CHAPTER 7

PUBLISHED PAPERS
Magnetic studies on erbium bromate and the crystal field

D. Neogy *, A. Chatterji, P.K. Chakrabarti, K.N. Chattopadhyay

*Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India

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D. Neogy *, A. Chatterji, P.K. Chakrabarti, K.N. Chattopadhyay
Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India
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Abstract

Measurements of the principal magnetic susceptibilities of erbium bromate single crystals in the temperature range 300–15.5 K have been made. The anisotropy at 300 K is high (|ΔX/ΔX| = 0.15) and it increases very rapidly with decreasing temperature. The variation of X⊥ is nearly Curie-type down to the lowest temperature attained, whereas the X∥ versus T plot is nearly flat. Smooth variation of X⊥ down to 15.5 K does not indicate any structural phase transition of the crystal. The observed magnetic properties were analyzed for the first time invoking an effective electrostatic interaction of the Er³⁺ ion with its diamagnetic surroundings; the crystal field (CF) conforms to the approximate site symmetry of Er³⁺, i.e. D₃h. The CF J–J mixing was included through term diagonalization and intermediate coupling effects were partly taken care of using appropriate reduced matrix elements. The computed values are in very good agreement with the corresponding observed values. Our computed values of X∥ in the range 60–500 mK reproduced the same sort of behavior as predicted by Simizu et al. in 1984. The thermal and hyperfine properties have been worked out.

1. Introduction

Recently the rare earth bromate (REBR) single crystals have been the subject of detailed studies to determine their magnetic properties and crystal structure. The earliest known work on the REBR was that of Spedding et al. [1] on the absorption spectra of samarium bromate. The crystal structures of a number of REBR [2–5] have already been reported. There are some recent conflicting reports [6] on the crystal structure which contradict these findings in principle. However, a detailed consideration of various results and the smallness of deviations from ideal D₃h symmetry and their uncertainties allow us to take the site symmetry of RE³⁺, D₃h and the crystal pseudohexagonal, i.e. uniaxial at least magnetically in the first approximation. The low-temperature susceptibilities of REBR (RE = Pr, Tb, Dy, Er and Tm) from 0.06–4.2 K have been measured by Simizu et al. [7,8] but no attempt was made to provide a quantitative theoretical explanation of the observed properties. In some recent work on the magnetic properties of RE bromates [9–13] we have covered the temperature range 300–77 K and have also provided a tentative explanation to the observed results invoking crystal field interaction. In the present paper we describe the results of our magnetic measurements on the single crystal of ErBR carried out for the first time in the temperature rage 15.5–300 K. The wide deviation

* Corresponding author.

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from the free-ion behavior is explained in the light of crystal field (CF) theory. Stark patterns of the low-lying \( J \)-multiplets of \( \text{Er}^{3+} \) in this pure crystal (ErBR) were obtained by term diagonalization of the CF Hamiltonian following the procedure adopted in earlier work \[14\]. Theoretical excursions into the magnetic, thermal and hyperfine properties of \( \text{Er}^{3+} \) ion in the bromate lattice are made using the results of CF analyses of the observed magnetic susceptibilities.

2. Experimental details

Erbium bromate single crystals were obtained by slow evaporation of ErBR solution at room temperature. The latter was prepared by the double decomposition of erbium sulfate and barium bromate in a hot aqueous solution. Light pink transparent needle-shaped crystals of \( \text{Er} \left( \text{BrO}_3 \right)_3 \cdot 9\text{H}_2\text{O} \) were obtained with elongation along the \( c \)-axis, the symmetry axis of the crystal. The crystals were then checked under a polarizing microscope for twinning. The absolute magnetic susceptibility perpendicular to the symmetry axis in the isotropic plane of the crystal was measured from \( 300 \) K down to \( 15.5 \) K by suspending the crystal with a thin quartz fibre in a magnetic field with a constant vertical field gradient produced by a pair of Faraday pole caps \[15\]. A highly sensitive microprocessor-controlled self-nulling taut band electromagnetic balance was fabricated for the Faraday measurements. The low-temperature environment was generated by an APD closed-cycle helium refrigerator. Temperature control was provided by a Scientific Instruments temperature controller using a gold-chrome thermocouple. The crystal was placed in the sample chamber nearly 12 cm below the second cold station. The calibration of the temperature of the sample chamber was performed by measuring the susceptibility of a \( \text{Mn(NH}_4\text{)}_2\text{(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) single crystal which is virtually magnetically isotropic and follows the Curie law (with \( \theta = 0 \)) down to 1 K \[16\]. The measurements were carried out in a helium atmosphere maintained at optimum pressure for good heat exchange and minimal disturbance of the balance by convection currents. With this procedure, the sample chamber temperature was found to follow the temperature of the second cold station monitored constantly by the APD temperature controller. In low-pressure environment at low temperatures, the crystal tended to lose its water of crystallization. This was prevented by coating the crystal with high-vacuum silicone grease.

The magnetic anisotropy \( (\Delta X = X_\perp - X_\parallel) \) was measured from room temperature down to \( 90 \) K employing the torsion balance described earlier \[9\]. Since \( X_\perp > X_\parallel \) and the anisotropy is quite high, the crystal rotated in the magnetic field when it was suspended with \( X_\parallel \) in the field direction with a less rigid quartz fibre in order to keep the suspension light. The susceptibilities at very low temperatures were corrected for demagnetization.

3. Results, analysis and discussion

The effective magnetic moment \( P_{\text{eff}} = 9.39 \) at \( 300 \) K was calculated from the observed results using the relation \( P_{\text{eff}} = (7.9971 \bar{X}T)^{1/2}, \) where \( \bar{X} = (X_\perp + 2X_\parallel)/3. \) This is only slightly lower than the free-ion value of 9.58; the corresponding value observed for \( \text{Er}^{3+} \) in \( \text{LaF}_3 \) \[17\], which has a closely resembling structure, is 9.34. The variation of \( P_{\text{eff}} \) with temperature is not appreciable; at 90 K the observed value is 8.99. Values of \( P_{\text{eff}} \) at different temperatures are shown in Table 1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( X_\perp )</th>
<th>( \Delta X )</th>
<th>( X_\parallel )</th>
<th>( \bar{X} )</th>
<th>( P_{\text{eff}} )</th>
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<td>300</td>
<td>36.60</td>
<td>-5.50</td>
<td>33.10</td>
<td>36.77</td>
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<td>260</td>
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<tr>
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<td>205.00</td>
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<td>85.00</td>
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<td>40</td>
<td>311.70</td>
<td>-247.00</td>
<td>98.70</td>
<td>148.40</td>
<td>8.99</td>
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<tr>
<td>30</td>
<td>402.80</td>
<td>-338.00</td>
<td>112.00</td>
<td>160.80</td>
<td>8.99</td>
</tr>
<tr>
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<td>573.20</td>
<td>-513.00</td>
<td>125.20</td>
<td>172.40</td>
<td>8.99</td>
</tr>
<tr>
<td>15.5</td>
<td>695.40</td>
<td>-638.00</td>
<td>138.40</td>
<td>184.80</td>
<td>8.99</td>
</tr>
</tbody>
</table>
least-squares fit of $\bar{X}$ to the Curie-Weiss law was tried and an excellent fit obtained (Fig. 1). The Curie constant and the paramagnetic Curie temperature ($\theta$) turned out 10.93 emu K and $-8.02$ K, respectively, with an rms deviation of 0.001 cm$^3$/mol. In this case $\theta$ is negative, as in many other RE bromates, which is due to the change in population among the CF levels rather than any exchange or dipolar effect.

The crystallographic c-axis sets perpendicular to the applied magnetic field, indicating that $X_\perp > X_\parallel$ at room temperature; the magnetic anisotropy is high, the relative magnetic anisotropy $|\Delta X/\bar{X}|$ at 300 K being 0.15. The rate of increase of $\Delta X$ with decreasing temperature is rather high; it becomes 14 times at 90 K (Table 1) and $|\Delta X/\bar{X}| = 0.67$, which is 4.5 times the value at 300 K. The explanation of the observed wide departure in the magnetic behavior of Er$^{3+}$ in this lattice from that of the free ion obviously leans heavily on the electrostatic interaction of the ion with the lattice, usually approximated by a one-electron crystal field. This has proved quite adequate for magnetic and other bulk properties, although for very precise spectroscopic results more sophisticated treatments may be necessary [18].

The 4f$^{11}$ electronic configuration of Er$^{3+}$ yields $^4I$ as the ground term. The ground multiplet splits into eight Kramers doublets under the influence of the crystal field of D$_3h$ symmetry [19] for which the CF interaction term in the Hamiltonian is given by

$$H_{\text{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{66}(C_{66} + C_{6-6}),$$

where the $B_{KQ}$'s are all real constants that parametrize the CF, and the $C_{KQ}$'s are tensor operators. For determination of the physical properties of the ion in the crystal it is sufficient to consider the low-lying energy levels and corresponding eigenvectors; for this we work in the basis of 52 $|4f^n, L, S, J, J_z\rangle$ kets spanned by the set of states of the ground and all three excited multiplets of the ground term. This adequately takes into account the CF J-mixing of the ground

![Graph](image-url)  

Fig. 1. Least-squares fit to $\bar{X}$ of Er(BrO$_3$)$_2$9H$_2$O.
multiplet states. The Hamiltonian $H = H_{SO} + H_{CF}$, $H_{SO}$ being the spin–orbit interaction term diagonal in $J$, is then block-diagonalized taking into consideration the intermediate coupling (IC) effects introducing the IC-reduced matrix elements; the approximate baricenters of the multiplets of the ground term are introduced to replace $H_{SO}$ in setting up the Hamiltonian matrix. Details of the procedure have been discussed in an earlier report [14]. With the resulting $J$-mixed Stark states and energies (shown in Table 2) the first- and second-order Zeeman energies were calculated for magnetic fields applied parallel and perpendicular to the symmetry axis of the crystal. Only the ground multiplet was considered for computing the susceptibilities since the highest temperature in the present study is only 300 K, at which the occupation of the higher multiplets would be less than 0.01%. The values of $X_{\parallel}$ and $X_{\perp}$ are calculated at different temperatures by using Van Vleck's well-known expression. We concentrated first on the determination of the CF parameters for the precise simulation of the observed values of $X_{\perp}$ from 15.5 to 300 K and $\Delta X$ from 90 to 300 K. The CF parameters were adjusted to obtain magnetic susceptibilities in close agreement with our observed values. However, this failed to produce exactly the results obtained below 0.5 K by Simizu et al. [7]. The final set of parameters that was arrived at is

\[ B_{20} = 120, \quad B_{40} = -580, \quad B_{60} = -380, \quad B_{66} = 700 \text{ (all in cm}^{-1}). \]

![Fig. 2. Experimental and theoretical variations of the principal magnetic susceptibilities ($X_\parallel$ and $X_\perp$) of Er$^{3+}$ in Er(BrO$_3$)$_3 \cdot 9$H$_2$O with temperature.](image)
Using the above CF parameters we calculate the CF strength parameter defined as [20]:

\[
S = \left( \frac{1}{3} \sum_k \frac{1}{2k+1} \right)^{1/2} \times \left[ B_{x0}^2 + 2 \sum_{m>0} \left( R B_{x+m}^2 + I B_{x-m}^2 \right) \right]^{1/2},
\]

which is a quantitative measure of the strength of the CF interaction of a particular RE ion in a given host lattice; in the present case it turns out to be 205.5 cm\(^{-1}\), which is about 28% greater than in HoBR [13]. The thermal variation of the susceptibilities is depicted in Fig. 2 along with the observed results. The calculated and observed values of \(\Delta X\) at different temperatures are presented in Fig. 3. From Figs. 2 and 3 it is evident that the computed values of \(X_\perp\) and \(\Delta X\) are in very good agreement with the corresponding experimental results, and consequently the observed behavior of \(X_\parallel\) is also reproduced quite faithfully by our theoretical values. The variation of \(X_\perp\) (Fig. 2) is nearly Curie-type down to the lowest temperature attained. Although the variation of \(X_\perp\) with temperature is largely due to the rearrangement of populations in the various CF levels, incidentally, it is very nearly Curie type down to 15.5 K. Simizu et al. [7] have measured \(X_\parallel\) from 500 to 60 mK, and state that the variation is of Curie-Weiss type; our theoretical values also give a Curie-type variation in this range. Since the spread of the experimental points in the graph in Ref. [7] is rather high it is difficult to retrieve the observed values for comparison. However, a rough estimate shows their values to be somewhat higher than our computed values. This is quite likely due to slight error in orientation of the crystal in the magnetic field. As \(X_\perp\) is nearly 50 times \(X_\parallel\) at 15 K even a small orientational error may lead to a large contribution from \(X_\perp\) to the observed susceptibility, i.e. \(X_\parallel\). The ground Stark doublet is nearly 40 cm\(^{-1}\) below the first excited state and hence spin resonance can only be observed for the ground state for which

![Graph](image-url)
the transition probability is found to be quite high. Considering the ground state wavefunction, the spectroscopic splitting factors \(g_1\) and \(g_\perp\) turn out to be 1.24 and 8.87, respectively. This wide difference in \(g\)-values is quite in keeping with the large observed magnetic anisotropy.

4. Thermal and hyperfine properties

The electronic heat capacity is computed using the relation

\[
C_s = N_A \left( \frac{d}{dT} \right) \frac{\text{Tr}(H\rho)}{\text{Tr}(\rho)} ,
\]

where \(H\) is the Hamiltonian matrix, \(\rho\) is the statistical density matrix, and \(N_A\) is Avogadro's number. The variation of \(C_s\) with temperature is shown in Fig. 4. The Schottky heat capacity shows a broad hump in which a low peak at 46 K is located; the peak value is 6.025 J/g·atom K. The rapid fall of \(C_s\) after attaining the maximum value indicates the possibility of easy experimental verification of the anomaly.

The hyperfine properties of the \(^{167}\text{Er}\) in erbium bromate are strongly influenced by the 4f-electrons and the lattice. In the present case the nuclear ground state spin is \(7/2\) and the electric quadrupole moment is 2.83 barn. The nuclear level would split by the quadrupole interaction between the nucleus and the electric field gradient (EFG) at the nuclear site produced by the 4f-electrons and the lattice. For fast electronic relaxation the 4f contribution to the EFG would be the time-averaged effect of all the low-lying CF Stark states because of the probability of occupying the excited states during the finite nuclear lifetime. Thus the quadrupole splitting \(\langle \Delta E_Q \rangle_T\) between any two adjacent nuclear states \(|I, I_z\rangle\) and \(|I, I_z + 1\rangle\) due to the 4f contribution to the EFG would be highly temperature dependent, whereas the lattice contribution is more or less constant. The quadrupole splitting \(\langle \Delta E_Q \rangle_T\) is
Fig. 5. Thermal variation of the nuclear electric quadrupole splitting between the lowest two doublets \([I \pm 7/2]\) and \([I \pm 5/2]\) due to time-averaged EFG of \(^{167}\text{Er}\) in erbium bromate.

Fig. 6. Hyperfine heat capacity \((C_N)\) of \(^{167}\text{Er}\) in erbium bromate at various temperatures.
Table 2
Crystal field Stark splitting of the ground term $^4I$ of the Er$^{3+}$ ion in Er bromate and its ground state wavefunction

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>Energy (cm$^{-1}$)</th>
<th>Wavefunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{13/2}$</td>
<td>0</td>
<td>$0.7087(15/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>39.90</td>
<td>$-0.0752(15/2,\mp 5/2)$</td>
</tr>
<tr>
<td></td>
<td>101.6</td>
<td>$0.0069(15/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>118.1</td>
<td>$0.0160(13/2,\mp 5/2)$</td>
</tr>
<tr>
<td></td>
<td>282.3</td>
<td>$-0.0010(11/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>6596</td>
<td>$-0.0026(11/2,\mp 5/2)$</td>
</tr>
<tr>
<td></td>
<td>6614</td>
<td>$0.0007(9/2,\pm 5/2)$</td>
</tr>
<tr>
<td></td>
<td>6721</td>
<td>$0.0000(9/2,\mp 5/2)$</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>10259</td>
<td>$0.7052(15/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>10262</td>
<td>$-0.7052(15/2,\mp 7/2)$</td>
</tr>
<tr>
<td></td>
<td>10265</td>
<td>$+0.0091(15/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>10285</td>
<td>$+0.0160(13/2,\mp 5/2)$</td>
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<tr>
<td></td>
<td>10291</td>
<td>$-0.0010(11/2,\pm 7/2)$</td>
</tr>
<tr>
<td></td>
<td>10307</td>
<td>$-0.0026(11/2,\mp 5/2)$</td>
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<td>$^4I_{9/2}$</td>
<td>12392</td>
<td>$0.0007(9/2,\pm 5/2)$</td>
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<td>$0.0000(9/2,\mp 5/2)$</td>
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<td>12528</td>
<td>$0.0000(9/2,\pm 5/2)$</td>
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<td>$0.0000(9/2,\mp 5/2)$</td>
</tr>
<tr>
<td></td>
<td>12672</td>
<td>$0.0000(9/2,\pm 5/2)$</td>
</tr>
</tbody>
</table>

expressed as [21]:

$$\langle \Delta E_Q \rangle_T = \left\{ -3e^2Q(2I_z + 1)/(4I(2I - 1)) \right\}$$

The magnetic hyperfine Hamiltonian is given by

$$H_{hf} = A\langle N,I \rangle = -\beta_N H_e \cdot \mu_N.$$  

$A = 2\beta_N g_N \langle r^{-3} \rangle_{hf}$ is the hyperfine structure parameter, $g_N = \mu_N/\mu$, and the other symbols have their usual meanings [22]; the z-component of $H_e$ is given by

$$H_{ez} = -(A/\beta_N g_N) \langle N_z \rangle,$$

where $\langle N_z \rangle$ is the quantum mechanical average of $N_z$ over the occupied electronic states of the ion [23], which behaves much like $(L + 2S)$. Due to J-mixed CF states the value of $\langle N_z \rangle$ would depend on the off-diagonal elements in $J$. In presence of a magnetic field and at very low temperatures, the value of $\langle N_z \rangle$ can be calculated by using the lowest electronic Zeeman state which only will be occupied. The value of $H_e$ in this case is only 0.55 MG, whereas in pure metal it is 7.64 MG [24]. The hyperfine Hamiltonian for $D_{3h}$ symmetry in the presence of a magnetic field along the symmetry axis is given by [25]:

$$H_n = A^P Z, I, + (A/2)(S_+I_- + S_-I_+ + P[I^2 - I(I + 1)/3]),$$

$H_n$ was diagonalized to calculate the hyperfine energies and hence the nuclear specific heat ($C_N$). The temperature variation of $C_N$ is depicted in Fig. 6. A Schottky-type anomaly is seen at 4.4 mK with the peak value 2.76 J/g·atom K.

5. Conclusions

The observed magnetic properties of Er (BrO$_3$)$_3$·9H$_2$O have been explained quite satisfactorily by the electrostatic interaction of Er$^{3+}$ ion with the lattice. The smooth variation of $X_\perp$ from 300 K down to 15.5 K does not suggest any structural phase transition or deviation from $D_{3h}$ site symmetry about the Er$^{3+}$ ion. The observed values of $X_\parallel$ in the temperature range 0.06–0.5 K [7] obey the Curie–Weiss law and our theory reproduced the same sort of behavior with relatively lower values. This discrepancy between theoretical and observed values of $X_\parallel$ may arise due to crystal mounting and orientational effects, since
the values of $X_L$ are exceptionally high (nearly 50 times) compared with the values of $X_1$ in this temperature range. The ground Stark state, a Kramers doublet well separated from the first excited state, yields highly anisotropic g-values, i.e. $g_\parallel = 1.24$ and $g_\perp = 8.87$. The hyperfine properties of $^{167}$Er in erbium bromate display the strong influence of its crystalline environment.

References

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Magnetic Measurements and Crystal Field Investigations on Yb(BrO₃)₃ · 9 H₂O

By
D. NEOGY, P. K. CHAKRABARTI, K. N. CHATTOPADHYAY, and A. CHATTERJI
(Received October 24, 1994; in revised form January 30, 1995)

Ytterbium bromate (Yb(BrO₃)₃ · 9 H₂O) single crystals were grown, and the magnetic susceptibility perpendicular to the symmetry axis (χ₄) and the magnetic anisotropy (Δχ = χ₁ - χ₄) were measured in the temperature range 300 to 14 K and 300 to 90 K, respectively. The magnetic anisotropy at 300 K is considerable (≈23%). The smooth variation of χ₄ down to 14 K does not suggest any structural phase transition or symmetry breaking. An analysis of the observed results undertaken for the first time invoking crystal field theory based on rare-earth site symmetry D₃h provides a satisfactory explanation to the experimental results.

1. Introduction

The rare-earth (RE) bromates [RE(BrO₃)₃ · 9 H₂O] which form an isomorphous series have been investigated extensively for their interesting behaviour particularly in the area of crystal structure, magnetic ordering, spectroscopy, and thermal behavior. The first reported work on rare-earth bromates (REBR) is that of Spedding and Bear [1] on the absorption spectra of samarium bromate. Later Hellwege and Hellwege [2], and Hellwege and Kahle [3] also carried out spectroscopic studies on some RE bromates. The crystal structure and site symmetry of the RE ions have been a subject of some controversy. Whereas some works [4 to 7] assume a hexagonal unit cell, some spectroscopic [2, 3] and a recent crystal structure [8] studies point to a lower-symmetry space group. However, the structural refinements lending credence to such a conclusion could not be called definitive due to experimental uncertainties [8]. Thus, as discussed in detail in earlier reports [9, 12], it is reasonable to consider the crystal as pseudohexagonal, i.e., uniaxial, with the site symmetry about the coordinated rare-earth ion, within experimental uncertainties, being D₃h.

The low-temperature susceptibilities of some REBR (RE = Pr, Tb, Dy, Er, and Tm) for T = 0.06 to 4.2 K have been measured by Simizu et al. [10]; they observed a ferromagnetic ordering of TbBR and DyBR below the temperature 0.125 and 0.170 K, respectively. Very recently the ordering of several REBR (RE = Nd, Yb, Er) has been reported by Xu and Corruccini [11]; Yb³⁺ and Er³⁺ order antiferromagnetically below 15 and 50 mK, respectively, while no order has been noticed in NdBR down to ≈6.5 mK.

In this communication we present our studies on the Yb³⁺ ion in Yb(BrO₃)₃ · 9 H₂O single crystals. The principal magnetic susceptibility perpendicular to the pseudo-hexa-
gonal $c$-axis of the crystal $\chi_{||}$ and the magnetic anisotropy $\Delta\chi$ have been measured for the first time in the temperature range 300 to 14 K and 300 to 90 K, respectively. The susceptibility parallel to the symmetry axis ($\chi_{||}$) was determined from these data. A theoretical analysis has been carried out to simulate the experimental data considering the electrostatic interaction of the rare-earth ion with its diamagnetic neighbors.

