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ESR absorption spectrum of Gd^{3+} in single crystal Y_2O_3

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Two electron-spin-resonance absorption spectra, each due to trivalent gadolinium, have been observed in single crystals of yttria, Y_2O_3. These spectra were observed at room temperature, 77 K, and 4.2 K with a spectrometer operating at 0.85-cm wavelength. One of these spectra exhibits trigonal symmetry with its principal direction being parallel to a crystal body diagonal. The other spectrum exhibits orthorhombic symmetry whose three mutually orthogonal directions are along a crystal cube edge and two crystal face diagonals. Both spectra exhibit resolved hyperfine structure. Fine-structure and hyperfine-structure parameters are given for both spectra. For the orthorhombic gadolinium ion, a slight displacement in the fine-structure spectrum of ^{157}Gd from the spectrum due to the even-numbered isotopes is observed. This displacement can be expressed as a relative increase of about six parts in 10^4 in the value of B_2^0. No analogous shift is observed in the trigonal spectrum of ^{157}Gd.

I. INTRODUCTION

Electron-spin-resonance absorption spectroscopy is a scientific technique whose usefulness as a microscopic probe for uncovering symmetry and crystalline perfection in the neighborhood of a paramagnetic ion is well established.[1,2] Its use in the solid state has been applied to a diversity of problems which extend from the study of magnetic point detects of low concentration in otherwise nearly-perfect crystalline hosts to the study of dynamical processes in which one or more components of the host lattice may undergo some form of motion not necessarily associated with the normal heat waves of the lattice.[3-16]

The work presented in this report was motivated by a need to understand the local environment of the metal atom sites in unstressed, nearly-perfect single crystals of yttria, Y_2O_3. This oxide was chosen as an object of study because it was felt that it has certain physical properties which could make it a reasonably good coating material for vessels to be used as containers in electrical power generation reactors. It was planned that after studying single crystals of this material which are virtually free of iron group and rare-earth group impurities (say less than 1 ppm), specimens would be produced having slight amounts of trivalent gadolinium ion. As it turned out, the purest specimens made available for this study were found to contain enough gadolinium to yield resonance lines readily observable by direct video detection and yet were of concentration low enough in this ion to yield central resonance lines ($M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$) having full widths between inflection points of 0.2 Oe. The wish to study trivalent gadolinium was motivated by the need to uncover as much information as possible on the local site symmetry of the substituted ion. Since trivalent gadolinium has a ground electronic term designated by ^8S, its probability density function $\Psi^*\Psi$, characterized by $J = 7$, would be expected to interact with crystal-field components of order $J = 2$, 4, and 6 as well as with M_J values limited by J and by local point symmetry considerations.

During the course of this investigation, an ESR absorption spectrum was observed consisting of about 70 spectral lines in single crystals of yttria. As will be demonstrated, these spectral lines can be associated with two distinct sites, each occupied by trivalent gadolinium ions, one site having trigonal symmetry with its z axis directed along a crystal body diagonal and another site having orthorhombic symmetry with one of the three mutually orthogonal axes being parallel to a cube edge direction and the remaining two being parallel to appropriate cube face diagonals. Since this structure is known to exhibit two types of yttrium ion sites, one having C_{2v} symmetry and the other having D_{3d} symmetry, it is deduced that the gadolinium ion substitutes for the yttrium ion without causing a sensible distortion of the local point symmetry.

Another aspect of this ESR spectrum is the gadolinium hyperfine-structure spectrum. In the case of the trigonal gadolinium ion, the hyperfine-structure spectrum appears to be normal except that the magnitudes of the spittings seem to be a bit small thereby suggesting a somewhat lower than normal electron-spin density at the gadolinium nucleus.[17–19] On the other hand, the orthorhombic gadolinium ion exhibits an unusual hyperfine-structure spectrum in that for some orientations of the Zeeman field vector relative to the crystal coordinates, the separations between hyperfine-structure components are unequal. It is suggested that this phenomenon arises from the nuclear quadrupole interaction whose orthorhombic component mixes nuclear spin states to an extent sufficient to cause this effect. In addition, ^{157}Gd located at the orthorhombic sites exhibits a shift in its fine structure spectrum from that of the even isotopes. This spectral shift is interpreted as a relative increase in the magnitude of B_2^0 of roughly six parts in 10^4 over that of the even-numbered isotopes.

Finally, it is determiend that the two types of metal ion sites in this structure, the C_{2v} and the D_{3d} sites, have a gadolinium ion occupation ratio of approximately 3:5 with the C_{2v} sites having the higher probability of being occupied.

