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NEUTRON DIFFRACTION AND THE MAGNETIC STRUCTURES OF SOME RARE EARTH DIBORIDES AND TETRABORIDES*

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Summary

The crystal structures and magnetic structures of tetragonal ErB_4 and DyB_4 were studied by neutron diffraction on polycrystalline materials. For ErB_4 the crystal structure data were verified by single-crystal measurements. Both compounds are ordered antiferromagnetically with the Shubnikov space group *Pb'am*, which belongs to the orthorhombic crystal system.

TbB_2 was studied in the form of polycrystalline samples. TbB_2 shows ferromagnetism below T_C = 151 K with a moment μ of 8.3 $\mu_B(Tb^{3+})^{-1}$, which is about 7% below the free-ion value. Therefore the influence of an applied magnetic field was studied and as a result we concluded that in a zero field the magnetic moments are ordered on a cone, the cone axis being parallel to the *c* axis and with a half-cone opening angle of 20°. When a field is applied the cone gradually closes and at about 5 kOe the moments are aligned parallel to the *c* axis. A further increase in the magnetic field (up to 65 kOe) yields a further increase in magnetization without reaching saturation. In agreement with earlier magnetization measurements we observed a relatively strong magnetocrystalline anisotropy in TbB_2.

1. Introduction

The magnetic properties of rare earth borides have been neglected by scientists for a long time despite their interesting behaviour and their potential use in many applications. Systematic investigations have been reported by Etourneau and his coworkers [1, 2] on several rare earth tetraborides and hexaborides and by Buschow [3] on rare earth diborides, tetraborides and hexaborides. These studies were limited to measurements of the bulk magnetic properties, the magnetization and the susceptibility. They indicated magnetic ordering at low temperatures to ferromagnetic or antiferromagnetic configurations in many cases. However, many questions about

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the magnetic behaviour are still unresolved. The magnetic interactions in these compounds are quite complex and are only partly understood at the moment.

In cooperation with the above groups we have begun to study rare earth borides in more detail by neutron diffraction in order to establish their magnetic structures in the ordered state and their magnetic interactions. The experiments are aimed not only at a better and more detailed understanding of the magnetic properties but also at the verification and refinement of the crystal structures (this cannot be achieved with X-rays).

2. Principles of neutron diffraction

X-ray diffraction is based on the electromagnetic interaction between the electromagnetic radiation and the charge of the electrons; hence X-rays "see" the electrons and probe the electron density. Neutrons interact via nuclear interactions with the nuclei and thus are used to locate the nuclei, *e.g.* they can also be used to determine the crystal structures. However, it is now possible to locate light elements, such as boron, in a matrix of heavy elements, such as the rare earth ions. In addition to this nuclear interaction there is also a simultaneous dipole–dipole interaction between the magnetic moment of the neutron and the magnetic moments of the ions; this interaction is the basis of a study of magnetic structures and magnetic properties [4]. In our study of rare earth borides the interaction is with the spin–orbit-coupled magnetic moments of the rare earth ions.

The magnetic moment of the neutron is utilized as a probe on an atomic scale to demonstrate the magnetic behaviour of the crystal. We can measure the value of the rare earth moments, their direction in the crystal and their orientation relative to each other, including the magnetic symmetry of the crystal. Investigations as a function of temperature yield the transition temperatures and the type of transition for the individual sublattices; with applied fields the inner fields and magnetic anisotropies can be studied and conclusions about the type of interaction can be drawn.

3. The crystal structure of ErB_4 and DyB_4

Using X-rays boron which has a total of five electrons cannot be safely located in a structure containing erbium or dysprosium which have 68 and 66 electrons. (The scattering power is proportional to the square of the number of electrons.) However, boron can be easily seen with neutrons since the neutron scattering powers of boron and erbium or dysprosium are comparable.

ErB_4 and DyB_4 are isostructural with UB_4 [5]. They crystallize in the tetragonal space group $P4/mbm$ D_{4h}^5 with four formula units per cell. Their crystal structures were refined by least-squares methods from neutron

diffraction powder data collected at room temperature [6]. The results are summarized in Table 1.

