (1). In particular, the shift of the center of gravity does not disappear when all spectrum lines are taken into account.

For  $Tm^{3+}$ ,  $J = 6$  and  $I = \frac{1}{2}$  in the nuclear ground

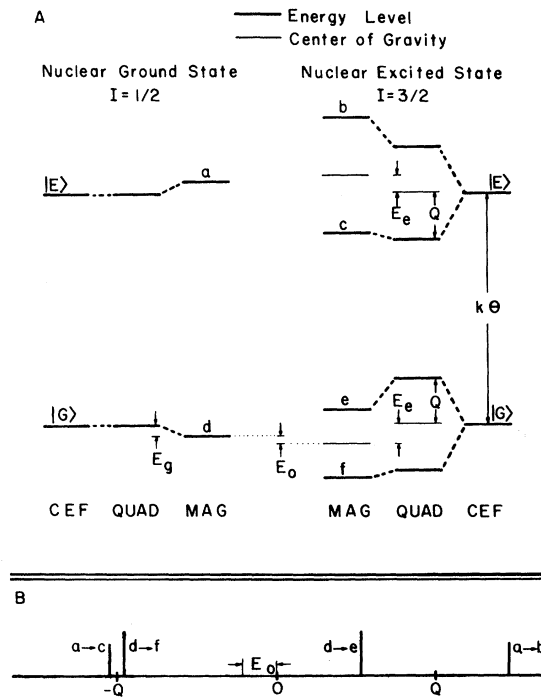


FIG. 1. Electronic and nuclear energy-level scheme and gamma-spectrum lines in trivalent  $Tm^{169}$ . The levels labeled "CEF" are the lowest two electronic levels that would occur in the presence of a crystalline electric field and in the absence of hyperfine interactions. The "QUAD" and "MAG" levels show the successive influence of a first-order electric-quadrupole and a second-order magnetic-dipole interaction. The latter produces displacements  $E_g$  and  $E_e$  of the centers of gravity of the nuclear levels. For simplicity the first-order quadrupole interactions of the two electronic levels were assumed to be identical. This appears to be a good assumption for the salts studied here. Nuclear gamma-absorption transitions occur between levels  $a \rightarrow b$ ,  $a \rightarrow c$ ,  $d \rightarrow e$ ,  $d \rightarrow f$ . Transitions such as  $a \rightarrow e$  have not been observed in our spectra. Electronic transitions occur between levels  $a \rightarrow d$ ,  $b \rightarrow e$ ,  $c \rightarrow f$ . The positions of the gamma resonance-spectrum lines that would result from these energy levels are shown in Fig. 1(b).

state,  $I = \frac{3}{2}$  in the nuclear excited state. Typical gamma resonance spectra are shown in Fig. 2. The four spectrum lines shown in Fig.

