

Three-dimensional ordering, spin excitations, and dilution effects in the quasi-1D ferromagnetic (DMeFc)(TCNE)

K. S. Narayan, K. M. Chi, and A. J. Epstein

Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106

Joel S. Miller

E. I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0328

The linear chain $S = \frac{1}{2}$ molecular ferromagnet decamethylferrocenium tetracyanoethanide [(DMeFc)(TCNE)] has been studied by frequency-dependent ac susceptibility experiments. $\chi'(T)$ and $\chi''(T)$ exhibit maxima in the temperature range of 4.8–4.9 K, which corresponds to the transition temperature to the three-dimensional (3D) ferromagnetic ground state. The 3D ordering is due to the presence of a finite interchain ferromagnetic interaction, as determined earlier by dc magnetic susceptibility and specific heat experiments. The results of ac susceptibility measurements below T_c are analyzed in terms of a Debye-like model to investigate the presence of gaps in the spin excitation spectrum of the system. Considerable changes are observed in the critical temperature on introducing spinless sites into the system. The transition temperature of the dilution series (DMeFc) $_x$ (DMeCo) $_{1-x}$ (TCNE), where (DMeCo) $^+$ = (decamethylcobaltocenium $^+$) has spin $S=0$, decreases with increasing $(1-x)$.

INTRODUCTION

There is increasing interest in the field of molecular and polymeric ferromagnetism. Several models have been developed to account for the ferromagnetic exchange. In nearly all cases, attempts to synthesize such ferromagnets have been unsuccessful. An important exception is decamethylferrocenium tetracyanoethanide [(DMeFc)(TCNE)]. It can be modeled as a linear chain $S = \frac{1}{2}$ anisotropic Heisenberg ferromagnet with a Curie temperature of 4.8 K.^{1,2} The system consists of $S = \frac{1}{2}$ (DMeFc) $^+$ donors and $S = \frac{1}{2}$ (TCNE) $^-$ acceptors.

(DMeFc)(TCNE) crystallizes with stacks of alternating cations and anions parallel to the long-needle axis of the solution-grown crystals.³ A schematic view of the type of stacking arrangement is shown in Fig. 1. The donor DMeFc consists of two $C_5(CH_3)_5$ rings surrounding a Fe^{III} ion. The acceptor TCNE is essentially planar. Earlier studies indicate that the Landé g factors for (DMeFc) $^+$ are $g_{\parallel} \sim 4.0$ and $g_{\perp} \sim 1.3$ as measured by electron paramagnetic resonance techniques, where the g_{\parallel} and g_{\perp} refer to the g factor obtained for magnetic fields parallel and perpendicular to the molecular axis.⁴ In contrast the (TCNE) $^-$ has $g=2$ and is isotropic. The dc susceptibility, magnetization, specific-heat, and neutron-diffraction studies show that the system becomes a three-dimensional (3D) ferromagnet below the transition temperature $T_c \approx 4.8$ K.^{1,5,6} The hysteresis curves obtained by plotting M vs H at 2.2 K indicate that the material is a hard ferromagnet with a coercive field of ~ 1 kG. At higher temperatures the susceptibility versus temperature can be fit to a 1D Heisenberg model for an intrachain exchange integral $J_{\text{intrachain}}$ value of approximately 28 K.¹ The temperature-dependent specific heat $C(T)$ has a cusp at the 3D ferromagnetic transition temperature with a crossover to primarily 1D behavior at higher temperatures.⁶

The magnetic properties of the individual chains have

been described by a Heisenberg-form spin Hamiltonian with a near-neighbor interaction and an orientational dependence of the (DMeFc) $^+$ moment:^{1,6}

$$H = -J \sum_i [g_{\parallel}^D g^A S_z^i S_z^{i+1} + g_{\perp}^D g^A (S_x^i S_x^{i+1} + S_y^i S_y^{i+1})],$$

where $g^{\text{TCNE}} = 2.0$ and is isotropic, and $g_{\parallel}^{\text{DMeFc}} = 3.9$ and $g_{\perp}^{\text{DMeFc}} = 1.3$. Substituting these values, the Hamiltonian can be rewritten as

$$H = -2J_{\text{intrachain}} \sum_i [S_z^i S_z^{i+1} + \gamma (S_x^i S_x^{i+1} + S_y^i S_y^{i+1})]$$

where $\gamma \sim 0.35$. Hence even though $J_{\text{intrachain}}$ is isotropic in spin space, the final Hamiltonian is anisotropic. The above Hamiltonian does not distinguish between the J and g anisotropies.

