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NEUTRON DIFFRACTION STUDIES OF TbB_4 AND ErB_4*

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Summary

Neutron diffraction data are presented on the rare earth tetraborides TbB_4 and ErB_4 which crystallize with the tetragonal space group *P4/mbm*. Positional and thermal parameters were refined by full matrix least-squares analysis from single-crystal measurements to agreement values R of 0.018 and 0.030 respectively. Collinear antiferromagnetic ordering was derived from the low temperature powder data ($T_N = 43$ K for TbB_4 and $T_N = 13$ K for ErB_4). The magnetic structures differ in their absolute moment orientations, which are perpendicular to the tetragonal c axis for TbB_4 and along the c axis for ErB_4.

1. Introduction

Boron reacts with almost all metallic elements to form compounds with a large number of different metal-to-boron atomic ratios and a great variety of crystal structure types [1]. In recent years the rare earth borides have attracted considerable scientific attention because of their remarkable electrical and magnetic properties which, in combination with their high thermal stabilities, make them valuable materials for application in electronic technology.

Neutron diffraction methods are well suited for investigating the crystallographic and magnetic properties of the rare earth borides. In the presence of the heavy rare earth atoms, the positions of the light boron atoms can be located much more accurately by means of neutron diffraction than by X-ray diffraction. Furthermore, the magnetic scattering of neutrons provides detailed information on the ordered magnetic structures occurring at lower temperatures.

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In continuation of our previous investigations on rare earth borides [2] we present here the results from neutron diffraction studies of the tetraborides TbB_4 and ErB_4. Positional and thermal vibration parameters for the atoms were refined from room temperature single-crystal diffractometer data. From previous macroscopic magnetic measurements [3, 4] both compounds are known to exhibit antiferromagnetic order at low temperatures. The magnitude and orientation of the ordered magnetic moments were determined from low temperature neutron powder diffraction data.

2. Experimental details

Polycrystalline material was prepared by borothermal reduction of the metal oxides at 2100 K under vacuum. Single crystals of TbB_4 and ErB_4 were grown by a flux method [5, 6]. Because of the strong absorption of thermal neutrons by natural boron ($\sigma = 430 \times 10^{-24}$ cm^2) boron enriched with the ^{11}B isotope (97%) had to be used. Room temperature diffraction data of TbB_4 and ErB_4 single crystals were collected on the computer-controlled four-circle neutron diffractometer Nancy [7] at the DIDO research reactor in Jülich. The measurements were performed in the θ–2θ scan mode with a wavelength $\lambda = 1.287$ Å. A detailed summary of the experimental data is given in Table 1.

TABLE 1

Experimental data for the single-crystal measurements ($T = 300$ K)

Parameter	*TbB_4*	*ErB_4*
Crystal diameter (mm)	0.8	1.0
Wavelength (Å)	1.287	1.287
$\{(\sin\theta)/\lambda\}_{\max}$	0.673	0.704
Number of steps per scan	24	24
Stepwidth $\Delta(2\theta)$ (deg)	0.1	0.1
Counting time per step (s)	300	300
Monitor reflection interval	9	9
Number of octants involved	5	3
Number of reflections recorded	399	249
Number of unique reflections	38	43
Number of unobserved reflections	7	7
Internal R value	0.013	0.024

Neutron diffraction diagrams of the polycrystalline samples were taken at 300 and 4.2 K on the two-circle neutron diffractometer Katinka. The neutron wavelength was 1.203 Å. The samples were contained in a cylindrical sample holder of 7 mm diameter and 20 mm height. The measured absorption rate at the centre of the sample was about 80%, corresponding to a linear absorption coefficient μ of 2.3 cm^{-1}.

3. Crystal structure

TbB_4 and ErB_4 crystallize at room temperature with the tetragonal space group *P4/mbm* (D_{4h}^5), isostructural with UB_4 [8]. The lattice constants were calculated by least-squares methods from the observed peak positions in the powder diagrams at 300 and 4.2 K. The room temperature values were checked with the single crystals on the eulerian cradle from independently optimized settings of ten reflections. The unit cell data are summarized in Table 2.

