

ELECTRONIC SHIELDING OF THE CRYSTALLINE FIELD IN THULIUM ETHYL SULFATE*

R. G. Barnes,[†] E. Kankleit, R. L. Mössbauer, and J. M. Poindexter
California Institute of Technology, Pasadena, California

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The method of recoilless nuclear resonance absorption of gamma radiation was employed in investigating the temperature dependence of the nuclear quadrupole interaction in the 8.4-keV level of Tm^{169} in thulium ethyl sulfate, $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The experiment reveals a strong influence of electronic shielding resulting from the polarization induced in the closed electron shells by the crystalline electric field.

In a paramagnetic crystal the rare earth ion (Tm^{+3} in the present case) interacts with the crystalline electric field (CEF) produced by the charges (ligands) surrounding the rare earth ion in the crystal. The CEF contributes to the nuclear quadrupole interaction by a variety of effects:

(1) The CEF due to the ligands interacts with the electrons in the partially filled $4f$ shell of the rare earth ion which induces a distortion in the electron shell. As a result each electronic multiplet of the ion is split into a series of levels. The point symmetry of the CEF at the ion determines the number of crystalline field levels, while the strength of the CEF determines the level spacing. The distorted $4f$ electron shell produces an electric field gradient $eq^{(4f)}$ at the nuclear site, which interacts with the nuclear quadrupole moment Q .

(2) The nuclear quadrupole moment of the rare earth ion interacts directly with the gradient $eq^{(\text{lig})}$ of the CEF at the nuclear site.

(3) The CEF interacts with electrons in the closed shells (core electrons), thereby inducing a distortion (polarization) in the closed shells. The quadrupole part of this polarization produces a contribution $-\gamma_\infty eq^{(\text{lig})}$ to the electric field gradient at the nuclear site. The proportionality factor $-\gamma_\infty$ is the Sternheimer¹ shielding ($\gamma_\infty > 0$) or antishielding ($\gamma_\infty < 0$) factor.

(4) The distorted $4f$ electron shell interacts with the core electrons, thereby inducing another polarization in the closed shells. The quadrupole part of this polarization likewise contributes to the electric field gradient at the nucleus, through the term $-Req^{(4f)}$, where $-R$ represents a shielding ($R > 0$) or antishielding ($R < 0$) factor.²

Any component eq_{ij} of the field gradient tensor at the position of the nucleus may then be written as $(1 - \gamma_\infty)eq_{ij}^{(\text{lig})} + (1 - R)eq_{ij}^{(4f)}$, where the first factor in each term gives the direct contribution, while the second factor gives the contribution from

electronic shielding.

Recoilless nuclear resonance absorption was measured in the temperature range $10^\circ\text{K} < T < 300^\circ\text{K}$, using a source of activated ErF_3 and an absorber of thulium ethyl sulfate. The source was kept at 550°K in order to restrict the emission spectrum to a single line. Details of the experimental arrangement and of the evaluation of the data will be described elsewhere.³ The temperature dependence of the nuclear quadrupole interaction is based upon the temperature dependence of $q^{(4f)}$. Each crystalline field level contributes its individual share to the field gradient $eq^{(4f)}$, weighted with its proper Boltzmann factor. As a result one observes only a net quadrupole splitting which is the average of the contributions from all crystalline field levels; the averaging process results from the presence of spin-lattice relaxation times which are short in comparison with all other relevant times.⁴

The nuclear quadrupole interaction for the C_{3h} point symmetry of a thulium ion in thulium ethyl sulfate may be described by the Hamiltonian

$$H_Q = \frac{e^2Q}{4I(2I-1)} [3I_z^2 - I(I+1)] \times [(1-R)q_{zz}^{(4f)} + (1-\gamma_\infty)q_{zz}^{(\text{lig})}], \quad (1)$$

where Q and I represent the nuclear quadrupole moment and spin, respectively. The spins of the nuclear ground state and of the 8.4-keV excited state in Tm^{169} are $\frac{1}{2}$ and $\frac{3}{2}$, respectively; thus only the excited state contributes to the quadrupole interaction. The hyperfine splitting, ΔE , of the 8.4-keV level and hence the splitting of the gamma absorption line in Tm^{169} is then according to Eq. (1)

$$|\Delta E(T)| = \frac{1}{2}e^2Q \left[(1-R)\langle q_{zz}^{(4f)} \rangle_T + (1-\gamma_\infty)q_{zz}^{(\text{lig})} \right], \quad (2)$$

