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Crystal-field studies of magnetic susceptibility, hyperfine, and specific heat properties of a $Ho_2Ti_2O_7$ single crystal

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Accurate measurement of the magnetic susceptibility of a single crystal and a powder sample of nearly cubic pyrochlore $Ho_2Ti_2O_7$ (HoT) were performed between 300 and 70 K. A crystal field (CF) of D_{3d} symmetry was considered to analyze the results of magnetic susceptibility, magnetization, and magnetostriction studies quite consistently. The best fitted CF parameters were found as $B_{20}=-980$, $B_{40}=1640$, $B_{43}=-1800$, $B_{60}=-1000$, $B_{63}=700$, $B_{66}=-500$ (all in cm^{-1}). The separation (Δ) between the lowest non-Kramers' CF doublet and the first excited level was found to be $\sim 150\ \mathrm{cm}^{-1}$, which explained reasonably well the absence of giant magnetostriction, the Jahn-Teller effect, and the fall of the Young modulus in a HoT crystal at low temperatures, unlike TbT for which Δ is small ($\sim 12\ \mathrm{cm}^{-1}$). It was found that the effective hyperfine magnetic field set up at the Ho^{3+} nucleus is 7.2 MG and the total width of the nuclear ground level is ~2 K. The calculated hyperfine and Schottky components of specific heat showed a maximum at 0.3 and 130 K, respectively. The heat-capacity contributions from dipolar interactions in the limit of high temperatures was found to be $12.2 \pm 0.4\ \mathrm{K}^2$. The magnetic energy gains associated with the antiferromagnetic ordering at 1.35 K and that due to Heisenberg exchange interactions ($J\sim 1$ K) were calculated and found to be 4.82 and 1.5 K, respectively. Specific-heat C_T studies of HoT at low temperatures are suggested.

I. INTRODUCTION

Different thermophysical properties of paramagnetic Ho^{3+} compounds[1–16] are quite sensitively dependent on the crystal field (CF) effect, which arises due to the Stark effect of the nearest anions on the electronic levels of the $4f^{10}$ electronic configuration of the Ho^{3+} atom in the host lattice. Consequently, from the CF analysis of these properties, studied over a sufficiently wide range of temperature, it has been possible to determine the values of CF parameters quite accurately and the corresponding CF energy pattern and wave functions as have been shown by us[7–10,16] and others.[1–6,11–15] This paper reports a coordinated effort to measure accurately the magnetic susceptibility ($\overline{\chi}$) of powder and single crystals of holmium titanate ($Ho_2Ti_2O_7$) or HoT between 300 and 70 K, and the theoretical analysis of the magnetic results as well as other available experimental results [17–19] for evaluating as accurately as possible the correct CF level pattern of the $^5I_8$ ground and few excited multiplets of Ho^{3+} ions in the titanate host, which have not as yet been reported, to our knowledge.

HoT belongs to an isomorphous series of rare-earth titanate (RET) compounds, having the general formula $R_2O_3 \cdot 2TiO_2$ or $R_2Ti_2O_7$ ($R=$Sm–Lu).[20] In recent years, the members of the RET series have drawn much attention of the physicists because of several interesting and potent thermophysical properties exhibited by RET compounds at low temperatures, for example occurrence of giant magnetostriction in the paramagnetic region and structural phase transition of the Jahn-Teller (JT) type in TbT caused by the strong $4f$ electron-phonon coupling and closely spaced CF energy levels,[21,22] interesting dielectric,[19] electrical,[22–24] and elastic[22] properties in GdT, TbT, YbT, and a large Goldanskii-Karyagin effect in the Mössbauer spectra (MS) of EuT (Refs. 25, 26) and GdT.[27] From adiabatic demagnetization studies, DyT and YbT were found to be very favorable as efficient working substances of a magnetic refrigerator, cycling between liquid-helium and boiling liquid hydrogen and that these are very suitable for evaluating the efficiency of a particular refrigerator design[28] and the adiabatic refrigerating technique.[20] Studies on HoT that have been reported before now are the investigations of the external field dependence of magnetostriction and magnetization,[18] temperature dependence of magnetic susceptibility,[17,18] dielectric properties and lattice parameters[19] of polycrystalline samples of HoT, and x-ray (XRD) and neutron-diffraction studies on trivalent RET,[20,24,25,29,30] which showed that HoT has a nearly cubic mineral pyrochlore structure with space group $Fd\overline{3}m$ and unit-cell dimension $a_0=10.095$ Å,[24] and that the cubic structure remains stable all the way down to liquid-helium temperature.[19,21] Unlike most of the previously studied oxides, e.g., $SrCr_{8-x}Ga_{4+x}O_{19}$ and the fluoride pyrochlores, e.g., $CsNiCrF_6$, $CsMnFeF_6$, HoT is found to be chemically well ordered, electrically insulating[31,32] and shows p-type semiconduction at higher temperatures.[24]

XRD studies of HoT showed that HoT crystallizes into a face-centered-cubic structure with eight formula units, i.e., 16 Ho^{3+} ions per conventional unit cell. Each Ho^{3+} ion has six nearest neighbors[20,30] and is surrounded by eight oxygen ions which form a trigonally distorted cube of D_{3d} symmetry and the trigonal axis along the [1,1,1] direction is the principal axis of the g tensor ($g_\parallel$ direction).[20] The CF having D_{3d} symmetry in HoT modifies the free ion energy levels of Ho^{3+} ions, breaking up the 17-fold degenerate $^5I_8$ ground multiplet into five singlets and six non-Kramers' doublets.[18]