II. EXPERIMENT

Electron-spin-resonance absorption spectral measurements were, for the most part, made at room temperature and at 77 K. Some measurements were made at 4.2 K for the purpose of determining the signs of crystalline electric field splitting energies. Two spectrometers were used to take data for this study. One operated at 0.85-cm wavelength, made use of homodyne microwave detection, and 100-kHz magnetic field modulation coupled with the use of phase sensitive lock-in-type detection of the ESR signal. The other spectrometer operated at 3.3-cm wavelength and was used almost exclusively for the purpose of checking the spectral analysis carried out on the 0.85-cm wavelength spectrometer.

Single crystals of yttria having dimensions of a few millimeters on an edge were oriented by means of x-ray Laue-pattern analysis. A crystal of proper size was selected and upon completion of orientation was cut into a parallelepiped of rectangular cross section having dimensions of approximately $0.3 \times 0.3 \times 2$ mm^3. The cutting was done such that a crystal cube face diagonal was parallel to the long edge of the crystal and a cube face diagonal and cube edge were parallel, respectively, to the remaining two short edges of the specimen. With a specimen cut in this fashion and placed in the spectrometer cavity resonator (the mode of cavity operation being TE_{011}) the Zeeman field could be rotated about a cube face diagonal thereby making it possible to align the Zeeman field vector along either a cube edge, a cube body diagonal, or a cube face diagonal. Along any of the various symmetry directions of the cube, spectral degeneracies are expected. From these symmetry imposed degeneracies, orientations within a {110} plane were obtained which provided for reproducibility of degeneracy to within a spectral linewidth after such rotations of the crystal were made as would take it from one symmetry direction to one which is its crystallographic equivalent. Typically, the resonance lines used for such degeneracy tests of orientation exhibited widths of the order of an oersted and some were as narrow as 0.2 Oe.

III. RESULTS AND DISCUSSION

It was first pointed out by Goldschmidt that there exists an extensive series of metal sesquioxides that crystallize in the cubic class with the unit cell containing 16 M_2O_3 formulas.[20] Subsequently, Zachariasen[21] assigned the cubic or *C* modification to crystals of the compounds Sc_2O_3, Mn_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and $(Fe,Mn)_2O_3$ the latter being the mineral bixbyite.[22] In 1930, Pauling and Shappell determined the crystal structure of bixbyite to belong to the space group $T_h^7(Ia3)$ and concluded that all of the sesquioxides assigned the *C* modification by Zachariasen belonged to the same structure.[23] More recent refinements have been made on the sesquioxide structures exhibiting the *C* modification, the latest being on In_2O_3.[24–26]

Of the 32 metal atom sites per unit structure in Y_2O_3, all are coordinated to 6 oxygen atoms with 24 *d* sites having C_{2v} local point group designation and with yttrium-to-oxygen distances given by 2.34, 2.27, and 2.25 (Å) and 8 *b* sites having D_{3d} local point group designation with yttrium-to-oxygen distance given by 2.25 (Å),[25,26] see Fig. 1. From this description of the metal ion sites in Y_2O_3 and from an inspection of Fig. 1 it seems likely that if a magnetic

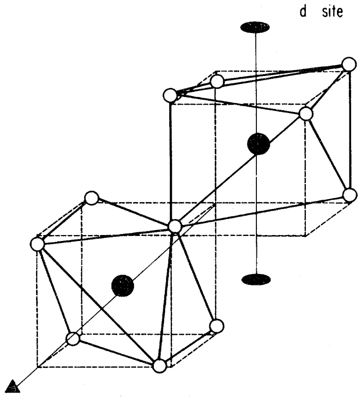

FIG. 1. Schematic representation of the two yttrium ion sites in yttria.

ion substitutes for the yttrium ion, its total ESR spectrum should be a composite of two distinct spectra, one characteristic of the symmetry properties of the *d* sites and the other of the *b* sites.

For the Zeeman field oriented along a nonsymmetry direction of the crystal, there should be observed four distinct spectra due to the *b* sites and six distinct spectra due to the *d* sites. Then, assuming that no mixing of any significance occurs in the electron-spin states, each gadolinium ion will exhibit 7 spectral lines thereby providing a total spectrum of 70 lines.

