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Thermal and nuclear hyperfine properties of $Ho(OH)_3$

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A reasonable explanation for the findings of Catanese and Meissner [Phys. Rev. B **8**, 2071 (1973)] regarding the (hyperfine) heat capacity in the low-temperature region of $Ho(OH)_3$ is given. The Schottky specific heat in the high-temperature region observed calorimetrically by Chirico *et al.* [J. Chem. Thermodyn. **13**, 1092 (1981)] is explained statisfactorily. Nuclear hyperfine constants for Ho^{3+} ions in $Ho(OH)_3$ are determined.

I. INTRODUCTION

Holmium hydroxide[1,2] and erbium hydroxide[3] are the heaviest lanthanide hydroxides whose magnetic, optical, and thermal properties have been investigated. The crystals of holmium hydroxide show good chemical and mechanical stability and are being used in many practical devices as laser host materials and in devices using optical Faraday rotation or birefringence. Since holmium hydroxide has been found to be a highly anisotropic ferromagnet with Curie point at a readily accessible temperature (2.54 K) in the liquid-helium range, its crystals are being widely used as a low-temperature, nonmetallic ferromagnet with large saturation magnetization.[4]

The hyperfine interactions in the rare-earth elements have been studied extensively.[5-9] In the excited states, they have been studied by photoexciting them and then performing electron spin resonance (ESR) experiments.[10] The investigation of the hyperfine interaction by optical absorption and emission spectroscopy was possible since the lines were found to be as narrow as those observed in the spectra of free atoms.[9] But detection is not always possible since the hyperfine interactions give energy-level splittings $\sim 1\ \mathrm{cm}^{-1}$ which is about the residual linewidth due to strains in the crystal. Ho^{3+} is the only one of the rare earths whose resolved nuclear hyperfine structure has been observed in the optical spectra. The compounds thus investigated were $HoCl_3$, $Ho{:}Y(NO_3)_3\cdot 6H_2O$ (Ref. 11), $Ho{:}LaCl_3$, $Ho(C_2H_5SO_4)_3\cdot 9H_2O$, and $Ho{:}Y(C_2H_5SO_4)_3\cdot 9H_2O$.[12] These observations were possible due to the simultaneous occurrence of several facts: firstly, the residual linewidth was very small; secondly, the nuclear angular momenta of the ground and first excited states of Ho^{3+} ion are very large; thirdly, the g factor of the ground crystal field level is highly anisotropic; and fourthly, there occurs only one isotope of holmium (^{165}Ho) with large isotopic spins in the ground ($\frac{7}{2}$) and first excited ($\frac{9}{2}$) states. Magnetic Sternheimer factor and hyperfine constants of the nuclear states were deduced from these measurements.

The half-life period of the excited state of ^{165}Ho when excited by 94.7 keV is 0.022 nsec.[13] This is in contrast to 28.1 and 920 nsec, the half-life periods of the excited states of ^{161}Dy when excited by 25.65 and 43.84 keV, respectively. That is why numerous Mössbauer-effect experiments have been performed for dysprosium compounds,[14] but only few have been reported for holmium.[13,15]

With accurate knowledge of the interaction of the rare-earth ion with the crystal field,[1] the electric-field-gradient (EFG) tensor can be calculated at various temperatures. Thereby the nuclear quadrupole interaction in the ground and first excited states of ^{165}Ho nucleus may be determined. The hyperfine constant for $Ho(OH)_3$ was previously reported to be $0.0305\ \mathrm{cm}^{-1}$.[4] So, the hyperfine field at the nucleus can be estimated. The nuclear hyperfine Hamiltonian was solved and the different nuclear levels in the ground and first excited states of Ho^{3+} ion were determined. The thermal variation of the hyperfine specific heat was calculated from 0.1 to 20 K, and a reasonable explanation for the sharp rise below 1 K, observed by Catanese and Meissner,[4] was obtained. The thermal variation of the Schottky heat capacity[16] was calculated from 5 to 350 K, and the large discrepancy observed by Chirico, Boeiro-Gates, and Westrum[17] between the calorimetrically deduced and calculated values was removed.