2. Experimental Details

Yb bromate was prepared and crystals were grown by slow evaporation of the concentrated aqueous solution [12]. Colorless, transparent, needle-shaped crystals of Yb(BrO$_3$)$_3$·9H$_2$O, about 4 mm long and 1 mm$^2$ in cross section were obtained with elongation along the $c$-axis, the symmetry axis of the pseudo-hexagonal system.

The magnetic anisotropy ($\Delta\chi = \chi_{||} - \chi_{\perp}$) was measured from room temperature down to liquid oxygen temperature employing a torsion balance described earlier [13]. The absolute magnetic susceptibility $\chi_{\perp}$ (here $\chi_{\perp} > \chi_{||}$) in the isotropic plane of the crystal was measured in the temperature range 300 to 14 K by suspending the crystal with a thin quartz fibre in a magnetic field with a constant vertical field gradient (i.e., $H_z \frac{dH_z}{dx} = \text{const}$) produced by a pair of Faraday pole caps [14]. For measuring the absolute susceptibility a highly sensitive taut-band balance with a microprocessor controlled self-nulling mechanism was fabricated in our laboratory. A digital power supply for the electromagnet and the balance were interfaced with a PC to make the measuring process fully programmable. The low-temperature environment was provided by a closed-cycle helium cryocooler supplied by APD cryogenics. The measurements were carried out in helium atmosphere at an optimum pressure. The temperature of the crystal chamber was calibrated using the standard sample Mn(NH$_4$SO$_4$)·6H$_2$O which strictly obeys the Curie law down to about 1 K. Several runs with this sample were taken for calibration. The lowest crystal temperature attained was $\approx$14 K. In low-pressure environment at low temperatures, the crystal tended to lose its water of crystallization. This was prevented by coating the crystal with high-vacuum silicone grease. The overall accuracy of measurements is better than 1%.

3. Experimental Results

In Yb(BrO$_3$)$_3$·9H$_2$O there are two formula units per unit cell and the two paramagnetic clusters have their symmetry axes parallel to each other. Thus, $\chi_{||}$ and $\chi_{\perp}$, the principal magnetic susceptibilities of the crystal are identical with the gram-atomic susceptibilities of the paramagnetic cluster, $K_{||}$ and $K_{\perp}$, respectively. The results of magnetic measurements are given in Table 1. The effective magnetic moment of Yb$^{3+}$ in YbBR at room temperature calculated with $\bar{\chi} = (\chi_{||} + 2\chi_{\perp})/3$ is $\mu_{eff} = 4.44$ which is slightly lower than the free ion value 4.53; for Yb ethylsulfate (YbES) it is 4.37 [15]. The relative magnetic anisotropy $|\Delta\chi|/\bar{\chi}$ at 300 K is 0.23 and at 90 K 0.45 (Table 1). The observed variation of $\chi_{||}$ and $\chi_{\perp}$ is depicted in Fig. 1. The variation of $\chi_{\perp}$ with decrease of temperature is nearly Curie type down to $\approx$150 K below which the rate of increase slows down and deviates more from the Curie law. The explanation of the observed behavior of $\chi_{||}$ and $\chi_{\perp}$ should naturally be sought in the interaction of Yb$^{3+}$ ion with its neighbors in the first instance; this so-called crystal field (CF) effect is considered in the following section.
Magnetic Measurements and Crystal Field Investigations on Yb(BrO$_3$)$_3$ · 9 H$_2$O

Table 1
The results of magnetic measurements on Yb(BrO$_3$)$_3$ · 9 H$_2$O

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\chi_\perp$</th>
<th>$\Delta \chi$</th>
<th>$\chi_\parallel$</th>
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<td>14</td>
<td>114.9</td>
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</tbody>
</table>

The susceptibilities are in $10^{-3}$ cm$^3$/mol.

4. Crystal Field Interaction

The ground electronic configuration of Yb$^{3+}$ [Xe]4f$^{13}$ gives the ground manifold $^2$F$_{7/2}$ which is $\approx$10000 cm$^{-1}$ below the first excited state $^2$F$_{5/2}$. Group theoretical considerations show the ground manifold split up into four Kramers doublets under the influence of the crystal field of D$_{3h}$ symmetry [16] for which the CF interaction term in the Hamiltonian is given by

$$B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{66}(C_{66} + C_{6-e}).$$

Here $C_{kj}$ are tensor operators and $B_{kj}$ are real constants [13]. In this case as the first excited $J$-multiplet is situated far above, the crystal field mixing of the ground multiplet with the excited states is negligible and hence we confine our calculations to the ground multiplet ($J = 7/2$). The matrix elements are computed using the tensor operator techniques [12, 13]. Diagonalization of the CF matrix yields the energies of the four Kramers doublets. The Zeeman interaction term $\beta g \mathbf{J} \cdot \mathbf{H}$, gives the first- and second-order Zeeman energies of the different Stark states for the magnetic field parallel and perpendicular to the symmetry axis of the crystal. The susceptibilities $\chi_\parallel$ and $\chi_\perp$ are obtained through the well-known expression of van Vleck. We adjust the CF parameters carefully for a precise simulation of our experimental results together with the reported $g$-values [11]. The best fit to the observed results was obtained with the following set of parameters:

$$B_{20} = 230, \quad B_{40} = -400, \quad B_{60} = -371, \quad B_{66} = 860 \quad (\text{all in cm}^{-1}).$$

The Stark energies and the corresponding eigenfunctions appear in Table 2. Our theoretical values for both $\chi_\parallel$ and $\chi_\perp$ are presented in Fig. 1 along with the observed results. The excellent agreement of experimental and theoretical values is self-evident. The splitting of the ground Kramers doublet gives the spectroscopic splitting factors $g_\parallel = 2.49$ and $g_\perp = 2.57$. From magnetization measurements below 0.1 K, Xu and Corruccini [11] find $g_\parallel = 2.5$ and $g_\perp = 2.9$. They take the ground state of Yb bromate to be $| \pm 3/2 \rangle$, a Kramers doublet, following the work of Elliott and Stevens [17] on YbES.
Table 2
The crystal field energies and the corresponding wave functions of the $^2F_{7/2}$ ground state of the Yb$^{3+}$ ion in Yb bromate

<table>
<thead>
<tr>
<th>Stark energy (cm$^{-1}$)</th>
<th>eigenfunctions</th>
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<td>0</td>
<td>0.8744 $</td>
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<td>$</td>
</tr>
<tr>
<td>112.47</td>
<td>$</td>
</tr>
<tr>
<td>271.5</td>
<td>0.8744 $</td>
</tr>
</tbody>
</table>

which gives $g_\perp = 0$. They argue that there is symmetry breaking so that in the lower symmetry there is mixing of different $|J_z\rangle$ states giving nonvanishing $g_\perp$. However, we find that although the symmetry in the two systems is considered to be the same, the CF parameters in the present case are quite different from that for YbES [15] and this gives the ground Kramers doublet with an admixture of $|\pm5/2\rangle$ and $|\mp7/2\rangle$ states yielding nonvanishing $g_\perp$ with a value quite close to that obtained by Xu and Corruccini. Moreover, in the temperature range of our measurement, viz. 300 to 14 K, we did not find any indication which would suggest a structural phase change; a sudden change of site symmetry to orthorhombic [8] would turn the isotropic plane anisotropic (unless the crystal is a multidomain one) giving rise to a discontinuity in the observed susceptibility, and also there would be no axial symmetry for the $g$-factors as Xu and Corruccini [11] reported (in fact then there would be three principal $g$-factors and not two). It is interesting to note that the CF splitting of the ground multiplet gives rise to a relatively sharp peak at $\approx 7$ K and a broad one at $\approx 100$ K in the electronic heat capacity [12].

Fig. 1. Experimental (○, △) and theoretical (——) variation of the principal magnetic susceptibilities ($\chi_{\parallel}$, $\chi_{\perp}$) of Yb$^{3+}$ in Yb(BO$_3$)$_3 \cdot 9$H$_2$O with temperature
5. Conclusion

Our measurements of $\chi_L$ from 300 down to 14 K do not show any discontinuity or abrupt change at any point suggesting a structural phase transition. A theoretical analysis of our results invoking crystal field theory based on $D_3h$ symmetry about the Yb$^{3+}$ ion provides an excellent fit to the observed principal susceptibilities $\chi_{\parallel}$ and $\chi_L$ over the entire range of temperature of our study. Moreover, it also explains the $g$-factors obtained indirectly by Xu and Corruccini [11] from sub-Kelvin magnetization experiments without the need to invoke any symmetry breaking as proposed by the latter. It turns out that even if the RE site symmetry in Yb ethylsulfate and the present sample is the same, the CF parameters differ considerably.

References

Magnetic behavior of Ho$^{3+}$ in HoAl$_3$(BO$_3$)$_4$

D. Neogy $^a$, K.N. Chattopadhyay $^a$, P.K. Chakrabarti $^a$, H. Sen $^a$, B.M. Wanklyn $^b$

$^a$ Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India
$^b$ Clarendon Laboratory, The University of Oxford, Oxford OX1 3PU, UK

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Magnetic behavior of Ho$^{3+}$ in HoAl$_3$(BO$_3$)$_4$

D. Neogy a,*, K.N. Chattopadhyay a, P.K. Chakrabarti a, H. Sen a, B.M. Wanklyn b

a Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India
b Clarendon Laboratory, The University of Oxford, Oxford OX1 3PU, UK

Received 31 January 1995; revised 26 June 1995

Abstract

Single crystals of HoAl$_3$(BO$_3$)$_4$ were flux grown and their principal magnetic susceptibilities, parallel and perpendicular to the symmetry axis of the crystal, $\chi_\parallel$ and $\chi_\perp$, measured in the range 300–14.5 K. The principal anisotropy $\chi_\parallel - \chi_\perp$ turns out to be positive throughout. A theoretical analysis of the experimental results invoking the crystal field interaction of the Ho$^{3+}$ ion with D$_3$ site symmetry, obtained from structural data, provide an excellent explanation of the observed behavior of the ion over the entire temperature range in our study; this rules out exchange or dipolar effects of any significance down to 14.5 K. The energy level structure of this potential laser crystal for all the low lying multiplets of the ground term is given and the anomalies in the electronic heat capacity located. The quadrupole splitting of $^{165}$Ho due to crystal field effects has been computed, which gives rise to a peak in the hyperfine heat capacity at about 5.5 mK.

1. Introduction

For more than a decade rare earth (RE)–aluminium borates [REAI$_3$(BO$_3$)$_4$] have attracted considerable attention for their luminescence properties, concentration quenching in particular, and their possible application as single crystal mini lasers [1]. Some of them (e.g. NdAl$_3$(BO$_3$)$_4$) have already been established as laser materials [2,3], and others are subject of intensive study for their immense potential in different optical applications. Trivalent neodymium is the most sought after activator ion in laser crystals, followed by the trivalent holmium (Ho$^{3+}$) ion. In order to have a clear understanding of the role played by RE$^{3+}$ ions in different situations it is essential to have a precise knowledge of the interactions of the ion in the host lattice. In laser physics, information on the crystalline Stark levels of the activator ions, their degeneracies and wave functions are extremely important, and these are best obtained from optical, magnetic and EPR studies. This naturally leads one to investigate, primarily, the effect of the charges situated immediately around the RE$^{3+}$ ion on the electrons in its incomplete 4f shell which brings about spectacular changes in the electronic spectra, magnetism and all manifestations of the domain of influence of 4f electrons.

The RE–aluminium borates form an isomorphous series having structures similar to that of the mineral huntite [Ca Mg$_3$(CO$_3$)$_4$], a rhombohedral double-carbonate with space group R32 [4,5]. The structures of nearly all RE–aluminium borates have been determined. The RE$^{3+}$ ion is surrounded by a trigonal prism of six oxygens, each belonging to a different borate group and not shared by neighboring RE$^{3+}$ ions. The RE site symmetry in this structure is C$_{3h}$ considering nearest-neighbor oxygens only; the sym-
metry reduces to $D_3$ if one includes nearest (BO$_3$) groups [5,6]. This simple crystal structure makes this system an ideal choice for magnetic and crystal field (CF) studies. In this paper we report our results of magnetic measurements on holmium aluminium borate single crystals from room temperature down to 14.5 K, which find an excellent explanation in the CF interactions. On the basis of these findings theoretical excursions into related fields allow us to make important predictions on some electronic and nuclear properties.

2. Experimental

Single crystals of holmium aluminium borate [HoAl$_2$(BO$_3$)$_4$] were grown using standard flux-growing techniques [6]. The crystals are well-defined prismatic and elongated along the crystallographic c-axis. The light yellow holmium aluminium borate crystals about 3 mm long were tested under a polarizing microscope for twinning.

The principal magnetic susceptibilities, $\chi_\parallel$ and $\chi_\perp$, parallel and perpendicular to the crystallographic symmetry axis $c$ were measured from room temperature down to 14.5 K with the help of a highly sensitive electronic balance fabricated in our laboratory [7]. The crystal was suspended with a thin quartz fibre in the constant vertical magnetic field gradient $(H_zdx/dz)$ produced by a pair of specially designed Faraday pole caps [8]. The low-temperature environment was provided by a closed-cycle helium refrigerator from APD Cryogenics. For measurement of susceptibility at different temperatures, the temperature was held steady at desired points within ±0.2 K with the help of a Scientific Instruments temperature controller and a chromel-gold/Fe thermocouple. Temperature calibration of the sample chamber and other details of measurements are discussed elsewhere [7].

$\chi_\perp$ was measured suspending the crystal with the $c$-axis vertical, while $\chi_\parallel$ was measured with the $c$-axis in the horizontal plane so that in a magnetic field $\chi_\parallel$ automatically sets in the direction of the field, since in this case $\chi_\parallel > \chi_\perp$ and the torsional constant of the quartz fibre was very small. Demagnetization corrections were made for the very low-temperature results, and these turned out to be very small indeed. Diamagnetic corrections were made for all the measured values.

The magnetic anisotropy $\Delta \chi (= \chi_\parallel - \chi_\perp)$ of the single crystal of holmium aluminium borate was also measured directly using a quartz torsion balance down to liquid nitrogen temperature as a check on the absolute measurements.

3. Results

The variation of $\chi_\parallel$ and $\chi_\perp$ with temperature is displayed in Fig. 1. The crystallographic c-axis sets along the applied external magnetic field, indicating $\chi_\parallel > \chi_\perp$ at room temperature similar to holmium bromate [9] and holmium phosphate [10] and this helps us to measure $\chi_\parallel$ and $\chi_\perp$ individually by the Faraday balance down to 14.5 K, the lowest temperature attained with our arrangement. $\chi_\parallel$ is greater than $\chi_\perp$ throughout the temperature range of our study, unlike in holmium bromate, where Ho$^{3+}$ is in a $D_3h$ site [9]. The variations of $\chi_\parallel$ and $\chi_\perp$ with decreasing temperature are similar in nature, with $\chi_\parallel$ increasing slightly faster than $\chi_\perp$ (Table 1).

The effective magnetic moment $P_{\text{eff}}$ at room temperature is calculated by the relation $P_{\text{eff}} = 2.828(\chi/T)^{0.5}$, where $\chi = (\chi_\parallel + 2\chi_\perp)/3$, turns out to be 10.52, which is slightly lower than the free-ion value of 10.6, and drops slowly with decreasing temperature. As is commonly found in polycrystalline samples with strong crystal field effects [16], here the average magnetic susceptibility, $\bar{\chi}$, also

![Fig. 1. Observed and theoretical variation of $\chi_\parallel$ and $\chi_\perp$ of Ho$^{3+}$ in HoAl$_2$(BO$_3$)$_4$.](image-url)
follows the Curie–Weiss law quite closely. A least-squares fit of the observed $\chi$ in the range 300–14.5 K to the Curie–Weiss law yields the Curie constant $C = 13.53$ emu K and the paramagnetic Curie temperature $\Theta = -2.74$ K (Fig. 2). Obviously, in the temperature range of our study the origin of $\chi$ should be sought mainly in the crystal field effects, i.e. changes in the populations in the different Stark states, rather than in any exchange or dipolar effects.

The relative magnetic anisotropy ($\Delta \chi/\chi$) at room temperature is 0.152 and that at 14.5 K is 0.361. At 77 K it is 0.224, which is rather small compared with that for holmium phosphate, i.e. 0.725 [10]. This wide difference may be traced to the difference in the asymmetry of the crystal field at Ho$^{3+}$ sites in the two systems.

### Analysis and discussion

As reported earlier [4,5], holmium aluminium borate is isostructural with other RE–aluminium borates and hence the site symmetry of Ho$^{3+}$ in this crystal matrix is assumed to be $D_3$, following earlier works [4–6,11,12]. The ground electronic configuration of Ho$^{3+}$ is $4f^{10}$, this gives the Hund ground state $^5I_8$. Group theoretically, the ground multiplet is found to split into 11 levels. This is easily seen from the reduction of the 17-dimensional representation of the $D_3$ group spanned by the degenerate states of the ground multiplet with $J = 8$ into its irreducible representations as follows:

$$\Gamma_J = 8 \rightarrow 3 \Gamma_1 + 2 \Gamma_2 + 6 \Gamma_3 \quad (\Gamma_3 \rightarrow \text{doublet}).$$

The crystal field Hamiltonian of Ho$^{3+}$ ion in holmium aluminium borate for $D_3$ symmetry is expressed as

$$\mathcal{H}_{\text{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{43}(C_{43} - C_{4-3}) + B_{63}(C_{63} - C_{6-3}) + B_{66}(C_{66} - C_{6-6}),$$

where $C_{kj}$ are tensor operators and $B_{kj}$ are the real parameters. The matrix elements of the tensor operators $C_{kj}$ are computed using the relation

$$\langle f'\chi'LLJ'J' | C_{kj} | f\chi LLLJ \rangle = (-1)^{J-J'} \delta_{SS'} \times (-1)^{S+L+J+k} \left\{ \begin{array}{ccc} J & J' & k \\ L & L & S \end{array} \right\}.$$

The 3–$j$ and 6–$j$ symbols are generated and the doubly reduced matrix elements, which differ from those of the unit tensors $U_{kj}$ by a constant factor $N_k$, were obtained from appropriate tables [13].

In order to calculate the magnetic and other physical properties strongly influenced by crystal field, first the low-lying Stark levels and their eigenvectors are determined. The Hamiltonian $\mathcal{H} = \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{CF}}$ is directly diagonalized in the 65-dimensional basis of the ground term; $\mathcal{H}_{\text{SO}}$ is the spin–orbit coupling interaction term diagonal in $J$. The intermediate coupling (IC) factors for the reduced matrix elements are introduced to take care of the IC effects. $\mathcal{H}_{\text{SO}}$ is

---

**Table 1**

Results of magnetic measurements on HoAl$_3$(BO$_3$)$_4$ (unit for susceptibilities: 10$^{-2}$ cm$^3$/mole)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
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<th>$X_L$</th>
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<td>14.5</td>
<td>97.5</td>
<td>69.1</td>
<td>78.5</td>
<td>9.54</td>
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</table>

---

Fig. 2. Curie–Weiss simulation of $\chi$ of HoAl$_3$(BO$_3$)$_4$. 

---
replaced by the approximate baricenters of the different J-multiplets of the ground term. The Zeeman energies for the different CF states are obtained through the magnetic interaction term $\beta H \cdot (L + 2S)$ for the two cases, $H$ parallel and perpendicular to the symmetry axis of the crystal; and the susceptibilities are obtained through the well-known Van Vleck expression. No report on the absorption spectra of this crystal has come to the notice of the authors. In order to fix the crystal field the six parameters $B_{kq}$ were varied carefully to get a precise fit to the observed variation of $\chi^\parallel$ and $\chi^\perp$ from room down to 14.5 K; this was achieved by minimizing the rms deviation of the theoretical values from those observed. The best-fit CF parameters are $B_{20} = 447.5$, $B_{40} = 298.5$, $B_{60} = 66$, $B_{43} = 895.5$, $B_{53} = -298.5$, $B_{66} = 149$ (all in cm$^{-1}$). Here a few words regarding the uniqueness of the best-fit set of parameters is probably in order. A fairly good test would be to vary the parameters one by one and see how the rms deviation behaves. It is observed that for every parameter a 0.5% change from the best-fit value leads to an appreciable increase in the rms deviation for both $\chi^\parallel$ and $\chi^\perp$ (e.g. for the most sensitive parameter, $B_{20}$, rms deviation increases by $\sim 50\%$ for $\chi^\parallel$); hence the uncertainties in the values of the parameters may be safely said to be less than 0.5%.

The computed Stark energies and the ground state wave function are given in Table 2. Our CF analysis of the magnetic data yields a singlet ground state and the first excited state, a doublet, lies only 1.2 cm$^{-1}$ above. A very good simulation of the observed $\chi^\parallel$ and $\chi^\perp$ by our theoretical values (Fig. 1) proves the adequacy of our crystal field treatment. Our computed $\Delta \chi$ fits well with the observed $\Delta \chi$ in the temperature range 300–77 K and predicts a reversal at about $\sim 2$ K. This interesting feature acts as a very sensitive index of the CF parameters which may be easily verified experimentally; our present low-temperature facilities do not permit this.

5. Thermal and hyperfine properties

As the electronic heat capacity $C_S$ is strongly influenced by the crystal field, the latter leaves its bold signature on the Schottky anomalies. Using the relation

$$C_S = N_A \frac{d}{dT} \left[ \text{Tr}(\mathcal{H} \rho)/\text{Tr}(\rho) \right],$$

**Table 2**

Crystal field Stark splitting of the ground term $^5I_1$ of the Ho$^{3+}$ in holmium aluminium borate and its ground state wave function (asterisks indicate doublets)

<table>
<thead>
<tr>
<th>Multiplet $^5I_k$</th>
<th>Energy (cm$^{-1}$)</th>
<th>Wave function</th>
</tr>
</thead>
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<tr>
<td>$^1g$</td>
<td>0.0</td>
<td>$+0.3429(8,6) + 0.6115(8,0)$</td>
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<td>$^1e$</td>
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<td>$-0.4421(8,3) + 0.4421(8,-3)$</td>
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<tr>
<td>$^1e$</td>
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<td>$+0.3429(8,-6) - 0.0003(7,6)$</td>
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<tr>
<td>$^2g$</td>
<td>28.3*</td>
<td>$+0.0024(7,3) + 0.0024(7,-3)$</td>
</tr>
<tr>
<td>$^2e$</td>
<td>36.6</td>
<td>$+0.0003(7,-6) - 0.0004(6,6)$</td>
</tr>
<tr>
<td>$^4g$</td>
<td>86.4*</td>
<td>$-0.0014(6,3) - 0.0024(6,0)$</td>
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<td>$^4e$</td>
<td>129.7</td>
<td>$+0.0014(6,-3) - 0.0004(6,-6)$</td>
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<td>$^6g$</td>
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<td>$-0.0009(5,3) - 0.0009(5,-3)$</td>
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<tr>
<td>$^6e$</td>
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where $N_A$ is Avogadro's number, $\mathcal{H}$ is the Hamiltonian matrix and $\rho$ is the statistical density matrix, the heat capacity is computed at different temperatures. The variation of $C_s$ with temperature is shown in Fig. 3. $C_s$ has two sharp peaks at 13 and 0.7 K, and one broad peak centred around 77 K. These anomalies are easily amenable to experimental verification.

