Viscous Behavior in a Quasi-1D Fractal Cluster Glass

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The spin glass transition of a quasi-1D organic-based magnet ([MnTPP][TCNE]) is explored using both ac and dc measurements. A scaling analysis of the ac susceptibility shows a spin glass transition near 4 K, with a viscous decay of the thermoremanent magnetization recorded above 4 K. We propose an extension to a fractal cluster model of spin glasses that determines the dimension of the spin clusters (D) ranging from $\sim$0.8 to over 1.5 as the glass transition is approached. Long-range dipolar interactions are suggested as the origin of this low value for the apparent lower critical dimension.

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Recent failures [1,2] of mean-field models for spin glass behavior have renewed interest in non-mean-field interpretations. One such non-mean-field interpretation is the fractal cluster model [3–6] which provides a physical meaning for the results, the fractal dimension of the spin clusters. This cluster fractal dimension can be calculated from critical exponents obtained through a scaling analysis of the glass transition, and knowledge of the effective dimension of the system. Previous results based on this model have concentrated on traditional 3D spin glass materials, including GdAl and $Fe_{0.25}Zn_{0.75}F_2$, generally obtaining a cluster dimension of $\sim$2.5 [5,7]. In this paper, we propose a method for obtaining the fractal dimension of the spin clusters in a quasi-1D spin glass without any prior knowledge of the effective dimensionality of the system.

The organic-based magnet $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ (TPP is tetraphenylporphyrin, TCNE is tetracyanoethylene) is an electron transfer salt which forms 1D polymers of alternating donors (MnTPP) and acceptors (TCNE) with large interchain spacings [8,9]. Previous magnetic data show 1D chain behavior above $\sim$50 K with a transition to more complex behavior, including spin glass behavior at lower temperatures [9–11]. Because of weak interchain interactions in this class of materials, dipolar interactions between neighboring chains is the suggested mechanism for bulk magnetic ordering [11–13]. However, the transition to the spin glass phase has yet to be fully investigated.

We report here a dynamic scaling analysis of the ac susceptibility of [MnTPP][TCNE] together with thermoremanent magnetization (TRM) decay data. The ac data support a spin glass transition near 4 K. The TRM decay was measured for temperatures above this transition and shows unusually long relaxation times near the glass transition. We propose an extension of the fractal cluster model which allows a determination of the fractal dimension of the spin clusters within this material at various temperatures. Calculated values range from $\sim$0.8 to over 1.5 near the glass transition, consistent with quasi-1D behavior. This anomalously low value for the apparent lower critical dimension is suggested to result from long-range dipolar interactions between clusters beyond the nearest neighbor.

Polycrystalline samples of $[MnTPP]^+[TCNE]^- \cdot 2(1,3\text{-}C_6H_4Cl_2)$ were synthesized according to Ref. [9]. The polycrystalline powder was constrained for study by dispersing in eicosane (melting point 36–38°C) and heating above 40°C and subsequently cooled. The sample was then sealed in a quartz tube (for ac susceptibility measurements) or an airtight Delrin® sample holder (for TRM measurements). The ac susceptibility was measured with a LakeShore 7225 ac susceptometer/dc 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 dc measurements were recorded on a Quantum Design PPMS-9 with the ACMS option.

The ac susceptibility data were taken from 4.5 to 50 K, at frequencies from 11.0 Hz to 11.0 kHz with an ac field of 1.0 Oe and zero applied dc field. In order to probe the glass transition, a dynamic scaling analysis of the out-of-phase component was performed according to the fractal cluster model [14] following the linear method proposed by Geschwind, Huse, and Devlin [15]. Only data points above the peak temperature were included in the scaling plot in order to avoid an overestimation of the critical exponents [16].

The linear method [15] enables independent determination of the ratio of the critical exponents $\beta/z\nu$ (where β, ν, and z have their usual definitions [17]) by examining the frequency dependence of the $\chi''(T,\omega)$ peak. As pointed out in Ref. [15], the amplitude (χ''_p) and temperature (T_p) of the peak should satisfy the relation $\chi''_p(\omega)T_p(\omega) \propto \omega^{\beta/z\nu}$. Figure 1(a) shows a plot of $\log_{10}[\chi''_p(\omega)T_p(\omega)]$ versus $\log_{10}(\omega)$. The slope of a linear

