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Magnetic measurement and a crystal field investigation of $Ho_2(SO_4)_3.8H_2O$ crystal

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Abstract. Magnetic measurements of octahydrated Holmium sulphate have been carried out in the temperature range 80-300 K and analysis of the results has been performed using a crystal field of C_{1h} symmetry which is the major point symmetry of the ion inferred from the polarized optical absorption studies. The most rigorous approach of direct diagonalization of the Hamiltonian matrix constructed in the complete basis of states belonging to all atomic terms of the Ho^{3+} ion has been employed. A new set of crystal field parameters some of which are widely different from that reported from optical studies, has been evaluated for consistent interpretation of both the magnetic and optical data.

PACS. 71.70.Ch Crystal and ligand fields – 75.10.Dg Crystal-field theory and spin Hamiltonians

1 Introduction

The information obtained from the observation on optical spectra, epr, specific heat and hyperfine interactions (from Mössbauer spectra) of the rare earth (RE) ions in crystalline salts may be supplemented by magnetic susceptibility and anisotropy experiments. The latter studies provide a useful check on the validity of the crystalline electric field parameters obtained from other experiments mentioned above. Therefore, a unified study of the different physical quantities within a single theoretical framework is necessary. Magnetic measurements on $Ho_2(SO_4)_3.8H_2O$ crystals have not yet been done. In the present paper we report the measurements on the principal magnetic susceptibilities and hence anisotropies of $Ho_2(SO_4)_3.8H_2O$ single crystals in the range of temperature 80 to 300 K and present a unified description of the optical and magnetic properties with a single set of parameters.

In connection with the analysis of the experimental data we would like to mention the work of Bleancy *et al.* [1] which enables one to correlate the ionic with the crystalline anisotropies in a monoclinic crystal under uniaxial symmetry of the ion. Knowledge of any two of the three principal crystalline anisotropies can immediately give the principal ionic anisotropy in the case of uniaxial symmetry of the ion in a monoclinic crystal [1] even without the knowledge of the relative orientation of the ionic and crystalline tensors.

We shall attempt to interpret the magnetic susceptibility and anisotropy behaviour of holmium sulphate octahydrate in a way consistent with the available spectroscopic data [2]. The theoretical analysis of the magnetic data has been performed with a site symmetry of C_{1h} which has been inferred from the study of polarized optical spectra by Stöhr and Gruber [2].

2 Experimental

2.1 Preparation of $Ho_2(SO_4)_3.8H_2O$ single crystals

Sample of holmium sulphate octahydrate was a gift from Prof. M Kato of Aichi Prefectural University, Japan. Powdered sample of Ho-sulphate octahydrate was dissolved in cold water and one or two drops of pure concentrated sulphuric acid was added to facilitate crystallisation. Single crystals were obtained by slow evaporation of the solution and recrystallized several times to obtain the pure form. The crystals are needle-shaped, about 5 mm × 1.5 mm × 1 mm in size and of honey yellow colour. The crystals were finely powdered for the mean susceptibility measurement.

2.2 Correlation between the crystalline and ionic anisotropies

The crystals are monoclinic with space group C^6_{2h}. The unit cell dimensions [3] are $a = 13.42$ Å, $b = 6.69$ Å, $c = 18.19$ Å and the monoclinic angle $\beta = 102\,°6'$; the diad axis is along b. One of the three principal crystalline susceptibilities χ_1, χ_2, χ_3 coincides with the b axis and it is denoted by χ_3, χ_1 and χ_2 lie in the ac plane, χ_1 being taken to be greater than χ_2 by convention. For uniaxial

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symmetry of the ion, the principal ionic susceptibilities are denoted by $K_\parallel$ and $K_\perp$ which lie parallel and perpendicular to the symmetry axis z respectively *i.e.* $K_\parallel = K_z$, $K_\perp = K_x = K_y$.

