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Dynamical properties of a crystalline rare-earth boron cluster spin-glass system

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Dynamical properties of the magnetic B_{12} cluster compound $HoB_{22}C_2N$ were investigated. $HoB_{22}C_2N$ is taken to be representative of the class of trigonal and rhombohedral B_{12} cluster compounds which were found to exhibit spin-glass behavior as measured by dc superconducting quantum interference device magnetometer and specific-heat measurements. These are examples of magnetic glassiness being observed in rare earth boron-rich crystalline cluster compounds. Well defined maxima in the in-phase linear ac susceptibility χ' curves were observed, indicative of the spin-glass transition. Strong frequency dependence of the cusp temperature T_f was found. The dependence of T_f could not be analyzed satisfactorily by the dynamical scaling theory of a three-dimensional spin glass. A more detailed investigation of the behavior of relaxation times by Cole-Cole analysis showed that the behavior in $HoB_{22}C_2N$ is different from the simple blocking of a superparamagnetic system, because of the temperature dependence of the parameter α representing the width of the relaxation-time distribution function $g(\tau)$. The median relaxation time was also determined and the data were found to be described well in terms of a generalized Arrhenius law $\ln \tau \propto T^{-2.5}$. These results indicate that $HoB_{22}C_2N$ is a two-dimensional spin-glass system, which supports what has been speculated previously.

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I. INTRODUCTION

The study of spin-glass systems has been a fascinating topic in magnetism for many years[1–3] with recent exciting discoveries in the "spin ice" compounds.[4,5] The magnetic properties of rare earth B_{12} icosahedral cluster compounds have also attracted growing interest because a number of magnetic transitions have been discovered at moderate temperatures despite the nonmetallic and magnetically dilute nature of the compounds. Antiferromagnetic transitions have been found for the RB_{50},[6,7] TbB_{25},[8] $RB_{44}Si_2$-type compounds,[9–11] and $GdB_{18}Si_5$.[12] An interesting feature of these transitions is that the B_{12} icosahedra are indicated to mediate the magnetic interaction[6–10] which is a new phenomenon in the boride compounds. It has also been reported that La doped CaB_6 (Ref. 13) and CaB_2C_2 (Ref. 14) exhibit high temperature ferromagnetism. However, we have demonstrated that the observed ferromagnetism in the two boride systems are indicated to be of nonintrinsic origin,[15,16] with the magnetism in the former case indicated to be due to iron impurities electrochemically plated onto the CaB_6 crystal surface during the flux removal procedure.

Quite recently it was discovered that a series of B_{12} cluster compounds $RB_{17}CN$, $RB_{22}C_2N$, and $RB_{28.5}C_4$ exhibit spin-glass behavior.[17–19] These are examples of magnetic glassiness being observed in a boron-rich crystalline cluster compound, where rare-earth atoms reside in boron frameworks. It has been observed that since the configuration of the rare-earth atoms in the basal planes of the three compounds is similar, they display basically the same spin-glass behavior with some minor variations attributed to the differences in basal plane lattice constants.[19] The structure of $RB_{22}C_2N$ has 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. The unit cell contains three sets of two flat triangular rare-earth atom layers closely stacked on top one another in *AB* configuration. In this configuration, each rare earth metal atom has as nearest neighbors three rare-earth metal atoms forming a triangle in the adjacent layer. However, it has been indicated that the interaction in the two-dimensional flat triangular planes is dominant.[17,19]

In this work, the dynamical properties of $HoB_{22}C_2N$ as representative of this series of compounds was investigated using ac susceptibility as a probe over five decades of frequency.

II. EXPERIMENT

Synthesis of the single phase polycrystalline samples of $HoB_{22}C_2N$, was carried out as described previously.[17] The samples were characterized by a high resolution powder x-ray diffractometer (Rigaku Co.; RINT2000) with Cu $K\alpha$ radiation and chemical analysis. $HoB_{22}C_2N$ is rhombohedral (space group *R-3m*) with lattice constants of $a=b=5.614$ Å, $c=44.625$ Å. The nearest-neighbor distances for $HoB_{22}C_2N$ are around 3.54 Å while the second-nearest-nearest-neighbor distance is the separation within the triangular layers, 5.62 Å.

ac susceptibility measurements were made using a superconducting quantum interference device (SQUID) magnetometer in which the residual field was reduced below 1.0 Oe by resetting the magnet. Both the in-phase component χ' and out-of-phase component χ'' were measured. The amplitude of applied ac field was 3.0 Oe while frequencies were varied from 0.08 to 801 Hz.