where $\langle q_{zz}^{(4f)} \rangle_T$ is the z component of the temperature-dependent field gradient properly averaged over the crystalline field levels. The field gradient $eq_{zz}^{(\text{lig})}$ may be expressed in terms of the parameter A_2^0 which appears in the usual expansion of the potential,

$$V = \sum_{n,m} A_n^m r^n Y_n^m(\theta, \varphi),$$

produced by the ligands at position r, θ, ϕ . In the case of C_{3h} symmetry the parameters A_2^0, A_4^0, A_6^0 , and A_6^6 suffice to describe the crystalline field splitting of the Tm^{+3} ion. We then have $q_{zz}(\text{lig}) = -4A_2^0/e^2$. The gradient $eq_{zz}(\text{lig})$ may be obtained by using the optically determined relevant crystal field parameter of Wong and Richman.⁵ It must be realized, however, that the parameter A_2^0 derived from optical measurements differs from the parameter A_2^0 defined above. This difference arises from the shielding effect which the core electrons (predominantly the $5s^2p^6$ electrons) exercise upon the potential produced by the ligands at the position of the $4f$ electrons. It is this partially shielded potential which actually produces the crystalline field splitting of the electronic ground multiplet. We therefore introduce another shielding factor through the relation $A_2'^0 = (1 - \sigma_2)A_2^0$.

Figure 1 shows the experimental data points and two theoretical curves. Plotted in each case is the ratio

$$\frac{\Delta E(T)}{\Delta E(0)} = \frac{[\langle q_{zz}^{(4f)} \rangle_T - 4\rho A_2'^0/e^2]}{[\langle q_{zz}^{(4f)} \rangle_0 - 4\rho A_2'^0/e^2]}, \quad (3)$$

where $\rho = (1 - \gamma_\infty)/(1 - R)(1 - \sigma_2)$. The difference

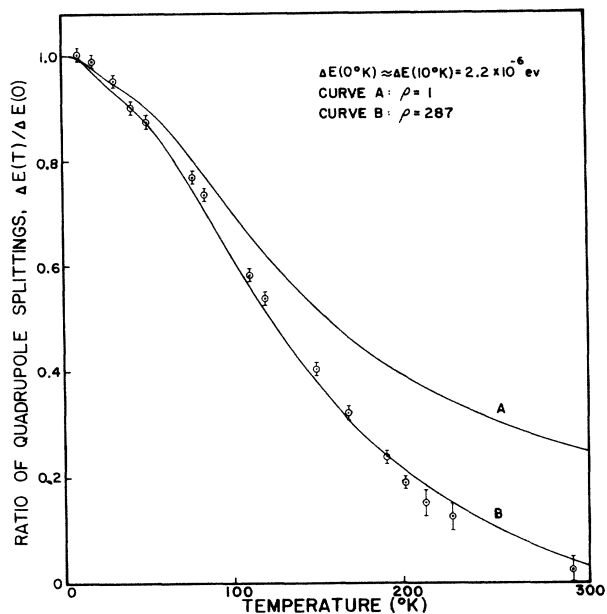


FIG. 1. Temperature dependence of quadrupole splitting in thulium ethyl sulfate. The zero-temperature splitting $\Delta E(0)$ corresponds to a relative velocity of 7.9 cm/sec between source and absorber.

between the two curves demonstrates the strong influence of electronic shielding effects upon the nuclear quadrupole interaction. Curve A was obtained by plotting the theoretical ratio $\Delta E(T)/\Delta E(0)$ for the case $\rho = 1$, thereby disregarding entirely the influence of electronic shielding. In this calculation we used the values $\langle r^2 \rangle_{4f} = 0.19 \text{ \AA}^2$ (Judd and Lindgren⁶), $\langle r^{-3} \rangle_{4f} = 75.5 \text{ \AA}^{-3}$ (Lindgren⁷), and the crystalline field parameters by Wong and Richman,⁵ which were employed in calculating the wave functions required in the evaluation of $\langle q_{zz}^{(4f)} \rangle_T$. The effects of electronic shielding are included in curve B, obtained in a similar way as curve A, but where now the parameter ρ of Eq. (3) was adjusted so as to obtain a best fit to the experimental data. We obtain $\rho = 287$. Furthermore, by using the theoretical value $Q = 1.5$ barn,⁸ the value $\gamma_\infty = -61.5$ as calculated by Wikner and Burns,⁹ and our experimental value $\Delta E(0) = 2.2 \times 10^{-7}$ eV, we obtain $R = 0.12$. This value compares with the value $R = 0.16$ obtained by interpolation from papers by Sternheimer.² With $\gamma_\infty = -61.5$ and $R = 0.12$ we obtain $\sigma_2 = 0.75$, which reflects the strong shielding exerted by the core electrons upon the A_2^0 term in the potential expansion.

