Nuclear quadrupole resonance measurement of the anisotropic magnetic shielding and quadrupole coupling constants of $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ dilute in $YAlO_3$ single crystal

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The nuclear quadrupole resonance spectra of Eu^{3+} in $YAlO_3$ single crystal at ~ 10 K are reported. From the ratio of the quadrupole interaction parameters of ^{151}Eu and ^{153}Eu, the ratio of the quadrupole moments corrected for the pseudoquadrupole interaction is obtained $Q^{153}/Q^{151} = 2.5812 \pm 0.0010$. With low-magnetic-field studies the anisotropic magnetic shielding factors are measured. They are $\alpha_x = 0.58$, $\alpha_y = 0.80$, $\alpha_z = 0.47$ compared to an estimate of $\alpha_z = 0.89$ by Elliott. A measured value $\langle r^{-3} \rangle = 39$ Å^{-3} is obtained using Elliott's formulation and the experimental values of the anisotropic magnetic shielding factors.

I. INTRODUCTION

It is commonly believed that nuclear quadrupolar resonance measurements (NQR) of the europium nucleus in a solid have not been successful because of a large diamagnetic shielding of the nucleus from external static and rf magnetic fields by the crystal-field split f^6 electron shell. Elliott[1] suggested that second-order interactions which are cross terms of the electronic Zeeman and the magnetic hyperfine interactions between the singlet $^7F_0$ ground state and other states $^7F_J (J \neq 0)$ of the ground manifold were responsible for this shielding. Judd[2] has found that other similar interactions were responsible for the anomalously large quadrupole splitting of ^{152}Eu and ^{154}Eu observed via angular correlation studies of radioactive decay products. Edmonds[3] in a room-temperature NMR study of La^{3+} in several different host crystals established that the anomalously large *quadrupole* splitting parameter P for the La nucleus (and also the lattice contribution to P for other rare-earth nuclei) is due to an unusually large *antishielding* of the *nucleus* from *the field gradients* of the host lattice by the closed-shell electrons of the rare-earth ion. Macfarlane *et al.*[4] has demonstrated that magnetic dipole transitions in Eu (in EuP_5O_{14}) could be observed optically if a large pulsed (8 G, 25 msec) resonant rf magnetic field is applied to the sample. However, to our knowledge, no measurements have been made of the anisotropic diamagnetic shielding of Eu^{3+} in a solid.

In this paper, we report cw nuclear quadrupole resonance measurements of the two naturally occurring isotopes of $^{151,153}Eu^{3+}$ which are substituted for 0.25% of the Y in a $YAlO_3$ single crystal, in both zero field and in a low static magnetic field. A detailed magnetic field study of one transition $(I_z = \frac{1}{2})$-$(I_z = \frac{3}{2})$ of one isotope, yielded all three anisotropic shielding factors for the Eu nucleus in the host crystal.

The ground term of Eu^{3+} (f^6), ^7F is split into seven multiplets by the spin-orbit interaction. In a solid host, each of the multiplets is further split by the action of the crystalline electric field. In $YAlO_3$, the ground term $J = 0$ is separated from the $^7F_1$ triplet by only 378 cm^{-1}.[5] The usual Hamiltonian for a rare-earth ion in a solid is written

$$\mathcal{H} = A\vec{J}\cdot\vec{I} + P\{[I_z^2 - \tfrac{1}{3}I(I+1)] + \eta(I_x^2 - I_y^2)\} + \beta\vec{H}\cdot(\vec{J}+\vec{S}) + \hbar\gamma\vec{H}\cdot\vec{I} \quad , \tag{1}$$

where the terms are the magnetic hyperfine, nuclear quadrupole, and finally the electronic and nuclear Zeeman interactions. If one considers only the $J = 0$ state, it appears as if only the nuclear quadrupole and nuclear Zeeman terms remain, leaving a simple spectrum with an isotropic nuclear Zeeman effect. However, Elliott[1] has pointed out that second-order interactions which couple the Zeeman and magnetic hyperfine terms via $^7F_1$ and higher levels produce a nuclear Zeeman-like term which results in an anisotropic γ. The simplified Hamiltonian for this ion may be written

$$\mathcal{H} = P'\{[I_z^2 - \tfrac{1}{3}I(I+1)] + \eta(I_x^2 - I_y^2)\} + \hbar(\gamma_x H_x I_x + \gamma_y H_y I_y + \gamma_z H_z I_z) \quad , \tag{2}$$

