PHYSICAL REVIEW B VOLUME 24, NUMBER 1 1 JULY 1981

Optical and magnetic studies of HoF_3

K. K. Sharma,* F. H. Spedding, and D. R. Blinde†
Ames Laboratory, Iowa State University, Ames, Iowa 50011

(Received 2 March 1981)

Absorption spectra of HoF_3 at 0 and 9.05 T have been measured for optical transitions from the ground multiplet $^5I_8$ to the excited multiplets $^5G_4$ and $^3K_8$. All the Stark levels of these excited multiplets and the lowest three levels of the ground multiplet have been identified. A crystal-field Hamiltonian appropriate to the Ho site symmetry (C_{1h}) has been fitted to the observed zero-magnetic-field energies. The rms deviation for 26 levels of the excited multiplets is 2.15 cm^{-1}. The principle of spectroscopic stability has been used to obtain absolute magnetic shifts of electronic singlet states produced by higher-order effects. The $^5G_4$ multiplet shows rather small magnetic shifts, whereas large shifts are observed for the $^5I_8$ and $^3K_8$ multiplets. This is in complete agreement with the calculated results. The calculated Zeeman shifts are obtained from a simultaneous diagonalization of the crystal-field and magnetic interactions. Crystal-field parameters obtained from a least-squares fit to the zero-magnetic-field data are presented.

I. INTRODUCTION

Recent years have seen a rapid growth of interest in the optical and magnetic studies of rare-earth ions in crystalline environment.[1-4] Most of these studies are however devoted to crystals of relatively high symmetry. Attention[5,6] is now being given to such studies in low-symmetry crystals. The standard procedure[1] for interpreting rare-earth spectra is to express the Hamiltonian in terms of single-particle operators within a single $4f^n$ configuration. Attempts[7,8] have been made to extend this description to include many particle interactions. All these methods tend to increase the number of adjustable parameters. Computations involving large-size matrices with several parameters are expensive and cumbersome even with the present day fast computers. Crosswhite *et al.*[9] have recently analyzed the spectra of Ho^{3+}, Np^{3+}, and U^{3+} in relatively-high-symmetry host crystals. Stohr and Gruber[5] have reported results of their investigation on $Ho_2(SO_4)_3 \cdot 8H_2O$. They concluded from polarization considerations that the Ho^{3+} local site symmetry is C_{1h}. These authors used the free-ion parameters obtained by Rajnak and Krupke[10] for their calculations.

In this paper, we report optical absorption and Zeeman spectra at 9.05 T of a low-symmetry crystal of HoF_3. We have confined ourselves to the study of the ground multiplet $^5I_8$ and two excited multiplets $^3K_8$ and $^5G_4$. Although these states are not pure states, we have retained Russell-Saunders labels of the leading eigenstate for easy reference. The zero-field absorption spectrum is interpreted in terms of a crystal-field Hamiltonian neglecting J mixing and using the free-ion parameters of Rajnak and Krupke.[10] The crystal field of C_{1h} symmetry gives rise to only diamagnetic (electronic singlet) states for the non-Kramers Ho^{3+} ion. The magnetic shifts of these singlet states can be calculated from second-order perturbation theory. However, at a magnetic field of 9.05 T, the shifts of individual Stark levels in some cases are comparable to their zero-field separations. In view of this, the Zeeman shifts are calculated from a simultaneous diagonalization of crystal field and magnetic interactions. The singlet electronic states are particularly interesting for enhanced nuclear studies.[11,12] Ho^{3+} ion has some unique features in this respect. HoF_3 seems to be a good candidate for these studies.

II. CRYSTAL STRUCTURE

The crystal structure of HoF_3 has been reported by Zalkin and Templeton[13] to be orthorhombic having space group $P_{nma}(D_{2h}^{16})$ with the holmium ions occupying the sites at $\pm(x,\frac{1}{4},z)$ and $\pm(\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z)$ where x and z are $0.367a$ and $0.058c$, respectively. The unit-cell dimensions are $a = 6.404$ Å, $b = 6.875$ Å, and $c = 4.379$ Å. Each Ho^{3+} ion in the unit cell is surrounded by eight equidistant and one slightly farther off fluorine neighbors. The site symmetry at each rare-earth ion is "C_{1h}" with the reflection plane normal to the crystallographic b axis. The local coordinates (x,y,z) of the Ho^{3+} ions are along (c,a,b) crystallographic axes, respectively.