TABLE 2

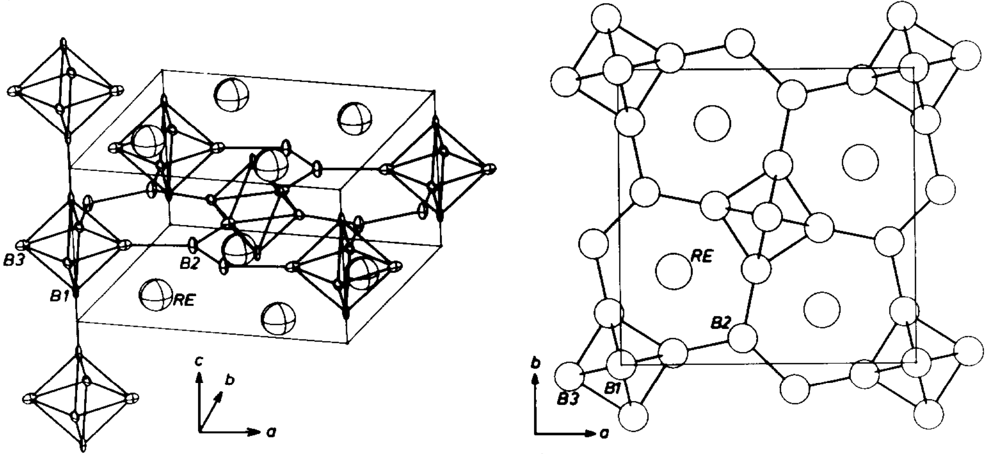
Crystallographic data based on single-crystal refinements at 300 K

Parameter		*TbB$_4$*	*ErB$_4$*
Unit cell data			
a (Å)		7.120(3)	7.071(1)
c (Å)		4.042(2)	4.000(1)
c/a		0.5677	0.5657
V (Å^3)		204.9(2)	200.0(1)
M		202.17	210.50
Z		4	4
ρ_N ($\times 10^3$ kg m^{-3})		3.95	4.21
Atomic parameters			
x Tb, Er 4g		0.3175(11)	0.3183(9)
z B(1) 4e		0.2017(17)	0.2031(13)
x B(2) 4h		0.0875(16)	0.0859(18)
x B(3) 8j		0.1758(7)	0.1767(4)
y B(3) 8j		0.0387(7)	0.0382(6)
Atomic distances (Å)			
B(1)–B(1)	Along c	1.630(10)	1.625(1)
B(1)–B(3)	Octahedron	1.760(6)	1.745(4)
B(3)–B(3)		1.813(7)	1.808(5)
B(2)–B(2)	Seven-membered ring	1.762(16)	1.718(18)
B(2)–B(3)		1.721(12)	1.712(13)
⟨B–B⟩	Octahedron	1.774(2)	1.760(1)
⟨B–B⟩	Seven-membered ring	1.775(4)	1.784(3)
⟨(Tb, Er)–B⟩	18 coordination	2.818(2)	2.754(1)

Values in parentheses are standard deviations.

The structure refinements based on the single-crystal data were carried out using the full matrix least-squares program YORFLS. Isotropic secondary extinction was included in the refinement according to Zachariasen [9] by putting a correction value g into the list of variables. The final values were $g = 2.9(3) \times 10^{-5}$ and $g = 1.7(1) \times 10^{-5}$ for TbB_4 and ErB_4 respectively. The final R values were $R = 0.023$ and $R_{ou} = 0.018$ for TbB_4 and $R = 0.032$ and $R_{ou} = 0.030$ for ErB_4 (ou, omitting unobserved reflections). Lists of observed and calculated intensity data will be provided on request. The refined positional parameters and the resulting atomic distances are given in Table 2.

The rare earth tetraboride structure is depicted in Fig. 1. The covalently bonded boron atoms form chains of boron octahedra (four B(3) atoms, two B(1) atoms) along the c axis connected by the B(1) atoms. The octahedra are linked in the (001) plane by pairs of B(2) atoms forming together with the B(3) atoms rigidly bonded seven-membered boron rings. The weighted mean B–B distances are 1.774 Å in TbB_4 and 1.766 Å in ErB_4. Between the planar B(2)–B(3) atomic layers parallel to the (001) plane there are large voids where the rare earth atoms are accommodated. The rare earth atoms are surrounded by six B(2) atoms and eight B(3) atoms belonging to one seven-membered ring from each of the two adjoining planar layers and by four B(1) atoms from two neighbouring boron octahedra. The average of the 18 Tb–B distances in TbB_4 is 2.818 Å and the corresponding value for ErB_4 is 2.754 Å.



