

Paramagnetic Susceptibility of Terbium Hexa-Antipyrene Tri-Iodide

J. A. WHITE*

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts

AND

H. J. WILLIAMS AND R. C. SHERWOOD

Bell Telephone Laboratories, Murray Hill, New Jersey

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Terbium hexa-antipyrene tri-iodide has a large temperature-dependent susceptibility parallel to the crystal hexagonal symmetry axis and at low temperatures a very much smaller temperature-independent susceptibility perpendicular to this axis. This behavior is interpreted on a hexagonal crystal field model. The parallel susceptibility, which between 1.4 and 150°K is given by $\chi_{\text{par}} = 8.7\beta(H_0^2 + H^2)^{-1/2} \tanh[8.7\beta(H_0^2 + H^2)^{1/2}/kT]$ with $H_0 = 3400$ Oe, corresponds to a nondegenerate terbium $J_z = \pm 6$ doublet with a zero field splitting of 4°K. The remaining crystal field levels lie more than 150°K above the doublet. The crystal field is found to have strong axial components, with somewhat weaker hexagonal distortions responsible for the doublet splitting. Distortions from hexagonal symmetry, although known to be appreciable in hexa-antipyrene at low temperatures, make only a small contribution to the Tb^{3+} susceptibility.

THE rare-earth hexa-antipyrene tri iodides (RE HAPI's) are a homologous series of compounds with the general formula $\text{RE}(\text{C}_{11}\text{H}_{12}\text{ON}_2)_3\text{I}_3$ in which Re can be any of the rare-earth ions or yttrium. The crystal symmetry is known from x-ray measurements to be $C_{3i}^2 = R\bar{3}$ at room temperature with the rare-earth ion at a site of $S_6 = C_{3i} = \bar{3}$ symmetry.¹ Paramagnetic resonance measurements have been reported for RE=Gd, Ce, Nd, Er, and Yb.^{2,3} These show that there is a transition to lower symmetry below about 100°K with several ions per unit cell, and the spectra below this transition are correspondingly complicated and difficult to interpret. In this paper we report static susceptibility measurements on Tb HAPI and interpret them on a hexagonal crystal field model. As the Tb^{3+} susceptibility is rather insensitive to distortions of the crystal field from pure hexagonal symmetry, it is possible to determine the lowest-lying states in Tb^{3+} and to determine some of the general features of the crystal field. In particular, it is found that both the axial and hexagonal components are stronger than in other hexagonal crystals in which Tb^{3+} ions have been studied.

The measurements were carried out on a single crystal of Tb HAPI by Williams and Sherwood⁴ using the pendulum magnetometer of Bozorth, Williams, and Walsh.⁵ The results are presented in Figs. 1 through 3. These show, respectively, the low-temperature magnetization parallel to the crystal axis of symmetry, the

susceptibility perpendicular to this axis, and the temperature dependence of the susceptibility up to room temperature.

The most striking feature of the susceptibility is its anisotropy. This amounts to as much as a factor of 100 between directions parallel and perpendicular to the crystal symmetry axis at low temperatures, and to about a factor of 2 at room temperature. Between 10 and 150°K the parallel susceptibility is about 90% of that to be expected for a doublet $J_z = \pm 6$ state and 30% larger than for a $J_z = \pm 5$ doublet. This indicates that in HAPI, as has been found previously in the ethyl sulfate⁶ and trichloride,⁷ the lowest Tb^{3+} levels are comprised of $J_z = \pm 6$ states. The exceptionally small perpendicular susceptibility corresponds to a separation of more than 150°K between the $J_z = \pm 6$ and $J_z = \pm 5$

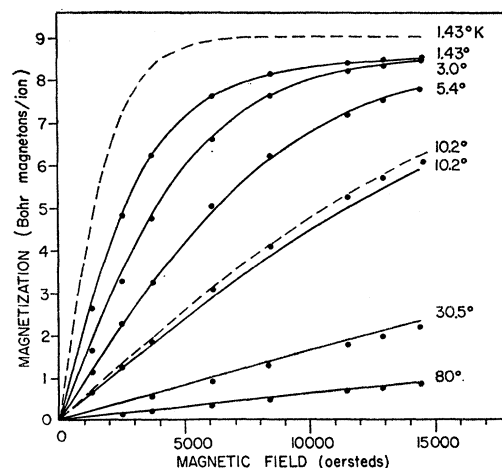


FIG. 1. Magnetization per ion parallel to the crystal symmetry axis. The dashed curves give the theoretical magnetization for a degenerate $J_z = \pm 6$ doublet; the solid curves correspond to Eq. (1), with $J_z g \cos \omega = 8.7$ and $H_0 = 3400$ Oe.

