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Physical properties of layered homologous *RE*–B–C(N) compounds

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Abstract

Physical properties of a series of homologous *RE*–B–C(N) B_{12} cluster compounds $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$ (RE = Er, Ho) were investigated. The structures of the compounds are layer-like along the *c*-axis, with rare earth and B_6 octahedral layers separated by B_{12} icosahedral and C–B–C chain layers whose number increases successively from two B_{12} layers for the $REB_{17}CN$ compound to four for the $REB_{28.5}C_4$ compound. The rare earth atoms are configured in two triangular flat layers which are stacked on top of one another in AB stacking where the nearest-neighbor rare earth directions are the three atoms forming a triangle in the adjacent layer. The series of homologous compounds exhibit a spin glass transition with T_f shifting in correspondence with variations of the basal plane lattice constants, consistent with the magnetic interaction being effective in the basal planes. The isothermal remanent magnetization shows a stretched exponential decay $I_m(t) \propto \exp[-Ct^{-(1-n)}]$. Exponents determined for the different homologous compounds were scaled as a function of $T_r = T/T_f$ and found to follow the empirical dependency determined for typical spin glasses. It is indicated that a mixture of disorder originating from the partial occupancy of the rare earth sites and frustration of interactions due to the unique configuration is responsible for the manifestation of spin glass transitions in these homologous systems.

Keywords: Rare earth boron-rich borides; B_{12} icosahedra; Spin glass

1. Introduction

Recently, the magnetic properties of rare earth B_{12} icosahedral cluster compounds have attracted growing interest because a number of magnetic transitions have been discovered at moderate temperatures despite the non-metallic and magnetically dilute nature of the compounds. Antiferromagnetic transitions have been found for the REB_{50}-type compounds [1–3], TbB_{25} [4], and $GdB_{18}Si_5$ [5]. It has also been reported that $Ca_{1-x}La_xB_6$ [6] and CaB_2C_2 [7] exhibit high-temperature ferromagnetism. However, we have demonstrated that the observed ferromagnetism in the two systems are indicated to be non-intrinsic phenomena [8,9].

Quite recently as a new development, it was discovered that the rhombohedral B_{12} cluster compounds $ErB_{22}C_2N$ and $HoB_{22}C_2N$ exhibit spin glass behavior [10]. This is the first example of magnetic glassiness being observed in a boron-rich cluster compound, where rare earth atoms reside in boron frameworks. The $REB_{22}C_2N$ compound has been found to be one in a series of layered homologous compounds, $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$. In this report the glassy properties of the series of compounds were measured and compared.

2. Experimental

$REB_{17}CN$ was the first compound discovered of the homologous *RE*–B–C(N) compounds [11]. Following this discovery, the series of *RE*–B–C(N) homologous compounds was also synthesized [12]. Synthesis of the single phase polycrystalline samples of $REB_{17}CN$, $REB_{22}C_2N$, and $REB_{28.5}C_4$ (RE = Er, Ho) measured in this work were carried out in the following way. The purity of all starting materials was the same as described in Ref. [11], this issue. As a first step, the powders of

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$RE\mathrm{B}_m$ ($m: 12-16, RE = \mathrm{Er, Ho}$) were synthesized by the borothermal reduction of rare earth oxide under vacuum using BN crucibles:

$$RE_2\mathrm{O}_3 + (2m+3)\mathrm{B} \rightarrow 2RE\mathrm{B}_{(m)} + 3\mathrm{BO}. \quad (1)$$

