Novel physical properties of rare earth higher borides

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Abstract. Boron forms various compounds with metal atoms occupying voids in the boron framework. We are particularly interested in the rare earth borides, of which many new and varied compounds have been discovered within the span of 10 years, and where the shell of f electrons supplies additional interesting properties. The following recently emerging topics in these borides will be covered: 1. Unexpectedly strong magnetic coupling discovered in dilute f-electron insulators. 2. Attractive high temperature thermoelectric properties. 3. Discovery of intrinsic building defects.

1. Introduction
The traditional focus on boron-rich cluster compounds has tended to be on their striking structural and mechanical properties. These compounds are attractive as materials for their typical high hardness and great stability in extreme environments such as high temperatures, which originate from the particular strong covalent bonding of boron. Boron forms various compounds with metal atoms occupying voids in the boron framework. We are particularly interested in the rare earth borides, of which many new and varied compounds have been discovered within the span of 10 years [1], and where the shell of f electrons supplies additional properties. As a new development, novel functions in the form of exciting electronic and magnetic physical properties have been found in the newly discovered rare earth boron compounds [1].

Rare earth B12 icosahedra-containing compounds are magnetically dilute semiconducting/insulating f-electron compounds, but it has been revealed that they display a wide variety of magnetism with surprisingly strong magnetic coupling [1-4]. A new aspect discovered for the homologous series of 2 dimensional (2D) spin glasses will be reported in this paper.

We have also been investigating the potential of these novel borides as possible thermoelectric materials, since the boron cluster compounds generally exhibit low thermal conductivity [5-7]. Analysis on the origin/mechanism of this intrinsic low thermal conductivity has recently been done on some rare earth borides, comparing effects of “crystal complexity” (the “amorphous concept”), possible “rattling” phenomena, and disorder. It was concluded that disorder was playing a dominant role [8]. In regard to the recently discovered rare earth borides, in a striking new development, the anomalous and attractive n-type behavior was observed in a homologous series of rare earth boron carbonitrides, REB17CN, REB22C2N, and REB28.5C4 without any need for extreme doping [9,10]. These compounds have similarities in crystal structure to boron carbide which is an excellent p-type material [11] and these rare earth boron carbonitrides may embody the long awaited n-type counterpart.
Morphology of the samples of these compounds was investigated and the effects will be presented and discussed.

As the third topic, intrinsic building defects were discovered to be generated for some layered borides like TmAlB$_4$ and found to have a significant effect on the physical properties, resulting in, i.e. multiple transitions at low temperatures. This phenomenon will be reviewed.

2. Experimental details

Details on the synthesis of the borides dealt with in this paper have been published elsewhere (for a review see ref. [1] and references therein), but the basic approach can be described as the following.

First of all powders of REB$_n$ are prepared with the borothermal reduction method at 2000 K in BN crucibles:

$$\text{RE}_2\text{O}_3 + (2n+3)\text{B} \rightarrow 2\text{REB}_n + 3\text{BO}$$

Binary rare earth borides like REB$_5$0 can be made directly with this one step. For ternary borides, in the next step the desired amounts of boron, carbon, and hexagonal BN, in the case of the rare earth boron carbonitrides, REB$_1$7CN, REB$_2$3C$_2$N, and REB$_{28.5}$C$_4$, and silicon in the case of REB$_{44}$Si$_2$, are added and fired again at a reaction temperature of around 1900 to 2100 K. Crystals of rare earth borosilicides, REB$_{44}$Si$_2$, can also be grown by the floating zone (FZ) method. Samples are characterized by X-ray diffraction (XRD) measurements and chemical analysis. Magnetic measurements were made using a superconducting quantum interference device (SQUID) magnetometer. ac susceptibility measurements were made after reducing the residual field below 1.0 Oe by resetting the magnet. Both the in-phase component $\chi'$ and out-of-phase component $\chi''$ were obtained. Resistivity and thermoelectric power were measured with an ULVAC ZEM-2 by using the four probe method. Thermal conductivity was measured by a laser flash method with an ULVAC TC-7000. Scanning electron microscope (SEM) pictures were taken with a JEOL SM-67F 10 kV.