* Summer visitor at the Bell Telephone Laboratories, Murray Hill, New Jersey, 1960/1961.

¹ R. G. Treuting, Bell Telephone Laboratories (private communication); G. Garton and J. W. Jeffrey have independently found the same symmetry, see Baker and Williams reference 2.

² J. M. Baker and F. I. B. Williams, Proc. Phys. Soc. (London) **78**, 1340 (1961).

³ J. M. Baker and R. S. Rubins, Proc. Phys. Soc. (London) **78**, 1353 (1961).

⁴ J. A. White, H. J. Williams, and R. C. Sherwood, Bull. Am. Phys. Soc. **7**, 263 (1962).

⁵ R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

⁶ J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

⁷ C. A. Hutchison and E. Wong, J. Chem. Phys. **29**, 754 (1958).

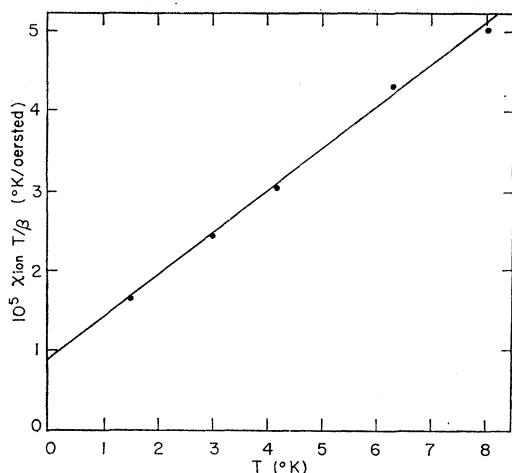


FIG. 2. Susceptibility per ion perpendicular to the crystal symmetry axis.

states. The persistence of a large parallel susceptibility to 150°K indicates that the remaining levels with $|J_z| < 4$ also lie more than 150°K above the ground doublet. This is to be contrasted with a total crystal field splitting of about 100°K in the ethyl sulfate and trichloride.

Since terbium has an even number of electrons, the $J_z = \pm 6$ levels cannot, in general, be expected to be degenerate. Figure 1 shows that the parallel magnetization at 1.43°K saturates less rapidly with increasing field than for a degenerate doublet. The magnetization per ion is given to good accuracy by the expression

$$M_{\text{par}} = \frac{J_z g \beta H \cos \omega}{(H_0^2 + H^2)^{1/2}} \tanh \left[\frac{J_z g \beta (H_0^2 + H^2)^{1/2} \cos \omega}{kT} \right], \quad (1)$$

with $J_z = 6$, $\cos \omega = 0.97$, and $H_0 = 3400$ Oe. Here g has been assigned the value $3/2$, corresponding to a pure

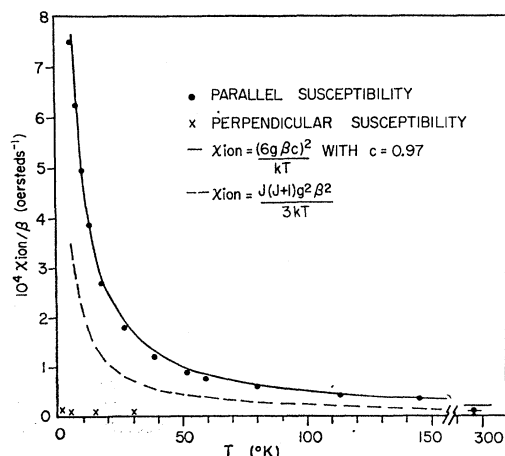


FIG. 3. Susceptibility per ion at 14 400 Oe as a function of the temperature. The dashed curve is the Tb^{3+} free-ion susceptibility. The solid curve corresponds to Eq. (1) with $J_z g \cos \omega = 8.7$, as in Fig. 1.