The general fine-structure spin-Hamiltonian operator used to analyze the ESR spectra observed in this study is given by

$$H=\mu_B\vec{S}\cdot\hat{g}\cdot\vec{H}+\sum_n\sum_m B_n^m O_n^m \ , \qquad (1)$$

where μ_B is the Bohr magneton, $\vec{S}$ is the electron-spin vector operator, $\hat{g}$ is the spectroscopic splitting factor tensor, $\vec{H}$ is the Zeeman field vector, n can take on all positive integer values, m is limited in magnitude by n, B_n^m are crystalline electric field splitting energy parameters, and the O_n^m are the Racah polynomial operators of order n in the spin variables S_z, S_+, and S_-.[27–29] The Racah polynomial operators transform upon a three-dimensional rotation as

$$P_r O_n^m=\sum_{m'=-n}^{n} D^{(n)}(\alpha,\beta,\gamma)_{m',m}O_n^{m'} \ , \qquad (2)$$

where P_r is the three-dimensional rotation transformation operator for the rotation designated by the three Euler angles (α,β,γ) and where $D^{(n)}(\alpha,\beta,\gamma)_{m',m}$ is the $(2n+1)$ dimensional matrix representation of P_r.[30–33]

For the *d* sites in yttria which have C_{2v} point symmetry, the values of m must be restricted to $m=2$, 4, and 6 as required by the C_2 symmetry element of this group. Furthermore, the two vertical planes of reflection require that the B_n^m be real. Hence, for the *d* sites the crystalline electric field operator given by the double sum in Eq. (1) may be rewritten as

$$V_{\mathrm{cf}}=\sum_{n=2}^{4,6}\left\{B_n^0O_n^0+\sum_m B_n^m(O_n^m+O_n^{-m})\right\} \ . \qquad (3)$$

For the *b* sites which have the point group symmetry designation D_{3d}, the values of m are restricted to $m=3$ and 6 as required by the C_3 symmetry element. For this point group there exist three vertical planes of reflection which require that B_6^6 be real and that the B_n^3 be pure imaginary.[34] As a consequence of these requirements the crystalline electric field potential operator for the *b* sites may be rewritten as

$$V_{\mathrm{cf}}=\sum_{n=2}^{4,6}[B_n^0O_n^0+B_n^3(O_n^3+O_n^{-3})+B_n^6(O_n^6+O_n^{-6})] \ , \qquad (4)$$

where for both Eqs. (3) and (4) it is understood that in effect, B_n^m vanishes for $m > n$.

Two distinct spectra, each due to trivalent gadolinium, are observed in single crystals of yttria. In both spectra, the identity of this rare-earth ion is established by its nuclear hyperfine-structure signature[35] and by the magnitude of its nuclear hyperfine structure splittings.[36] For one of these spectra, the absorption lines exhibit extremum field positions along a cube body diagonal, a crystal-ion *z* axis, as well as along a cube face diagonal, a crystal-ion *x* axis. This spectral information is interpreted to imply that gadolinium ions substitute for yttrium ions at the *b* sites of Y_2O_3, see Fig. 1. In the second spectrum, extremum field positions are observed along a cube face diagonal, a crystal-ion *z* and *y* axis and along a cube edge, a crystal-ion *x* axis. This spectrum is attributed to gadolinium ions substituted for yttrium ions at the *d* sites of Y_2O_3, see Fig. 1. The coordinate systems for these two crystal ions as well as the plane in which the Zeeman field is rotated are given in Figs. 2 and 3.

For both of these spectra, ESR data were obtained by rotating the Zeeman field vector in a {110} plane which is one that contains a cube edge, a cube body diagonal, and a cube face diagonal. Isofrequency data of spectral lines field strength positions versus polar angle coordinate taken for the *b*-sites gadolinium ion are given in Fig. 4. The maximum extention of this spectrum occurs along the *z* axis and is of the order of 12 000 Oe. These data, as well as most reliable data, were taken along the crystal-ion coordinates, *x*, *y*, and *z*, see the Obs. columns of Table I.[37] It will be noted from Table I that the *x* and *y* data for this spectrum are not identical. This lack of invariance of

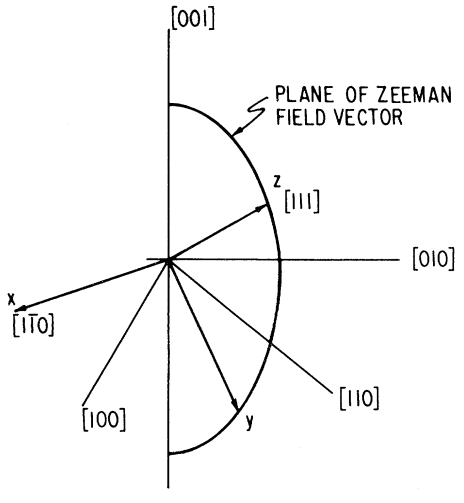

FIG. 2. Plane of rotation of the Zeeman field vector and the local coordinates of the *b* sites in yttria.

