Magnetization and dynamics of reentrant ferrimagnetic spin-glass $[MnTPP]^{\cdot+}[TCNE]^{\cdot-}\cdot 2PhMe$

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We present direct current (dc) magnetization $M(T,H)$ and alternating current (ac) susceptibility $\chi_{ac}(T,H,f)$ data for the quasi-one-dimensional molecule-based ferrimagnet $[MnTPP]^{\cdot+}[TCNE]^{\cdot-}\cdot 2PhMe$ (TPP=*meso*-tetraphenylporphyrinato, TCNE=tetracyanoethylene). Static scaling of the real part χ' of the ac susceptibility and data collapse of $M(T,H)$ over a limited reduced temperature range above $T_c \approx 13$ K lead to the critical exponents $\gamma \approx 1.6$, $\beta \approx 0.5$, and $\delta \approx 4.2$. Below T_c, χ_{ac} depends sensitively on frequency and exhibits a striking double-peak structure similar to that found in reentrant spin glasses. Possible models for the frequency dependence of the peaks observed in χ_{ac} are discussed. © *1996 American Institute of Physics.* [S0021-8979(96)23208-X]

INTRODUCTION

Interest in molecule-based magnets has expanded rapidly as materials with novel physics and technological potential continue to be realized.[1] The first molecular systems possessing bulk magnetization at room temperature were the disordered, organic-based compounds $V(TCNE)_x \cdot y(solvent)$ (TCNE=tetracyanoethylene).[2] More recently, magnetism in the vicinity of room temperature has also been observed in the $M[M'(CN)_6]\cdot nH_2O$ Prussian Blue class of materials.[3]

The relative ease of synthesis of molecule-based magnets also yields unique opportunities for studying low-dimensional magnets. In the one-dimensional case, the properties of integral vs half-integral spin chains,[4] alternating quantum-classical ferrimagnetic chains,[5] and low-dimensional spin glasses[6] are currently of great theoretical interest.

The class of metalloporphyrin-TCNE electron-transfer compounds is of interest for its unusual structural and magnetic properties.[7,8] The parent compound, $[MnTPP]^{\cdot+}[TCNE]^{\cdot-}\cdot 2PhMe$ (TPP=*meso*-tetraphenylporphyrinato) is comprised of chains of alternating [MnTPP] ($S_1 = 2$) and [TCNE] ($S_2 = 1/2$) molecular units with direct metal-CN bonds similar to those in V(TCNE).

In this paper, we present detailed measurements of direct current (dc) magnetization $M(T,H_{dc})$ and alternating current (ac) susceptibility $\chi_{ac}(T,f,H_{ac},H_{dc})$ for $[MnTPP]^{\cdot+}[TCNE]^{\cdot-}\cdot 2PhMe$. A state of long-range ferrimagnetic order builds up as T is decreased below ~20 K toward a critical temperature of $T_c \approx 13$ K as determined from a static scaling analysis. The broad temperature region of incipient ferrimagnetism above T_c may result from the presence of highly anisotropic coherent clusters of spins and the effects of disorder. At lower temperatures ($T < 10$ K), a distinct second peak appears in the out-of-phase ac susceptibility, indicative of the "reentrant" transition to a spin-glass "phase" which coexists with ferrimagnetic order in the field-cooled state. The frequency dependence of this lower-temperature peak, however, is stronger than that observed in the canonical spin glasses[9] as well as known reentrant alloys.[10] The field dependence of the low-temperature state is similar to that of a metamagnet: spins of disordered ferrimagnetic chains reorient coherently over a temperature-dependent critical field range $[\Delta H_c(T)]$ to a state with saturated ferrimagnetic order. These results are compared to the expectations of a model of anisotropic, interacting superparamagnetic clusters.

EXPERIMENT

The preparation of [MnTPP][TCNE] has been described earlier.[7] The dc magnetization was measured with a Quantum Design MPMS5 superconductory quantum interference device magnetometer in the ranges $2 \leqslant T \leqslant 400$ K and $0 \leqslant H_{dc} \leqslant 5$ T. The ac susceptibility was measured via the mutual inductance technique with a LakeShore 7225 ac Susceptometer/dc Magnetometer in the ranges $4 \leqslant T \leqslant 30$ K and $0 \leqslant H_{dc} \leqslant 1$ T. The real and imaginary components of the linear susceptibility were recorded for an ac field of 0.1 Oe and a range of frequencies (5 Hz$\leqslant f \leqslant$40 kHz). The dominant source of uncertainty in determining the magnitude of the molar susceptibilities was the sample mass, estimated to be accurate to within 2%.