The correlation between ionic and crystalline anisotropies in a monoclinic crystal with uniaxial symmetry of the ion can be obtained from the works of Bleancy *et al.* [1]. Noting that there are two rare earth ions per formula unit the relevant relations are given as follows. When the symmetry axis of the ion lies in the $\chi_2\chi_3$ plane , $K_\perp > K_\parallel$ and

$$K_\perp - K_\parallel = 1/2\left[(\chi_1 - \chi_2) + (\chi_1 - \chi_3)\right]. \tag{1}$$

On the other hand when the symmetry axis lies in the $\chi_1\chi_3$ plane, $K_\parallel > K_\perp$ and

$$K_\parallel - K_\perp = (\chi_1 - \chi_2) - 1/2\,(\chi_1 - \chi_3). \tag{2}$$

If the angle made by the symmetry axis with the ac plane be denoted by ϕ [1,4,5] we have

$$\cos 2\phi = [(\chi_1 - \chi_2) - (\chi_1 - \chi_3)]/[(\chi_1 - \chi_2) + (\chi_1 - \chi_3)] \quad \text{when } K_\perp > K_\parallel \tag{3}$$

$$\cos 2\phi = (\chi_1 - \chi_3)/[2\,(\chi_1 - \chi_2) - (\chi_1 - \chi_3)] \quad \text{when } K_\parallel > K_\perp. \tag{4}$$

Equations (3, 4) are used to test whether $K_\parallel > K_\perp$. For the holmium sulphate octahydrate crystals, the experimental results indicate that $K_\perp > K_\parallel$ at all temperatures, since for the other case (*i.e.* $K_\parallel > K_\perp$) $\cos 2\phi$ given by equation (4) assumes an absurd value of magnitude greater than unity. Further, we have the general relation between the crystalline and mean ionic susceptibilities

$$\overline{K} = (K_\parallel + 2K_\perp)/3 = \overline{\chi}/2. \tag{5}$$

2.3 Magnetic measurement

The crystals grow in such a way that no crystallographic planes or axes excepting the symmetry axis b could be identified. Hence conventional method of anisotropy measurement with an anisotropy balance [6] which requires identification of more than one crystallographic axis or plane could not be used for the magnetic anisotropy measurement. Therefore we first determined the values of χ_1, χ_2 and χ_3; then calculated their differences to get the principal crystalline anisotropies.

Magnetic susceptibility measurements for both crystals and powdered sample were made in a jewel mounted susceptibility balance [7] at a magnetic field of about 4 kgauss. First of all the mean magnetic susceptibility $\overline{\chi}$ of the powdered sample is measured. Then the monoclinic crystal is suspended with the b axis vertical in a magnetic field and the freely suspended crystal sets its maximum susceptibility (χ_1) in the ac plane along the direction of the magnetic field (horizontal) and the susceptibility is measured. We thus obtain χ_1. Next to measure χ_3, the crystal is suspended with the b axis horizontal. Biswas and Bhattacharyya [8] devised a specially designed suspension system for the susceptibility balance to align the crystal in any desired direction parallel to the magnetic field. Using this suspension system, we measured the susceptibility along b axis *i.e.* χ_3. Knowing χ_1 and χ_3, χ_2 can be evaluated from the mean susceptibility using the relation $\overline{\chi} = 1/3\,(\chi_1 + \chi_2 + \chi_3)$. All the measurements were carried out in a liquid bath type cryostat. An automatic temperature controller was used to keep the temperature steady at any desired value within an accuracy of ±0.1 K. The estimated accuracy of the susceptibility measurement is $\sim 5\%$.

3 Theoretical calculation

The effective Hamiltonian for the crystal field energy level calculation of the Ho^{3+} ion in the absence of the external field is given by

$$H_{\mathrm{eff}} = H_{\mathrm{r}}^{ij} + H_{\mathrm{so}} + H_{\mathrm{cf}} \tag{6}$$

where H_{r}^{ij} is the electrostatic repulsion energy, H_{so} is the spin orbit interaction energy and H_{cf} is the crystal field energy. Considering the point group symmetry $\mathrm{C}_{1\mathrm{h}}$ [2] for the holmium sulphate ion the crystal field Hamiltonian is written in terms of tensor operators C_q^k as defined by Judd [9] and Wybourne [10] as

$$H_{\mathrm{cf}} = \sum_{\substack{j\\k=2,4,6\\0<q\leq k}} \left\{ B_{k0}\left(C_0^k\right)_j + B_{kq}\left[\left(C_q^k\right)_j + \left(C_{-q}^k\right)_j\right] + iB_{k-q}\left[\left(C_q^k\right)_j - \left(C_{-q}^k\right)_j\right]\right\} \tag{7}$$

