



NRC Publications Archive Archives des publications du CNRC

Lattice and electronic contributions to the quadrupole interaction of trivalent europium

Erickson, L. E.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1103/PhysRevB.34.36>

Physical Review B, 34, 1, pp. 36-40, 1986-07

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=652c33fa-ce09-4686-ab5d-834365019aed>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=652c33fa-ce09-4686-ab5d-834365019aed>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.



Lattice and electronic contributions to the quadrupole interaction of trivalent europium

L. E. Erickson

National Research Council, Ottawa, Canada K1A 0R8

(Received 6 June 1985; revised manuscript received 19 February 1986)

A measurement of the $^{151}\text{Eu}^{3+} \ ^5D_0$ excited-state hyperfine splittings in the host crystal YAlO_3 using an optical-rf nuclear double-resonance method, is combined with previously measured values of the quadrupole interaction in the 7F_0 electronic states to obtain separately the lattice and the electronic contributions to the quadrupole coupling constant D . The ratio D_{latt}/D_{4f} is equal to -2.03 for 7F_0 in the crystalline host YAlO_3 . For the 5D_0 level, the ratio $D_{\text{latt}}/D_{4f} > 30$.

I. INTRODUCTION

Since the first measurements^{1,2} of the hyperfine splitting of the stable isotopes of Eu^{3+} , there has been a significant interest in this hitherto elusive ion.³⁻⁵ One problem which has received much theoretical attention, even before the first resonance results,⁶⁻⁸ is the magnitude of the quadrupole splittings. This interest grew out of the complete lack of success in attempts to observe the expected nuclear magnetic resonances in this $J=0$ ground-state ion. Elliot⁶ showed, in 1957, that this was due to a partial quenching of the nuclear moment by a second-order interaction with nearby $J=1$ levels, which reduced the resonance absorption signal by a factor of 100. He also pointed out that a large electronic quadrupole interaction results because the crystal field produces small admixtures of the $J=2$ state in the $J=0$ ground state. He estimated that the contribution to the quadrupole splitting by the electric field gradient of the lattice charges was negligible. Judd *et al.*⁷, in an analysis of the decay of radioactive nuclei, argued that the primary contribution to the quadrupole constant is an interaction which excites a $5p$ electron to the $6p$ shell and was three times larger and of opposite sign to the electronic term of Elliott. Edmonds,⁸ in an unrelated NMR study of La^{3+} , demonstrated that the lattice electric field gradient at the nucleus is 2 orders larger than had been previously thought, due to antishielding by the closed-shell electrons, so that the lattice contribution to the quadrupole interaction of Eu^{3+} should be quite large and could explain the experimental results of Judd.⁷ Edmond's hypothesis was confirmed by rf-optical double-resonance studies⁵ of the europium ion in two different crystals, which demonstrated that the quadrupole interaction is strongly affected by the host electric field gradient. Blok and Shirley⁹ have given expressions for both the electronic and lattice contributions to the quadrupole interaction constant in *axial* symmetry and the lattice component (and the electronic part for $J>0$) has been generalized to a nonaxial situation by Barnes *et al.*¹⁰ In all of these expressions, there are atomic constants and shielding parameters ($1-\gamma_\infty$) (lattice at the nucleus by closed shells), $\langle r^2 \rangle_{4f}(1-\sigma_2)$ (lattice at the $4f$ electron by closed shells), $\langle r^{-3} \rangle_{4f}(1-R_Q)$ (closed shell with $4f$ electrons) that have not been accurately determined¹¹ so that an estimate by Sharma and Erickson⁵

of the ratio $D_{\text{latt}}/D_{4f} = -2.9$ for the ground state needs to be established experimentally. In this paper, the separate contributions to the quadrupole interactions are derived from a measurement of the total quadrupole splitting in the 5D_0 state and a previous measurement of the ground state using a model first given by Barnes.¹⁰ It was assumed that the electronic contribution to the excited-state 5D_0 quadrupole constant could be ignored and this assumption was tested by calculating (in axial symmetry) the ratio of the lattice to the electronic terms.