RECENT RESULTS AND DISCUSSION

Apart from $J_{\text{intrachain}}$ there is a weak but finite interchain interaction $J_{\text{interchain}}$ which drives the system to 3D long-range order below 4.8 K. On using a simple approximation⁷ of $T_c \sim (J_{\text{inter}} J_{\text{intra}})^{1/2}$, we obtain a $J_{\text{interchain}} \sim 1$ K and a spatial anisotropy of $J_{\text{interchain}}/J_{\text{intrachain}}$ in the range of $\frac{1}{15}$ to $\frac{1}{75}$.

Ferromagnetic transitions can be closely studied by measuring the ac susceptibility in the vicinity of the transition temperature. The χ_{ac} results summarized here have been measured using a mutual inductance bridge as described.⁸ A ferromagnetic transition is characterized by a sharp maximum in the real and imaginary parts of the ac susceptibility $\chi(T)$ at the transition temperature. As shown in Fig. 2, a sharp maximum in χ' vs T is observed at $T \sim 4.9$ K recorded at 89 Hz.⁹ The divergence is associated with the transition to the ferromagnetic ground state. The imaginary part of the susceptibility recorded at 89 Hz is displayed in Fig. 3. It also peaks at approximately 4.9 K.

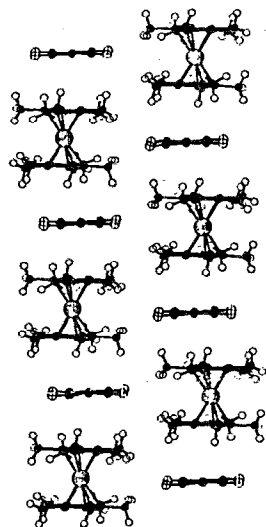


FIG. 1. Stacking arrangement of donor and acceptor molecules for out-of-registry chains of the compound (DMeFc)(TCNE). Other stacks are in registry (from Ref. 3).

The higher-frequency data are similar, the curve, however, becoming less peaked as the frequency is increased.

Using static scaling theory to analyze the divergence of $\chi'(T)$ at temperatures for $5.8 \text{ K} > T > T_c$ with a T_c of $4.90 \pm 0.15 \text{ K}$, yields a critical exponent $\gamma_c \approx 1.31 \pm 0.018$. This value differs from the results in Ref. 1 and reflects our choice of a much more restricted range of temperature for the evaluation. Further, these data were taken at zero field as compared to the 2 kG for Ref. 1. The value obtained for γ_c lies inbetween the 3D Ising and the 3D Heisenberg values consistent with the anisotropy in J discussed above.¹⁰ The decrease in $\chi'(T)$ below T_c can be explained by the relatively high coercive field of approximately 1 kG, resulting in hard ferromagnetic behavior.¹

The response of domains to an alternating field can be interpreted in terms of a Debye-like model for a two-level system with a single relaxation time τ . This model has been used for paramagnetic systems where the process is char-

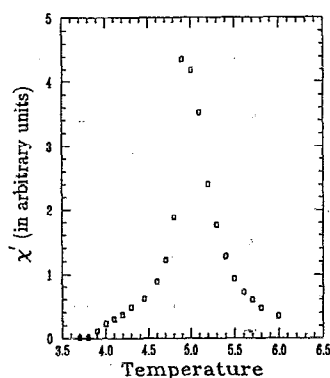


FIG. 2. Real part of the ac complex susceptibility of (DMeFc)(TCNE) as a function of temperature.

