Short Communications

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A note on the crystal and magnetic structure of $BaTbO_3$.*

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$BaTbO_3$ is rhombohedral, $a_0=6{\cdot}050$ (5) Å, $\alpha=60{\cdot}13$ (5)°, at 298°K. Neutron powder diffraction patterns between 11°K and room temperature have been refined in space group $R\bar{3}c$ by least-squares calculations and the x parameter of oxygen, which is in the neighborhood of 0·710, has been obtained as a function of temperature. The magnetic structure is G-type antiferromagnetic (collinear) and the magnetic moment of Tb^{4+} is calculated to be 6·66 (11) Bohr magnetons, only 5% below the value expected for an ion in the $^8S_{7/2}$ ground state. A Néel temperature of 36°K was derived from the diffraction data. Correction of the Tb^{4+} moment for temperature yields a value of $7{\cdot}01\mu_B$, the theoretical value.

The crystal structure of $BaTbO_3$ has recently (Jacobson, Tofield & Fender, 1972) been shown to be rhombohedral ($R\bar{3}c$) at room temperature, with a reported oxygen x parameter of 0·7124 (6). These authors also report that the compound orders antiferromagnetically with a G-type structure at a Néel temperature of 36°K. This note is presented to confirm their results and to present data on the temperature dependence of the oxygen positional parameter. The sample was prepared as a fine yellow powder by essentially the same method as Jacobson *et al.*, heating $BaCO_3$ and Tb_2O_3 in pure oxygen at 1000°C.

Neutron powder-diffraction data were obtained at 11, 15, 46, 80 and 298°K at the Brookhaven High-Flux Beam Reactor. Magnetic ordering was observed to occur in the low temperature patterns by the appearance of enhanced intensity of neutron-diffraction peaks corresponding to pseudocubic indices having h, k, l all odd, plus the appearance of a strong 111 reflection (pseudocubic, based on a doubled perovskite cell with $a_0=8{\cdot}564$ Å, $\alpha=90{\cdot}055°$ at room temperature) which is completely absent above the Neél temperature. The transition temperature was estimated to be 36°K by monitoring the intensity of this 111 peak as a function of temperature.

The positional and thermal parameters above the Néel temperature were obtained at 46°K, where the most complete set of data were available, by a least-squares refinement using a program (Ibers & Hamilton, 1966) for refinement of powder data with overlapping intensities. The data at 11°K were refined to include magnetic and nuclear intensities. Occupancy factors for Ba and Tb were varied in the refinement at 46°K. Temperature factors were fixed in the 11 and 80°K refinements at values judged to be reasonable with respect to those obtained in the refinements at 46 and 298°K, because of insufficient data. The positional and thermal parameters are shown in Table 1. It will be noted that our room-temperature value of the oxygen positional parameter agrees well with that reported by Jacobson *et al.*, in spite of our lower accuracy at that temperature. The oxygen x parameter shows a slow monotonic increase with temperature in the direction of the cubic value of 0·75. One might anticipate a transition to a higher symmetry above room temperature. If the values of the parameter were linearly extrapolated, a very high transition temperature would be expected. However, it is reasonable to suppose that the parameter should behave in the manner of a Brillouin function and begin to approach the ideal cubic value more rapidly as the temperature is raised. The occupation numbers in the table do not necessarily indicate departures from stoichiometry; they may reflect uncertainties in the scattering lengths and in the form factor used in the refinement of the magnetic and nuclear data (11°K).

The magnetic reflections observed at 11 and 15°K can be indexed on a doubled pseudocubic cell h, k, and l odd. (The very small departure from cubic symmetry has a negligible effect on magnetic intensities and will be ignored in the treatment of magnetic scattering.) The indexing, by itself, implies that the spins are collinear and that the magnetic structure is of the G-type. This result can be seen in the following way: In the doubled pseudocubic cell, atoms with magnetic vectors $\mathbf{K}_i$, assumed to be arbitrarily directed, are located at positions $x_l,y_l,z_l=0,0,0;\ \frac{1}{2},0,0;\ 0,\frac{1}{2},0;\ 0,0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$. The magnetic 'structure factor' $\mathbf{K}_{hkl}=\sum_l \mathbf{K}_l \exp{(hx_l+ky_l+lz_l)}$ is thus:

$$\begin{aligned}\mathbf{K}_{hkl}=\mathbf{K}_1+\mathbf{K}_2\exp(\pi ih)+\mathbf{K}_3\exp(\pi ik)+\mathbf{K}_4\exp(\pi il)\\ +\mathbf{K}_5\exp[\pi i(h+k)]+\mathbf{K}_6\exp[\pi i(k+l)]\\ +\mathbf{K}_7\exp[\pi i(h+l)]+\mathbf{K}_8\exp[\pi i(h+k+l)].\quad(1)\end{aligned}$$

Since $\mathbf{K}_{hkl}$ depends only on the parities of h, k and l, the reflections are conveniently divided into eight groups determined by these parities, within which $\mathbf{K}_{hkl}$ is a constant. Of these groups, only the h-odd, k-odd, l-odd reflections have non-zero intensities. If a magnetic reflection vanishes, it implies that $\mathbf{e}_{hkl}\times\mathbf{K}_{hkl}=0$ for that reflection ($\mathbf{e}_{hkl}$ is the

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Table 1. *Positional and thermal parameters in* $BaTbO_3$

Space group $R\bar{3}c$, $a=6{\cdot}050\ (5)^*$ Å, $\alpha=60{\cdot}13\ (5)^\circ$ at 298°K.