II. RESULTS AND DISCUSSION

The temperature dependence of the nuclear quadrupole interaction energy P_{gr} for the ground state of ^{165}Ho in $Ho(OH)_3$ is shown by curve A in Fig. 1. With the decrease of temperature, it increases sharply below 200 K and attains a maximum value around 4 K. Curve B has been plotted disregarding the lattice contribution to the electronic shielding which is a temperature-independent term. The difference between the two curves shows the large contribution of the lattice part $(1-\gamma_\infty)\, q_{zz}^{(\mathrm{lat})}$ to the electric field gradient at the nucleus.

The effective hyperfine field at the nuclear site was found to be 8.23 MG which is in reasonable agreement with the value reported by Gerdau *et al.*[13] For Dy^{3+} this field was found to be 5.68 MG.[14] It is noted that the nuclear hyperfine field for the transition-metal ions is of the order of kilogauss,[18] whereas in rare earths it is of the order of megagauss.[19]

The magnetic field and the electric field gradient set up at the nucleus by the distorted $4f$ electron and closed electron shells interact with the nuclear magnegtic dipole and electric quadrupole moments, respectively, and split the nuclear state. The extent of splitting is dependent on the EFG and thus is very sensitive to the crystal field (CF). This is because the magnitude of EFG is determined by CF levels and their eigenstates. The hyperfine structure so produced was computed at various temperatures from 0.1 to 20 K for the

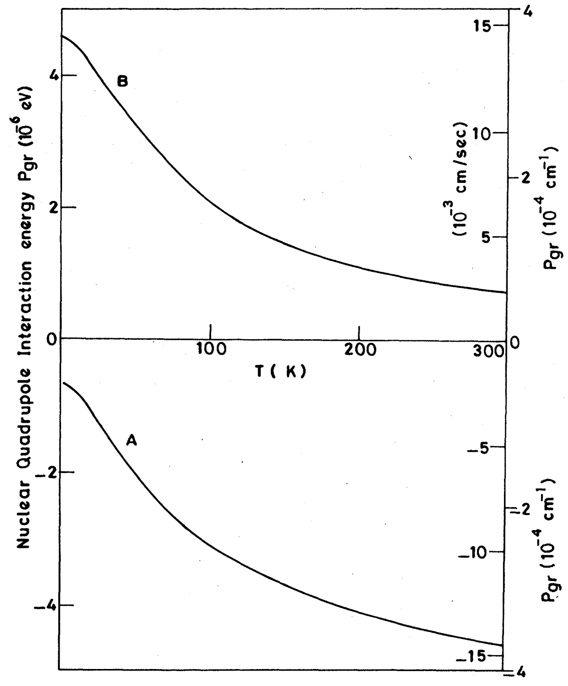
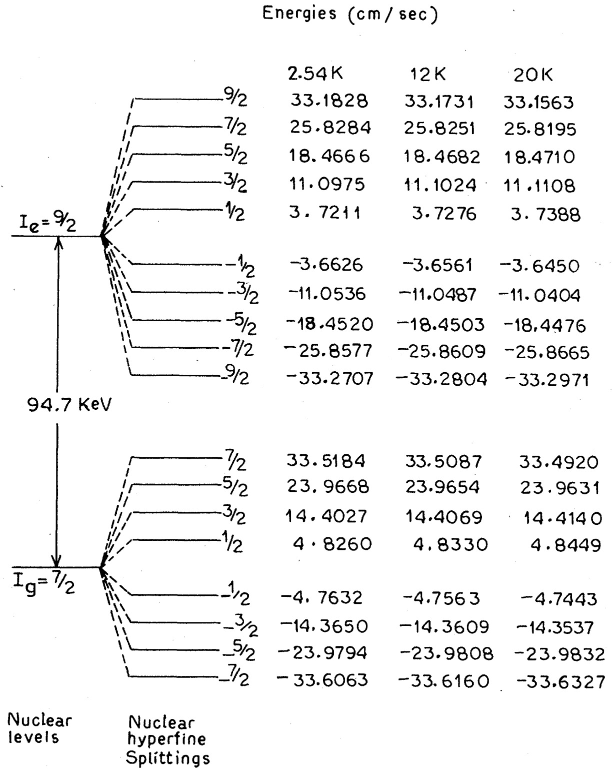


FIG. 1. Temperature dependence of the nuclear quadrupole interaction energy (curve A). Curve B was plotted disregarding the lattice contribution to the electronic shielding.