After this, the desired amounts of boron, carbon, and hexagonal BN, were added and the mixture reacted again at a temperature of around 1700°C. The samples were characterized by a high-resolution powder X-ray diffractometer (Rigaku Co.; RINT2000) with Cu$K\alpha$ radiation. $RE\mathrm{B}_{17}\mathrm{CN}$ is trigonal (space group *P*-3*m*1) while $RE\mathrm{B}_{22}\mathrm{C}_2\mathrm{N}$ and $RE\mathrm{B}_{28.5}\mathrm{C}_4$ are rhombohedral (space group *R*-3*m*). The lattice constants of the homologous compounds are given later in Table 1 together with magnetic parameters. The structures are depicted in Fig. 1. The compounds have a layered structure along the *c*-axis with rare earth and B_6 octahedral layers separated by B_{12} icosahedral and C–B–C chain layers whose number increases successively from two B_{12} layers for the $RE\mathrm{B}_{17}\mathrm{CN}$ compound to four for the $RE\mathrm{B}_{28.5}\mathrm{C}_4$ compound. The configuration of the rare earth atoms with respect to each other is the same for all the *RE*–B–C(N) homologous compounds. The unit cells contain two triangular layers of rare earth atoms stacked in AB configuration, which in projection along the *c*-axis appear as a honeycomb array. In this configuration, each rare earth metal atom has as nearest neighbors three rare earth metal atom forming a triangle in the adjacent layer. In the case of $\mathrm{ErB}_{17}\mathrm{CN}$ for example, the nearest-neighbor distances are around 3.46 Å while the second nearest-nearest-neighbor distance is the separation within the triangular layers, 5.59 Å. Measurements were made using a SQUID magnetometer from 1.8 to 300 K and fields up to 5.5 T.

Table 1
Crystallographic data and magnetic parameters of homologous *RE*–B–C(N) ($RE = \mathrm{Er, Ho}$) compounds

	a (Å)	*c* (Å)	μ_{eff} (μ_B/RE atom)	θ (K)	T_f (K)
$\mathrm{ErB}_{17}\mathrm{CN}$	5.589	10.880	8.89	−4.0	6.1
$\mathrm{ErB}_{22}\mathrm{C}_2\mathrm{N}$	5.624	44.681	9.02	−7.1	5.1
$\mathrm{ErB}_{28.5}\mathrm{C}_4$	5.640	56.868	8.79	−7.5	4.5
$\mathrm{HoB}_{17}\mathrm{CN}$	5.588	10.878	9.84	15.6	28.8
$\mathrm{HoB}_{22}\mathrm{C}_2\mathrm{N}$	5.614	44.625	10.1	−16.9	22.5
$\mathrm{HoB}_{28.5}\mathrm{C}_4$	5.638	56.881	9.60	9.7	19.3

3. Results and discussion

The magnetic susceptibility of $\mathrm{ErB}_{17}\mathrm{CN}$, $\mathrm{ErB}_{22}\mathrm{C}_2\mathrm{N}$, and $\mathrm{ErB}_{28.5}\mathrm{C}_4$ are shown in Fig. 2. Similar to what was