The nuclear ground state of the isotope $^{165}$Ho is split by the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) at the site of the nucleus set up by both ligand charges and the 4f electrons. Here, the lattice and 4f contributions are opposite in sign down to $\sim 2.6$ K; as the 4f contribution increases with decreasing temperature, the EFG initially goes to the lowest value at $\sim 20$ K.

The quadrupole splitting $\langle \Delta E_Q \rangle_T$ between two adjacent split levels is expressed as [14]

$$
\langle \Delta E_Q \rangle_T = \left\{ -3e^2Q \frac{2L_z + 1}{4I(2I - 1)} \right\} \times \left[ (1 - R_Q) \langle r^{-3} \rangle_{4f} \left\{ \sum_i (3z^2_i - r^2_i) / r^2_i \right\} + e^2 \langle r^2 \rangle_{4f} (1 - \sigma^2) \right].
$$

The variation of the quadrupole splitting $\langle \Delta E_Q \rangle_T$ between the lowest two levels, i.e. $|I_z| = \pm 7/2$ and $|I_z| = \pm 5/2$ is shown in Fig. 4. $\langle \Delta E_Q \rangle_T$ shows a slow decrease with temperature and is minimum at about 20 K; below 5 K it increases sharply.

At very low temperatures when only the singlet ground state is occupied the hyperfine magnetic field vanishes. However, this is strictly true only in the absence of an external magnetic field; in the presence of a field perpendicular to the symmetry axis, the nucleus sees a highly enhanced field from a large induced dipole moment due to a strong Zeeman mixing of the states of the very close lying doublet with the ground stark singlet. In the absence of a field, therefore, only quadrupole splitting contributes towards the nuclear heat capacity $C_N$ and it would be appreciable only in the milli-kelvin range. The temperature variation of $C_N$ shows (Fig. 5) a sharp anomaly at $\sim 5.5$ mK with a peak value 7.38 J/g.atom K, which is comparable to the peak value of $C_N$ in Ho$^{3+}$ in LaCl$_3$ (7.43 J/g.atom K) [15].
6. Conclusions

A suitable single crystal field of $D_3$ symmetry, the site symmetry of the Ho$^{3+}$ ion in HoAl$_3$(BO$_3$)$_4$, provides an excellent fit to the observed principal magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$ over the entire temperature range 300–14.5 K. This leads us to conclude that there is almost no ordering effect of any consequence among the Ho$^{3+}$ ions down to ~14.5 K, even though this is not a highly diluted system like the hydrated samples. $\Delta \chi = (\chi_\parallel - \chi_\perp)$ is positive throughout our observed temperature range; however, our theory predicts a changeover around 2 K if no ordering effects set in. The Stark energy levels of all the multiplets of the ground term of Ho$^{3+}$ in this lattice are given, which are of considerable importance in laser-crystal physics. The ground Stark state is a singlet and the first excited state, a doublet, lies only 1.2 cm$^{-1}$ above; at very low temperatures this is likely to show a pseudo-quadrupole-type magnetic hyperfine interaction.

Our calculations show interesting electronic heat capacity and hyperfine properties of $^{165}$Ho which are quite amenable to experimental verification.

References

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THE EFFECTS OF CRYSTAL FIELD ON Tm$^{3+}$ IN Tm(BrO$_3$)$_3$·9H$_2$O: AN EXPERIMENTAL AND THEORETICAL STUDY

D. NEOGY, R. K. SAHA, P. K. CHAKRABARTI and K. N. CHATTOPADHYAY
Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India

(Received 13 April 1995; accepted 2 August 1995)

Abstract—Crystals of thulium bromate enneahydrate were grown and the magnetic susceptibility $\chi_1$ and the magnetic anisotropy $\Delta \chi (= \chi_1 - \chi_2)$ were measured in the range 300–14 K and 300–80 K, respectively. $\chi_2$ and $\chi_1$ show widely divergent thermal variation; the $\chi_1$ versus $T$ plot is nearly flat compared to that of $\chi_2$. Smooth variation of $\chi_1$ down to 14 K does not suggest any structural phase transition or symmetry breaking. Our observed data and that of Simizu et al. [J. Appl. Phys. 55, 2333 (1984)] below 4 K were analyzed for the first time invoking an effective crystal field. Our theoretical values in general provide excellent agreement to the observed data. Very brief comment on the behavior of $\chi_1$ below 4 K by Simizu et al. is borne out qualitatively by our theory, but their absolute value seems abnormally high, which makes us suspect. The computed crystal field spectra led us to locate the peaks in the electronic heat capacity and to find the quadrupole splitting of the 8.42 keV nuclear excited state of $^{169}$Tm; high magnetic field enhancement at the nucleus suggests complex Mössbauer spectra in the presence of a magnetic field perpendicular to the symmetry axis.

1. INTRODUCTION

For the past several years keen interest has been shown in the structure and magnetic properties of rare-earth (RE) bromate (REBR) single crystals. RE-bromates with the chemical formula RE(BrO$_3$)$_3$·9H$_2$O form an isomorphous series and, being structurally similar to RE-ethylsulfates (REES), are ideally suited for studying crystal-field (CF) interactions, which are so important for understanding various electronic and nuclear properties and development in this direction, for being a non-Kramers ion on which the signature of the interactions is particularly bold. Recently the crystal structure of some REBR's has been determined [1–4] and magnetic properties of several RE-bromates studied over a wide range of temperatures [2–14]. Simizu et al. [8] have conducted measurements below 4.2 K using SQUID magnetometer on a number of RE-bromates; they have also reported [14] calorimetric measurements above 90 mK to investigate magnetic order in the REBR. Xu et al. [13], employing a fluxgate magnetometer, have probed magnetic order in NdBR, ErBR and YbBR below 100 mK. It is interesting to note that while YbBR and ErBR order antiferromagnetically [13], DyBR and the non-Kramers compound TbBr exhibit dipolar ferromagnetic order [8, 14]; the ordering in the latter is that of an electron nucleus system in the mixed regime [14]. Many RE-bromates show widely divergent magnetic behavior along different principal directions [5–8, 10, 13] indicating high asymmetry of the CF.

The crystal structure and site symmetry of the RE ions have been a subject of some controversy. Whereas earlier works [1–3, 15] give the unit cell hexagonal, some optical and crystal structure [4] studies point to a lower symmetry space group (Cmcm). The structural refinements lending credence to such a conclusion could not be called definitive due to experimental uncertainties [4]. Thus, as discussed earlier [10], it is reasonable to consider the crystal uniaxial approximately, and the symmetry about the co-ordinated rare-earth ion, within experimental uncertainties, $D_{3h}$.

In this communication we present our studies on Tm$^{3+}$ in TmBR. For the first time the principal magnetic susceptibility perpendicular to the hexagonal $'c'$ axis of the crystal, $\chi_1$, has been measured from 300 to 14 K and the magnetic anisotropy $\Delta \chi (= \chi_1 - \chi_2)$ from 300 to 80 K which yield $\chi_1$, the susceptibility parallel to the symmetry axis. Simizu et al. [8] have reported magnetic measurements on TmBR and some other RE-bromates below 4.2 K. Unlike TbBR [8, 14] no ordering has been observed in TmBR; the behavior of $\chi_2$ and $\chi_1$ has been discussed, but rather briefly. Data on CF levels of TmBR, either from spectroscopic or inelastic neutron scattering experiments have not come to the notice of the authors. We look for an explanation to the observed results over the whole temperature range mainly in the
interaction of the Tm$^{3+}$ ion with the ligand charges; as no ordering has been observed down to 60 mK [8], the dipolar effects do not seem to have any role to play at least down to 14 K. Various quantities evolving out of our analysis help us to compute related electronic and nuclear properties which give an insight into the electronic and nuclear hyperfine behavior of Tm$^{3+}$ in the bromate lattice.

2. EXPERIMENTAL DETAILS

Thulium bromate was prepared by double decomposition of thulium sulfate and barium bromate prepared separately. The crystals were grown from the concentrated aqueous solution by slow evaporation in a relatively dry atmosphere. The crystals grow in a needle shaped prismatic form with a purple tinge, the long axis being the hexagonal (pseudo-hexagonal) symmetry axis as evidenced by the magnetic isotropy of the plane perpendicular to it.

The magnetic anisotropy was measured with a quartz torsion balance down to liquid nitrogen temperatures. The absolute susceptibility $\chi_\perp$ (here, $\chi_\perp > \chi_\parallel$) was measured with a microprocessor controlled self-nulling taut band balance fabricated by us. The low temperature environment was provided by an APD Cryogenics He-refrigerator. Measurements were carried out in helium atmosphere at an optimum pressure for good heat conduction and minimal convectional disturbances. An Au-Fe(0.07%)/Chromel thermocouple monitored the temperature of the second cold station to which the hang-down tube was thermally strapped. The calibration of the sample chamber temperature was performed by measuring the susceptibility of Mn(NH$_4$SO$_4$)$_2 \cdot 6$H$_2$O single crystals which strictly obey the Curie law down to about 1 K. Several runs with this specimen were taken for calibration.

3. RESULTS

In the unit cell there are two formula units with the symmetry axes of the paramagnetic clusters parallel; the ionic susceptibilities $K_\parallel$ and $K_\perp$ are, therefore, identical with the crystal molar susceptibilities $\chi_\parallel$ and $\chi_\perp$, noting of course that there is only one rare-earth ion per formula unit.

The observed values of $\chi_\perp$ near 14 K were corrected for demagnetization effects which were indeed very small. Unlike bromates of other non-Kramers ions, viz. Pr and Ho, $\chi_\perp > \chi_\parallel$ at room temperature in the present case. This prevented us from measuring $\chi_\parallel$ directly by Faraday balance, since at very low temperatures the anisotropy was so high that quartz suspension could not prevent the crystal from rotating in the magnetic field.

The relative anisotropy $|\Delta \chi|/\bar{\chi} = 0.285$ at 300 K is comparable to that of the structurally similar Tm-ethylsulfate [16]. $\Delta \chi$ at 80 K is nearly 11 times the value at 300 K (Fig. 1). Interestingly, the effective magnetic moment at room temperature calculated with $\bar{\chi} = (\chi_\parallel + 2\chi_\perp)/3$ is 7.41, which is only slightly lower than the free ion value 7.61; it shows a slow decrease with fall of temperature. The observed variation of $\chi_\parallel$ and $\chi_\perp$ is depicted in Fig. 2. The striking feature is the wide difference in the nature of variation of the two principal susceptibilities. $\chi_\perp$ displays more or less a Curie type variation over nearly the entire range of temperature, viz. 300–20 K; $\chi_\parallel$ shows very slow rise from 300 K down to about 100 K, below which it shows a slight decrease. This is not
The effects of crystal field on Tm$^{3+}$ in Tm(BrO$_3$)$_3$·9H$_2$O

4. CRYSTAL-FIELD INTERACTION

The ground electronic configuration of Tm$^{3+}$ is 4f$^{12}$, with, of course, the closed shell xenon structure which is a common feature with all lanthanides. A precise determination of energy level structure of Tm$^{3+}$ in TmBR would involve the diagonalization of the Hamiltonian consisting of 13 free ion parameters and the CF parameters in the complete basis of 4f$^{12}$ configuration. The different groups of levels normally characterized by “terms” are, strictly speaking, no longer valid due to the breakdown of Russell–Saunders coupling, evidenced by the departure from the Lande interval rule; still, conventionally, we refer to them by their original names. Thus the ground term of Tm$^{3+}$ turns out to be $^3$H$_6$. In order to compute magnetic susceptibilities and other physical properties of the ion it is sufficient to diagonalize the Hamiltonian $\mathcal{H} = \sum_n \lambda_n (L \cdot S)^n + \mathcal{H}_{\text{CF}}$ in the truncated basis of 33 $|L, S, J, J_z\rangle$ state vectors spanning the ground term. The first term is an effective spin-orbit operator producing the observed baricenters of different multiplets. In fact one often circumvents this term by introducing the available values of baricenters in the diagonal elements of the Hamiltonian; the baricenters are dependent mainly on the free ion parameters and very little on the host lattice. The $\mathcal{H}_{\text{CF}}$ conforming to $D_{3h}$ symmetry is given in the one-electron tensor operator formalism as follows:

$$B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{66}(C_{66} + C_{6,-6})$$

Here $C_{kq}$s are tensor operators and $B_{kq}$s are real constants that parametrize the crystal-field. Here we use the traditional one-electron crystal field and do not include the correlated crystal field [17] (CCF) or spin-correlated crystal-field [17] (SSCF) operators, which although they give a more complete description of the interactions, make computations much too involved; these are important for very precise spectroscopic work, but hardly affect the susceptibilities or other aggregate physical properties. Since $B_{kq}$ parameters are adjusted to produce the best fit to the observed results, they are in a way effective parameters partly absorbing the effects of the neglected interactions, viz. CCF, SCCF. The matrix elements of the tensor operators are computed using the relation:

$$\langle f'' \alpha'S'L'J'J''|C_{kq}|f''\alpha'S'LJJ'\rangle = (-1)^{j'-J} \left( \begin{array}{c} J' \\ J \\ J'' \\ J'' \\ J' \\ J \\ J'' \\ J'' \end{array} \right) \delta(SS') \langle SL'\rangle \langle L'J' \rangle \langle J'k|C_{kq}|J'' \rangle$$

The $3-j$ and $6-j$ symbols are generated and the doubly reduced matrix elements which differ from that of the unit tensors $U_{kq}$ by constant factors $N_{kq}$, are obtained from appropriate tables [18]. The intermediate coupling (IC) effects were partly taken care of by introducing IC coefficients to be multiplied with the reduced matrix elements appearing with the $3-j$ symbols; in the present case the IC coefficients for the first excited state $^3$H$_4$ are widely different from unity showing large effects of intermediate coupling. Diagonalization of the CF Hamiltonian with the approximate baricenters of the different $J$ multiplets led to the CF Stark energies and corresponding eigenvectors. The first- and second-order Zeeman energies of the Stark states were obtained using the interaction term $\beta \mathbf{H} \cdot (L + 2S)$ with $H_\parallel z$ and $H \perp z$; $K_4$ and $K_6$ were finally computed with the well-known susceptibility expression of Van Vleck.

Using different trial sets of CF parameters and
working through the steps stated above, the observed behavior of Tm$^3^{+}$ was simulated very closely with the following set of parameters.

The Stark energies and the ground state wave function appear in Table 1.

Table 1. Crystal field Stark splitting of the ground term $^2$H of the Tm$^{3+}$ ion in Tm-bromate

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<th>Energy (cm$^{-1}$)</th>
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</table>

†Doublet: the singlet ground state is 0.2471$\pm$0.0006(4), 0.$\pm$3.

The Stark energies and the ground state wave function appear in Table 1.

In a brief reference to TmBR in their magnetic measurements on REBRs below 4K, Simizu et al. [8] state that $\chi_1$ remains essentially constant which points to a singlet ground state. Again, appreciable increase of $\chi_1$ down to 14 K (our measurements) and below 4 K [8] hints at an excited state close to the ground singlet; this is well supported by our theoretical results. We find that the ground state is a singlet and $\approx 3.4$ cm$^{-1}$ just above it lies a doublet giving rise to a high second-order contribution to the Zeeman energy of the ground state. It is the increase of occupation of the ground state making large contributions to the Van Vleck temperature independent susceptibility with a fall in temperature that renders $\chi_1$ behavior similar to the Curie type behavior. The excellent simulation of the experimental results for both $\chi_1$ and $\chi_4$ by our theoretical values is depicted in Fig. 2. Although qualitatively our theoretical results partly explain Simizu et al.'s observation on $\chi_1$, their reported constant value is surprisingly high. Here it is worth noting that our theoretical results show $\chi_1$ to be more than 50 times $\chi_2$ at $\approx 4$ K, and hence any slight error in the orientation of the crystal while measuring $\chi_1$ may bring in large contributions from $\chi_1$ leading to an abnormally high value of $\chi_1$. Unfortunately, no detailed information of low temperature measurements on $\chi_1$ has been given by the authors [8].

The other plausible explanation could probably be sought in a cooperative Jahn–Teller phase (CJTP) transition which is exhibited by concentrated RE compounds crystallizing in the tetragonal zircon structure [19]. However, no CJTP transition has been reported for the hydrated RE bromates, a dilute system, by any worker so far; neither do the smooth variation of susceptibilities observed by us suggest any such effect. Simizu et al. report $\chi_1$ to be 2.2 cm$^3$/mole at 4.2 K. Our theory gives the same value slightly below 3 K and at 4.2 K it gives 1.456 cm$^3$/mole; it also predicts $\chi_1$ to become constant below 0.8 K. This difference cannot be attributed to molecular field arising from dipolar and induced dipolar effects which are rather weak. Recently, ferromagnetic ordering in TbBR, which is also a non-Kramers compound, has been reported at 125 mK [8, 14]; however, no such ordering in the present crystal has been observed. In fact using the expression $\lambda = (1/\chi_c - 1/\chi_o)$, the molecular field constant turns out to be 0.231 cm$^{-3}$ mole which is large indeed (here, $\chi_c$ and $\chi_o$ are the calculated CF and observed molar susceptibilities, respectively). A thorough experimental study below 4 K is called for in order to sort out the discrepancies.

5. THERMAL AND HYPERFINE PROPERTIES

5.1. Electronic specific heat

The low lying CF stark levels give rise to high electronic heat capacity $C_v$ with characteristic thermal variation in the form of so-called Schottky anomalies. $C_v$ is computed using the relation

$$ C_v = N_A \frac{d}{dT} [Tr(\mathcal{H})/Tr(\rho)]. $$

Here $\mathcal{H}$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N_A$ is the Avogadro number. The plot of $C_v$ versus $T$ (Fig. 4) displays three maxima. A broad maximum is centered about 120 K and further down $C_v$ peaks at $\approx 31$ K; $C_v$ displays a spike with high peak value 6.26 J/g atom K at 2 K (not to be confused with a $\lambda$-type anomaly associated with a phase transition). This suggests very interesting heat capacity measurements.

5.2. Hyperfine properties

With the Stark ground state being a singlet, as such, there is no hyperfine magnetic field at very low temperatures, but this is strictly true only in the
The effects of crystal field on Tm\(^{3+}\) in Tm(BrO\(_3\))\(_3\) \(\cdot\) 9H\(_2\)O

![Graph](image)

**Fig. 4.** Temperature dependence of electronic heat capacity \((C_v)\) of Tm\(^{3+}\) in thulium bromate.

absence of an external field; in the presence of a field perpendicular to the symmetry axis, the effective field seen by the nucleus is a highly enhanced field due to a strong induced dipole moment of Tm\(^{3+}\) in the ground Stark state; the enhancement factor actually turns out to be \(\approx 568\) which is far greater than that for Tm-ethylsulfate, viz. \(\approx 77\) [16, 20]. Thus the effective magnetic field would be of the order of mega-gauss if the applied field is only in the kilo-gauss range, and this is sufficiently strong to produce magnetic hyperfine splitting, which is much greater than the quadrupole splitting. The field dependent magnetic hyperfine splitting of both the nuclear ground \((I = 1/2)\) and the first excited state \((I = 3/2)\) in the form of equispaced levels (for the excited state slightly modified by quadrupole interaction) should appear more conspicuously in the Mössbauer spectra than for TmES [20].

The nuclear ground state being a half spin state, remains unaffected by the electronic field gradient (EFG) produced by the 4\(f\) electrons and the ligand charges. The 8.42 KeV first excited state \((I = 3/2)\) suffers a quadrupole splitting; the separation between the two doublets (with \(I_x = \pm 1/2\) and \(I_z = \pm 3/2\)) \((\Delta E_Q)_T\), follows from the diagonalization of the temperature averaged quadrupole interaction Hamiltonian [21]. Obviously the temperature dependence of \((\Delta E_Q)_T\) arises from the variation of 4\(f\) contribution to the EFG with temperature; the lattice contribution is largely independent of temperature. The quadrupole splitting of the excited state is given by [22]:

\[
\langle \Delta E_Q \rangle_T = \left\{ -3e^2 Q(2I_z + 1)/[4I(2I - 1)] \times \left[ (1 - R_Q)(r^3 \psi (\Sigma_i r_i^2 - r_i^2)/r_i^2 \right) \right. \\
\left. + 2(1 - \gamma_0)B_{20} \right\} e^2 (\Sigma_i r_i^2) \psi (1 - \sigma_2) \\
\]

The quadrupole splitting is seen (Fig. 5) to increase smoothly as temperature decreases and below \(\approx 0.8\) K, levels off at a constant value \(\approx 0.011\) cm\(^{-1}\); this is a very good case for Mössbauer study.

**Fig. 5.** The thermal variation of the nuclear electric quadrupole splitting of the first excited state \((I = 3/2)\) of \(^{169}\)Tm in Tm(BrO\(_3\))\(_3\) \(\cdot\) 9H\(_2\)O.

6. CONCLUSION

The magnetic susceptibilities of thulium bromate observed over a wide range of temperatures find a very good interpretation in the electrostatic interaction of Tm\(^{3+}\) with its ligands. \(\chi_\perp\), which was measured down to 14 K, displayed a smooth variation and there was no indication to suggest a structural phase transition of any significance. Below 4 K our theoretical values give the magnetic behavior qualitatively similar to that observed by Simizu et al. [8] which is characteristic of Van Vleck high temperature paramagnetism. Justly, the ground Stark state turns out to be a singlet as in TmES [16, 20] but the first excited state, a doublet, is situated at only \(\approx 3.4\) cm\(^{-1}\), unlike in the ethylsulfate (\(\approx 31\) cm\(^{-1}\)); this renders the behaviour of Tm\(^{3+}\) at very low temperatures, in the present case, considerably different from that of ethylsulfate. The \(\chi_\perp\) value reported by Simizu et al. at 4.2 K is the same as our theoretical value, slightly below 3 K. However, the \(\chi_\parallel\) value at 4.2 K stated by the same authors is too high to be accounted for. A detailed study below 4.2 K is necessary to resolve the discrepancies. Hyperfine properties of \(^{169}\)Tm worked out suggest interesting Mössbauer studies.

