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^{161}Dy hyperfine parameters for C_2 and C_{3i} site symmetries in Dy_2O_3

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Low-temperature Mössbauer spectra of ^{161}Dy in Dy_2O_3 reveal for the first time a resolved magnetic hyperfine structure (hfs) associated with Dy^{3+} at sites with $C_{3i}(S_6)$ point symmetry. The magnetic hfs parameter is near that expected for a pure $|J_\xi = \pm 15/2\rangle$ Kramers doublet and is about 10% higher than for Dy^{3+} ions at sites with C_2 point symmetry in Dy_2O_3. A crystal-field parameter B_2^0 is deduced from the lattice part of the C_{3i} quadrupole splitting. Both the sign of this parameter and the almost pure $|J_\xi = \pm 15/2\rangle$ character of the ground state are shown to be inconsistent with earlier Mössbauer results and crystal-field calculations.

I. INTRODUCTION

In previous studies of Er, Tm, and Dy sesquioxides[1-3] the hyperfine structure (hfs) spectra for ions with C_2 point symmetry were readily observed. However, neither magnetic nor quadrupolar hfs parameters for the C_{3i} sites have been obtained. We report the first observation of hfs spectra for a rare-earth ion at lattice sites having $C_{3i}(S_6)$ symmetry in a rare-earth (R) sesquioxide (R_2O_3). One earlier study[3] of Dy_2O_3 noted additional spectral intensity near zero relative Doppler velocity and mistakenly (as we show below) attributed this to a collapsed, unresolved hfs from C_{3i} ions. Also the C_2 site magnetic hfs in that study was quoted as being the "full hyperfine interaction" corresponding to a ground ionic Kramers state with g-tensor components $g_x, g_z \cong 0$, $g_y \cong 19.7$. We note here that $g_y \cong 19.7$ is the maximum g factor obtainable for Dy^{3+} and corresponds to a pure $|J_y = \pm\frac{15}{2}\rangle$ state.

Dy_2O_3 has the C-type crystal structure[4] which is cubic with 16 molecules in the unit cell [space group $Ia3(T_h^7)$]. 24 of the R ions occupy sites with C_2 symmetry while eight are at sites with C_{3i} point symmetry.

Using optical and far-infrared spectroscopy, considerable data on energy-level spacings and a limited amount of data on Zeeman splitting of these levels have been obtained for the C_2-site ions in several R sesquioxides.[5-9] Relatively intense forced electric dipole transitions are allowed in this symmetry. On the other hand, only relatively weak magnetic dipole transitions are allowed for ions at C_{3i} sites because of the inversion symmetry. Few optical transitions have been observed for ions with this symmetry. Er_2O_3, Tm_2O_3, and Y_2O_3:Er or Y_2O_3:Tm have received the most attention both experimentally and theoretically. Various sets of the 15 crystal-field parameters (B_n^m) required to describe the C_2-site optical and infrared spectra have been derived. These sets are not always consistent and unfortunately the literature to date provides more confusion than illumination. No published attempt has been made to deduce the crystal-field parameters for C_2- or C_{3i}-site ions in Dy_2O_3. However, these can be estimated from those of other R sesquioxide ions, e.g., Er^{3+}, by using

$$B_n^m(Dy^{3+}) \cong B_n^m(Er^{3+})(\langle r^n\rangle_{Dy}/\langle r^n\rangle_{Er}). \tag{1}$$

Although there is not sufficient spectral data to give reliable values for the C_{3i}-site crystal-field parameters in any of these oxides, estimates have been made for Er_2O_3 using a superposition model.[9] This model assumes that the crystal field at any ion site may be constructed using a superposition of single-ion fields due to nearest-neighbor ligands. The data for both C_2 and C_{3i} sites are then fitted simultaneously to obtain better estimates for the C_{3i} spectra alone. Two sets of crystal-field parameters calculated[8,9] for the Er^{3+} C_{3i}-site ions are shown in Table I along with the observed energy levels on which the calculations were based. We note first of all the large difference between the two sets. Secondly, we note that B_2^0 is negative for both sets. Thirdly, we note that only six parameters were used whereas eight are actually required for the C_{3i} symmetry.