II. EXPERIMENT

The ground-state 7F_0 hyperfine constants of the two stable isotopes of Eu^{3+} dilute in the YAlO_3 host crystal have been obtained previously.^{1,2} Shelby and Macfarlane also reported hyperfine constants for the 5D_0 state, which they obtained using an optical hole-burning technique. Since their accuracy was limited by the dye-laser stability, an optical-rf double-resonance method¹ whose accuracy (but not sensitivity) is independent of the dye-laser stability was used to obtain the quadrupole constants. For this nuclear spin $I = \frac{5}{2}$ ion, there are three hyperfine levels separated by tens of MHz for each nondegenerate electronic level. These are not normally resolved optically in the strain-broadened spectral line. However, a narrow-band cw stabilized dye laser, tuned to the 5D_0 - 7F_0 transition, pumps an individual hyperfine level which quickly produces a large polarization of the hyperfine levels in both the ground and excited states. In effect, a hole is burned in the optical transition because ions are removed from the optical absorption. They are either in the excited state, or in decay from the excited state they sometimes return to a different ground-state hyperfine level due to I_z mixed levels. A rf magnetic field induces magnetic dipole transitions within either the excited or the ground state at the appropriate frequencies. Since excited-state magnetic dipole transitions increase the probability of return to a different ground hyperfine level, more ions are removed from the optical absorption, leading to a *decrease* in the optical absorption and consequently in the luminescence from the crystal. On the other hand, a ground-state magnetic dipole transition returns an ion to the pumped level, leading to an *increase* in the luminescence at resonance. In order to pump individual hyperfine levels, both the

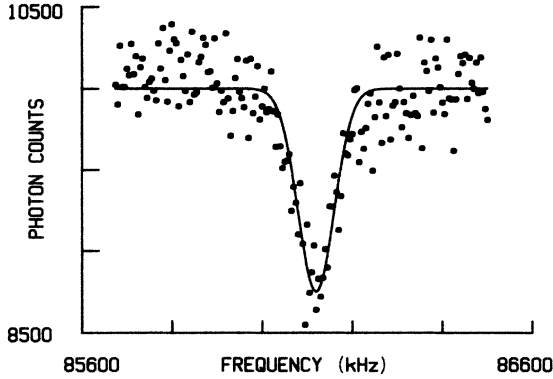


FIG. 1. The $I_z = \frac{3}{2} - I_z = \frac{5}{2}$ nuclear-quadrupole-resonance transition of $\text{YAlO}_3:\text{Pr}^{3+}$ in the excited 5D_0 electronic state. For this measurement, the cw dye-laser light was resonant with the $^7F_0 \rightarrow ^5D_0$ transition (17186.7 cm^{-1}). A radio-frequency magnetic field was applied to the crystal by current flowing in a two-turn coil. Broadband luminescence was observed at 16270 cm^{-1} as a function of the radio frequency. The sample temperature was about 5 K. The dwell time at each point was 1.6 sec.

laser spectral width and the energy levels must be narrow compared to the hyperfine splitting. Thus low crystal temperatures are required to reduce lifetime-limiting processes such as the phonon interactions which broaden the energy levels.

A typical signal for the excited 5D_0 electronic state is shown in Fig. 1. As was noted above for the *excited* state, a *reduction* in luminescence is observed at resonance. The zero-field frequencies are 59029 ± 16 and $86098 \pm 20 \text{ kHz}$ for ^{151}Eu , compared to 61 and 89 MHz, as reported by Shelby.² (A ground-state resonance of $^{153}\text{Eu}^{3+}$ at 59600 kHz almost interferes with the detection of the 59029-kHz line.) This yields quadrupole coupling constants $|D| = 22715 \pm 7 \text{ kHz}$ and $|E| = 4273 \pm 5 \text{ kHz}$.