Energies (cm/sec)

	2.54 K	12 K	20 K
9/2	33.1828	33.1731	33.1563
7/2	25.8284	25.8251	25.8195
5/2	18.4666	18.4682	18.4710
3/2	11.0975	11.1024	11.1108
1/2	3.7211	3.7276	3.7388
−1/2	−3.6626	−3.6561	−3.6450
−3/2	−11.0536	−11.0487	−11.0404
−5/2	−18.4520	−18.4503	−18.4476
−7/2	−25.8577	−25.8609	−25.8665
−9/2	−33.2707	−33.2804	−33.2971
7/2	33.5184	33.5087	33.4920
5/2	23.9668	23.9654	23.9631
3/2	14.4027	14.4069	14.4140
1/2	4.8260	4.8330	4.8449
−1/2	−4.7632	−4.7563	−4.7443
−3/2	−14.3650	−14.3609	−14.3537
−5/2	−23.9794	−23.9808	−23.9832
−7/2	−33.6063	−33.6160	−33.6327

FIG. 2. Hyperfine structure of the ground and first excited nuclear manifolds.

ground and first excited nuclear states (94.7 keV transition) (see Fig. 2). The splitting of the eight nuclear levels is found to be 1.7 cm^{-1} or 2.4 K. The hyperfine field at the holmium nucleus was studied by Mackenzie[20] and the total splitting found to be approximately 2.2 K. The quadrupole interaction of states of higher J with the ground multiplet by the crystal electric field yields a second-order perturbation. The calculation of this contribution gave a negligibly small value. The ratio of the nuclear magnetic moments of the first excited state to the ground state was assumed to be the same as for Ho metal, viz., 0.77.[13] The quadrupole mo-

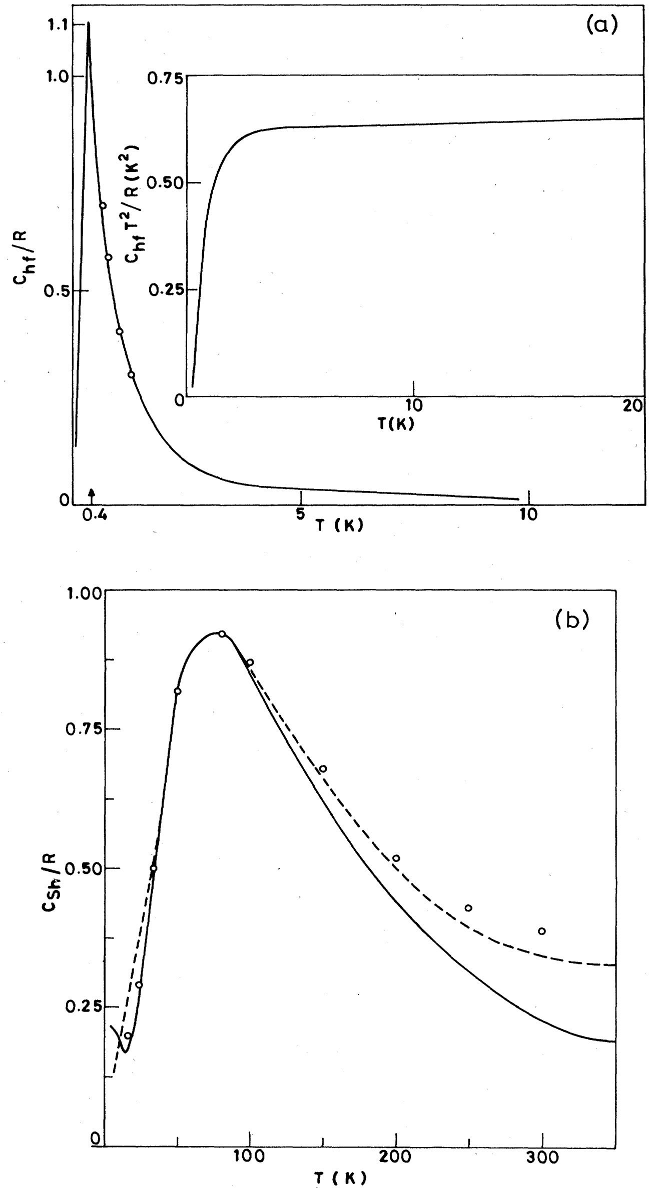


FIG. 3. (a) Thermal variation of the hyperfine specific heat. Insert shows the temperature dependence of $C_{hf}T^2/R$. (b) Thermal variation of Schottky specific heat. Circles represent the calorimetrically observed values by Chirico *et al.*[17] Solid and broken lines represent the calculated values using the CFP of Ho:Y(OH)$_3$ and the present CFP, respectively.