where P' is the effective quadrupole interaction parameter, $\gamma_i = \gamma(1-\alpha_i)$ $(i = x,y,z)$ is the effective gyromagnetic ratio and α_i are Elliott's[1] shielding parameters. This reduction in γ from the bare nuclear value reduces the sensitivity of NQR experiments by the γ_i/γ ratio squared. The nuclear quadrupole interaction P is dominated not by the crystal-

field gradient directly but by an electronic distortion which is proportional to the nuclear quadrupole moment.[1] The pseudoquadrupole effect which is predominant in $Pr^{3+}(J=4)$ is estimated to be much smaller than P for Eu^{3+}. In Sec. III, we calculate the very small pseudoquadrupole corrections and obtain a ratio of the quadrupole moments for the two isotopes.

II. EXPERIMENT

The NQR measurements were made using an optical rf double-resonance technique previously described.[6] A single crystal of $YAlO_3$:Eu^{3+} (0.25 at.%) at ~ 10 K was illuminated by a 5815-Å single-mode, frequency-stabilized laser beam to selectively excite hyperfine levels of the $^7F_0$-$^5D_0$ transition. The optical excitation produced a substantial redistribution of population in the ground-state hyperfine levels which was probed by an ~ 0.5-G rf magnetic field. This rf field was derived from a frequency synthesizer, 20-W amplifier, and a 2-turn coil surrounding the sample. The rf-induced magnetic dipole transitions tend to equalize the populations and this results in a large change in the optical absorption and therefore the crystal fluorescence. The $^5D_0$-$^7F_1$ fluorescence was monitored. In Fig. 1, a NQR of ^{153}Eu at 23.007 MHz is shown. This measurement consists of the sum of two 2-min sweeps of the peak in the absence of an external magnetic field. Each sweep consists of 250 frequency steps. The effective time constant is 1 sec. Four such resonances were observed at 22.993 ±0.003, 45.970 ±0.006, 59.594 ±0.006, 119.150 ±0.012 MHz, when the laser was exciting the inhomogeneously broadened $^5D_0 \leftarrow {}^7F_0$ transition ~ 0.5 GHz below line center. The linewidths full width at half maximum (FWHM) are 28, 56, 56, 110 kHz, respectively. The 23.0-MHz line position was observed to vary at +10 kHz/GHz when the laser frequency was varied from −5 to +5 GHz in relation to line center. Only two isotopes, ^{151}Eu ($I=\frac{5}{2}$) and ^{153}Eu ($I=\frac{5}{2}$) occur naturally. The ratio of natural abundances is 0.48/0.52. We interpret the two lowest observed transitions as those of ^{151}Eu, ($I_z=\frac{1}{2},-\frac{3}{2}$) and $I_z=(\frac{3}{2},-\frac{5}{2})$. Since the ratio of zero field frequencies is *almost exactly* 2, the quadrupole splitting parameters are very nearly axially symmetric as was observed for the ground state of Pr^{3+} in this host. The two higher frequency transitions are then $^{153}Eu^{3+}$. The observed ratio of these two higher frequencies is 1.9994, differing slightly from the 1.9993 ratio between the two lower frequencies. ($^{153}\eta = 0.0157 \pm 0.0030$, $^{151}\eta = 0.0164 \pm 0.0030$.) The ratio of the quadrupole parameters P for the two isotopes (at line center) is equal to

$$^{153}P'/{}^{151}P' = 2.5919 \pm 0.0005 \ .$$

This compares to the ratio of quadrupole moments measured by Baker and Williams[7] in an ENDOR study of Eu^{2+}, $Q^{153}/Q^{151} = 2.5835 \pm 0.0191$ and by Sandars and Woodgate[8] in an atomic beam experiment $Q^{153}/Q^{151} = 2.5445 \pm 0.0194$. If the estimates of Elliott are correct, then the measured ratio $^{153}P'/{}^{151}P'$ quadrupole should be nearly equal to the measured ratio of the nuclear quadrupole moment. The difference is due to the contribution of the pseudoquadrupole moment to P' which he estimates as $\frac{1}{1500}$ of the total. The zero-field linewidths are approximately proportional to the resonance frequency. This would indicate that these linewidths are due primarily to an inhomogeneous crystal-field broadening rather than being dominated by magnetic dipolar broadening as in the case of Pr^{3+}. This is also consistent with the large variation in resonant frequency depending on which part of the inhomogeneous line is excited. The measured ratio of quadrupole parameters is independent of line position. It is obvious then that this site-selective technique enables one to obtain a more accurate determination of the ratio of quadrupole parameters than is possible if the entire line is observed as in conventional NQR. A corollary is that for nonsite selective techniques the resonances would be significantly broader than observed here. A crystal with a different residual strain would likely give a