7F_6 ground term for Tb^{3+} . This expression, which except for the factor $\cos \omega$ is the same as that used by Becquerel, de Haas, and Kramers⁸ in discussing the optical rotatory power in xenotime, takes into account the zero field doublet splitting $\Delta W/k = 2J_z g \beta H_0 \cos \omega$. The origin of the splitting is different here, however, than in xenotime. Here, for Tb^{3+} , which has an even number of electrons, the splitting is due to a nonaxial term in the crystal field, whereas in xenotime, in which the rare-earth ion is Gd^{3+} with an odd number of electrons, the splitting must be due to exchange or magnetic interactions, as twofold degeneracy always persists in purely electrostatic fields for ions with an odd number of magnetic electrons. The magnitude of the splitting in HAPI, $\Delta W/k = 4^\circ\text{K}$, is considerably greater than in the ethyl sulfate⁶ and trichloride⁷ where the splittings are, respectively, 0.56 and 0.3°K.

If, following Baker and Bleaney,⁶ we designate the difference in axial crystal field energy for $J_z = 0$ and $J_z = \pm 6$ states by $d = \langle 0 | V_{\text{axial}} | 0 \rangle - \langle \pm 6 | V_{\text{axial}} | \pm 6 \rangle$ and the hexagonal perturbation term connecting the $J_z = 0$ and $J_z = \pm 6$ states by $c = \langle 0 | V_{\text{hex}} | \pm 6 \rangle$, then, since $\cos \omega$ differs but little from unity, we obtain for the doublet splitting $\Delta W = 2c^2/d$ and for $\cos \omega$ the expression $\cos \omega = 1 - c^2/d^2$. Inserting the values given above for ΔW and $\cos \omega$, we find for c and d the values

$$\begin{aligned} c/k &= 12^\circ\text{K}, \\ d/k &= 67^\circ\text{K}. \end{aligned} \quad (2)$$

These values are certainly too small, since the $J_z = 0$ level lies not at 67°K but more than 150°K above the $J_z = \pm 6$ doublet. The above expression for ΔW ignores matrix elements of the crystal field perturbation connecting different terms in the multiplet. Baker and Bleaney find that there is a contribution $-22c^2/3000^\circ\text{K}$ to the doublet splitting from the matrix elements of V_{hex} between the ground doublet and the $J = 5$, $J_z = 0$ state. When this term is taken into account, the above values for c/k and d/k are increased to 25 and 145°K, respectively. The additional contributions from $J < 5$, $J_z = 0$ states are of comparable importance, however, and alternately increase and decrease the splitting. The positions of the multiplet terms are not known well enough to determine the net contribution with any certainty. The order of magnitude of the contribution, however, is indicated by the size of the term calculated by Baker and Bleaney.

The values for c and d are very sensitive to the value used for $\cos \omega$; an increase in $\cos \omega$ by 1.5% would result in a factor of 2 increase in d . Since the spin-orbit interaction is relatively large in the rare-earth ions, the lowest term is not a pure 7F_6 Russell-Saunders term, and hence does not have a g value precisely equal to 1.50.

⁸ J. Becquerel, W. J. de Haas, and H. A. Kramers, *Proc. Acad. Sci. Amsterdam* **32**, 1206 (1929), or H. A. Kramers, *Collected Scientific Papers* (North-Holland Publishing Company, Amsterdam, 1956), p. 515.

Baker and Bleaney mention that Judd has found $g=1.49$ for a Tb^{3+} ground-state configuration ${}^7F_6 + \alpha({}^5G_6)$ with $\alpha^2=0.06$. This is a step in the right direction, as it makes $\cos\omega$ closer to 0.98 than to 0.97.

So far the theory has taken no account of distortions from hexagonality. Baker and Rubins³ have found from paramagnetic resonance measurements on Gd^{3+} ions in Tb HAPI that there is a phase transition below 100°K to a symmetry lower than S_6 and to several magnetically inequivalent ions per unit cell. Either rhombic or trigonal distortions from hexagonal symmetry will mix states with lower J_z values into the $J_z=\pm 6$ doublet and thereby reduce the low-temperature susceptibility. For example, trigonal distortion terms would mix $J_z=\pm 3$ into the $J_z=\pm 6$ states. If the corresponding perturbation energies were 15% of the separation between the $J_z=\pm 6$ and $J_z=\pm 3$ states, i.e., 30°K if this separation is 200°K, then the magnetic moment in the doublet states would be reduced by a little more than 1% and the part of $\cos\omega$ corresponding to admixture of $J_z=0$ state would be somewhat more than 0.98 rather than 0.97. This would suffice to make d larger than 100°K, while increasing c by about 20%. A rhombic perturbation of $\sim 30^\circ\text{K}$ connecting the $J_z=\pm 6$ and $J_z=\pm 4$ terms would have a similar, though somewhat smaller, effect.

