

Further studies of the enhanced nuclear magnet HoVO_4

I. The crystal field and the Zeeman spectrum

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A novel approach is adopted to fit the experimental results for the Van Vleck paramagnet HoVO_4 . Within the ground manifold 5I_8 , $J = 8$, the five parameters for a crystal field of tetragonal symmetry are adjusted to give values in agreement with the optical spectrum for the lowest energy levels: the ground singlet, the first excited doublet at 21 cm^{-1} , and the (accidental) triplet at 47 cm^{-1} . Within experimental error (of order 1 cm^{-1}), this agreement is not impaired by a small modification in which all the crystal field parameters are multiplied by a factor 1.0225. This factor is introduced to give the correct value of the enhanced nuclear magnetic resonance frequency for the stable isotope ^{165}Ho ($I = \frac{7}{2}$), known to 0.3% (Bleaney *et al.* *Proc. R. Soc. Lond. A* **362**, 179 (1978)). The optical Zeeman effect, calculated therefrom, is in good agreement with that observed experimentally for the lowest levels in magnetic fields up to 15 T, directed along the [100], [110] and [001] axes (Battison *et al.* *Phys. Lett. A* **55**, 173 (1975); *J. Phys. C* **10**, 323 (1977)).

1. INTRODUCTION

A systematic examination at low temperatures of the thermal, magnetic and crystallographic properties of the rare-earth vanadates, general formula RVO_4 , began in 1969 following the production of good single crystals by a flux-growth technique (Garton & Wanklyn 1970). In one compound, DyVO_4 , it resulted in the discovery of Jahn–Teller and antiferromagnetic transitions (Cooke *et al.* 1970, 1971). The predominant interest continued to lie in similar properties: in addition to DyVO_4 , crystallographic phase transitions were observed in TmVO_4 and TbVO_4 , and ordered magnetic states in GdVO_4 , TbVO_4 and DyVO_4 . An ironical consequence was that Van Vleck paramagnetism appeared to be of little interest, and a detailed investigation of the magnetic properties of the compound HoVO_4 commenced only with the realization that it should exhibit large anisotropy, both in the electronic paramagnetism (Battison *et al.* 1975) and the enhanced nuclear paramagnetism (Bleaney *et al.* 1976, 1977).

The first suggestion that enhancement of the effective nuclear moment (Baker & Bleaney 1958) could be used for nuclear cooling (Al'tshuler 1966) was followed by experiments at Kazan on a number of lanthanide compounds (see Teplov 1977). Most of these contain ^{141}Pr ($I = \frac{5}{2}$) or ^{169}Tm ($I = \frac{1}{2}$), but a general survey (Bleaney 1973) suggested that many materials with a singlet electronic ground

state and low-lying states (typically $10\text{--}50\text{ cm}^{-1}$) would have much larger enhancements of their nuclear magnetism. In particular ^{165}Ho is attractive because of its larger nuclear spin ($I = \frac{7}{2}$) and moment (4.173 nm); experiments on HoVO_4 (Bleaney *et al.* 1978) that used novel NMR techniques (Robinson 1977) showed that the enhancement of the effective nuclear moment in the (001) plane by a factor $(1+K)$ was about 175. A significant consequence is that the interactions between the nuclear spins are increased by a factor $K^2 \approx 3 \times 10^4$, leading to a cooperative nuclear state at millikelvin temperatures. This has been confirmed by adiabatic demagnetization and nuclear orientation experiments (Suzuki *et al.* 1978; Allsop *et al.* 1980); the onset of a nuclear antiferromagnetic state occurs at $T_n = 4.8\text{ mK}$, as predicted by Bleaney (1980).

