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The hyperfine splitting of the ground state and first excited state of holmium in yttrium hydroxide

D St P Bunbury†, C Carboni†, R L Cone‡, M A H McCausland†,
S Mroczkowski§ and J W Ross†

† The Schuster Laboratory, The University, Manchester M13 9PL, UK

‡ Physics Department, Montana State University, Bozeman, MT 59717, USA

§ Department of Applied Physics, Yale University, New Haven, CT 06525, USA

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Abstract. We have studied the field dependence of the hyperfine splitting of ^{165}Ho in yttrium hydroxide by spin echo NMR at liquid helium temperatures and in fields up to 8 T. Hyperfine spectra have been obtained from the electronic ground state and from the first excited state. The measured hyperfine splittings are compared with theoretical results obtained by diagonalizing the complete electronic–nuclear Hamiltonian for the nominally $^5\text{I}_3$ ground multiplet of Ho^{3+} , using crystal field parameters derived from optical spectroscopy. There is close agreement between the measured and calculated quadrupolar and octupolar splittings, but we find a significant difference between the measured and calculated dipolar splittings, especially when allowance is made for J mixing. Agreement is restored, to within the uncertainties, if the currently accepted value of the dipolar hyperfine coupling coefficient for the free Ho^{3+} ion is reduced by 1.3%. Independent evidence for a reduction of that order will be presented in a later publication. The ratio of nuclear to electronic antishielding factors for Ho^{3+} is found to be $\gamma_N/\gamma_E = 148 \pm 10$, in close agreement with the value obtained in pure holmium hydroxide.

1. Introduction

The rare earth hydroxides, $\text{R}(\text{OH})_3$, form an isostructural series of uniaxial magnetic insulators which are well suited for testing and refining theoretical models of the behaviour of rare earth ions in insulating crystals. (Skjeltorp *et al* 1973, Cone and Wolf 1978, Tigges and Wolf 1987, Kahle *et al* 1986, Bunbury *et al* 1989, Jacquier *et al* 1989, Bischoff *et al* 1991, Pilawa *et al* 1994.) The structure is hexagonal, with two equivalent rare earth sites of C_{3h} point symmetry in the unit cell. $\text{Tb}(\text{OH})_3$, $\text{Dy}(\text{OH})_3$ and $\text{Ho}(\text{OH})_3$ have Ising-like properties at low temperatures and order ferromagnetically at liquid helium temperatures, with moments along the crystallographic c axis (Catanese and Meissner 1973, Catanese *et al* 1973). Scott (1970) has studied the optical spectra of Tb^{3+} , Dy^{3+} and Ho^{3+} as dilute substituents in $\text{Y}(\text{OH})_3$. In the case of Ho^{3+} he made use of the free-ion wave functions obtained by Rajnak and Krupke (1967) from the optical spectrum of Ho^{3+} in LaCl_3 to derive the crystal field parameters for the hydroxide. The three lowest crystal field states for Ho^{3+} in $\text{Y}(\text{OH})_3$ consist of a non-Kramers doublet $\{|E_0\rangle, |E_1\rangle\}$ and a singlet $|E_2\rangle$ about 16 K higher. All other states are at least 100 K above the ground doublet.

The magnetic behaviour of heavy rare earth ions in solids at and below room temperature is determined almost entirely by the properties of the lowest-lying J multiplet. Δ_{SO} , the spin–orbit splitting between the ground multiplet and the first excited multiplet, is $\gtrsim 3000$ K;

all excited multiplets, therefore, are insignificantly populated. However, admixture of different J multiplets by the crystal field may not be entirely negligible. Scott, in the work cited above, finds that the effect of J mixing on the energy levels is appreciable for Tb^{3+} ($\Delta_{SO} \simeq 2900$ K), almost negligible for Dy^{3+} ($\Delta_{SO} \simeq 4700$ K) and insignificant for Ho^{3+} ($\Delta_{SO} \simeq 7500$ K). To a close approximation, therefore, we may take J to be a good quantum number for the nominally $^5\text{I}_8$ ground multiplet of Ho^{3+} in $\text{Y}(\text{OH})_3$. (The same cannot be said of L or S : intermediate coupling is not negligible for Ho^{3+} , and is allowed for in our analysis.)

In a previous paper (Bunbury *et al* 1989, to be referred to as BCM), we described the field dependence of the hyperfine splitting of the electronic ground state $|E_0\rangle$ of Ho^{3+} in ferromagnetic $\text{Ho}(\text{OH})_3$ at liquid helium temperatures. We were unable to observe the spectrum from the excited state $|E_1\rangle$, partly because of rapid relaxation and partly because of the depopulation of the state associated with cooperative order†. Both problems have been mitigated in the present work by using a 1% solution of Ho in $\text{Y}(\text{OH})_3$. The slower relaxation in the dilute material and the absence of a cooperative splitting of the ground doublet more than compensate for the reduced holmium content, and have enabled us to study the excited state NMR spectrum in fields up to 0.9 T. We have also studied the ground state spectrum up to the highest available field (8 T). Our results will be compared with hyperfine splittings calculated from crystal field parameters derived from optical spectroscopy. The observation of distinct ground- and excited-state spectra conclusively confirms the indirect evidence given by BCM that the hyperfine field is not thermally averaged. The behaviour of the excited state hyperfine splitting also provides a critical test of our theoretical model.

