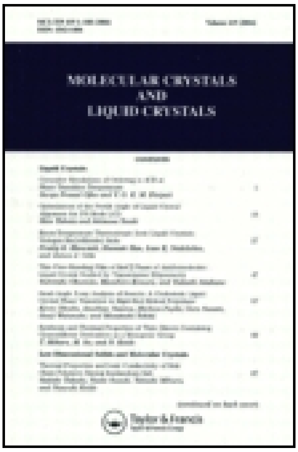

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Properties of Molecular-Based Frustrated Magnets

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PROPERTIES OF MOLECULAR-BASED FRUSTRATED MAGNETS

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Abstract The magnetic properties of cobalt complexes of BTCA (BTCA = 1,3,5 benzenetricarboxylic acid) have been investigated. The trianion of the BTCA ligand has the ability to create lattices with competing interactions leading to frustration. A dodecahydrate phase, $Co_3BTCA_2(H_2O)_{12}$, is obtained from room temperature aqueous solutions and consists of pendant chains with very small interactions. Varying the reaction conditions leads to an amorphous phase which displays many of the features of a spin glass: hysteresis, remanent magnetization, frequency dependent susceptibility, aging effects, and an inverse field dependence of the dc susceptibility.The dehydration state and corresponding magnetic properties are strongly dependent on the temperature of the original reaction. Reaction temperatures below 78 °C lead to the pendant chain while temperatures greater than 78 °C yield more interesting glassy phases. These phases exhibit many properties of reentrant spin glasses.

INTRODUCTION

The physical properties and underlying theory of disordered and/or spin glass-like systems have been the subject of an immense amount of experimental and theoretical investigation during the past two decades. Although some of the answers to the spin glass problem remain to be discovered, it is clear that the essential ingredients necessary to generate a spin glass are disorder and frustration.[1] It has also been shown via computer simulations, theory, and experiment that given this combination, a three dimensional Ising system undergoes a phase transition into the glass state at a finite temperature referred to as the freezing temperature, T_f.[2,3] Typically a sharp, frequency dependent peak in the in-phase component of the ac susceptibility occurs in the vicinity of T_f, along with a corresponding absorption peak. Below the transition temperature, a variety of effects occur including hysteresis, irreversibility, long relaxation times, and aging. In general, the system becomes extremely dependent on not only its thermal history, but also the time spent at a given temperature.

Competing interactions which ultimately lead to a frustrated state are necessary to produce the glassy behavior. There are, however, different ways of obtaining these interactions. To date, most spin glasses are produced via melt spinning or metal doping techniques. These systems are typically alloys with exchange pathways governed by Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. The long range oscillatory nature of RKKY interactions implies both next-nearest and further neighbor interactions, usually providing the source of frustration.

In contrast, the compound whose properties are reported here is a molecular spin glass. Typically, superexchange interactions between nearest neighbors only are found in molecular based magnets, necessitating that the local geometry (lattice) provide frustration. This project began as a search for purely frustrated systems. The BTCA (BTCA = 1,3,5 benzenetricarboxylic acid) ligand was chosen since with its three carboxylate binding sites it could provide the superexchange pathways necessary to create the highly frustrated Kagomé lattice. The Kagomé lattice is interesting in that it is theoretically the most frustrated two dimensional lattice possible. In addition, the carboxylate groups of the BTCA ligand can coordinate to metal ions in a variety of ways: chelating, monodentate, bridging, and bibridging bidentate. Initial attempts to produce transition metal complexes using the BTCA trianion in an aqueous solution did not achieve a frustrated lattice due to the presence of water molecules coordinating to the metals. Instead, when using the highly anisotropic cobalt as the metal, they produced a dodecahydrate phase with a pendant chain structure and weak antiferromagnetic behavior.[4] Attempts to reduce the number of waters in this complex yielded a novel amorphous spin glass, whose propeties are reported here.