In a number of other experiments, the properties of HoVO_4 have been investigated by using radio-frequency measurements of the susceptibility (Bleaney *et al.* 1980); acoustic enhanced nuclear magnetic resonance of ^{165}Ho (Bleaney *et al.* 1983); NMR of ^{51}V ($I = \frac{7}{2}$) in both the paramagnetic (Bleaney *et al.* 1978) and the ordered nuclear state (Bleaney *et al.* 1987). There are also more detailed nuclear orientation measurements on $^{166\text{m}}\text{Ho}$ (Clark *et al.* 1987), as well as further theoretical investigations (Bleaney *et al.* 1982; Bowden & Clark 1983). Battison *et al.* (1977) measured the effect of applied stress on the optical adsorption spectrum; they observed that the doublet at 21 cm^{-1} is not split by B_{1g} stress along [100], but that the initial splitting was approximately doubled by B_{2g} stress of 20 kg mm^{-2} along [110]. They suspected the presence of but found no evidence for a cooperative Jahn–Teller transition; however, Goto *et al.* (1986) using acoustic measurements have observed anomalies in several of the elastic constants; the anomalies vanish at lower temperatures (approaching 1.7 K) such that the thermal population of the 21 cm^{-1} doublet falls to zero. They also list a set of energy levels obtained from a crystal field, but the parameters quoted for the latter are not only mutually inconsistent ($B_{40} = 0$, but $B_{44}/B_{40} = 3.715$) but appear to give energy separations smaller by a factor of *ca.* 100 than those listed in their table II.

In this paper, we attempt a new approach in which a crystal-field calculation is combined with the parameters measured by enhanced nuclear magnetic resonance. The advantage is that the accuracy of the latter, *ca.* 0.3%, is greater than that of the optical energy-level separations (*ca.* 1 in 50 cm^{-1}). The values of the energy levels and Zeeman effect up to 15 T, obtained from this calculation, are compared with those observed by optical absorption spectroscopy for HoVO_4 . Also, new optical spectroscopic measurements have been made by using emission lines to determine the positions of the higher levels in the ground manifold $^5\text{I}_g$ for (10% Ho, 90% Y) VO_4 .

2. THE OPTICAL ENERGY LEVELS

In HoVO_4 the Ho^{3+} ion, $4f^{10}$, $^5\text{I}_g$, occupies a site of tetragonal symmetry in the zircon structure. The hamiltonian has the form

$$H = Z_{\text{cf}} + Z_e + Z_{\text{hfs}} + Z_Q + Z_I, \quad (1)$$

where Z_{cf} represents the crystal field, $Z_e = g_J \mu_B \mathbf{B} \cdot \mathbf{J}$ the electronic Zeeman

interaction, $Z_{\text{hfs}} = A_J \mathbf{J} \cdot \mathbf{I}$ the magnetic hyperfine interaction, Z_Q the nuclear electric quadrupole interaction, and $Z_I = -\gamma_I \hbar \mathbf{B} \cdot \mathbf{I}$ the nuclear Zeeman interaction. In tetragonal symmetry, only five terms with $k = 2, 4, 6$ and $q = 0, 4$ are required. Various estimates of the accompanying parameters B_{kq} have been made, the most recent being those of Andronenko *et al.* (1985), and of Goto *et al.* (1986). For $J = 8$ in D_{2d} symmetry, Z_{cf} splits the $2J + 1 = 17$ levels into four doublets and nine singlets, as shown in table 1. In principle, it should be possible to decide

TABLE 1. EXPERIMENTAL AND THEORETICAL VALUES FOR THE CRYSTAL FIELD LEVELS IN RECIPROCAL CENTIMETRES OF $J = 8$ IN HoVO_4 AND IN (10% Ho, 90% Y) VO_4

(S, singlet; D, doublet. References are: measured, HoVO_4 , Battison *et al.* (1975); calculated HoVO_4 , Goto *et al.* (1986); measured, 10%, Battison *et al.* (1977) (the two levels at 117 and 132 cm^{-1} are attributed in this paper to Schlaphof (1970)); measured, 10%, this paper; calculated, this paper.)