III. EXPERIMENTAL DETAILS

The absorption and Zeeman spectra of HoF_3 single crystals were obtained with a Jarrell-Ash 3.4-m Ebert Spectrograph. The 300 grooves/mm plane grating is

©1981 The American Physical Society

blazed at an angle of 59°. The $^3K_8$ and $^5G_4$ multiplets were photographed in the 12th and 15th orders with dispersions of 2.00 and 2.18 cm^{-1}/mm, respectively. Details of the technique used to align the crystals may be seen in Ref. 14. The samples used for obtaining the spectra measured $2.5 \times 2.5 \times 0.1$ mm^3 with light propagating along the short dimension. The zero-field polarized spectra were measured as a function of temperature from 1.6 to 40 K, whereas all Zeeman plates were taken at 20 K. Here we report the analysis of the Zeeman spectrum taken at a field of 9.05 T. The Zeeman shifts have been measured for magnetic field applied along directions parallel to the three crystallographic axes. An RCA superconducting magnet type SM2818 capable of producing a magnetic field up to 10 T with field to current ratio of 1.10 kG/A was used. Accurate zero-field energy determinations were made using a Jarrell-Ash model 23-500 microphotometer in conjunction with a Bristol model 560 chart recorder. Specific wavelengths to an accuracy of a few hundredths of a cm^{-1} were assigned to the absorption peaks by obtaining accurate wave number dispersion relationships in the vicinity of individual lines. The wavelengths of the lines of a hollow iron cathode were used as standards. An approximate technique was, however, used to find Zeeman shifts at 9.05 T to an accuracy of a few tenths of a cm^{-1}.

IV. FREE-ION SPECTRA

The free-ion energy calculations for the $J=8$ and $J=4$ multiplets were carried out in the intermediate coupling scheme with parameters of Rajnak and Krupke[10]: $E^0=20\,770$ cm^{-1}; $E^1=6682.6$ cm^{-1}; $E^2=30.6$ cm^{-1}; $E^3=620.1$ cm^{-1}; $\zeta=2127.1$ cm^{-1}; $\alpha=23.5$ cm^{-1}; $\beta=-811.2$ cm^{-1}; and $\gamma=0$. The calculated free-ion level positions of the $^5G_4$ and $^3K_8$ multiplets at 25 648 and 21 150 cm^{-1} are lower by 191 and 133 cm^{-1} from their respective observed centers of gravity. Despite this disagreement, a least-squares analysis could not be carried out for lack of sufficient data on free-ion levels.

V. ZERO-FIELD SPECTRA

The crystal field consistent with the site symmetry "C_{1h}" for Ho^{3+} in HoF_3 when expressed in terms of the tensor operators,[1] C_q^k will have 15 terms. Here we neglect the odd terms of the crystal-field Hamiltonian. With the restriction, $|q| \leqslant k$, the Hamiltonian can be written as

$$H_{\text{cryst}} = \sum_{\substack{i \\ k=2,4,6 \\ q=2,4,6}} \{B_0^k (C_0^k)_i + B_q^k [(C_q^k)_i + (C_{-q}^k)_i] + iB_{-q}^k [(C_q^k)_i - (C_{-q}^k)_i]\} \; .$$

The fifteen radial quantities B_q^k are real and in the absence of any good way of calculating their values, will be treated as adjustable parameters to fit the experimental data. The point group "C_{1h}" appropriate for an even electron configuration (Ho^{3+} has ten $4f$ electrons) is characterized by two one-dimensional irreducible representations Γ_1 and Γ_2. An even J state will split into $(J+1)$ and J Stark levels with transformation properties of Γ_1 and Γ_2, respectively. The former set of levels corresponds to the crystal quantum number $\mu=0$ and the latter to $\mu=1$. The selection rules for the electric dipole radiation among these levels can be worked out. If E_a, E_b, and E_c represent the polarizations of the incident radiation with electric field parallel to the a, b, and c axes, respectively, then the selection rules applicable for the three directions of light propagation are given in Table I. We prefer this notation to the usual σ, π notation because sometimes it is necessary to distinguish between the two σ polarizations (E_a, E_c). The magnetic selection rules are also included in Table I.

If we assume all but the lowest level of the ground multiplet to be essentially depopulated at 1.6 K, then the seventeen lines observed near 21 500 cm^{-1} and the nine lines observed near 26 000 cm^{-1} at this temperature exactly match the expected number of transitions from the ground level to the crystal-field (CF) levels of $^3K_8$ and $^5G_4$ multiplets, respectively. The identification of the symmetry types of levels of the excited multiplets is facilitated by the following observations. For light propagating parallel to the a axis (hereafter referred to as $\vec{K} \parallel a$), we observe only four and eight lines in E_c polarization and five and nine lines in E_b polarization for the $^5G_4$ and $^3K_8$ multiplets, respectively. However, for light propagating parallel to the b axis ($\vec{K} \parallel b$), there are only five and nine prominent lines in either polarization. This immediately leads us to conclude that the ground level wave function has the transformation properties of Γ_1 and not of Γ_2. There are several cross checks for this assignment. The sum of the observed CF splittings as measured from the multiplet center for all Γ_1 type levels for each multiplet is found equal and opposite in sign to the corresponding sum for Γ_2 type levels as expected. From the temperature-dependent spectra, it was possible to establish the positions and symmetry types of the first two excited CF levels of the ground state.