According to Lacorre's proposal,[32–34] the pyrochlore lattice presents the strongest possible degree of geometrical

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frustration due to antiferromagnetic interactions. It was also noted that even in the case of the ferromagnetic pyrochlore lattice of HoT such frustration was present even at 0.35 K, because of the presence of a large ionic axial anisotropy directed along the [1, 1, 1]-type direction.[31,32] However, in the presence of a small external magnetic field, magnetic order sets in around 1.35 K.[17,18,31] The large ionic anisotropy was due to a strong crystal field (CF) of D_{3d} symmetry acting on the Ho^{3+} in HoT but the effect of the CF in HoT had not been fully studied. This motivated the present study involving a determination of the CF parameter (CFP), CF energies and the corresponding wave functions of this compound from fitting simultaneously the experimental results of magnetic susceptibility,[17,18] magnetization, and magnetostriction studies[18] on HoT. On the basis of these findings, it was further aimed to simulate a few other electronic and nuclear thermophysical properties of HoT which depend on the CF very sensitively, as have been done by us[7–10,16,36–43] and others[2,4,11,13,15,35] in the case of some compounds of Ho^{3+} and other rare earths.

II. THEORY

The magnetic susceptibilities of Ho^{3+} in HoT are mainly described by CF which act as a major perturbation on the free ion ground state ${}^5I_8$ of Ho^{3+} especially in our experimental range of temperature since the ground term ${}^5I_8$ of Ho^{3+} is followed by the next excited term ${}^5I_7$, lying about 5200 cm^{-1} above it.[14,44] Because of the electrostatic, spin-orbit, and configurational interactions, the free ion terms of Ho^{3+} are mixed and form intermediately coupled (IC) states, and the percentage of admixture varied for different levels.[45–47] The low-lying levels are generally nearly pure Russell-Saunders states, for example, the IC ground state $|{}^5I_8'\rangle$ of Ho^{3+} in HoCl_3 (Ref. 48) (C_{3h} symmetry) is

$$|{}^5I_8'\rangle = 0.967|{}^5I_8\rangle \tag{1a}$$

and in the trigonal (D_3) $\mathrm{Na}_3[\mathrm{Ho}(\mathrm{C}_4\mathrm{H}_4\mathrm{O}_5)_3]\cdot 2\mathrm{NaClO}_4\cdot 6\mathrm{H}_2\mathrm{O}$ or Ho^{3+}-diglycollate (HoDG) (Ref. 49)

$$|{}^5I_8'\rangle = 0.97|{}^5I_8\rangle - 0.22|{}^3K_8^{(2)}\rangle . \tag{1b}$$

Consequently, the effect of the host on the IC ground term is around 1%. Thus the free ion states do not vary much with the host and as there are no report of spectroscopic results of HoT, we substituted the values of the electrostatic and spin-orbit parameters[47] reported for Ho^{3+}:LaCl_3 for simulating the free ion IC states of HoT and for calculating the reduced CF matrix elements using the Wigner-Eckart theorem[46,47]

$$\langle \alpha LSJM | U_{kq} | \alpha' L' S J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \times \langle \alpha LSJ || U^{(k)} || \alpha' L' S J' \rangle , \tag{2a}$$

where the reduced matrix element is given as

$$\langle \alpha LSJ || U^{(k)} || \alpha' L' S J' \rangle = (-1)^{L'+S+J+k} \sqrt{(2J+1)(2J'+1)} \times \begin{Bmatrix} L & J & S \\ J' & L' & k \end{Bmatrix} \langle \alpha LS ||| U^{(k)} ||| \alpha' L' S \rangle \tag{2b}$$

and the CF Hamiltonian (H_{CF}) for D_{3d} symmetry is expressed as

$$\begin{aligned} H_{\mathrm{CF}} &= \Sigma_{km} B_{km} U_{km} \\ &= B_{20}U_{20} + B_{40}U_{40} + B_{43}(U_{43} - U_{4-3}) + B_{60}U_{60} \\ &\quad + B_{63}(U_{63} - U_{6-3}) + B_{66}(U_{66} + U_{6-6}), \end{aligned} \tag{3}$$

where the U's are the one-electron intraconfiguration unit tensor operators (Table 8 of Ref. 44) and B_{km} are even-parity CF interaction parameters ($=\overline{B_{km}}$ of Ref. 45).

The $4f^{10}$ configuration of an Ho^{3+} ion has a total of 1001 $|LSJM\rangle$ states.[44] While analyzing optical, magnetic or other thermophysical properties of the compounds, it is therefore impossible to consider all these states and usually a suitable truncation is necessary for obtaining meaningful theoretical analysis of experimental results of Ho compounds. Following the usual procedure,[49] the atomic Hamiltonian was first diagonalized within 39 $|LSJ\rangle$ basis states with the principle LS percentages derived from the 11 different Russell-Saunders terms (${}^5S, {}^5D, {}^5F, {}^5G, {}^5I, {}^3P, {}^3G, {}^3H, {}^3K, {}^3L, {}^3M$).[50] The eigenvectors obtained from this calculation were then used to consider a suitably truncated 397 $|LSJM\rangle$ IC basis states within which the total Hamiltonian comprising the atomic and CF Hamiltonian was finally diagonalized, thus allowing for CF mixing between the IC states. In this method of matrix diagonalization, the mixing between the ground multiplet and the higher J multiplets, is least affected by the energy truncation.[14,49]