TABLE 1

Lattice parameters and atomic parameters at room temperature of ErB_4 and DyB_4

	ErB_4	DyB_4
a_0	7.0705(7)	7.021(1)
c_0	4.0000(4)	3.972(1)
x for Er(Dy); 4g; x, $\frac{1}{2}+x$, 0	0.3183(9)	0.319(2)
z for B(1); 4e; 0, 0, z	0.2031(13)	0.196(7)
x for B(2); 4h; x, $\frac{1}{2}+x$, $\frac{1}{2}$	0.0859(18)	0.086(2)
x for B(3); 8j; x, y, $\frac{1}{2}$	0.1767(4)	0.175(2)
y for B(3); 8j; x, y, $\frac{1}{2}$	0.0382(6)	0.039(2)

For ErB_4 we repeated the neutron diffraction measurements recently on a single crystal enriched by ^{11}B, the isotope with a low absorption. The crystal was kindly provided by Professor Etourneau, University of Bordeaux. The values for ErB_4 given in Table 1 are the results from this single-crystal measurement.

The characteristic feature of the structure, shown in Fig. 1, are boron octahedra connected by seven-member boron rings at $z = \frac{1}{2}$. The AB_4 tetraboride structure is a synthesis of the AB_2 diboride structure (hexagonal boron nets) with the AB_6 hexaboride structure. In the hexaborides boron octahedra are connected by B–B bonds between all octahedral corners along all the three axes of the unit cell. In the tetraborides we find boron octahedra forming chains along the tetragonal c axis. The combination of seven-member rings with the four-member rings in the octahedra is the closest approach possible to an h.c.p. structure. The result is a densely packed plane of boron atoms at $z = \frac{1}{2}$ with the rare earth ions in $z = 0$ ($z = 1$) and at positions below and above the centres of the seven-member boron rings.

The B–B distances in the boron octahedra vary between 1.72 and 1.78 Å, with a mean value of 1.745 Å. In the seven-member boron rings we find distances ranging from 1.67 to 1.77 Å (ErB_4) and from 1.71 to 1.78 Å (DyB_4) with a mean value of 1.73 Å. The B(1)–B(1) distance along the c axis between two octahedra is much shorter and measures only 1.59 Å in ErB_4 and 1.56 Å in DyB_4.

It has been shown by Berrada *et al.* [2] that the magnetic phase transition of ErB_4 at $T_N = 16$ K is accompanied by a contraction of the lattice parameter a_0 by $\Delta a_0 = 0.0005$ Å; however, no splitting in a_0 (this would indicate orthorhombic distortion) could be detected. In contrast our neutron diffraction measurements [7, 8] require the Shubnikov space group *Pb'am* (which is derived from *Pbam* D_{2h}^9 in the orthorhombic crystal system) for the magnetic structure. New experiments are at present under way in order to clarify this point.

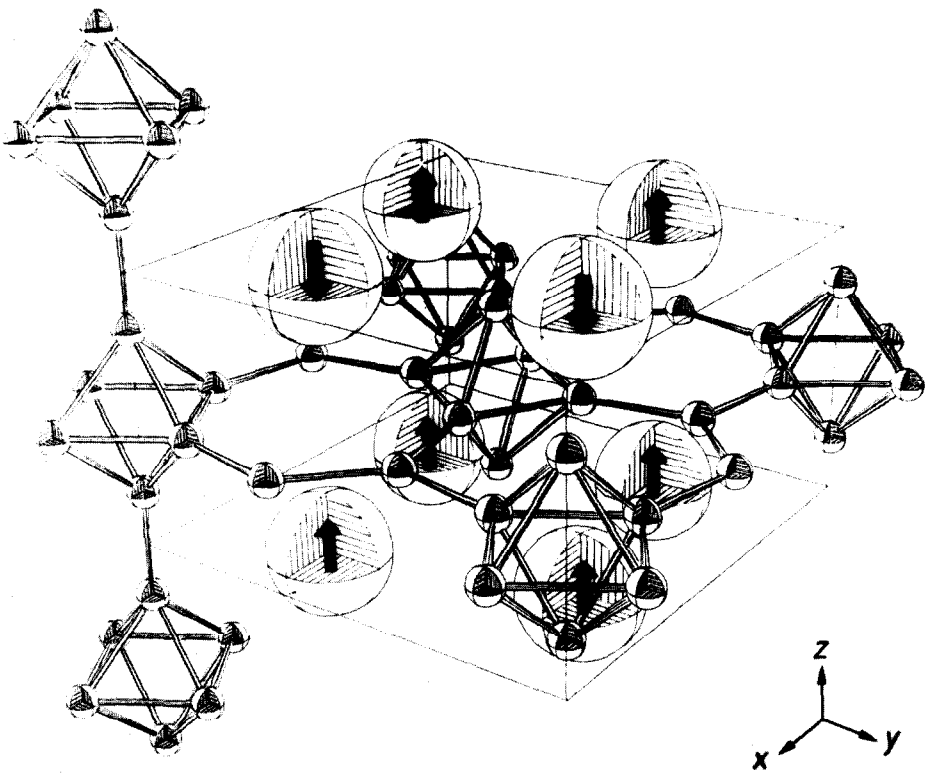


Fig. 1. The crystal structure and the magnetic structure of ErB_4. The magnetic moments are indicated by arrows. The magnetic structure is observed below 16 K. DyB_4 has the same structure.