2. Theory

The theory outlined below extends that given by BCM in two respects. First, the hyperfine interaction is recast in a form which circumvents the partial breakdown of the customary perturbative method (section 2.2); second, we include an assessment of the effect of J mixing on the hyperfine splitting (section 4.1 and appendix).

2.1. The effective Hamiltonian for the electronic ground multiplet

Insofar as J remains a good quantum number, the electronic ground multiplet of a rare earth ion at a site with C_{3h} symmetry may be described by an effective Hamiltonian comprising crystal field and Zeeman terms expressed as functions of the operator \mathbf{J} :

$$\mathcal{H}_{el}(\mathbf{J}) = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 + g_J \mu_B \mathbf{B} \cdot \mathbf{J} \quad (1)$$

The crystal field parameters B_n^m have been derived from the parameters of Scott (1970) and the operator-equivalent coefficients of Rajnak and Krupke (1967). Like the Landé factor g_J , they include corrections for intermediate coupling. Numerical values of these and all other parameters used in our calculations are given by BCM, whose notation we follow here. \mathbf{B} , the total field seen by the ion, is the sum of the applied field \mathbf{B}_a and the molecular field \mathbf{B}_m , but the latter is negligible in the dilute system under consideration, so $\mathbf{B} \simeq \mathbf{B}_a$. As in the work described by BCM, \mathbf{B}_a is collinear with the crystallographic c axis.

† $|E_0\rangle$ and $|E_1\rangle$ are the only states from which we could possibly obtain NMR signals at liquid helium temperatures. The population of the singlet $|E_2\rangle$ is not negligible at 4.2 K, but its hyperfine splitting is much smaller than that for $|E_0\rangle$ and $|E_1\rangle$ and would fall well below the frequency range of our spectrometer. The population of all higher states is insignificant.

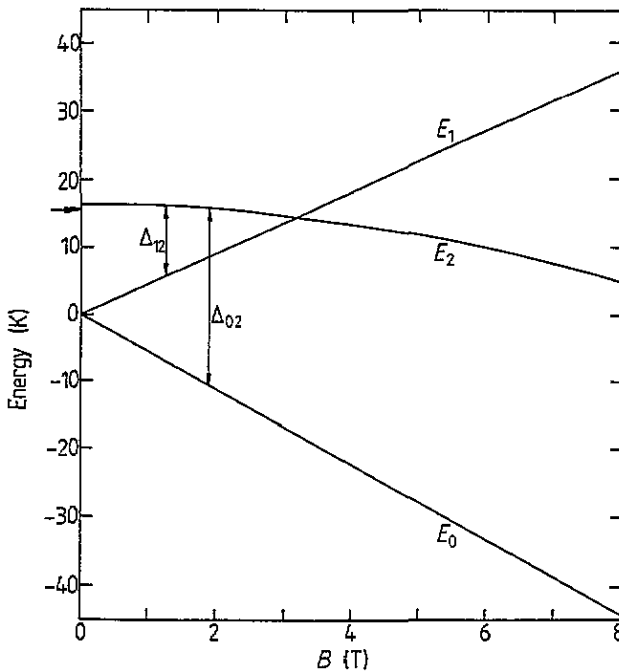


Figure 1. Calculated field dependence of the three lowest energy levels of Ho^{3+} in $Y(OH)_3$. The field is parallel to the c axis. The arrow indicates the measured position of the singlet in zero field, as determined by optical spectroscopy. The second-order contributions to the hyperfine splittings of $|E_0\rangle$ and $|E_1\rangle$ are inversely proportional to the electronic energy gaps Δ_{02} and Δ_{12} .

In figure 1 we show the computed field dependence of the three lowest eigenvalues of \mathcal{H}_{el} for Ho^{3+} in $Y(OH)_3$. The corresponding eigenstates at $B = 0$ and at $B = 8$ T are given in table 1, along with expectation values relevant to the first-order hyperfine splitting. We note in passing that the calculated position of the singlet is 2.5% higher than that measured by optical spectroscopy. This has an appreciable effect on the calculated quadrupole splitting for the excited state, to be discussed in section 4.2.

Table 1. Low-lying energy levels, eigenstates and expectation values.