Expressions of magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ (emu/ion), along and perpendicular to the D_{3d} axis, respectively, at different temperatures were obtained by substituting the computed Zeeman energies and CF wave functions of the 17-fold degenerate $|{}^5I_8\rangle$ ground term, in the Van Vleck expression[51]

$$\chi_j = (g_J^2 N \mu_B^2 / Z) \sum_i \{[(E_i^{(1)})^2/kT - 2E_i^{(2)}] \exp(-E_i^{(0)}/kT)\}, \tag{4}$$

where $j=\parallel$ or $\perp$, respectively, refer to the direction of the applied magnetic field parallel and perpendicular to the D_{3d} axis, g_J is the intermediately coupled value of the Lande' g factor for HoT, Z is the partition function, and $E_i^{(0)}, E_i^{(1)}, E_i^{(2)}$, are, respectively, the zeroth-, first-, and second-order perturbed energies. $\overline{\chi} = (\chi_{\parallel} + 2\chi_{\perp})/3$ and the ionic anisotropy $\Delta\chi = (\chi_{\parallel} \sim \chi_{\perp})$. The magnetic susceptibilities are therefore, functions of the six CF parameters (CFP's), e.g., B_{20}, B_{40}, B_{43}, B_{60}, B_{63}, and B_{66} which are conventionally assumed to be temperature independent. A computer program was developed to analyze all results simultaneously by varying the CFP.

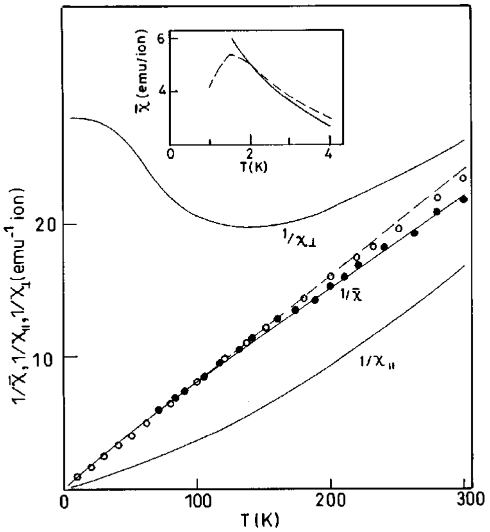

FIG. 1. Solid lines are the theoretical curves of $1/\chi_{\parallel}$, $1/\chi_{\perp}$, and $1/\bar{\chi}$ of HoT (○ and ● are experimental points of Ref. 18 and this work, respectively). Dashed line shows the Curie-Weiss-type behavior of $1/\bar{\chi}$ of HoT in the temperature range 8–220 K (Ref. 18). Inset shows that $\bar{\chi}$ (dashed curve) of HoT reaches a maximum at 1.35 K (Ref. 17) and the solid line is our theoretical curve.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Single crystals of HoT were prepared by hydrothermal process[52] by Dr. B. M. Wanklyn in the Clarendon Laboratory. HoT single crystals were reddish-brown with well developed planes. The powder susceptibility ($\bar{\chi}$) was measured between 300 and 70 K in a sensitive electrodynamically controlled Curie-type balance using the Faraday method,[53] the accuracy of the results was ~0.5%. Figure 1 shows the temperature dependence of the inverse of the susceptibility $\bar{\chi}$, which was 0.0458 emu/ion at 300 K and increased by ~3.2 times at 70 K. A large increase of $\bar{\chi}$ on cooling had been also found in other Ho^{3+} compounds, viz, $Ho(OH)_3$, $HoPO_4$, $Ho(BrO_3)_3 \cdot 9H_2O$, $HoAl_3(BO_3)_4$, $Ho_2Ge_2O_7$.[8,12,13,15,16] Inspection of Fig. 1 shows that although the value of $\bar{\chi}$ of HoT at 300 K obtained by us are around ~5% higher than the earlier reported values,[18] but on cooling the deviations between these results decreased and vanished below 150 K. Our experimental results showed that $\bar{\chi}$ of HoT obeyed a Curie-Weiss-type law and the Curie constant was found to be 14.35 ± 0.03 emu K per ion. The Curie temperature was found to be dependent on the range of temperature studied, as also noted by others in the case of polycrystalline DyT and HoT.[20,21] The effective magnetic moment $\bar{\mu}_{\text{eff}} = 2.828\sqrt{\bar{\chi}T}$ around 300 K was found to be $10.48\mu_B$ (the free ion value is $10.61\mu_B$). In comparison to Ho^{3+} in other hosts,[8,12,13,15,16] the thermal variation of $\bar{\mu}_{\text{eff}}$ of HoT is large, being 9.62 and $9.20\mu_B$ at 70 and 10 K, respectively.

The static torque method was used to detect and measure magnetic anisotropy in different planes.[53] No crystalline anisotropy was detected as expected for these nearly cubic crystals of HoT for which reason $\Delta\chi$ per ion could not be experimentally determined and used to obtain very accurate values of CFP's, as in other noncubic crystals of Ho^{3+} compounds.[8,12,13,15,16] It is relevant to mention here that $\bar{\chi}$ being an average property, there can be different sets of $\chi_{\parallel}$ and $\chi_{\perp}$ which will produce identical $\bar{\chi}$ vs T curves. Thus, the $\bar{\chi}$ vs T curve for HoT could be fitted with a maximum deviation of 4% with the same set of CFP's, e.g., $B_{20} = -88$, $B_{40} = -836$, $B_{43} = -578$, $B_{60} = 531$, $B_{63} = 777$, $B_{66} = 672$, which were determined from spectral analyses of HoDG.[49] However, it was found that the corresponding lowest CF level was a combination of $(|\pm 7\rangle)$ which would not explain the magnetization results[18] and g values reported for polycrystalline HoT. Furthermore, the separation (Δ) between the ground doublet and the first excited CF level was only ~10 cm^{-1}, which did not simulate the magnetostriction[18] and Jahn-Teller (JT) behaviors[22] of HoT. For such reasons, although we considered the above values of the six CF parameters as the starting values, these parameters were varied quite exhaustively to satisfy all observed results of HoT and we noted the following:

TABLE I. The value of B_{20} (cm^{-1}), nature and crystal quantum number μ_c (Ref. 44) of the ground CF level of different holmium compounds.