Temperature (°K)	11	46	80	298
Wavelength (Å)	1·2016	1·2016	1·3642	1·2016
Oxygen x parameter	0·7073 (3)	0·7096 (12)	0·7104 (4)	0·7131 (15)
Ba occupancy factor	1·000 (†)	1·000 (4)	1·000 (†)	1·000 (†)
Tb occupancy factor	1·002 (20)	0·979 (3)	0·979 (†)	0·979 (†)
Ba temperature factor	0·13 (†)	0·26 (26)	0·28 (†)	0·54 (9)
Tb temperature factor	0·06 (†)	0·12 (18)	0·13 (†)	0·40 (7)
O temperature factor	0·33 (†)	0·65 (13)	0·70 (†)	1·06 (24)
$R=\dfrac{\sum\omega(I_{\text{obs}}-I_{\text{calc}})^2}{\sum I^2_{\text{obs}}}$	0·031 (‡)	0·044	0·108	0·027
Number of observations	11	20	9	12

* Figures in parentheses give the estimated standard deviation in the last significant figure.

† This parameter not varied in refinement.

‡ Simultaneous refinement of nuclear and magnetic intensities (the magnetic moment is an additional variable here).

scattering vector); if one of the parity classes is absent, however, it follows that $\mathbf{K}_{hkl}$ is zero since $\mathbf{e}\times\mathbf{K}$ must vanish for constant $\mathbf{K}$ and variable $\mathbf{e}$. Thus, setting $\mathbf{K}_{hkl}$ in equation (1) equal to zero for all but the all-odd class of reflections, we obtain a set of eight relations connecting the individual moments, which on further manipulation yield the following relations among the atomic moments: $\mathbf{K}_1=-\mathbf{K}_2=-\mathbf{K}_3=-\mathbf{K}_4=\mathbf{K}_5=\mathbf{K}_6=\mathbf{K}_7=-\mathbf{K}_8$. These relations demonstrate that the moments must be collinear; placing the moments at the positions as labeled above shows them to be arranged in the *G*-type antiferromagnetic structure. The magnetic moment of Tb^{4+} was obtained by a least-squares refinement of the magnetic and positional parameters from the data at 11°K. The form factor for Tb^{4+} was estimated by a linear extrapolation of theoretical values for the isoelectronic Eu^{2+} and Gd^{3+} (Blume, Freeman & Watson, 1962). The value of $\langle q^2\rangle$, the parameter related to spin orientation, was taken to be $\frac{2}{3}$, the average over cubic forms (Shirane, 1959), inasmuch as the rhombohedral splittings of the magnetic reflections were not resolved. The refined value of the Tb^{4+} moment is $6{\cdot}66\ (11)\mu_B$, which is less than 5% below the free-ion value for an $^8S_{7/2}$ ground state.

At 11°K, the temperature is about one third of the Néel temperature. For an ion with $S=\frac{7}{2}$, the reduced magnetization at this temperature should be about 0·95. Applying this factor to the calculated value of the terbium moment yields a value of $7{\cdot}01\mu_B$ for Tb^{4+} at 0°K, which is the theoretical value within 0·15%.

It is of some interest to compare the Néel temperature of 36°K for this compound with the value of 2·4°K in $LaErO_3$ (Moreau, Mareschal & Bertaut, 1968). Although the magnetic moment of Er^{3+} is larger than that of Tb^{4+}, and the distances are comparable, the Tb^{4+} compound has a 15-fold stronger magnetic interaction. This may be due to the appearance of superexchange mechanisms resulting from the polarization of the metal–oxygen bond induced by the higher formal charge on the Tb^{4+} (greater covalency).

References

BLUME, M., FREEMAN, A. J. & WATSON, R. E. (1962). *J. Chem. Phys.* **37**, 1245.

IBERS, J. A. & HAMILTON, W. C. (1966). *J. Chem. Phys.* **44**, 1748.

JACOBSON, A. J., TOFIELD, B. C. & FENDER, B. E. F. (1972). *Acta Cryst.* B**28**, 956.

MOREAU, J. M., MARESCHAL, J. & BERTAUT, E. F. (1968). *Solid State Commun.* **6**, 751.

SHIRANE, G. (1959). *Acta Cryst.* **12**, 282.

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2,4,5-Trichloro-6-(methylthio)isophthalonitrile.

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$C_9H_3N_2SCl_3$, monoclinic, $P2_1/c$, $a=7{\cdot}705\ (6)$, $b=32{\cdot}356\ (28)$, $c=8{\cdot}901\ (7)$ Å, $\beta=99{\cdot}86\ (4)^\circ$, 25°C, $M=277{\cdot}56$, $Z=8$, $D=1{\cdot}682$ g.cm^{-3}. Bond distances and angles are normal but the molecules show significant deviations from planarity. Unusually short intermolecular contacts are found between cyanide and chloride functions.

Introduction

This crystal structure determination was undertaken to identify positively the substituent positions in a compound known to be a trichloro(methylthio)isophthalonitrile (Domenico, 1970), but which could not be unambiguously identified by conventional spectroscopic methods. Solution of the structure showed the isomer to be 2,4,5-trichloro-6-(methylthio)isophthalonitrile. The structure study also revealed the presence of unusually short interatomic dis-

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