The CF energy matrices were first diagonalized using the parameters of Stöhr and Gruber.[5] They were found inadequate in our case because the crystal-field interaction is considerably stronger in HoF_3 than in $Ho_2(SO_4)_3 \cdot 8H_2O$. A least-squares fit to the 26 CF levels of $^3K_8$ and $^5G_4$ multiplets paying due attention to their symmetry types yielded several sets of parameters with identical rms deviation of 2.15 cm^{-1}. These sets were found to correspond to different choices for the x and y axes.[15] The local symmetry at

TABLE I. Selection rules for HoF_3.

	Electric Dipole[a,b]							
	"$\vec{k}\|a$"			"$\vec{k}\|b$"			"$\vec{k}\|c$"	
	Γ_1	Γ_2		Γ_1	Γ_2		Γ_1	Γ_2
Γ_1	E_c	E_b	Γ_1	E_a,E_c	X	Γ_1	E_a	E_b
Γ_2	E_b	E_c	Γ_2	X	E_a,E_c	Γ_2	E_b	E_a

	Magnetic dipole[c] "$\vec{k}\|b$"	
	Γ_1	Γ_2
Γ_1	X	E_a,E_c
Γ_2	E_a,E_c	X

[a] "$\vec{k}\|a$" refers to light propagation along the crystallographic a axis; "$\vec{k}\|b$" and "$\vec{k}\|c$" have similar meanings.

[b] "E_c" refers to the polarization for which the electric field of the incident radiation is along the crystallographic c axis; "E_b" and "E_a" have similar meanings.

[c] The magnetic and electric dipole selection rules for "$\vec{k}\|a$" and "$\vec{k}\|c$" are identical.

TABLE II. Crystal-field parameters for HoF_3 obtained by a least-squares fit to 26 stark levels of the $^3K_8$ and $^5G_4$ multiplets.

Parameters	Set 1[a] (cm^{-1})	Set 2[a] (cm^{-1})
B_0^2	78.5[b]	78.5[b]
B_2^2	−199.6	−136.3
B_{-2}^2	272.7	309.2
B_0^4	17.9[b]	17.9[b]
B_2^4	−101.7	−79.7
B_{-2}^4	−33.4	71.4
B_4^4	265.8	−215.9
B_{-4}^4	−95.9	−182.2
B_0^6	224.6[b]	224.6[b]
B_2^6	156.6	−400.1
B_{-2}^6	−552.3	−411.8
B_4^6	58.1	−70.7
B_6^6	−405.9	405.9
B_6^6	−31.3	31.3

[a] Set 1 and set 2 are related by 30° rotation about the z axis. They give identical rms deviations.

[b] Parameters, B_0^2, B_0^4, and B_0^6 are independent of the choice of axes in the xy plane.

the Ho^{3+} site fixes only the z axis and leaves the remaining axes unspecified in the xy plane. For all such sets, the values of B_0^2, B_0^4, and B_0^6 remain unchanged as they are independent of the choice of x and y axes. Two sets of such parameters are given in Table II. The second set can be obtained from the first by a 30° rotation about the z axis. When these parameters were used to predict the CF splittings of the ground multiplet, very good agreement was found for levels whose energies and symmetry types could be inferred from the temperature-dependent spectra (Table III). The calculated and observed order of all CF levels for the $^5G_4$ multiplet are in exact agreement. The rms deviation for this multiplet is 1.41 cm^{-1} (Table IV). The agreement for the $^3K_8$ multiplet is satisfactory though not as good as for the $^5G_4$ multiplet. The calculated and observed order of levels within the pairs of levels marked (H_4,H_5), (H_6,H_7), (H_{10},H_{11}), and (H_{12},H_{13}) in Table V is reversed. Of course, the levels in each of these pairs are very close in energy. This reversal of order has no drastic effect on the rms deviation (2.5 cm^{-1}) for this multiplet but it has a profound effect on the Zeeman shifts as we shall see later.

VI. ZEEMAN EFFECT

Since the crystal field in HoF_3 removes the electronic degeneracy of the levels completely, we have only "Zeeman shifts" and no "Zeeman splittings." For external magnetic field of the order of 10 T, the

TABLE III. Observed and calculated crystal-field splittings and Zeeman shifts for the levels of $^5I_8^{\mathrm{c}}$ multiplet ($g_{\mathrm{eff}}=1.2415$).