State	B (T)	Energy (K)	Eigenstates in terms of the eigenstates $ M\rangle$ of J_c	$\langle J_c \rangle$	$\langle O_2^0 \rangle$
$ E_0\rangle$	0.0	0.0	$0.9380 7\rangle + 0.3126 1\rangle + 0.1494 -5\rangle$	6.1457	59.32
	8.0	-44.7	$0.9638 7\rangle + 0.2499 1\rangle + 0.0926 -5\rangle$	6.5226	65.40
$ E_1\rangle$	0.0	0.0	$0.9380 -7\rangle + 0.3126 -1\rangle + 0.1494 5\rangle$	-6.1457	59.32
	8.0	36.6	$0.8817 -7\rangle + 0.3962 -1\rangle + 0.2561 5\rangle$	-5.2712	47.67
$ E_2\rangle$	0.0	16.6	$0.5890 6\rangle + 0.5532 0\rangle + 0.5890 -6\rangle$	0.0000	2.95
	8.0	5.3	$0.7927 6\rangle + 0.5017 0\rangle + 0.3464 -6\rangle$	3.0499	8.82

2.2. Calculation of the hyperfine splitting

The hyperfine interaction for the ground manifold of the free ion is described by the Hamiltonian

$$\mathcal{H}_{hf}(\mathbf{J} \cdot \mathbf{I}) = h \left\{ A, \mathbf{J} \cdot \mathbf{I} + C, [2(\mathbf{J} \cdot \mathbf{I})^2 + \mathbf{J} \cdot \mathbf{I} - \frac{2}{3}J(J+1)I(I+1)] \right\} \quad (2)$$

where I is the nuclear spin operator; the constants A , and C , respectively define the strengths of the dipolar and quadrupolar couplings, in frequency units. In the solid we must add to \mathcal{H}_{hf} the extraionic contribution to the hyperfine interaction. This, in the uniaxial situation under discussion, may be written in the form

$$\mathcal{H}''(I) = -g_i \mu_N \mathbf{B}'' \cdot \mathbf{I} + h P'' [I_c^2 - \frac{1}{3}I(I+1)] \quad (3)$$

where g_i and μ_N are respectively the nuclear g factor and the nuclear magneton and I_c is the component of I along the crystallographic c axis. \mathbf{B}'' , the extraionic hyperfine field, is the sum of the applied field B_a and the dipolar field B''_{dip} . The dipolar field, though significant in the pure compound discussed in BCM, is negligible in the magnetically dilute system considered here. Thus $\mathbf{B}'' \simeq \mathbf{B} \simeq B_a$ (cf. equation (1) *et seq.*). P'' is the extraionic quadrupole parameter, in frequency units.

If J mixing is negligible, the hyperfine splitting in the solid can be computed by adding $\mathcal{H}_{hf}(\mathbf{J} \cdot \mathbf{I}) + \mathcal{H}''(I)$ to the electronic Hamiltonian $\mathcal{H}_{el}(\mathbf{J})$ and diagonalizing the resulting electronic-nuclear Hamiltonian

$$\mathcal{H}_{en}(\mathbf{J}, \mathbf{I}) = \mathcal{H}_{el}(\mathbf{J}) + \mathcal{H}_{hf}(\mathbf{J}, \mathbf{I}) + \mathcal{H}''(I). \quad (4)$$

In most cases $\mathcal{H}_{hf}(\mathbf{J}, \mathbf{I})$ and $\mathcal{H}''(I)$ are small perturbations on $\mathcal{H}_{el}(\mathbf{J})$ and it is then convenient to describe the hyperfine splitting of each electronic level by a purely nuclear effective Hamiltonian of the form given by BCM:

$$\mathcal{H}(I) = h \left\{ a_i I_z + P_i [I_z^2 - \frac{1}{3}I(I+1)] + w I_z^3 \right\}. \quad (5)$$

The z axis is by definition coincident with the direction of $\langle \mathbf{J} \rangle$ for the state under consideration. In the case under discussion $\langle \mathbf{J} \rangle$ is parallel to the c axis for $|E_0\rangle$ and antiparallel to the c axis for $|E_1\rangle^\dagger$. The dipolar parameter a_i and the quadrupolar parameter P_i are sums of intra- and extraionic terms, respectively labelled by single and double primes:

$$a_i = a' + a'' \quad P_i = P' + P''. \quad (6)$$

The octupolar parameter w is purely intraionic.

