

## Magnetic properties in some holmium compounds

M. Saha and D. Ghosh

*Magnetism Department, Indian Association for the Cultivation of Science, Calcutta 700 032, India*

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In continuation of our previous studies on the magnetic susceptibilities in  $\text{Tb}(\text{OH})_3$  and  $\text{Dy}(\text{OH})_3$ , this work reports the results of a study of the isomorphous  $\text{Ho}(\text{OH})_3$  crystalline complex. Using the crystal-field parameters (CFP) reported from earlier optical studies, calculations were made for the principal magnetic susceptibilities  $K_{\parallel}$  and  $K_{\perp}$ , their anisotropies ( $K_{\parallel} - K_{\perp}$ ), and their average values  $\bar{K}$ ,  $g$  values, the crystal-field splitting of the ground  $^5I_8$  term, and the Schottky specific heat  $C_s$  for  $\text{Ho}(\text{OH})_3$ ,  $\text{Ho}(\text{ES})_3$ , and  $\text{HoCl}_3$  between 300 and 80 K. The study showed that the anisotropy ( $K_{\parallel} - K_{\perp}$ ) was much more sensitive than  $\bar{K}$  or  $g$  values to the values of the CFP. The effect of variation of CFP on ( $K_{\parallel} - K_{\perp}$ ) was studied, and interesting limiting values for some of the CFP were obtained; this is applicable to any crystalline complexes of  $\text{Ho}^{3+}$  in a  $C_{3h}$  field.

### I. INTRODUCTION

We reported earlier the results of our studies on magnetic susceptibilities in single crystals of  $\text{Tb}(\text{OH})_3$  (Ref. 1) and  $\text{Dy}(\text{OH})_3$ .<sup>2</sup> The principal susceptibilities  $K_{\parallel}$  and  $K_{\perp}$  were obtained from the simultaneous measurements of magnetic anisotropies ( $K_{\parallel} - K_{\perp}$ ) and the average susceptibilities  $\bar{K} = \frac{1}{3}(K_{\parallel} + 2K_{\perp})$  in the temperature range 300–80 K. Using these experimental results, we estimated the corresponding crystal-field parameters (CFP) by varying them individually to get the best fit in this temperature range. We observed that the values of CFP thus obtained differed from those reported from earlier optical studies, the deviation being prominent in  $\text{Dy}(\text{OH})_3$ . Such a type of discrepancy between the CFP values as obtained from the optical and magnetic data was also reported<sup>3</sup> in  $\text{Dy}(\text{ES})_3$ . It is to be mentioned that for these rare-earth complexes the spectra are very complicated, especially at higher energies. Consequently, assignments of the levels and the determination of the CFP from such studies are not always reliable. Furthermore, it is found that in many instances the crystal-field splitting is markedly improved if different sets of CFP are used for different multiplets.<sup>4</sup> We have noted<sup>1,2</sup> that the magnetic anisotropy, in particular, and its thermal variations are very sensitive to the values of CFP chosen. Consequently, this property can be studied to determine accurately the CFP for the ground term. As a continuation of previous work,<sup>1,2</sup> we have calculated ( $K_{\parallel} - K_{\perp}$ ),  $\bar{K}$ ,  $g$  values, and the Schottky specific heat  $C_s$  of  $\text{Ho}(\text{OH})_3$ . Since experimental data on the magnetic anisotropies at high temperatures are not available for this crystal, we studied here the effect of variations of CFP on ( $K_{\parallel} - K_{\perp}$ ) in the temperature range 300–80 K.

CFP are also reported from optical spectra on  $\text{Ho}^{3+}$  in  $\text{LaCl}_3$  (Refs. 5 and 6) and  $\text{Ho}(\text{ES})_3$ .<sup>7,8</sup> We have calculated the principal magnetic susceptibilities,  $g$  values, and specific heat  $C_s$  for these complexes also. Similar type of calculations have been reported<sup>9</sup> for several rare-earth hydroxides; however, the effect of CFP variation has not been considered therein. Since the CFP in these three  $\text{Ho}^{3+}$  compounds differ widely, it was expected that the magnetic and thermal properties would differ.