where the sum over j includes all the $4f$ electrons. Terms involving both odd q and even k are not allowed for $\mathrm{C}_{1\mathrm{h}}$ point group symmetry [9,10] and there exist fifteen crystal field parameters. The matrix of the total Hamiltonian is constructed with all the states arising out of all the atomic terms [10] of f^{10} ion as the basis states in the $|SLJJ_z\rangle$ scheme. The energy matrix of Ho^{3+} ion comes out to be of the order 1001×1001. The matrix is then diagonalized with the help of a computer (Vax 3400). The fifteen crystal field parameters B_{kq}'s are adjusted by the computer to fit the observed crystal field levels and magnetic data with the calculated ones. The diagonalization yields seventeen Stark levels from the ground manifold which are all singlets. These are the only levels considered for the calculation of the magnetic susceptibility. The next higher multiplet is of the order of $5\,000$ cm^{-1} above the ground multiplet and contributes negligibly to the magnetic susceptibility.

Zeeman perturbation is now applied on the lowest seventeen crystal field states and the paramagnetic susceptibility upto second order along and perpendicular to the symmetry axis of the ion at different temperatures is calculated using Van Vleck's formula [11]. The theoretical calculations of the principal ionic susceptibilites K_x, K_y

and K_z indicate that K_x and K_y are equal, since the matrix elements of $(L_x + 2S_x)$ and $(L_y + 2S_y)$ between the states represented by $|LSJJ_z\rangle$ are equal whatever may be the symmetry of the ions. This justifies the assumption of uniaxial symmetry of the ions.

4 Results and discussion

For a satisfactory fit between the calculated and experimental results of Stark splittings in absorption spectra and magnetic susceptibility values $(K_\parallel, K_\perp)$ of the ion simultaneously, we started at first with the same set of electrostatic [12], spin orbit [12] and crystal field (CF) parameters as used by Stöhr and Gruber. But we failed to achieve this. The deviation from the experimental values ranges from 2% to 29% for $\overline{K}$ and 20% to 30% for $K_\parallel$ and from 10% to 25% for $K_\perp$. Then we varied the CF parameters keeping the free ion parameters the same as above so that a reasonable agreement between the theoretical and experimental results of both magnetic susceptibility and optical data is obtained. The CF parameters used by us are quoted below. Stöhr and Gruber's parameters are also given for comparison.

Crystal field parameters

	Our parameters	Gruber's parameters
B_{20}	$= 591.89 \pm 6$ cm^{-1}	160 ± 6 cm^{-1}
B_{22}	$= 124.18 \pm 5$ cm^{-1}	125 ± 8 cm^{-1}
B_{2-2}	$= 219.35 \pm 4$ cm^{-1}	-220 ± 15 cm^{-1}
B_{40}	$= -995.24 \pm 10$ cm^{-1}	-680 ± 25 cm^{-1}
B_{42}	$= -20.95 \pm 5$ cm^{-1}	-215 ± 20 cm^{-1}
B_{4-2}	$= -379.24 \pm 2$ cm^{-1}	380 ± 25 cm^{-1}
B_{44}	$= 272.38 \pm 10$ cm^{-1}	260 ± 20 cm^{-1}
B_{4-4}	$= 269.24 \pm 6$ cm^{-1}	270 ± 20 cm^{-1}
B_{60}	$= -399.55 \pm 5$ cm^{-1}	-400 ± 25 cm^{-1}
B_{62}	$= 59.28 \pm 5$ cm^{-1}	-60 ± 7 cm^{-1}
B_{6-2}	$= -230.95 \pm 3$ cm^{-1}	-135 ± 15 cm^{-1}
B_{64}	$= 232.49 \pm 2$ cm^{-1}	240 ± 25 cm^{-1}
B_{6-4}	$= -152.43 \pm 5$ cm^{-1}	-14 ± 7 cm^{-1}
B_{66}	$= 184.76 \pm 5$ cm^{-1}	190 ± 20 cm^{-1}
B_{6-6}	$= 159.36 \pm 15$ cm^{-1}	-160 ± 20 cm^{-1}

It is to be noted that the values of a number of CF parameters obtained by us (particularly B_{20}, B_{40}, B_{42}, B_{6-2}, B_{6-4}) are different from that reported by the optical workers. To justify the difference between the old and new CF parameters we note the following:

i) Optical workers did not include all the terms of Ho^{3+} ion for their energy level calculation. They restricted their calculation within the $^5I_8$, $^5S_2$, $^5F_3$, $^5F_2$, $^3K_8$, $^5G_4$ and $^5G_2$ manifolds only, whereas we used a more rigorous approach by taking all the manifolds arising from all the terms of Ho^{3+} ion [10].

ii) Moreover, the old CF parameters were evaluated from the optical data only, but the set of new parameters is consistent with both the available Stark splittings in absorption spectra and magnetic data simultaneously. It would have been quite interesting if we could compare the above two sets of parameters with those evaluated using a point charge model. But it has not been possible due to lack of the detailed X-ray data.