RESULTS

The temperature dependence of the zero-field cooled (ZFC) molar magnetization of $[MnTPP]^{\cdot+}[TCNE]^{\cdot-}\cdot 2PhMe$ for different applied fields is shown in Fig. 1. The lowest temperature state is demagnetized (M is near zero at 5 K). The magnetization goes through a broad maximum centered between 8 and 11 K depending on field. As T increases above 15 K, M drops quickly; the intermediate temperature ($100 < T < 250$ K) $M(T)$ data (not shown) follow Curie–Weiss behavior with $\chi_{dc} = M/H = C/(T-\theta)$, with $\theta = +61$ K. At room temperature, $C \approx 3.1$ emu K mol^{-1}, consistent with molecular units with $S_1 = 2$ (MnTPP) and $S_2 = \frac{1}{2}$ (TCNE). The large negative Curie–Weiss temperature $\theta < -100$ K for $T > 250$ K indicates antiferromagnetic coupling between adjacent spins. The inset of Fig. 1 shows field cooled (FC) and

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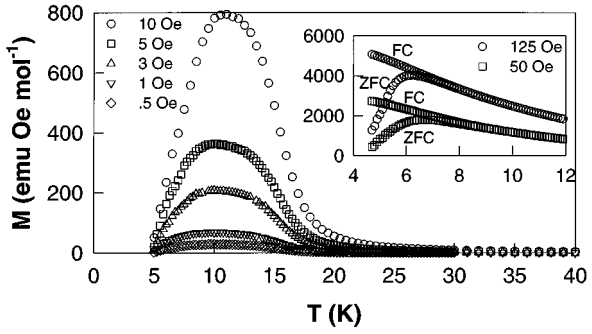

FIG. 1. Temperature dependence of zero-field cooled (ZFC) magnetization at small applied fields. Inset: FC vs ZFC magnetization at 50 and 125 Oe.

ZFC magnetization data at two fields. While the ZFC curves are only obtained on warming, the FC magnetization, which lies above the ZFC magnetization at low temperatures, is reversible at the sweep rate of ~ 0.1 K min^{-1}. The point where the FC and ZFC data merge is taken as the irreversibility temperature $T_f(H)$.

Isothermal magnetization data were recorded in a ZFC state (initial curves) for several temperatures $2 \leqslant T \leqslant 35$ K (Fig. 2). The saturation magnetization ($H > 4$ T) is $M_S \approx 17\,000$ emu Oe mol^{-1}, consistent with the expected value ($M_S = 16\,755$ emu Oe mol^{-1}) for a ferrimagnet of net spin $\frac{3}{2}$ per repeat unit. The S-shaped approach to saturation occurs at lower fields as T increases from 2 K.

The zero dc field susceptibility data are presented in Fig. 3. The real χ' and imaginary χ'' parts of χ_{ac} were recorded on warming from a ZFC state. An ac field of amplitude $H_{ac} = 0.1$ Oe was applied in a sequence of frequencies (5 Hz$\leqslant f \leqslant$40 kHz). Due to the small ac amplitude, a low signal-to-noise ratio was obtained at certain frequencies. A limited frequency range (20 Hz$\leqslant f \leqslant$1 kHz) is included in Fig. 3 to maximize clarity. The real part χ' becomes strongly frequency dependent below $\sim$14 K. In addition, a distinct shoulder appears in χ' at lower temperatures. This feature is isolated in the imaginary part χ'' as a separate peak. The "double-peak" structure in these data is discussed below.