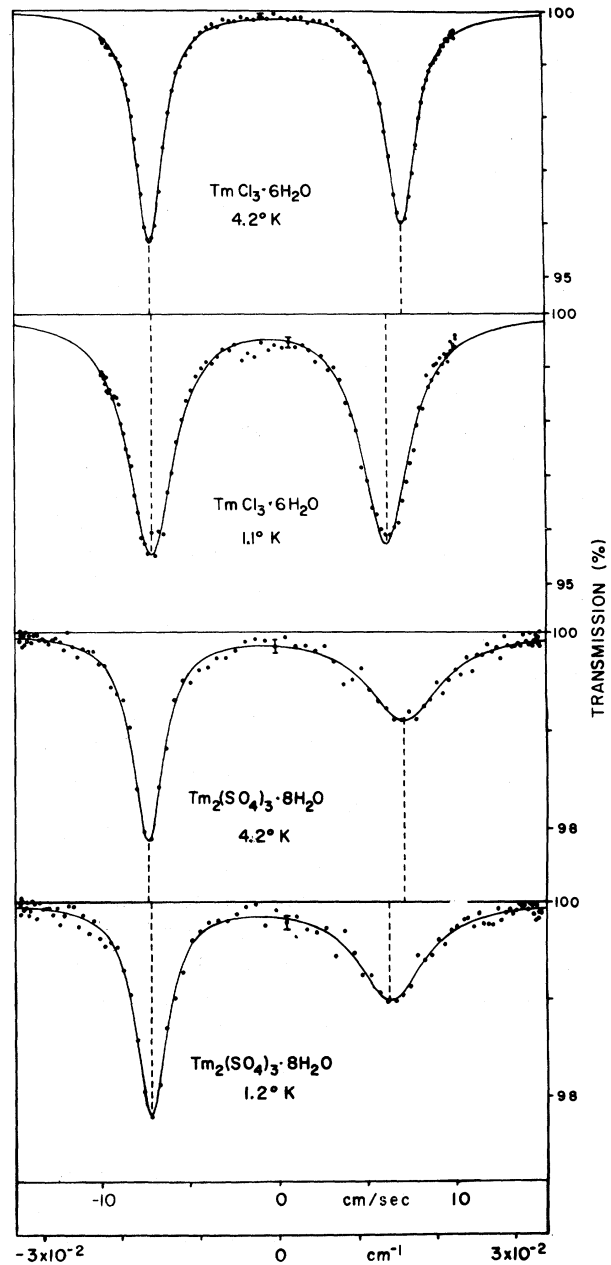


FIG. 2. Typical hyperfine spectra of  $TmCl_3 \cdot 6H_2O$  and  $Tm_2(SO_4)_3 \cdot 8H_2O$  absorbers at low temperatures. The single-line sources used were  $Er^{169}$  in  $ErF_3$  at 550°K. The  $Tm^{3+}$  in  $Tm_2(SO_4)_3 \cdot 8H_2O$  was diluted by 82 at.%  $Y^{3+}$ . The spectra were assumed to consist of two Lorentzians of equal areas (the solid curves). Slight deviations from this assumption would not appreciably affect our analysis. The pseudoquadrupole shift is then the average shift of the centers of these Lorentzians (the dashed lines).

1(b) are "narrowed" by relaxation between the two electronic states into the two lines seen in the observed spectra. The asymmetries exhibited by the spectra of Fig. 2 are due to the combined effects of the pseudoquadrupole interaction and incomplete motional narrowing of the gamma lines. Similar distorted spectra have been observed in  $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  up to  $T = 300^\circ\text{K}$ . The temperature independence and concentration dependence of the line widths obtained when the  $\text{Tm}^{3+}$  is diluted in isomorphous salts of  $\text{Y}^{3+}$  strongly indicate that the relaxation is due to spin-spin interactions. We obtain<sup>7</sup>  $\tau/(k\theta)^2 = (2.0 \pm 0.3) \times 10^{-11} \text{ cm}^2 \text{ sec}$  where  $\tau$  is the electronic relaxation time. From this an order-of-magnitude estimate of  $\tau$  may be obtained; using the value  $k\theta = 1 \text{ cm}^{-1}$  (see Fig. 3), we obtain  $\tau = 2 \times 10^{-11} \text{ sec}$ .

The observed shifts for  $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$  have been plotted versus temperature in Fig. 3. As can be seen from the graph,  $\theta$  cannot presently be determined with any accuracy. The measurements are being extended to lower temperatures where the curves are more sensitive to  $\theta$ . We can determine with good accuracy the quantity  $E_0 k\theta = (2.30 \pm 0.07) \times 10^{-2} \text{ cm}^{-2}$ . Using the value<sup>8</sup>  $\langle r^{-3} \rangle = 75 \text{ \AA}^{-3}$ , we obtain  $\langle G | \vec{J} | E \rangle^2 = 30$  from Eq. (3) for  $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ .

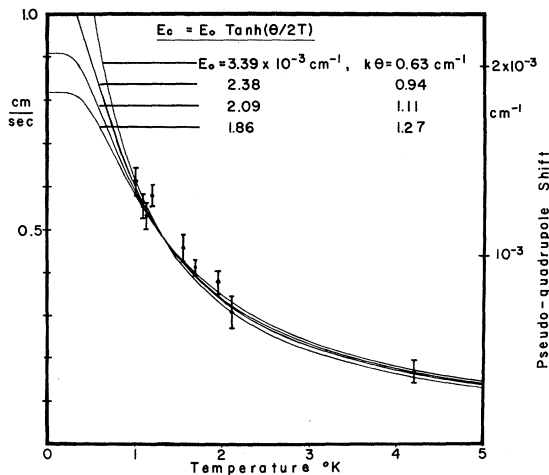


FIG. 3. Pseudoquadrupole shifts as a function of temperature for  $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$ . The experimental points shown here include some results from Tm diluted in  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ . The dilution has no measurable effect on the positions of the peaks. The solid curves are plots of  $E_0 \tanh(\theta/2T)$  for several values of  $\theta$ ; for each value of  $\theta$ ,  $E_0$  was chosen to fit the measured shifts best. The best over-all fit is obtained with  $k\theta = 1.11 \text{ cm}^{-1}$ ,  $E_0 = 2.09 \times 10^{-3} \text{ cm}^{-1}$ .