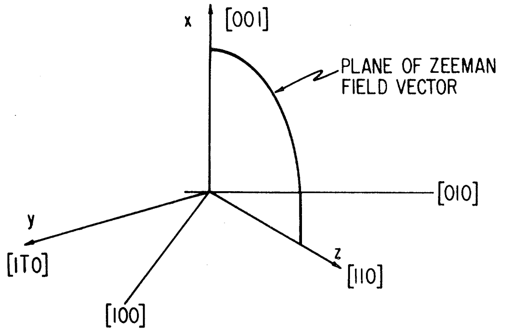

FIG. 3. Plane of rotation of the Zeeman field vector and the local coordinates of the *d* sites in yttria.

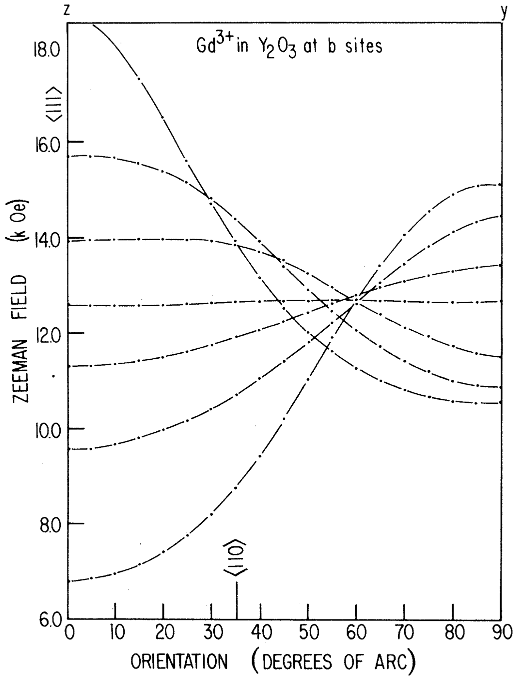

FIG. 4. Isofrequency plot of the *b*-sites ESR spectral lines taken in the *zy* plane.

spectral data for observations made in the xy plane ($\theta=\frac{1}{2}\pi$, $\phi=0\rightarrow\frac{1}{2}\pi$) arises from the transformation properties of the crystalline electric field potential function component V_6^6 which is given by the last term of Eq. (4). This term transforms upon rotation in such a manner[28,29] as to yield the following diagonal crystal field component which is the only one that does not vanish identically at $\theta=\frac{1}{2}\pi$ [38,39]:

$$P_r V_6^6 \big|_{m'=0} = [2/(12)^{1/2}] B_6^6 P_6^6(\cos\theta) x \cos(6\phi) O_6^0 \quad . \tag{5}$$

The case of trivalent gadolinium located at the *d* sites of yttria is considerably different. For this crystal-ion system the three mutually orthogonal coordinates *x*, *y*, and *z* are located, respectively, along a cube edge and along two cube face diagonals, see Fig. 3, with the *z* axis chosen to be that for which the spectrum exhibits maximum Zeeman field strength extension. Isofrequency data are taken with the Zeeman field vector rotated from the *z* axis to the *x* axis, see Fig. 5, and from the *x* axis to the *y* axis, see Fig. 6. As in the case of the *b*-sites gadolinium ion, the most reliable data were obtained from spectral observations made along each of the three crystal-ion coordinates, see Obs. column in Table II. An interesting point here is the maximum extention of this spectrum which is roughly one-sixth of the *b*-sites gadolinium ion spectrum.

TABLE I. ESR spectral line Zeeman field strength values for Gd^{3+} in Y$_2$O$_3$ at sites of trigonal symmetry. Data taken at room temperature. (Data taken at 35 465 MHz and field strengths given in oersteds.)

x		*y*		*z*	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
15 253	15 251	15 235	15 237	6 870	6 871
14 540	14 540	14 569	14 567	9 620	9 622
13 517	13 517	13 498	13 495	11 383	11 383
12 439	12 438	12 432	12 431	12 727	12 725
11 548	11 547	11 571	11 572	14 067	14 064
10 957	10 959	10 938	10 938	15 829	15 826
10 594	10 595	10 603	10 602	a	18 578

[a] Not observed due to inability of magnet to reach this field strength.

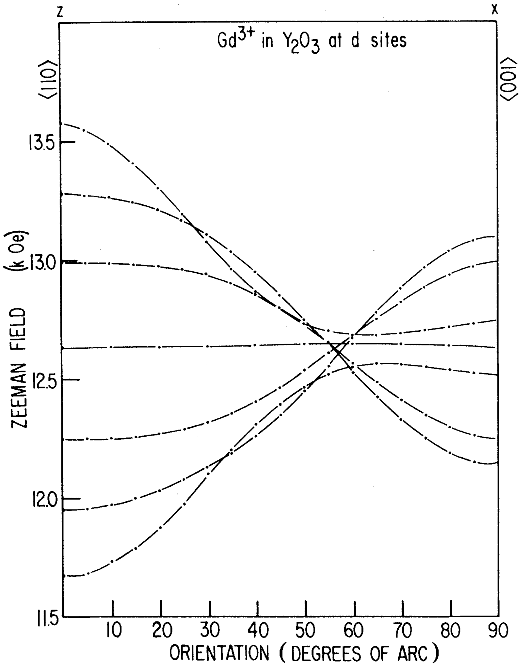

FIG. 5. Isofrequency plot of the *d*-sites ESR spectral lines taken in the zx plane.