EXPERIMENTAL

The synthesis of the spin glass was carried out as follows. $Co(ClO_4)_2(H_2O)_6$ (2.764 g, 7.6 mmol) was dissolved in 20 ml of water. BTCA (1.065 g, 5 mmol) and KOH (0.95 g, 17 mmol) were dissolved in 26 ml of water and the resulting solution added to the cobalt perchlorate. A precipitate formed immediately. The product was isolated by filtration, washed with acetone and dried. The temperature of the reagents when combined affects the course of the reaction. Temperatures less than 78 °C result in $Co_3BTCA_2(H_2O)_{12}$ which is the pendant chain.[4] As the temperature of the reaction is increased from 78 to 100 °C, two very distinct changes are observed: the color of the product becomes increasingly more purple, and the compound exhibits increasingly enhanced magnetically glassy behavior. Both the color and magnetic properties are further enhanced by putting the precipitate in an oven at 125 °C for about four hours. Most likely, the color change is due to a change in hydration state of the cobalt ion. Powder X-ray analysis of the compounds produced above 78 °C indicate that the material becomes progressively more amorphous, with the 100 °C, oven dried compound being the most amorphous. The analysis is not conclusive however. Accurate scattering data is hindered by the fluorescence of the cobalt ions which could be masking faint scattering lines. The molecular weight for all samples was calculated assuming six waters. However, the exact number of waters is still undetermined, hence the formula $Co_3BTCA_2(H_2O)_n$. It is known that the BTCA ligand is unchanged by the heating procedure since digestion of the sample in HCl recovers the original ligand intact.

Magnetic measurements were taken on a vibrating sample magnetometer and an alternating current susceptometer. Because of the irreversibility and history dependent behavior of spin glasses, it is necessary to clearly define the measurement processes. Irreversibility is usually observed by comparing the zero field cooled (ZFC) and field cooled (FC) susceptibilities. A ZFC curve is obtained by cooling a compound through its transition temperature in zero applied field, applying a fixed field, and subsequently recording the moment of the compound while the sample is warmed. In contrast, a FC curve is obtained by cooling the sample through its transition temperature in a fixed applied field, and again recording the moment while the sample is being warmed in the same field. Aging effects may also be measured using FC and ZFC techniques in two simple ways. One is to FC a sample through T_f, wait a time t_w before setting the field to zero, then record the moment of the sample as a function of time, t. The other is to ZFC the sample through T_f, wait t_w before switching the field on, and again record the moment as a function of time. In both cases the moment is a function of both t and t_w.

RESULTS AND DISCUSSION

Striking evidence for the effect of reaction temperature on magnetic properties is seen by comparing the hysteresis shapes and susceptibilities of the different preparations. Fig. 1 displays the product of the molar susceptibility (measured at H=1000 Oe) and temperature, $\chi_m T$, as a function of temperature, T, for compounds with various reaction temperatures. All curves show an upward curvature in the $\chi_m T$ product indicating the presence of ferromagnetic interactions. The interactions appear to increase as the reaction temperature is increased, as is evidenced by the 96 °C oven dried prep which has a $\chi_m T$ maximum value of about 77 cm^3K/mol, almost 10 times its paramagnetic value. A remarkable dependence of the $\chi_m T$ product on the applied field is seen for all preparations. As the magnetic field is decreased, the magnitude of $\chi_m T$ actually increases (see inset Fig.1).Low field measurements of the most strongly interacting compounds exhibit a $\chi_m T$ maximum of nearly 350 cm^3K/mol. Table 1 displays more evidence of the dramatic effect of changing the reaction temperature. It lists the coercive fields obtained during an hysteresis loop as a function of reaction temperature. It should be noted that because of the long relaxation times of some of these compounds, these values are dependent on how long one waits at a particular field. To avoid any time related discrepancies, all data were collected by waiting five minutes before changing the applied field. Table 1 also displays the maximum value of the $\chi_m T$ product measured in a 1000 Oe field. The last entry in the table represents a crystalline phase that was formed by evaporating an aqueous solution of the compound at 96 °C. Interestingly, this compound exhibits no glassy behavior; in fact, both its magnetic behavior and X-ray pattern indicate that it is the pendant chain.