	Zero-field position (in cm^{-1})		Zeeman shift at 9.05 T[a] (in cm^{-1})					
			$\vec{H}\parallel b$[b]		$\vec{H}\parallel c$[b]		$\vec{H}\parallel a$[b]	
Level	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$Z17$		377.27 (Γ_1)		13.0		22.5		21.9
$Z16$		370.58 (Γ_2)		3.0		−7.6		−8.7
$Z15$		350.89 (Γ_1)		−6.3		−5.6		−5.7
$Z14$		281.44 (Γ_2)		12.1		4.1		10.2
$Z13$		275.67 (Γ_1)		2.0		7.4		7.9
$Z12$		264.23 (Γ_2)		1.1		−3.3		−5.3
$Z11$		242.76 (Γ_2)		4.1		4.2		6.0
$Z10$		242.21 (Γ_1)		−4.0		0.7		−2.9
$Z9$		217.95 (Γ_2)		−13.6		2.2		−12.7
$Z8$		193.43 (Γ_1)		1.5		11.3		6.2
$Z7$		180.53 (Γ_2)		−4.8		−8.2		0.0
$Z6$		174.72 (Γ_1)		1.1		−20.9		−10.7
$Z5$		96.65 (Γ_1)		3.8		14.0		4.6
$Z4$		93.45 (Γ_2)		2.0		−16.2		−1.3
$Z3$	37.99 (Γ_1)	42.96 (Γ_1)	1.1	−0.6	2.0	0.3	0.8	−6.7
$Z2$	5.90 (Γ_2)	6.86 (Γ_2)	−3.2	−3.8	6.6	5.5	21.6	26.7
$Z1$	0 (Γ_1)	0 (Γ_1)	−10.9	−10.6	−14.0	−10.4	−31.2	−29.5

[a] The observed Zeeman shifts are anisotropic.

[b] "$\vec{H}\parallel b$" refers to magnetic field along the crystallographic b axis; "$\vec{H}\parallel c$" and "$\vec{H}\parallel a$" have similar meanings.

[c] Only three levels of this multiplet have been established from the temperature-dependent spectrum.

TABLE IV. Observed and calculated crystal-field splittings and Zeeman shifts for the levels of $^5G_4$ multiplet ($g_{\mathrm{eff}}=1.1233$)

	Zero-field position (in cm^{-1})		Zeeman shift at 9.05 T[a] (in cm^{-1})					
			$\vec{H}\parallel b$		$\vec{H}\parallel c$		$\vec{H}\parallel a$	
Level	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$K1$	81.24 (Γ_2)	79.61 (Γ_2)	0.6	1.4	1.5	2.9	1.2	2.8
$K2$	71.91 (Γ_1)	70.89 (Γ_1)	1.2	2.9	−1.7	0.6	0.7	1.1
$K3$	20.64 (Γ_1)	19.57 (Γ_1)	3.5	2.7	4.7	2.7	2.7	4.1
$K4$	17.70 (Γ_2)	18.40 (Γ_2)	−1.4	−0.6	−1.4	−2.6	0.7	−1.6
$K5$	2.46 (Γ_1)	3.41 (Γ_1)	−0.6	−1.5	0.6	0.6	−0.5	0.8
$K6$	−14.62 (Γ_1)	−16.10 (Γ_1)	−2.9	−0.8	3.2	4.9	−3.1	−3.6
$K7$	−27.98 (Γ_2)	−25.60 (Γ_2)	1.2	0.6	0.1	−6.2	−1.4	0.0
$K8$	−51.52 (Γ_1)	−52.15 (Γ_1)	−1.4	−3.3	−4.5	−0.7	0.7	−2.1
$K9$	−99.86 (Γ_2)	−98.04 (Γ_2)	0.0	−1.4	−2.8	−2.3	−1.4	−1.4

[a] Zeeman shifts for this multiplet are quite small.

TABLE V. Observed and calculated crystal-field splittings and Zeeman shifts for the levels of $^3K_8$ multiplet ($g_{\text{eff}} = 1.1064$).

