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Magnetic Transitions in B_{12} Icosahedral Cluster Compounds $REB_{41}Si_{1.2}$ (RE=Gd, Tb)

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Synthesis and magnetic properties measurements were carried out on $REB_{41}Si_{1.2}$(RE=Gd, Tb) compounds which take the new 9th type of structure of the B_{12} icosahedral compounds. Two different kinds of preparations were made of $TbB_{41}Si_{1.2}$; a polycrystalline sample and a successfully grown FZ crystal. The Gd phase of the REB_{50} structure type compounds was not known to exist up to now, however, it was also successfully synthesized in this work. The compounds were all observed to undergo an antiferromagnetic transition, with transition temperatures ranging up to 18.5 K for the $TbB_{41}Si_{1.2}$ FZ crystal. These are the first family of higher boride compounds which exhibit a magnetic transition. While the $TbB_{41}Si_{1.2}$ comparison of the magnetic behavior is consistent with the previous conclusion that the shortness of the B_{12} icosahedral axis is an important factor in the appearance of the magnetic transition, the variation of rare earth indicates that this is not the sole factor, while also showing a different dependence from variation of the de Gennes factor.

1. INTRODUCTION

Cluster compounds have attracted much interest as systems which can yield new and useful materials for the future. In particular, carbon based materials such as the "buckeyballs" C_{60} fullerenes have been the most extensively researched system (1). Our particular interest lies in boron based compounds which also contain cluster-like structural components such as the B_{12} icosahedra. Quite recently, we have synthesized and investigated the magnetic properties of higher boride compounds (2,3) which contain the B_{12} icosahedra. As a result we have discovered that an antiferromagnetic transition occurs in the TbB_{50} compound. This was a striking result, because TbB_{66} compounds synthesized at the metal rich end of the homogeneity region which have comparable magnetic atom concentration to TbB_{50} and TbB_{25} compounds which have a denser concentration showed no transition

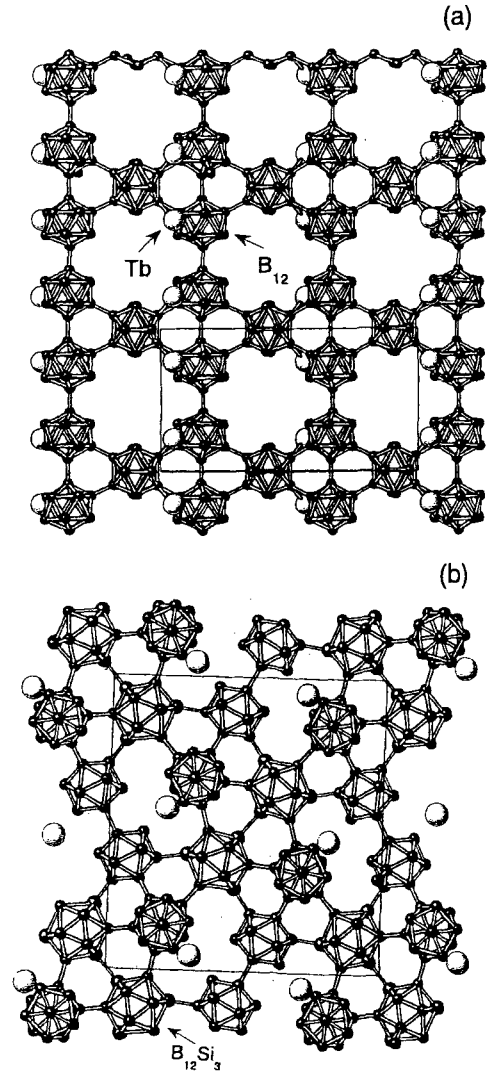

Figure 1: (a) Icosahedral B_{12} and terbium atom arrangement as seen along the a-axis, within the range of x = 0.09-0.41, and (b) a view along the c-axis, within the range of z = 0.30-0.92. The small circles indicate boron atoms, the large circles indicate terbium atoms, and the medium sized circles in (b) represent silicon atoms in the $B_{12}Si_3$ polyhedra.

down to 2 K. The transition observed in TbB_{50} had the relatively high transition temperature of 17.5 K. This is the first magnetic transition observed in the higher borides.

