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LETTER TO THE EDITOR

Synthesis and magnetic properties of binary boride REB_{25} compounds

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Abstract

Binary REB_{25} (RE = Gd, Tb, Dy, Ho, Er) B_{12} icosahedral compounds were successfully synthesized and magnetic properties were measured. Measurements down to 1.8 K revealed that an antiferromagnetic-like transition occurs in TbB_{25} at 2.1 K. This transition temperature is almost one order of magnitude lower than that of the transition in the more magnetically dilute TbB_{50}. The structure of TbB_{25} is refined and, from the differences of structure, the previous conclusion that B_{12} icosahedra are indicated to play an important role in the transition of TbB_{50} is further supported. The other magnetic rare-earth compounds show Curie–Weiss behaviour down to the lowest temperatures, with values of the effective moment close to that expected for trivalent rare-earth compounds.

1. Introduction

The physical properties of binary boride compounds have recently been attracting much interest due to the discovery of striking phenomena such as the high-temperature superconductivity in MgB_2 ($T_C = 39$ K) [1] and the magnetic transitions in lanthanum-doped CaB_6 [2] and the magnetically dilute higher-boride system REB_{50} (RE = rare earth) [3, 4]. In this work, we report on the synthesis, crystallographic parameters, and magnetic properties of the series of magnetic rare-earth compounds REB_{25} (RE = Gd, Tb, Dy, Ho, Er).

The YB_{25}-type compound was first synthesized in the yttrium phase [5]. The structure of YB_{25} was not solved but it was suggested that the structure is similar to the orthorhombic $MgAlB_{14}$-type structure. Using parameters determined from recent work on carbon-containing yttrium boride YB_{25}-type single crystals [6] as an initial starting point for the refinement, we were able to satisfactorily refine the atomic positions of TbB_{25}. The structure is depicted and the previous assumption is found to be correct. The magnetic properties are also investigated and it is newly found from measurements down to 1.8 K that TbB_{25} has an antiferromagnetic-like

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transition at 2.1 K. This transition temperature is almost one order lower than that of TbB_{50} and the indication that the B_{12} icosahedra play an important role as regards the magnetic transition appearing in TbB_{50} is further supported.

2. Experimental procedure

REB_{25} (RE = Gd, Tb, Dy, Ho, Er) was synthesized by the borothermal reduction of rare-earth oxide under vacuum:

$$RE_2O_3 + (2n + 3)B \rightarrow 2REB_{(n)} + 3BO \qquad RE = Dy, Ho, Er \tag{1}$$

$$Tb_4O_7 + (4n + 7)B \rightarrow 4TbB_{(n)} + 7BO \tag{2}$$

where $n = [B]/[RE]$ is the ratio of the mixing composition. The raw starting material with $n = 25$ was found to yield the samples with the purest YB_{25}-type phase. Rare-earth oxide (99.9%) powder and B (99.9%) powder were pressed into pellets at 300 MPa. The reaction was performed under vacuum in a BN crucible surrounded by an inductively heated composite susceptor at ∼1900 °C. Samples were washed in nitric acid and boiled for short times to remove small impurities such as REB_6 and REB_{12}. The samples were characterized by using a high-resolution powder x-ray diffractometer (Rigaku Company; RINT2000) with Cu Kα radiation.

Chemical analyses of the samples were done with inductively coupled plasma (ICP) atomic emission spectroscopy after the samples were dissolved in nitric acid for 16 hours at 110 °C. The analyses yielded compositions of [B]/[RE] = 30.7, 26.9, 24.4, 26.3, and 25.4 for the GdB_{25}, TbB_{25}, DyB_{25}, HoB_{25}, and ErB_{25} samples, respectively. The value of [B]/[Gd] of 30.7 is larger than the ratios for the other compounds and might be due to a lower occupancy of the gadolinium sites. But it is not clear whether this is an intrinsic effect due to the large size of the gadolinium atom, the gadolinium phase being at the large-size end of the series of rare-earth atoms possible for producing the REB_{25} phase. Magnetic susceptibility was measured by using a SQUID magnetometer from 2 K to 300 K.