Compounds	B_{20}	Ground state	μ_c	References
$Ho_2Ti_2O_7$	-980 ± 20	Doublet	± 1	This work
$HoPO_4$	-550		± 1	12, 14
$Ho\,YPO_4$	-466		± 1	11 (a), 45
HoDG	-88		± 1	49
$Ho(OH)_3$	-546		± 1	2, 7, 8, 45
$Ho\,Y(OH)_3$	-672		± 1	2, 8, 45
$Ho^{3+}{:}CaWO_4$	-596		± 1	1
$Ho^{3+}{:}LiYF_4$	-560		± 1	3, 45
Ho-E.S.	-341		± 1	7, 44, 45
$Ho\,Cl_3$	-310		± 1	6, 45, 48
$Ho^{3+}{:}Y_2O_2S$	-82		± 1	11 (b), 45
$Ho_2Ge_2O_7$	200	Singlet	0	16
$Ho\,VO_4$	224		0	14
$Ho(BrO_3)_3 \cdot 9H_2O$	130		0	13
$Ho\,Al_3(BO_3)_4$	447.5		0	15

(i) The value of Δ depends mainly on B_{20}, because the wave function of the lowest CF level as well as the position of the first excited state of the ground multiplet $|^5I_8\rangle$ changed abruptly with the change of the value as well as the sign of this parameters, thereby changing the $g_{\parallel}$ values randomly. Ho^{3+} compounds with a negative value of B_{20} have a magnetic-doublet ground state of crystal quantum number[44] $\mu_c = \pm 1$, while those with a positive value of B_{20} have a singlet and hence nonmagnetic ground state of $\mu_c = 0$ (Table I). Table I also shows that B_{20} has also a significant effect on lattice properties due to the quadrupole effect of the crystal field, involving interactions of Ho^{3+} moments with the crystal lattice.[14]

(ii) The thermal characteristic of $\bar{\chi}$ is dependent sensitively on B_{20}, B_{40}, and B_{43}, but more so on B_{60} at low temperatures.

(iii) As in case of YbT,[54] the cubic ratios between the CF parameters $B_{43}/B_{40} = -1.195$, $B_{63}/B_{60} = 0.6038$, and $B_{66}/B_{60} = 0.633$ were nearly satisfied.[55]

The best fitted set of CF parameters that were obtained are $B_{20} = -980 \pm 20$, $B_{40} = 1640 \pm 30$, $B_{43} = -1800 \pm 20$, $B_{60} = -1000 \pm 20$, $B_{63} = 700 \pm 20$, $B_{66} = -500 \pm 10$ (all in cm^{-1}). Figure 1 shows the close matching of the best fitted

TABLE II. Energies (E_i in cm^{-1}) and CF wave functions (ψ_i) of the 17-fold degenerate ground multiplet $^5I_8$ of $Ho_2Ti_2O_7$ are shown. For comparison corresponding quantities, CFP values, and C.G. (in cm^{-1}) of excited terms $^5I_{7-4}$ of HoDG (Ref. 49), and $HoCl_3$ (Refs. 44, 48) were also included. ($<$) represents the CF doublet level. (Only those states having admixtural coefficients greater than 4% were included in ψ_i.)