Spectroscopic data from the lowest level up to 28 369 cm^{-1} are available. All the seventeen Stark levels of the ground manifold $^5I_8$ could not be observed. The first order crystal field splittings for the J manifolds calculated by us are given in Table 1. Values calculated by optical workers are also included in the same table for comparison. It is to be noted that our values give better fit to Stark splittings of the ground manifold in comparison to the theoretical results of optical workers. For the multiplets $^5G_2$, $^5G_4$, $^3K_8$, $^5F_2$, $^5F_3$, $^5S_2$ the observed overall splittings are 126.9 cm^{-1}, 113.4 cm^{-1}, 91.6 cm^{-1}, 78.8 cm^{-1}, 112.6 cm^{-1} and 26.7 cm^{-1} respectively. Our theoretically evaluated splittings are 100.42 cm^{-1}, 110.7 cm^{-1}, 117.35 cm^{-1}, 126.52 cm^{-1}, 113.39 cm^{-1} and 38.33 cm^{-1} in contrast to Stöhr and Gruber's calculated results 98.4 cm^{-1}, 137 cm^{-1}, 97.4 cm^{-1}, 86.3 cm^{-1}, 105.6 cm^{-1} and 10.8 cm^{-1} respectively. Defining the relative splitting by the separation of a split component from the centre of gravity of the group of components into which a $^{2S+1}L_J$ level splits, the calculated relative splittings for $^5S_2$, $^5F_3$ and $^5G_4$ manifolds are in better agreement with observed values in comparison with the calculated results of the optical workers (see Tab. 1). But in $^3K_8$ and $^5F_2$ manifolds, the splittings as evaluated by the optical workers are closer to the observed values compared to the splittings calculated by us. In $^5G_2$ manifold, out of five levels, our calculated results of relative splittings of two levels are in good agreement with experimental results whereas the calculated splittings of other three levels obtained by optical workers are in better position.

Figure 1 shows the experimental thermal variation of $\overline{\chi}$, χ_1 and χ_3. The agreement between the observed and theoretically computed thermal variation of the mean ionic susceptibility $\overline{K}$ and principal ionic susceptibilities $K_\parallel$ and $K_\perp$ are shown in Figure 2. The figure shows that the agreement is fairly good for all the three quantities. Deviation of the calculated values from the observed values are (0.0% – 6.0%), (3.0% – 9.9%) and (0.0% – 5.0%) for $\overline{K}$, $K_\parallel$ and $K_\perp$ respectively within the temperature range studied. It is further observed that the agreement at temperatures from 280 to 120 K is very good and perceptible deviation only occurs between temperature 100 K and 90 K which amounts to about 9.0% at most. At temperature 300 K, the deviation is 5.0% for $\overline{K}$, 4.8% for $K_\parallel$ and 5.3% for $K_\perp$.

The small deviation between the calculated and observed values may be attributed to the slight local distortion from the major symmetry of CF at the site of the ion. The slight distortion can also be inferred from the crystalline anisotropy results. If the point symmetry of the RE ion were pure C_{1h}, the symmetry axis of the ion would have been exactly perpendicular to the *ac* plane *i.e* $\phi = 90°$ and both the equations (3, 4) give $\chi_1 = \chi_2$. But we could get a value of anisotropy $\chi_1 - \chi_2$ derived

Table 1. Crystal field splitting of $Ho_2(SO_4)_3.8H_2O$.