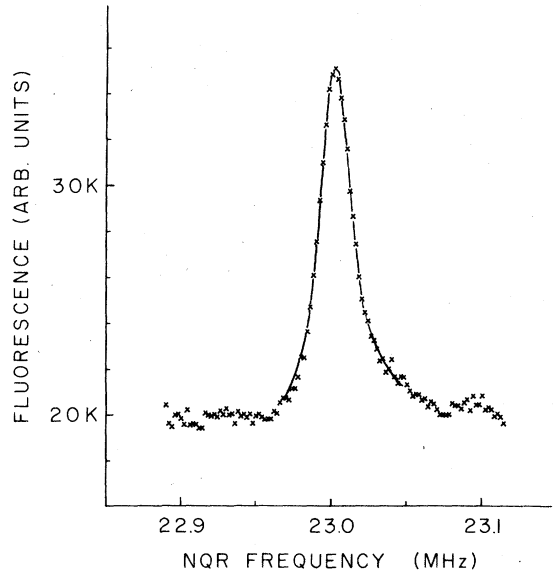

FIG. 1. Optically detected zero-field ground state NQR of the ($I_z=\pm\frac{1}{2} \rightarrow I_z=\pm\frac{3}{2}$) transition of $^{151}Eu^{3+}$ (0.25 at.%) in $YAlO_3$ at 10 K. The linewidth is 28 kHz (FWHM). The solid line is a smooth curve drawn through the experimental points. The slight asymmetry which is present is due to rapid sweeping of the transition. Each point represents two 0.5-sec stops on a staircase of 2-kHz steps. The center frequency is dependent upon the position of the exciting laser in the inhomogeneously broadened $^7F_0 \rightarrow {}^5D_0$ transition which is 1 GHz above line center.

different set of zero-field frequencies, but the ratios of those parameters should be the same as that measured in this work within the accuracy of the experiments.

Detailed magnetic resonance studies were made in a static magnetic field of 50.0 G on the 23-MHz transition (^{151}Eu) as a function of the angle between the crystal axes and the field. This isotope was studied because its magnetic moment is a factor of 2 larger than the other and also because the linewidth of the lowest-frequency transition is 2 times smaller. Indeed, at 50 G no splitting was resolved for the 59.6-MHz transition. The 23-MHz transition was studied because the $\frac{1}{2}$-$\frac{3}{2}$ transition is sensitive to all three magnetic splitting factors in first order unlike the $\frac{3}{2}$-$\frac{5}{2}$ where only γ_z is effective. Figure 2 shows a typical NQR result for an external static field of 50 G at an angle of 75° to the z axis of the Eu^{3+} site. The small magnetic splitting factors do not give clearly resolved spectra in this low magnetic field. This limits the accuracy of the experiment somewhat. Figure 3 shows the resonance frequencies versus the field direction where the field lies in the xz plane of the Eu site. Figure 4 gives similar data for the field in the xy plane of the site. Only one Eu^{3+} site is observed. The Hamiltonian (2) was fitted to the data. The solid curves are those calculated by diagonalizing a complex 6×6 matrix of $\mathcal{H}$ assuming $\eta=0$ using our best-fit parameters. $P=11.500\pm0.002$ MHz, $\gamma_x/2\pi=0.44\pm0.02$, $\gamma_y/2\pi=0.21\pm0.02$, $\gamma_z/2\pi=0.56\pm0.02$ kHz/G. ($\alpha_x=0.58\pm0.02$, $\alpha_y=0.80\pm0.02$, $\alpha_z=0.47\pm0.02$.) This clearly demonstrates the anisotropy of the magnetic shielding parameters as predicted by Elliott. They differ significantly in magnitude from his estimated $\alpha_z=0.89$. Judd[2] has pointed out that the $\langle r^{-3}\rangle$ used by Elliott is too large. The accuracy of these measurements is limited somewhat by the low field in which the measurements were made. The resonance linewidths are about $\frac{1}{10}$ of the maximum splitting. This leads to some scatter in Figs. 3 and 4.