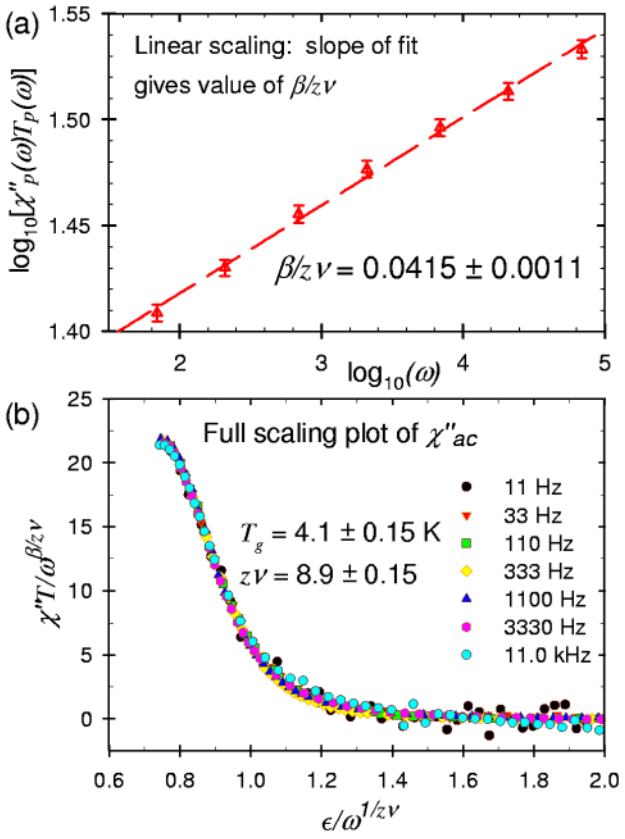

FIG. 1 (color online). (a) A plot of $\chi''(\omega)T(\omega)$ at the peak temperature vs $\omega^{\beta/z\nu}$; the slope of the fitted line gives the ratio $\beta/z\nu$. (b) A full scaling plot using the scaling function of Ref. [15]. Good data collapse was observed for temperatures from the peak temperature to ~30 K.

fit to this data gives a value for $\beta/z\nu = 0.0415 \pm 0.0011$. The value of this ratio was used to guide the selection of $z\nu$ and β in the full scaling plot.

The scaling function [15] $\chi''T/\omega^{\beta/z\nu} \sim f(\epsilon/\omega^{1/z\nu})$ $[\epsilon = (T/T_g - 1)]$ was used to plot the ac susceptibility data above the peak temperature. Good data collapse occurs over the three measured decades of frequency for the values of $z\nu = 8.9 \pm 0.15$ and $T_g = 4.1 \pm 0.15$ K giving $\beta = 0.369 \pm 0.012$ using the value for the ratio $\beta/z\nu$ found from Fig. 1(a). Scaling was observed over a large range of temperatures, from the peak temperature (~ 9 K) up to 30 K. The full scaling plot of $\chi''T/\omega^{\beta/z\nu}$ vs $\epsilon/\omega^{1/z\nu}$ with the values of the critical exponents and transition temperature given above is shown in Fig. 1(b).

Thermoremanent magnetization 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. Because of limitations of the instrument, the first measurement was taken approximately 30 sec after reaching zero field. The magnetization decay was then recorded for periods of 45 min to over 120 h depending on the temperature of the sample. The magnetization decay was fit to a stretched exponential of the form

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

where M_0, σ_0, τ, and n are the fitting parameters. In particular, M_0 is a parameter required to compensate for a small nonzero remanent magnetization ($M_0 \sim 0.01\sigma_0$) due to the presence of cluster glass behavior [11]. Stretched exponential relaxation has been observed experimentally in other spin glass and quasi-1D systems [18], as well as predicted by theoretical models, including the fractal cluster model [19,20].

Fits of the TRM data to Eq. (1) were made for temperatures from 4 to 6 K and were valid over the entire measured time range. Above 6 K, the magnetization relaxes too quickly to observe relaxation with this method. Data were generally taken until the magnetization appeared constant with time plotted on a logarithmic scale. However, the unusually long relaxation times observed near T_g made this experimentally unachievable at some temperatures. Typical relaxation curves and the corresponding fits are shown in Fig. 2. In particular, these fits allow a direct estimation of the characteristic response time (τ) of [MnTPP][TCNE] at different temperatures.