III. RESULTS AND DISCUSSION

High temperature Curie Weiss fit of the dc susceptibility yields a Curie-Weiss temperature of $\theta=-16.9$ K and an

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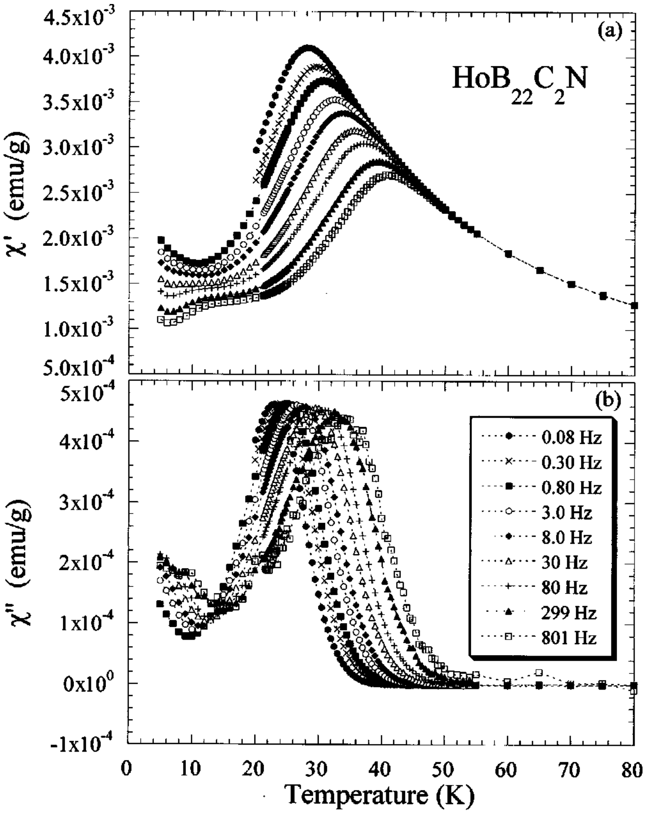

FIG. 1. Temperature dependence of the (a) in-phase χ', (b) out-of-phase χ'', linear ac magnetic susceptibility of $HoB_{22}C_2N$. The amplitude of the ac magnetic field is 3 Oe, while the ac measuring frequencies are 0.08 Hz (closed circles), 0.30 Hz (×), 0.80 Hz (closed squares), 3.0 Hz (open circles), 8.0 Hz (closed diamonds), 30 Hz (open triangles), 80 Hz (crosses), 299 Hz (closed triangles), and 801 Hz (open squares).

effective moment of $\mu_{\mathrm{eff}}=10.1\mu_{\mathrm{B}}/\mathrm{f.u.}$[17] The effective moment is close to the value expected for trivalent Ho ions and indicates that the moments in this system are located on the holmium sites.

Measured values of the in-phase χ', and out-of-phase χ'', linear ac susceptibilities are plotted in Figs. 1(a) and 1(b) for a frequency range of 0.08 to 801 Hz. χ' shows a well defined peak as is expected for a spin glass or superparamagnet, while the absorption χ'' shows a rise from zero as temperature is lowered, with maximum slope occurring around the peak temperature in χ' indicating that the existence of relaxation processes in this magnetic system.

The χ' curves exhibit frequency dependence which is also a characteristic shared by the two systems. As frequency is increased, the cusp temperature T_f increases. We can approximately estimate the relative variation of T_f per frequency decade

$$K=\Delta T_f/[T_f\Delta\ln(f)], \tag{1}$$

where T_f is determined from the derivative of χ' (where $d\chi'/dT=0$), f is the frequency, and Δ points to the difference between measurements at different frequencies.

K is estimated to be around 9×10^{-2} for $HoB_{22}C_2N$ which is an insulator. This is close to the value $K=8\times10^{-2}$ found for (Fe,Mg)Cl_2, for example, which is an insulating spin glass.[2] Metallic spin glasses have typically been found to take smaller values such as 1×10^{-2} or less. In the case of typical superparamagnets larger values of K such as $K=0.28$ for holmium borate glass a-$[Ho_2O_3(B_2O_3)]$ have been observed.[2] Although this is not a rigid criteria and the difference is not large, it points to our system being an insulating (or cluster) spin glass versus a superparamagnet. The fact that interactions observed in the B_{12} cluster compounds up to now, including this compound[17] have been antiferromagnetic[6–12] is another point against this compound being a superparamagnetic system. And yet another argument against what we are observing being simple blocking phenomena of a superparamagnet is that we have observed wait time effects in the remnant magnetization.[17]