III. THEORY

The hyperfine levels of each electronic state may be described by a quadrupolar Hamiltonian^{1,2}

$$H = D[I_z^2 - I(I+1)/3] + E(I_x^2 - I_y^2). \quad (1)$$

There are three contributions to the quadrupole parameters. The pseudoquadrupole interaction terms D_a and E_a arise from a second-order magnetic hyperfine interaction.

The electric-field gradient of the lattice, antishielded by the closed-shell electrons, acts on the quadrupole moment of the nucleus giving D_{latt} and E_{latt} . A third term D_{4f} and E_{4f} is due to the moment of the 4f electrons induced by the crystal field (with shielding by the closed shells) acting on the nucleus. When it can be assumed that the three interactions have a common z axis,

$$D = D_a + D_{4f} + D_{\text{latt}}. \quad (2)$$

The limitations imposed by this assumption are considered in Sec. IV. The pseudoquadrupole contribution D_a (and E_a) is less than 100 kHz and will be ignored.⁵

The direct and antishielded lattice contribution is given by^{5,9,10}

$$D_{\text{latt}} = -\frac{3Q(1-\gamma_\infty)B_{20}}{2I(2I-1)(1-\sigma_2)\langle r^2 \rangle_{4f}}, \quad (3)$$

$$E_{\text{latt}} = +(6B_{22}/3B_{20})D_{\text{latt}}. \quad (4)$$

For the shielded 4f electronic contribution to first order,

$$D_{4f}^{(1)} = -\frac{3e^2Q}{4I(2I-1)}\langle r^{-3} \rangle_{4f}(1-R_Q) \times \langle J||\alpha||J \rangle \langle 0|3J_z^2 - J(J+1)|0 \rangle, \quad (5)$$

$$E_{4f}^{(1)} = +[\langle 0|J_+^2 + J_-^2|0 \rangle / 2 \langle 0|3J_z^2 - J(J+1)|0 \rangle] D_{4f}^{(1)}. \quad (6)$$

Here, Q is the nuclear quadrupole moment, $\langle r^n \rangle_{4f}$ are radial integrals over the 4f electrons, B_{2m} are crystal-field parameters, and $|0\rangle$ represents the eigenfunction of the lowest level of the $2S+1L$ manifold. For a pure $J=0$ state, Eqs. (5) and (6) give a null result. They are included here to accommodate calculations on eigenstates mixed by the crystal field.

Estimating the nuclear quadrupole splitting in the $J=0$ level, Elliot⁶ considered the crystal field mixing together with the hyperfine interaction to give a second-order expression for D_{4f} (in axial symmetry). This, refined to include the various shielding terms by Blok and Shirley⁹ and Sharma and Erickson,⁵ is

$$D_{4f}^{(2)} = \frac{(6e^2QB_{20})}{2I(2I-1)}\langle r^{-3} \rangle_{4f}(1-R_Q) \frac{|\langle LS2||\alpha||LS0 \rangle|^2}{E_{20}-E_{00}}. \quad (7)$$

Thus for axial symmetry where only a single $J=2$ level has a $J_z=0$ component, the ratio

$$D_{\text{latt}}/D_{4f}^{(2)} = -[(1-\gamma_\infty)/2e^2\langle r^2 \rangle_{4f}(1-\sigma_2)\langle r^{-3} \rangle_{4f}(1-R_Q)](E_{20}-E_{00})/|\langle LS2||\alpha||LS0 \rangle|^2, \quad (8)$$