	Zero-field position (in cm^{-1})		Zeeman shift at 9.05 T (in cm^{-1})					
			$\vec{H} \parallel b$		$\vec{H} \parallel c$		$\vec{H} \parallel a$	
Level	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$H1$	74.71 (Γ_1)	73.62 (Γ_1)	18.4	17.1	14.8	12.9	30.1	29.0
$H2$	70.10 (Γ_2)	71.10 (Γ_2)	7.7	7.3	−0.6	−2.3	−19.3[a]	−22.1[a]
$H3$	59.58 (Γ_1)	57.65 (Γ_1)	2.5	4.3	1.7	0.6	11.0[a]	12.5[a]
$H4$	39.12 (Γ_1)	38.08[b] (Γ_1)	−8.3[a]	−6.2	−12.3[a]	−10.3[a]	0.7	0.1
$H5$	36.68 (Γ_2)	39.27[b] (Γ_2)	−0.4[a]	−3.0	15.1	15.2	−8.1	−5.1
$H6$	9.19 (Γ_2)	7.59[b] (Γ_2)	16.1	13.4[a]	0.8	5.4	−3.5[a]	−1.9[a]
$H7$	2.78 (Γ_1)	9.47[b] (Γ_1)	10.8	1.0[a]	33.3[a]	25.3[a]	17.6	12.7
$H8$	0.75 (Γ_1)	2.92 (Γ_1)	−2.8[a]	−4.3[a]	−8.8	3.6	12.0[a]	11.4[a]
$H9$	−7.86 (Γ_2)	−6.44 (Γ_2)	9.5[a]	10.5[a]	−4.2	−0.7	7.2	3.0
$H10$	−16.15 (Γ_1)	−15.65[b] (Γ_1)	−3.0	4.9[a]	2.9	−3.7	2.6	−2.3
$H11$	−17.25 (Γ_2)	−15.33[b] (Γ_2)	−3.6	−0.1[a]	−0.6	−0.7	1.2	3.9
$H12$	−22.89 (Γ_1)	−27.37[b] (Γ_1)	−8.0	−2.0	−15.8[a]	−13.5[a]	−13.1[a]	−9.9
$H13$	−25.53 (Γ_2)	−23.21[b] (Γ_2)	−1.2	−2.6	−3.3	−6.1	5.6[a]	0.9
$H14$	−28.85 (Γ_2)	−29.77 (Γ_2)	−18.2	−19.4	−4.8[a]	−5.6[a]	−25.9[a]	−15.8[a]
$H15$	−51.40 (Γ_1)	−54.80 (Γ_1)	3.8	3.0	8.3	8.4	7.5[a]	10.8[a]
$H16$	−60.22 (Γ_2)	−62.27 (Γ_2)	−5.4	−6.0	−5.4	−5.1	−5.8	−3.6
$H17$	−63.54 (Γ_1)	−64.87 (Γ_1)	−17.2	−18.0	−27.1	−23.1	−19.4	−23.4

[a] The calculated order not in agreement with the observed.

[b] The levels cross as the applied field strength increases.

Zeeman interaction $H_z = \mu_\beta \vec{H} \cdot (\vec{L} + 2\vec{S})$ is no longer a small perturbation over the crystal-field interaction. The two interactions must be considered simultaneously as perturbations of comparable strengths. For Ho ion in HoF_3, the only symmetry axis is the crystallographic b axis. The fluorine ions surrounding each Ho ion have a reflection plane of symmetry perpendicular to this axis. If the magnetic field is applied parallel to this direction, the symmetry of the Hamiltonian (preferred direction in space) is maintained. In this case, the magnetic field interaction is diagonal in J_z. Its matrix elements can be expressed as

$$\langle JJ_z | L_z + 2S_z | JJ_z' \rangle = \delta(J_z, J_z') g_{\text{eff}} J_z \ ,$$

where g_{eff}, the effective Landé g factor of a state in intermediate coupling, is given by

$$g_{\text{eff}} = \nu g(\gamma J) = \sum_{\alpha,S,L} R^2(\alpha SLJ | \gamma J) g(SLJ) \ .$$

The coefficients $R(\alpha SLJ | \gamma J)$ are obtained from the diagonalization of the free ion energy matrices in the intermediate coupling scheme. The new energy matrices are the same as the CF energy matrices with the magnetic terms added to the diagonal elements.

Introduction of the magnetic field in a direction normal to the b axis, specifies an additional direction in space, consequently the CF representations are no longer good representations. One has now to solve a $(2J+1) \times (2J+1)$ matrix for each multiplet. This leads to a 17×17 complex matrix for $J = 8$ and a 9×9 complex matrix for $J = 4$. For "$\vec{H} \parallel c$"[16] the nonzero matrix elements of the magnetic interaction are given by

$$\langle JJ_z | L_x + 2S_x | JJ_z' \rangle$$
$$= \pm \tfrac{1}{2} g_{\text{eff}} [(J \mp J_z)(J \pm J_z + 1)]^{1/2} \delta(J_z', J_z \pm 1) \ .$$

The nonzero matrix elements for "$\vec{H} \parallel a$" are related to those for "$\vec{H} \parallel c$."

$$\langle JJ_z | L_y + 2S_y | JJ_z' \rangle = \mp i \langle JJ_z | L_x + 2S_x | JJ_z' \rangle \ .$$

These matrix elements appear in the off-diagonal positions. The Zeeman shifts can be calculated by diagonalizing these matrices with and without the magnetic interaction terms. These shifts were calculated for applied fields from 0 to 9.05 T.

