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Anomalous cluster glass behavior in a quasi-one-dimensional organic-based magnet

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Abstract

The spin glass transition of the quasi-one-dimensional (1D) organic-based magnet $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ (TPP is tetraphenylporphyrin dianion, TCNE is tetracyanoethylene) is explored using both a.c. and d.c. measurements. The a.c. susceptibility shows a strong frequency dependent peak consistent with a clustered spin glass state. Application of a d.c. magnetic field suppresses the peak in the a.c. susceptibility. Magnetic relaxation data can be fit to a stretched exponential, with the results reflecting a spin glass transition near 4 K. The spin cluster dimension and the effective dimension of the system are calculated within a fractal cluster model of spin glasses with values for the spin cluster dimension ranging from ~ 0.8 to over 1.5 as the glass transition is approached.

Keywords: Organic-based magnet; Spin glass; Tetracyanoethylene; Low-dimensional magnetism; Susceptibility; Fractal cluster

1. Introduction

Organic-based magnets have long been of interest due to the ability to chemically tune both structural and magnetic properties. The ability to modify the range of properties of the material provides flexibility not normally found in traditional materials. One class of materials providing this flexibility is the maganese porphyrin family of organic-based magnets, consisting of electron transfer salts formed from organic acceptor units and manganese porphyrin donor units.

The manganese porphyrin family of magnets has been shown to form one-dimensional (1D) polymers with large, chemically tunable (~ 10 to over 20 Å) interchain spacing [1,2]. High temperature magnetic data reveal behavior consistent with a model [3] for a chain of alternating quantum and classical spins [4]. Bulk magnetic order has been attributed to dipole–dipole interactions between chains, due to the large interchain spacing leading to a lack of viable exchange pathways [4–6].

A typical member of this family is $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ (TPP is tetraphenylporphyrin dianion, TCNE is tetracyanoethylene). This material recently has been shown to exhibit complex magnetic behavior at low temperatures, including spin glass behavior [5,7]. The spin glass ordering has been attributed to frustration induced from competition between interchain dipole–dipole interactions and the single-ion anisotropy of the metal ion.

We report here results of a further investigation of the a.c. susceptibility, d.c. magnetic relaxation, and the spin glass phase of $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$. The a.c. susceptibility exhibits a broad peak which is strongly frequency dependent. The application of a d.c. magnetic field suppresses this peak consistent with a spin glass freezing process. Magnetic relaxation data taken at lower temperatures show behavior which can be explained [7] with a fractal cluster model for spin glasses [8–11]. The results from this model provide physical insight into the behavior of the system in terms

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of a spin cluster dimension and an effective spatial dimension.

2. Experimental

Polycrystalline samples of $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ were synthesized according to the literature [2]. In order to avoid contamination of degradation the polycrystalline powder was handled and stored in an argon environment at all times during sample preparation. The powder sample was constrained for study by dispersing in eicosane (m.p. 36–38 °C), heated above 40 °C and subsequently cooled. The sample was then sealed in a quartz tube (for a.c. susceptibility measurements) or an airtight Delrin® sample holder (for d.c. measurements).

The a.c. susceptibility was measured with a Lake-Shore 7225 a.c. susceptometer/d.c. magnetometer. Phase-sensitive detection allowed both the in-phase (χ') and out-of-phase (χ'') components of the susceptibility to be extracted. The instrument was calibrated for both phase and relative amplitude at each frequency by the use of a paramagnetic standard. The presence of a superconducting magnet in the system allowed the measurement of the susceptibility at d.c. applied fields up to 5 T. The a.c. susceptibility data were taken in a temperature range of 4.5–50 K, at frequencies from 11.0 Hz to 11.0 kHz with an a.c. field ($H_{a.c.}$) of 1.0 Oe and various applied d.c. fields ($H_{d.c.}$).

The d.c. magnetic relaxation measurements were recorded on a Quantum Design PPMS-9 with the ACMS option. Thermoremanent magnetization (TRM) measurements were made upon cooling in a field of 1000 Oe from 60 K to the desired measurement temperature. The sample was held at the desired temperature in the field for 5 min prior to reducing the field to zero. The magnetization decay was then recorded for periods of 45 min to over 120 h depending on the temperature of the sample. Due to limitations of the superconducting magnet, the first measurement was taken approximately 30 s after reaching zero field.