Each electronic state $|E_N\rangle$ has its own set of hyperfine parameters. The intraionic terms are normally obtained by treating the free-ion hyperfine interaction $\mathcal{H}_{hf}(\mathbf{J} \cdot \mathbf{I})$ as a perturbation (carried to second order) on the eigenstates of the electronic Hamiltonian \mathcal{H}_{el} . The first-order contributions to a' and P' are given by

$$a'^{(1)} = A_i \langle J_z \rangle = A_i | \langle J_c \rangle | = A_i | \langle E_N | J_c | E_N \rangle | \quad (7)$$

and

$$P'^{(1)} = C_i \langle O_2^0 \rangle = C_i \langle E_N | 3J_c^2 - J(J+1) | E_N \rangle. \quad (8)$$

Representative values of $\langle J_c \rangle$ and $\langle O_2^0 \rangle$ for $|E_0\rangle$ and $|E_1\rangle$ are given in table 1. Expressions for the second-order contributions to a' , to P' and to w (which vanishes in first order) can be found in appendix 1 in BCM. The extraionic dipolar term a'' is straightforwardly related to the applied field but P'' cannot be calculated *a priori* and must be treated as a free parameter. P'' depends only on the nuclear quadrupole moment and on the crystalline

† Following BCM, we define the positive c axis to be antiparallel to the applied field.

electric-field gradient and is therefore independent of the applied field. (The field gradient could in principle be altered by magnetostriction but such an effect would be insignificant in the magnetically dilute system under discussion.)

In the case of the first excited state $|E_1\rangle$ it is clear that the perturbation method will break down in the vicinity of the intersection of E_1 with E_2 (see figure 1). In general, this implies not only that perturbation theory will give incorrect values for a' , P' and w , but also that it may no longer be possible to describe the hyperfine splitting by just three parameters. By diagonalizing the 136-dimensional matrix of the electronic-nuclear Hamiltonian \mathcal{H}_{en} we have found that the computed hyperfine splitting of the excited state is adequately described by three parameters up to the highest field at which our measurements were made on the excited state. However, the numerical values of a' and w obtained from perturbation theory deviate significantly from those obtained by diagonalization, not only in the excited state but also in the ground state in low fields (see figures 3 and 5). In the analysis of our measured hyperfine splittings all intraionic hyperfine parameters (including P') have been calculated by exact diagonalization of \mathcal{H}_{en} . Perturbation calculations are included only for comparison.

Representative values of the various contributions to the hyperfine parameters are shown in table 2. Note that whereas higher-order contributions account for less than 0.3% of the intraionic dipolar splitting, they can amount to as much as 40% of the intraionic quadrupolar splitting.

Table 2. Calculated contributions to the hyperfine parameters (MHz).

State	B (T)	Dipolar				Quadrupolar			Octupolar	
		Intraionic			Total	Intraionic			Total	Total ^c
		First order	Higher order	Extra-ionic		First order	Higher order ^a	Extra-ionic ^b		
$ E_0\rangle$	0.0	4991.1	-0.2	0.0	4990.9	31.0	12.6	-26.2	17.4	0.42
	1.0	5043.0	4.1	8.9	5056.0	31.5	9.9	-26.2	15.2	0.30
	8.0	5297.2	2.1	71.3	5370.6	34.2	5.5	-26.2	13.5	0.13
$ E_1\rangle$	0.0	4991.1	-0.2	0.0	4990.9	31.0	12.6	-26.2	17.4	0.42
	1.0	4932.3	-11.8	-8.9	4911.6	30.4	18.1	-26.2	22.3	0.62
	8.0	4280.8	-5.5	-71.3	4204.0	24.9	-6.5	-26.2	-7.8	-0.01

^a Almost entirely second order.

^b Average value obtained by subtracting the total intraionic term from the measured quadrupole parameter (see section 4.2).

^c The octupole parameter is a purely intraionic term and vanishes in first order.

3. Experimental details

The crystals of $Ho:Y(OH)_3$ were grown at Yale University using the hydrothermal technique described by Mroczkowski *et al* (1970). The nominal concentration of holmium is 1% atomic. The specimen selected for our NMR measurements was a clear transparent needle, with well developed faces, 10 mm long and 0.5 mm in diameter.

The NMR measurements were performed at liquid helium temperatures with magnetic fields up to 8 T applied along the crystallographic c axis. Details of the 2–8 GHz spin echo spectrometer are given by Carboni *et al* (1989). Strong signals from the ground state $|E_0\rangle$ were observed at 4.2 K in fields greater than 1 T. The transverse relaxation time, of the order

of a few microseconds in high fields, decreased rapidly as the field was reduced. Echoes could not be detected at 4.2 K in fields below 0.5 T, but it was possible to obtain spectra down to 0.1 T by reducing the temperature to 1.5 K. We have also obtained a distinct NMR spectrum from the excited state $|E_1\rangle$ in fields between 0.1 T and 0.9 T and at temperatures between 1.5 K and 4.2 K. The temperature had to be increased as the field was increased in order to maintain an adequate population in the excited state. Above 0.9 T it was no longer possible to find an acceptable compromise between population and relaxation rate.

