Long Range Magnetic Order in Magnetic B$_{12}$ Boron Cluster Compounds

Takao MORI* **

*National Institute for Materials Science, Advanced Materials Laboratory, 1-1, Namiki Tsukuba 305-0044, Japan
**PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

GdB$_{12}$Si$_6$ is a member of an emerging family of rare earth B$_{12}$ icosahedral cluster compounds in which magnetic transitions have been discovered at moderate temperatures despite their non-metallic and magnetically dilute nature. B$_{12}$ icosahedra have been indicated to mediate the magnetic interaction possibly through a superexchange mechanism. In order to make a systematic comparison between gadolinium B$_{12}$ compounds, the GdB$_{12}$Si$_6$ compound (Pbnm) which is isostuctural to the well known TbB$_{12}$-type compounds was synthesized and its properties compared with the GdB$_{12}$Si$_6$ compound. In a striking contrast, GdB$_{12}$Si$_6$ with fully occupied gadolinium atomic sites exhibits short range order compared to GdB$_{12}$Si$_6$ which shows long range ordering despite the partial occupancy of the gadolinium sites. Magnetization of long range ordered GdB$_{12}$Si$_6$ was also investigated and a low magnetic field dependence was observed. [Received July 23, 2003; Accepted December 26, 2003]

Key-words: Borides, Boron cluster, Magnetic susceptibility, Specific heat, Long range order

1. Introduction

Magnetic properties of rare earth B$_{12}$ icosahedral cluster compounds such as TbB$_{12}$ have attracted growing interest because magnetic transitions have been discovered at moderate temperatures, despite their non-metallic and magnetically dilute compounds. It has also been reported that boron compounds like doped-CaB$_6$ exhibit high temperature ferromagnetism, but we have demonstrated that the observed magnetic properties originate from impurity effects.

In a new development on magnetism in boron compounds we have also discovered a class of trigonal and rhombohedral B$_{12}$ cluster compounds such as REB$_2$C$_2$N to exhibit spin glass behavior.

Quite recently an antiferromagnetic transition was observed in the B$_{12}$ cluster compound GdB$_{12}$Si$_6$ (R-3m) with $T_N = 3.2$ K. In this work, we make a systematic comparison of this system with another gadolinium $S_{7/2}$ system of the compound GdB$_{12}$Si$_2$, which is isostuctural to TbB$_{12}$. Magnetic field dependence of GdB$_{12}$Si$_6$ is also investigated.

2. Experimental

Single crystals of GdB$_{12}$Si$_6$ were prepared as described previously. With the addition of Si, it is known that the REB$_2$Si$_2$ compound forms which is isostuctural to REB$_2$Si$_2$ (R3m). Polycrystalline GdB$_{12}$Si$_6$ samples were also prepared in this way by arc melting. The samples were checked by pulverising the samples used for measurements into powder and measuring them with a high resolution powder x-ray diffractometer (Rigaku Co.; RINT2000) with Cu Kα radiation whether their phase is single or not.

The structure of GdB$_{12}$Si$_6$ is rhombohedral (space group R-3m) with lattice constants of $a = 10.07$ and $c = 16.45$ Å. In the shortest metal-metal spacing, the gadolinium sites form a zigzag chain along the [1 1 0] axis with a separation of 5.04 Å. The TbB$_{12}$-type compound GdB$_{12}$Si$_2$ is orthorhombic (space group Pbnm) with $a = 16.746$, $b = 17.731$, and $c = 9.565$ Å. B$_{12}$ icosahedral chains are aligned linearly along the c-axis, while Gd atoms occupy spaces among the icosahedra and are also aligned along the c-axis. To make a comparison, the shortest gadolinium-gadolinium site spacing is 5.04 Å for GdB$_{12}$Si$_6$ and 4.40 Å for GdB$_{12}$Si$_2$, respectively. An important difference between the compounds is that the gadolinium sites of GdB$_{12}$Si$_6$ are partially occupied (occupancy of 0.68) while the sites in GdB$_{12}$Si$_2$ have full occupancy of 1.