S or D	measured HoVO_4	calculated HoVO_4	measured 10%	measured 10%	calculated
S	0	0	0	0	0
D	21	20.9	20.8	21.0	21.43
S	47	46.0	46.5	47.4	48.3
D	47	46.0	46.8	47.4	48.4
S	—	79.11	117	—	120
S	—	118	132	132.5	131
S	—	150.5	—	—	222
D	—	183.9	—	236.2	226
S	—	191.5	—	—	229
S	—	200	—	—	230
D	—	200	—	—	260
S	—	298	—	275.2	263
S	—	298	—	—	292

between these by calculating the energy levels and fitting them to the known experimental values. The main difficulty is that higher levels are appreciably broadened at temperatures where the populations are sufficient for optical absorption spectroscopy (Battison *et al.* 1975, 1977). This gave the energies only of the lowest levels: the ground singlet, the doublet at about 21 cm^{-1} , and a doublet at *ca.* 48 cm^{-1} almost coincident with another singlet.

This has now been complemented by the observation of emission lines from higher multiplets, populated by optical absorption, down to upper levels in the ground manifold. Through a series of mirrors and lenses, light is directed onto a crystal in a helium cryostat from an xenon discharge lamp. This broad-band (white light) source is filtered to allow transmission only of frequencies greater than *ca.* 21 000 cm^{-1} , giving absorption to the multiplets 5F_3 and above. In the subsequent decay transitions are observed from the lowest levels in 5I_4 and 5S_2 to excited levels in the ground multiplet 5I_8 . The clearest lines, with maximum intensity for a crystal of composition (0.1 Ho, 0.9 Y) VO_4 , are enhanced by reducing the temperature of the helium bath to 1.4 K, because bubbling is absent in the superfluid phase. Even so, only five lines are clearly visible on polaroid film

and are analysed by a grating spectrograph, though one more could be detected by eye.

These six lines have energy separations up to 276 cm^{-1} , and maximum energy 18374 cm^{-1} . A further line at the higher frequency $18395.0 \pm 1.0\text{ cm}^{-1}$, observed by photoelectric detection, corresponds to absorption from the lowest level. Thus seven energy levels in the ground manifold are determined, as shown in the fifth column in table 1. A magnetic field up to 9 T, parallel to the [001] axis, is used to confirm the multiplicity shown in the table. The level at 236.2 cm^{-1} is broad, and at least a doublet; it probably corresponds to four of the levels in the last column.

3. FITTING THE EXPERIMENTAL DATA

In a Van Vleck paramagnet, a singlet ground state gives no EPR spectrum, but if the ion has a nuclear spin, the system can be investigated by NMR. For the nucleus ^{165}Ho , $I = \frac{7}{2}$, (abundance 100%), the enhanced NMR spectrum is fitted to the hamiltonian

$$H = -\hbar[\gamma_{\parallel} B_z I_z + \gamma_{\perp}(B_x I_x + B_y I_y)] + P[I_z^2 - \frac{1}{3}I(I+1)] \quad (2)$$

with the parameters (Bleaney *et al.* 1978) listed in table 2. The shift for LuVO_4 is significant, and confirms that enhanced NMR is very sensitive to small changes in

TABLE 2. VALUES OF $(\gamma_{\perp}/2\pi)$, THE RESONANT FREQUENCY FOR A FIELD OF 1 T IN THE (001) PLANE, AND OF THE NUCLEAR ELECTRIC QUADRUPOLE PARAMETER P/h AT *ca.* 1.6 K; AT *ca.* 4.2 K THE FORMER IS REDUCED BY *ca.* 3 MHz T^{-1} THROUGH THE RESIDUAL POPULATION OF THE DOUBLET AT 21 cm^{-1} ; P/h IS NOT APPRECIABLY DIFFERENT AT THE TWO TEMPERATURES, AND IS KNOWN TO BE POSITIVE

