Ferromagnetism in Molecular Decamethylferrocenium Tetracyanoethenide (DMeFc TCNE)

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The temperature and magnetic field dependence of the magnetization and susceptibility of single-crystal decamethylferrocenium tetracyanoethenide demonstrate that this material is the first molecular compound with a ferromagnetic ground state. A spontaneous magnetization is observed for $T < 4.8$ K. The results are consistent with a crossover from a dominance of one-dimensional ferromagnetic exchange interaction to a 3D mean-field-like interaction at $\simeq 16$ K. The critical exponents are in accord with mean-field behavior. A generalized Hubbard model is proposed to account for the unusual ferromagnetic exchange interactions in this system.

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In the past decade extensive study of quasi one-dimensional molecular charge-transfer salts has led to considerable insight into the physics of these systems,[1] especially segregated-stack conductors. Less emphasis has been placed upon mixed-stack systems where the donor molecule alternates with the acceptor molecule. Interaction among the unpaired electrons in such systems generally leads to antiferromagnetic exchange.[2] In parallel activity, there has been extensive study of few-dimensional magnetic interactions in inorganic linear-chain compounds, for example, the 1D ferromagnet $CsNiF_3$ and the 2D ferromagnet K_2CuF_4.[3]

We report here the first extensive magnetization and susceptibility study of single crystals of the first molecular ferromagnet, decamethylferrocenium tetracyanoethenide (DMeFc TCNE), $[Fe(C_5(CH_3)_5)_2]^+[C_2(CN)_4]^-$. The data show a dominance of one-dimensional exchange interactions for $T > 16$ K with a crossover to a mean-field-like 3D interaction for $16\text{ K} > T > 4.8$ K. For $T < 4.8$ K, a spontaneous magnetization is observed with a substantial coercive field. It is shown that the data for $T > 16$ K can be analyzed in terms of a 1D Heisenberg model with ferromagnetic exchange, J, of 27.4 K. Below 16 K agreement is shown with a mean-field divergence, $\chi \propto (T-T_c)^{-\gamma}$, with $\gamma \simeq 1.22$. For $T < 4.8$ K, the spontaneous magnetization is proportional to $(T_c - T)^{-1/2}$. At the transition temperature of $\simeq 4.8$ K, $M \propto H^{1/\delta}$ with $\delta \simeq 4.42$. It is shown that the presence of ferromagnetic exchange in these systems can be understood within a generalized Hubbard model taking into account the presence of degenerate or nearly degenerate energy levels.

DMeFc TCNE crystallizes in an orthorhombic structure with the stacks of alternating $DMeFc^+$ and $TCNE^-$ molecules parallel to the long needle (a) axis of the solution-grown crystals.[4,5] The magnetization, M, and susceptibility, χ, were measured on a single crystal (1.35×10^{-3} gm) with a Faraday technique.[6] Data reported here are for the magnetic field parallel to the needle axis; in this case the demagnetization field may be approximated as zero. A separately controlled magnetic field, H, up to 80 kG (uniform to one part in 10^5 over 1 cm) and a field gradient dH/dz up to ± 0.8 kG allow considerable sensitivity over the full range of magnetic fields, H, of interest. Spontaneous magnetization was measured in the absence of an applied field ($H=0$), with a field gradient dH/dz varying between ± 15 G/cm. Hence the field at the sample during nominally zero-field experiments was less than ~ 3 G. The contribution of the aluminum sample holder and sample core diamagnetism[7] (-2.57×10^{-4} emu/mole) were subtracted in order to obtain the data presented here.

The reciprocal of the experimentally measured spin susceptibility, χ^{spin}, defined as M/H, is plotted versus T in Fig. 1. The data for $T > 30$ K were taken at $H=65$ kG while those for $T < 30$ K were at $H=2.0$ kG, to avoid saturation effects. The logarithm of the susceptibility data for $T < 30$ K at several low magnetic fields is shown in Fig. 2, with the temperature scale plotted as $\log(T-T_c)$ for $T_c = 4.8$ K. As T decreases, an increasing spontaneous magnetization is observed in the absence of magnetic field below a transition temperature $T_c \simeq 4.8$ K (Fig. 3). At the transition temperature, a very strong dependence of M on H is observed (inset, Fig. 3). Below T_c, a substantial hysteresis in $M(H)$ is recorded (Fig. 4). A Honda analysis[6] at 290, 150, and 80 K yields a modest magnetic impurity concentration equivalent to the