Magnetic susceptibility was measured by using a SQUID magnetometer in a temperature range of 1.8–300 K and in magnetic fields up to 50 kG. Specific heat measurements were made by a transient heat pulse method with a small temperature increase of 2% relative to the system temperature.

3. Results and discussion

3.1 Magnetic susceptibility

It has already been observed that the antiferromagnetic transition occurs in GdB$_{12}$Si$_6$ at $T_N = 3.2$ K. Following this, we focus on the in-plane magnetic susceptibility of GdB$_{12}$Si$_6$, making a comparison with that of GdB$_{12}$Si$_2$ (Fig. 1). The inverse magnetic susceptibilities are plotted in the inset figure. The effective number of Bohr magnetons $\mu_{eff}$ is determined to be $8.16 \mu_B$/Gd atom and $7.89 \mu_B$/Gd atom for GdB$_{12}$Si$_6$ and GdB$_{12}$Si$_2$, respectively. These values both agree fairly well with that for trivalent free gadolinium ions. The Curie-Weiss temperatures $\theta$ are determined to be $-0.3$ and $-7.2$ K for GdB$_{12}$Si$_6$ and GdB$_{12}$Si$_2$, respectively.

As these compounds are insulating compounds, the RKKY mechanism is not expected to be effective. It has been previously indicated that the B$_{12}$ icosahedra play a role for mediating the magnetic interaction in the non-metal magnetic B$_{12}$ compounds and that the spacing of the magnetic rare

![Fig. 1. Temperature dependence of the magnetic susceptibility of GdB$_{12}$Si$_6$ (closed circles) and GdB$_{12}$Si$_2$ (open circles). The insets are enlarged views of inverse susceptibilities.](image)
earth atoms along the B\textsubscript{12} icosahedra is a critical factor of the transition.\textsuperscript{1,2,12} We note that the stronger magnetic interaction is observed for the GdB\textsubscript{2}S\textsubscript{i} which has the shorter gadolinium spacing of 4.40 Å than 5.04 Å for GdB\textsubscript{2}S\textsubscript{i} as is expected. Theoretical work is presently being done to generally solve the explicit mechanism of the mediated magnetic interaction in B\textsubscript{12} icosahedral compounds which we suspect to be a superexchange mechanism mediated by boron clusters. An obvious difference between the two compounds is that GdB\textsubscript{2}S\textsubscript{i} has a sharp peak at the transition temperature of 3.2 K, while the peak of GdB\textsubscript{2}S\textsubscript{i} is broad and not well defined despite the higher Curie-Weiss temperature, although a small shoulder is observed in the inverse susceptibility around 4 K. It has been observed previously that there is a sizable low temperature tail in the TbB\textsubscript{2}R-type compounds which tends to obscure susceptibility peaks at low temperatures.\textsuperscript{2,31} We were not successful in separating the low temperature component of GdB\textsubscript{2}S\textsubscript{i} in an absolutely non-subjective manner. The unequivocal existence of such transition for GdB\textsubscript{2}S\textsubscript{i} will be made clearer in the following specific heat section.

3.2 Specific heat

Magnetic specific heats $C_m$ of GdB\textsubscript{2}S\textsubscript{i} and GdB\textsubscript{2}S\textsubscript{i} were determined by subtraction of the phonon contributions which were estimated from the specific heat values of the respective yttrium non-magnetic analog compounds after correction due to the R-mass difference. The temperature dependences of $C_m$ are compared with each other in Fig. 2. Decisively different behavior is observed between these compounds. For GdB\textsubscript{2}S\textsubscript{i}, $C_m$ shows a very broad peak around 4 K with an obvious rise in the specific heat at temperatures well above 4 K. In contrast to this, $C_m$ of GdB\textsubscript{2}S\textsubscript{i} exhibits a very sharp $\lambda$-like peak at 3.2 K.