3. Results and discussion

3.1. Structural properties

The structure of the recently discovered YB_{25} compound was determined from x-ray powder diffraction and electron diffraction analyses to be monoclinic (space group $I112$ (No 5), $I11m$ (No 8), or $I112/m$ (No 12)) with lattice constants of $a = 0.58570(2)$ nm, $b = 0.82842(3)$ nm, $c = 1.03203(3)$ nm, and $\gamma = 90.402(3)^\circ$ [5]. Since the unit-cell dimensions were close to those of $YAlB_{14}$ [7] and the actual [B]/[Y] ratio in the $YAlB_{14}$ structure was nearly 25, it was speculated [5] that the crystal structure of YB_{25} is close to that of $YAlB_{14}$. $YAlB_{14}$ has the orthorhombic $MgAlB_{14}$-type structure [8, 9] with space group $Imma$ and lattice constants $a = 0.58212(3)$ nm, $b = 1.03950(4)$ nm, $c = 0.81825(3)$ nm. B_{12} icosahedral chains are aligned linearly along the b-axis with the yttrium atoms forming a zigzag chain in the direction of the a-axis.

The structure of the YB_{25}-type compounds has been further investigated by very recent structural studies on yttrium boride single crystals containing carbon [6]. By using the parameters determined in the single-crystal work as an initial starting point for the refinement, we were able to satisfactorily determine the atomic positions for our TbB_{25} sample. However, it should be noted that there is a large difference in that while the yttrium boride single crystals always contained carbon and the yttrium position was split, our samples are carbon free and the rare-earth positions are not split.

Powder x-ray diffraction data on TbB_{25} for the refinement were collected with a scanning step width of 0.02° and a sampling time of 8.6 s per step. The FULLPROF program [10] was used for the refinement. The least-squares refinement included the eight atomic positions, background parameters, lattice parameters, diffractometer zero point, parameters for fitting the peak profiles with pseudo-Voigt functions, and the isotropic thermal parameters of the boron atoms which were set to be the same, and that of the terbium atom. The occupancy of the terbium site was also refined while the boron sites are considered fully occupied. The refinement results converged with final agreement factors of $R_p = 6.78\%$, $R_{wp} = 8.99\%$, and $R_e = 3.72\%$. The refined lattice parameters of TbB_{25} are determined as $a = 0.58550(1)$ nm, $b = 1.033\,54(3)$ nm, $c = 0.828\,08(2)$ nm, and $\beta = 89.512(2)^\circ$ and the space group was found to be $I12/m1$. We follow the notation for $MgAlB_{14}$ and $YAlB_{14}$ in this work, which is equivalent to switching the b- and c-axes compared to the notation given above for YB_{25}. Table 1 lists the atomic parameters of TbB_{25}, while the observed and calculated diffraction patterns and their difference are shown in figure 1.

Table 1. Refined structure parameters from powder x-ray Rietveld analysis for TbB_{25} in the space group $I12/m1$; $Z = 1$, $R_p = 6.78\%$, $R_{wp} = 8.99\%$, $R_e = 3.72\%$, and the goodness of fit $\chi^2 = 5.84$. (The occupancy of Tb atoms is 0.53458.)

Atom	Site	x	y	z	b (Å^{-2})
Tb(1)	4i	0.25941	0	0.10064	0.72350
B(1)	8j	0.75891	0.35676	0.07970	1.25051
B(2)	8j	0.49296	0.35486	0.20572	1.25051
B(3)	8j	0.58385	0.20472	0.07869	1.25051
B(4)	8j	0.50466	0.17471	0.29471	1.25051
B(5)	8j	0.74291	0.41430	−0.13248	1.25051
B(6)	8j	0.73134	0.42287	0.27070	1.25051
B(7)	8j	0.90641	0.19227	0.08132	1.25051