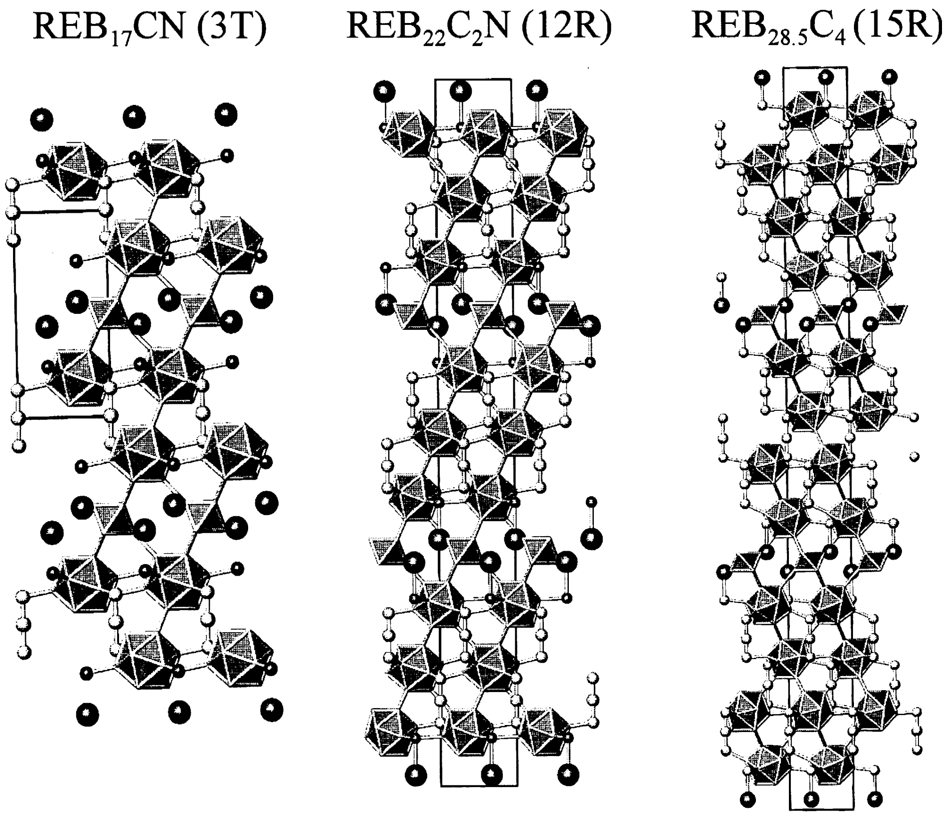

Fig. 1. Crystal structure of $RE\mathrm{B}_{17}\mathrm{CN}$, $RE\mathrm{B}_{22}\mathrm{C}_2\mathrm{N}$, $RE\mathrm{B}_{28.5}\mathrm{C}_4$, views perpendicular to the *c*-axis. The large polyhedra are B_{12} icosahedra, smaller polyhedra indicate B_6 octahedra, small dark circles indicate nitrogen atoms, the three bonded atoms along [001] are C–B–C chains, and the large dark circles indicate rare earth atoms.

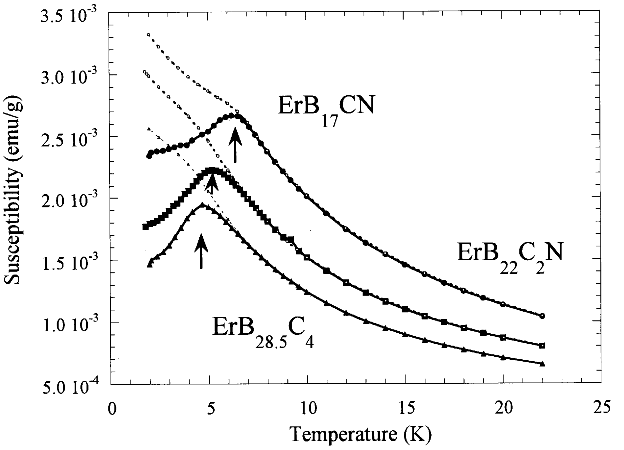

Fig. 2. Temperature dependence of the magnetic susceptibility of $ErB_{17}CN$ (squares), $ErB_{22}C_2N$ (circles), and $ErB_{28.5}C_4$ (triangles) for zero field cooled (ZFC) (closed symbols) and field cooled (FC) curves (small open symbols). The magnetic field is 50 G. The data for $ErB_{22}C_2N$ are the same as that in Ref. [10].