REFERENCES

SINGLE CRYSTAL MAGNETIC PROPERTIES AND THE CRYSTAL FIELD INTERACTIONS OF \textit{Er}^{3+} \textit{IN ErVO}_4

P. K. CHAKRABARTI,* D. NEOGY,* K. N. CHATTOPADHYAY* and B. M. WANKLYN†

*Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan 713 104, West Bengal, India
†Clarendon Laboratory, Oxford OX1 3PU, U.K.

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Abstract—Crystals of erbium vanadate were flux-grown and magnetic measurements carried out on the single crystals for the first time in the temperature range 300–13.2 K. At room temperature $\chi_M > \chi_L$; a crossover in $\Delta \chi$ is observed at about 130 K. Our magnetic data and that of Kuse on crystal field excitations were analyzed invoking an effective crystal field of $D_{4h}$ symmetry; the theoretical values provide an excellent agreement to the observed data. The principal susceptibility ($\chi_M$) did not show any sharp change in its behavior down to 13.2 K, which rules out a structural or magnetic phase transition in this range. The computed Stark energies led us to locate a Schottky anomaly in the electronic heat capacity. The quadrupole splitting of $^{167}$Er due to crystal field effects has been computed; the hyperfine heat capacity displays a sharp peak at about 4.8 mK. © 1997 Elsevier Science Ltd. All rights reserved

Keywords: erbium vanadate, magnetic susceptibility, crystal field, hyperfine properties.

1. INTRODUCTION

The trivalent rare earth (RE) ions in RE orthovanadates ($\text{REVO}_4$) and yttrium orthovanadates ($\text{YVO}_4$) have been under active study for quite some time now as they find numerous applications in different fields and for their interesting magnetic and other thermophysical properties. The use of Eu doped $\text{YVO}_4$ in high pressure mercury vapour lamps improves the appearance and colour rendering[1]. Ho : $\text{YVO}_4$ crystals have been proposed as a laser medium [2]. Recently, Bleaney [3] reported that Pr$\text{VO}_4$ and Ho$\text{VO}_4$ are also suitable for enhanced nuclear cooling. The RE orthovanadates are ideally suited for the study of cooperative Jahn–Teller effects (CJTE) because of their transparency to visible light; also cooperative JT phase transitions take place at low temperatures (of the order of 10 K) so that it is possible to make observations of, say, specific heat anomalies or spectral lines which are not masked by thermal effects [4]. Gd$\text{VO}_4$ orders antiferromagnetically with the sublattice magnetizations aligned along the four fold symmetry axis having the Neel temperature $T_N = 2.495$ K [5]. The antiferromagnetic transition of Dy$\text{VO}_4$ below 3.066 K has been confirmed by Will and Schäffer [6] using neutron diffraction techniques. All of these phenomena are, in one way or another, strongly influenced by the environment of the RE ions; thus, in order to have a clear understanding of the magnetic and optical behavior of these materials, it is essential to understand the interactions of these ions in the given crystal lattice.

The REVO$_4$ compounds ($\text{RE} = \text{Ce to Lu}$) and $\text{YVO}_4$ crystallize in the tetragonal zircon structure with the space group $I4_1/amd$ ($D_{4h}$) [7]. There are four molecular units per unit cell. All four RE sites with the unique point group symmetry $D_{4h}$ are magnetically equivalent.

The optical absorption spectra of trivalent erbium in isostructural single crystals of YPO$_4$ and YVO$_4$ have been carried out by Kuse [8]. Very recently, Skanthakumar et al. [9] studied the crystal field excitations and magnetic properties of Ho$^{3+}$ in HoVO$_4$. Guo et al. [10] have carried out magnetic measurements on the powder samples of rare earth orthovanadates including erbium vanadate. In the present communication we report for the first time magnetic measurements on the single crystals of erbium vanadate and present a precise theoretical explanation for its interesting anisotropic behavior. The results of the analysis have been used to study the thermal and hyperfine behavior of $^{167}$Er$^{3+}$ in ErVO$_4$.

2. EXPERIMENTAL

The single crystals of ErVO$_4$ were grown by flux method [11]. The light pink colored transparent crystals are elongated along their four-fold symmetry axis. The magnetic anisotropy was measured with a
quartz torsion balance in the temperature range 300–80 K. The absolute magnetic susceptibility $\chi_L$ was measured from room temperature down to 13.2 K with an on-line Faraday setup fabricated by us [12]. The low temperature environment was generated by an APD Cryogenics He-refrigerator. Measurements were carried out in helium atmosphere at an optimum pressure.

3. RESULTS

The average magnetic moment $P_{\text{eff}} = 2.828 \, (\chi T)^5$ where $\chi = (\chi_\parallel + 2\chi_L)/3$ turns out 9.30 at room temperature while the free ion value is 9.58. $P_{\text{eff}}$ decreases slowly with the fall of temperature. The anisotropy $(\Delta \chi = \chi_\parallel - \chi_L)$ at room temperature is small unlike other erbium crystals; the relative magnetic anisotropy $\Delta \chi/\chi$ turns out 0.05 at 300 K. The magnetic anisotropy increases slowly down to $\sim 220$ K, below which it starts decreasing; a cross-over in $\Delta \chi$ is located at about 130 K, below which $\chi_L$ exceeds $\chi_\parallel$. This offers a very sensitive test for the theoretical explanation proposed for the observed magnetic behavior of the Er$^{3+}$ in this crystal matrix. The variation of $\chi_\parallel$ and $\chi_L$ with temperature is depicted in Fig. 1. $\chi_\parallel$ displays a Curie type behavior down to $\sim 30$ K below which the rate of increase falls behind $1/T$ variation while $\chi_L$ shows a slower rise compared to $\chi_\parallel$. A least squares fit of $\chi = (\chi_\parallel + 2\chi_L)/3$—which is in agreement with Guo et al.'s powder values—to the Curie–Weiss law is displayed in Fig. 2; the fit is pretty good. The Curie constant turns out 11.2 cm$^3$ K/mole and the paramagnetic Curie temperature $\theta = -11.7$ K. Here the origin of $\theta$ is more likely to be traced to the interaction of the Er$^{3+}$ ion with the electrostatic field exerted mainly by its diamagnetic neighbors rather than to any exchange or dipolar effects. This so-called crystal field (CF) interaction is considered in detail in the next section in order to elucidate the interesting anisotropic magnetic behavior of the crystal.

4. ANALYSIS AND DISCUSSION

4.1. Crystal field interaction

The ground electronic configuration of Er$^{3+}$ is [Xe] 4f$^{11}$. The Hund’s ground term is $^4I_1$, which splits into four $J$-multiplets under the spin–orbit interaction namely, $\Sigma \zeta_l s_l$, the multiplet with $J = 15/2$ being the ground state; this also mixes to some extent the multiplets with the same $J$ value belonging to different terms, the so-called intermediate coupling or term mixing. Further, the CF of $D_{2d}$ site symmetry, the site symmetry of the Er$^{3+}$ ion, lifts the degeneracy of the $^4I$-manifolds to yield Kramer’s doublets and in the process also mixes the states belonging to different multiplets; this is the CF $J$–$J$ mixing. In order to find the ground term splitting for computation of the magnetic susceptibilities and other thermophysical properties of the ion, it is sufficient to diagonalize the Hamiltonian $\mathcal{H} = \sum_n \lambda_n (L \cdot S)^n + \mathcal{H}_{\text{CF}}$ in the truncated basis of $52 |L, S, J, J_z\rangle$ state vectors spanning the ground term. The first term is an effective spin–orbit operator producing the observed barycenters of different multiplets. In the actual calculation, the spin–orbit interaction ($\mathcal{H}_{\text{SO}}$) term has been replaced by the approximate barycenters of the different $J$-multiplets. The CF interaction term, $\mathcal{H}_{\text{CF}}$ conforming to $D_{2d}$ site symmetry in the one-electron tensor operator...
formalism is given by
\[ B_{20}C_{20} + B_{40}C_{40} + B_{60}(C_{44} + C_{6-4}) + B_{60}(C_{44} + C_{6-4}) \]

\[ C_{kq} \] are tensor operators and \( B_{kq} \) are real constants that parametrize the crystal field. Here we use the traditional one-electron crystal field and do not include the correlated crystal field or the spin-correlated crystal field operators which are of importance only for very precise spectroscopic computations and hardly affect the susceptibilities or other aggregate physical properties. The matrix elements of the tensor operators are calculated by normal tensor operator techniques [14]. All reduced matrix elements were computed using the doubly reduced matrix elements tabulated by Nielson and Koster [15]. The intermediate coupling (IC) effects are partly taken care of by introducing IC coefficients for the reduced matrix elements. Using the resulting \( J \)-mixed Stark states the first and second order Zeeman energies were obtained for the two cases, \( H \parallel z \) and \( H \perp z \) which yielded the expressions [16] of \( \chi_I \) and \( \chi_\perp \) through the Van Vleck formula.

The CF parameters were varied to minimize the weighted rms deviation between theory and experiment in order to get a precise fit to the observed susceptibilities and the cross-over temperature of the magnetic anisotropy. The CF excitations of the ground multiplet of \( \text{Er}^{3+} \) were also kept close to that reported for \( \text{YVO}_4 \) [8] by Kuse; it may be noted that Kuse’s spectroscopic data on the CF level structure of \( \text{Er}^{3+} \) is in similarly constituted \( \text{YVO}_4 \) and hence cannot be taken to provide a precise description of the situation existing in \( \text{ErVO}_4 \). The set of parameters thus arrived at is,

\[ B_{20} = -186, \quad B_{40} = 280, \quad B_{60} = -702, \quad B_{44} = 890, \quad B_{64} = 10 \text{ all in cm}^{-1}. \]

The Stark energies and the ground state wave functions appear in Table 1. Incidentally, our CF provides a lower rms deviation from the observed spectra of \( \text{Er}^{3+} \) in \( \text{YVO}_4 \) than that of Kuse [8]. Also our set of

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>( E^{\text{obs}} )</th>
<th>( E^{\text{cal}} )</th>
<th>Wave functions</th>
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<tr>
<td>( ^5J_{15/2} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0 ( 0.3963[15/2, \pm 9/2] )</td>
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<tr>
<td></td>
<td>42.21</td>
<td>46.5</td>
<td>44.1 ( 0.3284[15/2, \pm 1/2] )</td>
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<tr>
<td></td>
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<td>52.1</td>
<td>45.8 ( 0.8201[15/2, \mp 7/2] )</td>
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<tr>
<td></td>
<td>64.84</td>
<td>86.4</td>
<td>74.2 ( 0.2498[15/2, \mp 15/2] )</td>
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<tr>
<td></td>
<td>143.05</td>
<td>144.8</td>
<td>147.2 ( 0.0042[13/2, \pm 9/2] )</td>
</tr>
<tr>
<td></td>
<td>249.60</td>
<td>257.0</td>
<td>253.1 ( 0.0051[13/2, \pm 1/2] )</td>
</tr>
<tr>
<td>( ^4J_{13/2} )</td>
<td>293.0</td>
<td>282.9</td>
<td>( 0.0012[13/2, \mp 7/2] )</td>
</tr>
<tr>
<td></td>
<td>320.0</td>
<td>308.5</td>
<td>( 0.0004[11/2, \pm 9/2] )</td>
</tr>
<tr>
<td></td>
<td>6540</td>
<td>6541</td>
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<tr>
<td></td>
<td>6587</td>
<td>6590</td>
<td>( 0.0008[9/2, \pm 9/2] )</td>
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<td>6637</td>
<td>6695</td>
<td>( 0.0002[9/2, \pm 1/2] )</td>
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<td>6712</td>
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<tr>
<td>( ^4J_{11/2} )</td>
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<td>12,512</td>
<td>12,583</td>
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</table>

\( a \) Kuse, Ref. [8].

\( b \) This work; the barycenters of the different multiplets chosen are at 6, 6470, 10,087 and 12,312 cm\(^{-1}\) for \( J = 13/2, 15/2, 11/2, 9/2 \), respectively. The calculated levels have been raised by 145.82 cm\(^{-1}\) while tabulating for ease in comparison with the observed levels.
parameters differs considerably from that of Guo et al. This is quite expected since powder results provide too little information to fix the CF precisely; also, our theoretical approach differs from that of Guo et al. who do not seem to have considered IC effects which are appreciable and the CF $J-J$ mixing. In general the magnitude of parameters is seen to differ appreciably in different similarly constituted crystals, ErPO$_4$, Er$^{3+}$: YPO$_4$ [18] and the present one. The simulation of the observed $\chi_\parallel$ and $\chi_\perp$ is depicted in Fig. 1; the theoretical curves run through nearly all experimental points over the entire range of temperature. The observed cross-over in $\Delta \chi$ which is rather sensitive to the changes in the CF parameters is also correctly reproduced by our computed values indicating the adequacy of the chosen CF parameters. Thus, a comprehensive agreement with the available experimental data is obtained through the crystal field interaction of the Er$^{3+}$ ion and our measurements do not reflect any CJTE or magnetic phase transition effects at least down to 13.2 K.

4.2. Electronic specific heat

The effect of the CF on the heat capacity of the crystal is profound. This is reflected in the characteristic thermal variation of the electronic heat capacity $C_e$ in the form of Schottky anomalies given rise to by the low lying CF Stark levels. $C_e$ is computed using the expression

$$N_A \frac{d}{dT} [\text{Tr}(\mathcal{H}\rho)/\text{Tr}(\rho)].$$

Here $\mathcal{H}$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N_A$ is the Avogadro number.

4.3. Hyperfine properties

$^{167}$Er isotope has a ground state with nuclear spin $I = 7/2$ and an electric quadrupole moment of 2.83 barn. The nuclear level is split by the quadrupole interaction between the nucleus and the electric field gradient (EFG) at the nuclear site produced by the quadrupole moment of the $4f$ electrons and the lattice.
The computed quadrupole splitting, \((\Delta E_Q)_{\gamma}\) \cite{17} between the lowest two nuclear doublets \(|I_z = \pm 1/2\rangle\) and \(|I_z = \pm 3/2\rangle\) is displayed in Fig. 4; it attains a constant value below \(\sim 7\, \text{K}\). This is easily amenable to quadrupole resonance study. The hyperfine Hamiltonian \(\mathcal{H}_n\) for \(D_{2d}\) symmetry in the presence of magnetic field along the symmetry axis, \(\mathcal{H}_n = (1/2)A_{||} I_z + P[I_z^2 - I(I + 1)/3]\) was diagonalized to calculate the hyperfine energies and hence the thermal variation of the nuclear specific heat. A Schottky type anomaly is seen in the heat capacity at \(\sim 4.8\, \text{mK}\) with the corresponding peak value \(5.101\, \text{J/g atom K}\) (Fig. 5).

5. CONCLUSIONS

The magnetic susceptibilities of erbium vanadate are accounted for very well by considering electrostatic interaction of \(\text{Er}^{3+}\) with its immediate neighbors. The crystal becomes magnetically isotropic at about \(130\, \text{K}\) and this was reproduced exactly by the CF analysis. Below \(130\, \text{K}\), the larger of the two principal susceptibilities, \(\chi_{\parallel}\), which was measured down to \(13.2\, \text{K}\), displayed a smooth variation and there was no indication to suggest a structural or magnetic phase transition of any significance.

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Experimental and theoretical studies on the magnetic behavior of \( \text{Nd}^{3+} \) in \( \text{NdPO}_4 \)

D. Neogy\textsuperscript{a,\ast}, P.K. Chakrabarti\textsuperscript{a}, K.N. Chattopadhyay\textsuperscript{a}, B.M. Wanklyn\textsuperscript{b}

\textsuperscript{a} Solid State Research Laboratory, Department of Physics, Burdwan University, Burdwan 713 104, West Bengal, India
\textsuperscript{b} Clarendon Laboratory Oxford, Oxford OXI 3PU, UK

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Experimental and theoretical studies on the magnetic behavior of Nd$^{3+}$ in NdPO$_4$

D. Neogy$^a$,*, P.K. Chakrabarti$^a$, K.N. Chattopadhyay$^a$, B.M. Wanklyn$^b$

$^a$Solid State Research Laboratory, Department of Physics, Burdwan University, Burdwan 713 104, West Bengal, India
$^b$Clarendon Laboratory Oxford, Oxford OX1 3PU, UK

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Abstract

The monoclinic monazite-type single crystals of NdPO$_4$ were grown by flux technique. The molar principal susceptibilities ($\chi_1$ and $\chi_3$) of the crystal have been measured in the temperature range 300–13 K; the principal magnetic anisotropies ($\chi_1 - \chi_2$, $\chi_1 - \chi_3$) were obtained from the observed anisotropies in different modes of suspension of the crystal. The ionic susceptibilities are computed using the spectroscopic crystal-field parameters of Rukmini et al. (J. Phys.: Condens. Matter 6 (1994) 5919). The observed crystal susceptibilities are correlated to the ionic values determining the proper orientation of the ionic susceptibilities with respect to that of the crystal; the agreement between the experimental and theoretical values is excellent which incidentally rules out ordering effects of any consequence down to 13 K. g-factors computed for the ground doublet are found to be highly anisotropic. The electronic-heat capacity at different temperatures was calculated using the Stark energies which did not show any Schottky-type anomalies.

PACS: 75.10.Dg; 75.20.Ck; 71.70.Ch; 65.40.-f

Keywords: Neodymium phosphate; Susceptibility; Anisotropy; Crystal field

1. Introduction

Recent interest in rare-earth orthophosphates (REPO$_4$) is due to their multidirectional applications in different branches of physics. Structural and chemical stability, long-term corrosion resistance, and high melting point (~2000°C) of these materials make them suitable for use as high-temperature components in various devices and as a primary encapsulation medium for the permanent disposal of certain types of radioactive wastes [1–3]. Rare-earth activated luminescence in lanthanide orthophosphates makes these materials potential candidates for application as phosphors and lasers [4, 5]. The optical and magnetic properties of the (rare earth) RE-ions in REPO$_4$ hosts, magnetic-phase transitions and Jahn–Teller (JT) effects, have promoted numerous theoretical and experimental studies on these materials.
Orthophosphates of rare earths are divided into two classes: those of the first-half of the series have the monoclinic monazite structure, while those of the second-half have the tetragonal zircon structure. TbPO$_4$ is at the transition position of these RE-orthophosphates which can be grown in either of the two structures, monazite or zircon, depending on the method of preparation.

We reported in the earlier papers [6, 7] magnetic measurements and crystal-field investigations on TbPO$_4$ and HoPO$_4$. The long-range antiferromagnetic ordering has been observed in TbPO$_4$, DyPO$_4$ and HoPO$_4$ with corresponding Neel temperatures $T_N = 2.28$, 3.4 and 1.39 K, respectively [8-10]. The antiferromagnetic phase has a simple two-sublattice structure with the direction of RE magnetic moments lying parallel/antiparallel to the crystallographic c-axis. TbPO$_4$ also exhibits JT phase transition at 2.15 K where the Tb ion-lattice coupling induces a distortion of the tetragonal lattice to a monoclinic structure with a corresponding tilting of the Tb moments away from the tetragonal c-axis in the (1 1 0) plane [11-14]. In the past few years there has been extensive work on NdPO$_4$ mostly connected with its application in laser physics. Recently, optical absorption studies have been carried out by Fidancev et al. [15] on Nd$^{3+}$ in NdPO$_4$ and NdVO$_4$, and also on Eu$^{3+}$ in EuVO$_4$, EuPO$_4$ and LaV$_2$O$_4$; they also provided a crystal-field (CF) analysis of the observed energy levels. More recently, Rukmini et al. [16] have improved on the theoretical explanation of the spectra changing the CF parameters and invoking correlated crystal-field (CCF) interactions. In this communication we present the results of our magnetic measurements carried out for the first time on a monoclinic RE phosphate single crystal viz., NdPO$_4$; determination of the principal magnetic susceptibilities is much more involved in this case and correlation of these with the ionic values is rather complex compared to the zircon-structure phosphates where both the crystal and the site of the RE-ion have axial symmetry. An explanation to the observed results has been sought in the crystal-field interaction of the Nd$^{3+}$ ion with its diamagnetic neighbors which turns out to be quite encouraging.

2. Experimental

The single crystals of NdPO$_4$ were grown by flux method [17]. The monoclinic NdPO$_4$ was obtained as very small crystals from Pb$_2$P$_2$O$_7$ flux with PbF$_2$ as an additive. The deep violet prismatic crystals are between 10 and 20 mg each with a prominent (1 0 0) plane. The magnetic anisotropies for different modes of suspension (b-axis vertical, c-axis vertical, and (1 0 0) plane horizontal) were measured with a quartz torsion balance in the temperature range 300–80 K employing a microprocessor-based automatic temperature controller. The principal molar susceptibilities $\chi_1$ and $\chi_2$ were measured from room temperature down to $\sim 13$ K with a computerized Faraday setup [18]. Here, a highly sensitive taut-band electromagnetic balance fabricated in the laboratory was employed to measure the force acting on the crystal in the magnetic field; the balance was continuously nulled by a programmed current controller. The low-temperature environment was provided by a Displex closed-cycle helium cryo-cooler from APD Cryogenics. Temperature was maintained by a Scientific Instruments temperature indicator/controller where an Au–Fe(0.07%)/Chromel thermocouple was used as a sensor. The calibration of the crystal chamber temperature was performed by measuring the susceptibility of the Mn(NH$_4$SO$_4$)$_2$·6H$_2$O single crystals which strictly follow the Curie law down to $\sim 1$ K.