	$HoCl_3$	HoDG	$Ho_2Ti_2O_7$		
Multiplet	E_i	E_i	E_i	μ_c	Ψ_i
$^5I_8$	0<	0<	0<	±1	$\psi_g=-0.88\lvert\mp 8\rangle\pm 0.4\lvert\mp 5\rangle -0.12\lvert\mp 2\rangle-0.05\lvert\pm 1\rangle$
	12.5	9	150±5<	±1	$\psi_1=\mp 0.5\lvert\pm 7\rangle-0.76\lvert\pm 4\rangle\mp 0.17\lvert 1\rangle -0.3\lvert\mp 2\rangle+0.06\lvert\mp 8\rangle$
	43.8	71<	160	3	$\psi_2=-0.3(\lvert +6\rangle-\lvert -6\rangle)-0.6(\lvert +3\rangle+\lvert -3\rangle)$
	66.4<	109	240	0	$\psi_3=-0.4(\lvert +6\rangle+\lvert -6\rangle)-0.5(\lvert +3\rangle+\lvert -3\rangle) -0.3\lvert 0\rangle$
	89.9<	183<	274<	±1	$\psi_4=0.2\lvert\pm 7\rangle\pm 0.08\lvert\pm 4\rangle+0.42\lvert\pm 1\rangle \mp 0.7\lvert\mp 2\rangle+0.4\lvert\mp 5\rangle\mp 0.3\lvert\mp 8\rangle$
	104.1	189	335<	±1	$\psi_5=-0.05\lvert\pm 8\rangle\pm 0.13\lvert\pm 5\rangle-0.47\lvert\pm 2\rangle \pm 0.77\lvert\mp 1\rangle+0.2\lvert\mp 4\rangle\mp 0.22\lvert\mp 7\rangle$
	118.4	256<	346	0	$\psi_6=0.3(\lvert +3\rangle-\lvert -3\rangle)-0.88\lvert 0\rangle$
	154.2<	273	434<	±1	$\psi_7=0.3\lvert\pm 8\rangle\mp 0.8\lvert\pm 5\rangle+0.3\lvert\pm 2\rangle \pm 0.35\lvert\mp 1\rangle+0.1\lvert\mp 4\rangle-0.16\lvert\mp 7\rangle$
	155.4<	356	461	3	$\psi_8=-0.6(\lvert +6\rangle-\lvert -6\rangle)+0.3(\lvert +3\rangle+\lvert -3\rangle)$
	203.7<	359<	500	1	$\psi_9=-0.55\lvert +7\rangle+0.36\lvert +4\rangle+0.25\lvert +1\rangle -0.4\lvert -2\rangle-0.55\lvert -5\rangle$
	212.8	404<	504<	±1	$\psi_{10}=0.75\lvert\pm 7\rangle\mp 0.55\lvert\pm 4\rangle-0.06\lvert\pm 1\rangle -0.2\lvert\mp 2\rangle+0.11\lvert\mp 5\rangle$
$^5I_7$	5155	5240	5390		
$^5I_6$	8660	8745	9000		
$^5I_5$	11210	11300	11610		
$^5I_4$	13260	13375	13600		
B_{20}	−310	−88	−980±20		
B_{40}	−306	−836	1640±30		
B_{43}		−578	−1800±20		
B_{60}	570	531	−1000±20		
B_{63}		777	700±20		
B_{66}	−372	672	−500±10		

values of $\overline{\chi}$ with the experimental results. CF splits the ground multiplet $\lvert ^5I_8\rangle$ into five singlets and six non-Kramers' doublets with a total-energy splitting of 504 cm^{-1} and the ground CF level (ψ_g) is a doublet consisting of 88% $\lvert 8,\ \pm 8\rangle$ component and the contributions from the other $J_z \neq 8$ states are as given in Table II. For want of space, it was not possible to include all the computed CF levels of the different multiplets in Table II. The separation Δ for HoT was found to be $\sim$150 cm^{-1} which was large enough to inhibit giant magnetostriction,[18,21] JT behaviors and anomalous behavior in the thermal characteristics of Young modulus[22] in HoT in the paramagnetic region unlike TbT, for which Δ is $\sim$12 cm^{-1}, and $Tb_{0.5}Ti_{1.5}O_7$.[21,22]

The g tensors for the ground magnetic-doublet CF level of HoT were found to be $g_{\parallel}=18.3\pm 0.2$ and $g_{\perp}=0$, with $g_{\parallel}$ direction being the easy magnetization axis.[18,28] As the ground CF level is well isolated at low temperatures, hence in a large applied magnetic field the value of the saturated magnetization[2,8] $M_{\mathrm{sat}}=N\mu_B g_{\parallel}/2$ for the ground doublet was found to be 1320 emu/c.c. where $N(=15.55\times 10^{21})$ is the number of Ho ions per c.c. in HoT. This value of M_{sat} for HoT compared well with that for other Ho^{3+} compounds.[2,8,16]

The calculated thermal characteristics of the ionic susceptibilities $\chi_{\parallel}$, $\chi_{\perp}$, and $\Delta\chi=\chi_{\parallel}-\chi_{\perp}$ (emu/ion) of HoT have been shown in Fig. 1. It was found that on cooling from 300 to 10 K, the values of $\Delta\chi$ were 45% and 285% of $\overline{\chi}$ and the ratio of $\chi_{\parallel}/\chi_{\perp}$ were 1.2 and 85. Thus, there was a clear evidence of an easy magnetization axis along trigonal D_{3d} symmetry axis.[18] The presence the large single ion anisotropy ($\sim$25 emu/ion around 1 K) results in a very high degree of geometrical frustrations for the ferromagnetic interactions with a nearest-neighbor exchange energy of $J\sim 1$ K found in HoT.[31,32] $\chi_{\parallel}$, $\chi_{\perp}$, and $\Delta\chi$ could not be measured directly because of the cubic symmetry of HoT crystals, but comparison shows that the characteristic and order of the anisotropy $\Delta\chi$ of HoT were close to the experimental values reported for noncubic crystals of other Ho^{3+} compounds.[2,8,12,13,15,16]

Muon-spin resonance (μSR), neutron-scattering studies

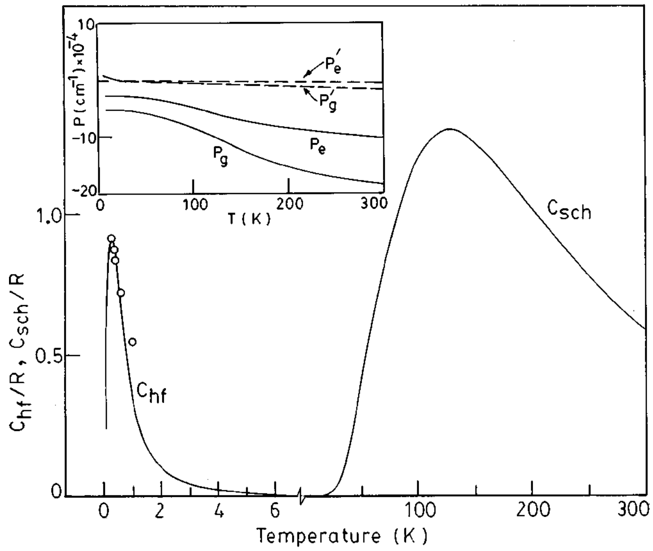

FIG. 2. Solid lines are the calculated thermal characteristics of hyperfine component ($C_{\rm hf}$) and Schottky component ($C_{\rm Sch}$) of specific heat of HoT, and the experimental results (○) of Ho_2GaSbO_7 (Ref. 20) are shown for comparison (see text). The inset shows the thermal variations of the quadrupole interaction parameter of ground (P_g) and first excited (P_e) nuclear level in which solid lines and dashed lines stand for HoT and HoDG, respectively.