	$(\gamma_{\perp}/2\pi)/(\text{MHz T}^{-1})$	(P/h) MHz
HoVO_4	1529(3)	25.9
(2% Ho, Y) VO_4	1526(3)	25.2(2)
(0.1% Ho, Y) VO_4	1525(2)	25.2(2)
(1% Ho, Lu) VO_4	1406(3)	27.9(2)

the crystal field. The ionic size of the trivalent ion Lu is smaller than that of Ho, but those of Ho and Y are almost identical. The resonance results for HoVO_4 and Ho in YVO_4 agree within experimental error, and confirm that Ho is an excellent fit in the YVO_4 lattice. The average value of $(\gamma_{\perp}/2\pi)$ for the three samples at 1.6 K is 1527 MHz T^{-1} , accurate to *ca.* 0.2%, and this is used in the calculations below. Parallel to the *c*-axis there is almost no enhancement; $(\gamma_{\parallel}/2\pi)$ is determined only as less than 20 MHz T^{-1} . The wavefunction of the ground singlet is almost wholly $|J_z = 0\rangle$; if there were no admixtures of $|\pm 4\rangle$, $|\pm 8\rangle$, the induced electronic moment along the *c*-axis would be zero, and the measured value of $(\gamma_{\parallel}/2\pi)$ would be equal to the free nucleus value $(\gamma_I/2\pi) = 9.0(1)\text{ MHz T}^{-1}$. The theory below (§4) gives a more precise value of 15 MHz T^{-1} for the parallel direction.

The principal values of the electronic susceptibility can be found from the relation

$$m/(\mu_B B) = (g_J/A_J) \hbar (\gamma - \gamma_I) \quad (3)$$

with $g_J = 1.2417$, $A_J/h = 812.1(\pm 1)$ MHz, both known to 0.1%. The induced moments, proportional to $(1527 - 9) = 1518$ and $15(5) - 9 = 6(5)$ MHz T^{-1} perpendicular and parallel respectively, have values $2.32(1)$ and $0.01(1)\mu_B \text{T}^{-1}$ per ion. This method of estimating them from the NMR measurements is precise; for the c -axis it avoids the error in making a direct measurement of a very small principal susceptibility when the anisotropy is large. For the perpendicular plane the accuracy of the NMR result is high, and will now be used to obtain an improved crystal field fit.

A difficulty in any simple crystal potential theory is that second-order effects from matrix elements of Z_{cf} to excited manifolds ($J = 7, 6$, etc.) may produce displacements of the levels by several reciprocal centimetres. A further problem is that the optical spectra yield values for the energy levels of accuracy *ca.* 1 cm^{-1} . In the perpendicular plane the large enhanced nuclear resonance frequency is inversely proportional to the crystal-field splitting between the ground singlet and the first excited doublet, and is very sensitive to this splitting. For example, the calculation of Andronenko *et al.* (1985), giving 17.4 cm^{-1} rather than 21.4 cm^{-1} for HoVO_4 produces an error of *ca.* 20% in the enhanced frequency for the perpendicular direction. Our approach therefore will be to obtain a good crystal-field fit, restricted to the one manifold $J = 8$, to the lowest levels at 0, 21 and 48 cm^{-1} , and then make a final adjustment to give a resonant frequency in the perpendicular plane equal to the value measured by NMR. Because these values differ only by 0.2% for concentrated HoVO_4 and for dilution in YVO_4 , no distinction is made between them.

The starting point is an approximate set of values of B_{kq} . A computer diagonalization is repeated with small adjustments such as a *ca.* 20% change in B_{60} to make the singlet and doublet at 48 cm^{-1} almost coincident. The results are checked by repetition with the signs of B_{44} and B_{64} reversed (equivalent to rotating the axes by 45° about the c -axis); this gives identical eigenvalues. From these, a calculation that uses perturbation theory gives 1546 MHz T^{-1} for the enhancement in the perpendicular plane, from matrix elements to the lowest doublet alone, and inclusion of contributions from other doublets produces an increase of only 0.4%. To fit this to the measured value of $1527(3) - 9 = 1518(3)$ MHz T^{-1} , all the crystal field elements are multiplied by 1.0225; this gives the energies shown in the last column in table 1. The eigenfunctions are not of course changed by inclusion of this factor, and are listed in table 3, together with the final values of the crystal field parameters B_{kq} .