ments of the two states were found to be the same, viz., 3.53 barns.[21]

In Mössbauer spectroscopy, the transitions from one of the levels of excited states to a level in the ground state are observed. The selection rule for the dipole radiation is $\Delta m_I = 0, \pm 1$. The relative energies of different possible nuclear transitions at temperatures from 2.54 to 20 K are listed in Table I. The γ-ray intensities were computed. The spectrum will consist of 24 hyperfine lines. Eight lines corresponding to $\Delta M_I = 0$ transitions would be absent if the propagation direction of the γ rays is parallel to the crystal c axis.

The thermal variation of the hyperfine specific heat is shown in Fig. 3(a) from 0.1 to 10 K. The circles representing the experimental points obtained by Catanese and Meissner[4] lie very close to this curve. A hyperfine peak is found at 0.4 K. The specific heat at 0.4 K is 27.5 times its value at 4 K. The spin entropy associated with the peak is 2.08. The insert shows the thermal variation of $C_{\mathrm{hf}} T^2/R$. It remains constant over a wide region from 3 to 20 K. The constant of proportionality is 0.63 ± 0.01 K^2. Consequently, this property may be utilized for low-temperature thermometry. It is pointed out here that the C_{hf} estimated by the experimentalists failed to account for the sharp increase in the hyperfine specific heat below 1 K. They even varied the value of the hyperfine constant, yet were not successful. The reason being that they used the following approximate expression given by Mattis and Wolf:[22]

$$C_{\mathrm{hf}} = -\frac{AI}{2}\frac{d}{dT}B_I\left(\frac{AI}{kT}\right) .$$

TABLE I. Different possible nuclear transitions with their relative energies and intensities.

Transition	Relative energy (cm/sec)			Average intensity (powder sample)	Relative intensity (crystalline samples)	
	2.54 K	12 K	20 K		C axis∥	C axis⊥
$-\frac{5}{2} \to -\frac{7}{2}$	15.1543	15.1657	15.1851	$\frac{1}{36}$	$\frac{1}{24}$	$\frac{1}{48}$
$-\frac{3}{2} \to -\frac{5}{2}$	12.9258	12.9321	12.9428	$\frac{1}{12}$	$\frac{1}{8}$	$\frac{1}{16}$
$-\frac{1}{2} \to -\frac{3}{2}$	10.7024	10.7048	10.7087	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{8}$
$\frac{1}{2} \to -\frac{1}{2}$	8.4843	8.4839	8.4831	$\frac{5}{18}$	$\frac{5}{12}$	$\frac{5}{24}$
$-\frac{7}{2} \to -\frac{7}{2}$	7.7486	7.7551	7.7662	$\frac{2}{9}$	0	$\frac{1}{3}$
$\frac{3}{2} \to \frac{1}{2}$	6.2715	6.2694	6.2659	$\frac{5}{12}$	$\frac{5}{8}$	$\frac{5}{16}$
$-\frac{5}{2} \to -\frac{5}{2}$	5.5274	5.5305	5.5356	$\frac{7}{18}$	0	$\frac{7}{12}$
$\frac{5}{2} \to \frac{3}{2}$	4.0639	4.0613	4.0570	$\frac{7}{12}$	$\frac{7}{8}$	$\frac{7}{16}$
$-\frac{3}{2} \to -\frac{3}{2}$	3.3114	3.3122	3.3133	$\frac{1}{2}$	0	$\frac{3}{4}$
$\frac{7}{2} \to \frac{5}{2}$	1.8616	1.8597	1.8564	$\frac{7}{9}$	$\frac{7}{6}$	$\frac{7}{12}$
$-\frac{1}{2} \to -\frac{1}{2}$	1.1006	1.1002	1.0993	$\frac{5}{9}$	0	$\frac{5}{6}$
$-\frac{9}{2} \to -\frac{7}{2}$	0.3356	0.3356	0.3356	1	$\frac{3}{2}$	$\frac{3}{4}$
$\frac{9}{2} \to \frac{7}{2}$	−0.3356	−0.3356	−0.3357	1	$\frac{3}{2}$	$\frac{3}{4}$
$\frac{1}{2} \to \frac{1}{2}$	−1.1049	−1.1054	−1.1061	$\frac{5}{9}$	0	$\frac{5}{6}$
$-\frac{7}{2} \to -\frac{5}{2}$	−1.8783	−1.8801	−1.8833	$\frac{7}{9}$	$\frac{7}{6}$	$\frac{7}{12}$
$\frac{3}{2} \to \frac{3}{2}$	−3.3052	−3.3045	−3.3032	$\frac{1}{2}$	0	$\frac{3}{4}$
$-\frac{5}{2} \to -\frac{3}{2}$	−4.0870	−4.0894	−4.0939	$\frac{7}{12}$	$\frac{7}{8}$	$\frac{7}{16}$
$\frac{5}{2} \to \frac{5}{2}$	−5.5002	−5.4972	−5.4921	$\frac{7}{18}$	0	$\frac{7}{12}$
$-\frac{3}{2} \to -\frac{1}{2}$	−6.2904	−6.2924	−6.2961	$\frac{5}{12}$	$\frac{5}{8}$	$\frac{5}{16}$
$\frac{7}{2} \to \frac{7}{2}$	−7.6900	−7.6836	−7.6725	$\frac{2}{9}$	0	$\frac{1}{3}$
$-\frac{1}{2} \to \frac{1}{2}$	−8.4866	−8.4891	−8.4899	$\frac{5}{18}$	$\frac{5}{12}$	$\frac{5}{24}$
$\frac{1}{2} \to \frac{3}{2}$	−10.6816	−10.6793	−10.6752	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{8}$
$\frac{3}{2} \to \frac{5}{2}$	−12.8693	−12.8630	−12.8523	$\frac{1}{12}$	$\frac{1}{8}$	$\frac{1}{16}$
$\frac{5}{2} \to \frac{7}{2}$	−15.0518	−15.0405	−15.0210	$\frac{1}{36}$	$\frac{1}{24}$	$\frac{1}{48}$

