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## Magnetic properties of terbium vanadate

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**Abstract.** Terbium vanadate is a paramagnet with the tetragonal zircon structure (Wyckoff R W 1965 *Crystal Structures* vol 3 (New York: Interscience)), with space group  $I4_1/amd$  ( $D_{4h}^{19}$ ). The ground state  ${}^7F_6$  is split by the crystal field into three doublets and seven singlets. At a temperature of 33 K, a cooperative Jahn–Teller interaction produces a lattice distortion with extensive changes in the electronic energy levels. At the lowest temperatures the ground levels are two singlets, split by nearly 30 GHz. The present paper reports a new determination by means of electron spin resonance of this splitting; this is correlated with earlier measurements, in particular that of the heat capacity below 1 K. Magnetic hyperfine interaction, not previously considered, produces a complex ground state with large enhanced nuclear moments. The antiferromagnetic state below  $T_N = 0.61$  K is attributed to spin–spin interaction between these moments.

### 1. Introduction

Terbium vanadate,  $TbVO_4$ , is a member of a series of lanthanide vanadates that have attracted considerable interest because of the diverse crystallographic and magnetic phase transitions which occur at low temperatures. A detailed review of the miscellaneous properties of the lanthanide vanadates ( $RVO_4$ ), arsenates ( $RA_sO_4$ ), and phosphates ( $RPO_4$ ), has been given by Gehring and Gehring (1975). For  $TbVO_4$ , changes in the crystal structure caused by cooperative effects of the Jahn–Teller interaction were first reported by Gehring *et al* (1971). The crystallographic distortion temperature,  $T_D = 33.1(1)$  K, was determined quite precisely from the anomaly in the heat capacity (Wells and Worswick 1972). Observations by infra-red spectroscopy (Ergun *et al* 1976) were supplemented by optical absorption spectroscopy and further measurements of the heat capacity (Gehring *et al* 1976). The ground manifold of the trivalent terbium ion  $4f^8$ ,  $L = 3$ ,  $S = 3$ , is split by spin–orbit coupling into states  $J = 0$  to 6, for which the values of  $g_J$  are all close to 1.5. The lowest state is  $J = 6$ , for which corrections from intermediate coupling (Judd and Lindgren 1961) reduce  $g_J$  to 1.491.

At ambient temperatures  $TbVO_4$  has tetragonal symmetry, with space group  $I4_1/amd$ , with lattice parameters  $a = a' = 0.71772$  nm,  $c = 0.63289$  nm (Wyckoff 1965). The lowest manifold  $J = 6$  is split by the crystal field into three doublets and seven singlets. Their energies and wave-functions are listed in table 1, from a crystal-field calculation of Gehring (1975), based on the behaviour of trivalent dysprosium ions in  $YVO_4$ . According to Gehring *et al* (1976), the ground state is a singlet,  $\Gamma_1$ ; the nearest level is a non-Kramers doublet,  $\Gamma_5$ , at  $8.0(5)$   $cm^{-1}$ , with another singlet,  $\Gamma_3$ , at  $19.1(5)$   $cm^{-1}$ . These levels are in broad agreement with those in table 1.

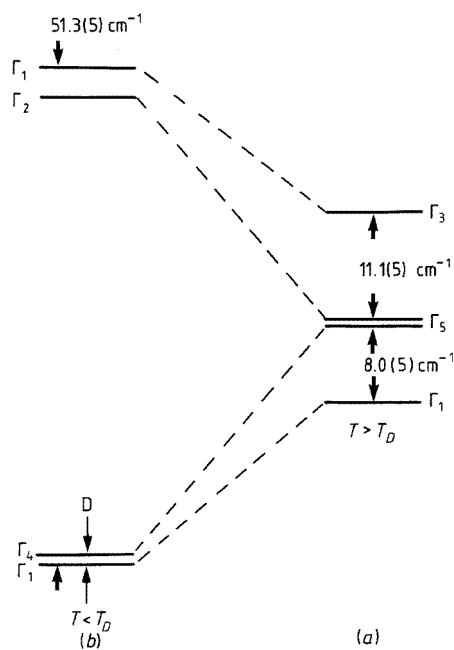
**Table 1.** Energies and wave-functions for the levels of terbium vanadate, at temperatures above that of the Jahn–Teller distortion.