4. The magnetic structure of ErB_4 and DyB_4

Below the Néel transition temperatures T_N = 16 K and T_N = 21 K for ErB_4 and DyB_4 respectively, additional new lines were observed in the neutron diffraction diagrams of both compounds, whereas other lines were strongly enhanced as a result of the long range order of the rare earth magnetic moments. From the diffraction diagrams the magnetic structure as shown in Fig. 1 was derived. From the measured intensities we calculated that the magnetic moments are pointing along the tetragonal c axis with parallel and antiparallel orientation to each other, as shown in Fig. 1. Thus we have puckered ferromagnetic (010) planes (or non-distinguishable (100) planes) which are stacked antiparallel to each other along [100] (or along [010]). The alternative configuration, which can be excluded, would have ferromagnetic planes approximately along (110). The values of the magnetic moments (at 4.2 K) are $8.2 \pm 0.2\,\mu_B\ (Er^{3+})^{-1}$ and $9.8 \pm 0.4\,\mu_B\ (Dy^{3+})^{-1}$.

5. Magnetic symmetry

At present there is no crystallographic evidence for a crystallographic phase transition to orthorhombic symmetry at the Néel transition temperatures. However, it can easily be seen from Fig. 1 that the fourfold c axis of $P4/mbm$ is lost. The configuration observed and depicted can only be described by the Shubnikov symmetry element $2'$ along the c axis, *e.g.* a twofold rotation axis with a change of direction. In the orthorhombic crystal system this leads to the space group $Pb'am$ or $Pba'm$. Both groups are equivalent as long as $a_1 = a_2$. At present we are studying this problem by neutron diffraction on the single crystal of ErB_4 to distinguish between the two space groups.

6. The magnetic structure of TbB_2

So far we have studied TbB_2 from the group of rare earth diborides. This class of borides crystallizes in the hexagonal AlB_2-type structure with a space group $P\bar{3}m\ D_{3d}^3$. The crystal structure consists of alternate h.c.p. terbium and h.c.p. boron layers (Fig. 2).

The RB_2 compounds with R ≡ Tb, Dy, Ho and Er have been studied by Buschow [3]. The compounds were prepared by arc melting of stoichiometric quantities of rare earths (of 99.9% purity) and boron (of 99.99% purity). Except for TbB_2 considerable differences were observed between T_C and the asymptotic Curie temperature. It was concluded therefore that the magnetic ordering phenomena are more complicated than simple ferromagnetic ordering. This also follows from the shape of the magnetization

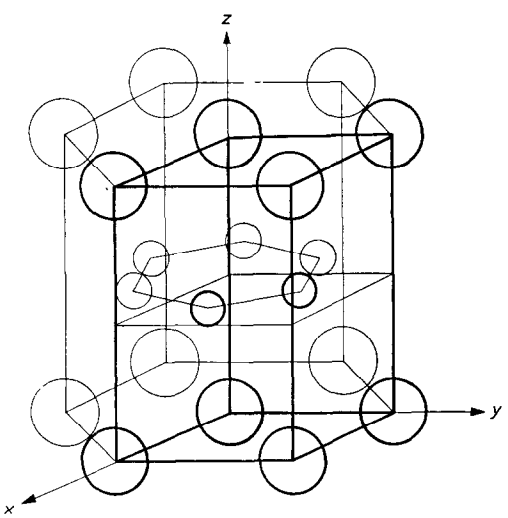
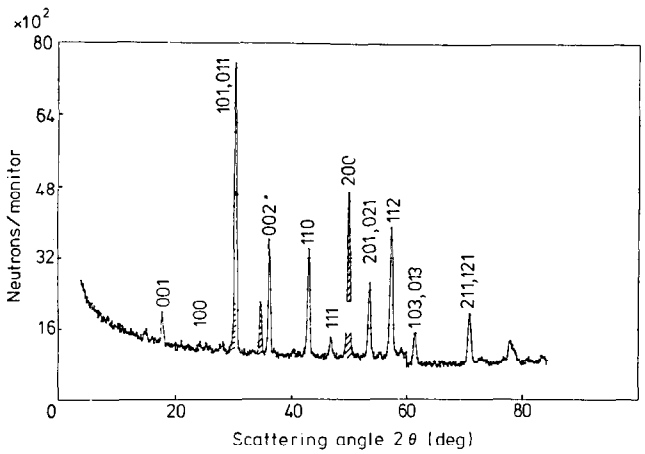


Fig. 2. The crystal structure of TbB_2 (AlB_2 type).