It should be noted that a calculation by Burns¹⁰ shows that the higher multipole terms ($n = 4$ and $n = 6$) in the expansion of the potential due to the ligands suffer a small shielding effect (of the order of 10% or less). A calculation by Lenander and Wong¹¹ of the shielding of the $4f$ electrons of Pr^{+3} in $LaCl_3$ yields a substantial shielding of the quadrupole term ($n = 2$) which is similar in magnitude to the one reported in this paper. The value

$$\gamma_\infty/(1 - \sigma_2) = \gamma_N/\gamma_E = -246$$

obtained in this work for thulium ethyl sulfate may be compared with the value ± 550 , deduced for lanthanum ethyl sulfate by Edmonds¹² from nuclear magnetic resonance measurements, and the average value -400 deduced for rare earth ethyl sulfate by Blok and Shirley¹³ from nuclear orientation measurements.

In summarizing we conclude that the effect of electronic shielding via the A_2^0 term plays a major role in both the crystalline field splitting and the quadrupole splitting. The electronic shielding effect is supposedly substantial for most rare earth ions and many values of nuclear quadrupole moments deduced from measurements of the nuclear quadrupole interaction require corrections due to electronic shielding.

Studies of recoilless resonance absorption in

thulium ethyl sulfate were simultaneously performed by Hüfner *et al.*¹⁴; in interpreting their data, Hüfner *et al.* did not take into account the electronic shielding factors σ_2 and R , which led to discrepancy between the experimental and theoretical value of the relevant nuclear quadrupole moment.

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†On leave from Iowa State University, Ames, Iowa.

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NUCLEAR MAGNETIC RESONANCE LINE NARROWING BY A ROTATING rf FIELD*

Walter I. Goldberg and Moses Lee

Osmond Laboratory, The Pennsylvania State University, University Park, Pennsylvania

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In most crystalline solids the breadth of the nuclear magnetic resonance (nmr) absorption line arises mainly from the dipole interactions between the nuclear spins. This interaction is often of sufficient strength to mask the effect of other, more interesting, interactions which broaden the absorption line or shift its frequency. We wish to report here a type of nmr measurement which is not very sensitive to the presence of the dipole interactions and therefore may facilitate observation of relatively small chemical shifts, Knight shifts, and various types of imperfection-induced line broadening which cannot be seen in solids by conventional nmr techniques.

Our experimental method is in many respects equivalent to the observation of a free-induction decay in a rotating sample. In such rotation experiments it has been shown both experimentally and theoretically¹ that the free-induction decay time is increased by this rotation provided the rotational velocity Ω is large compared to the linewidth, i. e.,

$$\Omega \gg \langle \Delta\omega \rangle, \quad (1)$$

where $\langle \Delta\omega \rangle$ is the square root of the second moment of the absorption line of the stationary sample. This increased decay time corresponds,

of course, to a narrowing of the absorption line. If the axis of sample rotation is inclined at an angle Φ with respect to the external field \vec{H}_0 so that

$$\cos^2\Phi = 1/3, \quad (2)$$

then the dephasing effect of the dipole interaction can be shown to vanish completely (in the limit $\Omega/\langle \Delta\omega \rangle \rightarrow \infty$), and the free-induction decay should persist for a time of the order of T_1 , the spin-lattice relaxation time.

The mechanical rotation experiments are quite difficult because of the very great angular velocities required to satisfy (1). With the line-narrowing technique described here this difficulty is absent, for it is a relatively small rf field which is "rotated" rather than the sample. In an analysis of our experiment there enters a frequency $\omega_1 \equiv \gamma H_1$, where γ is the gyromagnetic ratio of the resonant nuclei and $2H_1$ is the amplitude of an rf field applied in a direction perpendicular to \vec{H}_0 . The frequency ω_1 plays exactly the same role as does Ω in the mechanical rotation experiments. For example, it is found that line narrowing is appreciable when

$$\omega_1 \gg \langle \Delta\omega \rangle, \quad (3)$$