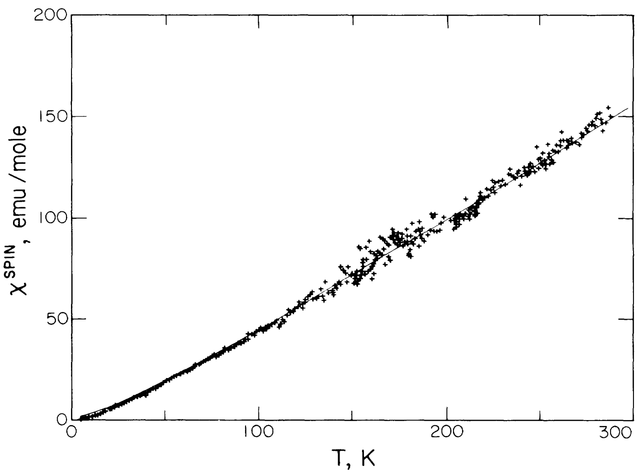

FIG. 1. $(\chi^{\rm spin})^{-1}$ vs T for DMeFc TCNE. The data for $T > 30$ K were taken at 65 kG, those for $T < 30$ K at 2.0 kG. The solid curve is a fit by a 1D Heisenberg $S=\frac{1}{2}$ ferromagnetic chain (see Eq. 3 in text).

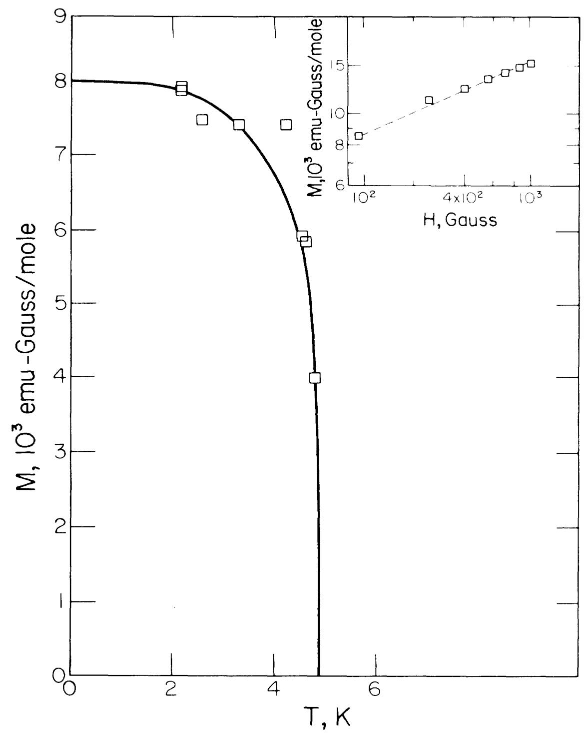

FIG. 3. Magnetization M vs T showing spontaneous magnetization. Solid curve is a fit by $M_0(T_c-T)^{0.5}$. Inset: log$M$ vs log$H$ at $T \approx 4.8$ K. The solid line is a fit by $M \propto H^{1/4.4}$.

presence of $\simeq 300$ ppm ferromagnetic iron by weight, insufficient to account for the low-temperature behavior.

DMeFc TCNE is composed of $S=\frac{1}{2}$ DMeFc$^+$ ions with an anisotropic g value of $g_\parallel^{\rm DMeFc} \simeq 4$ and $g_\perp^{\rm DMeFc} \simeq 2$,[6,8] and $S=\frac{1}{2}$ TCNE$^-$ ions with nearly isotropic $g^{\rm TCNE} \simeq 2$. Assuming independent (Curie) spins with H parallel to the stacking (molecular) axis, we have

$$\chi^{\rm spin} = \chi^{\rm spin}_{\rm DMeFc} + \chi^{\rm spin}_{\rm TCNE} = N[(g_\parallel^{\rm DMeFc})^2 + (g^{\rm TCNE})^2]S(S+1)\mu_{\rm B}^2/3k_{\rm B}T, \tag{1}$$

where N is Avogadro's number, $\mu_{\rm B}$ the Bohr magneton, and $k_{\rm B}$ Boltzmann's constant. The experimental $\chi_\parallel^{\rm spin}(290\ {\rm K}) = 6.67\times 10^{-3}$ emu/mole is in rough agreement with a χ of 6.46×10^{-3} emu/mole calculated with

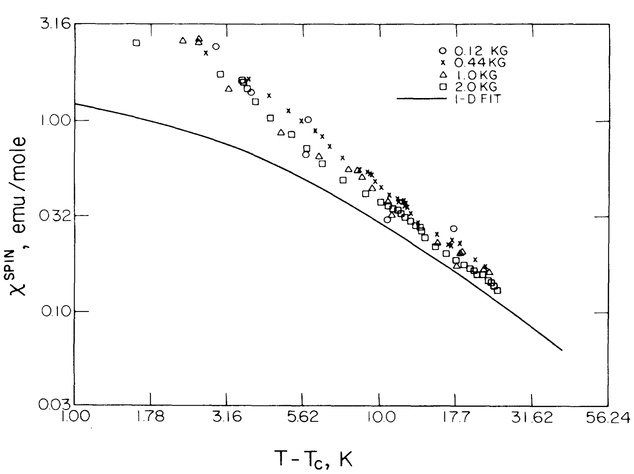

FIG. 2. log$\chi^{\rm spin}$ vs log$(T-T_c)$ with $T_c=4.8$ K at fields of 0.12, 0.44, 1.0, and 2.0 kG. The solid line is a continuation of the fit by the 1D model shown in Fig. 1.