From a comparison of the structures it was indicated that the particular structure of TbB_{50} was critical to the appearence of the transition. In Fig. 1 we show the crystal structure of $TbB_{41}Si_{1.2}$ which is isostructural to TbB_{50} and orthorhombic with lattice constants of a=16.648 Å, b=17.661 Å, and c=9.495 Å in the case of the FZ crystal described in this work. B_{12} icosahedral chains are aligned along the c-axis with metal atoms occupying spaces created among the icosahedra. The differences in the structure (4,5) between TbB_{50} and $TbB_{41}Si_{1.2}$ due to the different compositions are that the silicon interstitial and $B_{12}Si_3$ polyhedron sites in $TbB_{41}Si_{1.2}$ are replaced by boron sites in TbB_{50} and that the occupancies of these sites and partially occupied boron interstitial sites are larger in TbB_{50} than in $TbB_{41}Si_{1.2}$. The terbium sites in both compounds have an occupancy of 1. The existence of the B_{12} chains in these compounds themselves are not unique since B_{12} chains are included in all the higher boride compounds that we studied (2), however, the distinguishing feature of the YB_{50} type structure is that the lattice constant of the axis (c-axis) along which the B_{12} chain is aligned takes the shortest value ever observed for these icosahedral chain compounds (4,5). It was indicated that shortness of the B_{12} axis, i.e. the magnetic interaction along the B_{12} chain is critical for the magnetic transition to appear (2,3).

In this study we report further investigations on the magnetic transition in this system. Crystals of $TbB_{41}Si_{1.2}$:which are isostructural to TbB_{50} were successfully grown by the floating zone (FZ) method. A comparison between two different preparations of $TbB_{41}Si_{1.2}$; arcmelted $TbB_{41}Si_{1.2}$ and FZ $TbB_{41}Si_{1.2}$ crystal which have different lattice constants was made. Furthermore, variation of the rare earth constituent was also made. We compared $TbB_{41}Si_{1.2}$ with $GdB_{41}Si_{1.2}$.

2. EXPERIMENTAL

REB_{50} (RE=Tb, Dy) compounds were synthesized by the borothermal reduction method with sintering done at temperatures of 1700°C~1800°C. The $TbB_{41}Si_{1.2}$ samples were prepared in the following way. First of all TbB_{50} was synthesized by multiple sintering and then the samples were crushed and Si powder was added and synthesized again. As a final step the sample was arc melted. The polycrystalline samples were characterized by X ray powder diffraction and chemical analyses. Although the Gd phase for REB_{50} compounds could not be previously synthesized, we were able to synthesize the first gadolinium compound taking the REB_{50} type structure. $GdB_{41}Si_{1.2}$ was synthesixed in a similar way as $TbB_{41}Si_{1.2}$. We judge that this was possible due to the larger lattice constants of $REB_{41}Si_{1.2}$ compared to REB_{50}. This difference enabled occupation of the gadolinium atoms which are larger than terbium ions. $TbB_{41}Si_{1.2}$ crystals were grown by first preparing feed rods by the above two step sintering. These feed rods were used in the floating zone (FZ) method to obtain crystals. Our crystals were identified by X ray powder diffraction and chemical analyses to be of the $TbB_{41}Si_{1.2}$-type phase. Polished surface of the highest quality grown samples showed the existence of multigrains and any particular alignment could not be detected by Laue measurements.

Lattice constants for all the compounds are given in Table I. For reference the lattice constants of the REB_{50} compounds, TbB_{50} and DyB_{50} are also given.

Table I: Lattice constants of the compounds

	a (Å)	b (Å)	c (Å)
$TbB_{41}Si_{1.2}$(polyxtl)	16.776	17.798	9.591
$TbB_{41}Si_{1.2}$(FZ xtl)	16.648	17.661	9.495
$GdB_{41}Si_{1.2}$ (polyxtl)	16.746	17.731	9.565
TbB_{50}(polyxtl)	16.609	17.619	9.477
DyB_{50}(polyxtl)	16.608	17.623	9.472

Magnetic susceptibility was measured by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer from 300 K to 2 K.

3. RESULTS AND DISCUSSION

3.1 Comparison of $TbB_{41}Si_{1.2}$ samples

The magnetic susceptibility of arc melted polycrystalline $TbB_{41}Si_{1.2}$ and that of a crushed $TbB_{41}Si_{1.2}$ crystal is given in Fig. 2. The magnetic susceptibility increases as temperature is lowered, but shows significant decreases below 20 K indicating the antiferromagnetic transition.

