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Low-temperature magnetism of the compound $GdB_{18}Si_5$

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Abstract

Low-temperature magnetic properties of single crystals of the B_{12} cluster compound $GdB_{18}Si_5$ ($R\bar{3}m$) were investigated. A sharp drop in the a–b in-plane magnetic susceptibility is observed at $T_N = 3.2$ K indicating an antiferromagnetic transition. Anisotropy between the in-plane and c-axis susceptibilities is observed, consistent with the spins ordering in the a–b plane. The logarithm of the resistivity follows the hopping $T^{-0.25}$-behaviour which has been typically observed for B_{12} icosahedral boron-rich solids, and this indicates that the typical Ruderman–Kittel–Kasuya–Yosida interaction is not the mediating interaction. A λ-like peak is observed in the magnetic specific heat at 3.2 K and supports the notion of a long-range-order antiferromagnetic transition occurring in this system.

1. Introduction

The magnetism of rare-earth boride compounds such as the hexaborides has been an extensively researched topic over the years [1–5]. Previously, magnetic transitions at moderate temperatures in rare-earth borides have been observed in metallic compounds such as REB_2 [6], REB_4 [7], the aforementioned REB_6 [1–5], and REB_{12} [8] in which the Ruderman–Kittel–Kasuya–Yosida (RKKY) mechanism generally mediates the magnetic interaction [9]. However, recently the magnetic properties of the more boron-rich B_{12} icosahedral compounds have attracted interest following the discovery of an antiferromagnetic transition at relatively high temperatures in REB_{50} which is non-metallic and has relatively large rare-earth–rare-earth spacing [10, 11]. Magnetic transitions have also been observed in the ternary $REB_{44}Si_{0.7}$ phases [12, 13] which are isostructural with REB_{50} and are the only non-metallic ternary boride compounds that we are aware of in which magnetic transitions have been observed at relatively high temperatures.

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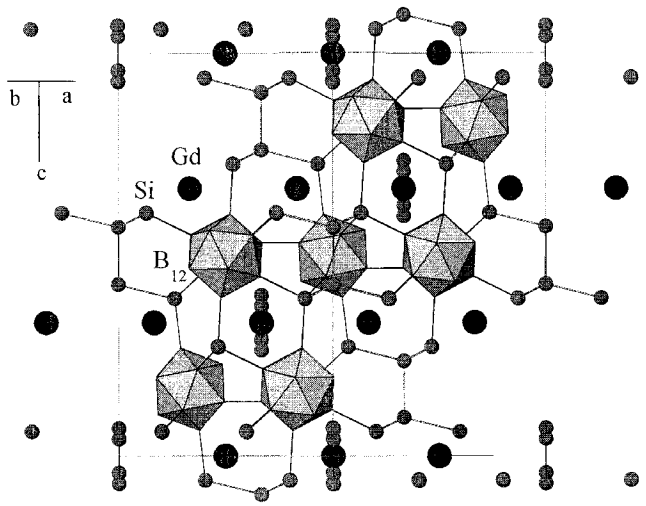

Figure 1. The crystal structure of $GdB_{18}Si_5$, projected onto the (110) plane. The polyhedra represent B_{12} icosahedra, small grey circles indicate silicon atoms, and the large black circles indicate gadolinium atoms.

In this work, we report on the low-temperature magnetic properties of the B_{12} cluster compound $GdB_{18}Si_5$. An antiferromagnetic transition at $T_N = 3.2$ K is observed. This is the third magnetic transition observed in the B_{12} icosahedral borides, following those found in the REB_{50}-type compounds [10, 11] and in TbB_{25} [14]. The specific heat of $GdB_{18}Si_5$ was measured together with that of the non-magnetic reference $YB_{18}Si_5$, and the resistivity of $GdB_{18}Si_5$ was also measured.

2. Experimental procedure

The synthesis and structure determination of $REB_{18}Si_5$ have been described previously [15]. Single crystals of $GdB_{18}Si_5$ were grown with a high-temperature solution method with Si flux and a starting composition of Gd:B:Si of around 1:20:100. That the samples were single phase was checked by pulverizing the crystals used for measurements into powder and measuring them with a high-resolution powder x-ray diffractometer (Rigaku Co.; RINT2000) with Cu Kα radiation.