which is independent of the crystal-field parameter B_{20} . It is noted that the ratio is dependent on the spin and orbital angular momentum, by virtue of the operator-equivalent factor $\langle LS2||\alpha||LS0 \rangle$ and by the separation of the $J=2$, $J_z=0$ level from the $J=0$ level, i.e., $E_{20}-E_{00}$. This, differing only slightly from the spin-orbit splitting of the $J=0$ and $J=2$ levels, may be obtained from the calculations of Morrison, Karaianis, and Wortman^{12(c)} for the YAlO_3 host crystal or by a measurement of the optical-absorption spectra. The operator equivalent factors are more difficult because of the complexity of the f^6 configuration. One can show that the operator equivalent factor (f electrons) is given by

$$\langle WULSJ || \alpha || W'U'L'SJ' \rangle = 2[-2(105)^{1/2}/15][J, J']^{1/2} \begin{Bmatrix} J & J' & 2 \\ L & L' & S \end{Bmatrix} \\ \times (\langle WULS || U^{(2)} || W'U'L'S \rangle (-1)^{S+L+J'+2} (\Omega_{J,J'})^{-1/2}, \quad (9)$$

where $\Omega_{J,J'}$ (Ref. 10) is given by

$$\Omega_{J,J} = (2J-1)(2J)(2J+1)(2J+2)(2J+3)/4, \quad (10)$$

$$\Omega_{J,J+1} = 2J(2J+1)(2J+2)(2J+3)(2J+4)/24, \quad (11)$$

$$\Omega_{J,J+2} = (2J+1)(2J+2)(2J+3)(2J+4)(2J+5)/6, \quad (12)$$

and $J < J'$. The reduced matrix elements ($WULS || U^{(2)} || W'U'L'S$) are tabulated in Nielson and Koster¹³ as are the 6J factors in Rotenberg *et al.*¹⁴ The $[J, J']$ symbol denotes $(2J+1)(2J'+1)$. Because Eq. (9) is expressed in terms of fractional parentage states and the lowest 5D term has significant amplitudes from 7F , ${}^5D_{1,2,3}$, ${}^3P_{1,3,6}$ states,¹⁵ the effective value of the operator equivalent factor was obtained using Porcher's¹⁵ lowest 5D eigenstates $\langle {}^5D_2 || \alpha || {}^5D_0 \rangle = +0.10487$. Similarly for the ground level,⁶ $\langle {}^7F_2 || \alpha || {}^7F_0 \rangle = 2/5(3)^{1/2}$ and with Porcher's 7F eigenstates, is equal to 0.20242.

For all practical purposes, the excited state is modeled by Eqs. (3) and (4). Using Eq. (8), it can be shown for the 5D_0 state that D_{4f} is approximately 3% D_{latt} , so that $D({}^5D_0) = D_{\text{latt}} = -22\,715$ kHz is a good approximation. One may conclude that

$$D_{4f}({}^7F_0) = D({}^7F_0) - D_{\text{latt}} = -11\,500 - (-22\,715) \\ = 11\,215 \text{ kHz}$$

if one assumes that the z axes of the two interactions coincide and that the sign of D_{latt} is negative. There is no doubt about the sign, but there is controversy about the directions of the various interactions. In a separate Raman-heterodyne study of this crystal,¹⁶ it has been shown that the z axes of the total quadrupole interaction D of 7F_0 and 5D_0 are coincident within the experimental error of $\pm 3^\circ$. The limits to the generalization of these results is discussed in Sec. IV. The ratio $D_{\text{latt}}/D_{4f} = -2.03$ value for the ground state is somewhat smaller than the predicted value of -2.9 (Ref. 5). One should note that the predicted value was obtained using the experimental value of Blok and Shirley⁹ for $(1-\gamma_\infty)/(1-\sigma_2) = 302$ for the ethyl sulphate crystal. The generally accepted Sternheimer antishielding value is $\gamma_\infty = -80$ for the rare-earth elements.¹¹ While there appears to be some variation with host material (published "experimental" values range from 0.5 to 0.8), a calculated value may be obtained by interpolation from Erdos¹¹ and from Sternheimer.¹¹ This yields $\sigma_2 = 0.63$,¹¹ which would give $(1-\gamma_\infty)/(1-\sigma_2) = 220$ or a theoretical ratio $D_{\text{latt}}/D_{4f} = 2.1$. In Sec. IV, we note that better agreement between the theory presented here and the experimental values is obtained using a value of $\sigma_2 = 0.57$.