3. Results and discussion

The measured a.c. susceptibility for $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ with zero applied field is displayed in Fig. 1. The results show a large broad peak in both χ' and χ'', with a strong shift in peak temperature (T_p) with frequency (f). The magnitude of the shift in χ', $\Delta T_p/(T_p \Delta \log f) \sim 0.14$, is consistent with cluster glass behavior with a similar shift observed in χ''. The susceptibility also displays a small constant value at low temperatures ($\lesssim 5$ K), consistent with a frozen spin glass state.

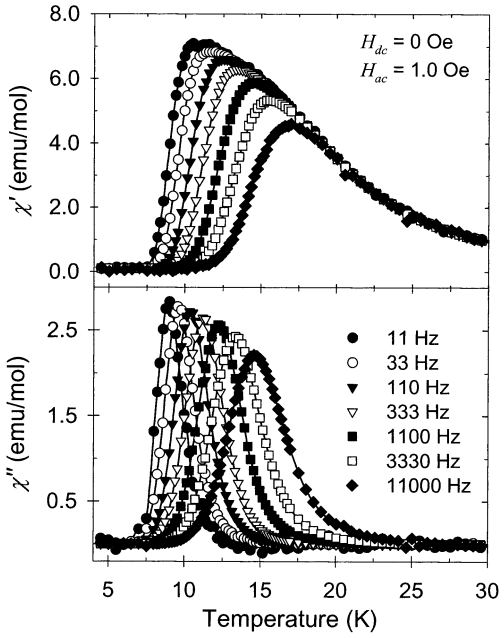

Fig. 1. Both the in-phase (χ') and out-of-phase (χ'') components of the a.c. susceptibility of $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ with $H_{ac} = 1$ Oe, $H_{dc} = 0$ Oe. The frequency dependence is consistent with a spin glass freezing process.

The application of a d.c. magnetic field (3 kOe shown) has the result of significantly suppressing the peak in the a.c. susceptibility (Fig. 2). The field also appears to resolve the broad peak observed at zero field into two distinct features, a frequency independent peak at ~ 25 K, and a frequency dependent shoulder at lower temperatures. The frequency dependent shoulder can be assigned to a freezing process in a spin glass transition, while the frequency independent peak is likely another weakly 3D ordered state. The presence of the higher temperature, frequency independent peak suggests that the lower temperature spin glass state observed in this material is reentrant.

The field dependence of the a.c. susceptibility for a frequency of 333 Hz is shown in Fig. 3. The results show

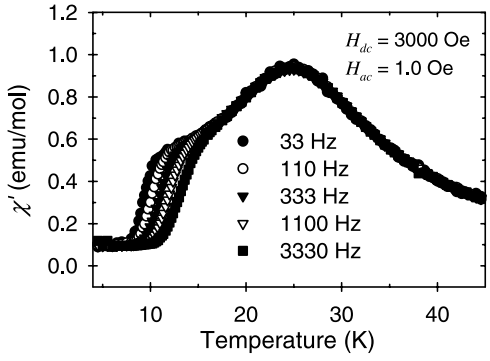

Fig. 2. The a.c. susceptibilty (χ') $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ in 3 kOe applied dc field ($H_{ac} = 1$ Oe, $f = 333$ Hz). The resolution of a second peak suggests reentrant behavior.

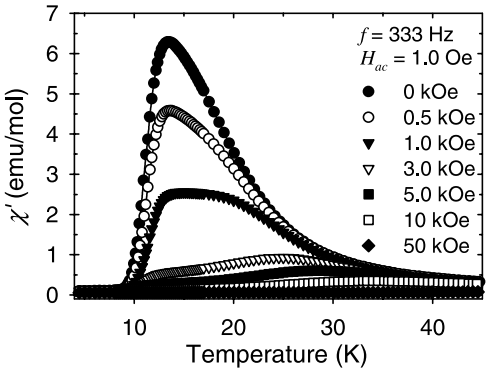

Fig. 3. The a.c. susceptibilty (χ') $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ in various applied dc fields ($H_{ac} = 1$ Oe, $f = 333$ Hz).

the evolution of the a.c. susceptibility suppression in the presence of an external magnetic field. The broad peak is resolved into the previously mentioned features, with both being reduced with larger applied field. The higher temperature peak appears to shift to the right (towards even higher temperatures) with the application of higher fields, suggesting the weak 3D order is ferromagnetic in nature. The lower temperature shoulder is reduced in smaller fields consistent with behavior expected for cluster glasses.