The structure of $GdB_{18}Si_5$ is rhombohedral (space group $R\bar{3}m$) with lattice constants of $a = b = 1.007$ nm, $c = 1.645$ nm, and is depicted in figure 1. With the shortest metal–metal spacing, the gadolinium sites form a chain along the [110] axis with a separation of 0.504 nm.

The [001] alignment of the crystal was successfully determined; however, we could not assign the explicit in-plane alignment of the crystals by Laue photography techniques, possibly due to the complicated structure and general weakness of reflection of the boron-rich compounds. Such difficulties have been noted previously for other boron-rich borides [12].

The magnetic susceptibility was measured by using a Quantum Design MPMS-XL SQUID magnetometer from 1.8 to 300 K. The two-probe method was used to measure the resistivity up to values of 1 MΩ cm. Measurements were made by a transient heat pulse method with a small temperature increase of 2% relative to the system temperature. To provide a non-magnetic reference, the specific heat of $YB_{18}Si_5$ was also measured.

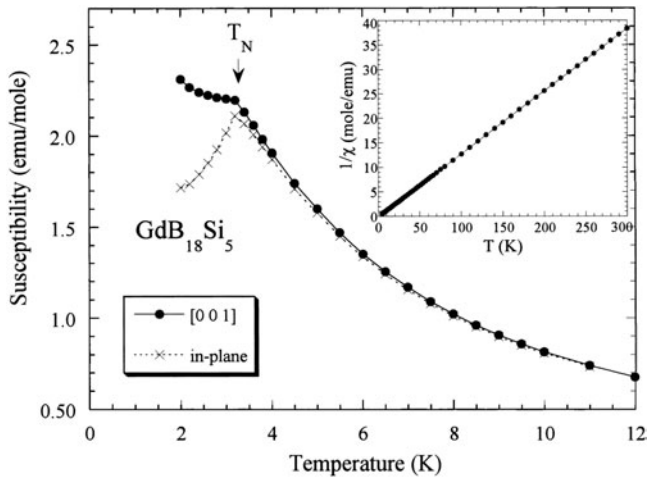

Figure 2. The temperature dependence of the static magnetic susceptibility of $GdB_{18}Si_5$ at low temperatures along the [001] direction (closed circles) and in the plane (crosses). The inset shows the inverse susceptibility along the [001] direction above 5 K. The applied magnetic field is 40 G.

3. Results and discussion

The magnetic susceptibility of $GdB_{18}Si_5$ is shown in figure 2 with a magnetic field of 40 G applied along the [001] *c*-axis and in the plane. A sharp drop in the in-plane susceptibility is observed at 3.2 K indicating that an antiferromagnetic transition occurs at this temperature. The anisotropy between the in-plane and [001] susceptibilities indicates that the spins are ordered in the *a*–*b* plane. This is the third boron-rich B_{12} icosahedral system in which a magnetic transition has been observed above 2 K, following REB_{50} [10, 11] and TbB_{25} [14]. The inverse magnetic susceptibility along the [001] axis above 5 K is plotted in the inset of figure 2. From the data on the [001] susceptibility, the effective number of Bohr magnetons $\mu_{\rm eff}$ per gadolinium atom is determined as 8.15 $\mu_{\rm B}$, which agrees fairly well with the value for trivalent free gadolinium ions, while the Curie–Weiss temperature θ is determined as -0.3 K.

The other magnetic $REB_{18}Si_5$ (RE = Tb–Yb) compounds do not show a transition down to 2 K.

The resistivity of $GdB_{18}Si_5$ measured along the [001] axis is plotted in figure 4. The resistivity follows Mott's three-dimensional variable-range-hopping (VRH) law [16]:

$$\rho = \rho_0 \exp[(T_0/T)^{1/4}] \tag{1}$$

with $\rho_0 = 8.4 \times 10^{-4}$ Ω cm and the characteristic temperature $T_0 = 6.7 \times 10^6$ K. This non-metallic behaviour is similar to the behaviour exhibited by other B_{12} icosahedral borides such as the REB_{66} and REB_{50}-type compounds [12, 17, 18]. T_0 takes a value of 4×10^7 K for example, for GdB_{66} [17]. In the 3D VRH theory, T_0 follows the relation

$$k_{\rm B}T_0 = 18.1/(D(E_{\rm F})\xi^3), \tag{2}$$

where $D(E_{\rm F})$ is the density of states at the Fermi energy $E_{\rm F}$ and ξ is the localization length at $E_{\rm F}$ [16]. Therefore, in this model $GdB_{18}Si_5$ appears to have a larger density of states at the Fermi energy or a longer localization length compared to GdB_{66}, indicating that it is less localized. This tendency seems to be reasonable, since the rare-earth atoms supply electrons to the electron-deficient boron clusters, and $GdB_{18}Si_5$ is less rich in boron. Significant anisotropy of the resistivity was not observed.