noted before for $ErB_{22}C_2N$ [10], the field cooled (FC) magnetic susceptibility was found to show surprising divergences from the zero field cooled (ZFC) magnetic susceptibility for the $ErB_{17}CN$ and $ErB_{28.5}C_4$ compounds also, indicating that spin glass transitions occur in these compounds too. The spin glass transition temperatures which we take to be the cusps of the ZFC susceptibilities, T_f, show a shift between the layered homologous compounds. The spacing of the rare earth layers along the *c*-axis is approximately 10, 15, and 19 Å for $ErB_{17}CN$, $ErB_{22}C_2N$, and $ErB_{28.5}C_4$, respectively (see Fig. 1). Considering that the spacing is substantial ($\geqslant 10$ Å) and above all, varies substantially among the homologous compounds, we can conclude that the magnetic interaction along the *c*-axis is indicated to be a negligible factor in this system and the transition is mediated in the basal plane. As can be seen in Table 1, T_f monotonically decreases as the basal plane lattice constant a increases (corresponding to an increase in the separation of the rare earth atoms in the basal plane). This is the fourth non-metallic B_{12} icosahedral system, following the $RE$$B_{50}$-type compounds [1–3], TbB_{25} [4], and $GdB_{18}Si_5$ [5], in which a sizable magnetic interaction has been observed resulting in transition temperatures above 2 K. Theoretically solving the explicit mechanism mediating the magnetic interaction is a work in progress, but it is clear that since these compounds are non-metallic exhibiting variable range hopping, the RKKY mechanism [13] which mediates interaction in typical magnetic boride compounds such as the REB_4 and REB_6 systems [14,15] is not effective here.

From the Curie–Weiss fitting $C/(T\text{-}\theta)$ of the susceptibility curve at high temperatures sufficiently above T_f, we obtain magnetic parameters θ and effective magnetic moments μ_{eff} which are also listed in Table 1. The low-temperature upturn in the susceptibility curves can be attributed to Curie tails which have been observed before for magnetic B_{12} compounds [1–3,10].

The holmium phase *RE*–B–C(N) homologous compounds show similar behavior to the erbium phases, with higher transition temperatures (Fig. 3). The determined magnetic parameters are also listed in Table 1 and the trend of T_f is observed to also follow the variation of basal plane lattice constants.

The magnetization of all the *RE*–B–C(N) homologous compounds showed hysteresis at low temperatures below T_f. For example, the enlarged magnetization curve of $ErB_{28.5}C_4$ at 2 K is plotted in Fig. 4. Sizable hysteresis is observed and the magnetization does not show a saturation even at the highest fields of 5.5 T in agreement with a spin glass state.

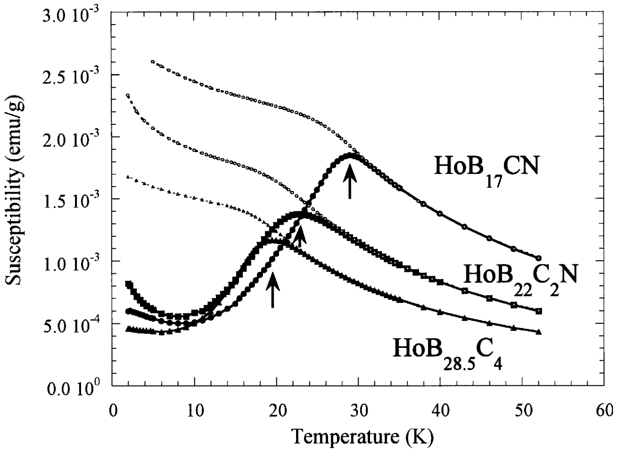

Fig. 3. Temperature dependence of the magnetic susceptibility of $HoB_{17}CN$ (squares), $HoB_{22}C_2N$ (circles), and $HoB_{28.5}C_4$ (triangles) for zero field cooled (ZFC) (closed symbols) and field cooled (FC) curves (small open symbols). The magnetic field is 50 G. The data for $HoB_{22}C_2N$ are the same as that in Ref. [10].

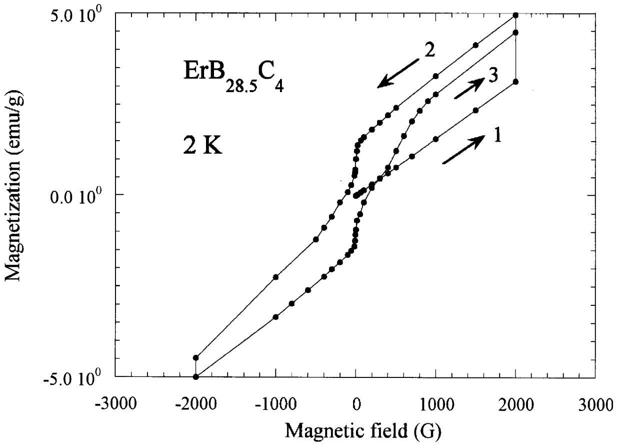

Fig. 4. Enlarged magnetization curves of $ErB_{28.5}C_4$ at 2 K. The arrows indicate the increase and decrease of magnetic field.