A notable feature of this approach is that the perpendicular resonance frequency cannot be fitted with the doublet at an energy lower than 21.43 cm^{-1} without either drastically altering the wavefunctions or noticeably reducing the value of $A_J/h = 812(1)$ MHz (Baker & Bleaney 1958). The higher energy levels are in approximate agreement with the 1987 measurements on 10% HoVO_4 .

4. THE OPTICAL ZEEMAN SPECTRUM

In the optical absorption spectrum of HoVO_4 the Zeeman effect has been observed by Battison *et al.* (1975). Magnetic fields up to 15 T were applied to a single crystal along the principal axes [001], [100] and [110], to measure the variation of the lowest levels in the $^5\text{I}_8$ manifold. Their results may be compared with those from a computer calculation based on the crystal field parameters listed in table 3. If the values of $\langle J || \infty || J \rangle$, etc. from Abragam & Bleaney (1970) are used, the crystal-field values are $B_{20} = -88.32$, $B_{40} = 39.75$, $B_{60} = -42.64$, $B_{44} = -773.4$, $B_{64} = +77.67$ (all in reciprocal centimetres); but with allowance for intermediate coupling (Rajnak & Kupke 1967), they become $B_{20} = -96.20$, $B_{40} = 42.97$, $B_{60} = -45.79$, $B_{44} = -836.1$, $B_{64} = +83.41$ all in reciprocal centimetres. Figures 1, 2 and 3 show that a good detailed fit is obtained, with only minor

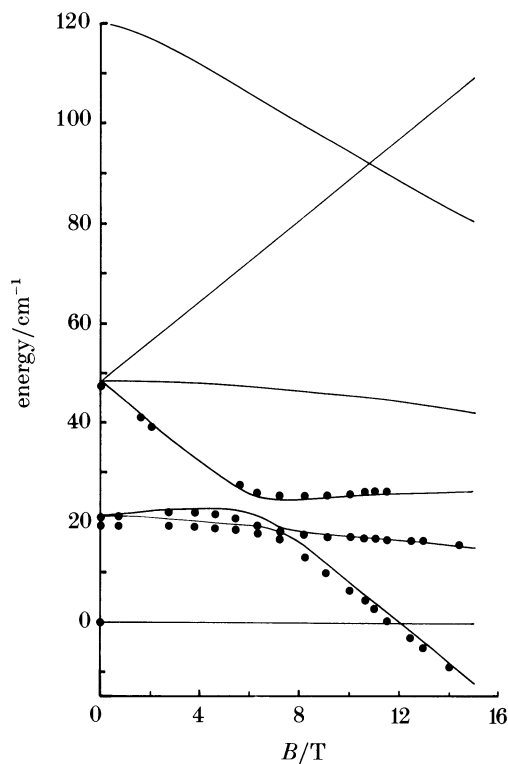


FIGURE 1. The Zeeman effect for HoVO_4 with magnetic field along the [001] axis. The continuous lines are computed from the crystal field parameters listed above; the experimental points are those of Battison *et al.* (1977).

discrepancies, over the whole range of fields for all three directions. Apart from this, some remarks may be made about other points of comparison. We consider first the results for magnetic field along the [001] axis.

Because a non-Kramers doublet has only one non-zero g -value, parallel to the

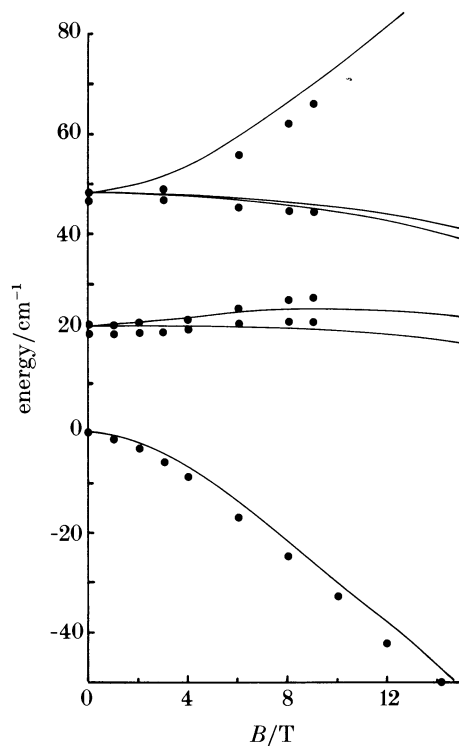


FIGURE 2. The Zeeman effect for HoVO_4 with magnetic field along a $[100]$ axis. The continuous lines are computed from the crystal field parameters listed above; the experimental points are those of Battison *et al.* (1977).