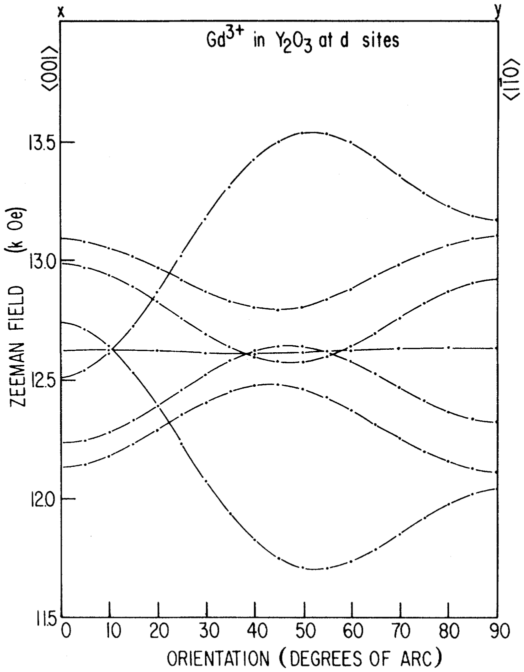

FIG. 6. Isofrequency plot of the *d*-sites ESR spectral lines taken in the xy plane.

Analysis of the spectra, that is, determination of spectral parameters from the observed x, y, and z spectral line data was carried out in a two step process. In the first, spectral lines were identified from linewidth considerations as well as by noting how well certain criteria were satisfied by using a truncated spin-Hamiltonian operator which contained only those terms that yield diagonal matrix elements. Generally, these criteria had to do with determining which lines of a given spectrum would be grouped together as conjugate pairs ($M_s = -b \rightarrow -a$, $M_s = a \rightarrow b$) such that the mean of a pair gave a reasonable g value while differences between pairs collectively gave approximate values of B_2^0, B_4^0, and B_6^0. For each of the two metal atoms sites, the spectral data for each of the three crystal-ion axes were put into proper order and then submitted to a machine for calculation; see Tables III and IV for calculated fine-structure spectral parameters. Resonance absorption line field strength values obtained from

TABLE II. ESR spectral line Zeeman field strength values for Gd^{3+} in Y$_2$O$_3$ at sites of orthorhombic symmetry. Data taken at room temperature. (Data taken at 35 465 MHz and field strengths given in oersteds.)

x		y		z	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
12 857	12 856	12 163	12 171	13 665	13 661
12 250	12 250	12 226	12 221	13 410	13 415
12 348	12 346	12 431	12 426	13 115	13 115
12 721	12 723	12 730	12 730	12 726	12 722
13 095	13 094	13 031	13 026	12 339	12 339
13 183	13 184	13 197	13 191	12 038	12 043
12 608	12 606	13 263	13 269	11 798	11 795

machine calculations using these parameters appear under column headed Calc. of Tables I and II. For an outline of the computing procedure the reader may consult Ref. 39.

In both ESR spectra the crystalline electric field splitting energies are dominated by the terms B_2^0. Furthermore, since the signs of the other parameters are fixed by the sign of B_2^0 as well as by the manner in which the crystal-ion coordinate system is chosen, it remains to fix the sign of B_2^0. By comparing, at 4.2 K, the relative intensities of conjugate pair transitions it was established that $B_2^0 > 0$ for the *b*-sites gadolinium and $B_2^0 < 0$ for the *d*-sites gadolinium.

The relative populations of the gadolinium ions at the two metal atom sites was determined by noting the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transitions for the Zeeman field vector directed along a crystal-ion *z* axis. Such a comparison demonstrated a 3:5 ratio in site populations with the greater probability of occupancy being given to the *d* sites of the lattice.