DISCUSSION

The results of the static scaling analysis are presented in Fig. 4. The Kouvel–Fisher[11] scaling function $X_{KF}(T) = -\chi'(d\chi'/dT)^{-1}$ [Fig. 4(a), left axis], obtained from the real zero-field ac susceptibility χ', has the linear (scaling) form $X_{KF}(T) = (T - T_c)/\gamma$ only above $\sim$16 K. The critical temperature $T_c \approx 12.5$ K and average susceptibility exponent $\gamma \approx 1.6$ are obtained from the T intercept and inverse slope of X_{KF}, respectively. The fact that χ' does not obey a power law in $|t|$ within $\sim$3 K above T_c may reflect the presence of strong spatial anisotropy ($J_{inter}/J_{intra} \sim 10^{-2}$)—the buildup of long-range intrachain correlations is particularly sensitive to defects and disorder, possibly leading to the formation of quasi-one-dimensional (1D) "domains" well above T_c. Consequently, the "core" (3D) critical region is not probed in this measurement and the observed γ is expected[11] to be enhanced over its true value. The effective exponent $\gamma(T) = (T - T_c)/X_{KF}$ [Fig. 4(a), right axis] elucidates the presence of a region ($T < 16$ K) where χ' does not scale, below an unusually wide range where $\gamma(T)$ is fairly constant, falling off slowly as T increases.

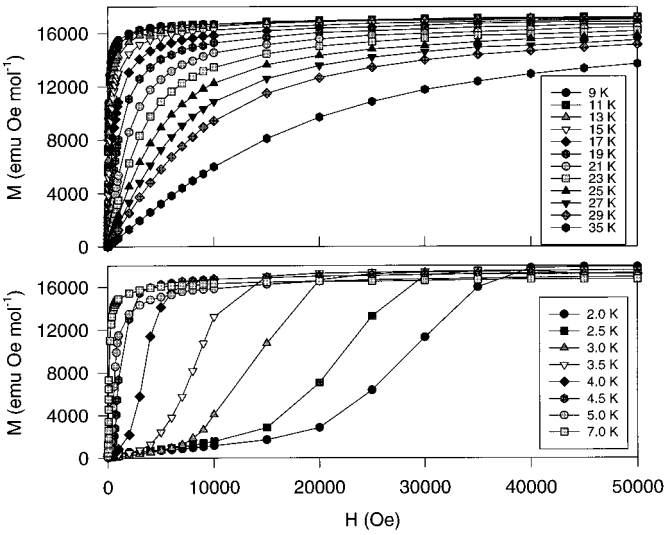

FIG. 2. Zero-field cooled (initial) isothermal dc magnetization.

The value $\gamma \approx 1.6$ is used to restrict the parameter space (β, δ) in the scaling of $M(T,H)$ [Fig. 4(b)] through the Griffiths–Rushbrooke relation[12] $\gamma = \beta(\delta - 1)$. The trial critical temperature T_c^{tr} for which the $M(T)$ data appear to coalesce for the three smallest applied fields (over a limited reduced temperature range above T_c^{tr}) is independently found to be $T_c \sim 13$–13.5 K. It is estimated that $\beta \sim 0.5$ and $\delta \sim 4.2$, though the accuracy and precision are limited by the relative insensitivity of the analysis to the choice of β and δ, and that the (possibly enhanced) γ is obtained from data above 16 K. The T_c value obtained is significantly lower than that ob-

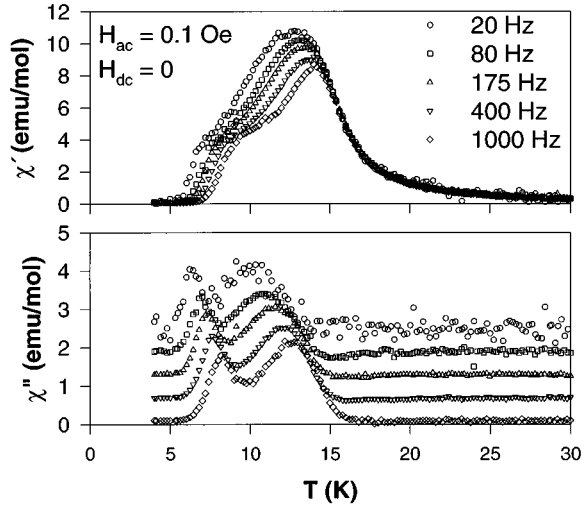

FIG. 3. Real (χ') and imaginary (χ'') parts of the ZFC ac susceptibility in zero bias field H_{dc} and 0.1 Oe excitation field $H_{ac} \cdot \chi''$ data are shifted for clarity; high temperature values show the approximate baseline for each curve.