3. Results and discussion

3.1. Magnetic measurements

Unlike uniaxial systems, determination of the principal magnetic susceptibilities in a monoclinic system is relatively difficult; not all the principal susceptibilities or the principal anisotropies can be measured directly. Symmetry considerations of this crystal in correlation to that of the susceptibility tensor-ellipsoid require that the crystallographic b-axis be a principal susceptibility axis which we call $\chi_3$. The other two principal susceptibilities viz., $\chi_1$ and $\chi_2$ ($\chi_1 > \chi_3$ by convention) lie in the b-plane but the orientation with respect to
the crystallographic axes $a$ and $c$ lying in the same plane is not known; this makes measurement of the principal $\Delta\chi$'s difficult. We adopted the following procedure to determine the principal anisotropies. The principal magnetic anisotropy ($\chi_1 - \chi_2$) was measured directly by suspending the crystal with the $b$-axis vertical. The anisotropies with $c$-axis vertical and $(1 0 0)$ plane horizontal were measured which yielded the following quantities, respectively,

$$\pm [\chi_3 - \chi_1 \sin^2 \psi - \chi_2 \cos^2 \psi],$$
$$\pm [\chi_3 - \chi_1 \cos^2 \psi - \chi_2 \sin^2 \psi].$$

(± sign for $\chi_3$ setting $\parallel$ or $\perp$ to $H$, respectively.) Here, $\psi$ is the angle between the crystal axis $c$ and $\chi_1$. In the present case, the $b$-axis sets parallel to $H$, the magnetic field, with $c$-axis vertical and perpendicular to $H$ with $(1 0 0)$ plane horizontal. Using the above relations the principal magnetic anisotropies were worked out from the observed values for the three modes of suspension. $\chi_1$ and $\chi_3$ were measured directly. The thermal variation of the molar susceptibilities is depicted in Fig. 1. The variation of $\chi_1$ and $\chi_3$ is nearly Curie-type down to ~200 K below which the rate of increase slows down. The increase of $\chi_2$ with decrease of temperature is much slower than $1/T$. A cross-over in ($\chi_1 - \chi_3$) is detected just below ~180 K. A least-squares fit of $\bar{\chi} = (\chi_1 + \chi_2 + \chi_3)/3$ to the Curie-Weiss law down to 80 K is displayed in Fig. 2; the fit is pretty good. The Curie constant turns out to be 1.65 cm$^3$ K/mole and the paramagnetic Curie temperature $\theta = -42.5$ K; here the origin of $\theta$ is likely to be found in the CF splitting of the ground multiplet rather than in any dipolar or exchange effects. The effective Bohr magneton number ($P_{eff} = 2.828 [\bar{\chi} T]^{0.5}$) at 300 K turns out to be 3.41 which is slightly lower than the free-ion value, viz., 3.64; it is found to decrease slowly with fall of temperature. In the following section we turn to CF interaction to seek an explanation to all observed deviations from the free-ion behavior of Nd$^{3+}$ in this crystal.

### 3.2. Crystal-field interaction

The site symmetry of RE ion in this crystal is $C_1$ [19] which may be approximated to $C_{2v}$ [15]; this means the paramagnetic cluster is not uniaxial and this renders correlation of the ionic
susceptibilities with the observed crystal susceptibilities rather involved.

The ground electronic configuration of Nd$^{3+}$ is [Xe]4f$^{3}$, the ground term being $^2$I; the spin-orbit coupling gives rise to four $J$ multiplets with $J = \frac{3}{2}$, the lowest. The crystal field (CF) of $C_{2v}$ symmetry splits all the multiplets into Kramers doublets. Using one-electron CF, the Hamiltonian conforming to $C_{2v}$ symmetry is as follows:

$$\mathcal{H}_{\text{CF}} = B_{20} C_{20} + B_{22} (C_{22} + C_{2-2}) + B_{40} C_{40} + B_{42} (C_{42} + C_{4-2}) + B_{44} (C_{44} + C_{4-4}) + B_{60} (C_{60} + C_{6-2}) + B_{62} (C_{62} + C_{6-2}) + B_{64} (C_{64} + C_{6-4}) + B_{66} (C_{66} + C_{6-6}).$$

$C_{xq}$'s are tensor operators and $B_{xq}$'s are real constants that parametrize the crystal field (use of one-electron CF is adequate for calculation of the magnetic properties). Employing the normal tensor operator techniques [20] the crystal-field Hamiltonian was set up and diagonalized in the ground term [$^2$I] manifold with important intermediate coupling corrections. The ionic susceptibilities ($K_x$, $K_y$ and $K_z$) were computed employing the spectroscopic CF parameters of Rukmini et al. [16] ($B_{20} = -618$, $B_{22} = 103$, $B_{40} = -785$, $B_{42} = 233$, $B_{44} = 728$, $B_{60} = -1078$, $B_{62} = 850$, $B_{64} = -305$ and $B_{66} = -67$, all in cm$^{-1}$) which are an improvement on the CF parameters given by Fidancev et al. [15]; incidentally, even one-electron CF with the parameters of Rukmini et al. brings about a remarkable decrease in the RMS deviation of the computed Stark energies of the ground term from those observed. The average values of the ionic susceptibilities agree very well with our observed average crystal susceptibilities. Employing a slightly modified procedure adopted for correlating ionic susceptibilities ($K$'s) with those of the crystal ($\chi$'s) in monoclinic systems with uniaxial paramagnetic cluster, the computed ionic susceptibilities are compared with our observed results. The computed ionic values led us to conclude that the crystal susceptibility $\chi_2$ and the ionic susceptibility $K_x$ are collinear, while the crystal susceptibilities $\chi_1$ and $\chi_3$ are related to the ionic values $K_x$ and $K_z$; the situation is depicted in Fig. 3. A comparison of the theoretical values with those observed gives the angle ($\phi$) between the principal susceptibility $\chi_1$ and the ionic susceptibility $K_x$, ~ 49°; $\chi_1$ and $\chi_3$ calculated from the computed values of $K$'s at different temperatures are compared with our experimental data in Fig. 1. The result is a complete agreement of the theoretical and observed principal susceptibilities over the entire range of temperature of our study which endorses the approximation of the site symmetry to $C_{2v}$ by the earlier workers [15, 16] for the analysis of the spectroscopic data. The very good explanation provided by the CF theory alone also indicates that ordering effects of any consequence are absent down to the lowest temperature of our study. Hence, a transition to an ordered state could be expected at a much lower temperature than those observed in other RE phosphates [8-10].

The principal spectroscopic splitting factors for the ground Kramers doublet were computed and found to differ widely. The values are, $g_x = 4.26$, $g_y = 0.97$ and $g_z = 1.38$. Consideration of the wave functions of the doublet shows that the transition probabilities for all the three $g$ factors are quite significant and hence, resonance should not be difficult to observe.

The low-lying CF states make a significant contribution to the heat capacity of the crystal; the change of occupation of different states with the temperature usually gives rise to characteristic anomalies. The electronic heat capacity $C_e$ of our
The electronic heat capacity $C_s$ system was computed using the relation

$$C_s = N_A \frac{d}{dT} \left[ \frac{\text{Tr}(\mathcal{H}\rho)}{\text{Tr}(\rho)} \right].$$

Here $\mathcal{H}$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N_A$ is the Avogadro number. The variation of $C_s$ with temperature is depicted in Fig. 4 which fails to show any Schottky anomaly so often encountered in such systems; however, a sharp drop in the large value of $C_s$ just below $\sim 50$ K should be quite amenable to heat-capacity measurement.

4. Conclusions

For the first time the magnetic properties of a nonuniaxial rare-earth phosphate crystal have been studied and a correlation established between the observed principal magnetic susceptibilities of the crystal and that of the RE-ion which is also in an environment without any axial symmetry. Further, an excellent agreement could be established between our observed magnetic behavior of the single crystal of NdPO$_4$ with those computed theoretically from the spectroscopically derived parameters for the crystal-field interaction of the Nd$^{3+}$ ion; the adequacy of the parameters lends support to the approximation of the site symmetry of the ion to be $C_{2v}$ by Fidancev et al. [15] and Rukmini et al. [16]. $g$-factors have been computed which are found to be quite amenable to experimental verification. Behavior of the electronic heat capacity $C_s$ computed from our above findings led us to conclude that $C_s$ suffers a steep drop just below 50 K but do not display any Schottky-type anomaly.

Acknowledgements

We would like to thank Dr. B. Lahiri for helping us confirm the crystal faces by X-ray diffraction. Our thanks are also due to Mr. D. Bisui for his help in the low-temperature measurements.

References

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STUDIES OF THE MAGNETIC BEHAVIOUR OF ErAl₃(BO₃)₄ AND THE EFFECTS OF THE CRYSTAL FIELD

D. NEOGY†*, K. N. CHATTOPADHYAY†, P. K. CHAKRABARTI†, H. SEN† and B. M. WANKLYN‡

†Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan-713104, West Bengal, India
‡Clarendon Laboratory, University of Oxford, Oxford OX1 3PU, UK

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Abstract—Single crystals of ErAl₃(BO₃)₄ were produced by flux growing techniques. The principal magnetic susceptibility, \( \chi_\perp \), perpendicular to the symmetry axis of the crystal was measured in the range 300–14.2 K, and the principal anisotropy \( (\chi_\perp - \chi_\parallel) \) was determined from 300 to 77 K, which turned out to be negative throughout. A crystal field conforming to \( D_3 \) site symmetry (obtained from structural data) accounts very well for the observed thermal variation of the magnetic susceptibilities; this yields \( g \) factors, \( g_1 \) and \( g_2 \), of 2.32 and 8.95, respectively. The electronic heat capacity is computed, and shows a Schottky anomaly at around 45 K. Calculated quadrupole splitting of \(^{167}\)Er due to crystal field effects shows a smooth decrease with decreasing temperature. The hyperfine heat capacity, contributed mainly by magnetic hyperfine splitting, displays a rounded maximum at about 8 mK.

Keywords: magnetic susceptibility, \( D_3 \) site symmetry, crystal field, hyperfine properties

1. INTRODUCTION

Rare earth (RE) aluminium borates \([\text{REAl}_3(\text{BO}_3)_4]\) are isostructural with the rhombohedral mineral huntite, \( \text{CaMg}_3(\text{CO}_3)_4 \), having the space group \( R\overline{3}2 \) [1, 2]. They have been attracting attention for their luminescence, concentration quenching in particular, and their possible application as single crystal minilasers [3]. \( \text{NdAl}_3(\text{BO}_3)_4 \) has already been established as a laser material [4, 5]; others are under intensive study for their immense potential in different optical applications. Although trivalent neodymium is the most sought-after activator ion in laser crystals, other are also finding increasing use. The rare earth activation ions in these crystals interact with the ligand charges, which split the degenerate multiplets into crystalline Stark levels; the position of these levels, their degeneracies and their wavefunctions greatly influence their role in device applications. Information on these aspects of the ions is best obtained from optical, neutron diffraction, magnetic and EPR studies. Thermal neutron diffraction and optical experiments provide the most direct evidence on the position of the crystal field (CF) levels; magnetic measurements over a wide temperature range and EPR studies also help in locating the levels and find their wavefunctions through CF analysis of the results. In fact, all these measurements play complementary roles for a complete and thorough understanding of the behaviour of the RE ions in the host matrix.

The RE aluminium borates form an isomorphous series. The structures of nearly all the RE aluminium borates have been determined. The \( \text{RE}^{3+} \) ion is surrounded by a trigonal prism of six oxygen atoms, each belonging to a different borate group and not shared by neighbouring \( \text{RE}^{3+} \) ions. The RE site symmetry in this structure is \( C_{3v} \), considering nearest-neighbour oxygen atoms only; the symmetry reduces to \( D_3 \) if one includes the nearest \( (\text{BO}_3) \) groups [2, 6]. The simple crystal structure makes this system amenable to crystal field (CF) studies in correlation with its magnetic properties. In the present communication, we report our results of magnetic measurements on erbium aluminium borate single crystals from room temperature down to 14.2 K, and their analysis invoking CF theory. On the basis of these findings, theoretical excursions into related fields allow us to make important predictions on some electronic and nuclear properties.

2. EXPERIMENTAL

Single crystals of erbium aluminium borate \([\text{ErAl}_3(\text{BO}_3)_4]\) were grown by standard flux-growing techniques [6]. The light pink crystals are well-defined, prismatic and elongated along the crystallographic \( c \) axis. The principal magnetic susceptibility perpendicular to the crystallographic symmetry axis \( c \), i.e. \( \chi_\parallel \), was measured from room temperature down to 14.2 K with the help of a highly sensitive electronic balance fabricated in our laboratory. The programmable digital
The magnet current control module and the balance were brought under single regulation with a PC to make the set-up fully automatic. The low-temperature environment was provided by an APD Cryogenics closed-cycle helium refrigerator and the temperature was measured with an Au–Fe/Chromel thermocouple; for further details, see our earlier work [7–9].

The magnetic anisotropy \( \Delta x = x_r - x_\perp \) of a single crystal of erbium aluminium borate was measured directly, using a quartz torsion balance, down to liquid nitrogen temperature [7].

3. RESULTS

The variation of \( x_\perp \) and \( x_r \) with temperature is displayed in Fig. 1. As \( x_\perp \) is greater than \( x_r \) throughout the temperature range of our study, we were unable to measure \( x_r \) directly with a freely suspended crystal in the Faraday system; we obtained \( x_r \) by comparing \( \Delta x \) and \( x_\perp \) data. The natures of the variation of \( x_\perp \) and \( x_r \) with decrease of temperature are quite different; whereas \( x_r \) increases gently, almost linearly, down to about 80 K, \( x_\perp \) undergoes a very rapid rise from 120 K with decreasing temperature (Fig. 1).

The effective magnetic moment \( P_{\text{eff}} \) at room temperature calculated by use of the relationship \( P_{\text{eff}} = 2.828(\chi T)^{1/2} (\chi = [x_\perp + 2x_\perp]/3) \) turns out to be 9.81 (Bohr magnetons) which is slightly greater than the free ion value of 9.58; \( P_{\text{eff}} \) drops slowly with decrease of temperature. As is commonly experienced in polycrystalline samples with strong crystal field effects [10], here also the average magnetic susceptibility, \( \bar{\chi} \), follows the Curie–Weiss law quite closely. A least squares fit of the observed \( \bar{\chi} \) in the range 300–77 K to the Curie–Weiss law yields a Curie constant of 12.26 e.m.u. K and a paramagnetic Curie temperature of \( \theta = -4.96 \) K; the fit is pretty good (Fig. 2). As will be shown later, this behaviour arises entirely from the change of occupation of the low-lying CF states contributing to the magnetic moment of the RE ion in the crystal and is influenced little by exchange effects.

The magnetic anisotropy \( \Delta x = x_r - x_\perp \) of ErAl\(_3\)(BO\(_3\))\(_4\) is quite high at 300 K, and at 77 K it is twelve times the room temperature value; the relative magnetic anisotropy \( \Delta x/\bar{\chi} \) at room temperature is 0.238 and that at 77 K is 0.779.

4. ANALYSIS AND DISCUSSION

As reported earlier [1, 2], erbium aluminium borate is isostructural with other RE aluminium borates and hence the site symmetry of Er\(^{3+}\) in this crystal matrix is assumed to be \( D_3 \) following earlier work [1, 2, 6, 11, 12]. The electronic configuration of Er\(^{3+}\) is \([Xe] (4f)^{11}\), and this gives \( 4 \) as the ground term. Group theoretical considerations show that the ground multiplet splits into eight Kramers doublets under the influence of a CF of \( D_3 \) symmetry according to a reduction of the 16 dimensional double-valued irreducible representation of the spherical rotation group spanned by the degenerate states of the ground multiplet of the Er\(^{3+}\) ion into eight two-dimensional irreducible representations of the \( D_3 \) crystal double group. The crystal field Hamiltonian of the Er\(^{3+}\) ion in erbium aluminium borate for \( D_3 \) symmetry is expressed as

\[
\mathcal{H}_{\text{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{43}(C_{43} - C_{4-3}) + B_{63}(C_{63} - C_{6-3}) + B_{66}(C_{66} + C_{6-6})
\]

where \( C_{ij} \) are tensor operators and \( B_{ij} \) are the real parameters.

The Hamiltonian \( \mathcal{H} = \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{CF}} \) is directly diagonalized in the 52-dimensional basis of the ground term; \( \mathcal{H}_{\text{SO}} \) is the spin–orbit coupling interaction term diagonal in \( J \). The matrix elements are computed using Racah tensor operator techniques [13]. Intermediate coupling (IC)
Table 1. Crystal field Stark splitting of the ground term $^4I$ of the Er$^{3+}$ ion in erbium aluminium borate and its ground state wave functions

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>Energy (cm$^{-1}$)</th>
<th>Wave functions</th>
</tr>
</thead>
</table>
| $^4I_{19/2}$ | 0.0 | $-0.036615/2, \pm 11/2 + 0.406715/2, \pm 5/2 >$
| | 28.4 | $+0.731015/2, \mp 1/2 \mp 0.523415/2, \pm 7/2 >$
| | 75.6 | $-0.157715/2, \mp 13/2 + 0.003115/2, \pm 11/2 >$
| | 98.1 | $-0.004513/2, \pm 5/2 \pm 0.002813/2, \mp 1/2 >$
| | 103.4 | $-0.001213/2, \mp 7/2 + 0.003613/2, \mp 13/2 >$
| | 124.6 | $-0.000911/2, \pm 11/2 \pm 0.002111/2, \pm 5/2 >$
| | 169.1 | $-0.001711/2, \mp 1/2 \mp 0.001411/2, \mp 7/2 >$
| | 220.7 | $+0.000419/2, \mp 5/2 + 0.000219/2, \mp 11/2 >$
| | 4 $^1I_{13/2}$ | 6512.5 | -
| | 6531.1 | -
| | 6549.7 | -
| | 6564.8 | -
| | 6585.3 | -
| | 6611.7 | -
| | 6652.6 | -
| | 10154.1 | -
| | 10161.7 | -
| | 10175.2 | -
| | 10191.8 | -
| | 10212.4 | -
| | 10242.4 | -
| | 12367.6 | -
| | 12373.9 | -
| | 12422.1 | -
| | 12453.6 | -
| | 12464.2 | -

All are Kramers doublets.

factors for the reduced matrix elements are introduced to take care of the term mixing to a large extent, which is a dominant feature of configuration diagonalization through the free-ion interaction term $\xi \sum I_i s_i$; it may be noted that $\xi$ and the other so-called free-ion parameters vary a little with the lattice that hosts the ion, and this may have some effect on the baricentres but usually very little on the term mixing and hence on the magnetic properties [16]. The Zeeman energies of the resulting CF states are obtained for the two cases, i.e. $H$ parallel and perpendicular to the symmetry axis of the crystal; the susceptibilities are obtained through the well-known van Vleck expression. No information on the absorption spectra or inelastic neutron scattering of the crystal is available. In order to fix the crystal field, the six parameters $B_{kq}$ were varied carefully to obtain a precise fit to the observed variation of the magnetic properties over the entire temperature range of our study; the r.m.s. weighted deviation between experiment and theory has been taken as the primary index of the fit achieved. Here, it must be borne in mind that we have two different susceptibilities to simulate and hence the deviations for them are computed separately; while fitting, the deviations for the two susceptibilities, as well as the total deviation, are tried to be minimized. In the case of HoAl$_3$(BO$_3$)$_4$, the susceptibilities were extremely sensitive to the change in CF parameters [8]; in the present case, however, the sensitivity is relatively less. A rough estimate of the uncertainty for each parameter is given in the best-fit set below.

$B_{10} = 600 \pm 3$, $B_{40} = 12 \pm 1$, $B_{60} = 16 \pm 1$,
$B_{43} = 30 \pm 1$, $B_{63} = -280 \pm 3$, $B_{66} = 50 \pm 2$ cm$^{-1}$

The computed Stark energies and the ground-state wave functions are given in Table 1. The excellent simulation of observed $\chi_\perp$ and $\chi_\parallel$ by our theoretical values (Fig. 1) proves the adequacy of our crystal field treatment. This also leads us to conclude that exchange or dipolar effects have very little role to play in this temperature range. No report on the spectroscopic splitting factors $g_\|$ and $g_\perp$ has come to our notice. The ground Kramers doublet yields $g_\| = 2.32$ and $g_\perp = 8.95$. A little consideration of the wave functions of the Kramers pair shows that the magnetic dipole transition probability for observing resonance absorption is quite favourable and hence experimental vindication of our results is anticipated. The first excited state is about 28 cm$^{-1}$ and its occupancy at liquid helium temperatures should be poor to respond to the resonance experiments; $g_\| = 6.54$ for this level but the transition probability is poor.

5. THERMAL AND HYPERFINE PROPERTIES

As the electronic heat capacity $C_e$ is strongly influenced by the crystal field, the latter leaves its bold imprint on the Schottky anomalies. The heat capacity $C_e$ was computed at different temperatures using the standard expression

Magnetic behaviour of ErAl$_3$(BO$_3$)$_4$
[14] Fig. 3 depicts the thermal variation which shows a rounded maximum at around 45 K with a peak value 8.30 J (g atom)$^{-1}$ K$^{-1}$ and this is easily amenable to experimental verification.

$^{167}$Er has a ground state with nuclear spin $I = 7/2$ and an electric quadrupole moment of 2.83 barn. The nuclear level is split by the quadrupole interaction between the nucleus and the electric field gradient (EFG) at the nuclear site produced by the quadrupole moment of the 4f electrons and the lattice. The quadrupole splitting ($\Delta E_{Q}$) [15] between the lowest two nuclear doublets $|l_z = \pm 5/2\rangle$ and $|l_z = \pm 7/2\rangle$ is computed at different temperatures. The thermal variation of $\Delta E_{Q}$ is depicted in Fig. 4.

The hyperfine Hamiltonian for $D_3$ symmetry in the presence of a magnetic field along the symmetry axis is given by $\mathcal{H}_F = \frac{1}{2} A_n I_n + P[I_z^2 - I(I + 1)/3]$. The hyperfine energies and hence the nuclear specific heat ($C_N$) were obtained by diagonalizing the hyperfine hamiltonian $\mathcal{H}_F$. The thermal variation of $C_N$ is depicted in Fig. 5 which shows a rounded maximum at around 8 mK.

6. CONCLUSIONS

Just as in the case of holmium aluminium borate [8], here, too, we find a single crystal field providing an excellent description of all the observed results, ruling out any ordering effects down to around 14.2 K although the aluminium borates do not belong to highly dilute systems. It is also interesting to note that this is so both for non-Kramers and Kramers systems. However, in the present case, the magnetic anisotropy is very high, rendering the behaviour of the two principal susceptibilities to differ widely; the spectroscopic splitting factors of the ground doublet also differ considerably. The overall splitting of the ground multiplet is small, i.e. 220$^{17}$ cm$^{-1}$, similar to the Ho compound. Locations of the crystal field levels suggest a rounded maximum in the thermal variation of the electronic heat capacity of this crystal around 45 K, which would provide an interesting study. Our work also predicts a rounded maximum in the nuclear heat capacity at around 8 mK and a slow decrease of the quadrupole splitting of the nuclear ground state with lowering of the temperature.