The crystal-field interaction potential may be

TABLE I. Erbium-oxide crystal-field parameters and energy-level data for C_{3i} sites. All are in units of cm^{-1}.

B_2^0	B_4^0	B_6^0	B_4^3	B_6^3	B_6^6	Energies (cm^{-1})
−326	−6	31	−327	274	330	0 80 [a]
−158	95	29	585	547	769	0 41 80 [b]

[a] Reference 7.
[b] Reference 8.

written as

$$-eV=\sum_{i}\sum_{n}\sum_{m=-n}^{n} A_n^m r_i^n \Phi_n^m(\theta_i,\phi_i)\ , \tag{2}$$

where the sum on i is over all $4f$ electrons. The Φ_n^m are linear combinations of the spherical harmonics. For $C_{3i}(S_6)$ symmetry, terms involving A_2^0, A_4^0, A_6^0, $A_4^{\pm 3}$, $A_6^{\pm 3}$, and $A_6^{\pm 6}$ are required[10] although one of these (e.g., A_4^{-3}) may be eliminated by a rotation about the threefold-symmetry axis. Therefore, eight parameters instead of the six used in Ref. 9 are required. The use of only eight parameters actually raises the symmetry to D_{3d} which has an operator equivalent crystal-field Hamiltonian

$$\mathcal{H}_{\text{crys}}=B_2^0\langle J\,\|\,\alpha\,\|\,J\rangle O_2^0+\langle J\,\|\,\beta\,\|\,J\rangle(B_4^0O_4^0+B_4^3O_4^3)$$
$$+\langle J\,\|\,\gamma\,\|\,J\rangle(B_6^0O_6^0+B_6^3O_6^3+B_6^6O_6^6). \tag{3}$$

The factors $\langle J\,\|\,\alpha\,\|\,J\rangle$, $\langle J\,\|\,\beta\,\|\,J\rangle$, and $\langle J\,\|\,\gamma\,\|\,J\rangle$ are the so-called Stevens coefficients. Following the usual definition, the B_n^m crystal-field parameters in Eq. (3) are related to the A_n^m parameters of Eq. (2) through a factor σ_n which accounts for shielding of the $4f$ electrons by the $5s^25p^6$ electrons[11]:

$$B_n^m \equiv A_n^m\langle r^n\rangle(1-\sigma_n). \tag{4}$$

Although Eq. (3) is only an approximate Hamiltonian we use it in the present discussion for comparison purposes because crystal-field parameters are not available for the more general C_{3i} Hamiltonian.

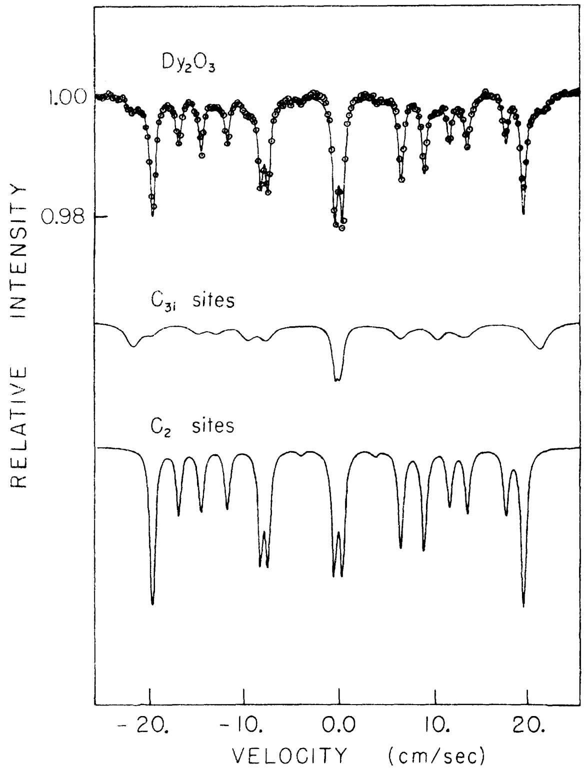

FIG. 1. ^{161}Dy Mössbauer spectrum taken at $T=7$ K. The solid curve through the data points is a computer fit using Eq. (5) for both C_{3i} and C_2 site ions. The two solid curves at the bottom are calculated C_{3i} and C_2 spectra which make up this composite fit.