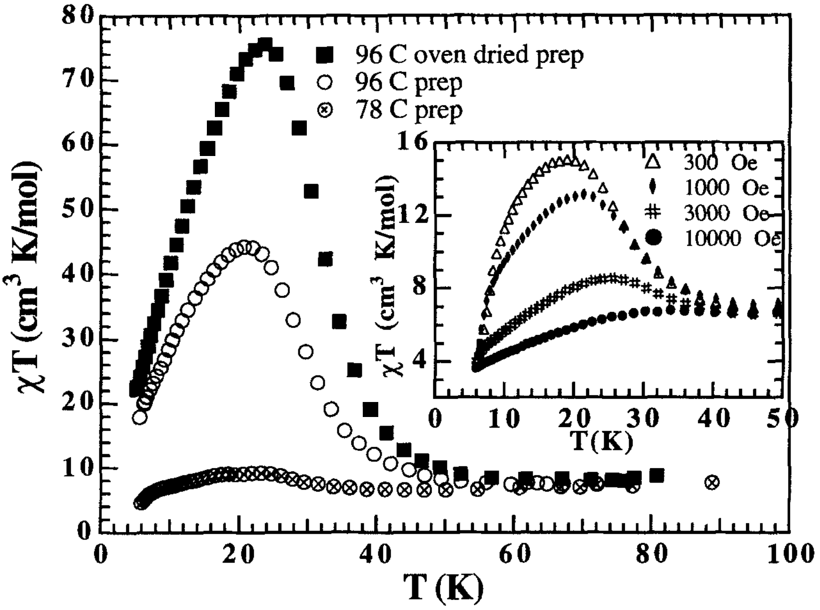

FIGURE 1 The product of the molar susceptibility (in a 1 kOe field) and temperature is plotted as a function of temperature for various reaction temperatures. Inset shows data obtained in various fields for the 78 °C preparation.

TABLE 1. Properties of the various phases of $Co_3(BTCA)_2(H_2O)_n$

Reaction Temp. (C)	Coercive Fields at 4.2 K (Oe)	Maximum value of χT (H = 1kOe) (cm^3 K/mol)
96, oven dried	4000,-4000	77
96	1500,-1500	45
78	400,-375	10
96, crystalline	0,0	8

In general, all purely crystalline samples (both lower temperature powders and higher temperature crystals) displayed no spin glass behavior. The reason for this lies in the fact that spin glasses require both frustration and disorder. The disorder in these complexes comes from the fact that they are amorphous. When the amorphous nature is removed, the compound ceases to behave as a spin glass. Most likely the higher reaction temperature combined with the rapid precipitation of the powder, results in a random coordination about the cobalt ions, forcing the system into an amorphous state. The 96 °C crystalline phase was formed by slow evaporation allowing regular coordination about the cobalt ions. The regular structure of the crystalline phase removes the disorder, thus destroying the glassy nature.

In addition to the above mentioned properties, the glassy phase exhibits history dependent effects such as a divergence of the FC and ZFC curves. The temperature at which these curves diverge is a function of not only the applied field but also the amount of time allowed for the sample to equilibrate at any one temperature. Both these properties are displayed by Fig. 2. The explanation behind these unusual properties of spin glasses lies in their 'rugged' free energy landscape[5], a consequence of the combination of disorder and frustration. This multivalued landscape allows the system to settle into metastable states from which relaxation into one of its many ground states may take infinitely long. Thus we see that as the waiting time is increased, the ZFC curve slowly approaches the FC curve, a curve believed to be the true equilibrium state.[6]