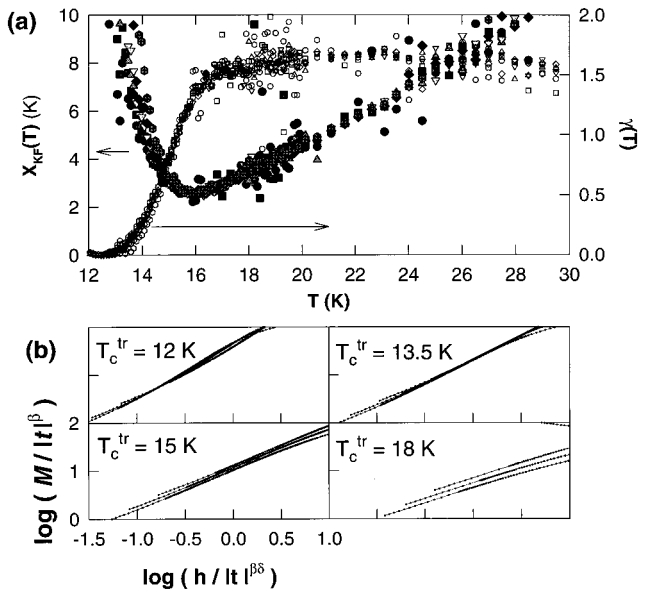

FIG. 4. (a) Kouvel–Fisher scaling function $X_{\mathrm{KF}}(T)=-\chi'(d\chi'/dT)^{-1}$ (left axis) and temperature-dependent effective critical exponent $\gamma(T)=(T-T_c)/X_{\mathrm{KF}}(T)$ (right axis). (b) Scaling of dc magnetization $M(T,H)$ above T_c^{tr} for $\beta=0.5$ and $\delta=4.2$, where $h=H/T$. See the text.

tained by extrapolating the maximum slope[8] of the low-field $M(T)$ curve to $M=0$, which gives $T_c\approx 18$ K.

As mentioned above, the experimental observation of a "slow" transition to long-range ferrimagnetic order in $[\mathrm{MnTPP}]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}\cdot 2\mathrm{PhMe}$ reflects the quasi-1D magnetism in this system. In chainlike magnets, significant long-range longitudinal spin–spin correlations build up well before 3D order is established. For instance, specific heat studies reveal that a very high fraction of the magnetic entropy of quasi-1D magnets lies above T_c.[13]

The low-temperature isothermal magnetization $M(H)$ and the appearance of the "reentrant" transition may be interpreted as resulting from the behavior of interacting, anisotropic superparamagnetic clusters. Superparamagnetism (SPM) describes the behavior of well separated, classical (large S) spin clusters which behave paramagnetically at high temperatures, but due to internal shape or dipolar anisotropy energy barriers are "blocked" from undergoing global spin flips below a characteristic temperature T_b. SPM leads to broad maxima around T_b in $M(T)$ and χ_{ac}, with the latter following an Arrhenius frequency dependence $\omega=\omega_0\exp(-E_a/k_BT)$, where E_a is a characteristic anisotropy energy. In contrast, [MnTPP][TCNE] is a magnetically concentrated system, so intercluster interactions are likely very important, and may be responsible for the spin-glass-like behavior.

The S-shaped crossover in $M(H)$ from low-M to saturation occurs in a range $\Delta H_c(T)$. If $H_c(T)$ is defined as the midpoint of the crossover, it is seen that both H_c and ΔH_c decrease as T increases from 2 to 7 K. The ΔH_c trend favors a disordered, spin-glass-like state at low T and H rather than a pure antiferromagnetic one as in the ideal metamagnetic case. Due to a strongly spatially anisotropic exchange J, spin clusters in [MnTPP][TCNE] are expected to be elongated. The increase in ΔH_c as T decreases indicates the presence of a broadening distribution of barriers to the rotation of spin cluster moments.

The appearance of a second, lower temperature peak in χ_{ac} is similar to that seen in "reentrant" spin-glass (RSG) alloys.[14] However, the frequency dependence of both lower (T_1) and upper (T_2) peak temperatures is quite strong, suggesting that [MnTPP][TCNE] lies somewhere between traditional RSGs and pure SPM. The fractional shifts in peak temperature per decade of frequency are $(\Delta T_1/T_1)/(\Delta\log f)\approx 0.23$ and $(\Delta T_2/T_2)/(\Delta\log f)\approx 0.14$. Fits to pure Arrhenius behavior give $E_{a1}/k_B\approx 112$ K and $f_{01}\approx 940$ MHz ($\tau_{01}\sim 10^{-9}$ s) for $T_1(\omega)$ and $E_{a2}/k_B\approx 247$ K and $f_{02}\approx 420$ GHz ($\tau_{02}\sim 2.4\times 10^{-12}$ s) for $T_2(\omega)$. ($\tau_0=1/f_0$ is the characteristic limiting relaxation time for a given frequency prefactor f_0). The peak positions are relatively close to the "typical" blocking temperatures obtained using $T_b\sim E_a/25k_B$.[10] The applicability of the model of transverse spin freezing[14] to [MnTPP][TCNE] is under investigation.