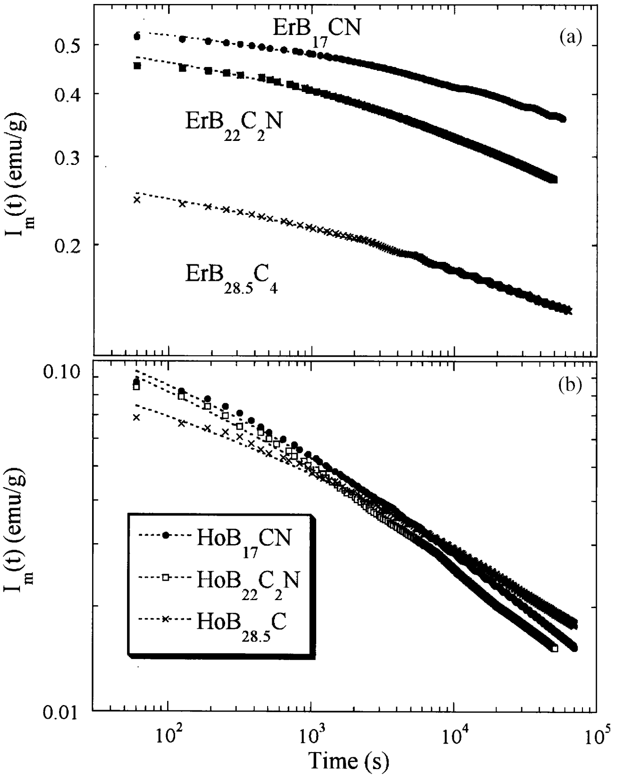

Fig. 5. Time decay of the isothermal remanent magnetization I_m of (a) $ErB_{17}CN$ (squares), $ErB_{22}C_2N$ (circles), $ErB_{28.5}C_4$ (crosses) and (b) $HoB_{17}CN$ (squares), $HoB_{22}C_2N$ (circles), $HoB_{28.5}C_4$ (crosses). The measurements were made at 2 K for the Er phase samples, and 5 K for the Ho phase samples. The lines depict the fit to $I_m(t) = I_0 \exp[-Ct^{-(1-n)}]$.

Table 2
Parameters determined from the stretched exponential fit Eq. (2) of the isothermal remanent magnetization of homologous *RE*–B–C(N) ($RE = \mathrm{Er, Ho}$) compounds

	I_0 (emu/g)	C ($s^{1/(1-n)}$)	$1-n$
$ErB_{17}CN$	0.612	0.0672	0.190
$ErB_{22}C_2N$	0.606	0.122	0.176
$ErB_{28.5}C_4$	0.372	0.229	0.127
$HoB_{17}CN$	0.525	1.13	0.102
$HoB_{22}C_2N$	0.534	1.16	0.104
$HoB_{28.5}C_4$	0.258	0.791	0.110

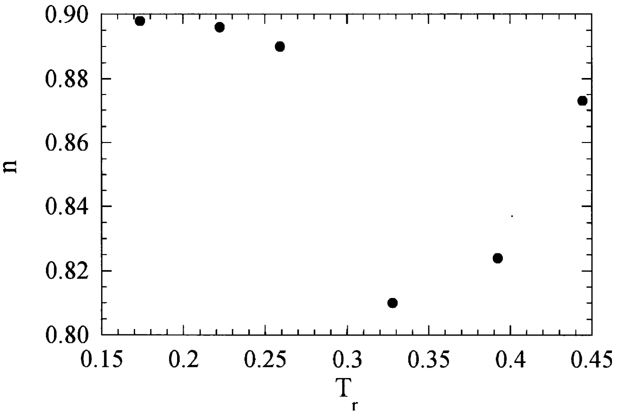

Fig. 6. Exponents n determined from the data of Fig. 5 for the different homologous compounds plotted as a function of the reduced temperature $T_r = T/T_f$.