This is in good agreement with the value of 35 calculated from angular wave functions obtained by Harrop.<sup>9</sup>

Previously several other mechanisms have been reported which produce shifts of the center of gravity of gamma resonance spectra. These may be divided into two categories: (1) mechanisms which change the position of the spectrum lines such as the isomer shift<sup>10</sup> and the second-order Doppler shift,<sup>11</sup> and (2) mechanisms which asymmetrically change the intensities of the spectrum, such as an anisotropic Debye-Waller factor,<sup>12</sup> and nuclear orientation.<sup>13</sup> The pseudoquadrupole shift of gamma lines involves both a shift of the line positions and an asymmetric change of the intensities of the spectrum. The pseudoquadrupole shift can be clearly distinguished from all the above shifts by its characteristic temperature dependence. In particular, this dependence can be used to distinguish isomer shifts from pseudoquadrupole shifts at low temperatures.

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## MAGNETOPIEZO-OPTICAL REFLECTION IN GERMANIUM

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We report the first observation of magneto-reflection for the direct transition in germanium. Among semiconductors, a study of magnetoreflexion was first made<sup>1</sup> in InSb but was not successfully extended to other higher energy-gap materials. We have examined the magnetoreflexion in germanium by the use of piezoreflection technique reported recently by Engeler *et al.*<sup>2</sup> In this technique, the sample is mounted rigidly on a piezoelectric transducer. By applying an alternating voltage to the transducer, the sample is subjected to a small sinusoidal strain. The resulting change in reflectivity,  $\Delta R$ , due to the applied strain, is detected synchronously with driving voltage on the transducer by using a phase-sensitive amplifier. In this manner, it is possible to measure fractional changes in reflectivity,  $\Delta R/R$ , as small as  $10^{-5}$ . Thus piezoreflection provides a much more sensitive probe for the investigation of magnetoreflexion effects in solids. It should be mentioned that one obtains an equally high sensitivity with the electroreflection technique.<sup>3,4</sup> A very high electric field  $\sim 10^5$  V/cm has to be applied at the surface of the sample in the latter technique. As pointed out by Vrethen,<sup>5</sup> a high electric field tends to smear out the magnetic structure present at the direct gap in germanium. This is due to the fact that the selection rules for optical transitions are modified and additional transitions occur in the presence of the electric field.<sup>6</sup> Another advantage of the magnetopiezoreflection technique is that it can be applied to metals as well.

We have performed a preliminary experiment for the effect of magnetic field on the piezoreflectance for the direct transition in ger-

manium. A Bitter-type magnet with a 4-in. bore provided magnetic fields up to  $\sim 90$  kG at 4 MW. The samples were in the Faraday configuration, the direction of light propagation being parallel to the magnetic field. The reflection measurements were made with samples at near-normal incidence using a Perkin-Elmer double-pass grating monochromator equipped with a Bausch and Lomb grating blazed at  $1.6 \mu$ . A lead sulfide cell operating at room temperature was used to detect infrared radiation. Samples of single-crystal "web" germanium<sup>7,8</sup> were used in the present investigation. Web material grows in the form of thin flat sheets and, therefore, no polishing and/or etching is needed for sample preparation. Thus web material, whenever available,<sup>9</sup> provides an as-grown surface of high quality necessary for the study of reflection effects.

For the experimental results reported in this Letter, 0.15-mm-thick samples were glued to one face of a 2.5-mm-thick lead-zirconate-titanate transducer using Duco-type cement. The transducer was operated at a frequency of 1000 cps and at a level such that the rms value of the strain,  $S$ , in the plane of the sample was  $\sim 5 \times 10^{-5}$ . In the above sample-transducer configuration, the stress on the sample is neither purely hydrostatic nor uniaxial, but a combination of the two types. The contribution of each component is determined by the crystallographic orientation of the sample and the elastic constants of the material. For the (111) germanium samples used in the present case, it can be shown<sup>10</sup> that the dilation,  $\Delta V/V$ , is equal to  $(2-\lambda)S$ , where

$$\lambda = 2 \frac{c_{11} + 2c_{12} - 2c_{44}}{c_{11} + 2c_{12} + 4c_{44}} = 0.37.$$