IV. DISCUSSION

The application of the approach of Barnes's *et al.*¹⁰ to other hosts of low Eu^{3+} site symmetry is controversial. They assumed that both interactions have principal axes common with the crystal electric field. There has been some discussion² indicating that the various contributions to the quadrupole interaction may have differing principal-axis systems. For a crystal of C_2 or lower site symmetry, only one common axis is required by symmetry for the various terms in the Hamiltonian and any two of these interactions may have differing labels on the common axis. Indeed, the cancellation of the asymmetry in the ground state 7F_0 has been attributed to differing axis directions for the lattice and $4f$ contributions to the quadrupole parameters.² Freeman and Watson¹⁷ note, however, that the usual linear (anti)shielding parameters used in the crystal-field theory merely scale the crystal field, so in the absence of an m dependence $B_{lm}(1-\sigma_{lm})$ of the shielding parameters, no rotation of the principal axes of the interaction from that of the field-gradient tensor is expected. Published parameters do not give an m dependence. In the approximation of no *nonlinear* (anti)shielding¹⁷ of the crystal electric field, for the interactions considered in Eqs. (1)–(8), the principal axes of each tensor are identical through the crystalline electric field. The electronic eigenfunctions (and their axes) are determined by the crystal-field interaction (shielded $1-\sigma_i$). The $(4f)^6$ -electron contribution to the field gradient at the nucleus has the same J_i dependence as the second-order crystal-field terms (with shielding $1-R_Q$). The lattice term (and its axes) are proportional to the same (antishielded $1-\gamma_\infty$) crystal-field terms. In this paper, the treatment of Barnes *et al.*¹⁰ has been followed in which the Hamiltonian is written in the principal-axes system of the electric-field-gradient tensor. This was validated by a measurement of the axes directions of the total quadrupole interaction in both electronic levels.¹⁶ Consequently, the relative sizes of the electronic and the lattice contribution to the electric field gradient are meaningful. If this model is used for a low-symmetry host, and the ratio of the lattice to the electronic contributions to the electric field gradient differs *widely* from -2 , this would likely be a result of differing principal-axes directions, rather than from host-dependent atomic or crystal-field parameters. A theoretical model below shows that a 10% ratio variation is obtained in going from an axial host LiYF_4 to YAlO_3 due to symmetry and crystal-field differences.

The expression [Eq. (7)] given for D_{4f} is valid only for axial symmetry. For a lower site symmetry such as C_{1h} in YAlO_3 , one requires a summation over the three Γ_1 levels of $J=2$ which have components of $J_z=0$. In order to analyze the C_{1h} example, a crystal-field matrix includ-