REFERENCES

Magnetism of neodymium trifluoromethanesulfonate nonahydrate and effects of the crystal field


Solid State Research Laboratory, Department of Physics, Burdwan University, Burdwan 713 104, West Bengal, India

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Abstract

The principal magnetic susceptibilities of neodymium trifluoromethanesulfonate nonahydrate (NdTFMS) were measured between 300.0 and 12.5 K. The hexagonal crystal structure of NdTFMS is very similar to that of the hydrated rare-earth ethylsulfates with the Nd$^{3+}$ ion occupying a site of $C_{3v}$ symmetry. An excellent description of the observed results was obtained using one-electron crystal field theory with the set of parameters derived from a fit to the observed absorption spectra. No ordering effects were noticed indicating the interionic interaction to be of predominantly dipolar type. The $g$-values were calculated to be 3.81 and 2.02 for $g_I$ and $g_J$, respectively. The nuclear quadrupole splitting, and the electronic and nuclear heat capacities were also computed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystal fields; Magnetic susceptibility

1. Introduction

Recently there has been considerable interest in the spectra and magnetic properties of the rare earth trifluoromethanesulfonate nonahydrates (RTFMS) [R(OH$_2$)$_9$(CF$_3$SO$_3$)$_3$] where R stands for a trivalent rare earth ion [1-4]. These crystals grow in the hexagonal system and are very similar in structure to those of the extensively studied rare-earth ethylsulfates nonahydrates (RES); in this respect they are also similar to the rare earth bromate nonahydrates (RB) to a certain extent although the detailed geometries of the cations in RES and RTFMS are significantly different from that in RB [1]. Both series of compounds, viz. RES and RTFMS have the space group symmetry $P6_3/m$ with $Z = 2$; all rare-earth ions in these structures have the site symmetry $C_{3v}$ and they are magnetically equivalent [1]. The unit cell dimensions and the density of R$^{3+}$ ions in RTFMS are nearly the same as in RES. In these crystals the R$^{3+}$ ions are surrounded by nine H$_2$O molecules forming a tricapped trigonal prism; the prisms in both RTFMS and RES are nearly identical.

* Corresponding author. Tel.: +91-342-62266; fax: +91-342-64452.
E-mail address: phydn@burdwan.emet.in (D. Neogy)

The magnetic ordering [2], electron paramagnetic resonance (EPR) [3] and heat capacity of a number of RTFMS were studied by the Friedberg group. HoTFMS order ferromagnetically along the $c$ axis at $T_c = 0.23$ K as does HoES which is of particular interest for this non-Kramers ion. EPR studies reveal an accidentally degenerate ground state which suffers a zero-field splitting because of Jahn–Teller distortion. The electronic absorption spectra of NdTFMS were observed and the energy-level and line strength data were analyzed by Quagliano et al. [4] quite exhaustively in terms of the interactions of the 4f electrons with the crystal field (CF). Magnetic, thermal and hyperfine properties are strongly influenced by the CF and a study of these properties provide very interesting data in understanding the behavior of the R$^{3+}$ ion in correlation to different interactions present in the crystal. We have not come across any data on the magnetic ordering or susceptibility at very low temperatures for this crystal.

In the present communication we report our measurements on the principal magnetic susceptibilities of NdTFMS single crystals. This is the first such study ever conducted on any of the compounds of this series. We first try to seek an explanation to our observed data over the entire range, 300–12 K, primarily in the crystal field interaction suggested by Quagliano et al. from their optical absorption studies and see
whether there is any influence of the ordering effects. Using our computed results of CF interaction we also undertake calculations of the electronic heat capacity and nuclear hyperfine properties of this system.

2. Experimental details

A solution of NdTFMS was prepared by adding anhydrous triflouromethanesulfonic acid (CF$_3$SO$_3$H) to a slurry of Nd$_2$O$_3$ in water [1] and heating it to 90°C with constant stirring until the solution became clear. Single crystals of NdTFMS were obtained by slow evaporation of the solution at room temperature. Needle like pink crystals elongated along the c-direction were on the average 8–10 mm in length.

The principal magnetic susceptibilities, $\chi_\parallel$ and $\chi_\perp$, parallel and perpendicular to crystallographic symmetry axis c, were measured from room temperature down to 12.5 K with the help of a highly sensitive electromagnetic balance fabricated in our laboratory [5]. The low temperature environment was provided by a closed-cycle helium cryocooler from APD cryogenics. The details of the fully computerized low temperature magnetic susceptibility setup developed by us with special reference to temperature calibration of the sample chamber are given in earlier articles [5,6].

$\chi_\perp$ was measured by suspending the crystal with a thin quartz fibre with the c-axis vertical in the constant vertical magnetic field gradient i.e., $H_z \frac{dH_z}{dx} = \text{const}$. $\chi_\parallel$ was measured with the c-axis in the horizontal plane; in the magnetic field, $\chi_\parallel$ automatically sets in the direction of the field as in this case $\chi_\parallel > \chi_\perp$, and care is taken to see that the torsional constant of the quartz fibre is very small.

The magnetic anisotropy ($\chi_\parallel - \chi_\perp$) is calculated with the values of $\chi_\parallel$ and $\chi_\perp$ at different temperatures; at room temperature the anisotropy was measured directly using a quartz torsion balance described earlier [7] as a check on the absolute susceptibility measurements.

3. Results

At room temperature the crystallographic c-axis sets along the applied external magnetic field indicating $\chi_\parallel > \chi_\perp$, as found in structurally similar NdES [8] and also in NdB [7]; however, for NdB there is a cross-over in anisotropy at ~155 K below which $\chi_\parallel > \chi_\perp$. There is no such cross-over in the present case and this helped us to measure $\chi_\parallel$ and $\chi_\perp$ individually down to the lowest temperature attained (i.e., 12.5 K) in our experiment. The variation of $\chi_\parallel$ and $\chi_\perp$ with the temperature is displayed in Fig. 1 from which it is clear that $\chi_\parallel$ is greater than $\chi_\perp$ at all temperatures. Although the magnetic anisotropy at room temperature is small, with lowering of temperature $\chi_\parallel$ increases more rapidly than $\chi_\perp$ giving rise to very high anisotropy at low temperatures; the relative magnetic anisotropy $\Delta E/N^2$ at room temperature is merely 0.063 while at 12.5 K it is 1.222.

The average magnetic moment (effective Bohr magneton
number) \( P_{\text{eff}} \) at room temperature calculated from the observed values of \( \chi_L \) and \( \chi_{\perp} \), is 3.65, almost the same as the free ion value 3.61. \( P_{\text{eff}} \) was calculated at different temperatures and it is noted that it varies quite appreciably with the temperature (at 12.5 K, \( P_{\text{eff}} = 2.46 \)).

A least squares fit of \( \chi \) \( = \sqrt{3(\chi_L + 2\chi_{\perp})} \) to the Curie–Weiss law was tried; it is seen that a single set of \( C \) (Curie constant) and \( \theta \) (paramagnetic Curie temperature) could not fit the observed \( \chi \) over the entire range of temperature of our study; this is definitely different from our experience with other rare-earth compounds that we have studied but it should not be construed as very unexpected.

4. Analysis and discussion

The ground electronic configuration of Nd\(^{3+}\) is \([Xe]4f^3\), the ground term being \( ^{1}I\); the spin–orbit coupling gives rise to four \( J \) multiplets with \( J = 9/2 \), as the lowest. The crystal field (CF) of \( C_{\text{th}} \) symmetry splits all the multiplets into Kramers doublets. Using one-electron CF, the CF Hamiltonian conforming to \( C_{\text{th}} \) symmetry is as follows:

\[
\mathcal{H}_{\text{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{66} + B_{66}(C_{66} + C_{20})
\]

\( C_{kl} \)'s are tensor operators and \( B_{mn} \)'s are real constants that parametrize the crystal field (use of one-electron CF is adequate for calculation of the magnetic properties). Employing the normal tensor operator techniques \[9\] the crystal field Hamiltonian was set up and diagonalized in the ground term \( ^{1}I \) manifold with important intermediate coupling corrections which take care of the term mixing through spin orbit interaction to a large extent. The ionic susceptibilities \( K_L \) and \( K_{\perp} \) (which are the same as the crystal molar susceptibilities \( \chi_L \) and \( \chi_{\perp} \) in the present case) were computed \[10\] employing the spectroscopic CF parameters of Quagliano et al. \[4\] \( (B_{20} = 135, B_{40} = -596, B_{60} = -819 \) and \( B_{66} = -635 \); all in cm\(^{-1}\)). The energies of all the Stark levels of the ground multiplet obtained agree exactly with those reported by Quagliano et al. using CF and configuration diagonalization; however, a comparison with the CCF values of the same workers show that only for two levels above 290 cm\(^{-1}\) the difference is \(-4 \) cm\(^{-1}\) which should be of little consequence as far as the calculation of the susceptibilities below 300 K is concerned and this proves the adequacy of our procedure.

The computed values of \( \chi \)'s at different temperatures are compared with our experimental data in Fig. 1. The result is an excellent agreement of the theoretical and observed principal susceptibilities over the entire range of temperature of our study which endorses that the site symmetry is indeed \( C_{\text{th}} \) considered by the earlier workers \[2–4,11\] for the analysis of their magnetic and spectroscopic data; this implies that the assumption that Nd\(^{3+}\) interacts mainly with the nine nearest water oxygens is valid. The very good explanation provided by the CF theory alone also indicates that ordering effects of any consequence are absent down to the lowest temperature of our study. A transition to an ordered state could be expected at a much lower temperature as observed in some RTFMS (\( R = \text{Tb, Dy, Pr and Ho} \)) \[2\]; this is the characteristic of dipolar systems.

The principal spectroscopic splitting factors for the ground Kramers doublet were computed; the values are, \( g_L = 3.81 \), and \( g_{\perp} = 2.02 \) which are quite close to the observed resonance values for NdES \[13\]. Consideration of the wave functions of the doublet shows that the transition probabilities for the \( g \) factors are quite significant and hence resonance should not be difficult to observe.
5. Thermal and hyperfine properties

5.1. Electronic specific heat

The low lying CF states make a significant contribution to the heat capacity of the crystal; the change in occupation of different states with the temperature usually gives rise to characteristic anomalies. The electronic heat capacity $C_e$ of our system was computed using the relation

$$C_e = N \frac{d}{dT} [\text{Tr}(\mathcal{H} \rho)/\text{Tr}(\rho)].$$

Here $\mathcal{H}$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N$ is the Avogadro number. The variation of $C_e$ with temperature is depicted in Fig. 2 which displays a broad Schottky anomaly around 100 K and below 75 K it drops down sharply to nearly vanish at ~ 20 K; this should be quite amenable to heat capacity measurements employing a differential scanning calorimeter.

5.2. Hyperfine properties

For nuclear precession times large compared to the electronic relaxation times, the nucleus sees a time averaged electric field gradient (EFG) produced by the 4f electrons which is temperature dependent; there is also a direct lattice contribution to the EFG but this is temperature independent. The nuclear quadrupole splitting $\langle \Delta E_q \rangle_T$ varies with the temperature because of the 4f component in the EFG [12]. The quadrupole splitting between the lowest nuclear doublets i.e., $| \pm 1/2 \rangle$ and $| \pm 3/2 \rangle$, for the two isotopes $^{143}$Nd and $^{145}$Nd are depicted in Fig. 3. In the present case the nuclear quadrupole splitting is rather small compared to the magnetic hyperfine splitting and hence the contribution to the nuclear specific heat $C_N$ comes almost entirely from the latter. The predictions for variation of $C_N$ with temperature [9,14] for the two isotopes is shown in Fig. 4. Unlike most cases there are no peaks but only broad maxima at ~ 30 mK and ~ 18 mK with peak values 7.37 and 7.39 J/g atom K for the two isotopes, $^{143}$Nd and $^{145}$Nd, respectively.

6. Conclusion

For the first time the principal magnetic susceptibilities of the single crystal of a rare earth TFMS were studied in the range 300–12.5 K. An excellent agreement could be established between the magnetic behavior of NdTFMS observed by us and those computed theoretically from the spectroscopically derived parameters for the crystal field interaction of the Nd$^{3+}$ ion in NdTFMS matrix; the adequacy of the parameters lends support to the site symmetry of the Nd$^{3+}$.
ion in the coordination unit Nd$^{3+}$(OH)$_2$$_9$ forming a slightly distorted tricapped prism to be $C_{3h}$ considered by earlier workers. The computed g-factors were found to be quite amenable to experimental verification. Behavior of the electronic heat capacity $C_e$ computed from our earlier findings led us to conclude that $C_e$ suffers a steep drop just below 75 K giving rise to a broad Schottky type anomaly around 100 K. The nuclear level splitting as a result of the hyperfine magnetic field and electric quadrupole interaction and its effect on the nuclear heat capacity have also been investigated which brings out much commonness with NdES.

References

Magnetic behavior of Sm$^{3+}$ in SmAsO$_4$: an experimental and theoretical study

P.K. Chakrabarti$^a$, D. Neogy$^{a, *}$, K.N. Chattopadhyay$^a$, D. Bisui$^a$, B.M. Wanklyn$^b$

$^a$Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan-713 104, West Bengal, India
$^b$Clarendon Laboratory Oxford, Oxford OX1 3PU, UK

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Magnetic behavior of Sm$^{3+}$ in SmAsO$_4$: an experimental and theoretical study

P.K. Chakrabarti$^a$, D. Neogy$^{a,*}$, K.N. Chattopadhyay$^a$, D. Bisui$^a$, B.M. Wanklyn$^b$

$^a$Solid State Research Laboratory, Physics Department, Burdwan University, Burdwan-713 104, West Bengal, India
$^b$Clarendon Laboratory, Oxford, Oxford OX1 3PU, UK

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Abstract

Samarium arsenate single crystals were grown by flux technique. The principal susceptibilities ($\chi_1$ and $\chi_2$) of the uniaxial system were measured in the temperature range 300-13 K. The room temperature anisotropy obtained from absolute measurements was checked by measuring the anisotropy directly. The magnetic anisotropy is not appreciable; the value of $(\Delta\chi/\chi_a)$ at 300 K is only 0.024. Because of the slow rise of the susceptibilities ($\chi_4$ and $\chi_5$) with the lowering of temperature the average susceptibility ($\chi_a$) cannot be accounted for by the Curie-Weiss law. The smooth variation of the susceptibilities down to 13 K rules out any structural phase transition or symmetry breaking. An analysis of the observed results undertaken for the first time invoking crystal field (CF) theory based on the rare-earth site symmetry $D_{4h}$ provides a satisfactory explanation to the experimental results; ordering effects of any consequence are absent. $g$-factors and the electronic heat capacity were computed theoretically. Various hyperfine properties, including the thermal variation of the Mössbauer spectra, were computed for both isotopes of Samarium ($^{147}$Sm and $^{149}$Sm) in the light of the proposed CF. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Single crystals; Crystal field theory; Mössbauer spectra; Hyperfine interactions

1. Introduction

Because of the interesting crystallographic and magnetic behavior at low temperatures, particularly the phase transitions, the rare-earth orthoarsenates (REAsO$_4$, RE = rare earth) have attracted considerable interest. The crystal structure of REAsO$_4$ changes from the monoclinic monazite (space group $P2_1/n$) to the tetragonal zircon (space group $I4_1/amd$) as one moves across the RE series and the exact point of transition depends on the cation-anion radii [1]. The transition from monoclinic to tetragonal occurs at Sm where SmAsO$_4$ has been prepared in the zircon form only. A detailed review of the similarly constituted rare-earth arsenates, vanadates and phosphates has been given by Gehring and Gehring [2].

The specific heat and magnetic properties of DyAsO$_4$ have been investigated by Kahle et al. [3]; the specific heat shows two $\lambda$-type anomalies, one at 11.2 K caused by crystallographic phase transition induced by cooperative Jahn-Teller effects...
and the other at the antiferromagnetic transition temperature $T_N = 2.44$ K. Mangum et al. [4] observed magnetically controllable cooperative Jahn-Teller effects (CJTE) in TmAsO$_4$. They have shown that TmAsO$_4$ undergoes crystallographic phase transition caused by CJTE from a high-temperature phase of tetragonal symmetry to a lower symmetry phase below 6 K and when a magnetic field is applied at $T < 6$ K, parallel or in the vicinity of the high-temperature tetragonal axis; the distortion is removed at some critical field, which is a function of temperature. The optical absorption spectrum of Tb$^{3+}$ in TbAsO$_4$ as a function of temperature down to $\sim 0.77$ K, and as a function of magnetic field along the principal crystallographic directions as well as any direction in the basal plane have been observed by Wuchner et al. [5]. The magnetic structure of TbAsO$_4$ has been determined by Schafer and Will [6] using neutron diffraction techniques; the crystal undergoes a crystallographic phase transition induced by CJTE at $T_d = 27.7 \pm 0.5$ K and an antiferromagnetic transition at $T_N = 1.48 \pm 0.04$ K and both transitions were extensively studied by thermal [6], spectroscopic [7], and magnetic [8] measurements.

Raman and infrared spectra of SmAsO$_4$ in the frequency regions of 20-4000 and 300-4000 cm$^{-1}$, respectively, have been observed by Pradhan and Chaudhary [9]. No magnetic measurements seem to have been carried out on this material. Sm$^{3+}$ has low-lying $J$-multiplets and these are split further by the electrostatic field of $D_{3d}$ symmetry in SmAsO$_4$ which should give rise to interesting magnetic properties; also effects due to ordering or crystallographic phase transitions are quite likely in view of the behavior of other RE ions in the arsenate lattice. In order to have a clear understanding of these interactions we undertook magnetic measurements on the single crystal of SmAsO$_4$. In this paper we report the results of our low-temperature magnetic measurements of SmAsO$_4$ single crystal. The principal magnetic susceptibilities parallel and perpendicular to the symmetry axis 'c' of the crystal ($\chi_\parallel$ and $\chi_\perp$) have been measured in the temperature range 300–13 K. The observed results are analyzed primarily in the light of the interaction of Sm$^{3+}$ with its diamagnetic neighbors. Further, theoretical excursions into the thermal and hyperfine behavior of Sm$^{3+}$ in SmAsO$_4$ are made using the results of our CF analysis to predict some interesting properties.

2. Crystallography and rare-earth environment

SmAsO$_4$ has tetragonal zircon structure with space group symmetry I$4_1$/amd. In tetragonal systems there are four-molecules per unit cell and all the four RE ions in these molecules are magnetically equivalent with the site symmetry $D_{3d}$. Here the lanthanoid metal atom is coordinated to eight oxygen atoms forming two unique orthogonal interpenetrating tetrahedra. The structural polyhedron formed from the O-O contact distances is a distorted dodecahedron ($D_{3d}$).

3. Experimental

The single crystals of SmAsO$_4$ were grown from Pb$_2$As$_2$O$_7$ flux by slow cooling [10]. The light yellow crystals of SmAsO$_4$ grow in the form of prisms with typical dimensions $4 \times 2 \times 2$ mm$^3$. The transparent crystals are elongated along their four-fold symmetry axis. The crystals used in our measurements are between 40 and 45 mg each. The crystallographic c-axis of the crystal sets along the applied magnetic field, indicating $\chi_\parallel > \chi_\perp$ at room temperature and this helps us to measure $\chi_\parallel$ and $\chi_\perp$ separately by the Faraday balance down to 13 K [11,12]. Here a highly sensitive taut-band electromagnetic balance fabricated in the laboratory was employed to measure the force acting on the crystal in the constant vertical gradient of the magnetic field, i.e., $H_\parallel (\partial H_\parallel / \partial X) = \text{constant}$. The low-temperature environment was provided by an APD cryogenics He-refrigerator. Measurements were carried out in helium atmosphere at an optimum pressure. The calibration of the temperature of the sample chamber was performed by measuring the susceptibility of a Mn(NH$_4$)$_3$(SO$_4$)$_2$·6H$_2$O single crystal which is virtually magnetically isotropic and follows the Curie law (with $\theta = 0$) down to 1 K. A fully programmable susceptibility measuring system was developed for carrying out the measurements [11,12]. The magnetic anisotropy
(\(\Delta \chi = \chi_\parallel - \chi_\perp\)) was measured with a quartz torsion balance in the temperature range 300-80 K and this helped us to check the anisotropies obtained from the absolute measurements.

4. Results

The variations of \(\chi_\parallel\) and \(\chi_\perp\) with lowering of temperature are displayed in Figs. 1 and 2. The magnetic anisotropy (\(\Delta \chi = \chi_\parallel - \chi_\perp\)) is very low; the relative magnetic anisotropy (\(\Delta \chi/\chi_{av}\)) at 300 K is only 0.024 and this was checked by measuring the anisotropy directly. A least-squares fit of the average susceptibility [\(\chi_{av} = (\chi_\parallel + 2\chi_\perp)/3\)] in the range 300–13 K to the Curie-Weiss law was tried and this is displayed in Fig. 3. The Curie constant (\(C\)) and the paramagnetic Curie temperature (\(\theta\)) turned out 0.35 emu K/mol and \(-131.9\) K, respectively; the high value of \(\theta\) clearly displays the large deviation from the free ion Curie-type behavior. In the temperature range of our study the origin of \(\theta\) should be sought mainly in the crystal field effects, i.e., changes in the population of the different CF Stark states rather than in any exchange or dipolar effects which are found to take place in RE arsenates at much lower temperatures. No CJTE induced or other crystallographic phase transition seems to be present as no peculiarity in the thermal variation of the susceptibilities which usually accompanies such a transition was noticed. The poor fit of \(\chi_{av}\) (Fig. 3) suggests that the susceptibility (\(\chi_{av}\)) cannot be accounted for by the Curie-Weiss simulation. The
The effective magnetic moment $P_{\text{eff}}$ at room temperature calculated by the relation $P_{\text{eff}} = 2.828(\chi_{\text{mT}}^0)^{0.5}$ turns out to be 1.57, which is slightly higher than the free ion value 1.55, a very rare case indeed. The variation of $P_{\text{eff}}$ with lowering of temperature is shown in Fig. 4; it decreases smoothly down to the lowest temperature attained in our study. In the next section, the observed behavior of $\chi_\parallel$ and $\chi_\perp$ in the wide range of temperature of our study, is treated by crystal field analysis since in this case the CF interaction is probably the only viable interaction influencing the magnetic properties in this range of temperature.