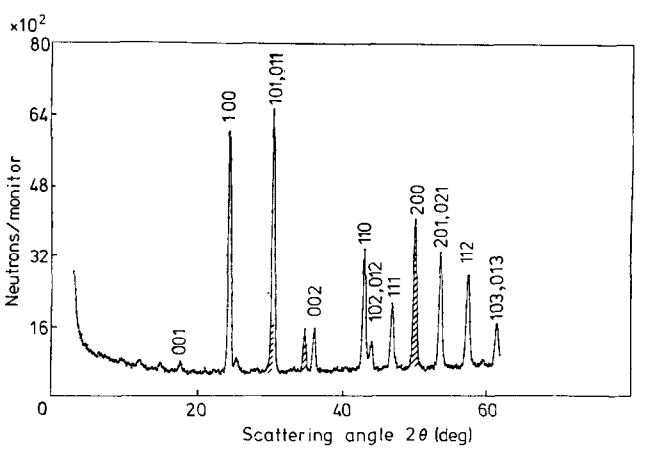
versus temperature curves, which involves two steps [9]. TbB_2 was selected as the first sample to be studied by neutron diffraction.

The neutron diffraction experiments were performed on a powdered sample enriched in ^{11}B (97%). The diffraction diagrams are shown in Fig. 3 for 300 and 5 K. They are indicative of ferromagnetic ordering with no indication at all of antiferromagnetism or of a helical moment configuration. A helical moment configuration would lead to satellite reflections which cannot be indexed on a simple unit cell.

The onset of ferromagnetic ordering begins at T_C = 151 K, which has been established from the temperature dependence of the (100) reflection and of the (101), (011) reflection [9]. From the measured intensities we calculated a magnetic moment value of μ = 8.3 ± 0.5 μ_B $(Tb^{3+})^{-1}$ at 5 K. This is about 7% below the free-ion value.



(a)



(b)

Fig. 3. Neutron diffraction diagrams of TbB_2 obtained (a) at 300 K and (b) at 4.2 K.

7. Neutron diffraction of TbB_2 in a magnetic field

In the magnetization *versus* temperature curves of DyB_2 and TbB_2 [3, 9] we observed two steps. In order to study this phenomenon we applied magnetic fields to the sample during the neutron diffraction experiments.

Figure 4 shows the temperature dependence of the purely magnetic reflection (100) without a field and with a field of 18 kOe. In both cases we found the same Curie temperature of 150 K. The same result was obtained for the (101), (011) reflection (this is not shown in Fig. 4).

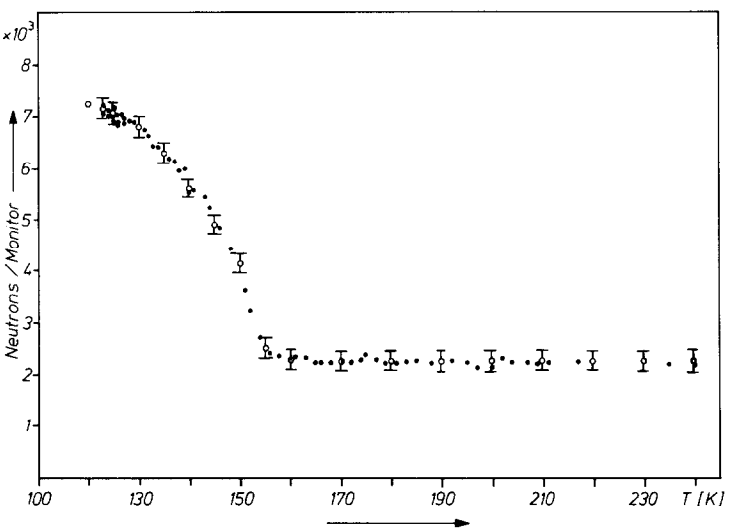


Fig. 4. The temperature dependence of the purely magnetic reflection (100) of TbB_2 without a magnetic field (Φ) and in a field of 18 kOe (●). In both cases T_N = 150 K.