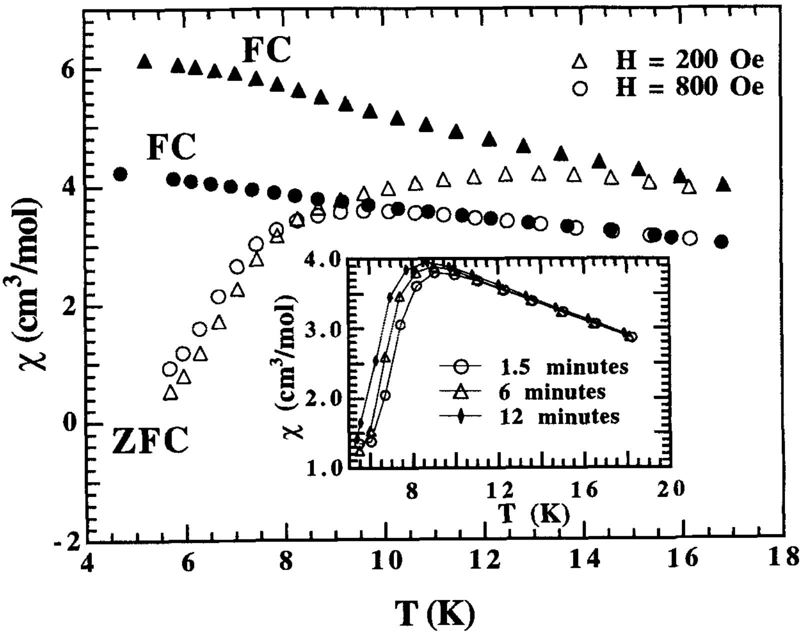

FIGURE 2 FC and ZFC susceptibilities in applied fields of 200 and 800 Oe for the 96 °C prep. Inset shows 800 Oe ZFC susceptibility for various times waited at each temperature.

Other manifestations of the rugged landscape which these samples display include aging effects (at 5 K) and remanent magnetizations which are history dependent. Remanent magnetization data obtained for these compounds[7] at 5.8 K are similar to those of other spin glasses[8], although the field necessary to force the convergence of the IRM and TRM is relatively large, being in excess of 10 kOe.

The glassy dynamics of these systems can be seen in the ac frequency response. The complex ac susceptibility has been measured in a 2.5 Oe ac field and a zero dc field for frequencies ranging from 10 to 1500 Hz. Fig. 3 displays both the in-phase, χ', and out-of-phase, χ'', susceptibilities as a function of temperature for a sample prepared at 96 °C.

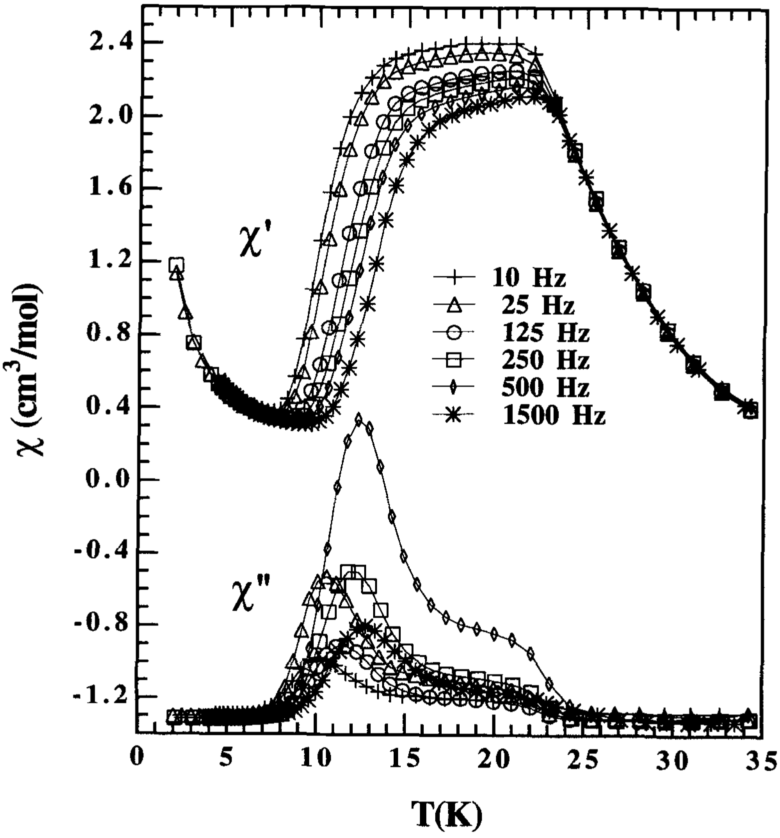

FIGURE 3 Complex ac susceptibilities of the 96 °C preparation as a function of temperature in frequencies varying from 10 to 1500 Hz . The upper set of data corresponds to the in-phase susceptibility, χ', while the lower set corresponds to the out-of-phase susceptibility, χ''. The zero of the lower curves has been shifted down by 1.3 in order to avoid overlap of the two data sets.