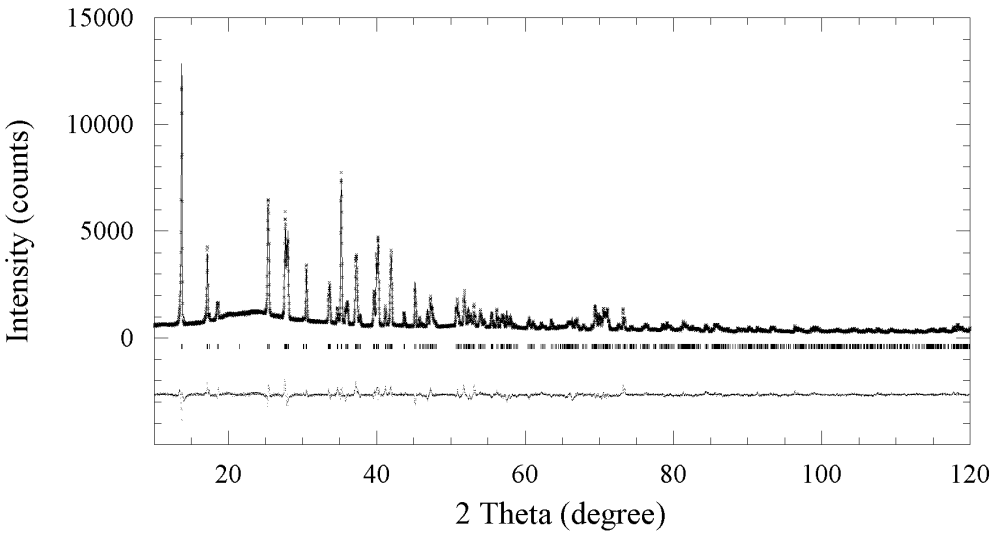
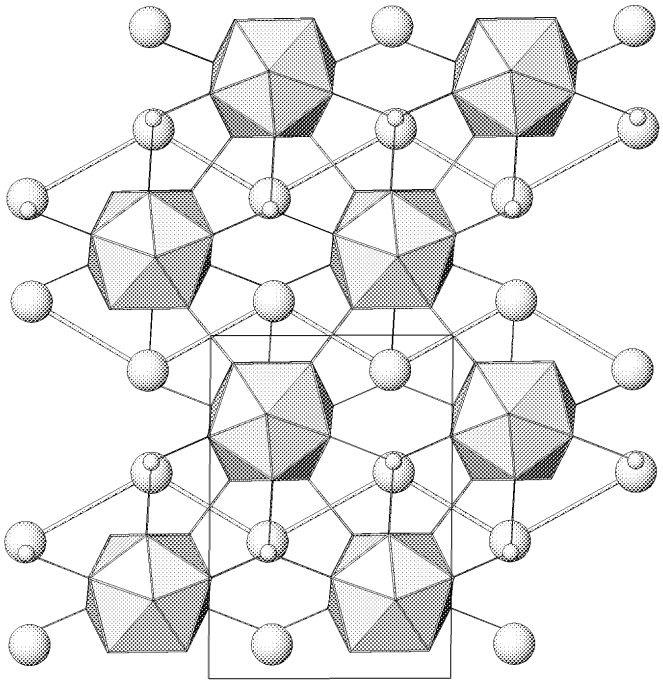
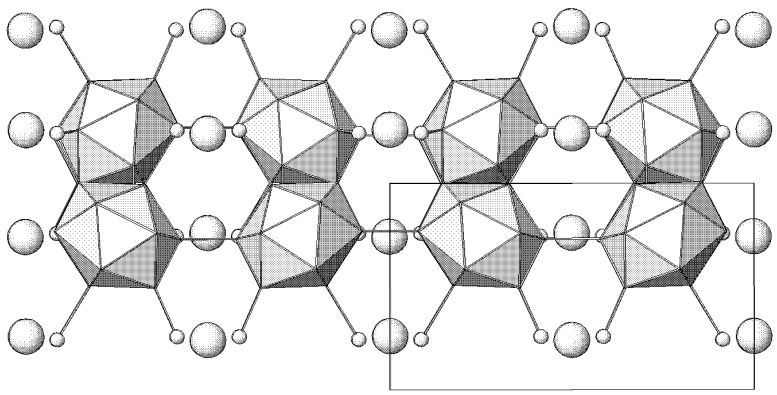


Figure 1. Observed, calculated, and difference x-ray powder diffraction profiles for the TbB_{25} compound.