But, $Ho(OH)_3$ is Ising-like only to a first approximation and the non-Ising terms in the Hamiltonian limit the above expression to being a first approximation to C_{hf}. The other reason was the use of eigenstates and energy levels of $Ho:Y(OH)_3$. Although the fact remains that they found a discrepancy of about 15% in the experimental and the theoretically calculated values of different magnetic properties due to the lack of complete correspondence of crystal fields in $Ho(OH)_3$ and $Ho:Y(OH)_3$, one cannot assume the Ho^{3+} ion to show the same low-temperature properties in different environments because of the small but significant effect of the crystal electric field.

Using the crystal field for $Ho(OH)_3$,[1] the Schottky specific heat was calculated and the thermal variation is shown by the broken line in Fig. 3(b), where the solid line represents the same using the crystal field parameters (CFP) of $Ho:Y(OH)_3$. Circles represent the calorimetrically observed values by Chirico *et al.*[17] It is seen that the experimetal points lie quite close to the broken lines. Hence, the large discrepancy at higher temperatures observed by Chirico[17] between the calorimetrically deduced and the calculated values is minimized if the exact crystal field for $Ho(OH)_3$ is used. Hence, it can be concluded that Chirico's lattice approximation scheme between 11 and 350 K can be successfully extrapolated to include the heavier lanthanides.

III. CONCLUSION

A single crystal field gives a remarkably good description of all the properties observed so far over a wide range of temperature from room temperature down to liquid-helium temperatures. There is no indication of any change of crystal field with temperature. It establishes the important fact that the hyperfine splitting in the paramagnetic and ferromagnetic states of $Ho(OH)_3$ are the same. This is quite unlike the case with compounds of the iron group.[23]

The highly anisotropic g values in the ground state of $Ho(OH)_3$ make the magnetic dipole interactions correspondingly anisotropic, the largest part being due to the two nearest neighbors which lie along the c axis. Therefore, the results for linear Ising chains of nearest neighbors can be used. But, at the same time, the smaller interactions with other neighbors should be taken into account by a molecular field,[14] because, for some thermophysical properties at low temperatures, the weaker long-range interactions become very significant.

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