The characteristic response time of the system at various temperatures is shown in Fig. 3. The response times obtained from both the ac data and the TRM measurements lie on the same curve. For the ac data, τ values were determined at the peak temperature by $\tau \sim 1/\omega$, while, for TRM measurements, τ values were determined from fits to Eq. (1).

Besides the determination of τ, fits of the data to Eq. (1) also allow a determination of the stretched exponential power (n). The measured values for both n and τ increase

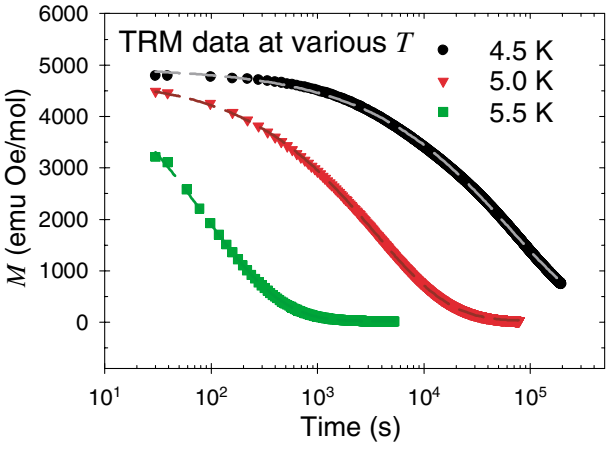

FIG. 2 (color online). Typical TRM decay curves at various temperatures. The symbols represent the data, while the solid lines are a fit to Eq. (1).

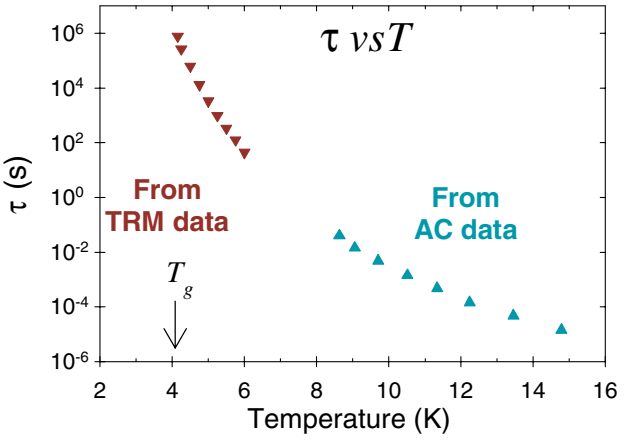

FIG. 3 (color online). The characteristic response time of [MnTPP][TCNE] versus temperature. Data from both dc and ac measurements can be seen on the curve. The data cover large ranges of both temperature and time, suggesting a slow, viscous transition.

with decreasing temperature. We discuss below the increase in n from ~0.35 to ~0.5 near the glass transition in terms of the fractal dimension of the spin clusters.

The fractal dimension of the spin clusters (D) is usually obtained from the relation [4,5]

$$d = D + \beta/\nu. \tag{2}$$

However, this equation requires knowledge of the effective spatial dimension (d) of the system. While $d = 3$ for most systems, it may be different from three, in fact, a noninteger (fractal) effective spatial dimension is also possible [4]. The chain structure of [MnTPP][TCNE] suggests quasi-1D behavior or $d \sim 1$ though the exact value is not explicitly known. We present here another approach for calculating the fractal dimension of the spin clusters which avoids placing assumptions on the value of d.

The stretched exponential power (n) can be used to obtain the fractal dimension of the spin clusters. Following Ref. [20], n can be written in terms of critical exponents as $n = z\nu/(z\nu + \phi\nu)$, where z, ν, and ϕ are standard critical exponents. The critical exponents ϕ and ν are related to the fractal dimension of the clusters by $\phi = \nu D$ [5]. Therefore we can relate D to n by

$$D = \frac{\phi^2}{z\nu}\left(\frac{n}{1-n}\right). \tag{3}$$

Equation (3) gives the fractal dimension in terms of critical exponents, and the stretched exponential power with no reference to the effective dimension of the system.

The critical exponent $z\nu$ (= 8.9) was obtained from the ac susceptibility measurements directly, while n is determined at various temperatures from fits of the TRM data to Eq. (1). The crossover exponent ϕ can be obtained from β through the use of scaling relations. The lack of a specific heat anomaly at the spin glass transition (as is typical of this material [21] and other spin glasses [22]) places certain restrictions on the scaling relations involving the specific heat exponent, α. In particular, Campbell points out that, for the specific heat to be regular at T_g, $\nu d = 4$ [23,24]. Using this result, and Eq. (2), ϕ can be related to β by $\phi = 4 - \beta$. This relation allows a determination of D from Eq. (3) using quantities determined experimentally.