### II. THEORY

The ground multiplet of the  $\text{Ho}^{3+}$  ion ( $4f^{10}$ ) is  $^5I_8$ , and the first excited term is about  $5030 \text{ cm}^{-1}$  higher.<sup>10</sup> The point-group symmetry at the rare-earth-ion site of the  $\text{Ho}^{3+}$  complexes considered is  $C_{3h}$ . A  $C_{3h}$  crystalline field splits the ground term into singlets and non-Kramers doublets. In the static-crystal-field model the Hamiltonian has the familiar form

$$H_c = B_2^0 V_2^0 + B_4^0 V_4^0 + B_6^0 V_6^0 + B_6^6 V_6^6 \quad (1)$$

The matrix elements of the crystal-field operators under different  $J$  manifolds in the intermediate coupling scheme have been worked out and tabulated by Dieke.<sup>11</sup> The resulting matrices were diagonalized to obtain the related eigenvalues and eigenfunctions. The energy-level schemes for the three  $\text{Ho}^{3+}$  compounds are shown in Table I ( $\mu$  is the crystal quantum number).

The magnetic-field matrix elements were then calculated using the Hamiltonian

$$H_m = g_0 \beta \vec{H} \cdot \vec{J} \quad (2)$$

where  $g_0 = 1.241$ .<sup>10</sup> The gram ionic or molar suscepti-

TABLE I. Crystal-field splittings of the ground-state multiplet  $^5I_8$  in some holmium compounds.

Ho <sup>3+</sup> in Y(OH) <sub>3</sub> <sup>a</sup>		Ho <sup>3+</sup> in LaCl <sub>3</sub> <sup>b</sup>		Ho(ES) <sub>3</sub> <sup>c</sup>	
$\mu$	Energy (cm <sup>-1</sup> )	$\mu$	Energy (cm <sup>-1</sup> )	$\mu$	Energy (cm <sup>-1</sup> )
$\pm 1$	-174.56	$\pm 1$	-107.64	0	-127.39
0	-162.93	0	-95.11	$\pm 1$	-127.06
0	-98.84	0	-61.60	0	-88.06
$\pm 1$	-71.61	$\pm 1$	-40.60	$\pm 1$	-58.35
$\pm 2$	-46.24	$\pm 2$	-18.03	$\pm 2$	-36.30
3	-26.44	3	-3.12	3	-23.30
0	+46.75	0	+10.38	0	+34.48
$\pm 2$	+48.74	$\pm 2$	+43.61	$\pm 1$	+67.13
$\pm 1$	+100.14	$\pm 1$	+49.35	$\pm 2$	+73.15
$\pm 2$	+168.66	$\pm 2$	+94.27	$\pm 2$	+116.99
3	+191.20	3	+107.54	3	+133.13
	$B_2^0 = 246 \text{ cm}^{-1}$		$B_2^0 = 113.6 \text{ cm}^{-1}$		$B_2^0 = 125 \text{ cm}^{-1}$
	$B_4^0 = -57 \text{ cm}^{-1}$		$B_4^0 = -33.9 \text{ cm}^{-1}$		$B_4^0 = -79 \text{ cm}^{-1}$
	$B_6^0 = -40 \text{ cm}^{-1}$		$B_6^0 = -27.8 \text{ cm}^{-1}$		$B_6^0 = -30 \text{ cm}^{-1}$
	$B_6^6 = 544 \text{ cm}^{-1}$		$B_6^6 = 276.7 \text{ cm}^{-1}$		$B_6^6 = 391 \text{ cm}^{-1}$

<sup>a</sup>P.D. Scott, Ph.D. thesis, Yale University, 1970 (unpublished).<sup>b</sup>References 5 and 6.<sup>c</sup>References 7 and 8.

bilities were obtained by means of Van Vleck's formula<sup>12</sup>

$$K_j = \frac{N}{Z} \sum_i [(E_i^1)^2/kT - 2E_i^2] \exp(-E_i^0/kT) \quad (j = \parallel \text{ or } \perp), \quad (3)$$

where  $E_i^0$  is the energy of the  $i$ th level when  $H=0$  and  $Z = \sum_i \exp(-E_i^0/kT)$ ;  $E_i^1$  and  $E_i^2$  are the first- and second-order perturbation-energy eigenvalues corresponding to  $H$  parallel or perpendicular to the  $C_{3h}$  symmetry axis. The magnetic anisotropy ( $K_{\parallel} - K_{\perp}$ ) and the mean susceptibility  $\bar{K} = \frac{1}{3}(K_{\parallel} + 2K_{\perp})$  were obtained from Eq. (3).

The  $g$  values are given by the expressions

$$g_{\parallel} = 2 \langle \psi_1 | g_0 J_z | \psi_1 \rangle, \quad (4)$$

$$g_{\perp} = 2 \langle \psi_1 | g_0 J_x | \psi_1' \rangle$$

for the lowest level. In the present case  $g_{\perp} = 0$ .