3. Properties of rare earth higher borides

3.1. Magnetism of B$_{12}$ icosahedral rare earth borides

The magnetism of rare earth borides like tetraborides REB$_4$, hexaborides REB$_6$, and dodecaborides REB$_{12}$ has attracted a lot of attention over the years [12], with recent interesting discoveries still being made such as the frustrated Shastry-Sutherland-type magnetic spin system revealed in RB$_4$ (R = Dy, Er) [13,14] and the complex magnetic structure discovered in the dodecaborides [15]. These compounds are all good metals in the case of trivalent rare earth elements, and their magnetic coupling has basically been described by the Ruderman-Kittel-Kasuya-Yoshida (RKKY) mechanism with possible secondary effects from dipole-dipole interaction and frustration.

As an emerging novel phenomenon, it has been found that borides, which contain the B$_{12}$ icosahedra as a structural building block, can exhibit unexpectedly strong magnetic interactions, although they are relatively magnetically dilute, f-electron insulators [1]. These compounds will be discussed in the next subsections.

3.1.1 RB$_{50}$-type compounds

The TbB$_{50}$ compound was discovered to exhibit the first magnetic transition in the higher borides [2]. TbB$_{50}$ has a transition temperature of $T_N = 17$ K, which is surprisingly high considering that these are magnetically dilute insulating f-electron compounds. Investigation of the rare earth series indicates that the magnetic coupling mechanism is different from that of conventional f-electron systems [1]. It has been proposed that the B$_{12}$ icosahedron is playing a role to mediate the interaction [1-4]. REB$_{50}$ and isostructural REB$_{44}$Si$_2$ compounds were also discovered to have similar transitions.

The invariance of the critical magnetic field with regards to non-magnetic dilution, indicated that the transition is dimer-like with magnetic ions forming pairs [4]. Electron spin resonance (ESR) results support one dimensionality of the system which indicates that magnetic dimer pairs are formed along a bond alternating chain parallel to the $c$-axis [16].
To summarize, RB₅₀-type compounds are found to be one dimensional dimer-like magnetic systems with surprisingly strong magnetic interaction for a dilute, localized f-electron insulator.

3.1.2 REB₁CN, REB₂₂C₂N, and REB₂₈.₅C₄

REB₂₂C₂N was found to exhibit irreversible magnetic behavior [17]. For example, as a characteristic physical property, the relaxation of isothermal remanent magnetization Iᵣ following the stretched exponential dependence was observed (figure 1):

\[ Iᵣ \propto \exp[-C(\omega t)^{1-n}]/(1-n) \]

(e.g., HoB₂₂C₂N, C = 0.033, 1-n = 0.10). Furthermore, the existence of wait time effects was also observed in the thermal remanent magnetization σ_TRM as can be seen in figure 2 which is another strong indication of a spin glass system.

**Figure 1.** Isothermal remanent magnetization of REB₂₂C₂N. **Figure 2.** Thermal remanent magnetization of HoB₂₂C₂N for different wait times.

Further investigations established REB₂₂C₂N as the first spin glass system observed for a non-doped boride [3]. The uniqueness of this system exhibiting spin glass behavior without doping among all the borides was laid down to strong frustration in the system originating from the triangular configuration of the rare earth atoms.

**Figure 3.** Relaxation time distribution of HoB₂₂C₂N. **Figure 4.** Temperature dependence of τᵣ.
Strong frequency dependence of the ac susceptibility was found, but could not be analyzed satisfactorily by the dynamical scaling theory of a three dimensional spin glass. A more detailed investigation of the relaxation behavior was carried out by a Cole-Cole analysis on the frequency dependence of the in-phase component $\chi'$ and out-of-phase component $\chi''$ of the ac susceptibility. A relaxation time distribution was determined as shown in figure 3. The temperature dependence of the median relaxation time $\tau_c$ could be described well in terms of a generalized Arrhenius law (figure 4):

$$\ln(\tau_c/\tau_0) \propto T^{(1+\phi_{\nu})}, \quad \tau_0 = 5.3\times10^{-6} \text{ s}, \quad 1+\phi_{\nu} = 2.5$$