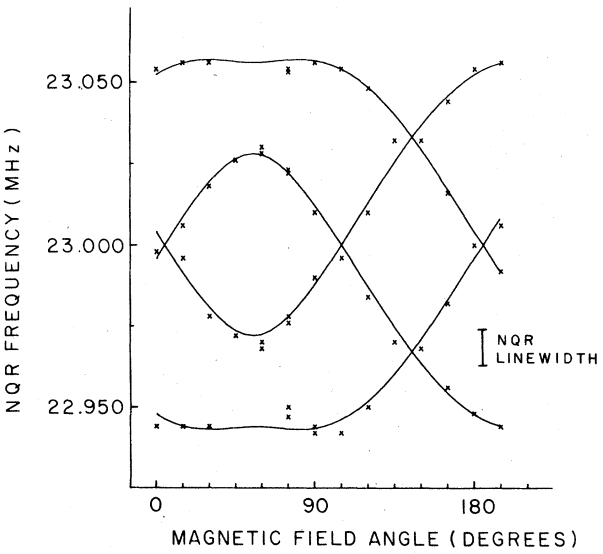

FIG. 3. $^{151}Eu^{3+}$ nuclear quadrupole resonance frequencies ($I_z=\frac{1}{2}$-$I_z=\frac{3}{2}$) in an external static magnetic field of 50.0 G. The field is always perpendicular to the y axis of the Eu^{3+} site. As the field approaches the z axis, the outer transitions become very weak. The solid lines are calculated using the best-fit data assuming the asymmetry parameter $\eta=0$.

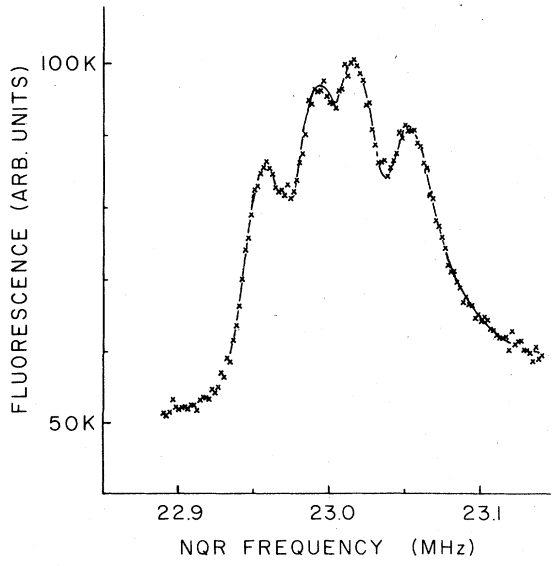

FIG. 2. Optically detected NQR line in a field of 50 G. The field lies in the xz plane of the Eu^{3+} site at an angle 75° to the z axis.

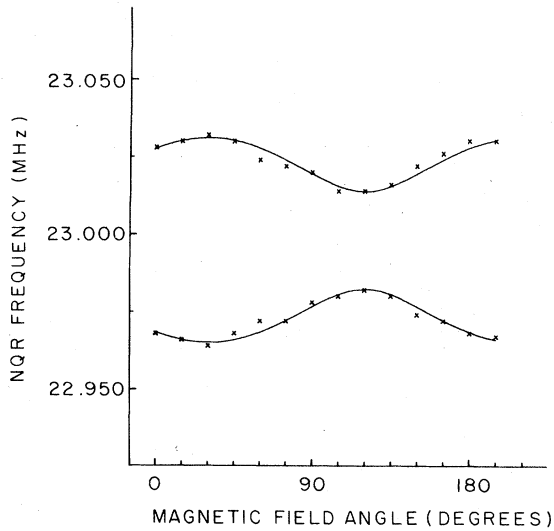

FIG. 4. $^{151}Eu^{3+}$ nuclear quadrupole resonance frequencies ($I_z=\frac{1}{2}$-$I_z=\frac{3}{2}$) in an external magnetic field of 50.0 G. The field is always perpendicular to the z axis of the Eu^{3+} site. The solid lines are calculated using the best-fit data.

In order to confirm the assignment of isotopes (beyond the quadrupole ratios), a single measurement of magnetic splitting in a field of 182 G was made for the 23-MHz and the 59.6-MHz transitions. The splitting of the 23-MHz transition was 2.16 ± 0.22 times that of the 59-MHz transition. The measured ratio of their respective magnetic moments is equal to 2.2632 ± 0.0026.[7]

III. DISCUSSION

Elliott[1] has given an expression for the anisotropic diamagnetic shielding which can be used to derive an experimental value for $\langle r^{-3} \rangle$ using measured values of α_i

$$\alpha_i = \frac{40\beta^2 \langle r^{-3} \rangle}{3\Delta_i} \quad , \tag{3}$$

where Δ_i is an energy level of $^7F_1$ and i indicates x, y, or z depending on which level is chosen. The $J_z = 0$ level at 500 cm^{-1} must be used to obtain α_z. From this we calculate

$$\langle r^{-3} \rangle_z = 40.8 \text{ Å}^{-3} \quad .$$

The shielding factors for x, y yield

$$\langle r^{-3} \rangle_x = 37.1 \text{ Å}^{-3} \quad , \quad \langle r^{-3} \rangle_y = 36.8 \text{ Å}^{-3} \quad .$$

This is to be compared with Judd and Lindgren's value[9] of 45.4 $Å^{-3}$.