We show the crystal structure of TbB_{25} in figures 2(a) and 2(b). Infinite B_{12} icosahedral chains run along the *b*-axis direction, with two icosahedra occupying the length of 1.0335 nm. Infinite zigzag chains of terbium sites with occupancy of 0.535 run along the direction of the *a*-axis. The approximate spacing of the terbium sites within the chain is 0.348 nm. The separation between terbium chains along the *b*-axis, which is the B_{12} icosahedral axis, is 0.517 nm. The structure is indeed similar to that of the $YAlB_{14}$ compound, with terbium occupying the yttrium site, and the previous assumption of the structure [3, 5] is found to be correct.



(a)



(b)

Figure 2. Crystal structure of TbB_{25}; (a) a view along the *b*-axis; (b) a view along the *c*-axis. The polyhedra are B_{12} icosahedra, small circles indicate boron atoms, and the large circles indicate terbium atoms. In (b), although the B_{12} icosahedra appear overlapped, since this is a complete projection onto the *a*–*b* plane, they are in fact of course separated.

The x-ray diffraction (XRD) patterns of GdB_{25}, DyB_{25}, HoB_{25}, and ErB_{25} are given in figure 3. Aside from a small impurity component of ErB_{50} being observed for ErB_{25}, the REB_{25} patterns show a single YB_{25}-type structural phase. The lattice parameters determined for the REB_{25} (RE = Gd, Tb, Dy, Ho, Er) compounds are given in table 2.

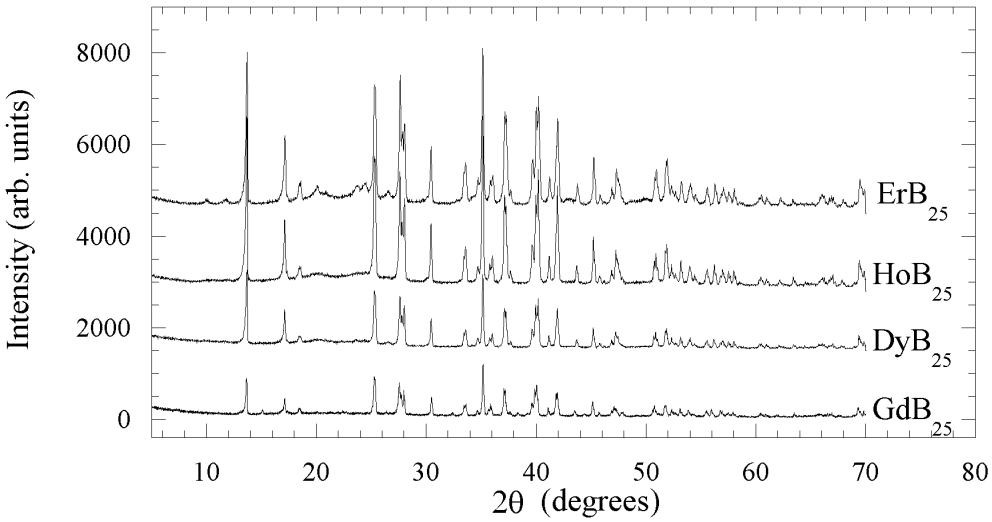


Figure 3. X-ray diffraction (XRD) patterns of GdB_{25}, DyB_{25}, HoB_{25}, and ErB_{25}.

Table 2. Lattice parameters of REB_{25} (RE = Gd, Tb, Dy, Ho, Er). The estimated standard deviation is given in parentheses. The powder XRD data were collected in steps of 0.02°, with 8.6 s/step in the case of TbB_{25}, 1.7 s/step for the other compounds.

	a (nm)	*b* (nm)	*c* (nm)	β (deg)
GdB_{25}	0.5853(2)	1.0339(2)	0.8313(2)	89.58(2)
TbB_{25}	0.58550(1)	1.03354(3)	0.82808(2)	89.512(2)
DyB_{25}	0.5856(1)	1.0325(2)	0.8277(2)	89.56(2)
HoB_{25}	0.5858(1)	1.0319(2)	0.8271(1)	89.54(1)
ErB_{25}	0.5856(2)	1.0309(2)	0.8262(2)	89.54(2)

