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Magnetism of Higher Borides

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Magnetism of borides which contain the B_{12} icosahedra as a structural building block are attracting increasing interest since they exhibit unexpectedly strong magnetic interactions, despite being magnetically dilute f-electron insulators. The magnetic behavior among the different compounds has also been found to be diverse. The f-electron dependence of magnetic B_{12} icosahedra borides is compared, and found to be different from conventional mechanisms. The TbB_{25} system is also investigated further and the transition is assigned to a typical antiferromagnetic transition.

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1. Introduction

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 [1–6], with recent interesting discoveries still being made such as the complex magnetic structure revealed in REB_{12} [7]. 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–Yosida (RKKY) mechanism with possible secondary effects from the dipole-dipole interaction. As an emerging novel phenomenon, it has been found that borides which contain the B_{12} icosahedra as a structural building block [8] can exhibit unexpectedly strong magnetic interactions, although they are relatively magnetically dilute, f-electron insulators. For example, $T_N = 18$ K for TbB_{50} [10] and the peak temperature in the zero field cooled (ZFC) susceptibility of $HoB_{17}CN$ is $T_* = 29$ K [9]. A wide variation of the magnetic behavior has also been observed, ranging from the one-dimensional dimer-like antiferromagnetic transition in REB_{50} and $REB_{44}Si_2$ [9, 11, 12], two-dimensional spin-glass behavior in $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$ [10, 13, 14] to three-dimensional long-range order in $GdB_{18}Si_5$ [15].

We analyze the f-electron dependence of some of the magnetic higher borides which contain the B_{12} icosahedra. Furthermore, a low temperature

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antiferromagnetic-like transition was previously reported in TbB_{25} [16], and we investigate the nature of this transition in more detail.

2. Experimental

In regards to synthesis, TbB_{25} was synthesized by the borothermal reduction of terbium oxide under vacuum; $Tb_2O_3 + 53B \rightarrow 2TbB_{25} + 3BO$, as described previously [16]. The reaction was performed under vacuum in a BN crucible surrounded by an inductively heated composite susceptor at 1900°C. Characterization was done by powder X-ray diffractometry and chemical analysis (AES-ICP). Magnetic properties were measured with a SQUID magnetometer (Quantum Design MPMS).

3. Results and discussion

First of all, the magnetic coupling mechanism in the insulating higher borides is considered. The characteristic temperatures of the magnetism for some B_{12} icosahedra containing rare earth borides are plotted in Fig. 1. The expected dependences in the case of the conventional f-electron mechanisms, RKKY mechanism and dipole–dipole interaction are also shown with the value for Er arbitrarily set as 4.5 K, which is the characteristic temperature of $ErB_{28.5}C_4$.

The RKKY interaction scales with the de Gennes factor [17]

$$Int_{\mathrm{RKKY}} \propto (g_J - 1)^2 J(J+1), \tag{1}$$

where g_J is the Lande factor and J — the total angular momentum. The dipole–dipole interaction can approximately be expressed by [18]

$$Int_{\mathrm{dipole}} \propto g_J^2 \mu_{\mathrm{B}}^2 J(J+1). \tag{2}$$

As shown in Fig. 1, we find that the f-electron dependences of the characteristic temperatures of the magnetic behavior observed for the higher borides do not simply follow either mechanism. This is also underlined by the fact that the Tb phase has the highest T_{N} for REB_{25} [16], while Gd has the highest for $REB_{18}Si_5$ [15].

As noted in the introduction, the magnetic behavior in higher borides manifests in a wide variety of forms. The reported transition at 2.1 K in TbB_{25} is investigated in more detail by varying the magnetic field.

The magnetic field dependence of χ of TbB_{25} is plotted in Fig. 2a. The transition temperature T_{N} shifts to lower temperatures as the magnetic field is increased. We determine T_{N} as the temperature, where $\mathrm{d}\chi/\mathrm{d}T = 0$ for each magnetic field. If we assume a simple quadratic suppression of T_{N} due to magnetic fields as determined, for example, by Shapira and Foner [19]

$$T = T_{\mathrm{N}}(1 - (H/H_{\mathrm{C}})^2), \tag{3}$$

we can obtain a good fitting curve as shown in Fig. 2b. Parameters are determined as $T_{\mathrm{N}} = 2.1$ K and $H_{\mathrm{C}} = 5.1$ kOe. This determined value of H_{C} is within the

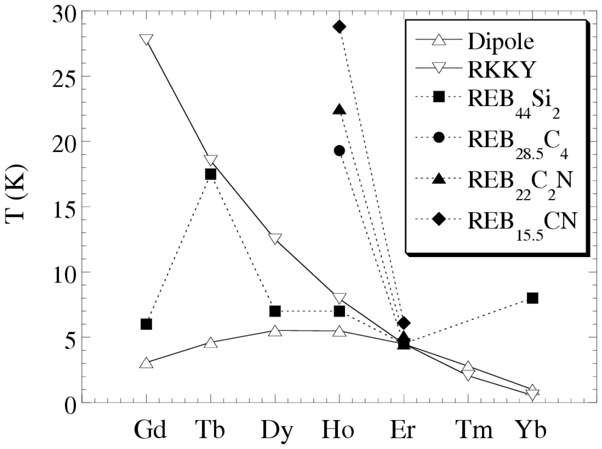

Fig. 1. Rare earth dependence of the characteristic temperatures of the magnetism of rare earth higher borides. T_N for $REB_{44}Si_2$ [11, 12] and the peak temperature T_* of χ_{ZFC} for $REB_{28.5}C_4$, $REB_{22}C_2N$, and $REB_{15.5}CN$ [13, 14, 10] are plotted. Theoretical values for the RKKY interaction and dipole-dipole mechanism are also plotted after normalizing at an arbitrary value of 4.5 K for erbium for visual clarity.

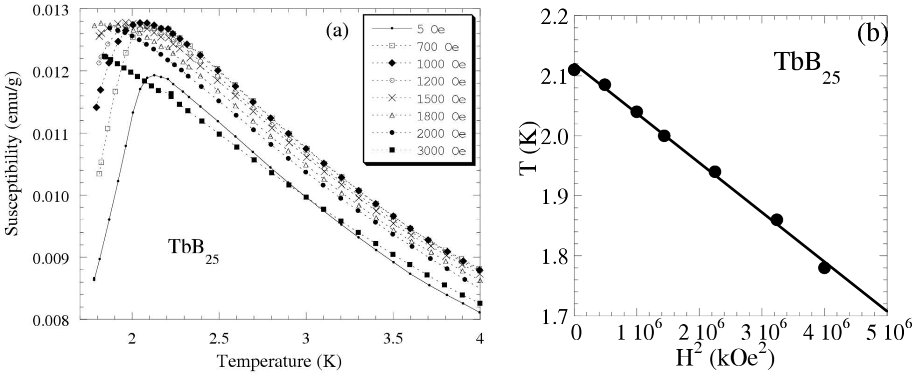

Fig. 2. (a) Magnetic field dependence of the magnetic susceptibility for TbB_{25}. (b) The fit to Eq. (4), $T = T_N(1-(H/H_C)^2)$, yields parameters of $T_N = 2.1$ K and $H_C = 5.1$ kOe.

magnitude of order which is expected for local moment antiferromagnets: $H_C \sim k_B T_N/\mu_B = 14$ kOe.

Hysteresis is not observed and it is indicated that the transition in TbB_{25} is a typical antiferromagnetic transition.

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