VII. PRINCIPLE OF SPECTROSCOPIC STABILITY AND ZEEMAN SHIFTS

The "multiplet centers" of both excited multiplets are found to shift in an identical manner between 0 and 9.05 T applied magnetic field for each of the three orientation sets. In this particular context, the term "multiplet center" is defined as the arithmatic average of the energies (in cm^{-1}) of the transitions from the lowest ground-state level to each of the CF levels of the excited multiplet. Since the $^3K_8$ and $^5G_4$ multiplets are well separated from other Ho^{3+} multiplets, the principle of spectroscopic stability asserts that the centers of these multiplets should not shift with the application of an external magnetic field. This basically implies that no significant interaction is introduced between these multiplets and the neighboring ones as the magnetic field is switched on. This argument rests upon the smallness of the magnitudes of the magnetic interaction matrix elements among the neighboring multiplets relative to the energy separations among them. The matrix elements between $^3K_8$ and neighboring multiplets ($^5F_2$ and $^5G_6$) are identically zero because of the $\Delta J = 0, \pm 1$ selection rule for the Zeeman effect. Similarly $^5G_4$ will not interact with the nearby $^3K_7$ multiplet and the remaining multiplets are too far away in energy to have any substantial interaction with it. For these reasons, multiplet centers for $^5G_4$ and $^3K_8$ are expected to show complete stability. However, as the center of the multiplets measured from the lowest ground-state level do shift with the magnetic field, these shifts must be entirely attributed to the shift of the lowest ground-state level. Based on this assumption, a very good one indeed, the shifts of three lowest ground-state levels have been determined for the three orientations of the magnetic field. The validity of this assumption is borne out by the fact that for any given field direction, both excited multiplets (Table VI) give identical shifts of the levels of the ground multiplet. The actual shifts (after subtracting the ground level shift) of the individual Stark levels of the excited multiplets are shown in Tables IV and V. The assignment of shifts to individual levels at 9.05 T were made by following the lines as a function of magnetic field. It is reassuring to note that for "$\vec{H} \parallel b$," the Zeeman levels satisfy the trace test for Γ_1 and Γ_2 groups of levels separately.

VIII. GROUND MULTIPLET $^5I_8$

Only three levels of this multiplet have been identified from the temperature dependent absorption spectrum. The Zeeman shifts for these levels are relatively large and anisotropic. The observed shifts at 9.05 T for the ground level are -10.9, -14.0, and -31.2 cm^{-1} for magnetic field along b, c, and a axes, respectively. Similar variations are observed for the remaining levels as well. Table III compares the observed and calculated Zeeman shifts of these levels. We find excellent agreement for the ground and the first excited levels for all orientations of the magnetic field used in these experiments. The agreement for the second excited level is not so good, but the shifts for this level are quite small.

IX. $^3K_8$ MULTIPLET

Like the ground multiplet, $^3K_8$ also shows reasonably large and anisotropic Zeeman shifts at 9.05 T. In some cases, these shifts and the crystal-field splittings are found to have comparable magnitudes, justifying our simultaneous treatment of the magnetic and CF interactions. Although the electronic magnetic moment for all levels is zero in the absence of external field, a few levels, especially those near the top and the bottom of the multiplet show fairly large Zeeman shifts even at low applied field. The superscript "b" in Table V indicates observed and/or cal-

TABLE VI. Zeeman shifts of the three levels of the ground multiplet (obtained from the apparent shift of the center of gravity of the $^3K_8$ multiplet).

Ground-state level	Zero-field energy (cm^{-1})		Zeeman shift at 9.05 T (in cm^{-1})					
			$\vec{H}\parallel a$		$\vec{H}\parallel b$		$\vec{H}\parallel c$	
Lowest^a	0^b	0^c	-31.2^b	-31.2^c	-10.9^b	-10.9^c	-14.0^b	-14.0^c
Second^a	15.85^b	5.90^c	21.6^b	21.7^c	-3.2^b	-3.3^c	6.6^b	6.5^b
Third^a	37.99^b	37.99^c	0.8^b	0.8^c	1.1^b	1.0^c	2.0^b	2.0^c

[a] The Zeeman shifts for each of the three levels in the three directions of the magnetic field as obtained from the apparent shifts of the center of gravity of the $^3K_8$ and $^5G_4$ multiplets are identical in agreement with the principle of spectroscopic stability.

[b] Obtained from the apparent shift of the center of gravity of the $^3K_8$ multiplet.