It is clear that a combination of a reduction in g value to less than 1.5 due to a breakdown of Russell-Saunders coupling, a negative contribution to the zero field splitting from excited multiplet terms, and a dilution of the $J_z=\pm 6$ states by smaller $|J_z|$ states due to trigonal or rhombic distortions can account for the discrepancy between the value of d found above and that required to explain the persistence of a large value for the parallel susceptibility to high temperatures.

Since the crystal field terms V_2^0 , V_4^0 , and V_6^0 all contribute to d , it is not possible to determine these axial components uniquely. A pure second-order field with $V_2^0=A_2^0\langle r^2\rangle=400\text{ cm}^{-1}$ would give a splitting between the lowest pair of doublet states ($J_z=\pm 6$ and $J_z=\pm 5$ in this case) of 190°K. There is no reason to expect that the contributions from V_4^0 and V_6^0 are negligible, however, so V_2^0 could, in particular, be considerably smaller than this. The hexagonal distortion comes entirely from V_6^0 . A value of 25°K for c/k would correspond to $V_6^0=A_6^0\langle r^6\rangle=1400\text{ cm}^{-1}$. This is considerably larger than in the ethyl sulfate and trichloride, though comparable to the values found for rare earth ions in the double nitrates.⁹

The perpendicular susceptibility has the form $\chi_{\text{perp}}=C_1+C_2/T$ with $C_1=5.2\times 10^{-6}\beta$ and $C_2=9.1$

$\times 10^{-6}\beta$. The small value for the temperature independent part of the susceptibility corresponds to a separation between the ground doublet and the $J_z=\pm 5$ states of at least 170°K. The temperature-dependent term could correspond to a misalignment of the crystal by 2°K from perfect perpendicularity to the field. Although this much misalignment is within experimental uncertainty, the term may, instead, be an indication of the phase transition mentioned above. If a hexagonal theory is used for each of the Tb^{3+} ions but with the hexagonal axis for each ion twisted slightly from the high-temperature crystal symmetry axis, then the above value for the temperature-dependent term suggests an average twist of 2°K.

Throughout the above discussion we have ignored the effect of hyperfine structure. The Tb^{159} nucleus has spin $I=3/2$ and a magnetic moment of 1.5 nuclear magnetons. In the $J_z=\pm 6$ ground doublet only the component of the nuclear moment parallel to the crystal axis is effective in producing a hyperfine interaction. The value of this interaction found by Baker and Bleaney⁶ corresponds to a nuclear magnetic field contribution $H_{\text{hfs}}=250I_z\text{ Oe}$ to be added to the externally applied field. This makes a contribution of only about 1% to the zero-field doublet splittings, and a correspondingly small contribution to the susceptibility.

We have also ignored the demagnetization correction. This correction depends on the shape of the crystal, and amounts to somewhat more than $4\pi M/3$ for fields parallel to the axis of the relatively flat crystal used in the measurements. Corresponding to the primitive unit cell volume in Tb HAPI of 1781 Å, this correction amounts to about 300 Oe at saturation. When this correction is taken into account, there is slightly better agreement between the theoretical susceptibility vs field curves at low temperatures and those observed, provided H_0 and $\cos\omega$ are reduced slightly. The change in $\cos\omega$ is very small, however, and that in H_0 is less than the 10% uncertainty in the value which best fits the data.

At no temperature was there any sign of ferro- or antiferromagnetism. This is no doubt due to the very large distance between Tb^{3+} ions in HAPI—more than 13 Å—and the fact that the crystal is a nonconductor.

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⁹ B. R. Judd, Proc. Roy. Soc. (London) **A232**, 458 (1955); M. J. M. Leask, R. Orbach, M. J. D. Powell, and W. P. Wolf, Proc. Phys. Soc. (London) (to be published).