We note that on attempting a fit of our data to an Arrhenius law

$$f=f_0\exp[-E_a/k_BT_f], \tag{2}$$

which has been used to describe blocking phenomena in typical non-interacting superparamagnets, a passable fit was obtained. Parameters such as $f_0=4.0\times10^{11}$ Hz and $E_a/k_B=820$ K are obtained. f_0 is on the large side for an insulating superparamagnet since it corresponds to a microscopic limiting relaxation time of only 2.5×10^{-12} s but it is not unphysical. E_a represents an energy barrier which depends on the magnetic anisotropy energy constant and particle volume,[20] but it is not simple to estimate whether this value would be appropriate or not for our particular system. However, our system is not considered likely to be a superparamagnet for reasons listed above, and further strong proof of this is obtained later from the Cole-Cole analysis.

Now we attempt to analyze our results in terms of the dynamical slowing down of the spin fluctuations above the glass transition temperature T_0 in a three-dimensional spin glass.[2,21] The well known result of dynamical scaling gives the relation $\tau\sim\xi^z$, where τ is the measured relaxation time, ξ the correlation length, and z the dynamic exponent.[2,21] The correlation length ξ diverges as $\xi\sim[T/(T-T_0)]^{\nu}$ with ν the critical exponent. From this we can obtain the relation

$$\tau/\tau_0=[(T-T_0)/T]^{-z\nu}, \tag{3}$$

where τ_0 is the shortest relaxation time of the system. This can be written as

$$T_f=T_0[1+(\tau_0 f)^{1/z\nu}]. \tag{4}$$

Because the least squares fitting to our data in this case is largely dependent on the starting values assigned to the three parameters and therefore not completely satisfactory, we assume $T_0=22.5$ K assigned from the dc measurements.[17] Then we obtain a fit with $\tau_0=2.5\times10^{-4}$ s, $z\nu=8.3$. The value of $z\nu$ agrees with the range of $z\nu\sim7.9\pm1$ determined by the simulations of Ogielski[22] for three-dimensional spin glasses with short-range magnetic interactions. However, the obtained value of $\tau_0=2.5\times10^{-4}$ s as the shortest relaxation time is too long to be satisfactory, since typically, values in

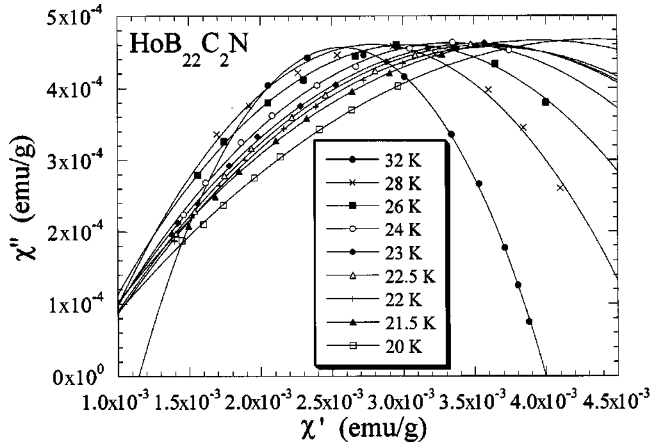

FIG. 2. Argand diagrams of $HoB_{22}C_2N$ for 32 K (closed circles), 28 K (×), 26 K (closed squares), 24 K (open circles), 23 K (closed diamonds), 22.5 K (open triangles), 22 K (crosses), 21.5 K (closed triangles), and 20 K (open squares). The lines are fits to Eq. (6).

the range of 10^{-11}–10^{-13} s have been obtained for canonical spin glasses such as CuMn,[2] while Bontemps *et al.* have determined $\tau_0 \sim 2\times10^{-7}$ s for $Eu_{0.6}Sr_{0.4}S$ which is an insulating system similar to ours.[23]

We note that although the criteria of using the cusp temperature T_f of χ' has been widely used to analyze the dynamics of spin-glass systems, it has been pointed out that this may not be the best criteria for analysis.[23–26] We have used the above general analysis method to make a comparison with contemporary results in other systems, but for example, even using the criteria proposed by Bontemps *et al.*,[23] we find that the dynamical scaling theory for three-dimensional systems does not describe our results well.