As the parameter n is evaluated at different temperatures, Eq. (3) gives D in a temperature dependent form. This allows physical insight into the evolution of the spin clusters that generally cannot be achieved using Eq. (2). A plot of D and n versus temperature for [MnTPP][TCNE] is shown in Fig. 4. Calculated values for D increase with decreasing temperature and range from ~0.8 to over 1.5 near T_g. In particular, D shows a rapid increase as the temperature approaches T_g.

These results can be understood in terms of an anisotropic cluster glass model. [MnTPP][TCNE] is a typical member of a broad class of materials which form linear chains with large (> 1.2 nm) interchain spacing [9]. This large interchain spacing results in a very weak exchange between neighboring chains with dipolar interactions having the dominant role in interchain interactions [10–13]. Structural data, as well as the strong magnetocrystalline anisotropy observed in this material [25], support that spin clusters lie predominantly along a chain.

The values obtained for D confirm this type of quasi-1D behavior. At higher temperatures ($T > 5.0$ K), the values for D (~ 0.8) indicate that spin clusters are generally constrained to a single chain. As the temperature is lowered, D becomes greater than 1 as clusters now include portions of neighboring chains. As the glass transition is approached from above, the increasing size of the

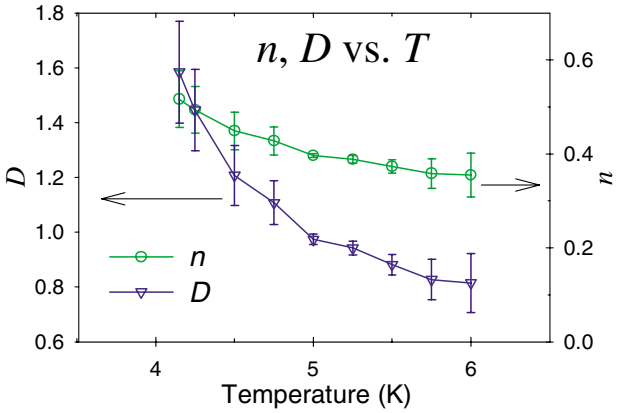

FIG. 4 (color online). Variation of the stretched exponential power n from Eq. (1) and the calculated values for the fractal cluster dimension D as a function of temperature. The arrows indicate the axis for a particular plot. The symbols represent the data, while the lines are merely a guide to the eye.

spin cluster leads to an increase in the strength of the dipolar interactions. This effective "dipolar exchange" with parallel chains beyond nearest neighbor, as well as the uniaxial anisotropy of [MnTPP][TCNE], may lead to the observed spin glass transition occurring for $d < 3$ [26].

The response times (τ) of the system shown in Fig. 3 provide insight into the nature of this glass transition. The τ from the ac and TRM data cover a large temperature range including temperatures up to $\sim 4T_g$ showing a slow transition to the frozen state. The slowness of the transition is also evident in the strong frequency dependent shift in the peak temperature of the ac susceptibility $[\Delta T_p/(T_p \Delta \log f) \sim 0.178)]$.

The TRM data show unusually long relaxation times ($\tau \sim 10^5$ sec) near T_g suggesting viscous behavior of the spin clusters. The long relaxation seen near T_g can be understood in terms of the dipolar interaction between spin clusters of neighboring chains. The interaction of the magnetic clusters will create some weak 3D order which will compete with and slow the glassy relaxation of the system.

In conclusion, we have reported a detailed scaling analysis of the ac susceptibility and TRM decay data for [MnTPP][TCNE]. Results indicate the presence of a glass transition near 4 K. Long characteristic times and strong frequency dependence of ac measurements suggest a slow, viscous transition to the glassy state. An extension of the fractal cluster model for spin glasses [3–6] enables a calculation of the fractal dimension of spin clusters in a temperature dependent form. Using this method, the spin system for [MnTPP][TCNE] was found to evolve from near linear spin clusters to higher dimensional clusters. The results were discussed in terms of the dipolar interaction between spin clusters of neighboring chains. Values for the fractal dimension obtained for [MnTPP][TCNE] are consistent with quasi-1D behavior, and are believed to be the first reported for a system of $d < 3$.

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