II. EXPERIMENTAL

Mössbauer spectra were taken in transmission geometry using a conventional constant-acceleration transducer driven in the triangular mode. The radioactive source matrix was $(^{160}\text{Gd}_{0.5}{}^{162}\text{Dy}_{0.5})\text{F}_3$ fabricated following the procedure of Cohen and Guggenheim.[12] The minimum room-temperature full width at half maximum linewidth observed using this source is $\Gamma=3.75$ mm/sec. The source was maintained at room temperature and the Dy_2O_3 absorber (enriched to 90% ^{161}Dy) was mounted in a variable-temperature liquid-helium Dewar. Temperatures were measured and controlled using calibrated platinum and germanium resistance thermometers. Temperature regulation was better than ±0.5 K.

^{161}Dy Mössbauer spectra obtained for Dy_2O_3 are shown at the top of Fig. 1 and the bottom of Fig. 2. The 256-channel spectrum in Fig. 1 was taken at $T=7$ K and there are more than 8×10^6 counts per channel. The 512-channel spectrum in Fig. 2 was taken at $T=2.5$ K with about 2×10^6 counts per channel. In both figures the predominant spectral features are associated with ions at sites with C_2 symmetry. However, a second, weaker and broadened spectrum is noted with an overall splitting greater than the C_2 site spectrum. The solid line drawn through the data in Fig. 1 is the result of a least-squares computer analysis using an effective spin $S=\frac{1}{2}$ hyperfine interaction Hamiltonian for each of the C_2 and C_{3i} sites[13]:

$$\mathcal{H}_{\text{hfs}}=f(t)A_zI_zS_z+P\{[3I_z^2-I(I+1)]+\tfrac{1}{2}\eta(I_+^2+I_-^2)\}. \tag{5}$$

Off-diagonal magnetic hfs components were neglected and A_z is related to the effective nuclear magnetic hyperfine field by $H_{\text{eff}}\equiv(A_z/g_N\mu_N)S_z$, where $Ig_N\mu_N$ is the magnetic moment of the nuclear state involved. P is the electric quadrupole interaction term given by

$$P=-\frac{e^2Q}{40}(1-R_Q)\left\langle\frac{1}{r^3}\right\rangle\langle J\,\|\,\alpha\,\|\,J\rangle\langle 3J_z^2-J(J+1)\rangle$$
$$-\frac{e^2Q}{10}\,\frac{B_2^0}{\langle r^2\rangle}\,\frac{1-\gamma_\infty}{1-\sigma_2}\ . \tag{6}$$