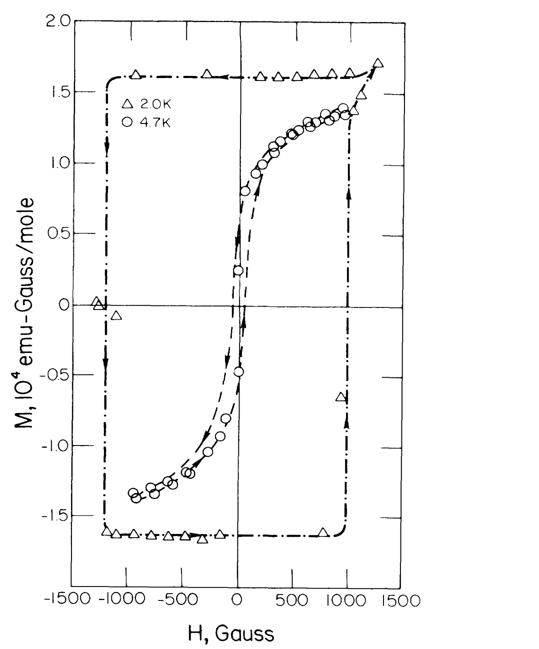

FIG. 4. Magnetization M vs applied magnetic field; circles, 4.7 K; triangles, 2.0 K.

use of this independent-spin expression, although the T behavior reported in Fig. 1 is not a simple Curie or Curie-Weiss type. For $T \ll T_c$ the saturation moment, M^{sat}, can similarly be compared to a sum expected for independent spins,

$$M^{\text{sat}} = N[g_{\parallel}^{\text{DMeFC}} + g^{\text{TCNE}}]S\mu_{\text{B}}. \qquad (2)$$

The experimental value of 1.63×10^4 emu G/mole, Fig. 4, is in very good agreement with that calculated for $g_{\parallel}^{\text{DMeFc}} = 4$ and $g^{\text{TCNE}} = 2$, 1.675×10^4 emu G/mole.

Several models exist for 1D magnetic chains, including Ising for $S = \frac{1}{2}$ [9] and Heisenberg for $S = \frac{1}{2}$.[10-12] If we fit the experimental data by a Padé[10] series expansion for the $S = \frac{1}{2}$ Heisenberg model,

$$\frac{T\chi(K)}{Ng^2\mu_{\text{B}}^2} = \left[\frac{1 + 5.8K + 16.90K^2 + 29.38K^3 + 29.83K^4 + 14.04K^5}{1 + 2.80K + 7.01K^2 + 8.65K^3 + 4.57K^4} \right]^{2/3}, \qquad (3)$$

where $K = J/2k_{\text{B}}T$, a good fit is obtained for $J = 27.4$ K despite the assumption that all spins are identical (not alternating $g = 4$ and $g = 2$). The fit shown by the solid line in Figs. 1 and 2 assumes one spin of $g = 3.9$ and one spin of $g = 2$ per repeat unit. Similar fits were obtained in the study of polycrystalline samples[5,6] with $J = 30$ K and a magnitude consistent with an averaging of the anisotropic DMeFc g tensor.

The deviation from one-dimensional behavior and the approach to the 3D ordered state is of fundamental interest. Figure 2 shows the susceptibility measured at several low fields for $T < 30$ K together with an extrapolation of the high-temperature one-dimensional behavior plotted as $\log\chi$ vs $\log(T - T_c)$. Below approximately 16 K, χ^{spin} increases much more rapidly than predicted by the 1D Heisenberg model, increasing as $(T - T_c)^{-\gamma}$, with $\gamma \simeq 1.22 \pm 0.02$. A γ of $\simeq 1.2$ is typical of 3D Heisenberg ferromagnets,[13] for example, the insulator CrBr_3.[13] The crossover from 1D to 3D behavior occurs as T is lowered below 16 K. An attempt to model the susceptibility as $\chi \propto \exp(bt^n)$ with $t = (T - T_c)/T_c$ and b and n constants of order 2.6 and 0.5, respectively, was unsuccessful, indicating the absence of an intermediate temperature regime where ferromagnetic interactions in two dimensions[14] dominate. The temperature variation of the magnetization at constant applied field was examined for fields of $1.0 \text{ kG} < H < 76$ kG. A critical temperature in the presence of the applied field, $T_c(H)$, was defined as T for maximum dM/dT. A plot of $T_c(H)$ vs H is a smooth, monotonically increasing function, demonstrating the absence of an easy plane of magnetization[15] perpendicular to the crystalline stacking (a) axis.