The Schottky specific heat  $C_s$  was calculated from the relation

$$C_s/R = \frac{1}{Z^2} \left[ Z \sum_i (E_i^0/kT)^2 \exp(-E_i^0/kT) - \left( \sum_i (E_i^0/kT) \exp(-E_i^0/kT) \right)^2 \right]. \quad (5)$$

The susceptibilities  $K_{\parallel}$  and  $K_{\perp}$ ,  $g$  values, and  $C_s$  are thus functions of  $B_2^0$ ,  $B_4^0$ ,  $B_6^0$ , and  $B_6^6$ .

### III. RESULTS AND DISCUSSION

Table I shows that the ground-state multiplet  $^5I_8$  in these Ho<sup>3+</sup> complexes splits into singlets and non-Kramers doublets under a crystal field of  $C_{3h}$  symmetry, the overall splitting being 215.17, 260.52, and 365.76 cm<sup>-1</sup>, respectively, for the chloride, ethylsulfate, and the hydroxide. In these three compounds, although the CFP vary widely, we find that the crystal-field level  $|\mu = \pm 1\rangle$  prefers to be lowest. In Ho(ES)<sub>3</sub> it is only 0.33 cm<sup>-1</sup> above the lowest level  $|\mu = 0\rangle$  (for which  $g$  values are zero) and, because of this near degeneracy with the  $|\mu = \pm 1\rangle$  level, the  $g$  values are nearly the same as in the other two compounds [ $g_{\parallel} = 15.24, 15.27,$  and  $16.01$  for Ho(ES)<sub>3</sub>, Ho<sup>3+</sup> in Y(OH)<sub>3</sub>, and Ho<sup>3+</sup> in LaCl<sub>3</sub>, respectively]. We have noted that several sets of CFP exist which make a particular level lowest, and as a result the  $g$  values are nearly the same. Consequently, paramagnetic-resonance studies in these compounds are not sufficient for determining CFP exactly. The mean susceptibilities  $\bar{K}$ , being an average effect, are also inadequate in this respect. However, inspection of Fig. 1 shows that there is a more sensitive dependence of the anisotropy values on the absolute values of these CFP. This is because the principal susceptibilities  $K_{\parallel}$  and  $K_{\perp}$ , and hence their difference, depend not only on the ground term but also on the relative positions of the higher levels and their contribution to the magnetic susceptibilities. Since the details of the  $^5I_8$  level splitting are sensitively affected

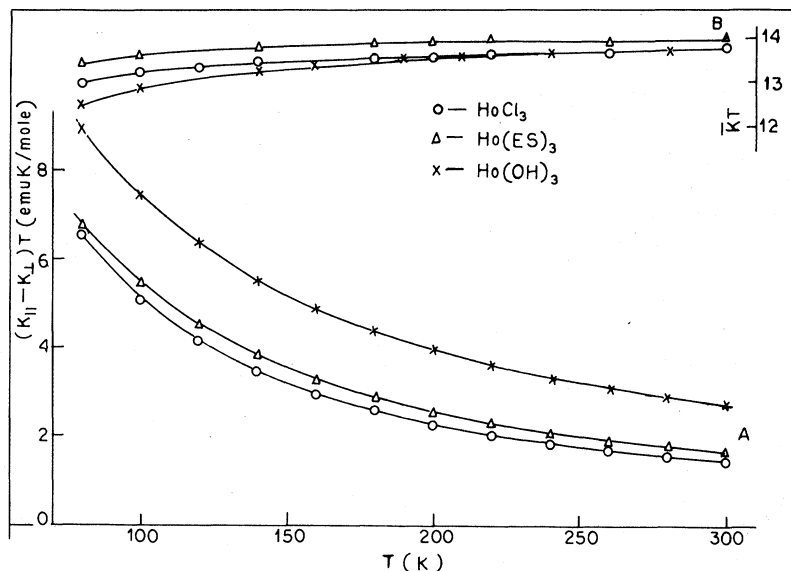


FIG. 1. Thermal variation of magnetic anisotropy  $(K_{\parallel} - K_{\perp})T$  and the mean susceptibility  $\bar{K}$  [O— $\text{HoCl}_3$ ,  $\Delta$ — $\text{Ho}(\text{ES})_3$ ,  $\times$ — $\text{Ho}(\text{OH})_3$ ].

by small variations in each of the CFP, such variations will affect not only the room-temperature values of  $(K_{\parallel} - K_{\perp})$  but also their thermal variations.