and low-field susceptibility measurements on HoT revealed that in the absence of an external magnetic field the ground state remained disordered down to at least 0.05 K but with frozen dynamics, rather like a conventional spin glass in zero field.[31,32] However, upon application of a field of 0.01 T, the degeneracy was completely broken and a striking series of order phases appeared. The study also showed that there was a tendency for some long-range antiferromagnetic order of the moments forming in chains perpendicular to the direction of the applied field due to 180° spin flips, but this was a highly metastable process and required a thermal energy of the order of 1.4 K. This involves a breaking of the face-centered symmetry of the magnetic structure so that the magnetic unit cell is larger than the chemical unit cell.[31,32] This may explain the peak in the susceptibility curve observed[17] at 1.35 K (Fig. 1, inset). The effect of such ordering in the presence of external field on the specific-heat properties of HoT has not been studied until now. Similarly, the effect of hyperfine interactions of HoT are also expected to be intriguing at such low temperatures, which was therefore studied theoretically as discussed in the following sections.

IV. NUCLEAR HYPERFINE INTERACTIONS

Nuclear recoilless absorption measurements of the 86.5 keV γ ray of ^{155}Gd in GdT, as also in case of 25.6 keV γ ray of ^{161}Dy in DyT, have shown that the electric-field gradient (EFG), which is very sensitive to the CF, is highest in the titanates compared to any other known compounds.[56] This provided the motivation for calculating the nuclear hyperfine effects and Mössbauer spectrum (MS) of HoT. Holmium -165 (relative abundance 100%, stable) is one of the rare earths, having well-resolved hyperfine patterns which have been detected from studies of the sharp electronic transitions[44,47] in several different crystal hosts, namely, $Ho^{3+}:LaCl_3$,[44,57] $Ho^{3+}(C_2H_5SO_4)_3\cdot 9H_2O$ (Ref. 58) (C_{3h} symmetry), $Ho^{3+}:CaF_2$ (Ref. 59) (C_{3v} symmetry). A well-resolved eight-line hyperfine structure characteristic of $^{165}Ho^{3+}$ appears for crystals with 0.01% or less Ho^{3+} ions in the C_{3h}/C_{3v} symmetry site for which the electronic ground states is a doublet.[60] The magnetic field and the electric-field gradient (EFG) set up at the site of the $^{165}Ho^{3+}$ nucleus in HoT by the aspherical charge distribution of the surrounding ions at the crystal lattice and the $4f^{10}$ electrons of Ho^{3+} ions in different Stark states,[47] interact with the nuclear magnetic moments ($\mu_g = 4.17\,\mu_N$ and $\mu_e = 4.09\,\mu_N$),[61] and quadrupole moments ($Q_g = 3.58$b and $Q_e = 3.43$b) (Ref. 61) of the ground ($I_g = 7/2^-$) and the excited ($I_e = 9/2^-$) nuclear levels of the Ho^{3+} nucleus and split the degenerate nuclear levels. The extent of the hyperfine splitting depends on EFG and magnetic hyperfine interaction parameter.[56] Thus from the knowledge of the EFG, we can estimate the CF levels and their eigenstates and vice versa. Therefore, a theoretical estimation of the effect of nuclear hyperfine interactions ($H_{\rm hf}$) on $^{165}Ho^{3+}$ in the titanate host was made using the standard form[47] of $H_{\rm hf}$ as

$$\begin{aligned} H_{\rm hf} &= H_m + H_q \\ &= [A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y)] \\ &\quad + P[I_z^2 - I(I+1)/3], \end{aligned} \tag{5}$$

where $S(=1/2)$ is the effective electronic spin[32] of the ground doublet and P is the quadrupole interaction parameter,[47] being the sum of the antishielded lattice contribution $P_{\rm latt}$ and the temperature-dependent P_{4f} where

$$P_{\rm latt} = \frac{-3QB_2^0}{I(2I-1)\langle r^2\rangle_{4f}}\,\frac{1-\gamma_\alpha}{1-\sigma_2} \quad [B_2^0 = \overline{B}_{20}/(-2.732\,52), \text{ Ref. 45}], \tag{6a}$$

$$P_{4f} = \frac{-3e^2Q}{4I(2I-1)}\langle J\|\alpha\|J\rangle\langle r^{-3}\rangle_{4f}(1-R_Q)\langle 3J_z^2 - J(J+1)\rangle_T . \tag{6b}$$