Note the frequency dependent absorption peaks near both 10 and 22 K. The temperature range which spans 10 to 22 K also defines a broad maxima in χ'. Below 10 K there is a frequency independent upturn in χ' that is believed to be due to a paramagnetic component. This upturn disappears in the most amorphous sample, with χ' approaching zero as the temperature goes to zero.

Early excitement in the physics community over spin glasses came in part due to their very sharp or cusplike peaks in the in-phase susceptibility[9] Clearly, this is not the situation in these compounds. A possible explanation for the rounded peak in χ' observed in these compounds is that there are actually two peaks in χ' merging to appear as one. This hypothesis is further supported by the two absorption peaks near 10 and 22 K. Behavior such as this is suggestive of a reentrant spin glass[10,11], in which the system undergoes two transitions, one from the paramagnetic state into a ferromagnetic state (or possibly a correlated spin glass state[12]), and a second from the ordered state into a spin glass state (sometimes referred to as the reentrant state). The higher temperature absorption peak is generally used to mark the phase boundary between the paramagnetic and ordered states. Further evidence for the existence of two phase transitions is provided by the temperature dependence of the field cooled remanent moment (FCRM). The FCRM persists for temperatures up to 22 K (Fig. 4), further supporting the idea of a ferromagnetic transition. The FCRM also displays a curvature near 10 K typical of reentrant systems undergoing a transition into the spin glass state.

The temperature at which the system enters the spin glass state, T_f, is more difficult to determine. The most widely accepted method of observing this transition is to measure the nonlinear susceptibility, which, being related to the four spin correlation function, should diverge at the critical temperature[13] The nonlinear susceptibility may be measured directly via the third harmonic of the ac response, or in a more indirect manner using the following dc techniques. In small fields, the magnetization may be expanded as follows

$$M = \chi_0 H + \chi_2 H^3 + \chi_4 H^5 + \dots \qquad (1)$$

where χ_0 is the zero field susceptibility. Defining the nonlinear susceptibility $\chi_{nl} = \chi_0 - M/H$, gives

$$\chi_{nl} = \chi_2 H^2 + \chi_4 H^4 + \dots \qquad (2)$$

If the applied field is small enough, an H^2 dependence of the nonlinear susceptibility can be obtained, allowing χ_2 to be ascertained. χ_2 should diverge as $t^{-\gamma}$, where $t = (T - T_f)/T_f$ and γ is a universal critical exponent. These quantities are obtained by measuring the FC susceptibility in various fields. Extrapolation of the low field susceptibility as a function of field at each temperature generates a good approximation of $\chi_0(T)$.

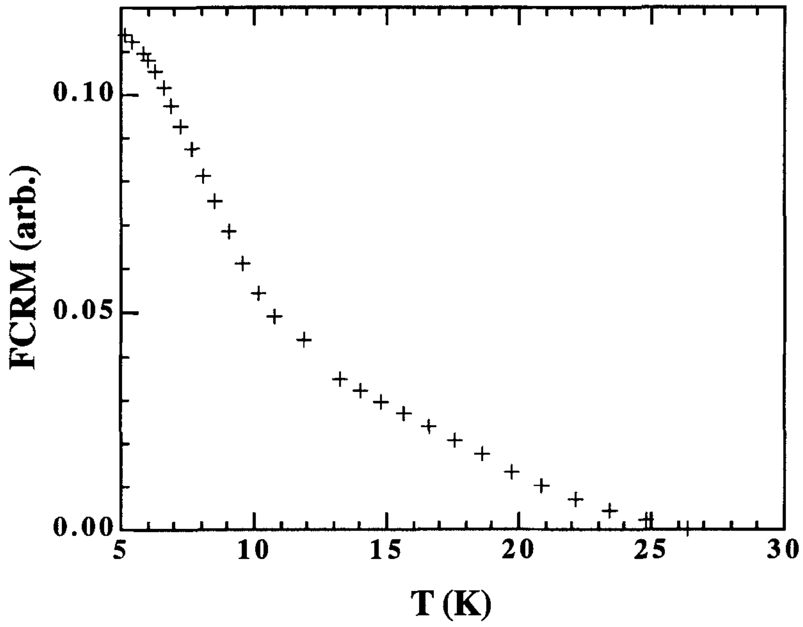

FIGURE 4 FCRM as a function of temperature for sample prepared at 96 °C. The sample was cooled in a 40 Oe field to 5 K. The field was then set to zero and the remanent moment was recorded as a function of temperature while the sample was warmed.