The relaxation exponent $1+\phi_{\nu}$ takes a value close to 2 and together with the temperature dependence observed for the width parameter of the relaxation time distributions it was demonstrated that this was not a super paramagnetic system (which also exhibits large frequency dependence) but a new 2 dimensional spin glass system [3]. Actually, it can be considered to be a dilute triangular lattice magnetic system. It was indicated that interaction within the triangular layers was dominant, despite it being the second nearest separation with significantly longer distances. This matches perfectly our theory of the B$_{12}$ icosahedra mediating the magnetic interaction.

Analogous magnetic behavior was observed for the homologous series of REB$_{17}$CN, REB$_{22}$C$_2$N, and REB$_{28.5}$C$_4$ and it was indicated that the magnetism is governed in the two dimensional metal layers [18]. However, in this paper, we consider this in more detail. The structure of the homologous series is plotted in figure 5. The compounds have a layered structure along the c-axis with B$_{12}$ icosahedra and C-B-C chain layers residing in between B$_6$ octahedral and rare earth atomic layers. The B$_{12}$ icosahedra and C-B-C chain layers increase successfully along the series of REB$_{17}$CN, REB$_{22}$C$_2$N, and REB$_{28.5}$C$_4$. In the limit of the boron icosahedra layers going to infinity, the compound is actually analogous to boron carbide.

One difference observed between the compounds in regard to the amount of boron icosahedra and C-B-C chain layers was that the cusp temperature of the zero field cooled susceptibility $T^*$, decreased monotonically as the number of boron icosahedra and C-B-C chain layers were increased. E.g., $T^*$ = 28.8 K, 22.5 K, and 19.3 K for HoB$_{15.5}$CN, HoB$_{22}$C$_2$N, and HoB$_{28.5}$C$_4$T, respectively. This was attributed in ref. 18 as possibly due to the change in spacing of the rare earth atoms. However, the absolute differences in the lattice constant $a(b)$ are only about 0.5% and in any imaginable functions of

![Figure 5. Structure of RE-B-C(N) homologous phases.](image-url)
magnetic interaction, this would be too small to explain the large differences in T* via interaction only in \(ab\) plane. Therefore, it is indicated that some correlation or effect exists beyond the rare earth layers. As noted above, spin glass behavior was thought to be caused by disorder from partial occupancies of the rare earth sites and frustration of magnetic interaction. The origin of disorder in these structures can also be surmised to come from their layered stacking nature. The more stacking layers the polytype member of homologous series has, the more frequent are mistakes in layer sequences and disorder in the structure. This means that the disorder becomes stronger as the boron icosahedra and C-B-C chain layers increase along the series, and this serves to depress T* more than would be expected from just a simple change in the magnetic interaction in the rare earth layer. In this way the observed anomalous dependency can be explained.

3.1.3 \(\text{GdB}_{18}\text{Si}_5\)

A three-dimensional long-range order antiferromagnetic transition was discovered to occur in \(\text{GdB}_{18}\text{Si}_5\). This is interesting because it is the only long range ordering observed for the higher borides and occurs despite the relatively low partial occupancy of the gadolinium sites [19]. The details of the magnetic ordering are under investigation at present.

An interesting dependence at low magnetic fields (applied along the \(c\)-axis) was observed when the field was varied in-plane, with a reorientation of the spin, a spin flip, appearing to occur at fields below 300 G. The origin of this behavior of course can be attributed to the round spin of the gadolinium ions, but the actual observation of a spin flip at such low magnetic fields is unusual and interesting [20].