To further investigate the behavior of relaxation times in this system in more detail, we attempt a Cole-Cole plot analysis[27] such as has been carried out by Huser *et al.*[28] and Dekker *et al.*[29] for spin glass systems. The complex susceptibility can be phenomenologically expressed as

$$\chi = \chi_s + \frac{\chi_0 - \chi_s}{1 + (i\omega\tau_C)^{1-\alpha}}, \tag{5}$$

where χ_0 and χ_s are the isothermal ($\omega = 0$) and adiabatic ($\omega \to \infty$) susceptibilities, respectively, τ_C is the median relaxation time around which a distribution of relaxation times (symmetric on the logarithmic scale) is assumed, while α ($0 < \alpha < 1$) is representative of the width of the distribution. $\alpha = 1$ for a distribution of infinite width, while $\alpha = 0$ for the Debye form of a single relaxation time. This equation can be decomposed into χ' and χ'' to obtain the relation

$$\chi'' = -\frac{\chi_0 - \chi_s}{2\tan[(1-\alpha)\pi/2]} + \sqrt{(\chi_0 - \chi')(\chi' - \chi_s) + \frac{(\chi_0 - \chi_s)^2}{4\tan^2[(1-\alpha)\pi/2]}}. \tag{6}$$

We use this equation to fit the Argand diagrams in Fig. 2, where the χ' and χ'' from Fig. 1 are plotted in the complex plane. The maxima of the diagrams give $\omega\tau_C = 1$, while the flatness of the arcs are a measure of the width of the distribution of relaxation times. We determine the actual values of τ_C at each temperature by using the refined values of χ_0, χ_s, α in the relation

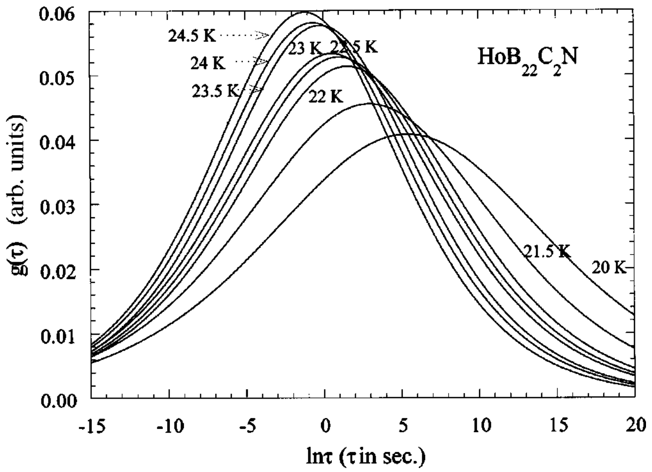

FIG. 3. Distribution of relaxation times $g(\tau)$ for several selected temperatures from 24.5 to 20 K.

$$\chi'' = \frac{\chi_0 - \chi_s}{2} \frac{\cos(\pi\alpha/2)}{\cosh[(1-\alpha)\ln(\omega\tau_C)] + \sin(\pi\alpha/2)}. \tag{7}$$

From this analysis we can determine the distribution function of relaxation times $g(\tau)$ at each temperature (Fig. 3). We observe that as temperature is lowered, the distribution of relaxation times $g(\tau)$ becomes broad while the median relaxation time is shifted to very long times below 22 K, indicating that the spin glass transition has occurred and the spins are frozen into "macroscopic" time scales. The qualitative behavior is similar to what has been observed for other spin glasses[28–30] and is obviously different from a superparamagnet in which α has been observed to have little temperature dependence.[2,28]

The distribution width parameter α and the extracted median relaxation time τ_C are plotted in Figs. 4(a) and 4(b) as a function of temperature T and $T^{-2.5}$, respectively. Sandlund *et al.* have previously systematically investigated Cu-Mn films and found a dimensional crossover in the dynamical behavior.[31] The relaxation times for two-dimensional films showed large frequency dependence (i.e., large K) similar to our system, and were successfully analyzed in terms of a generalized Arrhenius law

$$\ln(\tau/\tau_0) = A\mathrm{T}^{-(1+\psi\nu)}, \tag{8}$$

with $1 + \psi\nu = 2.6$.[31] The generalized Arrhenius dependence is derived from the droplet scaling theory of Fisher and Huse[32] and Monte Carlo simulations on 2D systems have given values of $1 + \psi\nu \sim 2$.[33,34] Anderico *et al.* has done work on diluted triangular antiferromagnetic lattices, which is very similar to the system considered here, and has also found a generalized Arrhenius dependence with an exponent of 2.[35] Dekker *et al.* has also obtained $\psi\nu = 1.9$ for a 2D