(cm <sup>-1</sup> )		
274	0.497{ +6> +  -6>} + 0.522{ +2> +  -2>}	
252	0.385 ±5> + 0.700 ±1> + 0.601 ±3>	
249	0.499{ +4> +  -4>} + 0.706 0>	
241	0.697{ +6> -  -6>} + 0.116{ +2> -  -2>}	
202	0.522{ +6> +  -6>} - 0.477{ +2> +  -2>}	
134	0.847 ±5> - 0.009 ±1> - 0.531 ±3>	
124	0.501{ +4> -  -4>}	
17.98	0.116{ +6> -  -6>} - 0.697{ +2> -  -2>}	(Γ <sub>3</sub> )
8.14	0.367 ±5> - 0.714 ±1> + 0.597 ±3>	(Γ <sub>5</sub> )
0	0.501{ +4> +  -4>} - 0.706 0>	(Γ <sub>1</sub> )

## 2. The Jahn–Teller effect

TbVO<sub>4</sub> undergoes a Jahn–Teller cooperative distortion at  $T_D = 33.1$  K, determined quite precisely from the anomaly in the heat capacity (Wells and Worswick 1972); later measurements by Raman spectroscopy (Harley *et al* 1980) gave  $T_D = 32.6$  K. Below this temperature, the structure is orthorhombic (Elliott *et al* 1972), with space group  $D_{2h}^{24}$ , resulting from a  $B_{2g}$  strain. The moments are constrained to lie parallel and antiparallel to the axes  $110$  and  $\bar{1}\bar{1}0$ . This produces equivalent domains, which can be reduced to a single domain by application of a magnetic field.

The changes in the lattice parameters are small; an x-ray diffraction experiment

**Figure 1.** The lowest four energy levels of terbium vanadate, at temperatures above and below the Jahn–Teller distortion; (a) at 77 K; (b) at 20.4 K.

(Will *et al* 1972) showed that the fractional difference between the principal axes rises fairly sharply at temperatures below 20 K to a maximum of  $21.7 \times 10^{-3}$ . The changes in the energy levels produced by the Jahn–Teller interaction are much more important; the lowest four electronic energy levels at 77 K and at 20.4 K are shown in figure 1, based on the work of Gehring *et al* (1971).

**Table 2.** The wave-functions of the two lowest electronic levels at temperatures below the Jahn–Teller distortion. (For the wave-functions for  $\Gamma_3$  and  $\Gamma_1$ , see table 1.)

$ u\rangle$	$0.367 5^a\rangle - 0.714 1^a\rangle + 0.597 3^a\rangle$ where $ 5^a\rangle = (2^{-1/2})[ +5\rangle -  -5\rangle]$ , etc
$ v\rangle$	$0.957 \Gamma_3\rangle + 0.290 \Gamma_1\rangle$

Below  $T_D$ , the  $\Gamma_3$  singlet is raised in energy from 18 to 51.3(5)  $\text{cm}^{-1}$ , becoming a  $\Gamma_1$  singlet. The  $\Gamma_5$  doublets are all split by the Jahn–Teller interaction. One component of the lowest doublet becomes a singlet  $\Gamma_2$  at 47.0(5)  $\text{cm}^{-1}$ ; the other is reduced in energy to become  $\Gamma_4$ , lying just above the  $\Gamma_1$  singlet. These four levels (see figure 1) determine the properties of the compound at temperatures below about 100 K. The electronic wave-functions and energies in table 2 are calculated from the Jahn–Teller interaction

$$O_{JT} = J_+^2 - J_-^2. \quad (1)$$

The two lowest singlets may be treated as a non-Kramers doublet,  $S = 1/2$ , with a splitting  $D$ . The upper level  $|u\rangle = \Gamma_4$ ; the lower level  $|v\rangle$  is an admixture of the wave-functions  $\Gamma_3$  and  $\Gamma_1$  produced by the Jahn–Teller interaction. Table 2 of Gehring *et al* (1976) shows that the electronic Zeeman interaction between  $|u\rangle$  and  $|v\rangle$  has a single matrix element, equivalent to  $g_y = 16.5(5)$ . The crystal-field calculation of Gehring (1975) gives 16.28; below, a mean value of 16.4 is used.

### 3. Nuclear aspects

The hyperfine Hamiltonian is

$$A_J(JI) + P[I_z^2 - I(I+1)/3]. \quad (2)$$

Terbium has a single stable isotope of mass 159, with  $I = 3/2$ , a nuclear magnetic moment +2.014(4) nm, and an electric quadrupole moment of +1.432 b (table 1 of Bleaney (1988)). For the free ion in the state  $J = 6$ ,  $A_J/h = 0.530$  GHz (Baker and Bleaney 1958), with  $P/h = +0.386$  GHz (table 13 of Bleaney (1988)) for the nuclear electric quadrupole interaction. Although the early papers on terbium vanadate contain extensive discussions of the electronic levels, there is no detailed treatment of the hyperfine interactions (2).