The symbols used bear their usual meanings.[47] As the g tensor of the ground CF doublet of HoT compounds showed strong anisotropy, the magnetic hyperfine interaction (H_m) may be observed at sufficiently low temperatures. The magnetic hyperfine constants $A_{\parallel}$ and $A_{\perp}$ may be found from the relation[2,62] $A_{\parallel}/g_{\parallel} = A_{\perp}/g_{\perp} = A_J/g_J$ which is independent of the particular CF within a given ground term. For most of the Ho^{3+} compounds, A_J was found to be 812 MHz which is larger than any other R compounds.[63] The effective hyperfine magnetic field[63] $H_{\rm eff}(=JA_J/g_N\mu_N)$ set up at the Ho^{3+} nucleus in HoT, was found to be (7.2 ± 0.3) MG, which is close to the value of 7.6 ± 0.2 MG reported for $HoAl_2$ and $HoYAl_2$.[64] Substituting the values of different nuclear hyperfine quantities given in Table III, the quadrupole interaction parameters of ground (P_g) and first excited (P_e) nuclear state of Ho^{3+} in HoT were calculated between 300 and 4 K. The inset of Fig. 2 shows that P_g and P_e of HoT each attained saturation below 20 K.

$H_{\rm hf}$ acting on the $|M_I, M_S\rangle$ state of the ground and first excited nuclear levels produces eight and ten doublets with

TABLE III. Important nuclear hyperfine quantities and the allowed Mössbauer transition lines between the ground ($\lvert M_1\rangle_g$) and the first excited ($\lvert M_1\rangle_e$) states of ^{165}Ho nucleus in HoT.

Hyperfine quantities	Mössbauer transitions $\lvert M_1\rangle_g \rightarrow \lvert M_1\rangle_e$	Relative energies (cm/s)	Relative intensity for powdered sample
$\langle J \Vert \alpha \Vert J\rangle = -1/450$	$\lvert 7/2\rangle \rightarrow \lvert 5/2\rangle$	7.86	1/36
$\langle r^{-3}\rangle_{4f} = 11.17$ a.u.	$\lvert 3/2\rangle \rightarrow \lvert 1/2\rangle$	7.86	1/6
$\langle r^{2}\rangle_{4f} = 0.696$ a.u.	$\lvert 5/2\rangle \rightarrow \lvert 3/2\rangle$	7.83	1/12
$R_Q = 0.27$	$\lvert 1/2\rangle \rightarrow \lvert -1/2\rangle$	7.73	5/18
$(1-\gamma_{\propto})/(1-\sigma_2) = 241$	$\lvert -1/2\rangle \rightarrow \lvert -3/2\rangle$	7.63	5/12
$A_e/A_g = \mu_e/\mu_g$	$\lvert -3/2\rangle \rightarrow \lvert -5/2\rangle$	7.54	7/12
$(g_N)_g = 0.118$	$\lvert -5/2\rangle \rightarrow \lvert -7/2\rangle$	7.54	7/9
$(g_N)_e = 0.094$	$\lvert -7/2\rangle \rightarrow \lvert -9/2\rangle$	7.03	1
(mm/s/T)	$\lvert 5/2\rangle \rightarrow \lvert 5/2\rangle$	0.2	7/18
	$\lvert 7/2\rangle \rightarrow \lvert 7/2\rangle$	0.18	2/9
	$\lvert 1/2\rangle \rightarrow \lvert 1/2\rangle$	0.03	5/9
	$\lvert 3/2\rangle \rightarrow \lvert 3/2\rangle$	0.01	1/2
	$\lvert -1/2\rangle \rightarrow \lvert -1/2\rangle$	−0.05	5/9
	$\lvert -3/2\rangle \rightarrow \lvert -3/2\rangle$	−0.12	1/2
	$\lvert -5/2\rangle \rightarrow \lvert -5/2\rangle$	−0.197	7/18
	$\lvert -7/2\rangle \rightarrow \lvert -7/2\rangle$	−0.37	2/9
	$\lvert 7/2\rangle \rightarrow \lvert 9/2\rangle$	−7.44	1
	$\lvert 5/2\rangle \rightarrow \lvert 7/2\rangle$	−7.48	7/9
	$\lvert 3/2\rangle \rightarrow \lvert 5/2\rangle$	−7.63	7/12
	$\lvert -1/2\rangle \rightarrow \lvert 1/2\rangle$	−7.76	5/18
	$\lvert -3/2\rangle \rightarrow \lvert -1/2\rangle$	−7.8	1/6
	$\lvert 1/2\rangle \rightarrow \lvert 3/2\rangle$	−7.82	5/12
	$\lvert -5/2\rangle \rightarrow \lvert -3/2\rangle$	−7.86	1/12
	$\lvert -7/2\rangle \rightarrow \lvert -5/2\rangle$	−8.11	1/36

total splitting 1.39 (≈ 2 K) and 1.76 cm^{-1}, respectively, around 4 K. These results are quite close to the observation made by Mackenzie (unpublished results).[10] The Mössbauer spectrum (MS) of the HoT compound consists of 24 transition lines ($E1+M2$ type)[61] restricted by the selection rule $\Delta M_I = 0, \pm 1$ and having corresponding relative average intensities as given in Table III.