TABLE 3. EIGENFUNCTIONS FOR HoVO_4 , CALCULATED FROM CRYSTAL FIELD PARAMETERS (REFERRED TO $[110]$, $[1\bar{1}0]$ AXES)

(The eigenvalues are in reciprocal centimetres and repeat those listed in table 1 in the last column.)

S or D	energy	eigenfunction
S	0	$-0.948 0\rangle + 0.320 4^s\rangle + 0.006 8^s\rangle$
D	21.43	$-0.189 \pm 5\rangle + 0.914 \pm 1\rangle - 0.354 \mp 3\rangle + 0.062 \mp 7\rangle$
S	48.3	$0.272 6^a\rangle - 0.963 2^a\rangle$
D	48.4	$0.998 \pm 7\rangle + 0.001 \pm 3\rangle - 0.064 \mp 1\rangle + 0.015 \mp 5\rangle$
S	120	$0.976 6^s\rangle - 0.216 2^s\rangle$
S	131	$0.963 6^a\rangle + 0.272 2^a\rangle$
S	222	$0.216 6^s\rangle + 0.976 2^s\rangle$
D	226	$0.015 \pm 7\rangle + 0.553 \pm 3\rangle + 0.042 \mp 1\rangle - 0.832 \mp 5\rangle$
S	229	$0.993 8^a\rangle + 0.116 4^a\rangle$
S	230	$0.023 0\rangle + 0.054 4^s\rangle + 0.998 8^s\rangle$
D	260	$+0.017 \pm 7\rangle + 0.754 \pm 3\rangle + 0.399 \mp 1\rangle + 0.522 \mp 5\rangle$
S	263	$+0.993 4^a\rangle - 0.116 8^a\rangle$
S	292	$+0.318 0\rangle + 0.946 4^s\rangle - 0.058 8^s\rangle$

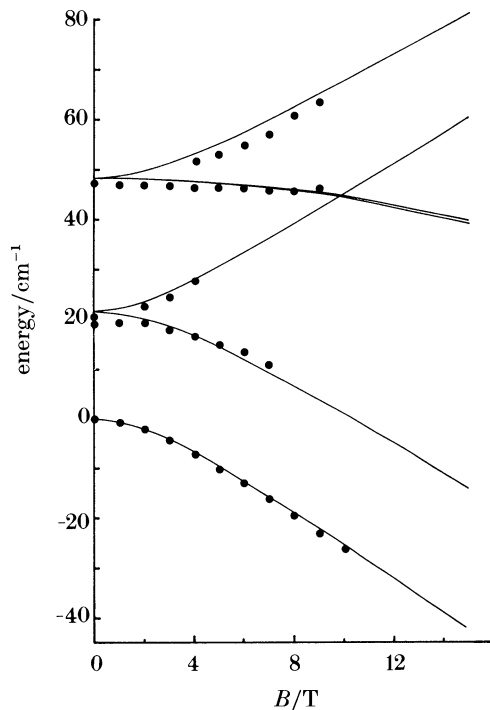


FIGURE 3. The Zeeman effect for HoVO_4 with magnetic field along a $[110]$ axis. The continuous lines are computed from the crystal field parameters listed above; the experimental points are those of Battison *et al.* (1977). In high fields the levels for magnetic fields along $[110]$ and $[100]$ axes differ considerably, reflecting the fact that the symmetry of the crystal field is not fully axial, but tetragonal.

c -axis, we denote this by g , without a subscript. We consider first the ground singlet.