In Figs. 5(a) and (b) are shown the isothermal remanent magnetization I_m of the *RE*–B–C(N) homologous compounds measured at low temperatures. As can be seen, I_m decays slowly over several decades of time. The measuring temperatures are 2 and 5 K for the Er and Ho phases, respectively. A field of 10 kG was applied for 5 min after which the field was charged to zero and I_m measured. The time dependences can be fitted well as stretched exponentials

$$I_m(t) = I_0 \exp[-Ct^{-(1-n)}], \tag{2}$$

which have been observed for typical spin glasses [16]. The fitting parameters are listed in Table 2. The exponents determined for the different homologous compounds were plotted as a function of the reduced temperature $T_r = T/T_f$ in Fig. 6. The dependency generally agrees with the empirical T_r dependence of 1-n determined previously for some typical spin glass systems in which n approaches 0.9 as T_r approaches zero and there appears to be a broad minimum around $T_r = 0.4$. [17]. Therefore, in this context, the behavior of the different homologous *RE*–B–C(N) compounds apparently can be scaled by T_r, although further extensive measurements should be made as the next step. As a physical picture, the stretched exponential relaxation in spin glasses has been explained by various models such as the cooperative–relaxation theory of Ngai [18], the fractal cluster model of Continentino and Malozemoff [19], or the disorder–diffusion theory of Grassberger [20], although absolute values of experimentally determined parameters have not always been satisfactorily explained.

The rare earth sites in the homologous compounds have partial occupancy [11,12] which can be considered to be a significant source of disorder which is necessary to cause a glassy state. Some degree of frustration of the magnetic interactions is also typically observed in spin glasses, such as the strong geometrical frustration in pyrochlores [21]. Although the explicit form of the magnetic interaction in these B_{12} compounds must be solved, the configuration of the rare earth sites in the *RE*–B–C(N) homologous compounds is also likely to cause frustration if antiferromagnetic interaction within the flat triangular layers is dominant, since there is no spin configuration which can simultaneously minimize the energy of all the bonds.

Making a comparison with some other B_{12} magnetic compounds, we see that (1) the REB_{50}-type compounds have full occupancy of *RE* sites and therefore no source of sizable disorder, (2) $GdB_{18}Si_5$ has partial occupancy of Gd sites but geometrically does not have frustration of the magnetic interactions, (3) $RE\mathrm{B}_{66}$ has large disorder [22] but only a small magnetic interaction [1]. Therefore, it is indicated that the *RE*–B–C(N) homologous compounds provide a unique system where there is both disorder originating from partial occupancy of rare earth sites and simultaneous frustration due to their configuration, which results in the first spin glass transitions observed in rare earth boron cluster systems.

4. Conclusions

$RE\mathrm{B}_{17}\mathrm{CN}$ and $RE\mathrm{B}_{28.5}\mathrm{C}_4$ as well as other homologous *RE*–B–C(N) compounds exhibit spin glass behavior. Magnetic interactions in these compounds are effectively mediated in the basal plane. Stretched exponents determined from analysis of relaxation of the isothermal remanent magnetization for different homologous compounds were scaled as a function of $T_\mathrm{r} = T/T_\mathrm{f}$ and found to follow the empirical dependency for typical spin glasses.

The uniqueness of the *RE*–B–C(N) homologous compounds compared to other borides which do not manifest such a spin glass state is a mixture of disorder originating from the partial site occupancy and frustration of relatively strong magnetic interactions due to the unusual configuration of the rare earth sites.

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