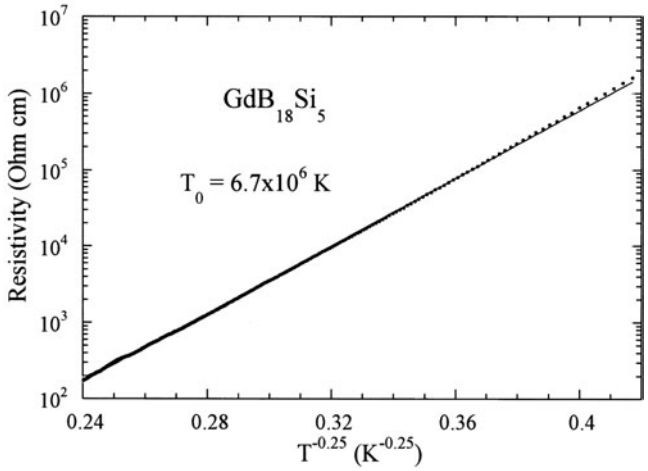

Figure 3. The temperature dependence of the resistivity along the [001] direction of $GdB_{18}Si_5$, plotted as the logarithm of the resistivity versus T to the $-1/4$ power. The line indicates the fit to equation (1).

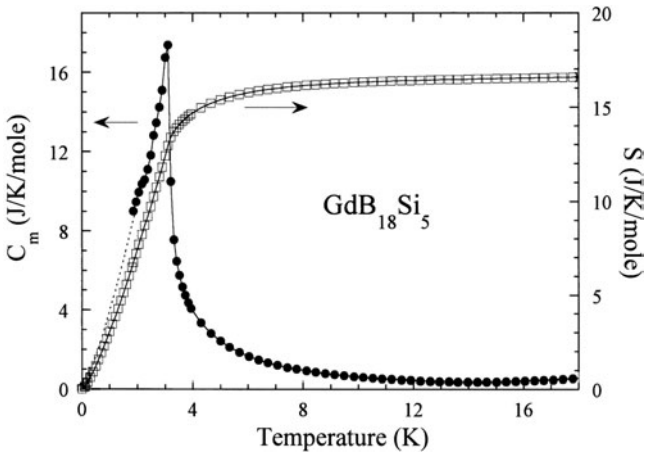

Figure 4. The temperature dependences of the magnetic specific heat C_m (closed circles) and entropy S (open squares) of $GdB_{18}Si_5$. The entropy S was calculated by extrapolating C_m to $T = 0$, using the power law function BT^{α} ($B = 3.94$ J K^{-1} mol^{-1}, $\alpha = 1.27$) which is indicated by the dotted curve.

It has been previously indicated that the B_{12} icosahedra play a role in mediating the magnetic interaction in the non-metal magnetic B_{12} compounds, and that the spacing of the magnetic rare-earth atoms along the B_{12} icosahedral axis is a critical factor in the transition [10, 11, 14]. Theoretical work is currently being done to establish the explicit mechanism of magnetic transitions in the B_{12} icosahedral compounds but, as a comparison, we note that the metal–metal spacing of the magnetic gadolinium atoms along the B_{12} icosahedral axis (figure 1) for $GdB_{18}Si_5$, which has $T_N = 3.2$ K, is 0.504 nm. This is shorter than the spacing for REB_{25} of $\sim$0.517 nm, for which GdB_{25} does not have a transition down to 1.8 K and TbB_{25} has a transition at $T_N = 2.1$ K [14]. The spacing of $GdB_{18}Si_5$ is sizably larger than the average spacing along the B_{12} icosahedral axis for REB_{50} of $\sim$0.474 nm, where TbB_{50} has

Table 1. A list of a number of B_{12} icosahedra compounds with magnetic transitions above 2 K. 'Separation' indicates the separation of the rare-earth atoms along the B_{12} icosahedral axis. GdB_{25} does not have a transition down to 2 K, and GdB_{50} does not exist.