1. The wavefunction is almost pure $|0\rangle$, for which the Zeeman effect should be zero. Experimentally it is very small, and the wavefunction in table 3 gives a quadratic Zeeman effect in small fields, corresponding to an induced moment of $0.008 \mu_B \text{ T}^{-1}$ per ion. This gives a value of 6 MHz T^{-1} as the enhanced contribution to the nuclear magnetic resonance frequency; together with the true nuclear value of $9.0(1) \text{ MHz T}^{-1}$, the value of $(\gamma_{\parallel}/2\pi)$ becomes 15 MHz T^{-1} , somewhat smaller than the upper limit of 20 MHz T^{-1} obtained by Bleaney *et al.* (1978).

2. For the doublet $|\pm 7\rangle$ at 48 cm^{-1} , the calculated value of g is 17.3, very close to the maximum value $g = 14 \times 1.242 = 17.39$ for pure $|\pm 7\rangle$ states. In the optical measurements, the splitting in a field of 14 T parallel to the c -axis, is $114 (\pm 2) \text{ cm}^{-1}$; this corresponds to $g = 17.4(3)$ in good agreement with the calculated value. A further point is that in this calculation the level $|-7\rangle$ crosses the ground singlet at a field of 11.7 T, in better agreement with the observed value 11.6 T than the 10.0 T of Andronenko *et al.* (1985).

3. For the first excited doublet of HoVO_4 , the wavefunction has the form

$$a|\pm 5\rangle + b|\pm 1\rangle + c|\mp 3\rangle + d|\mp 7\rangle,$$

from which

$$g/2g_J = 5a^2 + b^2 - 3c^2 - 7d^2.$$

For such an admixture, the value of g varies rapidly as a function of the coefficients. The various crystal field estimates give values ranging between -1.40 (Domann); -0.53 (Goto *et al.* 1986); -1.52 (calculated). It is difficult to deduce a value for this from the optical data, but the good agreement between the calculated Zeeman effect and the experimental points up to 15 T supports the calculated value.

Little needs to be said about the Zeeman effect in the (001) plane, except to remark that in small fields it is the same in all directions, a result most accurately established by the enhanced NMR measurements at *ca.* 0.3 T of Bleaney *et al.* (1978). In high fields the difference between the [100] and [110] axes reflects the fact that the crystal symmetry is tetragonal, not wholly axial. Along a [100] axis the optical measurement has been supplemented by observation of the resonant frequency of a circuit oscillating at 300–400 kHz, and containing a crystal of HoVO_4 . The frequency change is a measure of the differential electronic susceptibility in fields up to 7 T (Bleaney *et al.* 1980). Points taken at 4.2, 0.5 and 0.1 K show no detectable change with temperature. The results were fitted by an algebraic approximation previously used by Battison *et al.* (1977) for (10% Ho, Y) VO_4 . Our calculations may be compared with their measurements most simply in terms of their parameters h_1 , $h_2 = 2^{-\frac{1}{2}} g_J \mu_B B \times \alpha_1, \alpha_2$, respectively, the latter parameters being those of Bleaney *et al.* (1980). The values of Battison *et al.* (1977) are: for [100], $h_1 = 4.95 \mu_B B$, and for [110] $h_2 = 4.25 \mu_B B$, these being primarily fits to the high-field results. The values of Bleaney *et al.* (1980) are $4.59 \mu_B B$ and $4.05 \mu_B B$ respectively, primarily fitted to the (low-field) value of gamma. Our calculations give $4.98 \mu_B B$ and $3.44 \mu_B B$, respectively.