3.2. Thermoelectric properties of novel higher borides.

3.2.1 \(\text{REB}_{17}\text{C}_N, \text{REB}_{22}\text{C}_2\text{N}, \text{and REB}_{28}\text{.5C}_4\)

As noted in the introduction, the n-type RE-B-C(N) compounds are generating excitement because it may be developed as the long awaited high temperature thermoelectric counterpart to p-type boron carbide [9,10]. After the attractive thermoelectric properties of boron carbide were discovered, various rigorous efforts were made over the years however it was not possible to obtain similar n-type materials, unless through doping, for example, \(\beta\)-boron by extremely large amounts of transition metals like vanadium [21,22]. Boron carbide doped with nickel has also been reported to show n-type but only at a limited temperature range, and not at high temperatures [23]. Asides from the boron icosahedra cluster compounds, we note that divalent alkaline-earth hexaborides like CaB6 have been found to exhibit n-type behavior as first shown by Paderno et al [24,25] and Etourneau et al [26] (recently other groups have also reported and further investigated this behavior [27]). However, they are a different class of compounds compared to the boron icosahedra compounds, since they are basically dirty metals/small gap semiconductors with relatively large thermal conductivity. The n-type behavior is not unexpected, especially for inadvertently doped samples.

As noted above about the crystal structure of the RE-B-C(N) series of compounds, in the limit of the boron icosahedra layers going to infinity, the compound is actually analogous to boron carbide. This similarity of the structural blocks is also why we consider them to be compatible n-type counterparts to boron carbide which has been established to be an excellent p-type high temperature thermoelectric material. Recently, the origin of the anomalous n-type behavior is also becoming clearer [28].

These compounds will not melt stably and therefore, large crystals cannot be grown so sintered powders are compacted in various ways for measurements. Conventional hot press methods and cold pressing and annealing methods yield samples with densities of only around 50% of the theoretical value. Spark plasma sintering (SPS) has been found to easily increase the density to \(\sim 70\%\) [10]. The morphologies of a typical hot pressed and SPS-prepared RE-B-C(N) sample are shown in figure 6.

The SPS sample shows an increase of the grain size compared to hot pressed sample. A particularly interesting feature is that the grains in the SPS sample appear very thin and plate-like. Considering the
anisotropic structure of the compound (figure 5) we speculate that the growth is along the in-plane directions of the layered structure (the \( ab \) plane).

With such densification by SPS there is large improvement in electrical conductivity with resistivities decreasing by close to 2 orders of magnitude (figure 7). Accompanying the decrease in resistivity, the absolute values of the Seebeck coefficients also show small decreases, but the effect is much smaller than the resistivity improvement. In fact, the power factor at 1000 K increases by close to 2 orders.

The thermal conductivities of two SPS RE-B-C(N) samples (both approximately 70% of theoretical density) are compared with conventionally hot pressed samples as shown in figure 7. There is a sizable increase of the measured thermal conductivity compared to the hot pressed samples, however, this cannot be attributed simply to the effect of simple densification, because the two SPS samples have similar densities (in regard to their theoretical densities).

SPS-HoB_{17}CN actually exhibits almost 1.5 times the thermal conductivity of SPS-YB_{22}C_{2}N. From this result, the following can be surmised. First of all, it should be assumed that there is a very large anisotropy in the thermal conductivity of the rare earth boron carbonitrides. This is reasonable because of the crystal structure as noted before, and a hypothesis can be made that the thermal conductivity is low in the \( c \)-axis direction through the boron cluster layers, while being relatively high in-plane within

![Figure 6. SEM pictures of hot pressed and SPS HoB_{17}CN.](image)

![Figure 7. Resistivity and thermal conductivity of hot pressed and SPS RE-B-C(N) samples.](image)
the rare earth layers. As the grain size increases through SPS along this relatively high thermal conductivity direction and the sample becomes less “uniform” (more anisotropic), it becomes easier for significant differences in the thermal conductivity to manifest for different samples.

In such anisotropic systems, control of the nano/microstructure of the samples can be a powerful tool to enhance or tune the thermoelectric properties. Further investigations should continue into the processing of this promising system which is hoped to be a viable n-type counterpart to boron carbide, which is a well established high temperature p-type material.