(a) (b)

Fig. 1. The rare earth tetraboride structure. Chains of boron octahedra along the [001] direction are linked by planar seven-membered rings above and below the planes of rare earth atoms (RE): (a) three-dimensional view; (b) projection onto the tetragonal basal plane.

4. Thermal behaviour

The refinement calculations were performed by varying the anisotropic thermal parameters $\beta_{ij} = 2\pi^2 U_{ij} a^*_i a^*_j$, where the symmetrical tensor U_{ij} reflects the symmetry-dependent anisotropy of the mean square vibrations $\langle u^2 \rangle$ of the individual atoms. In reciprocal space, constant anisotropic thermal coefficients are represented by an ellipsoid whose Fourier transform results in an equiprobability surface in direct space. Mean thermal vibrational lengths of the atomic nuclei along the crystallographic axes are derived from $d_i = a_i(\beta_{ii}/2)^{1/2}/\pi$. Thermal coefficients and vibrational lengths are summarized in Table 3 for TbB_4 and ErB_4.

TABLE 3

Atomic thermal parameters $\beta_{ij} \times 10^4$ and mean vibrational lengths d (Å) for TbB_4 (upper lines) and ErB_4 (lower lines) ($T = 300$ K)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	d_a	d_c
Tb	43(17)	$(=\beta_{11})$	118(30)	1(11)	0	0	0.105	0.099
Er	26(23)	$(=\beta_{11})$	284(24)	26(11)	0	0	0.081	0.152
B(1)	1(16)	$(=\beta_{11})$	27(32)	0	0	0	0.018	0.048
	26(17)	$(=\beta_{11})$	71(27)	0	0	0	0.081	0.076
B(2)	3(23)	$(=\beta_{11})$	34(44)	0	0	0	0.028	0.053
	6(18)	$(=\beta_{11})$	227(30)	5(9)	0	0	0.039	0.136
B(3)	5(16)	5(13)	12(31)	3(15)	0	0	0.037	0.032
	16(12)	12(11)	168(25)	12(8)	0	0	0.064	0.117

Values in parentheses are standard deviations.

In general, we observe stronger thermal vibrations for the rare earth atoms than for the boron atoms, although the atomic weights of terbium and erbium exceed that of boron by a factor of 15. This experimental result is not biased by uncertainties in the non-spherical electron distribution of atoms, as could be the case in X-ray analysis: neutrons are scattered by the atomic nuclei and not by the electrons. The observed vibrations of the rare earth ions are believed to be connected with the large cages of about 4 Å diameter in the tetraboride structure, where the metal atoms are relatively free to vibrate, at least at room temperature. Calculating the lengths of the 99.9% probability ellipsoids along the principal axes we conclude that the terbium ions show basically isotropic vibrations whereas the erbium ions show a stronger vibration along the [001] direction (see Table 3). Considering the thermal behaviour of the boron atoms, the refinement calculations reveal thermal parameters that are systematically lower in TbB_4 than in ErB_4, although there are no essential differences between the positional parameters of the two compounds.

By comparing the lattice constants at 300 K determined by neutron diffraction on single crystals with those at 4.2 K (from powder measurements) a thermal volume contraction of about 0.7% is observed uniformly for TbB_4 and ErB_4, corresponding to 5×10^{-3} Å^3 K^{-1}. This is in agreement with the overall picture that the rigidity of the tetraboride structure is determined by the boron network: seven-membered planar rings in the (001) plane connected by boron octahedra along the [001] direction (Fig. 1(a)). Metal atoms or ions, in our case terbium and erbium, are merely filling the empty cages and in principle are rattling around in those cages.