Gadolinium has two nonzero spin isotopes. They are ^{155}Gd of $I = \frac{3}{2}$ with relative natural abundance 14.68% and ^{157}Gd also of $I = \frac{3}{2}$ and with relative natural abundance of 15.64%. The nuclear magnetic dipole moments of these two isotopes are $^{155}\mu = -0.25\mu_n$ and $^{157}\mu = -0.34\mu_n$ where μ_n is the nuclear magneton. The spectroscopic consequence of these nuclear characteristics is, under conditions of sufficient spectral resolution, an unambiguous nuclear hyperfine-structure signature to the fine-structure spectral components of trivalent gadolinium. This signature is characterized by a nonet spectrum composed of a singlet having a relative strength of 0.6968 due to a superposition of the singlet spectra of the even isotopes of gadolinium, and a pair of quartets due to ^{155}Gd and ^{157}Gd each having components of relative strengths 0.037 and 0.039, respectively.[40]

For both the *b*-sites and *d*-sites gadolinium ion spectra, resolved or partially resolved hyperfine-structure spectral lines were observed for the $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$, $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$ transitions provided observations were made along the principal directions of a specific site. The general spin Hamiltonian used to analyze the nuclear hyperfine-structure spectra is given by

$$H' = \vec{I} \cdot \hat{A} \cdot \vec{S} + \mu \vec{I} \cdot \vec{H} + \xi[3I_z^2 - I(I+1)] + \eta(I_x^2 - I_y^2) \ , \qquad (6)$$

where the first term is the electron-nuclear hyperfine interaction, the second is the nuclear Zeeman interaction, and the last two are the interactions of the nuclear quadrupole moment with the electric field gradient at the nucleus.[41]

A slight asymmetry in the separations of the hyperfine-structure spectral components is observed along the *x* and *y* axis of both the *b*- and *d*-sites spectra of gadolinium in this host, see Fig. 7. For either of these two odd-numbered isotopes, the spectral line positions asymmetry is defined as

$$\Delta = [H(-m) - H_0] - [H_0 - H(m)] \ , \qquad (7)$$

where H_0 is the field strength of the central line of a given nonet. This asymmetry can be explained by the off-diagonal nuclear quadrupole interaction and may be used to obtain the signs of the parameters ξ and η of Eq. (6) as well as to provide estimates of their magnitudes. It may be demonstrated readily that the observed asymmetry is too large to be explained by off-diagonal terms in the electron-nuclear hyperfine interaction.

If the crystal coordinates are transformed relative to the laboratory frame by the operator P_r in such a manner as to send the *z* axis into the *x* axis while leaving the *y*-axis invariant, then it is straightforward to demonstrate that

$$\begin{aligned} P_r\{\xi[3I_z^2 - I(I+1)] + \eta(I_x^2 - I_y^2)\} &= -\tfrac{1}{2}(\xi - \eta)[3I_z^2 - I(I+1)] \\ &\quad + \tfrac{1}{2}(3\xi + \eta)(I_x^2 - I_y^2) \ . \qquad (8) \end{aligned}$$

The results of that transformation which sends the *z* axis into the *y* axis while leaving the *x*-axis invariant may be obtained from this equation by changing the sign before η.

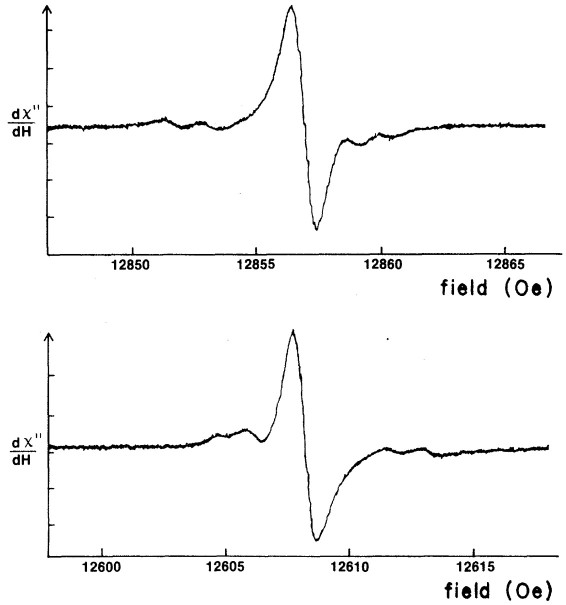

FIG. 7. Graphic recorder tracing of a conjugate pair of resonances of the *d*-sites Gd^{3+} spectrum for the *x* axis. The upper tracing is of the transition centered at 12 857 Oe and the lower is at 12 608 Oe. Zeeman field increases from left to right with a total of 20 Oe for each graph.