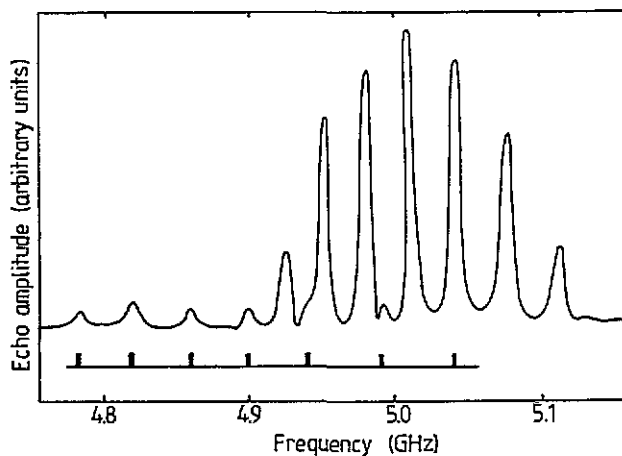


Figure 2. Composite NMR spectrum from the ground and excited states of Ho^{3+} in $\text{Y}(\text{OH})_3$ at 4.2 K with a field of 0.9 T applied along the c axis. Each state contributes seven lines, corresponding to the nuclear spin $I = \frac{7}{2}$ of ^{165}Ho . The vertical bars indicate the positions of the NMR lines from the partly obscured excited state spectrum.

4. Results and discussion

A representative composite spectrum is shown in figure 2. The seven strong lines from the ground state are easily identified; those from the excited state are much weaker and some of them are obscured by the ground state spectrum. When the field is reduced the NMR frequencies decrease for the ground state and increase for the excited state, thus increasing the degree of overlap between the two spectra. However, excited state lines which are obscured at one field are always visible at another field. We have recorded the positions of all observable lines at various fields and obtained the complete spectrum at any given field by interpolation. The hyperfine parameters were obtained by fitting the NMR frequencies to the effective Hamiltonian $\mathcal{H}(I)$ (equation (5)). In fields below 0.9 T the overlap problem becomes more pronounced and the uncertainties in the parameters are somewhat greater than at higher fields.

The field dependence of the hyperfine parameters is illustrated in figures 3 to 5. The data for the excited state are shown on the left-hand side of the figures, with the field increasing from right to left. (Since \mathbf{B} is antiparallel to $\langle \mathbf{J} \rangle$ for $|E_0\rangle$ and parallel to $\langle \mathbf{J} \rangle$ for $|E_1\rangle$, a 'positive' field for the ground state may be regarded as a 'negative' field for the excited state.)

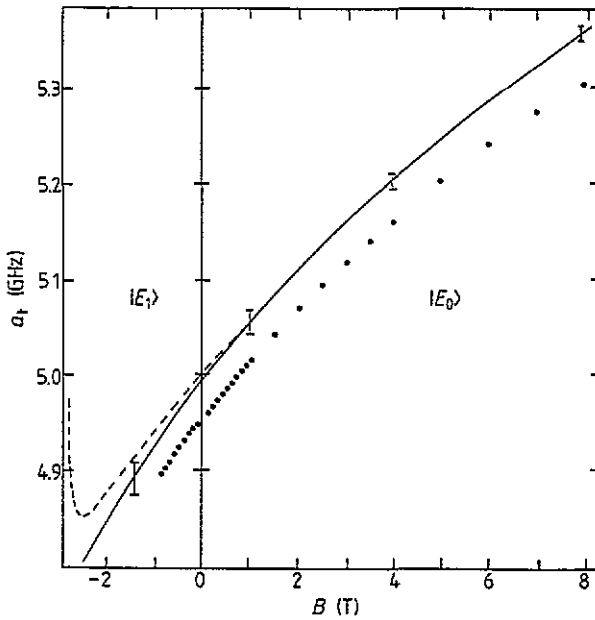


Figure 3. Measured and calculated field dependence of the dipolar hyperfine parameter a_t for Ho^{3+} in $Y(OH)_3$ at liquid helium temperatures. The experimental uncertainties (± 1 MHz) are smaller than the circles. The continuous line is obtained by diagonalization of the electronic-nuclear Hamiltonian \mathcal{H}_{en} . The broken line, obtained from second-order perturbation theory, illustrates the progressive failure of perturbation theory as the energy gaps Δ_{02} and Δ_{12} diminish (see figure 1).

4.1. The dipolar hyperfine splitting

The measured and calculated field dependences of a_t are shown in figure 3. The error bars on the calculated curve are derived from the error matrices for the crystal field parameters and from the uncertainties in all other parameters entering the calculation (see appendix 2 in BCM for details); the uncertainties in the experimental data are negligible by comparison. The difference between the calculated and measured hyperfine splittings is less than 1% but is statistically significant, ranging from about twice the standard deviation σ in low fields to nearly 5σ at 8 T. The discrepancy may be attributed to some or all of the following: (i) the neglect of J mixing in our calculations; (ii) an inaccurate value of the dipolar coupling coefficient A_j ; (iii), inaccuracies in the crystal field parameters. We consider these in turn.