ing $J=0$, $J=1$, and $J=2$ states of 7F_0 was diagonalized to obtain ground-state wave functions which could be used to calculate D_{4f} and E_{4f} , including all $|J=2, J_z=0\rangle$ components. Using Morrison's values¹² for the crystal electric field, and $\langle r^2 \rangle_{4f} = 0.233 \text{ \AA}^2$, $\sigma_2 = 0.57$, $\langle r^{-3} \rangle_{4f}(1-R_Q) = 41 \text{ \AA}^{-3}$, $1-\gamma_\infty = 81$, one obtains, using Eqs. (3)–(6), $D_{4f} = 11\,152$, $E_{4f} = -3591$, $D_{\text{latt}} = -22\,617$, $E_{\text{latt}} = 5637$, $D = -11\,465$ ($-11\,500$), $E = 2046$ (0) kHz, and the magnetic quenching terms $\alpha_x = 0.785$ (0.58), $\alpha_y = 0.622$ (0.80), and $\alpha_z = 0.468$ (0.47). The measured values are in parentheses. An interchange of the x and y axes gives good agreement for the magnetic quenching terms. The ratio of $D_{\text{latt}}/D_{4f} = -2.03$ is some 11% higher than predicted for the axial case. A similar calculation for $\text{LiYF}_4:\text{Eu}^{3+}$ using the crystal-field parameters from Gorller-Walrand¹⁸ gives $D_{4f} = 8100$, $D_{\text{latt}} = 14\,782$, $D_{\text{latt}}/D_{4f} = -1.82$, $D = -6683$ (-6539) kHz, and the magnetic quenching terms $\alpha_x = \alpha_y = 0.701$ (0.939) and $\alpha_z = 0.533$ (0.614). No experimental data are available for the 5D_0 state in $\text{LiYF}_4:\text{Eu}^{3+}$. The reasons for the large discrepancy in the magnetic quenching terms of the $\text{LiYF}_4:\text{Eu}^{3+}$ axial case is under study.¹⁹

It should be noted that this apparent agreement comes with atomic parameters in the accepted range. The ratio of D_{latt}/D_{4f} varies inversely as $(1-\sigma_2)\langle r^2 \rangle_{4f}$, as does D_{latt} . This parameter has shown some host dependence,^{10,11} so that a small variation in the ratio of lattice and electronic contributions should be expected as the host is changed. Secondly, the value of $\langle r^{-3} \rangle_{4f}(1-R_Q) = 41 \text{ \AA}^{-3}$ used is consistent with Lindgren's value²⁰ of 45 \AA^{-3} and a shielding parameter $R_Q = +0.1$.²¹ The YAlO_3 crystal-field parameters as used have been obtained¹² from an interpolation from other impurity ions in the crystal. Those for LiYF_4 have been obtained by fitting a crystal-field Hamiltonian to the data¹⁸ and disagree with the interpolated values¹² for LiYF_4 by as much as 13%. This would suggest that

within the bounds of the crystal-field theory and the available parameters, the overall accuracy is no better than 10%. One also notes that the calculated D_{latt}/D_{4f} ratio changes for deviation from axial symmetry in the $[\text{YAlO}_3]/[\text{LiYF}_4]$ case by $+10\%$. Finally, it is noted that for the $\text{YAlO}_3:\text{Eu}^{3+} {}^7F_0$ level, $E(\text{calc}) = 2046 \text{ kHz}$ is, significantly, not zero. The suitability of the crystal-field parameters^{12,22} used in these calculations may be tested by examining the measured and calculated parameters D and E because only the lattice interaction is significant in the excited state. The excited state, as modeled by Eqs. (3) and (4), gives the same values as the ground state $D_{\text{latt}} = -22\,617 \text{ kHz}$, $E_{\text{latt}} = +5637 \text{ kHz}$. While the $D_{\text{latt}} = D({}^5D_0)_{\text{meas}}$, E_{latt} is somewhat larger than the measured value $|E({}^5D_0)_{\text{meas}}| = 4273 \text{ kHz}$. This difference is similar in size to that in the ground state where two interactions are present. In order to get a match in the excited state, the B_{22} value should be reduced by 24%, but this would leave a problem with the optical spectra, particularly for the $J=1$ levels, which are controlled by only the B_{2m} values. The accuracy of these calculations is limited because there is no comprehensive crystal-field study of $\text{YAlO}_3:\text{Eu}^{3+}$.

V. CONCLUSIONS

The lattice and the electronic contributions to the quadrupole interaction in trivalent europium have been obtained by comparing a new measurement of the quadrupole interaction in the excited 5D_0 electronic state using a nuclear-optical double-resonance technique with a previously reported value for the ground 7F_0 state. The lattice term is shown to be completely dominant in the excited 5D_0 state, while the ratio of lattice to electronic contributions in the ground 7F_0 state is -2.03 for the YAlO_3 host lattice.