Diagonal terms for the electronic Zeeman effect or the magnetic hyperfine interaction for the two electronic singlet states  $|u\rangle$ ,  $|v\rangle$  are zero; between them there is a single electronic matrix element from  $J_y$ , with corresponding magnetic hyperfine terms. The energy matrix becomes

$$\begin{vmatrix} D + P_u & [G + Am]/2 \\ [G + Am]/2 & P_v \end{vmatrix} \quad (3)$$

where  $D$  is the separation in zero magnetic field between  $|u\rangle$  and  $|v\rangle$ , and  $G = g\mu_B B$ . The terms for the other axes are zero, and the subscripts  $y$  may therefore be omitted. In a magnetic field along the  $y$ -axis, the energy levels are

$$(1/2)D \pm (1/2)\{D^2 + (G + Am)^2\}^{1/2}. \quad (4)$$

The value  $g = 16.4$  implies a matrix element  $g/g_J = \langle v|J_y|u \rangle = 11.0(3)$ ; from the relation  $A/A_J = g/g_J$ , the magnetic hyperfine parameter  $A/h = 11.0 \times 0.530 = 5.83(3)$  GHz. The parameters  $P_u$  and  $P_v$  have equal values but opposite signs for  $m = \pm 3/2$  and  $m = \pm 1/2$  respectively. The contributions from the electric field gradient and from second-order effects of the magnetic hyperfine structure are of order 0.2 GHz, and are omitted below.

**Table 3.** Energies of the hyperfine levels in zero magnetic field, and the enhanced nuclear moments  $M$  in Bohr magnetons.

$m = \pm 3/2$	$W/h = \pm 15.8$ GHz or $W/k = 1.368$ and 0 $M/\mu_B = \pm 2.516$
$m = \pm 1/2$	$W/h = \pm 13.5$ GHz or $W/k = 1.339$ and 0.029 $M/\mu_B = \pm 0.876$

It follows from (4) that in each singlet electronic state, the magnetic hyperfine interaction produces a greatly enhanced nuclear moment, almost electronic in size. The values of the energy in zero magnetic field, and the enhanced nuclear moments, are listed in table 3.

#### 4. Electron paramagnetic resonance (EPR)

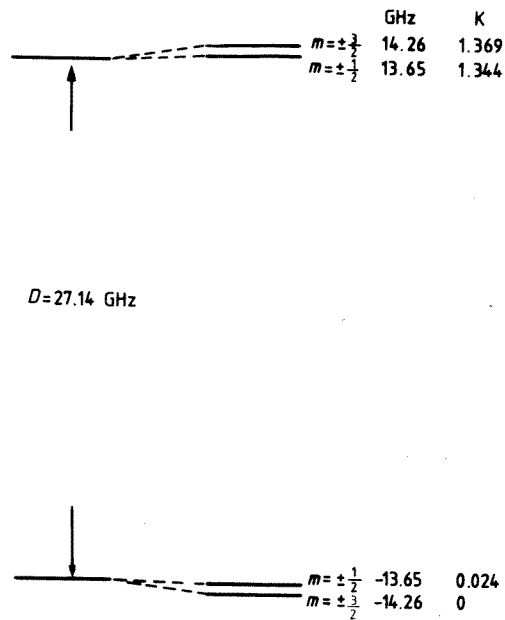
A strong magnetic resonance (EPR) transition between the two singlet levels in equation (4) is allowed with the radio-frequency field along the  $y$ -axis. Previous estimates of the splitting were close to 30 GHz, and an EPR experiment was carried out at a slightly higher frequency, 33.81 GHz. At a temperature of 4.2 K, an intense, broad resonance was observed, centred on a field of 0.249 T along a [010] axis. This result, combined with the optical value for  $g$ , gives  $D/h = 27.14$  GHz for the splitting in zero magnetic field, in good agreement with the previous value of  $0.95 \text{ cm}^{-1} = 28.5$  GHz, obtained from measurements of the heat capacity (Kahle *et al* 1974, Kahle 1996).

TbVO<sub>4</sub> is a relatively concentrated compound; in an electron spin-resonance experiment, the root mean square width from magnetic dipole interaction should be about 0.35 T for an electronic doublet with  $g = 16.4$ . However, inclusion of the magnetic hyperfine structure produces the levels in table 3, with enhanced nuclear moments, for which the root mean square width should only be about 0.018 T. The observed width is about 0.125 T, half-peak-to-peak in the line differential; this is probably due to unresolved hyperfine structure. The Jahn–Teller transition might produce additional width from random strains, but these appear to make no appreciable contribution to the heat capacity.