V. SPECIFIC HEAT

Low-temperature specific heat C_T of DyT, ErT, and YbT was studied by Blöte *et al.*[20] with particular emphasis on the magnetic ordering phenomena in these cubic compounds, since the cubic compounds are more accessible to theoretical interpretation than noncubic compounds. In the case of HoT, C_T is expected to have the following components:[2,65]

$$C_T = C_L + C_{\mathrm{Sch}} + C_M + C_{\mathrm{hf}}, \tag{7}$$

where C_L, C_{Sch}, C_M, and C_{hf} are, respectively, the lattice, Schottky (or the paramagnetic), magnetic [expected due to magnetic ordering at 1.35 K in HoT (Refs. 17,18)] and the hyperfine components of the specific heat. For HoT which is an insulator, $C_L/R = a_L T^3$, where a_L is of the order of 10^{-5}.[65] Figure 2 shows the calculated thermal characteristics of C_{Sch} defined as[66]

$$C_{\mathrm{Sch}} = \frac{R}{Z^2}\left[Z \sum_{i=1}^{n} x_i^2 \exp(-x_i) - \left\{ \sum_{i=1}^{n} x_i \exp(-x_i) \right\}^2 \right], \tag{8}$$

where $x_i = E_i^{(0)}/kT$, $E_i^{(0)}$ are the zeroth-order CF energies. Figure 2 shows that C_{Sch} vs T curve peaked at 130 K. Review on other Ho^{3+} compounds[7–10,45,48] revealed that the temperature of the peak depends on the separation (Δ) between the ground and the first excited CF level, for example in $\mathrm{Ho(OH)_3}$, $\mathrm{Ho^{3+}{:}Y(OH)_3}$, $\mathrm{HoCl_3}$, $\mathrm{Ho^{3+}(C_2H_5SO_4)_3 \cdot 9H_2O}$, the values of Δ are 21.7, 11.32, 12.5, 0.33 cm^{-1}, respectively, and corresponding peaks were between 50 and 80 K.[2,4,7–10]

The hyperfine specific heat C_{hf} for $^{165}\mathrm{Ho}^{3+}$ in HoT was calculated between 0.02 and 6 K by substituting the energies of the hyperfine levels in Eq. (8). In HoT, the C_{hf}/R curve increased quite sharply below 1.5 and showed a peak at 0.3 K with a peak value of 0.91 R (Fig. 2). It is relevant to mention here that in a similar cubic pyrochlore compound $\mathrm{Ho_2GaSbO_7}$, the hyperfine specific-heat peak of 0.9 R was observed at about 0.3 K (Fig. 2).[20] Both C_L and C_{Sch} fall off to zero value around 10 K, for which reason $C_T = C_{\mathrm{hf}}$ below 10 K. We found that between 10 and 50 K, $T^2 C_{\mathrm{hf}}$ has a constant value ($=0.429\ \mathrm{K}^2$) which is quite close to the value of 0.426 K^2 obtained using the expressions of C_{hf} in the Ising spin-1/2 system[20,67]

$$C_{\mathrm{hf}} T^2/R = 1/9 S(S+1) I(I+1) (A_{\parallel}^2 + 2A_{\perp}^2) \tag{9}$$

for $A_{\parallel}=0.3964\,\mathrm{cm}^{-1}=0.57\,\mathrm{K}$ and $A_{\perp}=0$. Thus due to the CF effect, HoT resembled an almost Ising spin-1/2 system at low temperatures. A similar situation occurred in $\mathrm{LiHoF_4}$, where the CF ground state is a doublet and the g tensor is highly anisotropic.[32]

Isotropic dipole-dipole interactions, the hyperfine splitting of the nuclear ground level of the Ho^{3+} nucleus as well as the isotropic exchange interactions modify the low-temperature characteristic of C_T significantly. According to Daniels,[68] the heat-capacity contributions from the dipolar contribution in the limit of high temperatures can be written as[20]

$$C_T T^2/R=(10.8g_{\parallel}^4+2.8g_{\parallel}^2g_{\perp}^2+12.2g_{\perp}^4)10^{-5}\mathrm{K}^2, \quad (10)$$

assuming 10 Å for the lattice parameter. According to this theory, substitution of the highest g values that may be expected for an ion, yields an upper limit for the $C_T T^2/R$ value, below which the heat capacity can be explained by dipolar interactions only, and above which we have to assume exchange interactions. On substitution of the values of $g_{\parallel}$ and $g_{\perp}$ in the HoT obtained by us, we found $C_T T^2/R$ to be $12.2\pm0.4\,\mathrm{K}^2$. In the case of DyT ($g_{\parallel}=18.73$, $g_{\perp}=0$),[69] this value is 13.3 K^2 whereas Van Geuns[20] observed experimentally $C_T T^2/R=2.5\,\mathrm{K}^2$ at high temperatures. Thus in the light of Daniels' theory if $g_{\parallel}$ is as large as 12, as in HoT, dipolar interaction predominates over the exchange interaction; the latter was found to be ~1 K in HoT.[31] However, it is reversed in the case of cubic pyrochlore Nd^{3+} compounds,[20] viz., $\mathrm{Nd_2GaSbO_7}$, $\mathrm{Nd_2Sn_2O_7}$, $\mathrm{Nd_2Zr_2O_7}$, for which the maximum g value is nearly 3. We next estimated the total energy gain $\Delta E_d/R=1.44\times10^{-2}\,g^2$ for the antiferromagnetic long-range ordering due to dipole interactions in the presence of an external field, with the approximation that the magnetic and the crystallographic unit cell are identical, and the energy gain $\Delta E_e/R=qs^2|J/k|$ for the Heisenberg exchange interaction in the zero magnetic field.[20] The corresponding values obtained were 4.82 and 1.5 K, which may be verified from future experimental measurements of the specific heat with and without an external magnetic field at low temperatures.

VI. CONCLUSIONS

(1) Crystal-field parameters and energy levels of $\mathrm{Ho_2Ti_2O_7}$, were determined with reasonable accuracy.

(2) Magnetic energy gain for the long-range antiferromagnetic dipolar ordering and exchange interaction were estimated with some approximations.

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