If, for the purpose of demonstration, the direction of the Zeeman field vector is taken to be the z axis then following the aforementioned transformation of the crystal, the only nondiagonal terms in the spin Hamiltonian H' arise from the hyperfine-structure and quadrupole interactions. Furthermore, using second-order perturbation theory, it may be demonstrated that the off-diagonal terms in the hyperfine-structure interaction can account for no more than 10% of the observed spectral line position asymmetry for either the b- or d-sites gadolinium. This leaves the off-diagonal quadrupole interaction, the last term of Eq. (8), as the only one remaining to provide for such an asymmetry. Again, using perturbation calculations, it is possible to predict spectral line asymmetry of sign and magnitude that depends upon the spectral parameters ξ and η. Furthermore, these calculations predict that the asymmetry for a transition $M_s = a \rightarrow b$ is equal to but opposite in sign to the transition $M_s = -b \rightarrow -a$. This happens to be consistent with observations.

In actual fact, the procedure followed to determine the parameters ξ and η was to diagonalize the full energy matrix rather than use perturbation calculations. It was felt that a full matrix diagonalization treatment would be less open to question than a perturbation approach. The results of such a treatment using data from both the b sites and d sites is given in Table V. For both sites, the signs of the matrix elements of the hyperfine interaction are taken to be positive.[17,36,42,43] In addition, the signs and magnitudes of ξ and η are chosen so as to provide for the proper spectral line asymmetry, see Eq. (7). A similar effect has been reported in the spectrum of trivalent gadolinium in YPO_4.[44]

The sign of ξ may be predicted by noting that $\xi = eqQ$ where e is the charge on the proton, q is the second derivative of the electronic potential function evaluated at the nucleus, and Q is the nuclear electric quadrupole moment.[45] Since e and Q are of opposite sign for both ^{155}Gd and ^{157}Gd, the sign of ξ is determined by the sign of q.[46] The argument is now made that q and the fine-structure spectral parameter B_2^0, see Table III, are of like sign, that is to say, q and B_2^0 are determined by the electronic charge distribution's prolateness or oblateness. The sign of ξ deduced in this manner is consistent with the result given in Table V for both the b- and d-sites gadolinium. It may also be argued that the ratios $[\eta/\xi]$ and $[B_2^2/B_2^0]$ are similarly dependent upon the electronic charge distribution and that by casting the quadrupole interaction in terms of irreducible tensor operator polynomials in the spin variables I_z, I_+, and I_- there results the relation

$$[\eta/\xi] = (6)^{1/2}[B_2^2/B_2^0] \ , \tag{9}$$

which may be used to predict the sign of η assuming the signs of ξ and $[B_2^2/B_2^0]$ are known, see Table IV.

TABLE III. ESR spectral parameters for Gd^{3+} in Y_2O_3 at the trigonal sites. The B_n^m are given in units of MHz.

$g_{xx} = g_{yy}$	1.9912 ±0.0001
g_{zz}	1.9916 ±0.0001
B_2^0	1603.8 ±0.2
B_4^0	12.42 ±0.02
B_4^3	$-i$(3.95 ±0.05)
B_6^0	0.040 ±0.001
B_6^3	~0
B_6^6	−0.032 ±0.004

Although this relation predicts the sign of η it fails to predict its magnitude, see Table V.[47,48]

One aspect of the z-axis spectrum of the d-sites gadolinium ion is the existence of a slight displacement in the mean spectral position of the ^{157}Gd quartet hyperfine structure from the singlet due to the even isotopes.[49] This displacement, which is an order of magnitude greater than what might be expected from second-order hyperfine-structure contributions at these Zeeman fields, is to be distinguished from that previously discussed in that it is a consequence of isotopic mass difference while the former is due entirely to nuclear quadrupole interaction. Furthermore, this displacement is most clearly manifested in the z-axis spectrum. To interpret this effect, a truncated spin-Hamiltonian operator is used consisting of only an electron-Zeeman term and an axial crystalline electric field of second degree in the electron spin. The following equations in differences result from

TABLE IV. ESR spectral parameters for Gd^{3+} in Y_2O_3 at the orthorhombic sites. The B_n^m are given in units of MHz.

g_{xx}	1.9912 ±0.0001
g_{yy}	1.9916 ±0.0001
g_{zz}	1.9910 ±0.0001
B_2^0	−308.8 ±0.1
B_2^2	−40.60 ±0.05
B_4^0	1.305 ±0.005
B_4^2	4.027 ±0.003
B_4^4	−5.560 ±0.005
B_6^0	−0.0350 ±0.0005
B_6^2	−0.0478 ±0.0005
B_6^4	0.0177 ±0.0002
B_6^6	~0

TABLE V. Hyperfine-structure parameters for ^{155}Gd and ^{157}Gd. All data are given in units of MHz. [The nuclear magnetic moment parameter $(g_n\beta_n/h)$ was taken to be −1.713 MHz/Oe for the isotope ^{157}Gd, see D. van Ormondt, J. Phys. C 11, 203 (1978).]