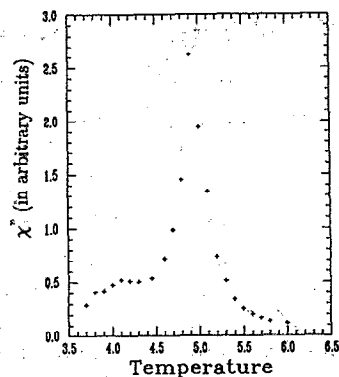


FIG. 3. Imaginary part of the ac complex susceptibility of (DMeFc)(TCNE) as a function of temperature.

acterized by a spin-lattice time constant, which is in the range of 0.1–1 ms.¹¹ In ferromagnetic materials, the magnetization relaxes on a much longer time scale. Consequently, there is a preferential ordering direction of magnetic domains and there is a loss of information about this preferential direction if the period of oscillation of the external field is longer than the spin-lattice time constant. The relaxation process in this regime is indicative of the domain-wall processes in the system and can fit to an Arrhenius expression with respect to the temperature $\exp(-\Delta/k_B T)$ (Ref. 12). Fitting the experimental values of τ measured for $T < T_c$ to the Arrhenius form yields a value of the activation energy of $\Delta \sim 35 \text{ K}$. A more detailed examination of the excitation spectrum by inelastic neutron scattering and χ_{ac} in a magnetic field will elucidate the effects of the strong spatial anisotropy of the exchange interaction, the domain-wall motions, and the possible existence of solitons in this system.

The (DMeFc)(TCNE) material is an ideal prototype system for study of quasi-1D ferromagnetism. For example, theorists have long been studying the effects of spin dilution on the 3D ferromagnetic ordering of low-dimensional systems.¹³ Replacement of $S = \frac{1}{2}$ sites by $S = 0$ sites in a chain causes substantial changes in the magnetic properties. The study of (DMeFc)(TCNE) with some spinless sites, achieved by doping (DMeFc)(TCNE) with (DMeCo)(TCNE) where the (DMeCo)⁺ = dekamethylcobaltocenium is spinless, has been a test of these theories.¹⁴ Experimental results show a dramatic decrease of T_c with increasing dopant concentration in a manner which is in accordance with the two-decade-old theoretical predictions.

We acknowledge the assistance of A. Chakraborty and K. R. Cromack. The project was supported in part by DOE Grant No. DE-FG02-86ER45271.

¹S. Chittipeddi, K. R. Cromack, J. S. Miller, and A. J. Epstein, Phys. Rev. Lett. **58**, 2695 (1987).

²J. S. Miller, A. J. Epstein, and W. M. Reiff, Science **240**, 40 (1988).

³J. S. Miller, J. C. Calabrese, H. Rommelmann, S. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, J. Am. Chem. Soc. **109**, 769 (1987).

⁴D. M. Duggan and N. Hendrickson, Inorg. Chem. **14**, 955 (1975).

- ⁵S. Chittipeddi, M. A. Selover, A. J. Epstein, D. M. O'Hare, D. M. Manriquez, and J. S. Miller, *Synth. Met.* **27**, B417 (1988).
- ⁶A. Chakraborty, A. J. Epstein, W. N. Lawless, and J. S. Miller, *Phys. Rev. B* **40**, 11422 (1989).
- ⁷S. H. Liu, *J. Magn. Magn. Mater.* **82**, 294 (1989).
- ⁸K. S. Narayan, A. J. Epstein, and J. S. Miller (unpublished).
- ⁹The difference between T_c of 4.9 K measured by χ_{ac} and 4.8 K earlier reported for static susceptibility measurements (Ref. 1) and 4.82 K determined from specific-heat measurements (Ref. 2) may reflect differences in T_c for finite magnetic fields (Ref. 1), powdered sample (Ref. 6), small crystals (Ref. 1), and large crystals (present work), as well as systematic instrumental differences.
- ¹⁰S. K. Ma, *Modern Theory of Critical Phenomena* (A. Benjamin, Reading, MA, 1976).
- ¹¹R. L. Carlin and A. J. van Duynvelt, *Magnetic Properties of Transition Metal Compounds* (Springer, New York, 1977).
- ¹²A. J. van Duynvelt, *J. Appl. Phys.* **53**, 8006 (1982).
- ¹³R. B. Stinchcombe, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 7.
- ¹⁴K. S. Narayan, K. M. Cai, A. J. Epstein, and J. S. Miller *Bull. Am. Phys. Soc.* **35**, 594 (1990); and (unpublished).

Journal of Applied Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/japo/japcr/jsp>
Copyright of Journal of Applied Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.