Magnetic relaxation data were taken for temperatures ranging from 3.5 to 6 K. The results of the TRM measurements [7] gave a magnetization versus time curve which could be fit with a stretched exponential of the form

$$M(t) = M_0 + \sigma_0 e^{-(t/\tau)^{1-n}} \tag{1}$$

where M_0, σ_0, t, and n are the fitting parameters. In particular, M_0 is a parameter required to compensate for a small non-zero remanent magnetization ($M \sim 0.01\sigma_0$) due to the presence of cluster glass behavior [4]. Stretched exponential relaxation has been observed in other spin glass and quasi-1D systems [12], as well as predicted by theoretical models, including the fractal cluster model [13,14].

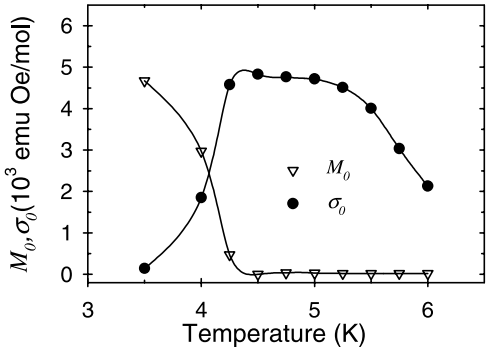

Fig. 4. Temperature dependencies of the fitting parameters M_0 and σ_0 from Eq. (1). The observed change in magnetic relaxation suggests a spin glass transition near 4 K.

The parameters M_0 and σ_0 obtained from these fits versus temperature are shown in Fig. 4. Near ~ 4 K the value for M_0 (corresponding to the value of the remanent magnetization) increases with decreasing temperature while σ_0 (a measure of the amount the spin system is able to relax) decreases. This change in spin relaxation suggests a transition in this region. Since the system shows little magnetic relaxation below 4 K, this transition is most likely a transition to the frozen cluster glass state. These findings are in agreement with the value for the spin glass transition obtained through a scaling analysis of the χ'' data shown in Fig. 1.

Values obtained for the parameter n can be used along with results from a scaling analysis [7,15–17] of the a.c. susceptibility shown in Fig. 1 to obtain the spin cluster dimension (D) and effective dimension (d_{eff}) of the system. The needed relations are [7,9]

$$D = \frac{\phi^2}{zv}\left(\frac{n}{1-n}\right) \tag{2}$$

and

$$d_{\text{eff}} = D + \beta/v \tag{3}$$

where β, zv, and ϕ are standard critical exponents [18].

The results (Fig. 5) are indicative of quasi-1D behavior. The graph shows the spin cluster dimension (D) growing from near 1 to over 1.5 as the spin glass transition is approached. This result, along with the chain-like structure of the material, suggests that spin clusters lie predominantly along a single chain of the material at higher temperatures. At lower temperatures the spin clusters extend out into neighboring chains, creating a highly anisotropic spin cluster. Similar behavior is observed in the effective dimension (d_{eff}) of the system.

4. Conclusions

Our detailed analysis of the a.c. susceptibility and d.c. magnetic relaxation of $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}$

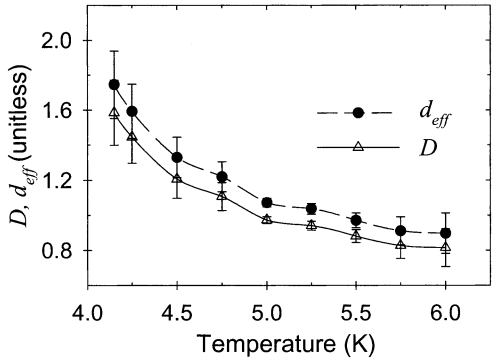

Fig. 5. The effective dimension (d_{eff}) and spin cluster dimension (D) versus temperature as calculated from Eqs. (2) and (3).

$C_6H_4Cl_2$) show a reentrant spin glass state. The application of an external d.c. field resolves a second feature in the a.c. susceptibility. The higher temperature peak shifts toward even higher temperatures with an increase of applied magnetic field suggesting that the weak 3D order is ferromagnetic in nature. The d.c. relaxation data can be fit to a stretched exponential, with the parameters reflecting a transition near 4 K. This behavior helps confirm the presence of the spin glass state at this temperature as predicted by a scaling analysis of the a.c. susceptibility. Other parameters from the stretched exponential fits allow the determination of the spin cluster dimension and effective spatial dimension of the system. The temperature dependence of these quantities support the presence of highly anisotropic spin clusters.

Acknowledgements

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