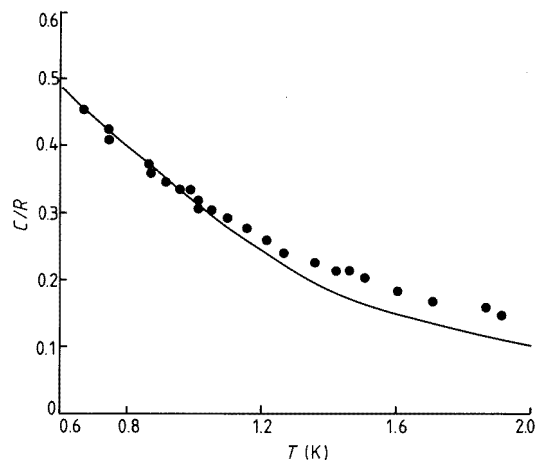
#### 5. The heat capacity

Immediately below 34 K, the heat capacity is dominated by the anomaly arising from the Jahn–Teller interaction. The measurements of Wells and Worswick (1972) show a sharp rise at  $T_D$ , for which their value was 33.1(1) K. Below this temperature the heat capacity falls steadily, until the two main contributions, from the Jahn–Teller effect and the lattice, become negligible. Using a cryostat cooled by liquid helium-3, they found that below 1 K

the heat capacity rises again. Their measurements, from 1.2 K down to 0.65 K, are shown in figure 2.



**Figure 2.** The electronic energy levels for the ground doublet with splitting  $D$ , together with the hyperfine levels for  $I = 3/2$ .



**Figure 3.** The heat capacity. The full circles represent the measurements made by Wells and Worwick. The full curve shows the variation calculated from the energy levels in table 3, including the small contribution from magnetic dipole interaction.

In zero magnetic field the energy levels given by equation (4) with  $G = 0$  are listed in table 3. These have been used in a new calculation of the heat capacity which gives values of  $C/R$  falling from 0.437 at 0.6 K to 0.025 at 4.2 K. The contribution from magnetic

dipolar interaction between the enhanced nuclear moments is quite small:

$$CT^2/R = 0.0164.$$

At 0.8 K this increases the heat capacity  $C/R$  from 0.373 to 0.398. The combined total agrees very well with the measured values below 1.2 K, as shown in figure 3, but falls somewhat lower at higher temperatures.

## 6. The ordered state

Just below the temperature range covered by Wells and Worswick, measurements of the heat capacity (Gehring *et al* 1976) revealed a sharp anomaly, ascribed to an antiferromagnetic transition with

$$T_N = 0.61(3) \text{ K}.$$

For the ordered state they suggested the space group  $Fdd'd'$ , as for terbium arsenate, for which  $T_N = 1.48(4) \text{ K}$  (Wüchner and Laugsch 1973). The principal axes are again  $[110]$  and  $[1\bar{1}0]$ , with domains oriented at  $90^\circ$  to each other.

It was assumed that this arose from ordering with a singlet electronic ground state, but inclusion of the hyperfine interactions, as discussed above, suggests that ordering results from the large enhanced nuclear moments.

Below  $T_D = 33 \text{ K}$ , the size of the crystallographic distortion was determined as a function of temperature using x-rays by Will *et al* (1972). The fractional difference between the two axes normal to the tetragonal axis reaches a maximum of  $21.7 \times 10^{-3}$  below about 20 K. There may also be changes in the lattice constants in a large magnetic field.

## 7. Magnetic dilution

In electron paramagnetic resonance, the large linewidths that prevent the resolution of hyperfine structure are usually overcome by magnetic dilution—replacing most of the magnetic ions by non-magnetic ions. The Jahn–Teller interaction is a cooperative effect which vanishes on dilution, so this cannot be applied to terbium vanadate. An experiment on a diluted crystal would need enhanced nuclear magnetic resonance, and would give detailed information about the ground state. From the wave-functions and energies in table 1, the principal values of the resonance frequency are  $0.05 \text{ GHz T}^{-1}$  (parallel to the tetragonal axis) and  $2.75$  to  $3.0 \text{ GHz T}^{-1}$  (normal to the tetragonal axis) respectively. The uncertainty in the latter arises because the energy of the  $\Gamma_5$  doublet is not known precisely. The nuclear electric quadrupole interaction, of order  $-0.1 \text{ GHz}$ , could also be determined. A measurement of the  $\Gamma_5$  doublet itself by means of electron spin resonance is theoretically possible, but  $g_z$  is only 0.34, and the levels are likely to be broadened by spin–lattice relaxation through an Orbach process.

## 8. Conclusion

A neutron diffraction experiment at low temperatures would determine the nature of the antiferromagnetic state, together with the field, about 0.1 T, needed to convert to a ferromagnetic configuration. An unusual feature is that the two ground electronic singlets have quite different wave-functions, with different scattering cross-sections.

## Acknowledgment

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