3.2. Magnetic properties

The terbium B_{12} icosahedra compounds were previously investigated and measurements to 2 K showed that the magnetism of TbB_{25} is Curie–Weiss-like with a Curie–Weiss temperature θ of -1.5 K [3]. In the present work the TbB_{25} compounds were prepared again as one of the series of REB_{25} (RE = Gd, Tb, Dy, Ho, Er) and washed in acid in the manner described above. The lattice constants are similar to those given for the previous work. By detailed measurement down to the low temperature of 1.8 K, a new fact which was not clear in the previous work is revealed. The low-temperature susceptibility of TbB_{25} is given in figure 4 and it can be seen that the susceptibility shows a drop around 2.1 K, indicative of an antiferromagnetic-like transition. Although the transition temperature is low, this is the first report of a magnetic transition being observed in a higher-boride B_{12} compound other than REB_{50}.

The transition temperature T_N of 2.1 K for TbB_{25} is almost one order lower than that for TbB_{50}. It has been previously concluded that the B_{12} icosahedra are indicated to play an

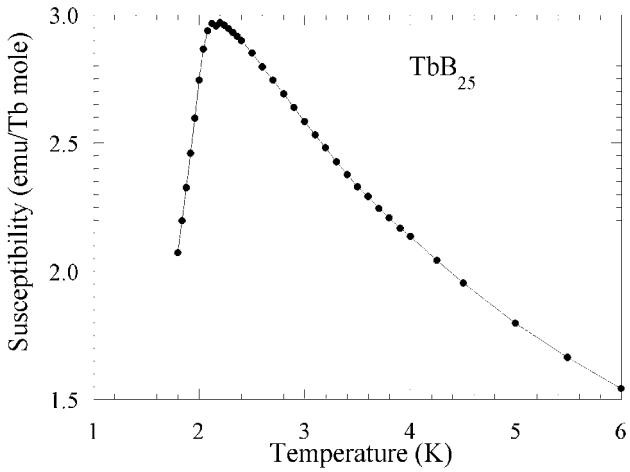


Figure 4. The temperature dependence of the static magnetic susceptibility of TbB_{25} at low temperatures. The magnetic field is 50 G.

important role (i.e. the magnetic interaction along the B_{12} icosahedra axis is important) as regards the magnetic transition appearing in TbB_{50} [3]. Since the TbB_{25} structure was refined, we can conclusively compare the two B_{12} compounds. Although there are shorter metal–metal distances in TbB_{25} (0.348 nm within the zigzag chain along the a-axis), the metal–metal distances along the B_{12} icosahedral chain are 0.573 nm for TbB_{25} ($T_N = 2.1$ K) and 0.512 nm and 0.436 nm alternating for TbB_{50} ($T_N = 17$ K), due to the differences of the lattice constants of the B_{12} icosahedral axis. These results are consistent with the previous conclusion that the interaction along the B_{12} axis is important. From the high-temperature fitting we obtain parameters of $\theta = -1.7$ K and an effective magnetic moment μ_{eff} of 9.75 μ_B/Tb atom.

The magnetic behaviours of the other REB_{25} (RE = Gd, Tb, Dy, Ho, Er) compounds do not show transitions down to 1.8 K. The inverse static magnetic susceptibilities of REB_{25} (RE = Gd, Dy, Ho, Er) are shown in figure 5. The data follow a straight line indicating that the magnetism can be described well as Curie–Weiss behaviour. The effective magnetic moments of GdB_{25}, DyB_{25}, HoB_{25}, ErB_{25} are determined as 7.85 μ_B/Gd atom, 9.05 μ_B/Dy atom, 10.54 μ_B/Ho atom, 9.79 μ_B/Er atom, respectively. The effective numbers of Bohr magnetons agree fairly well with the values for trivalent free rare-earth ions. A transition was not observed for the REB_{25} compounds other than TbB_{25}, and this is similar to the behaviour of REB_{50} (RE = Tb, Dy, Ho, Er) where the highest transition temperature was found for TbB_{50} [4].

