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 geometry of his arrangement.

4J. W. M. DaMond, Rev. Mod. Phys. 5, 11 (1933).

**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. This paper reports the first observation of the pseudoquadrupole shift of gamma lines.2

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\(^{169}\) in TmCl\(_3\)\( \cdot 6\)H\(_2\)O and Tm\(_3\)(SO\(_4\))\(_3\)\( \cdot 8\)H\(_2\)O. The sites of the non-Kramers Tm\(^{3+}\) ions in these salts have such a low symmetry (\( C_2 \) for TmCl\(_3\)\( \cdot 6\)H\(_2\)O) that all of the 4\( f \) electronic levels are nondegenerate.3 However, in both cases the separation \( k\theta \) of the lowest two levels is only of order 1 cm\(^{-1}\).4 The pseudoquadrupole interaction then causes the electronic ground state |\( G \rangle \) and excited state |\( E \rangle \) 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 electronic 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 \( a \sim b, a \sim c \) of Fig. 1(b) (which are associated with the excited electronic level) decrease, causing a shift of the center of gravity towards \( E_0 (E_0 < 0 \) for Tm\(^{169}\)), which is the center of lines \( d \sim e, d \sim f \). It is easy to show that the temperature dependence of the center of gravity \( E_c \) is given by

\[
E_c = E_0 \tanh(\theta/2T) = E_0 \theta/2T \text{ for } \theta \ll T. \tag{1}
\]

The magnetic hyperfine interaction is given by

\[
H_m = 2\beta(\gamma^{-3}) (J || N || J') g \beta_N \vec{I} \vec{J}, \tag{2}
\]

where \( \beta \) and \( \beta_N \) are the Bohr and nuclear magnetons, \( (\gamma^{-3}) \) is a radial matrix element of the 4\( f \) electrons, \( (J || N || J) \) is a reduced matrix element, \( g \) 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

\[
E_0 k\theta = \frac{3}{2}(\vec{H})_g^2 (\mu^2 - \mu^2_e),
\]

\[
\vec{H} = 3\beta(\gamma^{-3}) (J || N || J) (G || \vec{J} || E),
\]

\[
\mu^2 = g \beta_N^2 (J(J + 1)) \tag{3}
\]

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

![Diagram of energy levels and centers of gravity](image1.png)

**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 \(E_Q\) 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. 1b).

![Typical hyperfine spectra](image2.png)

**FIG. 2.** Typical hyperfine spectra of TmCl\(_2\)·6H\(_2\)O and Tm\(_2\)(SO\(_4\))\(_3\)·8H\(_2\)O 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\(_4\))\(_3\)·8H\(_2\)O 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 Tm₃(SO₄)₄·8H₂O up to T = 300°K. The temperature independence and concentration dependence of the line widths obtained when the Tm⁹⁺ is diluted in isomorphous salts of Y³⁺ strongly indicate that the relaxation is due to spin-spin interactions. We obtain \[ \tau /\hbar \theta = (2.0 \pm 0.3) \times 10^{-11} \text{cm}^2 \text{sec} \] where \( \tau \) is the electronic relaxation time. From this an order-of-magnitude estimate of \( \tau \) may be obtained; using the value \( \hbar \theta = 1 \text{ cm}^{-1} \) (see Fig. 3), we obtain \( \tau = 2 \times 10^{-11} \text{sec} \).

The observed shifts for TmCl₃·6H₂O 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 \( E_\theta = (2.3 \pm 0.1) \times 10^{-2} \text{ cm}^{-2} \). Using the value \( \langle \nu \rangle = 75 \text{ A}^{-3} \), we obtain \( \langle G \times J \rangle^2 = 30 \) from Eq. (3) for TmCl₃·6H₂O.

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

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 and the second-order Doppler shift, and (2) mechanisms which asymmetrically change the intensities of the spectrum, such as an anisotropic Debye-Waller factor, and nuclear orientation.¹³ 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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⁴S. Hühner, private communication of optical observations. See also I. H. Harrop, J. Chem. Phys. 42, 4000 (1955); and private communication.


⁹Harrop, Ref. 4.


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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 german-
ium. Among semiconductors, a study of mag-
netoreflection was first made in InSb but was
not successfully extended to other higher en-
ergy-gap materials. We have examined the
magnetoreflection in germanium by the use of
piezoreflection technique reported recent-
ly by Engel et al. In this technique, the
sample is mounted rigidly on a piezoelectric
transducer. By applying an alternating volt-
age to the transducer, the sample is subjected
to a small sinusoidal strain. The resulting
change in reflectivity, ΔR, due to the applied
strain, is detected synchronously with driv-
ing voltage on the transducer by using a phase-
sensitive amplifier. In this manner, it is pos-
sible to measure fractional changes in reflec-
tivity, ΔR/R, as small as 10⁻⁸⁻⁴. Thus piezo-
reflection provides a much more sensitive
probe for the investigation of magnetoreflec-
tion effects in solids. It should be mentioned
that one obtains an equally high sensitivity
with the electroreflectance technique. A very
high electric field ~10⁶ V/cm has to be applied
at the surface of the sample in the latter tech-
nique. As pointed out by Vrehen, a high elec-
tric field tends to smear out the magnetic struc-
ture present at the direct gap in germanium.
This is due to the fact that the selection rules
for optical transitions are modified and addi-
tional transitions occur in the presence of the
electric field. Another advantage of the mag-
netopiezoreflection technique is that it can be
applied to metals as well.

We have performed a preliminary exper-
iment for the effect of magnetic field on the piezo-
reflectance for the direct transition in ger-

\[ \lambda = \frac{2}{c_{11} + 2c_{12} - 2c_{44}} = 0.37. \]