### 5. Crystal field interaction

The ground electronic configuration of Sm$^{3+}$ is $[\text{Xe}]4f^6$; this gives $^6\text{H}$ as the ground term. The ground term splits into six $J$-multiplets under the spin–orbit interaction, viz., $\sum \gamma_i L_i \cdot S_i$, and yields the multiplet with $J = \frac{3}{2}$ as the ground state. The crystal field Hamiltonian ($H_{\text{CF}}$) conforming to $D_{2d}$ symmetry, the site symmetry of the Sm$^{3+}$ ion in this crystal, lifts the degeneracy of the $J$-manifolds to give rise to Kramers doublets and in the process also mixes the states belonging to different $J$-multiplets; the latter is the so-called CF $J-J$ mixing. In the present case (Sm$^{3+}$ ion) the $J$-multiplets are closely spaced compared to other ions (except Eu$^{3+}$) of the lanthanide series, making CF $J-J$ mixing large and its effects on the optical, magnetic and other thermophysical properties profound. In order to find the ground term splitting for computation of the magnetic susceptibilities and other physical properties of the ion it is sufficient to diagonalize the Hamiltonian $H = \sum \gamma_i (L \cdot S)^n + H_{\text{CF}}$ in the truncated basis of $66 |L, S, J, J_z\rangle$ state vectors spanning the ground term. The first term is an effective spin–orbit operator producing the observed baricenters of different $J$-multiplets. The CF interaction term, $H_{\text{CF}}$ conforming to $D_{2d}$ site symmetry is given by

$$B_{20}C_{20} + B_{40}C_{40} + B_{44}C_{44} + C_{4-4} + B_{60}C_{60} + B_{64}(C_{64} + C_{6-4}) \quad (\text{all in cm}^{-1}).$$

Here $C$'s are tensor operators and $B$'s are real constants that parametrize the crystal field. In the present calculation the spin–orbit interaction ($\gamma_{50}$) term has been replaced by introducing the available values of baricenters of the different $J$-multiplets in the diagonal elements of the Hamiltonian. The intermediate coupling (IC) effects were partly taken care of by introducing IC coefficients for the reduced matrix elements. The CF matrix elements were calculated by normal tensor operator techniques [13]. The Zeeman energies for the different CF states were obtained through the magnetic interaction term $\beta H \cdot (L + 2S)$ for the two cases viz., $H_\parallel$ and $H_\perp$ (i.e., magnetic field parallel and perpendicular to the symmetry axis of the crystal) and the susceptibilities were obtained through the well-known Van Vleck expression. In order to fix the crystal field the five CF parameters ($B_{kq}$) were varied carefully to get a precise fit to the observed variation of $\chi_\parallel$ and $\chi_\perp$ from room temperature down to 13 K; this was achieved by minimizing the rms deviation of the theoretical values from those observed. The best-fit CF parameters are

$$B_{20} = 90, \quad B_{40} = 475, \quad B_{60} = 315, \quad B_{44} = 575, \quad B_{64} = -305 \quad (\text{all in cm}^{-1}).$$

The computed Stark energies and the ground state wave functions are given in Table 1. The computed
Table 1
Stark energies of the multiplets of the ground \(^6\)H term and the ground state wave functions of Sm\(^{3+}\) in SmAsO\(_4\)

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>Stark energies (cm(^{-1}))</th>
<th>Ground state wave functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^6)H(_{5/2})</td>
<td>0</td>
<td>(-0.4658</td>
</tr>
<tr>
<td></td>
<td>48.75</td>
<td>(\mp 0.0546</td>
</tr>
<tr>
<td></td>
<td>96.83</td>
<td>(-0.0069</td>
</tr>
<tr>
<td></td>
<td>1026.6</td>
<td>(\mp 0.0049</td>
</tr>
<tr>
<td></td>
<td>1079.0</td>
<td>(\pm 0.0109</td>
</tr>
<tr>
<td></td>
<td>1121.2</td>
<td>(-0.0038</td>
</tr>
<tr>
<td></td>
<td>1129.4</td>
<td>(\pm 0.0019</td>
</tr>
<tr>
<td>(^6)H(_{7/2})</td>
<td>2230.7</td>
<td>(-0.0003</td>
</tr>
<tr>
<td></td>
<td>2290.7</td>
<td>(\pm 0.0093</td>
</tr>
<tr>
<td>(^6)H(_{9/2})</td>
<td>3298.2</td>
<td>(-0.0009</td>
</tr>
<tr>
<td></td>
<td>3232.9</td>
<td>(\pm 0.0083</td>
</tr>
<tr>
<td>(^6)H(_{11/2})</td>
<td>4982.1</td>
<td>(-0.0010</td>
</tr>
<tr>
<td></td>
<td>4982.5</td>
<td>(\pm 0.0009</td>
</tr>
<tr>
<td></td>
<td>5008.8</td>
<td>(-0.0008</td>
</tr>
<tr>
<td></td>
<td>5008.9</td>
<td>(\pm 0.0010</td>
</tr>
<tr>
<td></td>
<td>5045.7</td>
<td>(-0.0010</td>
</tr>
<tr>
<td></td>
<td>5050.0</td>
<td>(\pm 0.0010</td>
</tr>
<tr>
<td></td>
<td>5075.7</td>
<td>(-0.0010</td>
</tr>
<tr>
<td>(^6)H(_{13/2})</td>
<td>6355.5</td>
<td>(-0.0009</td>
</tr>
<tr>
<td></td>
<td>6366.3</td>
<td>(\pm 0.0010</td>
</tr>
<tr>
<td></td>
<td>6396.3</td>
<td>(-0.0009</td>
</tr>
<tr>
<td></td>
<td>6411.0</td>
<td>(\pm 0.0010</td>
</tr>
<tr>
<td></td>
<td>6521.3</td>
<td>(-0.0010</td>
</tr>
<tr>
<td></td>
<td>6536.3</td>
<td>(\pm 0.0010</td>
</tr>
<tr>
<td></td>
<td>6557.8</td>
<td>(-0.0010</td>
</tr>
<tr>
<td></td>
<td>6560.7</td>
<td>(\pm 0.0010</td>
</tr>
</tbody>
</table>

The baricenters of the different multiplets chosen are at 0, 1034, 2240, 3564, 4966, and 6403 cm\(^{-1}\) for \(J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}, \text{and} \frac{15}{2}\), respectively. The calculated levels have been raised by 56.01 cm\(^{-1}\).

values of \(\chi_{||}\) and \(\chi_{\perp}\) are displayed in Figs. 1 and 2 together with the observed values. The simulation of our observed \(\chi_{||}\) and \(\chi_{\perp}\) by the theoretical values is evidently very good (Figs. 1 and 2). This demonstrates that the CF interaction is adequate enough to explain the departure from the free ion behavior of Sm\(^{3+}\) ion in SmAsO\(_4\) matrix and that there is no strong exchange effect although SmAsO\(_4\) is not a dilute crystal; the ordering due to dipolar interactions usually takes place at a much lower temperature, viz., \(< 1\) K.

The ground Kramers doublet yields \(g_{||} = 3.01\) and \(g_{\perp} = 3.29\). A little consideration of the wave functions of the Kramers pair shows that the
magnetic dipole transition probability for observing resonance absorption is quite favorable for the determination of the $g$ values. The first excited state is at $\sim 49 \text{ cm}^{-1}$ above the ground state and its population at liquid-helium temperatures would be too small to observe a spin resonance.

6. Thermal and hyperfine properties

The change of population in the low-lying energy levels with temperature makes significant contributions to the heat capacity ($C_v$) and gives rise to the Schottky anomalies. $C_v$ at different temperatures is calculated using the relation

$$C_v = N(d/dt)[Tr(H\rho)/Tr\rho],$$

where $H$ is the Hamiltonian matrix, $\rho$ the statistical density matrix, and $N$ the Avagadro number.

The thermal variation of $C_v$ is depicted in Fig. 5. It shows a prominent maximum at $\sim 37 \text{ K}$ with the peak value $5.32 \text{ J/g atm K}$ which is quite amenable to experimental verification.

The eight-fold degenerate ground states ($I = \frac{7}{2}$) of the two isotopes ($^{147}\text{Sm}$ and $^{149}\text{Sm}$ both having the same nuclear spin $I = \frac{7}{2}$) of samarium undergo a splitting by the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) set up by both ligand charges and the 4f electrons. For fast electronic relaxation the 4f contribution to the EFG would be the time-averaged effect of all the low-lying CF Stark states because of the probability of occupying the excited states during the finite nuclear lifetime. Thus, the quadrupole splitting ($\langle \Delta E_Q \rangle_T$) between any two adjacent nuclear states $|I, I_z\rangle$ and $|I, I_z + 1\rangle$ due to the 4f contribution to the EFG would be highly temperature dependent, whereas the lattice contribution is more or less constant. The nuclear electric quadrupole splitting is then calculated by using the expression [14].

$$\langle \Delta E_Q \rangle_T = (2I_z + 1)[PN \cdot \langle PJZ \rangle_T + P_{\text{LATT}} \cdot (B_{20}/2)],$$

where $PN = -3e^2Q(1 - R_0)(r^{-3})_{4f}/[4I(2I - 1)]$, $\langle PJZ \rangle_T = \sum (3z^2 - I^2)/(r^2)^T$, $P_{\text{LATT}} = -3Q(1 - \gamma_{\text{eff}})/(2I^2 - 1)(r^{-3})_{4f}(I - \sigma_2)$. Here $\sigma_2$ and $\gamma_{\text{eff}}$ are the shielding and antishielding factors, respectively, and $Q$ is the quadrupole moment; other symbols have their usual connotations [14]. The first term within the square bracket of the above equation is the 4f contribution and the second term is the lattice contribution to the EFG. The nuclear level scheme depends on the sign of the value of the terms within the square bracket of the above equation. In $^{147}\text{Sm}$ nucleus the lattice contribution is positive and dominant over 4f contribution down to $\sim 1 \text{ K}$ and therefore the lowest nuclear levels are $| \pm 1/2 \rangle$ and $| \pm 3/2 \rangle$. Whereas in case of $^{149}\text{Sm}$ nucleus the lattice contribution is negative and is also dominant over 4f contribution and the lowest nuclear levels are $| \pm 7/2 \rangle$ and $| \pm 5/2 \rangle$. The quadrupole splittings ($\langle \Delta E_Q \rangle_T$) between the lowest two nuclear doublets for the two isotopes ($^{147}\text{Sm}$ and $^{149}\text{Sm}$) are shown in Fig. 6. $\langle \Delta E_Q \rangle_T$ decreases smoothly down to $\sim 70 \text{ K}$ below which it increases sharply; the values of $\langle \Delta E_Q \rangle_T$ in both cases are nearly constant below $\sim 10 \text{ K}$. This is a very interesting feature in the NQR and Mössbauer spectra of the crystal.

The magnetic hyperfine Hamiltonian is given by $H_{hf} = A(N \cdot I) - \beta N I \cdot \mu_N$, where $A = 2\beta N^2 g_N$. $\langle N_z \rangle r^{-3} \langle r^{-3} \rangle$ is the hyperfine structure parameter, $\mu_N = g_N \beta_N I$, and the other symbols have their usual connotations [14]; the $z$-component of...
Fig. 6. Thermal variation of the nuclear electric quadrupole splittings between the lowest two doublets \([I_f, I_z] \) and \([I_f, I_z + 1] \) due to time-averaged EFG of \(^{147}\text{Sm}\) and \(^{149}\text{Sm}\) in SmAsO₄.

Fig. 7. Hyperfine heat capacities \(C_N\) of \(^{147}\text{Sm}\) and \(^{149}\text{Sm}\) in SmAsO₄ at various temperatures.

\(H_z\) is given by \(H_\parallel = -\langle A/\beta N \rangle \langle N_z \rangle\), where \(\langle N_z \rangle\) is the quantum mechanical average of \(N_z\) over the occupied electronic states of the ion, which behaves much like \(\langle L_z + 2S_z \rangle\). Due to \(J\)-mixed CF states the value of \(\langle N_z \rangle\) would depend on the off-diagonal elements in \(J\). In presence of a magnetic field and at very low temperatures, the value of \(\langle N_z \rangle\) can be calculated by using the lowest electronic Zeeman state which only will be occupied. The hyperfine magnetic field at the nucleus turns out to be \(\sim 0.74\) MG which is much lower than the free ion value \(3.42\) MG [15]. The hyperfine Hamiltonian for \(D_{2d}\) symmetry \(0.5A_\parallel I_z + P(I_z^2 - I(I + 1)/3)\) in the presence of a magnetic field along the symmetry axis was diagonalized to calculate the hyperfine energies and hence the nuclear specific heat \(C_N\). The thermal variation of \(C_N\) for both the isotopes \(^{147}\text{Sm}\) and \(^{149}\text{Sm}\) is depicted in Fig. 7; Schottky-type anomalies are quite sharp and are located at \(\sim 6.9\) and \(\sim 5.8\) mK with the peak values 7.41 and 7.51 J/g atm K, respectively.

7. Conclusions

The magnetic properties of samarium orthoarsenate over the wide range of temperature studied find a very good interpretation in the electrostatic interaction of the \(\text{Sm}^{3+}\) ion with its immediate neighbors \(\chi_\parallel\) and \(\chi_\perp\) which were measured down to 13 K, displayed a smooth variation and there was no indication to suggest a structural or magnetic phase transition of any significance. The ground Strak state, a Kramers doublet, well separated from the first excited state, yields \(g\)-factors, i.e., \(g_\parallel = 3.01\) and \(g_\perp = 3.29\). The crystalline environment in samarium arsenate strongly influences the hyperfine properties of \(^{147}\text{Sm}\) and \(^{149}\text{Sm}\).

References

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Magnetic measurements on single crystals of Ho(CF$_3$SO$_3$)$_3$.9H$_2$O and crystal field investigation

D. Neogy*, P. Paul, K.N. Chattopadhyay, D. Bisui

Solid State Research Laboratory, Department of Physics, Burdwan University, Burdwan 713 104, West Bengal, India

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Abstract

Magnetic measurements on single crystals of holmium trifluoromethanesulfonate (HoTFMS) have been carried out from 300 to 12.5 K. The hexagonal crystal structure of HoTFMS is very similar to that of the hydrated rare earth ethylsulfates with the non-Kramers Ho$^{3+}$ ion occupying a site of $C_{3h}$ symmetry. A very good theoretical simulation of the principal magnetic susceptibilities, observed by us and the Friedberg group, over the wide range 300 to $\sim$1.0 K was obtained with the crystal field $J$-mixed eigenvectors taking into consideration intermediate coupling effects. No ordering effects were noticed by us down to $\sim$12.5 K indicating the interionic interaction to be of predominantly dipolar type consistent with the discovery of a ferromagnetic transition at $T_c = 0.23$ K by the Friedberg group. The $g$-values are found to be in reasonable agreement with those derived from other sources. The Schottky anomaly in the electronic heat capacity observed at $\sim$6 K by the Friedberg group is borne out excellently by our theoretical values computed from the crystalline Stark pattern. The thermal behavior of quadrupole splitting and hyperfine heat capacity is calculated and our computed values explain very well the principal anomaly in $C_H$ observed experimentally. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recently, keen interest has been shown in the spectra, magnetic properties and heat capacities of rare earth trifluoromethanesulfonate nonahydrates R(CF$_3$SO$_3$)$_3$.9H$_2$O or RTFMS where R stands for a trivalent rare earth ion [1-4]. These form hexagonal crystals very similar in structure [1] to those of the familiar rare earth ethylsulfate nonahydrates R(C$_2$H$_5$SO$_4$)$_3$.9H$_2$O or RES; in this respect they are also similar to the rare earth bromate nonahydrates (RB) to a certain extent, although the detailed geometries of the cations in RES and RTFMS are significantly different from those in RB [1]. Both families of compounds, viz. RES and RTFMS belong to the space group $P6_3/m$ with $Z = 2$. All rare earth ions in the structure are magnetically equivalent and occupy sites of $C_{3h}$ symmetry [2]. The unit cell dimension and the density of R$^{3+}$ ions in RTFMS are nearly the same as in RES. In these crystals, the R$^{3+}$ ions are surrounded by nine H$_2$O molecules forming a tricapped trigonal prism. The prisms in RTFMS and RES are nearly identical.

The magnetic ordering [3], electron paramagnetic resonance (EPR) [2] and heat capacity [3] of a number of RTFMS have been studied by the Friedberg group. They have measured magnetic properties and heat capacity of HoTFMS in the temperature range 0.08-20 K. The results show that these crystals order ferromagnetically along the c-axis as do crystals of HoES ($T_c = 0.23$ K) which is of particular interest for this non-Kramers ion. The observation of a ferromagnetic ordering in HoTFMS led to the measurement of the heat capacity in the range 1–20 K. Two Schottky anomalies appear in the heat capacity. The first rounded anomaly appears at 0.23 K (just below the cooperative $\lambda$ peak) due to nuclear spin states split by hyperfine interactions and the second Schottky anomaly near 6 K is evidence of thermal excitations from the ground doubled to the first excited singlet of the Ho$^{3+}$ ion. EPR studies reveal an accidentally degenerate ground state which suffers a zero field splitting due to Jahn–Teller distortion of the crystal field.

Our present interest is focused on the study of the susceptibility of this crystal in the higher range of temperature...
and in evolving a theoretical basis which gives a comprehensive analysis of all experimental data, magnetic properties and heat capacity in particular.

In an earlier communication [5] we reported the details of our magnetic studies on the first such crystal of the RTFMS series, viz. NdTFMS. In the present communication we present our measurements on the principal magnetic susceptibilities of HoTFMS, viz. \( \chi_\parallel \) and \( \chi_\perp \), over a wide range of temperature. We first try to seek an explanation to our observed data for \( \chi_\parallel \) and \( \chi_\perp \) in the entire range 300–12.5 K, as well as for the \( g \)-values and the heat capacity measured by the Friedberg group, primarily using the crystal field (CF) interaction. We then make an excursion into the nuclear hyperfine properties of this system.

2. Experimental details

A solution of HoTFMS was prepared by adding anhydrous trifluoromethanesulfonic acid (CF\(_3\)SO\(_2\)H) to a slurry of Ho\(_2\)O\(_3\) in water [1] and heating it to 90°C with constant stirring until the solution became clear. Single crystals of HoTFMS were obtained by slow evaporation of the solution at room temperature. Needle-like single crystals, elongated along the \( c \)-direction, were on the average 6–8 mm in length.

The principal magnetic susceptibilities, \( \chi_\parallel \) and \( \chi_\perp \), parallel and perpendicular to the crystallographic symmetry axis \( c \), were measured from room temperature down to 13.5 and 12.5 K, respectively, with the help of a highly sensitive electromagnetic balance fabricated in our laboratory [6].

The low temperature environment was provided by a closed-cycle helium cryo-cooler from APD cryogenics. The details of the fully computerized low temperature magnetic susceptibility setup developed by us with special reference to temperature calibration of the sample chamber are given elsewhere [6,7]. \( \chi_\perp \) was measured by suspending the crystal with a thin quartz fiber with the \( c \)-axis vertical in the constant vertical magnetic field gradient, i.e. \( H_z \frac{dH_z}{dx} \) = const. \( \chi_\parallel \) was measured with the \( c \)-axis in the horizontal plane; in the magnetic field, \( \chi_\parallel \) automatically sets in the direction of the field as in this case \( \chi_\parallel > \chi_\perp \) with care being taken to see that the torsional constant of the quartz fiber is very small.

The magnetic anisotropy \( \chi_\parallel - \chi_\perp \) is calculated with the values of \( \chi_\parallel \) and \( \chi_\perp \) at different temperatures; at room temperature the anisotropy was measured directly using a quartz torsion balance described earlier [8] as a check on the absolute susceptibility measurements.

3. Results

At room temperature, the symmetry axis, \( c \)-axis, sets along the applied external magnetic field indicating \( \chi_\parallel > \chi_\perp \) as found in structurally similar HoES. The variation of \( \chi_\parallel \) and \( \chi_\perp \) with temperature is depicted in Fig. 1; it is clear that \( \chi_\parallel \) is greater than \( \chi_\perp \) at all temperatures. Although the magnetic isotropy at room temperature is small, with lowering of temperature \( \chi_\parallel \) increases more rapidly than \( \chi_\perp \) giving rise to a very high anisotropy at low temperatures. The relative magnetic anisotropy \( \Delta \chi/ \)
\(X_{\text{e}}\) at room temperature is 0.1353, a little higher than in HoES, viz. 0.1071 [9]; at 20 K it assumes a value nearly 11 times that at room temperature.

The effective magnetic moment \(\mu_{\text{eff}}\) at room temperature calculated from the observed values of \(X_{\text{e}}\) and \(X_{\chi}\) is 10.33, which is smaller than the free ion value, namely 10.60. \(\mu_{\text{eff}}\) was calculated at different temperatures and it is seen that its value decreases slowly with decrease of temperature. A least square fit of the observed \(X_{\text{e}}\) \(=1/3(X_{\chi}+2X_{\chi})\) down to 20 K to the Curie–Weiss law yields the Curie constant \(C=11.79 \text{ emu K}^{-1}\) and the paramagnetic Curie temperature \(\theta=-2.78 \text{ K}\). The Curie–Weiss fit is quite good and yet it must be admitted that the implication of \(\theta\) as normally construed is not appropriate here. It arises largely due to the crystal field effects rather than any antiferromagnetic type of interaction, as would be amply clear from our analysis of the data given in the next section. In fact at very low temperatures the Ho\(^{3+}\) ions tend to align ferromagnetically in sign and the appearance of the \(\lambda\) peak in the heat capacity [3].

4. Analysis and discussion

The ground electronic configuration of Ho\(^{3+}\) is \([\text{Xe}]4f^{10}\), the ground term being \(^5\text{I}_1\). The first excited multiplet \(^5\text{I}_2\) is situated at about 5032 cm\(^{-1}\) above the ground state \(^5\text{I}_6\), the ground multiplet \(^5\text{I}_6\) is split by the strong electric field produced by the immediate neighbors, viz. the nine water molecules having high electric dipole moments. A group theoretical consideration shows that the 17 dimensional irreducible representation, \(\Gamma_{\text{J}=8}\), of the spherical rotation group spanned by the degenerate states of the ground multiplet \((^5\text{I}_6\)) reduces into the irreducible representations of the \(C_{3h}\) group as follows:

\[
\Gamma_{\text{J}=8} \rightarrow 2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5 + 3\Gamma_6
\]

where \(\Gamma_1\) and \(\Gamma_6\) are two dimensional representations giving rise to six doublets and the rest are one dimensional representations giving five singlets. The characteristic of magnetic behavior at very low temperatures is greatly dependent on whether a singlet lies lowest. With a singlet lowest the low temperature behavior is dominated by Van Vleck high temperature paramagnetism.