$^{2S+1}L_J$ level	Empirical label	Experimental energy levels (cm^{-1})	Centre of gravity (cm^{-1})	Relative observed splitting (cm^{-1})	Relative calculated splitting (cm^{-1})	Relative calculated splitting by optical observer (cm^{-1})
$^5I_8$	Z_1			0	0	0
	Z_2			2.6	2.37	5.1
	Z_3			9.9	11.39	14.9
	Z_4			28.3	19.03	21.2
	Z_5			29.8	21.62	36.3
	Z_6			101.0	89.12	91.1
					98.37	109.6
	Z_7			121.0	104.65	122.8
$^5S_2$	E^3_{11}	18451.3	18464	-12.7	-18.57	-0.8
	E^3_9	18455.7		-8.3	-13.93	-10.3
	E^3_7	18461.3		-2.3	-5.99	-3.4
	E^3_3	18473.5		9.5	6.89	4.6
	E^3_1	18478.0		14.0	19.66	10.0
$^5F_3$	F_{24}	20587.7	20653.9	-66.2	-64.06	-66.6
	F_{20}	20604.8		-49.2	-36.71	-41.8
	F_{17}	20624.6		-29.3	-20.03	-34.0
	F_9	20679.4		25.5	2.65	10.0
	F_7	20685.3		31.4	30.9	33.5
	F_3	20695.4		41.5	43.03	59.6
	F_1	20700.3		46.4	49.33	39.3
$^5F_2$	G_{14}	21074.1	21111.4	-37.3	-48.24	-39.2
	G_{10}	21090.0		-21.4	-13.12	-19.6
	G_7	21106.2		-5.2	-10.08	-10.7
	G_4	21133.9		22.6	-6.81	22.5
	G_1	21152.6		41.2	72.28	47.1
$^3K_8$	H_{40}	21348.8	21393.5	-44.7	-67.91	-48.3
	H_{38}	21352.0		-41.5	-67.41	-49.0
	H_{36}	21355.8		-37.7	-65.42	-42.6
	H_{32}	21366.5		-27.0	-63.31	-29.4
	H_{29}	21372.5		-21.0	-27.42	-37.4
	H_{27}	21377.5		-16.0	-26.96	-24.3
	H_{26}	21380.0		-13.5	-0.33	-11.4
	H_{23}	21384.2		-9.3	8.74	-19.5
	H_{21}	21389.8		-3.7	12.39	-0.8
	H_{18}	21393.0		-0.5	16.37	5.2
	H_{15}	21400.3		6.8	27.33	18.0
	H_{14}	21401.7		8.2	30.57	12.0
	H_9	21424.4		30.9	31.76	38.5
	H_7	21427.4		33.9	45.97	44.2
	H_2	21439.0		45.5	49.2	44.7
	H_1	21440.4		46.9	49.44	49.1
$^5G_4$	K_{30}	25842.0	25905.3	-63.3	-60.03	-82.0
	K_{20}	25882.8		-22.5	-57.49	-15.3
	K_{16}	25891.2		-14.1	-21.08	-2.5
	K_{15}	25891.9		-13.4	-10.95	-23.4
	K_{13}	25896.4		-8.9	0.93	-6.5
	K_{10}	25915.4		10.1	21.94	11.0
	K_8	25921.8		16.5	29.91	20.1
	K_3	25951.1		45.8	46.17	42.7
	K_1	25955.4		50.1	50.67	55.7
$^5G_2$	N_{15}	28241.4	28300.5	-59.1	-59.48	-42.7
	N_{11}	28268.3		-32.2	-37.71	-23.8
	N_8	28296.1		-4.4	-22.19	-16.3
	N_4	28328.5		28.0	34.34	27.2
	N_1	28368.3		67.8	40.94	55.7

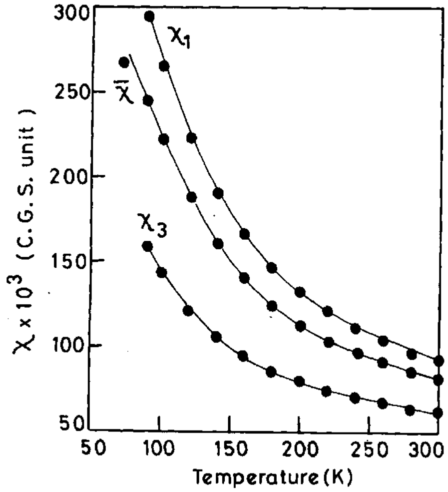

Fig. 1. Thermal variation of $\bar{\chi}$, χ_1 and χ_3 for holmium sulphate octahydrate: (•) experimental points. (Solid lines are fit to aid the eye.)