A striking result was obtained when small amounts of metal borides were doped into samples [10]. The densities of the doped and nondoped samples are all similar, being ~50% of theoretical density, but a significant decrease up to 2 orders in the resistivity, is obtained through the doping. The Seebeck coefficient and thermal conductivities do not show a large change, so this doping method is revealed to be an even more effective way to increase the figure of merit compared to simple densification. Since the percent of doping is small, it is unlikely that a percolation effect is the origin for the large reduction in resistivity, where the metal boride particles provide connecting channels of high electrical conductivity.

The investigation of the morphology of the samples (figure 8) reveals the origin of the behavior. The metal doped samples obviously have larger grain size. Therefore, it is indicated that the presence of metal borides appear to promote the growth of larger grains in the RE-B-C(N) samples. We note that compared to typical compounds in which in some cases it is preferred to inhibit grain growth so as to depress thermal conductivity, in the case of the boron cluster compounds, they are compounds which typically have intrinsic low thermal conductivity. Therefore, the grain growth is not necessary a detrimental effect when the overall effect is taken into account.

As noted above, control of the morphology of anisotropic compounds is a very important aspect to control their properties. The small addition of metal borides has been shown to change the morphology and this effect will be investigated in detail further.

3.3. Building defects in layered borides

The rare-earth metal aluminoboride system $\text{RAIB}_4$ has been attracting increasing attention with recent discoveries. Multiple magnetic transitions were reported to occur in $\text{TmAlB}_4$ at low temperatures below an antiferromagnetic transition temperature $T_N$ [29] while crystals with two different structure types were reportedly obtained from the same flux for $\text{YbAlB}_4$ and $\text{LuAlB}_4$ [30]. $\text{TmAlB}_4$ takes a well-known $\text{YCrB}_4$-type structure (space group $\text{Pbam}$) [31], and we have found that X-ray diffraction measurements point to an intrinsic tiling variation existing in the crystals [32] due to the presence of fragments of the closely related $\text{ThMoB}_4$-type structure (space group $\text{Cnmm}$) [33]. Both structures

![Figure 8. SEM pictures of $\text{YB}_2\text{C}_2\text{N}$ (left) and $\text{ErB}_2\text{C}_2\text{N}:\text{ErB}_4$ (right).](image-url)
have similarities to the AlB$_2$-type structure, with a planar boron network build of pentagonal and heptagonal rings having differently sized rare-earth and aluminum atoms. The difference between the YCrB$_4$-type (α-type) and ThMoB$_4$-type (β-type) structures is in the orientation of the pairs of condensed pentagonal rings. The previous work indicates that the existence of an intrinsic intergrown nanostructure influences physical properties and is the origin of multiple magnetic anomalies which are observed in TmAlB$_4$. This is striking because there are more than a hundred compounds reported with this type of structure, and it is possible that such indicated phenomenon of the intrinsic tiling variation is actually ubiquitous.

4. Conclusions

Interesting and striking physical properties have been discovered for novel rare earth higher borides. Topics covered in this paper deal with the magnetic behavior and unexpectedly strong coupling discovered for rare earth borides containing the B$_{12}$ icosahedra. It is newly pointed out that in the homologous series of two dimensional spin glasses, REB$_{17}$CN, REB$_{22}$C$_2$N, and REB$_{28.5}$C$_4$, contrary to what was assumed previously, it is indicated that some correlation or effect exists beyond the rare earth and octahedral layer. Stronger disorder in the polytypes with more boron icosahedra layer stacking can cause a more rapid depression of T* than normally expected.

The potential of novel rare earth borides as mid to high temperature thermoelectric materials is also a topic of interest. Morphology is indicated to play a large role in affecting the thermoelectric properties. The increase in the power factor of rare earth borocarbides doped with metal borides which was previously observed is indicated to originate from an increase in the grain growth.

Finally, the phenomena of building defects observed in layered borides and their effect on physical properties were briefly reviewed.

Acknowledgments

Dr. T. Nishimura is thanked greatly for his help with some of the experiments.

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