In order to determine the dependence of the magnetic anisotropies in  $\text{Ho}^{3+}$  in a  $C_{3h}$  field on CFP, we varied systematically each of these parameters within

reasonable limits. For example, we varied  $B_2^0$  from 250 to 100  $\text{cm}^{-1}$ ,  $B_4^0$  from  $-30$  to  $-60$   $\text{cm}^{-1}$ ,  $B_6^0$  from  $-20$  to  $-50$   $\text{cm}^{-1}$ , and  $B_6^6$  from 550 to 250  $\text{cm}^{-1}$ . These variations are shown in Figs. 2(a)–2(d). It is apparent from Figs. 2(a) and 2(b) that, by reducing the numerical values of  $B_2^0$ ,  $B_4^0$ , and  $B_6^0$ , the

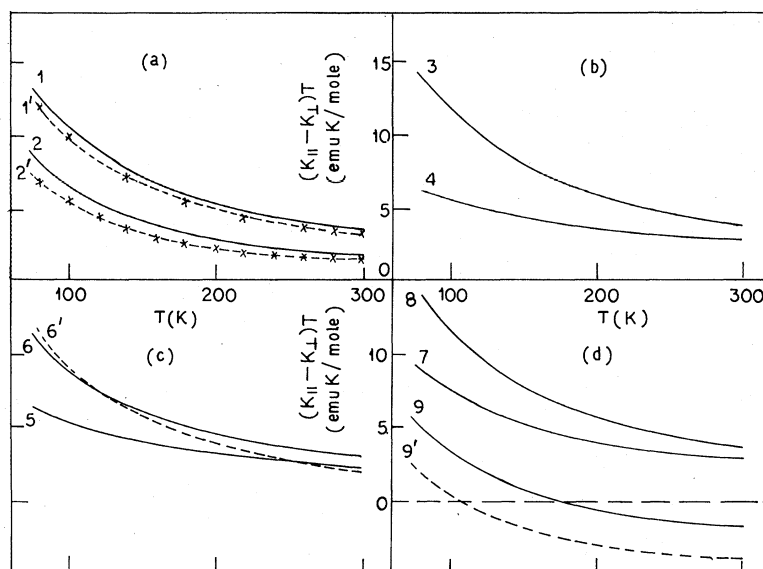


FIG. 2. Effect of CFP ( $\text{cm}^{-1}$ ) variation on  $(K_{\parallel} - K_{\perp})T$ : (a)  $B_2^0$  and  $B_4^0$  variation:  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -40$ ,  $B_6^6 = 400$  (curve 1);  $B_2^0 = 250$ ,  $B_4^0 = -30$ ,  $B_6^0 = -40$ ,  $B_6^6 = 400$  (curve 1');  $B_2^0 = 100$ ,  $B_4^0 = -60$ ,  $B_6^0 = -40$ ,  $B_6^6 = 400$  (curve 2);  $B_2^0 = 100$ ,  $B_4^0 = -30$ ,  $B_6^0 = -40$ ,  $B_6^6 = 400$  (curve 2'). (b)  $B_6^0$  variation:  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -50$ ,  $B_6^6 = 450$  (curve 3);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -20$ ,  $B_6^6 = 450$  (curve 4). (c)  $B_6^6$  variation:  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -30$ ,  $B_6^6 = 550$  (curve 5);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -30$ ,  $B_6^6 = 350$  (curve 6);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -30$ ,  $B_6^6 = 250$  (curve 6'). (d)  $B_6^6$  variation:  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -40$ ,  $B_6^6 = 550$  (curve 7);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -40$ ,  $B_6^6 = 350$  (curve 8);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -40$ ,  $B_6^6 = 250$  (curve 9);  $B_2^0 = 250$ ,  $B_4^0 = -60$ ,  $B_6^0 = -50$ ,  $B_6^6 = 250$  (curve 9').