Parameter	^{155}Gd	^{157}Gd
b site		
$A_{xx}=A_{yy}$	8.3 ±0.1	11.0 ±0.1
A_{zz}	11.3 ±0.1	14.9 ±0.1
ξ	4.0 ±0.5	5.5 ±0.1
d site		
A_{xx}	8.0 ±0.2	10.5 ±0.1
A_{yy}	10.1 ±0.2	13.4 ±0.1
A_{zz}	10.1 ±0.2	13.4 ±0.1
ξ	−30 ±4	−40 ±2
η	−3 ±4	−6 ±2

manipulating eigenvalues of such an operator:

$$
\begin{aligned}
g\beta\Delta H(\pm\tfrac{5}{2}\rightarrow\pm\tfrac{7}{2}) &= \mp 9\Delta B_2^0 \ , \\
g\beta\Delta H(\pm\tfrac{3}{2}\rightarrow\pm\tfrac{5}{2}) &= \mp 6\Delta B_2^0 \ , \qquad (10) \\
g\beta\Delta H(\pm\tfrac{1}{2}\rightarrow\pm\tfrac{3}{2}) &= \mp 3\Delta B_2^0 \ .
\end{aligned}
$$

These equations predict that conjugate transitions should exhibit shifts which are of equal magnitude but of opposite sign and that the shifts should stand in the ratios (3:2:1) with no shift in the $M_s=-\frac{1}{2}\rightarrow\frac{1}{2}$ transition.

Such shifts observed for six *z*-axis spectral lines in the spectrum of ^{157}Gd located at the *d* sites of yttria are listed in Table VI. Interpreted in terms of variations in only one fine-structure spectral parameter, the following result is obtained:

$$(\Delta B_2^0/B_2^0)=(6.4\pm0.3)\times10^{-4} \ , \qquad (11)$$

where it is observed that $B_2^0(157)$ is greater in magnitude than the effective B_2^0 for the $I=0$ composite spectrum. This shift is to be compared with $(\Delta B_2^0/B_2^0)=5.8\times10^{-5}$ for Fe^{3+} in $CaCO_3$,[50] $(\Delta B_2^0/B_2^0)=1.1\times10^{-4}$ for Cr^{3+} in MgO,[51] and $(\Delta B_4^0/B_4^0)=4.2\times10^{-5}$ for Gd^{3+} in ThO_2.[52] Much larger isotope effects in ESR spectra have been observed by Schirmer in the spectrum of a lithium paramagnetic center in ZnO,[53] by Watkins in the spectrum of a tin-vacancy pair center in silicon,[54] and by Lee, Dang, and Watkins in the ODMR spectrum of 6*H*-SiC(Ti).[55]

ESR measurements made on single crystals of yttria have demonstrated two distinct spectra due to gadolinium each being identified with one of two distinct metal ion sites in this structure. From spectral line intensity measurements it is deduced that the *d* site is slightly preferred over the *b* site by the gadolinium ion. Fine- and hyperfine-structure spectral parameters are presented for both the *b*- and *d*-site spectra. The investigation was carried out using data obtained from a 0.8-cm wavelength spectrometer. As a check, spectral predictions made from these data were checked against observations made at 3.2-cm wavelength. Such a comparison between observations and predictions for the longer wavelength suggests added confidence to the entries of Tables III and IV. Furthermore, spectral line data were computer generated for both the *b* and *d* sites at angle coordinate intervals of 5° for each of the planes depicted in Figs. 4, 5, and 6. Such data were compared with experimental data and found to be satisfactory considering estimated errors in the computer input parameters and experimental data. Finally, the hyperfine-structure spectral line field strength position asymmetry has been satisfactorily interpreted in terms of the nuclear quadrupole interaction, see Ref. 43, for both the *b*- and *d*-sites gadolinium ion and in terms of a slight isotope shift in the crystalline electric field parameter for the *d*-sites gadolinium ion. To within experimental error, no isotope shift was detected for the *b* sites.

TABLE VI. Shifts observed in the *z*-axis fine-structure spectrum of ^{157}Gd located at the *d* sites of yttria.

Spectral line	Shift in Oe
$-\frac{7}{2}\rightarrow-\frac{5}{2}$	−0.58 ±0.04
$-\frac{5}{2}\rightarrow-\frac{3}{2}$	−0.42 ±0.04
$-\frac{3}{2}\rightarrow-\frac{1}{2}$	−0.24 ±0.04
$\frac{1}{2}\rightarrow\frac{3}{2}$	0.22 ±0.04
$\frac{3}{2}\rightarrow\frac{5}{2}$	0.43 ±0.04
$\frac{5}{2}\rightarrow\frac{7}{2}$	0.60 ±0.04

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