¹L. E. Erickson and K. K. Sharma, Phys. Rev. B **24**, 3697 (1981).

²R. M. Macfarlane, R. M. Shelby, A. Z. Genack, and D. A. Weitz, Opt. Lett. **5**, 462 (1980); R. M. Shelby and R. M. Macfarlane, Phys. Rev. Lett. **47**, 1172 (1981).

³R. L. Cone, R. T. Harley, and M. M. Leask, J. Phys. C **17**, 3101 (1984).

⁴A. J. Silversmith and N. B. Manson, J. Phys. C **17**, L97 (1984).

⁵K. K. Sharma and L. E. Erickson, J. Phys. C **18**, 2935 (1985).

⁶R. J. Elliott, Proc. Phys. Soc. London Sect. B **70**, 119 (1957).

⁷B. R. Judd, C. A. Lovejoy, and D. A. Shirley, Phys. Rev. **128**, 1733 (1962).

⁸D. T. Edmonds, Phys. Rev. Lett. **10**, 129 (1963).

⁹J. Blok and D. A. Shirley, Phys. Rev. **143**, 278 (1966).

¹⁰R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poin-dexter, Phys. Rev. **136**, A175 (1964).

¹¹See P. Erdos and J. H. Kang, Phys. Rev. B **6**, 3393 (1972); R. M. Sternheimer, Phys. Rev. **146**, 140 (1967); R. M. Sternheimer, M. Blume, and R. F. Peierls, *ibid.* **173**, 376 (1968); A. J. Freeman and R. E. Watson, *ibid.* **127**, 2058 (1962).

¹²(a) C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam,

1982), Vol. 5; (b) N. Karaianis, D. E. Wortman, and C. A. Morrison, Solid State Commun. **18**, 1299 (1976); (c) C. A. Morrison, N. Karaianis, and D. E. Wortman, Harry Diamond Report No. HDL-TR-1788, 1977 (unpublished); (d) K. K. Deb, J. Phys. Chem. Solids. **43**, 819 (1982).

¹³C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n , d^n , and f^n Configurations* (MIT Press, Cambridge, 1963).

¹⁴M. Rotenberg, R. Bivens, N. Metropolis, and J. Wooten, Jr., *The 3J and 6J Symbols* (MIT Press, Cambridge, 1959).

¹⁵P. Porcher (private communication). The terms are labeled with subscripts indicating the parentage. Details are given in Ref. 13.

¹⁶L. E. Erickson (unpublished).

¹⁷A. J. Freeman and R. E. Watson, Phys. Rev. **139**, A1606 (1965).

¹⁸C. Gorller-Walrand, M. Behets, P. Porcher, O. K. Moune-Minn, and I. Laursen, Inorg. Chim. Acta **109**, 83 (1985).

¹⁹K. K. Sharma (private communication).

²⁰I. Lindgren, Nucl. Phys. **32**, 161 (1962).

²¹A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), p. 273.

²²It should be noted that Morrison's parameters [Ref. 12(c)] cor-

respond to the x axis perpendicular to the reflection plane. Deb [Ref. 12(d)], gives a set with the z axis perpendicular to the reflection plane. In order to confirm experimentally which parameter set corresponds to the z axis perpendicular to the mirror plane, one compares the observed polarizations with those obtained from the calculations. The emission to the 370-cm^{-1} level is of opposite polarization to the 265- and 500-cm^{-1} levels. This agrees with the calculations using the

parameters of Deb and not with those of Morrison (which gives the 500-cm^{-1} level as different from the other two $J = 1$ levels). The note added in proof by Karaianis [Ref. 12(b)] confirms this interpretation. Therefore the z axis of the crystal-field parameters given by Morrison is in the mirror plane as assumed in this analysis and is consistent with the principal axes of the observed nuclear Zeeman tensor of Refs. 1 and 2.