ACKNOWLEDGMENTS

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[1] J. S. Miller and A. J. Epstein, Angew. Chem. Int. Ed. Engl. **33**, 385 (1994); *Proceedings of the 4th International Conference on Molecule-Based Magnets*, J. S. Miller and A. J. Epstein, eds., Mol. Cryst. Liq. Cryst. **271–274** (1995). *Proceedings of the NATO ASI on Localized and Itinerant Molecular Magnetism* (to be published).

[2] J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein, and J. S. Miller, Science **252**, 1415 (1991); B. G. Morin, P. Zhou, C. Halm, A. J. Epstein, and J. S. Miller, J. Appl. Phys. **73**, 5648 (1993); P. Zhou, B. G. Morin, J. S. Miller, and A. J. Epstein, Phys. Rev. B **48**, 1325 (1993); W. B. Brinckerhoff, J. Zhang, J. S. Miller, and A. J. Epstein, Mol. Cryst. Liq. Cryst. **272**, 195 (1995).

[3] T. Mallah, S. Ferlay, C. Auberger, C. Helary, F. L'Hermite, R. Ouahes, J. Vaissermann, M. Verdaguer, and P. Veillet, Mol. Cryst. Liq. Cryst. **273**, 579 (1995).

[4] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).

[5] J. Curély, R. Georges, and M. Drillon, Phys. Rev. B **33**, 6243 (1986); M. Drillon, E. Coronado, R. Georges, J. C. Gianduzzo, and J. Curély, *ibid*. **40**, 10992 (1989); J. Curély and R. Georges, *ibid*. **49**, 1146 (1994); **49**, 1158 (1994).

[6] J. A. Lukin, S. A. Friedberg, S. Chadarlapathy, W. W. Brubaker, C. C. Cinquina, and G. C. DeFotis, J. Appl. Phys. **75**, 5529 (1994); A. N. Kocharian and A. S. Sogomonian, *ibid*. **76**, 6186 (1994); E. B. Kolomeisky, Phys. Rev. B **51**, 3047 (1995).

[7] J. S. Miller, J. C. Calabrese, R. S. McLean, and A. J. Epstein, Adv. Mater. **4**, 498 (1992); D. A. Summerville, T. W. Cape, E. D. Johnson, and F. Basolo, Inorg. Chem. **17**, 3297 (1978).

[8] P. Zhou, B. G. Morin, A. J. Epstein, R. S. McLean, and J. S. Miller, J. Appl. Phys. **73**, 6569 (1993).

[9] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor and Francis, London, 1993).

[10] T. Eckelt, Ch. Böttger, and J. Hesse, J. Magn. Magn. Mater. **104–107**, 1665 (1992); B. Özçelik, K. Kiymaç, J. C. Verstelle, A. J. van Duyenveldt, and J. A. Mydosh, J. Phys. Condensed Mater. **4**, 6639 (1992); S. Giri, K. Ghoshray, R. Ranganathan, A. Roy, B. Bal, and A. Ghoshray, Solid State Commun. **91**, 273 (1994).

[11] J. S. Kouvel and M. E. Fisher, Phys. Rev. A **136**, 1626 (1964); S. N. Kaul, J. Magn. Magn. Mater. **53**, 5 (1985).

[12] R. B. Griffiths, Phys. Rev. Lett. **14**, 623 (1965).

[13] A. Chakraborty, A. J. Epstein, W. N. Lawless, and J. S. Miller, Phys. Rev. B **40**, 11422 (1989).

[14] B. R. Coles, Philos. Mag. B **49**, L21 (1984); I. A. Campbell and S. Senoussi, Philos. Mag. B **65**, 1267 (1992); M. J. P. Gingras, in *Magnetic Systems with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994), p. 238.