The transition temperature T_N which we take to be the peak in the susceptibility is around 14.5 K and 18.5 K, for polycrystalline and FZ grown crystal, respectively, At further lower temperatures an upturn is observed which is attributed to paramagnetic impurities such as TbB_{66} impurities.

If we fit the susceptibility above 35 K as the

sum of a temperature independent term χ_0 and Curie-Weiss term:

$$\chi = \chi_0 + N\mu_{eff}/3k_B(T - \theta), \quad (1)$$

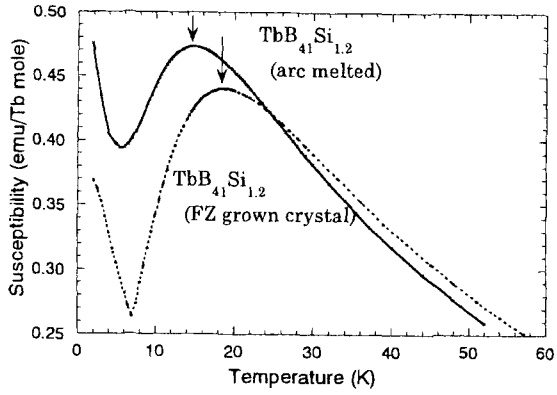

Figure 2: Temperature dependence of the static magnetic susceptibility of $TbB_{41}Si_{1.2}$ for a polycrystalline sample (round dots) and a FZ grown crystal (x). The transition temperatures T_N are indicated by arrows. T_N is defined as the temperature where the susceptibility takes a maximum before decreasing. The lines are guides to the eye.

the data can be described well with Curie-Weiss temperature θ of –12.7 K and –14.7 K for polycrystalline and FZ crystal, respectively,which agrees with the variation of the transition temperature. The effective magnetic moments are determined to be 11.9 μ_B and 12.4 μ_B for polycrystalline and FZ crystal, respectively. These values are larger than the theoretical value of 9.72 μ_B determined for free Tb^{3+}. The reason for this difference is not clear, since TbB_{50} samples typically gave lower values closer to the free ionic value (2,3), and impurity effects are negligible at this scale.

If we simply focus on the B_{12} icosahedral lattice constant which is of interest to us, we see that it is 9.591 Å and 9.495 Å for polycrystalline and FZ crystal, respectively. The results obtained are consistent with the previous conclusion that the shortness of the B_{12} axis is important for the magnetic transition to appear, although it can not be exclusively proved here again. Although the reason for the difference between the obtained values and that of free trivalent terbium ionic value of the effective moment is not clear, we also note that the sample with the larger effective magnetic moment has the higher transition (and Curie-Weiss) temperature. This will be discussed more in the following section.

3.2 Comparison of $TbB_{41}Si_{1.2}$ with $GdB_{41}Si_{1.2}$

Next we will investigate the effect of when the rare earth constituent is varied from terbium to gadolinium, by a comparison of polycrystalline $TbB_{41}Si_{1.2}$ with $GdB_{41}Si_{1.2}$. The temperature dependence of the magnetic susceptibility of the two compounds is shown in Fig. 3 (the data for $TbB_{41}Si_{1.2}$ is the same as that in Fig.2).

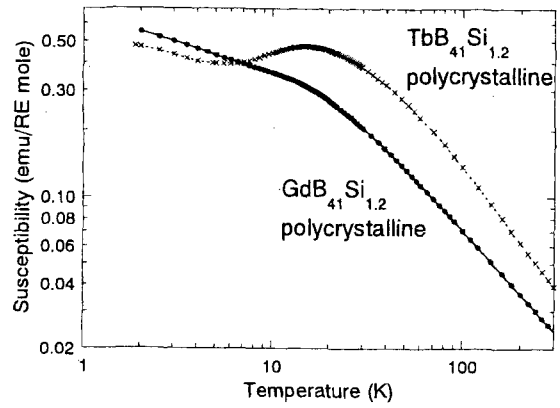

Figure 3: Temperature dependence of the static magnetic susceptibility of $TbB_{41}Si_{1.2}$ (x) and $GdB_{41}Si_{1.2}$ (round dots). The plot is log-log and the lines are guides to the eye.

$GdB_{41}Si_{1.2}$ does not show an obvious hump in the susceptibility. By fitting the high temperature susceptibility to Eq. 1 we obtain μ_{eff}=7.87 μ_B and θ = – 7.2 K. Although an obvious hump in the susceptibility is not observed, from the change in curvature below ~10 K, and the negative Curie-Weiss temperature, a transition is also indicated similar to the other magnetic REB_{50} type compounds. The hump appears to be obscured by a large low temperature paramagnetic tail. Whether this is due to impurities or intrinsic in this case is not clear at present.