(i) J mixing affects the electronic energy levels E_N only in second order but can affect the hyperfine splitting in first order through the eigenstates $|E_N\rangle$ (equations (7) and (8)). The fact that J mixing has an insignificant effect on the optical spectrum of Ho^{3+} in $Y(OH)_3$ does not, therefore, guarantee that its effect on the hyperfine splitting is negligible. In order to quantify the effect we have reanalysed Scott's optical data in order to obtain explicit expressions for the J -mixed components of the ground doublet. From these we have calculated the correction factor $(1 + \epsilon)$ to be applied to the right-hand side of equation (7). Details are given in the appendix, in which we find that $\epsilon \simeq 0.0058$. This correction increases the discrepancy between the calculated and measured values of a_t to 4σ in zero field and to $\sim 8\sigma$ at 8 T. We must therefore look to (ii) or (iii) (or both) for an explanation.

(ii) The currently accepted value of A_j for Ho^{3+} (see Bleaney 1972, 1988) is based on

EPR measurements on Ho^{3+} in yttrium ethylsulphate by Baker and Bleaney (1958). At that time it was not possible to quantify the corrections for J mixing because the requisite optical data were not available. A preliminary analysis of the data currently available, including the optical data of Grohmann *et al* (1961) and the NMR measurements of Carboni *et al* (1988) indicates that the value of A_j should be revised downwards by about 1.3%. That, when combined with the J mixing correction given above brings the measured and calculated values of a_j in zero field into almost perfect agreement; at 8 T the discrepancy is reduced to less than one standard deviation.

(iii) The evidence available at present indicates that Scott's crystal field parameters give a very satisfactory description of the field dependence of the dipolar splitting when the corrections considered in (i) and (ii) above are taken into account. It should be added, however, that the value of A_j may be subject to some further adjustment when we have completed a new determination of the electronic Zeeman splitting of Ho^{3+} in yttrium ethylsulphate.

4.2. The quadrupolar hyperfine splitting

Comparison between theory and experiment for the quadrupolar parameter P_i is not straightforward because the measured hyperfine splitting gives only the modulus of P_i and, as noted in section 2.2, the extraionic contribution P'' cannot be calculated *a priori*. As noted by BCM, the sign of P_i can be ascertained by recalling that P'' , hence $P_i - P'$ (see equation (6)), must be independent of the applied field. Figure 4 shows that whereas $|P_i|$ varies strongly with the field, $|P_i| - P'$ is almost constant. We conclude that $|P_i| = P_i$, i.e., that P_i is positive, as in pure $\text{Ho}(\text{OH})_3$.

Closer examination of figure 4(b) shows that $|P_i| - P'$ varies erratically in low fields and rises appreciably in the excited state. The erratic behaviour is due to the difficulty of determining the exact positions of the NMR lines in the region in which the ground and excited state spectra overlap (see section 3). The increase in $|P_i| - P'$ in the excited state may be explained as follows. The first-order contribution to P' for any state $|E_N\rangle$ is determined solely by the value of $\langle J_z^2 \rangle$ for that state. The second-order contribution involves all other states which are connected to $|E_N\rangle$ by the off-diagonal parts of the free-ion hyperfine interaction (2). The largest second-order contributions to the hyperfine splittings of $|E_0\rangle$ and $|E_1\rangle$ come from the low-lying singlet $|E_2\rangle$ (see figure 1). Since $\Delta_{12} < \Delta_{02}$, the second-order contribution to P' is larger for $|E_1\rangle$ than for $|E_0\rangle$. It turns out that the computed values of P' for $|E_1\rangle$ are significantly affected by the small discrepancy between the computed and measured positions of $|E_2\rangle$. The sign and order of magnitude of this effect are consistent with the observed increase in $|P_i| - P'$.

With the above considerations in mind, we have used only the data obtained in fields above 2 T to calculate P'' . We obtain $P'' = (-26.2 \pm 1.6)$ MHz, close to the value obtained by BCM in pure $\text{Ho}(\text{OH})_3$. ($\text{Y}(\text{OH})_3$ and $\text{Ho}(\text{OH})_3$ have similar lattice parameters and can therefore be expected to have similar values of the extraionic electric-field gradient.) The uncertainty in P'' comes almost entirely from the notional 5% uncertainty in the quadrupole coupling parameter C_j . The continuous line in figure 4(a) shows the resulting fit to the measured quadrupole splitting. The error bars indicate the uncertainties arising from the crystal field parameters alone; the highly correlated uncertainties in C_j and in the free parameter P'' have not been included. It is clear that Scott's crystal field parameters give a satisfactory account of the quadrupole splitting.