In Fig. 5 we show the field dependence of several reflections at a constant temperature of 4.2 K. The measurements were made with a four-detector bank [10], *i.e.* we measured simultaneously four different positions with four detectors. In Fig. 5 three curves for (001), for (100) and for the pair (101), (011) are shown together with the curve for the background value.

The results obtained are not easy to understand. With powdered samples there is a random orientation of the crystallites in the beam. The magnetic field was vertical in our experimental arrangement and was always perpendicular to the scattering plane which contains the incoming beam, the reflected beam and the scattering vectors of the reflecting planes. Crystallites which have their normals to the planes not in the scattering plane do not contribute to the diffraction.

The lowest curve in Fig. 5 shows the field dependence of (001), which is a purely nuclear reflection and thus is not affected by a field. The background is also included and this stays constant. These two values indicate

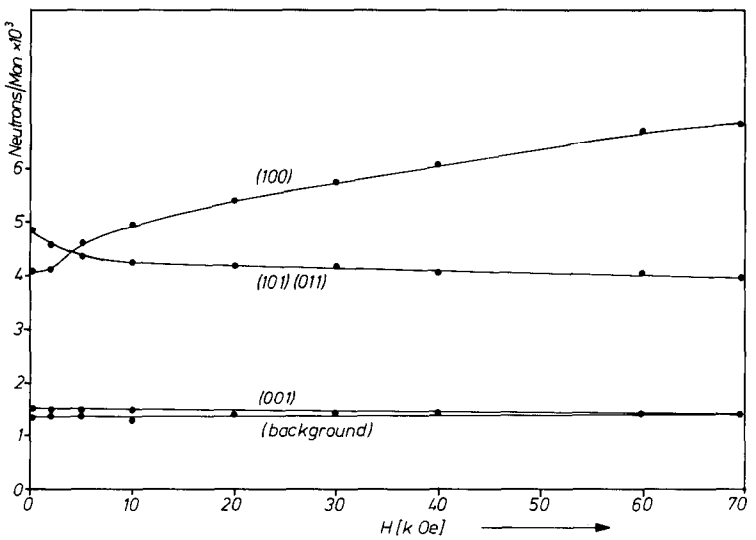


Fig. 5. The field dependence of several reflections of TbB_2 at a constant temperature of 4.2 K.

that no macroscopic effects such as the rotation of crystallites are superimposed on the magnetic diffraction measurements.

The observed magnetic intensity is proportional to $\sin \alpha = \sin(\epsilon, \kappa)$ where α is the angle between the reciprocal lattice unit vector ϵ (the scattering vector) and the magnetic moment direction κ [4]. Since the magnetic contribution to (001) is zero in a zero field, it follows directly that the magnetic moments in a zero field are parallel to the c axis. By the same arguments the reflection (100) must be maximum ($\sin \alpha = 1$), as is observed.

If we now consider the field dependence (Fig. 5) we observe a purely magnetic reflection for the (100) curve, *i.e.* a sharp increase in the intensity between 2 and 5 kOe followed by a slight but steady increase in the intensity. At the same time the intensity of the (101), (011) curve decreases.

We can divide the effect of a magnetic field into three regions. At the beginning there is no effect; between about 2 and 5 kOe there is a sharp increase; above about 5 kOe the field exerts only a slight influence.

To interpret this, we propose that at $H = 0$ the magnetic moments are arranged on a cone around the c axis. The orientation on the cone is random and therefore we can measure only the moment value projected onto the c axis. From the measured values we can calculate a half-cone opening angle of about 20°.

The increase in the intensity in the second region from 2 to 5 kOe we interpret as meaning that the cone gradually closes because of the influence of the magnetic field. At 5 kOe the moments are all aligned parallel to the c axis and we can calculate the full free-ion value of $8.8\,\mu_B$ $(Er^{3+})^{-1}$ from the observed neutron intensity.

A further increase in H will now force the moments to rotate out of the easy direction, the c axis, into the direction of the magnetic field. This yields a steady increase in the neutron intensity. At the limiting field strength of 65 kOe, magnetization is not yet reached.

The measured field dependence reported by Schäfer *et al.* [8] suggests that relatively strong magnetocrystalline anisotropies are involved in TbB_2. In these magnetization measurements a magnetic moment of only $4\,\mu_B$ could be attained at 18 kOe. From the hysteresis measurements an intrinsic coercive field of about 12 kOe was calculated. This high value, in combination with the value of the magnetization, constitutes a rather high anisotropy energy. Using the value $4\pi I_r = 13.6$ G for the observed remanence, a value of more than 40 MG Oe is derived from the energy product. This behaviour is clearly also represented in the observed neutron diffraction data.

Acknowledgments

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