[c] Obtained from the apparent shift of the center of gravity of the $^5G_4$ multiplet.

culated level crossings. We notice that the number of calculated level crossings does not always match the actually observed number of such crossings. This can happen in two ways whenever the observed and calculated order of two nearby Stark levels do not agree and if one of the following two conditions is satisfied. An apparent level crossing can be predicted by the calculations whenever in the above situation, the upper observed level has positive and the lower level has negative Zeeman shifts. On the other hand, a real crossing may not show up in the calculations if the signs of the Zeeman shifts are just the opposite. The former is the case for the apparent crossings of the pairs (H_6,H_7) and (H_{10},H_{11}) when the magnetic field is parallel to the b axis and the second conditions are responsible for the absence of the level crossings for the pair (H_{12},H_{13}) in "$\vec{H} \parallel a$" and the pair (H_4,H_5) in "$\vec{H} \parallel b$" are between levels of different symmetry. Out of the four level crossings observed for "$\vec{H} \parallel a$" and two for "$\vec{H} \parallel c$," only the crossings for the pair (H_4,H_7) in "$\vec{H} \parallel c$" is between levels of the same symmetry (Γ_1). Strictly, Γ_1, Γ_2 cease to have any meaning for the transverse Zeeman effect.

The experimental data are more certain for the levels near the top and bottom of the multiplet and extremely good agreement between the observed and calculated Zeeman shifts exists for these levels. In the absence of precise and complete analysis of the Zeeman data for intermediate magnetic fields, the assignment of Zeeman shifts for the levels near the center of the multiplet can be treated only tentatively at this stage. We may conclude this section by stating that the agreement between the calculated and observed shifts is excellent for the levels at the top and bottom of the multiplet and fair elsewhere.

X. $^5G_4$ MULTIPLET

The Zeeman shifts for this multiplet are comparatively small. No level crossings are predicted by the calculations and none are observed for any direction of the external field. The effective magnetic moments for practically all levels of this multiplet remain essentially zero up to a magnetic field of about 5 T and only towards the upper limit of the applied field, does one begin to observe characteristic "repulsion" among levels of the same symmetry. With the exception of two levels for "$\vec{H} \parallel c$" and three levels for "$\vec{H} \parallel a$," all observed and calculated Zeeman shifts agree in sign and the discrepancies in magnitude, if any, are within the range of disagreement of the CF least-squares fit. The only significant discrepancy exists for the level K_7 in the "$\vec{H} \parallel c$" case with -6.2 cm^{-1} calculated shift against 0.1 cm^{-1} actually observed. As has been pointed out earlier, the smallness of the Zeeman shifts in this case makes them more sensitive to the discrepancies in the calculated and observed crystal-field splittings. In fact, the level showing maximum discrepancy in Zeeman shift also shows maximum disagreement in the crystal-field analysis. It is not unreasonable to expect that such discrepancies might be considerably reduced if the CF fit can be improved by using better free-ion wave functions.

XI. MAGNETIC DIPOLE TRANSITIONS

The selection rules for the electric and magnetic dipole transitions are different only for light propagation along the b axis. The electric dipole operator in this case permits transitions between levels of same symmetry ($\Gamma_1 \rightarrow \Gamma_1$ and $\Gamma_2 \rightarrow \Gamma_2$). However, at 1.6 K, $\Gamma_1 \rightarrow \Gamma_2$ type transitions are also observed. These transitions, though always weaker than the $\Gamma_1 \rightarrow \Gamma_1$ type transitions are considerably stronger for the $^3K_8$ multiplet than for the $^5G_4$ multiplet. The appearance of these lines could be understood in terms of slight misalignment of the crystal with respect to the beam axis. However, a more plausible explanation is that these are magnetic dipole transitions since in the absence of appreciable J mixing such transitions are more likely to take place for the $^3K_8$ multiplet than for the $^5G_4$ multiplet in view of the selection rule $\Delta J = 0, \pm 1$ for the magnetic dipole transitions.

XII. HYPERFINE INTERACTION

Because of the low Ho^{3+} site symmetry in HoF$_3$, all electronic states are singlets with zero magnetic moment and hence first-order hyperfine interaction is identically zero in the absence of external magnetic field. The zero-field spectrum at 1.6 K consists of mostly sharp lines. Some of the lines are no more than a few tenths of a cm^{-1} wide indicating the absence of hyperfine broadening. However, a few lines in the $^3K_8$ multiplet are broad with sharp cutoff on both sides indicating possible incipient hyperfine structure due to higher-order magnetic hyperfine interaction. These lines correspond to levels which show relatively large Zeeman shifts. The Zeeman measurements have been carried out at 20 K where the overall line broadening would make it difficult for the hyperfine structure to be resolved, even if it was present.