The extraionic quadrupolar parameter P'' , like the crystal field parameter B_2^0 , is proportional to the electric-field gradient V_{cc} . By eliminating V_{cc} it is possible to obtain

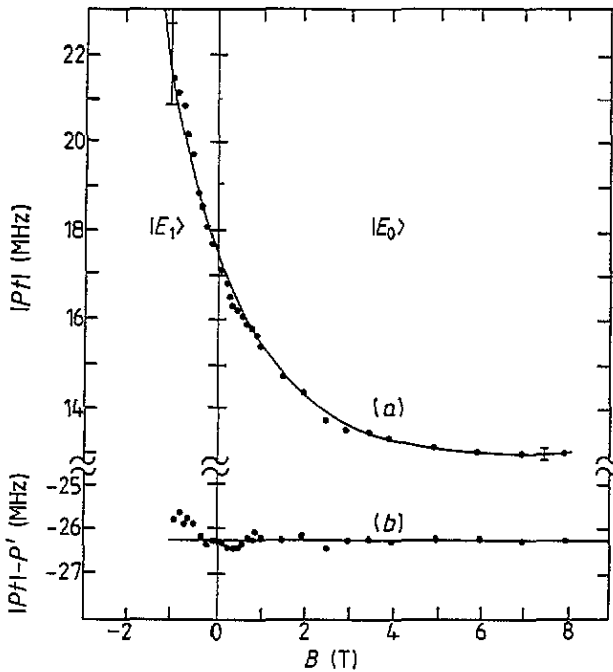


Figure 4. (a) Measured and calculated field dependence of the quadrupolar hyperfine parameter $|P_I|$ for Ho^{3+} in $Y(\text{OH})_3$ at liquid helium temperatures. The continuous curve is obtained by setting $|P_I| = P_I = P' + P''$ where P' is computed by diagonalizing the electronic-nuclear Hamiltonian \mathcal{H}_{en} and $P'' = -26.2$ MHz (see text and (b) below). The uncertainties in the measured points are small compared to those in the computed values of P_I . (b) Graph of $|P_I| - P'$ against field. The horizontal line represents our best estimate of P'' .

the ratio of the nuclear and electronic antishielding ratios, γ_N and γ_E , from P'' and B_2^0 (see equation (18) in BCM). In this way we obtain

$$\gamma_N/\gamma_E = 148 \pm 10 \quad (9)$$

in close agreement with the figure obtained by BCM for pure $\text{Ho}(\text{OH})_3$. We have ignored the correction for J mixing because it is much smaller than the uncertainty arising from C_J .

4.3. The octupolar hyperfine splitting

The computed and measured field dependences of the octupolar parameter are shown in figure 5. The uncertainty on the calculated parameter ($\sim 5\%$) is dominated by the uncertainty in C_J ; it is small compared to the experimental uncertainties. There are no free parameters in the calculation.

5. Summary and conclusions

We have made a detailed NMR study of the field dependence of the hyperfine splitting of holmium in yttrium hydroxide at liquid helium temperatures. The splitting of the ground state has been measured in fields up to 8 T; that of the first excited state has been measured up to 0.9 T, above which the population of the state becomes too small. We find that the crystal field parameters for the nominally 5I_8 ground manifold which Scott (1970) has

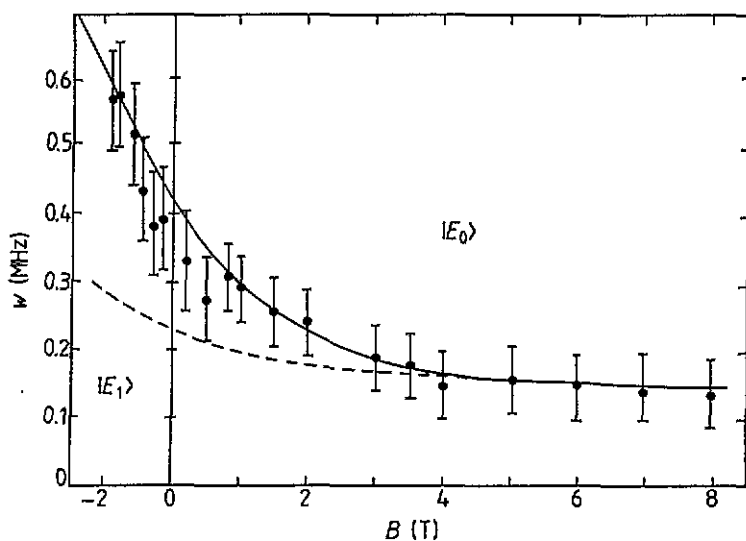


Figure 5. Field dependence of the octupolar hyperfine parameter w . The continuous line is obtained by diagonalization of the electronic–nuclear Hamiltonian \mathcal{H}_{en} . The broken line is obtained from second-order perturbation theory, which becomes increasingly inadequate as the energy gaps Δ_{02} and Δ_{12} diminish (see figure 1).

derived from optical spectroscopy at 77 K give a remarkably accurate description of the hyperfine splittings of both the ground and the excited state at liquid helium temperatures. Only one free parameter (the extraionic quadrupole term P'') is involved in the entire fit. The small discrepancy between the calculated and measured values of the dipolar parameter a_i is increased when allowance is made for J mixing, but practically disappears if the currently accepted value of the free-ion dipole coupling parameter A , is reduced by 1.3%. Evidence to support a reduction of that order will be presented in a later paper.