The first term in P is the ionic contribution and

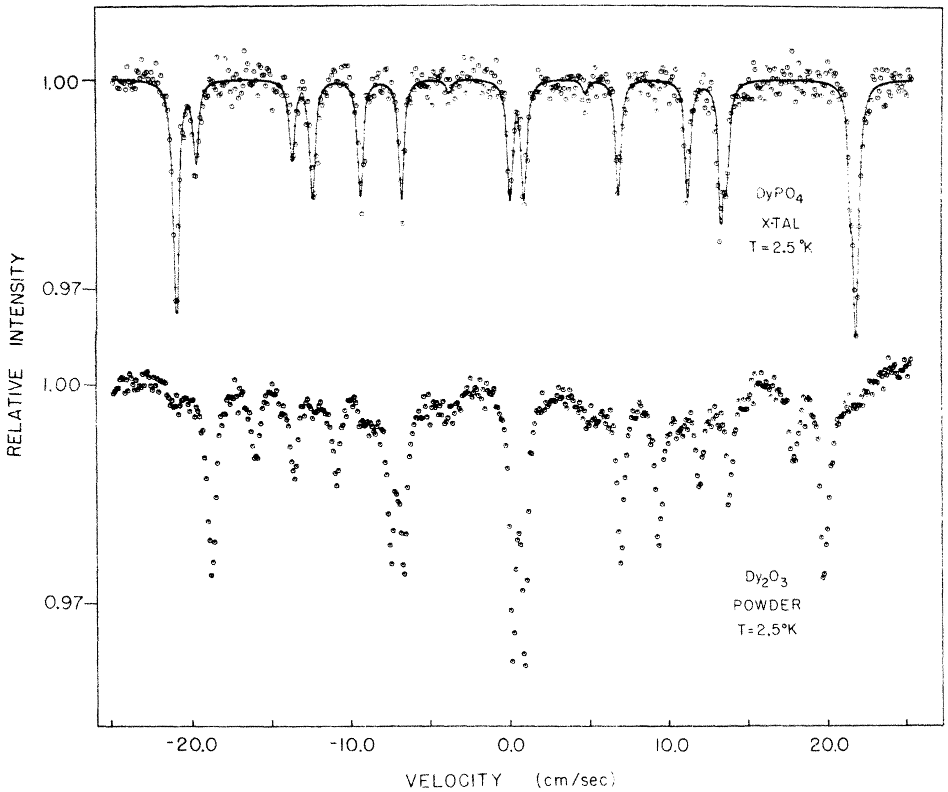

FIG. 2. ^{161}Dy spectra taken at $T = 2.5$ K for $DyPO_4$ and Dy_2O_3.

the second term represents the lattice contribution written in terms of B_2^0 and σ_2 [Eq. (4)], and R_Q and γ_∞ which are the ionic[14] and lattice[15] Sternheimer parameters. The asymmetry parameter is defined by $\eta \equiv (q_{xx} - q_{yy})/q_{zz}$, where q_{ii} are axial electric field gradients at the nucleus. For C_{3i} symmetry $\eta = 0$. For C_2 symmetry η may be nonzero. However, within the accuracy of our experiment, the effect of η was negligible and η was taken to be zero for the fitting procedure in Fig. 1. The C_{3i} spectrum is broadened considerably by relaxation effects which were included in the analysis by assuming random spin reversals [$f(t) = \pm 1$ in Eq. (5)] following the treatment of Blume.[16]

The two solid curves at the bottom of Fig. 1 are the individual C_2 and C_{3i} spectra obtained in the composite fitting of the data. The area ratio, $\text{Area}(C_2)/\text{Area}(C_{3i}) = 3/1$ is consistent with the ratio of sites within the crystallographic unit cell. The ground-state hyperfine parameters deduced for these two sites are listed in Table II. At $T = 7$ K the relaxation frequency associated with C_{3i} sites is $\Omega(C_{3i}) \cong 6 \times 10^8$ sec^{-1} whereas $\Omega(C_2) \sim 7 \times 10^7$ sec^{-1} (the frequency associated with the natural source-absorber linewidth.) There is some broadening of the C_2 spectrum beyond the natural source-absorber linewidth, but it is too small to extract a relaxation frequency.

In Fig. 2 the data for Dy_2O_3 at $T = 2.5$ K are shown. The spectral features for both ionic sites are sharper indicating a slower relaxation frequency for both at this lower temperature. A spectrum of $DyPO_4$ is included at the top of Fig. 2 for comparison because Dy^{3+} in that material has an almost pure $|J_z = \pm\frac{15}{2}\rangle$ ground state[17] with a corresponding $A_z/2h \equiv \mu_N g_N H_{\rm eff}/h = 831$ MHz. It is readily observed that the C_{3i} spectrum of Dy_2O_3 has the same splitting as $DyPO_4$ from which we deduce a ground state of almost pure $|J_z = \pm\frac{15}{2}\rangle$ character.