Comparing the specific heat with the magnetic properties for GdB\textsubscript{2}S\textsubscript{i}, the broad peak in $C_m$ at 4 K corresponds to the temperature where the small shoulder is observed in the inverse magnetic susceptibility (inset of Fig. 1). We take this temperature as the transition temperature of GdB\textsubscript{2}S\textsubscript{i}. The specific heat shows an increase well above 4 K as noted, and the susceptibility also deviates from the Curie-Weiss law above 4 K. These characteristics are indicative of a short range order transition, where the onset of short range magnetic order starts significantly above $T_N$. For GdB\textsubscript{2}S\textsubscript{i}, the sharp $\lambda$-like peak at 3.2 K coincides with the sharp peak in the magnetic susceptibility, indicating a typical long range order antiferromagnetic transition.

Extrapolations to T = 0 enable calculation of the entropies $S$, which are also respectively plotted in Fig. 2. It can be seen that in the GdB\textsubscript{2}S\textsubscript{i} case, S attains a value close to 17 J/K mole at 15 K. This value is close to the full magnetic entropy of Rln8 = 17.3 J/K mole which would be expected in this case, since the 5\textsuperscript{s}S\textsubscript{5/2} ground state of Gd\textsuperscript{3+} is spherically symmetric and degeneracy would not be lifted by crystalline electric field CEF effects. In contrast, for GdB\textsubscript{2}S\textsubscript{i} S only reaches a value around 11 J/K at 15 K, indicating that significant magnetic entropy remains to be loosed even at this temperature high above the transition at 4 K. This agrees with behavior expected for a short range order transition.

As a striking feature, we see that the GdB\textsubscript{2}S\textsubscript{i} compound which has partial occupancy of the gadolinium atomic sites (occupancy = 0.68) exhibits the long range order, while the GdB\textsubscript{2}S\textsubscript{i} compound which has full occupancy (occupancy = 1) of the gadolinium sites shows the short range order.

3.3 Magnetization

To further investigate the transition in GdB\textsubscript{2}S\textsubscript{i} we carefully examine the magnetization curve at a temperature (1.8 K) below the transition temperature as plotted in Fig. 3. As can be seen, the magnetization curve exhibits a change in curvature in the region from 70 G to 240 G. Above 240 G, the magnetization is linear to the fields of 10 kG, above which it rapidly saturates, taking the expected value of 7 $\mu_B$/Gd atom. This behavior is interesting because it indicates a reorientation of the arrangement of long range ordered spins at a low magnetic field, i.e. energy. We therefore find that the magnetic ordering of GdB\textsubscript{2}S\textsubscript{i} is of substantial interest for 2 aspects, namely, the partial occupancy of the magnetic sites and the very low field dependence observed.

Further extensive investigation into the nature of the magnetic ordering of this compound is desirable. Neutron scattering is a powerful technique, but due to the extremely large cross sections of both natural boron and gadolinium this is impossible for the as-prepared samples. We are presently attempting to synthesize isotope samples of GdB\textsubscript{2}S\textsubscript{i} in order to carry out the neutron scattering experiments and probe the magnetic structure.

4. Conclusions

Systematic comparison was made between two gadolinium B\textsubscript{12} icosahedral cluster systems. The TbB\textsubscript{2}R-type GdB\textsubscript{2}S\textsubscript{i} compound was synthesized and compared with GdB\textsubscript{2}S\textsubscript{i} which is
known to have an antiferromagnetic transition at 3.2 K. Short range order behavior is observed for GdB$_4$Si$_2$ with a transition indicated at 4 K. The magnetic behavior of GdB$_4$Si$_2$ is concluded to be very interesting for two aspects. Despite the partial occupancy of magnetic sites it exhibits long range order (in stark contrast to the GdB$_4$Si$_2$ compound which has full occupancy but exhibits short range order). Furthermore, a dependency is observed on low magnetic fields with a threshold range of 70 G to 240 G. Work on investigating the magnetic structure of GdB$_4$Si$_2$ is in progress.

References