anisotropy in general decreases between 300 and 80 K, although the rate of decrease is different in different cases. Figure 2(c) shows a different feature. With  $B_2^0 = 250 \text{ cm}^{-1}$ ,  $B_4^0 = -60 \text{ cm}^{-1}$ , and  $B_6^0 = -30 \text{ cm}^{-1}$  the anisotropy increases when  $B_6^0$  decreases from 550 to 350  $\text{cm}^{-1}$ . But when  $B_6^0 = 250 \text{ cm}^{-1}$ , the anisotropy (dotted line 6) is smallest around room temperature, then increases sharply on cooling and becomes highest below 110 K. In Fig. 2(d) a similar characteristic is observed when we vary  $B_6^0 = -40 \text{ cm}^{-1}$  [keeping  $B_2^0$  and  $B_4^0$  the same as before in Fig. 2(c)]; i.e., the anisotropy increases when  $B_6^0$  decreases from 550 to 350  $\text{cm}^{-1}$ ; however, when  $B_6^0 = 250 \text{ cm}^{-1}$ , (curve 9)  $K_{\parallel} - K_{\perp}$  is negative (i.e.,  $K_{\perp} > K_{\parallel}$ ) around room temperature. On cooling, the anisotropy decreases until around 173 K at which point the anisotropy is zero. This implies that for such a set of CFP values the magnetic tensors in a highly anisotropic  $\text{Ho}^{3+}$  compound with  $K_{\perp} > K_{\parallel}$ , becomes isotropic at some low temperature, and on further cooling the anisotropy reappears but with  $K_{\parallel} > K_{\perp}$ . This behavior of the anisotropy is again observed in curve 9, corresponding to  $B_6^0 = -50 \text{ cm}^{-1}$  with the other CFP being the same as before; the only difference is that  $K_{\perp}$  remains greater than  $K_{\parallel}$  over a wider range of temperatures. Thus the effect of increasing  $|B_6^0|$  beyond 30  $\text{cm}^{-1}$  is that the calculated anisotropy behaves anomalously between 300 and 80 K. It may be remarked here that to make  $K_{\parallel} > K_{\perp}$  with  $|B_6^0| > 30 \text{ cm}^{-1}$  throughout this range of temperature would require the other parameters to be increased by more than 100%.

Magnetic-anisotropy measurements have been reported for  $\text{Ho}(\text{ES})_3$  between 300 and 4 K,<sup>8</sup> with  $K_{\parallel} - K_{\perp} = 5800 \times 10^{-6} \text{ emu}$  at 290 K. The magnetic and optical data for  $\text{Ho}(\text{ES})_3$  were fitted with the same set of parameters. Low-temperature studies (below 20 K) on the hydroxide have shown that  $K_{\parallel} > K_{\perp}$ . No report on the magnetic susceptibilities

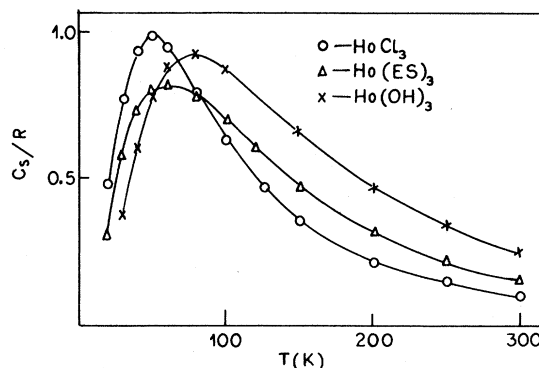


FIG. 3. Thermal variation of Schottky specific heat  $C_s/R$  [ $\circ - \text{HoCl}_3$ ,  $\Delta - \text{Ho}(\text{ES})_3$ ,  $\times - \text{Ho}(\text{OH})_3$ ].

or their anisotropies in the higher-temperature range is available for the chloride or the hydroxide compounds. However, the possibility of  $K_{\perp} > K_{\parallel}$  at higher temperatures cannot be ruled out since, from our earlier observations,<sup>6,7</sup> we have found that the CFP reported from optical studies may not satisfy the magnetic data in this temperature region. Consequently, measurements of the magnetic anisotropies in  $\text{HoCl}_3$  and  $\text{Ho}(\text{OH})_3$  are desirable, and in such cases the results of our calculations will be helpful in determining the actual set of CFP for these or any other  $\text{Ho}^{3+}$  compounds having  $C_{3h}$  symmetry.

Figure 3 shows the calculated Schottky specific heat  $C_s$  for the three  $\text{Ho}^{3+}$  compounds. Experimental data in this temperature range are not available since all the earlier work reported  $C_s$  near the critical regions. It is to be noted that in these  $\text{Ho}^{3+}$  compounds the specific-heat curves show peaks between 50 and 80 K. The more anisotropic system has a maximum in the cooler region, but the magnitude of  $C_s^{\text{max}}$  is, however, dependent on other factors which are not discussed in this work.

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