In order to have a comprehensive theoretical analysis of the magnetic and thermal data obtained by us and the Friedberg group we first block diagonalized the total Hamiltonian comprising of both CF and the spin orbit coupling. Using one electron CF, the CF Hamiltonian conforming to \(C_{3h}\) symmetry is as follows:

\[
H_{\text{CF}} = B_{20}C_{20} + B_{40}C_{40} + B_{60}C_{60} + B_{80}(C_{80} + C_{6–6})
\]

\(C_{6k}\) are tensor operators and \(B_{6k}\) are real constants that parametrize the crystal field. The total Hamiltonian \(H (=H_{50} + H_{\text{CF}})\) is directly diagonalized in the complete (65 dimensional) basis of the ground \(^5\text{I}_1\) term; here \(H_{50}\) is the spin orbit coupling interaction term diagonal in \(J\), and \(H_{\text{CF}}\) is the CF interaction. The intermediate coupling (IC) effects are taken care of to a large extent by using IC factors [10] for the reduced matrix elements in computing the matrix elements; the approximate barycenters of the different multiplets are introduced to replace \(H_{50}\). The Zeeman splitting of the CF Stark states are obtained introducing the magnetic interaction term \(\beta(L + 2SJ)\) and working out the first and Table 1

<table>
<thead>
<tr>
<th>Multiplets</th>
<th>Energy (cm(^{-1}))</th>
<th>Wave functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^5\text{I}_6)</td>
<td>(0.0^\circ)</td>
<td>(0.9491(8, \pm 7) + 0.2872(8, \pm 1))</td>
</tr>
<tr>
<td>(^5\text{I}_6)</td>
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<td>(+ 0.1265(8, \pm 5) + 0.0209(7, \pm 7))</td>
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<tr>
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<td>(+ 0.0051(6, \pm 1) + 0.0004(6, \pm 5))</td>
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<tr>
<td>(^5\text{I}_6)</td>
<td>(105.3^\circ)</td>
<td>(\pm 0.0016(5, \pm 1) + 0.0004(5, \pm 5))</td>
</tr>
<tr>
<td>(^5\text{I}_6)</td>
<td>(121.8^\circ)</td>
<td>(+ 0.0007(4, \pm 1))</td>
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\(\circ\) Indicates doublet.
second order energies. Substitution of these energies in the well-known Van Vleck formula yields the susceptibilities.

The best fit to the observed magnetic data is obtained with the following set of CF parameters in the tensor operator formalism $B_{20} = 280$, $B_{40} = -460$, $B_{60} = -538$, $B_{66} = 412$; all in cm$^{-1}$. The computed Stark energies and the eigenfunction of the ground CF state appear in Table 1.

The computed parallel and perpendicular components of the susceptibility $\chi_I$ and $\chi_\perp$ are shown in Fig. 1 along with the observed values. The excellent agreement of the theoretical values with the observed principal susceptibilities over the entire range of temperature of our study endorses that the site symmetry is indeed $C_3v$; this implies that the assumption that Ho$^{3+}$ interacts mainly with the nine nearest water oxygens is valid. The very good explanation provided by the CF theory alone also indicates that ordering effects of any consequence are absent down to the lowest temperature of our study. A transition to an ordered state was observed by the Friedberg group [3] at a much lower temperature ($T = 0.23$ K). This is the characteristic of a dipolar system. We found that $\chi_H$ obtained by the Friedberg group down to $\sim 1$ K is well explained by our theoretical values using a mean-field constant slightly different from theirs. Our analysis gives an accidentally degenerate non-Kramers doublet as the ground CF Stark state with an excited singlet at about 10 cm$^{-1}$ in very close agreement with the inferences of Bellesis et al. [3].

The computed spectroscopic splitting factors, i.e. $g_I$ and $g_\perp$ for the ground doublet are found to be 15.72 and 0.0, respectively, which compare very well with those deduced by Bellesis et al., from susceptibility measurements below 4 K, viz. $g_I = 15.7$ and $g_\perp = 0$ [3].

5. Thermal and hyperfine properties

5.1. Electronic specific heat

The CF strongly influences the electronic heat capacity $C_v$ and is quite often responsible for the anomalies observed in its thermal behavior. The Schottky anomalies which are computed from the thermal average of the energy over the CF-split states important features of the RE ions in crystalline hosts. $C_v$ is calculated using the expression

$$ C_v = N_A \frac{d}{dT} [\text{Tr}(H\rho)/\text{Tr}(\rho)] $$

where $H$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N_A$ the Avogadro number. Fig. 2 shows the variation of $C_v$ with temperature. The interesting feature in the $C_v$ of HoTFMS is a broad Schottky anomaly around 65 K with a high peak value 7.48 J g$^{-1}$ atom$^{-1}$ K$^{-1}$ and a second Schottky anomaly at around 6 K with a low peak value 2.0 J g$^{-1}$ atom$^{-1}$ K$^{-1}$. It is expected that the heat capacity measurements in this range of temperature should show up this anomaly. Bellesis et al. [3] have carried out measurements on specific heat of HoTFMS in the range 1–20 K and their results indeed confirm a peak at 6 K with a peak value which agrees exactly with our computed peak value at 6 K; this is really very encouraging as it confirms the adequacy of our proposed CF.
Fig. 3. Predicted thermal variation of nuclear electric quadrupole splitting of the ground state of $^{165}$Ho in HoTFMS.

Fig. 4. Predicted temperature dependence of hyperfine heat capacity ($C_N$) of $^{165}$Ho in HoTFMS.

5.2. Hyperfine properties

For nuclear procession times large compared to the electronic relaxation times, the nucleus sees a time averaged electronic field gradient (EFG) produced by the 4f electrons which is temperature dependent. There is also a direct lattice contribution to the EFG but this is temperature independent. The nuclear quadrupole splitting $<\Delta E_Q>_{\tau}$ varies with temperature because of the 4f component in the EFG [11]. The variation of $<\Delta E_Q>_{\tau}$ between the lowest two levels,
i.e. \[ |I_z = \pm 7/2 > \] and \[ |I_z = \pm 5/2 > \] for the isotope \(^{165}\text{Ho}\) is shown in Fig. 3.

The hyperfine heat capacity changes with temperature as the nuclear population in the different hyperfine energy levels varies with temperature. A Schottky type anomaly in the form of a large hump is predicted to appear in the heat capacity at about 250 mK, the height of the peak being 7.44 \( \text{J g}^{-1} \text{atom}^{-1} \text{K}^{-1} \) (shown in Fig. 4); and this explains conclusively the experimentally observed rounded anomaly in the heat capacity [3]. The experimental peak value at 250 mK, viz. 7.4 J g\(^{-1}\) atom\(^{-1}\) K\(^{-1}\) and the position of the rounded anomaly are in exact agreement with our theoretical values. It may also be noted that the broad anomaly is comparable to the anomaly in \( C_N \) at 290 mK for Ho metal [12] where the peak value is 7.0 J g\(^{-1}\) atom\(^{-1}\) K\(^{-1}\).

### 6. Conclusion

The magnetic measurements on the single crystals of HoTFMS were carried out for the first time in the range 300–12.5 K. This, together with the observed results of the Friedberg group, provides a complete description of the behavior of the principal magnetic susceptibilities of HoTFMS from 0.1 to 300 K. A crystal field analysis undertaken by us over nearly the entire range has been highly successful in simulating the susceptibilities quantitatively which vindicates earlier conviction that the site symmetry about the rare earth ions in RETFMS is indeed \( C_{3v} \). Our theoretical results also give correct g-values as obtained from the very low temperature magnetic data. Extension of our computations to thermal properties, both electronic and nuclear hyperfine, has been quite encouraging as the experimentally observed Schottky anomalies in the electronic and nuclear hyperfine heat capacities are comprehensively explained.

### References

Magnetic measurements on single crystals of dysprosium trifluoromethanesulfonate nonahydrate; effects of crystal field perturbed energy levels

D. Neogy*, P. Paul, K.N. Chattopadhyay, D. Bisui

Solid State Research Laboratory, Department of Physics, Burdwan University, Burdwan-713 104, Burdwan, West Bengal, India

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Abstract

Magnetic susceptibility measurements on single crystals of dysprosium trifluoromethanesulfonate (DyTFMS) have been carried out from 300 K down to 13 K. The hexagonal crystal structure of DyTFMS renders the crystal uniaxial with the Kramers ion Dy$^{3+}$ occupying a site of C$_{3h}$ symmetry. The principal magnetic susceptibilities, observed by us and the Friedberg group, over the wide range 300 to $\sim 1.0$ K find an excellent theoretical simulation by the crystal field perturbed J-mixed eigenvectors with due consideration of the intermediate coupling effects. No ordering effects were noticed down to $\sim 13$ K indicating the interionic interaction to be predominantly of the dipolar type which is consistent with the discovery of a ferromagnetic transition at $T \sim 0.111$ K by the Friedberg group. The g-values derived from other sources are reasonably accounted for. The thermal behavior of quadrupole splitting and that of electronic and nuclear heat capacities is also worked out. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dysprosium trifluoromethanesulfonate; Single crystals; Crystal field; Magnetic susceptibility; Hyperfine properties

1. Introduction

Several investigations have been carried out on the spectra, magnetic and thermal properties of a relatively new series of compounds, the rare-earth trifluoromethanesulfonate nonahydrates R(CF$_3$SO$_3$)$_3$·9H$_2$O or RTFMS where R stands for a trivalent rare-earth ion [1-4]. X-ray studies [1] show that their structure is very similar to that of the hexagonal rare-earth ethylsulfate nonahydrates R(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O or RES about which much is known including the crystal field (CF) perturbed energy level schemes of the various R$^{3+}$ ions. They are also similar to the rare-earth bromate nonahydrates (RB) to a certain extent although the detailed geometries of the cations in RES and RTFMS are significantly different from that in RB [1]. Both families of compounds, viz. RES and RTFMS belong to the space group P6$_3$/m with $Z = 2$. All rare-earth ions in the structure are magnetically equivalent and occupy sites of C$_{3h}$ symmetry [2]. The unit cell dimension and the density of R$^{3+}$ ions in RTFMS are nearly the same as in RES. In these crystals the R$^{3+}$ ions are surrounded by nine H$_2$O molecules as nearest neighbors; six form a triangular prism with three
above and three below the mirror plane containing
the remaining three water oxygens and the lanthanide ion. Actually, if all but the nearest
oxygen positions are neglected, the symmetry
about the lanthanide ion is nearly D$_{3h}$. The prisms
in RTFMS and RES are nearly identical.

The magnetic ordering [3], electron paramag-
netic resonance (EPR) [2] and heat capacity [3]
of a number of RTFMS have been studied by
the Friedberg group. They have measured
magnetic properties of dysprosium trifluoro-
methanesulfonate (DyTFMS) in the temperature
range 0.05–20 K. The results show that these
crystals order ferromagnetically along the c-axis
($T_c = 0.111$ K) as does DyES and considering
the very low temperature of transition it may be
concluded that the interaction bringing about the
alignment is dipolar in nature.

In an earlier communication [5] we reported the
details of our magnetic studies on the first such
crystal of the RTFMS series viz., the Kramers salt
NdTFMS; the striking feature has been the great
success of the CF theory to provide a very
comprehensive explanation of all aspects of the
observed behavior of the Nd$^{3+}$ ion in this new
crystal matrix. This encouraged us to undertake
the study of magnetic properties of DyTFMS in
the higher range of temperature and in evolving a
theoretical basis to have a comprehensive analysis
of all experimental data, magnetic properties in
particular. In this communication we present our
measurements on the principal magnetic suscept-
bilities, $\chi_{||}$ and $\chi_{\perp}$, parallel and perpendicular to crystallographic
symmetry axis c, were measured from room
temperature down to 13 K with the help of a
highly sensitive electromagnetic balance fabricated
in our laboratory [6]. The low temperature
environment was provided by a closed-
cycle helium cryo-cooler from APD cryogenics.
The details of the fully computerized low tem-
perature magnetic susceptibility setup developed
by us with special reference to temperature
calibration of the sample chamber are given in
earlier articles [6,7]. $\chi_{\perp}$ was measured by suspend-
ing the crystal with a thin quartz fiber with the
c-axis vertical in the constant vertical magnetic
field gradient i.e., $H, \frac{dH}{dx} = \text{const}$. $\chi_{||}$ was measured with the c-axis in the horizontal plane;
in the magnetic field, $\chi_{||}$ automatically sets in the
direction of the field as in this case $\chi_{||} > \chi_{\perp}$ with
care being taken to see that the torsional constant
of the quartz fiber is very small.

The magnetic anisotropy ($\chi_{||} - \chi_{\perp}$) is calculated
with the values of $\chi_{||}$ and $\chi_{\perp}$ at different
temperatures; at room temperature the anisotropy
was measured directly using a quartz torsion
balance described earlier [8] as a check on the
absolute susceptibility measurements.

3. Results

At room temperature the symmetry axis 'c' sets
along the applied external magnetic field indicating
$\chi_{||} > \chi_{\perp}$ as found in structurally similar DyES.
The variation of $\chi_{||}$ and $\chi_{\perp}$ with temperature is
depicted in Fig. 1; it is clear that $\chi_{||} > \chi_{\perp}$ at all
temperatures. Although the magnetic anisotropy
at room temperature is small, with lowering of
temperature $\chi_{||}$ increases more rapidly than $\chi_{\perp}$
upto 60 K giving rise to a very high anisotropy.
Below 60 K $\chi_{||}$ increases slightly slower than $\chi_{\perp}$
resulting in a decrease of anisotropy; yet again at
very low temperatures the anisotropy starts increasing to attain a very high value. The relative magnetic anisotropy of DyTFMS, $\Delta \chi / \chi_{av}$, at room temperature viz., 0.1877, is comparable with that of DyES (0.1672) and dysprosium bromate (0.1852).

The effective magnetic moment $\mu_{eff}$ at room temperature calculated from the observed values of $\chi_{I}$ and $\chi_{L}$ is 10.44, which is quite close to that observed for dysprosium ethylsulfate viz., 10.41 [9] while the corresponding free ion value is 10.47. $\mu_{eff}$ is calculated for different temperatures and it is seen that its value decreases slowly with decrease of temperature. We tried a least squares fit of the Curie-Weiss law to the observed $\chi_{av}[=(\chi_{I}+2\chi_{L})/3]$ down to 13 K which yielded the Curie constant $C = 12.99$ emu K and the paramagnetic Curie temperature $\theta = -5.09$ K. The Curie–Weiss fit is quite good and yet it must be admitted as in earlier cases [5] that the implication of $\theta$ as normally construed is not appropriate here. It arises largely due to the crystal field effects rather than any antiferromagnetic type of interaction, as would be amply clear from our analysis of the data given in the next section. In fact at very low temperatures the Dy$^{3+}$ ions tend to align ferromagnetically as may be concluded from the mean-field constant being ferromagnetic in sign [3].

4. Analysis and discussion

The 4f$^0$ ground electronic configuration of Dy$^{3+}$ yields $^6H_{15/2}$ as the ground state. The first excited multiplet $^6H_{13/2}$ is situated at about 3965 cm$^{-1}$ above the ground state. The ground multiplet $^6H_{15/2}$ is split by the strong electric field produced by the immediate neighbors of Dy$^{3+}$ viz., the nine water molecules having high electric dipole moments; the site symmetry of Dy$^{3+}$ conforms to $C_{3v}$. A group theoretical consideration shows that the 16-dimensional double-valued irreducible representation, $\Gamma_{J=15/2}$, of the spherical rotation group spanned by the degenerate states of the ground multiplet ($^6H_{15/2}$) reduces to the irreducible representations of the hexagonal crystal double group as follows:

$$\Gamma_{J=15/2} \rightarrow 3\Gamma_7 + 2\Gamma_8 + 3\Gamma_9,$$
where $\Gamma_7, \Gamma_8$ and $\Gamma_9$ are all two-dimensional representations giving rise to eight Kramers doublets.

In order to have a comprehensive theoretical analysis of the magnetic data obtained by us and the Friedberg group we first block diagonalized the total Hamiltonian comprising of both CF and the spin–orbit coupling. Using one electron CF, the CF Hamiltonian conforming to $C_{3v}$ symmetry is as follows:

$$H_{\text{CF}} = B_{2s}C_{2s} + B_{4s}C_{4s} + B_{6s}C_{6s} + B_{6\pm}(C_{6\pm} + C_{6-\pm}),$$

where $C_{\mu\nu}$ are tensor operators and $B_{\mu\nu}$ are real constants that parametrize the CF. The total Hamiltonian $H(= H_{\text{so}} + H_{\text{CF}})$ is directly diagonalized in the complete (52 dimensional) basis of the ground $^6H$ term; here $H_{\text{so}}$ is the spin–orbit coupling interaction term diagonal in $J$, and $H_{\text{CF}}$ is the CF interaction term. The intermediate coupling (IC) effects are taken care of to a large extent by using IC factors [10] for the reduced matrix elements in computing the matrix elements; the approximate baricenters of the different multiplets are introduced to replace $H_{\text{so}}$. The Zeeman splitting of the CF Stark states is obtained introducing the magnetic interaction term $\beta(L + 2S) \cdot H$ and working out the first- and second-order energies; substitution of these energies in the well-known VanVleck formula yields the susceptibilities.

Starting with the parameters of dysprosium ethylsulfate, we slowly varied the parameters to simulate the variation of $\chi_{||}$ and $\chi_{\perp}$ observed by us between 300 and 13 K, and by Simizu et al. between 5 and 1 K. The best fit is obtained with the following set of CF parameters in the tensor operator formalism:

$$B_{2s} = 245, \quad B_{4s} = -635, \quad B_{6s} = -1380$$

and $B_{6\pm} = 250$; all in cm$^{-1}$.

The computed Stark energies and the eigen functions of the ground CF state appear in Table 1.

The computed parallel and perpendicular components of the susceptibility, $\chi_{||}$ and $\chi_{\perp}$, are shown in Fig. 1 along with the observed values. The excellent agreement of the theoretical values with the observed principal susceptibilities over the entire range of temperature of our study endorses that the site symmetry is indeed $C_{3v}$; this implies that the assumption that Dy$^{3+}$ interacts mainly with the nine nearest water oxygens is valid. The very good explanation provided by the CF theory alone also indicates that ordering effects of any consequence are absent down to the lowest temperature of our study. A transition to an ordered state is observed by Friedberg group [3] at a much lower temperature $T = 0.111$ K; this is the characteristic of a dipolar system. Observed values of $\chi_{||}$ obtained by the Friedberg group from 1 to 5 K are also plotted as inset in Fig. 1. We found that $\chi_{||}$ obtained by the Friedberg group down to $\sim 1$ K is well explained by our theoretical values using a mean-field constant slightly different from theirs. Although the magnetic behavior at still lower temperatures has been observed by Simizu et al., we did not attempt to fit the same since it is strongly dominated by cooperative interaction (dipolar) and should, therefore, deviate widely from that expected from a consideration of purely electrostatic interactions of the R$^{3+}$ ions with its surroundings. Our analysis gives an excited doublet at about 9.5 cm$^{-1}$ above the ground state which is lower than the inferences of Bellesis et al. [3]. $\chi_{\perp}$ also exhibits a large temperature-independent term amounting to 1.22 emu/mol predicted fairly well by Simizu et al. viz., 1.13 emu/mol.

The computed spectroscopic splitting factors, i.e., $g_{||}$ and $g_{\perp}$ for the ground doublet turn out to be 11.71 and 0.0, respectively, which compare very well with that deduced by Bellesis et al. from susceptibility measurements below 4 K, viz. $g_{||} = 11.92$ and $g_{\perp} = 0$ but differ appreciably from that of DyES viz., $g_{||} = 10.8$ and $g_{\perp} = 0$ [3].

5. Thermal and hyperfine properties

5.1. Electronic specific heat

The change of population in the low-lying energy levels with temperature makes significant contributions to the electronic heat capacity, $C_v$, and is quite often responsible for the anomalies observed in its thermal behavior. The Schottky anomalies which are computed from the thermal
Table I
Crystal field Stark energies of the low-lying multiplets of the ground term $^6H$ of the Dy$^{3+}$ ion in dysprosium trifluoromethanesulfonate and its ground state wave functions

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<th>Multiplets</th>
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</table>

average of the energy over the CF-split states is an important feature of the RE ions in crystalline hosts. $C_s$ at different temperatures is calculated using the relation

$$C_s = N_A \frac{d}{dT}[\text{Tr}(\mathcal{H}\rho)/\text{Tr}(\rho)],$$

where $\mathcal{H}$ is the Hamiltonian matrix, $\rho$ the statistical density matrix and $N_A$ the Avogadro number. Fig. 2 shows the variation of $C_s$ with temperature; two anomalies occur. The interesting feature in the $C_s$ of DyTFMS is a broad Schottky anomaly at around 57 K with a peak value 5.0 J/g atom K and a second anomaly at 6 K with peak value 3.65 J/g atom K is rather sharp.
5.2. Hyperfine properties

Both isotopes of dysprosium, $^{161}$Dy and $^{163}$Dy have nuclear ground state spin $I = 5/2$. The nuclear quadrupole interaction with the electric field gradient (EFG) due to the 4f electrons and the lattice at the nuclear site splits the ground state in absence of a magnetic field. The temperature-dependent part of the EFG is due to the contribution of the 4f electrons whereas direct lattice contribution to the EFG is temperature independent. The nuclear quadrupole splitting $\langle \Delta E_Q \rangle_T$ varies with the temperature because of the 4f component in the EFG [11]. The variation of $\langle \Delta E_Q \rangle_T$ between the lowest two levels i.e. $|I_z = \pm 5/2\rangle$ and $|I_z = \pm 3/2\rangle$ for both the isotopes $^{161}$Dy and $^{163}$Dy are depicted in Fig. 3.

The magnetic hyperfine structure of the nuclear levels of both isotopes of Dy modified by the quadrupole interaction gives rise to anomalies in the hyperfine heat capacity ($C_N$) which is calculated using a formula similar to that of $C_3$ but using the hyperfine energies instead of the electronic energies. In the present case as the ferromagnetic transition takes place [3] at 111 mK the spins are already aligned along the c-axis in the range of temperatures where the anomalies in $C_N$ are usually obtained and hence $C_N$ would be indistinguishable for the two cases, viz., in the presence and absence of an external magnetic field. A sharp anomaly in $C_N$ for both the isotopes is seen in Fig. 4 at 24 and 33 mK for $^{161}$Dy and $^{163}$Dy, respectively, with the corresponding peak values, 8.1 and 7.9 J/g atom K.

6. Conclusion

The principal magnetic susceptibilities of the single crystals of DyTFMS were studied for the first time in the range 300–13 K; this along with the observed results of the Friedberg group provides a complete description of the behavior of the principal magnetic susceptibilities of DyTFMS from 0.1 to 300 K. A crystal field analysis undertaken by us over nearly the entire range has been highly successful in simulating the susceptibilities quantitatively which vindicates earlier conviction that the site symmetry about the rare-earth ions in RTFMS is indeed C3h. Our theoretical results also give correct g-values as obtained from the very low temperature magnetic data. We have extended our computations to nuclear quadrupole splitting and thermal properties, both electronic and nuclear hyperfine, based on our present state of knowledge on dysprosium trifluoromethanesulfonate; these are all amenable to experimental verification.
References