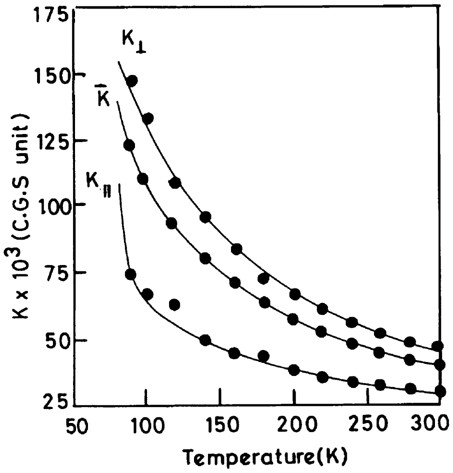

Fig. 2. Thermal variation of the mean ionic susceptibilities $\overline{K}$ and principal ionic susceptibilities $K_\parallel$ and $K_\perp$ for holmium sulphate octahydrate. (—) theoretical curve, experimental points are also shown.

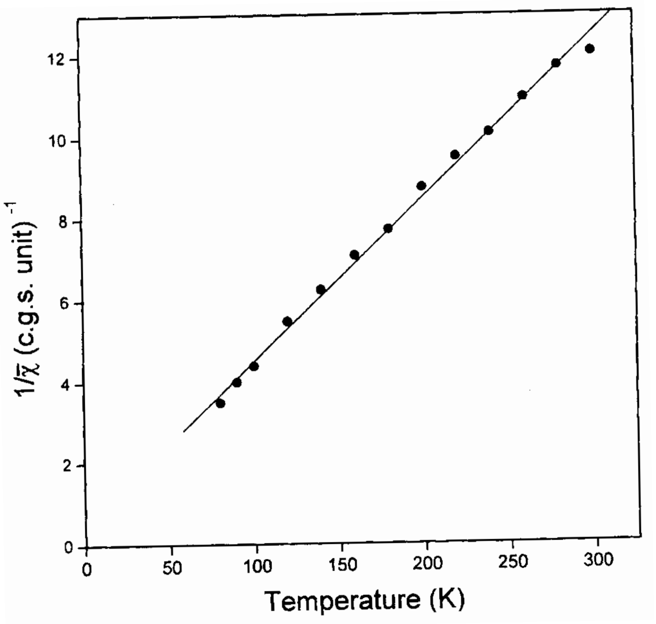

Fig. 3. Thermal variation of $1/\bar{\chi}$ for holmium sulphate octahydrate.

from the individual susceptibilities χ_1 and χ_2. At 300 K the anisotropy $\chi_1 - \chi_2$ is about 2.5% of individual susceptibilites. Susceptibility values are measured with an accuracy of about 5% only and hence the anisotropy derived from the susceptibility data lies within the experimental error. We would then be not able to infer whether χ_1 is equal to χ_2 from the susceptibility data. To establish whether χ_1 is equal to χ_2 we used a room temperature anisotropy balance and suspended the crystal with *b* axis vertical to test the anisotropy $(\chi_1 - \chi_2)$ if it exists at all. The crystal showed anisotropy and the room temperature anisotropy $(\chi_1 - \chi_2)$ was measured. The value of $(\chi_1 - \chi_2)$ is 2 221 c.g.s unit at 301.3 K from the anisotropy measurement. However, from observed susceptibility the value of $(\chi_1 - \chi_2)$ is 2 230 c.g.s. unit at 301.3 K. This indicates that slight distortion from the pure C_{1h} point symmetry exists in holmium sulphate octahydrate. The lowest level of all the ground manifold of holmium sulphate octahydrate is singlet and hence no question of epr *g*-values arises.

The mean susceptibility values at different temperatures are found to obey the Curie-Weiss law. The plot of $1/\bar{\chi}$ *versus* T as shown in Figure 3 is almost a straight line yielding a value of 24.98 emu K/g atom for the Curie constant and −12.26 K for the paramagnetic Curie temperature. Although the detailed structure and the Ho-Ho distance are not available in the literature we have made an attempt to evaluate an approximate estimate of Ho-Ho distance by the following procedure. We know from the works of Zachariasen [13] and Ivanov [14] that the rare earth sulphates are isostructural. Using the coordinates [13] of eight rare earth ions in the unit cell and lattice parameters [3], the nearest Ho-Ho distance comes out to be ~ 5 Å. The interatomic distances Ho-O range from 2.26 Å to 2.46 Å. If the nearest Ho-Ho distance that results from the above approximate calculation is close to the true value, the presence of superexchange will be marginal and its effect will be very small. Moreover the value of Curie temperature (−12.2 K) obtained from $1/\bar{\chi}$ *vs.* T graph indicates the validity of our assumption that holmium sulphate octahydrate is paramagnetic at least within the temperature range of our measurement.

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