5. Magnetic structure

The antiferromagnetic structures of TbB_4 [10] and ErB_4 [11] were evaluated from the additional magnetic reflections appearing in the powder diffractograms recorded at 4.2 K. For both compounds the coherent magnetic scattering peaks can be indexed on the basis of the original chemical unit cell with four magnetic ions at positions $(x, 1/2+x, 0)$, $(\bar{x}, 1/2-x, 0)$ $(1/2+x, \bar{x}, 0)$ and $(1/2-x, x, 0)$. Referring to these positions, a collinear antiferromagnetic spin sequence $(+--+)$ was evaluated both for the terbium moments and for the erbium moments from the observed crystallographic extinctions ($0kl$, $k=2n$; $h0l$, $h=2n+1$).

However, there is an essential difference in the antiferromagnetic structures with respect to the absolute orientation of the ordered moments relative to the crystallographic axes. An evaluation of the observed integrated intensities yields an orientation of the moments perpendicular to the tetragonal c axis in TbB_4 but along the c axis in ErB_4 (Fig. 2). These configurations are invariant under the symmetry operations of the Shubnikov groups *Pbam'* for TbB_4 and *Pb'am* for ErB_4. Both groups are derived from the crystallographic orthorhombic space group *Pbam*, a subgroup of the tetragonal space group *P4/mbm*.

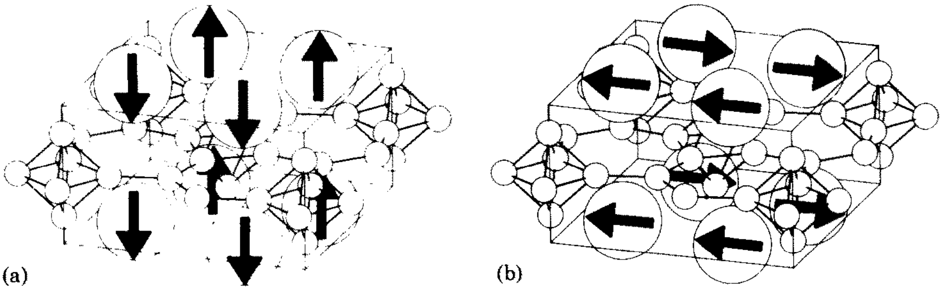


Fig. 2. A comparison of the antiferromagnetic structures of (a) ErB_4 with the moments oriented along the c axis and (b) TbB_4 with the moments oriented perpendicular to the c axis.

From the temperature dependence of several magnetic reflections the antiferromagnetic transition temperature of TbB_4 was determined as $T_N = 43 \pm 1$ K. Similar measurements recently performed on an ErB_4 single crystal (in addition to previous powder data) resulted in $T_N = 13.2 \pm 0.2$ K for ErB_4. The magnitudes of the antiferromagnetically ordered moments were determined by least-squares calculations with the 4.2 K powder data to give $\mu = 7.7 \pm 0.2\ \mu_B$ (Tb ion)$^{-1}$ and $\mu = 8.2 \pm 0.6\ \mu_B$ (Er ion)$^{-1}$. The agreement values between a total of 14 observed and calculated peak intensities each were minimized to $R = 0.044$ and $R = 0.068$ for TbB_4 and ErB_4 respectively.

6. Conclusions

Neutron diffraction proves to be an adequate method in providing reliable crystallographic and magnetic data especially for rare earth–boron compounds. The various structural data relate the known stability of these compounds to a network of stable boron octahedra and seven-membered boron rings. In terms of a linear combination of atomic orbitals model [12] the covalent boron bonds are constituted by 48 electrons of 16 trivalent boron atoms together with eight electrons from the four rare earth ions. The excess valence electrons of terbium and erbium are available for the conduction band, determining the strongly correlated electrical and magnetic properties.

A quantitative estimate of the possible magnetic exchange energies involved in the antiferromagnetically ordered state indicates the predominance of the indirect Ruderman–Kittel–Kasuya–Yosida exchange mechanism via conduction electrons. This was recently confirmed by the temperature and magnetic field dependences of the ordered magnetic moments in ErB_4 determined by low temperature neutron diffraction on a single crystal in an external magnetic field [13]. Similar measurements are in progress on TbB_4.

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