Knowing $\chi_0(T)$, the nonlinear susceptibility, $\chi_{nl}(H,T)$, may now be calculated at each temperature and field by taking the difference between M/H and χ_0. By next plotting χ_{nl} as a function of H^2 at each temperature and taking the slope of the linear low field regime, a plot of $\chi_2(T)$ may be extracted. Data generated in this fashion are shown in Fig. 5. Although it would be difficult to describe the behavior as a divergence, it is clear that χ_2 reaches a maximum near 9 K, approximately the same temperature as the low frequency limit of the absorption peak. It should be noted that the regime in which $\chi_2(H,T = \text{const.})$ is linear with H^2 is at best from 0 to 15 Oe, while the accuracy in our measurement of H was ±0.5 Oe. Furthermore, it is known that the region of H^2 dependence becomes vanishingly small (0.1 Oe) as T_f is approached[14] Uncertainties of this relative magnitude could certainly explain the absence of a clear divergence in χ_2, and necessitate further low field SQUID studies.

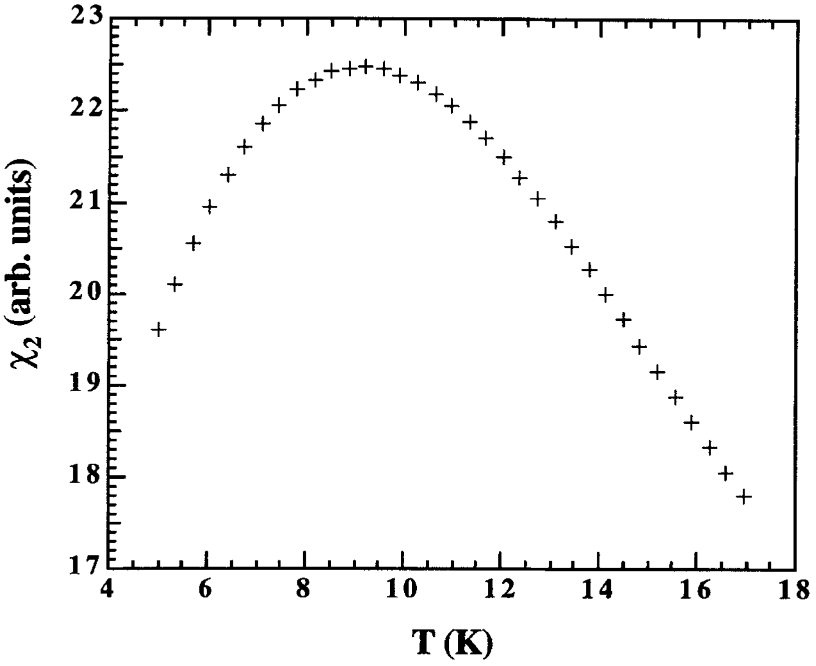

FIGURE 5 The nonlinear susceptibility, χ_2, of the 96 °C oven dried prep as a function of temperature.

In summary, the high reaction temperature phase of $Co_3BTCA_2(H_2O)_n$ displays the physical properties characteristic of a frustrated magnetic system. There are only a few other molecular based magnets known to be similar. The amorphous phase of $V(TCNE)_x{\cdot}y(sol)$[15] has a spontaneous moment and an ordering temperature approaching 400 K, when the solvent is CH_2Cl_2. Extensive studies[16] have shown the system to be well described as possessing random magnetic anisotropy, leading to a description as a *correlated spin glass.* A crystalline example of a molecular based magnet with frustration arising from the lattice is $Cu_9X_2(cpa)_6$,[17] described as a Kagomé-like structure with "triangles within triangles". This compound also has the strong inverse field dependence of the χ_mT product[18], as seen in Fig. 1 for the cobalt/BTCA complex. Research will continue on the $Co_3BTCA_2(H_2O)_n$ with the goal of correlating the magnetic properties with the connectivity of the lattice.

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