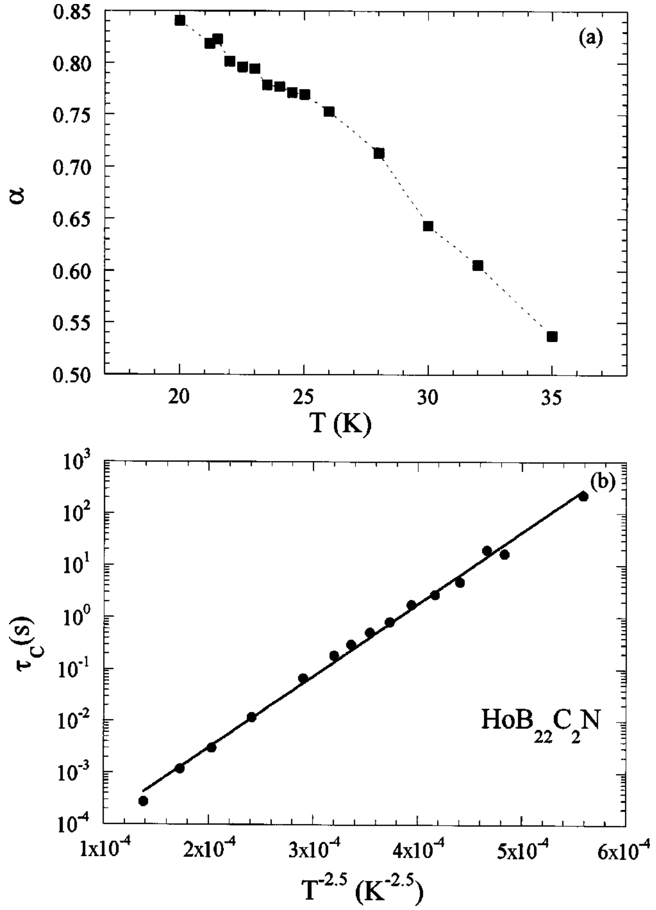

FIG. 4. Temperature dependence of (a) the parameter α plotted versus T and (b) the median relaxation time τ_C plotted versus $T^{-2.5}$. The bold line in (b) represents a fit to Eq. (8) with parameters of $1+\psi\nu=2.5$ and $\tau_0=5.3\times10^{-6}$ s.

spin-glass system $Rb_2Cu_{1-x}Co_xF_4$.[29] As we noted above, analysis of our data has not been successful in terms of the dynamical scaling of a 3D system. On the other hand, investigation of the homologous series of RB$_{17}$CN, RB$_{22}$C$_2$N, RB$_{28.5}$C$_4$ have yielded basically the same spin glass behavior, indicating that the configuration of the 2D triangular rare earth layers dictate the physics of this system.[19] Fitting our relaxation time data with Eq. (8), we obtain a good fit with $1+\psi\nu=2.5$ and $\tau_0=5.3\times10^{-6}$ s as is indicated by the bold line in Fig. 4(b). Our value of $1+\psi\nu$ is in accordance with that previously obtained for 2D systems and we are satisfactorily able to obtain a shorter τ_0 which is close to that determined for the insulating $Eu_{0.6}Sr_{0.4}S$ system, for example.[23]

From the Cole-Cole analysis we are able to definitely conclude that the dynamical behavior of $HoB_{22}C_2N$ is not that of a typical superparamagnet and we have also been able to extract reasonable parameters of the behavior of the determined relaxation time in terms of the generalized Arrhenius law used for two-dimensional systems. This is consistent with the previous results which indicate that the magnetism in $HoB_{22}C_2N$ and related homologous compounds is governed in the rare earth basal triangular planes.

IV. CONCLUSIONS

The dynamical properties of the rare earth B_{12} compound $HoB_{22}C_2N$ were investigated. Strong frequency dependence is observed and various typical methods were used to analyze the behavior. Applying the dynamical scaling theory for three dimensional systems to our data did not give a satisfactory description. From Cole-Cole analysis we were able to determine the relaxation time distribution and find qualitative behavior similar to some previously studied typical spin glass systems. From the temperature dependence of the width parameter α it can be concluded that the dynamical behavior of $HoB_{22}C_2N$ is different from the blocking of a typical superparamagnetic system despite the strong frequency dependence. It was found that the median relaxation time could be satisfactorily analyzed in terms of the generalized Arrhenius law with $1+\psi\nu=2.5$. Together with previous results, this indicates that $HoB_{22}C_2N$ is a two dimensional spin-glass system.

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