5. COMPARISON WITH NMR RESULTS

At liquid helium temperatures the average value (Bleaney *et al.* 1978) of the quadrupole parameter $P/h = +25.6(3)$ MHz. This comprises three contributions; the most accurate is that from the second-order effect of the magnetic hyperfine interaction

$$P_2/h = (A_J/2g_J \mu_B) (\gamma_{\perp} - \gamma_{\parallel})/2\pi = +35.3 \text{ MHz.} \quad (4)$$

The other two contributions are true NEQ effects; that from the field gradient of the $4f$ electrons is $P_{4f} = -35(2)$ MHz, based on a value of $+62.7(\pm 3)$ MHz for the stretched state $J_z = J$. To obtain the measured value of P/h , the lattice contribution must be $P_{\text{latt}}/h = +26(2)$ MHz. This may be compared with the electronic electric field gradient term B_{20} , through the relation

$$P_{\text{latt}} = -3QB_{20} (1 - \gamma_{\infty})/21 \langle r^2 \rangle (1 - \sigma_2).$$

From the values $Q = 3.53(2) b$, $\langle r^2 \rangle = 0.745$ AU (Freeman & Desclaux 1979), and our value $B_{20} = -88.5 \text{ cm}^{-1}$, we find $(1 - \gamma_{\infty})/(1 - \sigma_2) = 390(30)$, a surprisingly high result for the ratio of the shielding corrections, but in line with the results of Edmonds (1963).

Another point of comparison is the variation of the NMR parameters as the temperature is increased. The results listed in table 4 are those of Bleaney *et al.* (1978), except that a value of $(\gamma_{\perp}/2\pi)$ for 20.4 K is deduced indirectly from the

TABLE 4. MEASURED VARIATIONS WITH TEMPERATURE OF THE NMR PARAMETERS, $(\gamma_{\perp}/2\pi)$ IN MEGAHERTZ PER TESLA AND P/h IN MEGAHERTZ, COMPARED WITH THOSE COMPUTED FROM THE ENERGY LEVELS AND EIGENFUNCTIONS IN TABLE 3

(The values of the former are corrected for the internal magnetic field. Values in parentheses are identical with the measured values, having been used in the fit.)

T	$(\gamma_{\perp}/2\pi)$ measured	$(\gamma_{\perp}/2\pi)$ calculated	P/h measured	P/h calculated
1.6	1526	(1526)	25.6	(25.6)
4.2	1524	(1524)	25.6	(25.6)
11	1308	1324	20.6	21
14	1185	1230	~ 13	19
20.4	960	990		

shift in the ^{51}V resonance at this temperature, using the fact that the shifts at lower temperature are linearly proportional to the values of gamma for ^{165}Ho . The variation with temperature in column 3 is an approximation that allows only for the decrease in the net population of the ground singlet; this is inversely proportional to the partition function

$$Z = 1 + 2 \exp(-30.85/T) + 3 \exp(-69.5/T) \dots$$

The observed fall in $(\gamma_{\perp}/2\pi)$ with rising temperature is clearly mainly due to the increase in Z .

6. CONCLUSION

The measurements of Battison *et al.* (1975, 1977) of the optical absorption spectrum of HoVO_4 have been supplemented by lines observed in emission, to obtain values of several higher energy levels in the ground $^5\text{I}_8$ manifold. A set of crystal field parameters giving an approximate set of levels is modified to improve the fit, and to give the observed value of the enhanced nuclear resonance frequency perpendicular to the c -axis, this being the parameter determined with the highest accuracy (0.3%). A more precise value of the very small enhancement of the nuclear resonance frequency parallel to the c -axis is obtained from these calculations, together with an estimate of the antishielding effects in the electronic and nuclear quadrupole terms. The theory also gives a good fit to the optical Zeeman spectrum in fields up to 15 T, directed along the [100], [110] and [001] crystal axes.

This paper is based on results from several types of experiments by a number of authors. An appropriate comment is thus contained in the Roumanian proverb

‘Copilul cu mai multe moașe rămână cu buricul netaiat’

translated as ‘A child with too many midwives remains with his navel-string uncut’ (Fermor 1986, p. 220).

The purpose of this paper is *‘denimque quod diu multumque hinc de rebus cum pluribus ex qualis occasione diffuerim, quo factum est, ut copiosus fusiusque (absit*

verbis invidia) nonnunquam ea explicare necesse habuerim, que ab aliis quasi per transennam proposita verius quam explicat sint (Von Herberstein 1549). (Translated as 'to give a more copious and ample explanation of matters which have been exhibited by others obscurely and as it were through a lattice' (Von Herberstein 1851).)

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