Measurements of hyperfine splittings in rare earth compounds have now reached a level of precision which calls for more accurate hyperfine coupling constants than those currently available. Ideally, the measurements should be made on free ions, but there is scope for improvements in the values derived from magnetic resonance measurements on insulating crystals. The present work illustrates the potential of high-resolution optical spectroscopy not only to provide the necessary crystal field parameters but also to quantify the effects of J mixing.

Acknowledgments

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Appendix. The effect of J mixing on the hyperfine splitting

As noted in section 4.1, J mixing may have an appreciable influence on the hyperfine splitting even though its effect on the optical spectrum is insignificant. Scott's calculations (1970) avoid explicit reference to the energy eigenstates, so we have reanalysed his optical data, using the Hamiltonian of Crosswhite *et al* (1977), in order to obtain explicit expressions for the J -mixed states which we require. We express the members of the electronic ground doublet in terms of the eigenstates $|J, M\rangle$ of J^2 and J_z :

$$|E_0\rangle = \sum_{JM} c_{J,M}^0 |J, M\rangle \quad |E_1\rangle = \sum_{JM} c_{J,M}^1 |J, M\rangle. \quad (A1)$$

The components $c_{J,M}$ obtained from our analysis are given in table A1. They are necessarily restricted to zero field since the optical data on which they are based were taken in zero field.

Table A1. Components $c_{J,M}$ of $|E_0\rangle$ and $|E_1\rangle$ in zero field.

	$ E_0\rangle$			$ E_1\rangle$		
	$M = 7$	$M = 1$	$M = -5$	$M = -7$	$M = -1$	$M = 5$
$J = 8$	0.9413	0.3064	0.1386	0.9413	0.3064	0.1386
$J = 7$	-0.0216	-0.0125	-0.0066	0.0216	0.0125	0.0066
$J = 6$	—	0.0078	0.0007	—	0.0078	0.0007

For simplicity we shall consider only the first-order dipolar hyperfine parameter, which gives by far the largest contribution to the total hyperfine splitting (see table 2). In order to allow for J mixing it is necessary to replace the operator J in the free-ion dipolar interaction $hA_J J \cdot I$ (see equation (2)) by $(\langle J \| N \| J \rangle)^{-1} N$, where N is the vector operator which represents the electronic part of the dipolar hyperfine interaction and $\langle J \| N \| J \rangle$ is the corresponding operator-equivalent coefficient. (See, for example, chapter 17 in Abragam and Bleaney 1969). The first-order intraionic contribution to the dipolar hyperfine coefficient for the electronic ground state is given by

$$a^{(1)} = \frac{A_J \langle E_0 | N_z | E_0 \rangle}{\langle J \| N \| J \rangle}. \quad (A2)$$

Discarding terms of second order in the small quantities $c_{J,M}$ we obtain

$$a^{(1)} = A_J \langle J_z \rangle (1 + \varepsilon) \quad (A3)$$

(cf. equation (7)) where

$$\varepsilon = \left(\langle 8 \| N \| 7 \rangle \sum_M c_{8,M}^0 c_{7,M}^0 (8^2 - M^2)^{\frac{1}{2}} \right) / \left(\langle 8 \| N \| 8 \rangle \sum_M (c_{8,M}^0)^2 M \right). \quad (A4)$$

Setting $\langle 8 \| N \| 7 \rangle = -0.113$ and $\langle 8 \| N \| 8 \rangle = 0.725$ (figures based on those of Pelzl *et al* (1970) but corrected to allow for core polarization) and using the data in table A1, we obtain $\varepsilon = 0.0058$. Strictly speaking, this figure applies only in zero field, where the J mixing is due solely to the crystal-field interaction. However, we have estimated the additional J mixing due to the Zeeman interaction and find that, even at 8 T, it is negligible compared to that caused by the crystal-field interaction. The correction factor $1 + \varepsilon \simeq 1.0058$ is therefore valid over the entire range of fields used in our measurements. It should be added that the same correction factor applies to the excited state $|E_1\rangle$. The signs of the $c_{J,M}^1$ are opposite to

those of the $c_{J,M}^0$, but this is compensated by the reversed signs of the M in the denominator of equation (A4).

Evaluation of the J mixing correction for the quadrupolar splitting is more complicated than that for the dipolar splitting because of the substantial contribution of higher-order contributions to P' (see table 2). A rough calculation indicates that the fractional correction is of the same order as that for the dipolar term, and therefore negligible compared to the 5% uncertainty on the quadrupole coupling constant C_J . The J mixing correction for the octupolar term is almost certainly insignificant compared to the experimental uncertainties (see figure 5).

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