From the first part of Eq. (6) we calculate the ionic contribution to the quadrupole splitting of the C_{3i} sites using $R_Q = 0.124$,[18] $Q = 2.36 \times 10^{-24}$ cm^2,[19] $\langle r^{-3}\rangle = 62.087 \times 10^{24}$ cm^{-3},[20] and $\langle J \| \alpha \| J\rangle$

TABLE II. Hyperfine interaction parameters obtained for ^{161}Dy in C_2 and C_{3i} sites of Dy_2O_3. Parameters obtained for $DyPO_4$ in Ref. 17 are listed for comparison. All parameters are in MHz.

Material and site	$-\mu_g H_{\rm eff}/h$ (MHz)	P_g/h (MHz)
Dy_2O_3 (C_2)	755	28
Dy_2O_3 (C_{3i})	830	50
$DyPO_4$ (D_{2d})	831	60

$= -0.066\,215$. From this, $P_{\rm ion}(C_{3i})/h \cong 70$ MHz. Subtracting this from the measured P_z/h (Table II) we obtain the lattice contribution $P_{\rm lat}/h = -21$ Mhz. In the second part of Eq. (6), $P_{\rm lat}$ is related to the B_2^0 crystal-field parameter. Using $\langle r^2\rangle = 0.203 \times 10^{-16}$ cm^2,[21] and $\alpha \equiv (1-\gamma_\infty)/(1-\sigma_2) = 190$,[17] we deduce $B_2^0 \cong 290$ cm^{-1}. Although comparable in magnitude with the B_2^0 parameter for Er^{3+} in Er_2O_3 (Table I) the B_2^0 (Dy^{3+}) deduced from our Mössbauer data is of opposite sign. We would expect some scaling of B_2^0 following Eq. (1) because of the different $\langle r^2\rangle$ values for Dy^{3+} and Er^{3+}. However, the sign reversal indicates a gross error in the crystal-field parameters for C_{3i} sites in Er_2O_3 as deduced from optical and far-infrared studies.

To gain some insight into this disagreement for the B_2^0 parameters we diagonalized Eq. (3) as an approximation to the full C_{3i} Hamiltonian. The energy levels and wave functions for the lowest $^4I_{15/2}$ manifold of Er^{3+} and the lowest $^6H_{15/2}$ manifold of Dy^{3+} were calculated. For both sets of parameters in Table I we are in agreement with earlier calculations for the Er^{3+} ion. However, for the Dy^{3+} ion and using the scaling from Eq. (1), the ground state obtained does not have the required $|J_z = \pm\frac{15}{2}\rangle$ character. In fact the ground-state manifold is inverted with an almost pure $|J_z = \pm\frac{15}{2}\rangle$ state lying highest and an almost pure $|J_z = \pm\frac{1}{2}\rangle$ state lying lowest. A number of calculations were performed using Eq. (3) and covering a wide range of magnitudes for B_2^0, B_4^0, and B_6^0, both positive and negative. In the erbium calculations the level spacings and ground-state wave function were relatively insensitive to changes in B_2^0, but were sensitive to B_4^0 and B_6^0. The reverse was true in the Dy^{3+} calculation with the crystal-field manifold inverting when the sign of B_2^0 was reversed.

We also diagonalized the full C_2-site Hamiltonian. For the Er^{3+} ion our calculated energies and wave functions agree with previous calculations[6] when we use their crystal-field parameters. However, for the Dy^{3+} ion and using the scaling in Eq. (1) we do not find agreement with measured energy levels[22] and the ground-state wave function has a $\langle J_z\rangle$ much too small to be in agreement with the Dy^{3+} C_2-site hyperfine magnetic field.

III. CONCLUSION

In conclusion, we propose that the B_2^0 parameter obtained for the C_{3i} sites from optical and far-infrared studies has the wrong sign. Certainly, the Mössbauer results for Dy^{3+} in Dy_2O_3 are in disagreement with the present set of parameters as deduced for Er^{3+} in Er_2O_3. It seems likely that the relative insensitivity of the crystal-field ground state to changes of B_2^0 for the case of Er^{3+} and the lack of complete optical data have contributed to this error. Our Mössbauer results and crystal-field calculations for the C_2 site suggest that further analysis of the C_2-site crystal-field parameters is called for. The lack of complete optical and infrared magnetic Zeeman data may have introduced errors in these parameters.

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