To make the comparison between $TbB_{41}Si_{1.2}$ and $GdB_{41}Si_{1.2}$ more clear, we plot the inverse of the static magnetic susceptibility, after temperature independent terms χ_0 determined from the Curie-Weiss fit are subtracted from the data in Fig. 4. The differences in θ (7.2 K for $GdB_{41}Si_{1.2}$ and -12.7 K for $TbB_{41}Si_{1.2}$) can be seen more clearly. Since the the lattice constant of the B_{12} axis (c-axis) is shorter in $GdB_{41}Si_{1.2}$ compound, we see that this is not the sole factor of the magnetic interaction regardless of type of rare earth. Actually we have found that the transition temperatures varies from 17.5 K for TbB_{50} to 6.2 K for DyB_{50} (6), which is also different from a simple relation to the B_{12} axis constants given in Table I. We observe that in the $GdB_{41}Si_{1.2}$ to

$TbB_{41}Si_{1.2}$ comparison, the decrease in effective magnetic moment corresponds to a decrease in the magnetic interaction, which is also the case with the DyB_{50} comparison. This also does not contradict the results of 3.1 although it is not clear whether the difference in effctive magnetic moment observed in that case is actually intrinsic or not. We will not attempt to solve the interaction mechanism here, although the fact that it is an indirect mechanism as opposed to dipole-dipole mechanism is clear from transition temperatures and metal-metal spacing (2).

A major important new result that we obtain from the $GdB_{41}Si_{1.2}$ comparison is that the dependence apparently also does not follow the de Gennes factor dependence (Gd is 15.75 compared to 10.50 for Tb) which is observed in conduction electron mediated magnetic interaction systems. This is a fact not discernable from simply the DyB_{50} comparison.

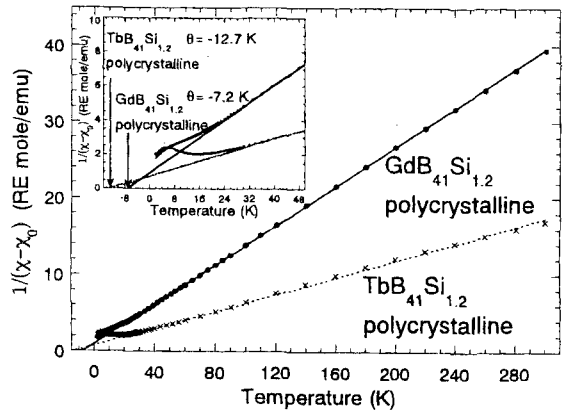

Figure 4: Temperature dependence of the inverse of the static magnetic susceptibility of $TbB_{41}Si_{1.2}$ (x) and $GdB_{41}Si_{1.2}$ (round dots) after temperature independent terms χ_0 determined from the Curie-Weiss fit are subtracted from the data. The inset is an enlarged view.

4. CONCLUSION

Synthesis was carried out on $REB_{41}Si_{1.2}$ (RE=Gd, Tb) compounds which take the new 9th type of structure of the B_{12} icosahedral cluster compounds. TbB_{50} has been found to exhibit the first magnetic transition ever observed in the higher boride compounds. From a careful comparison of the terbium higher borides it was concluded that the short icosahedral (c-axis) lattice constant is an important factor for the transition to occur in TbB_{50}.

In this work 2 different comparisons were made to further investigate the mechanism of the transition. A gadolinium phase of a YB_{50} type structure compound was also successfully synthesized for the first time. A comparison was made of two different kinds of preparations of $TbB_{41}Si_{1.2}$; a polycrystalline sample and a successfully grown FZ crystal which have different lattice constants. The results were consistent with the conclusion made previously. Effect of the variation of the rare earth constituent from terbium to gadolinium was also investigated. $TbB_{41}Si_{1.2}$ was compared with $GdB_{41}Si_{1.2}$. It was confirmed that the shortness of the B_{12} icosahedral axis is not the sole factor determining the transition. An important discovery was made in that the magnetic interaction appeared not to follow the variation of the de Gennes factor as would be expected for an RKKY interaction mediated system. Further work such as neutron scattering measurements to determine the spin structure, anisotropy measurements, and theoretical calculations should be fruitful to further make the mechanism of the transition clear.

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