Compound	Separation (nm)	T_N (K)
TbB_{25}	0.517	2.1[a]
$GdB_{18}Si_5$	0.504	3.2[b]
TbB_{50}	0.474	17[c]

[a] Reference [14].
[b] This work.
[c] Reference [10].

a transition at $T_N = 17$ K (the GdB_{50} phase does not exist) [11]. These parameters are listed in table 1. The general tendency of the transition temperature T_N to be higher for compounds with shorter spacing of the rare-earth atoms along the B_{12} icosahedral axis is followed. But it is interesting that in the $REB_{18}Si_5$ system the Gd phase has a transition above 2 K with no transition for the Tb phase, while the REB_{25} phase shows the opposite behaviour with a transition only observed for the Tb phase. This is an indication of the effect of the anisotropy of the rare-earth ions (in the Gd case, a lack of anisotropy) on the magnetic interaction and should be useful toward establishing the explicit mechanism of the magnetic transition in the B_{12} icosahedral compounds.

The magnetic specific heat C_m of $GdB_{18}Si_5$ was determined by subtraction of the phonon contribution from the measured total specific heat of $GdB_{18}Si_5$. The phonon contribution was estimated from the molar specific heat of the non-magnetic reference $YB_{18}Si_5$, which approximately followed a T^3-dependence in this temperature region, by correcting for the R-mass difference by multiplying by a factor of $(M_{Gd}/M_Y)^{3/2}$, where M_{RE} is the molar weight of $REB_{18}Si_5$. The temperature dependence of C_m is given in figure 4. The magnetic specific heat C_m shows a sharp λ-like peak at $T_N = 3.2$ K which supports the conclusion of a typical long-range-order antiferromagnetic transition occurring at this temperature. This behaviour is in contrast with that of the REB_{50}-structure-type $REB_{44}Si_{0.7}$ compounds which have only a broad peak in the specific heat around the transition temperature, which indicates that the transition in these compounds is of short-range-order type [18, 19]. An attempt to estimate the entropy S was made by extrapolating C_m to $T = 0$ by assuming a power law function of BT^α ($B = 3.94$ J K^{-1} mol^{-1}, $\alpha = 1.27$). The power is different from the T^3 of the specific heat of simple 3D antiferromagnetic spin waves without energy gaps, and we have also ignored any effect that nuclear specific heat contributions might have at $T \geqslant 1.8$ K on the parameters obtained for the C_m-extrapolation of BT^α. However, the resulting calculated S plotted in figure 4 attains a value close to 17 J K^{-1} mol^{-1} at 18 K, which is close to the full magnetic entropy of $R \ln 8 = 17.3$ J K^{-1} mol^{-1} expected in this case, since the $^8S_{7/2}$ ground state of Gd^{3+} is spherically symmetric and degeneracy is not expected to be lifted by crystalline electric field (CEF) effects. Therefore, it appears that our extrapolation yielded reasonable results, but for a more rigorous treatment, the low-temperature $T \leqslant 1.8$ K specific heat of $GdB_{18}Si_5$ should be measured to investigate this further.

4. Conclusions

Low-temperature magnetic properties of single crystals of the B_{12} cluster compound $GdB_{18}Si_5$ were investigated. A drop in the in-plane magnetic susceptibility is observed at $T_N = 3.2$ K indicating that an antiferromagnetic transition occurs in this system. Anisotropy is observed,

typical of an antiferromagnet with the spins ordered in the a–b plane. The resistivity follows the hopping $T^{-0.25}$-behaviour which has been typically observed for B_{12} icosahedral boron-rich solids. $GdB_{18}Si_5$ is the third non-metal boron-rich B_{12} icosahedral system in which a magnetic transition has been observed above 2 K. Although the explicit mechanism of the magnetic interaction in the B_{12} icosahedral rare-earth borides has yet to be established, the spacing of the magnetic ions along the B_{12} icosahedral axis and the transition temperature were compared and found to be consistent with what has been observed previously for the other magnetic B_{12} compounds.

Acknowledgments

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