Aside from the interesting fact that the B_{12} icosahedra are indicated to play an important role in mediating the magnetic transition in REB_{50}, the exact mechanism of interaction in these higher-boride systems has not been solved yet. The REB_{50} compounds from TbB_{50} to ErB_{50} appeared to follow a de Gennes factor dependence as given in reference [4]. However, although the Gd phase of REB_{50} cannot be obtained, recently we were successful in synthesizing the isostructural borosilicide phase $GdB_{41}Si_{1.2}$ due to the larger lattice constants, and found that the Curie–Weiss temperature is smaller than that of the terbium borosilicide analogue (-7.2 K versus -12.7 K) [11]. This of course is different from a de Gennes factor dependence. Moreover, a simple electron counting for the system (the icosahedra have an electron deficiency of two [12]) shows that the compound is electron deficient and resistivity measurements do not show good metallic conductivity [4, 13] (anisotropic measurements are in progress now).

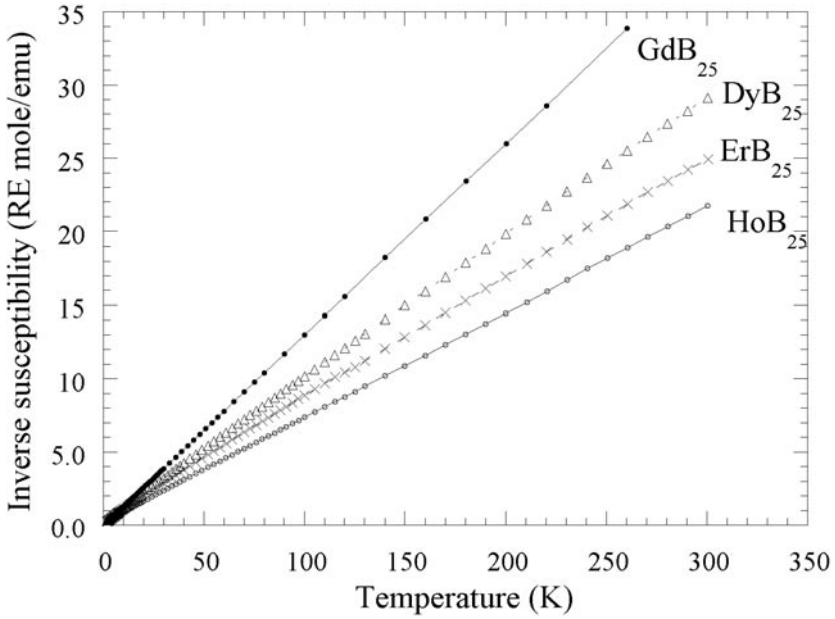


Figure 5. The temperature dependence of the inverse static magnetic susceptibility of GdB_{25} (closed circles), DyB_{25} (open triangles), HoB_{25} (open circles), and ErB_{25} (crosses). The magnetic field is 50 G.

These results obviously indicated that the magnetic interaction mechanism is not an RKKY mechanism which has explained the magnetic transitions in all previously known rare-earth boride compounds which have been metals. And therefore, that there is a new type of interaction for magnetic rare-earth borides that is effective in this system. The magnetic interaction mechanism in these systems remains a very intriguing problem to solve, and theoretical work to address this is in progress.

4. Conclusions

We synthesized the series of binary B_{12} icosahedral boride compounds REB_{25} (RE = Gd, Tb, Dy, Ho, Er). The structure of TbB_{25} was refined using the Rietveld method and the previous assumption of the structure of YB_{25} was confirmed. Measurements of the magnetic susceptibility of TbB_{25} at low temperatures revealed that an antiferromagnetic-like transition is indicated to occur at 2.1 K. This is one order of magnitude lower than the transition temperature of the B_{12} compound TbB_{50}, and from a comparison of the structure, the previous conclusion that B_{12} icosahedra are indicated to play an important role in the transition of TbB_{50} is further supported. GdB_{25}, DyB_{25}, HoB_{25}, and ErB_{25} did not show transitions down to a temperature of 1.8 K with a Curie–Weiss behaviour of the magnetic susceptibility and effective magnetic moments close to the free-ion values.

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