The ratio of nuclear quadrupole moments for the two isotopes differs from the measured ratio of quadrupole interaction constants $^{151}P'/^{153}P'$ due to the pseudoquadrupole interaction which is proportional to the nuclear magnetic moment of each isotope rather than the nuclear electric quadrupole moment. Elliott gives an equation for the pseudoquadrupole correction in second order,

$$P'' = \tfrac{5}{2}(\alpha_x + \alpha_y - 2\alpha_z) \langle r^{-3} \rangle \beta_N^2 \mu_N^2 / 6I^2 \quad . \tag{4}$$

If the mean of the experimental $\langle r^{-3} \rangle = 39$ $Å^{-3}$ and the Pichanick, Sandars, and Woodgate[10] values of μ_N for these two isotopes is used, one obtains

TABLE I. Europium quadrupole moment ratios Q^{153}/Q^{151}.

This work	2.5812 ± 0.0010
Sandars and Woodgate[a]	2.5445 ± 0.0194
Baker and Williams[b]	2.5835 ± 0.0191

[a] Eu atomic beam study. See Ref. 8.
[b] Eu^{2+} ENDOR study. See Ref. 7.

$^{151}P'' = 0.0515$ and $^{153}P'' = 0.0100$ MHz. This gives a quadrupole moment ratio

$$Q^{153}/Q^{151} = 2.5812 \pm 0.0010 \quad .$$

The error is due almost equally to the uncertainty in the measured ratio $^{153}P'/^{151}P'$ and an estimated 10% accuracy of the pseudoquadrupole correction.[11]

This result is compared with previously published values of the quadrupole moment ratio in Table I. It lies within the experimental precision of Baker and Williams, and just outside that of Sandars and Woodgate.

IV. CONCLUSION

NQR measurements of Eu^{3+} in solids are reported. The anisotropic diamagnetic shielding predicted by Elliott for a rhombic host are observed and agree very well with his second-order formalism. A "measured" value of $\langle r^{-3} \rangle = 39$ $Å^{-3}$ for Eu^{3+} is obtained which is approximately 15% less than the calculated value of Judd and Lindgren. Finally, with corrections to the measured values of the quadrupole interaction constant, a new value of the quadrupole moment ratio $Q^{153}/Q^{151} = 2.5812 \pm 0.0010$ is obtained.

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[1] R. J. Elliott, Proc. Phys. Soc. London Sect. B 70, 119 (1957).
[2] B. R. Judd, C. A. Lovejoy, and D. A. Shirley, Phys. Rev. 128, 1733 (1962).
[3] D. T. Edmonds, Phys. Rev. Lett. 10, 129 (1963).
[4] R. M. Macfarlane, R. M. Shelby, A. Z. Genack, and D. A. Weitz, Opt. Lett. 5, 462 (1980).
[5] Fluorescence from $^5D_0$ was observed at 5906, 5942.5, and 5989. This corresponds to energy levels of $^7F_1$ at 265, 369, and 500 cm^{-1}. C. A. Morrison, N. Karayianis and D. E. Wortman, in Harry Diamond Lab Report No. HDL-TR-1788, have calculated the three levels to be at 287, 371, and 473 cm^{-1} using crystal-field parameters extrapolated from best-fit values of other rare-earth ions in $YalO_3$.
[6] L. E. Erickson, Phys. Rev. B 19, 4412 (1979).
[7] J. M. Baker and F. I. B. Williams, Proc. R. Soc. London Ser. A 267, 283 (1962).
[8] P. G. H. Sandars and G. K. Woodgate, Proc. R. Soc. London Ser. A 257, 269 (1960).
[9] B. R. Judd and I. P. K. Lindgren, Phys. Rev. 122, 1802 (1961).
[10] F. M. Pichanick, P. G. H. Sandars, and G. K. Woodgate, Proc. R. Soc. London Ser. A 257, 277 (1960).
[11] Following Judd (Ref. 2) and Edmonds (Ref. 3), a negative value of P is chosen. The pseudoquadrupole correction is positive.