XIII. DISCUSSION OF RESULTS

A 15 parameter least-squares fit has been carried out to 26 Stark levels of HoF$_3$ neglecting J mixing. A rms deviation of 2.15 cm^{-1} so obtained is quite satisfactory. The observed polarizations are in complete agreement with the site symmetry. The calculated positions of the first two excited levels of the ground multiplet agree with the values inferred from the temperature-dependence spectrum. The agreement between the observed and calculated Zeeman shifts at 9.05 T for most levels is also very good. Disagreement remains for some levels of the $^3K_8$ multiplet. The absolute Zeeman shifts for such levels are, however, small. For magnetic fields of the order of 10 T, the Zeeman shifts of levels sometime exceed their zero magnetic field separations and unless the discrepancies (however small) among calculated and observed positions of the Stark levels are removed, the interpretation of Zeeman shifts and accompanying level crossings is not going to be unambiguous. The use of free ion wave functions appropriate to HoF_3 should help reduce whatever discrepancies remain. The crystal-field calculations place the ground level at 200 cm^{-1} below the center of gravity of the ground multiplet. Lowering the observed centers of gravity of the multiplets at 1.6 K by this amount leaves the calculated "free-ion" positions of $^5G_4$ and $^3K_8$ multiplets lower than their observed positions by 191 and 133 cm^{-1}, respectively. This is a fairly large discrepancy and "free-ion" wave functions obtained by using Rajnak and Krupke's parameters for $LaCl_3$ are not expected to be accurate for HoF_3. A least-squares analysis to the free-ion energy levels for HoF_3 is however not possible at the moment for lack of sufficient experimental data.

XIV. CONCLUSIONS

Absorption spectrum and Zeeman effect at 9.05 T for the $^5I_8 \rightarrow {}^3K_8$, $^5G_4$ transitions in HoF_3 have been obtained and analyzed in the limit in which the magnetic and crystal-field interactions are comparable in strength. A set of crystal-field parameters appropriate for C_{1h} symmetry of Ho^{3+} have been obtained. Only the axial parameters B_0^2, B_0^4, and B_0^6 have unique values in this low-symmetry case, the remaining 12 parameters depend upon the choice of x, y axes which are not fixed by the site symmetry. All such sets of parameters are, however, equivalent as they give identical "rms" deviation. The principal of spectroscopic stability has been used to obtain absolute second- (and perhaps higher) order magnetic shifts of individual crystal-field levels. The $^5G_4$ multiplet shows reasonably well separated CF levels and rather small Zeeman shifts. On the other hand, the $^3K_8$ and $^5I_8$ multiplets have rather closely positioned CF levels and fairly large Zeeman shifts. The large Zeeman shifts for the latter multiplets are consistent with the relatively large angular moments associated with them.

We acknowledge many useful discussions with Dr. W. J. Haas and the help provided by W. L. Sutherland in obtaining spectra. This work was supported by the U. S. Department of Energy, Contract No. W-7405-Eng-82, Division of Basic Energy Sciences, budget code AK-02-02-2.

---

[*] On leave from the Indian Institute of Technology, Kanpur, India.

[†] Fegles Power Serice Corp., Minneapolis, Minn.

[1] B. G. Wybourne, *Spectroscopic Properties of Rare-Earths* (Interscience, New York, 1965).

[2] G. H. Dieke, *Spectra and Energy Levels of Rare-Earth Ions in Crystals* (Interscience, New York, 1968).

[3] S. Hüfner, *Optical Spectra of Transparent Rare-Earth Compounds* (Academic, New York, 1978).

[4] F. H. Spedding, M. T. Rothwell, W. J. Haas, and W. L. Sutherland, J. Chem. Phys. 48, 4843 (1968).

[5] Joachim Stöhr and J. B. Gruber, Chem. Phys. 7, 336 (1975).

[6] D. Bauerle, G. Borstel, and A. J. Sievers, J. Appl. Phys. 49, 676 (1978).

[7] S. S. Bishton and D. J. Newman, J. Phys. C 3, 1753 (1970).

[8] B. R. Judd, Phys. Rev. Lett. 39, 242 (1977).

[9] H. M. Crosswhite, H. Crosswhite, N. Edelstein, and K. Rajnak, J. Chem. Phys. 67, 3002 (1977); W. T. Carnall, H. Crosswhite, H. M. Crosswhite, Jan. P. Hessler, N. Edelstein, J. G. Conway, G. V. Shalimoff, and R. Sarup, *ibid.* 72, 5089 (1980); H. M. Crosswhite, H. Crosswhite, W. T. Carnall, and A. P. Paszek, *ibid.* 72, 5103 (1980).

[10] K. Rajnak and W. F. Krupke, J. Chem. Phys. 46, 3532 (1967).

[11] B. Bleany, Physica 69, 317 (1973).

[12] J. B. Baltison *et al.*, Phys. Lett. 55, 173 (1975).

[13] Allan Zalkin and D. H. Templeton, J. Am. Chem. Soc. 75, 2453 (1953).

[14] F. H. Spedding, W. J. Haas, W. L. Sutherland, and C. A. Eckroth, J. Chem. Phys. 42, 981 (1965).

[15] D. N. Olsen *et al.*, J. Chem. Phys. 55, 4471 (1971).

[16] "$H \parallel c$" means H parallel to c axis.