$M(H)$ was measured for constant T for $T \simeq T_c$. The results for $T = 4.82 \pm 0.02$ K plotted on a logarithmic scale are detailed in the inset in Fig. 3. For modest fields, $96 \text{ G} < H < 1100$ G, we observe $M \propto H^{1/\delta}$ with $\delta = 4.42 \pm 0.06$. The experimental δ for the anisotropic molecular DMeFC TCNE is nearly identical to that for CrBr_3 [14] though larger than $\delta = 3$ obtained from mean-field theory.[13]

The zero-field magnetization increases rapidly as T is decreased below T_c. The solid curve in Fig. 3 is the fit by $M = M_0(T_c - T)^{\beta}$, with $\beta \simeq 0.5$, $T_c = 4.8$ K, and $M_0 = 8000$ emu G/mole. Though $\beta \approx 0.5$ is the mean-field result,[13] it is larger than that usually observed for 3D magnetic systems. The value of M is less than the saturation moment in the presence of applied field, 1.64×10^4 emu G/mole, consistent with ferromagnetic domain formation.

Measurement of magnetization as a function of applied field for $T < T_c$, Fig. 4, shows an increasingly well-defined hysteresis loop as T decreases. For $T = 4.7$ K, a hysteresis of $\simeq 30$ G is observed. At lower temperatures, a well-defined remnant magnetization nearly equal to the saturation moment is seen. As T is decreased to 2.0 K, a rectangular hysteresis loop is recorded, with a sizable coercive field (parallel to the stacking axis) of $H_c = 1000$ G.

The origin of the ferromagnetic exchange interaction in all three directions is of fundamental importance. In general, the antiferromagnetic exchange interaction present in linear-chain charge-transfer salts composed of identical molecules with nondegenerate highest-energy occupied orbitals, each with one electron in them, can be accounted for within a nearest-neighbor Hubbard model with transfer integral t_{ij} between near neighbors i and j, and energy cost ΔE for double occupancy of the nondegenerate orbital[2,16]:

$$H = \sum_i \Delta E n_{i\uparrow} n_{i\downarrow} - \sum_{i,j,\sigma} t_{ij}(C_{i\sigma}^{\dagger}C_{j\sigma} + C_{j\sigma}^{\dagger}C_{i\sigma}). \qquad (4)$$

Here $C_{i\sigma}^{\dagger}$ and $C_{j\sigma}$ are, respectively, creation and annihilation operators for an electron of spin σ on the ith and jth sites and $n_{i\sigma}$ is the number of electrons of spin σ on the ith site. For $\Delta E \gg t_{ij}$ and $\Delta E \gg k_{\text{B}}T$ the Hamiltonian in Eq. (4) reduces to the Heisenberg form,

$$H_{\text{eff}} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \qquad (5)$$

with $J_{ij} = t_{ij}^2/\Delta E$. If sites i and j are not identical ΔE depends upon direction of charge transfer: $J_{ij}^i = t_{ij}^2/\Delta E_i$ for charge transfer from j to i and $J_{ij}^j = t_{ij}^2/\Delta E_j$ for charge transfer from i to j. For singly occupied nondegenerate orbitals on each site, $J_{ij} > 0$, i.e., antiferromagnetic coupling dominates since the excited state is a singlet.

For DMeFc TCNE the exchange interaction is more complex. While TCNE^- has a single electron (spin) in the highest occupied b_{2g} orbital, $DMeFc^+$ has three electrons in the two (degenerate) highest-energy electron orbitals, $d_{x^2-y^2}$ and d_{xy}. Virtual reverse charge transfer from $TCNE^-$ to $DMeFc^+$ leads to antiferromagnetic exchange, $|J_{ij}^{DMeFc}| \approx t_{ij}^2/\Delta E_{DMeFc}$. However, a virtual transition from $DMeFc^+$ to $TCNE^-$ to form the doubly ionized excited state will lead to a ferromagnetic exchange,[17] $|J_{ij}^{TCNE}| \approx t_{ij}^2/\Delta E_{TCNE}$; thus the total exchange along a chain, $J_{ij} = J_{ij}^{TCNE} + J_{ij}^{DMeFc}$, can be ferromagnetic.[18] Similarly, the exchange interaction among spins in parallel chains will be antiferromagnetic between pairs in $TCNE^-$ ions but can be ferromagnetic between $DMeFc^+$ pairs and $DMeFc^+$-$TCNE^-$ pairs, resulting in a net ferromagnetic exchange.

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