Ferromagnetism in molecular materials: Decamethylferrocenium tetracyanoethanide (DMeFc) (TCNE) (invited)

A. J. Epstein
Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1106

Sailesh Chittipeddi and A. Chakraborty
Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106

Joel S. Miller
Central Research and Development Department, Experimental Station E328, E. I. DuPont de Nemours and Company, Wilmington, Delaware 19898

Ferromagnetism has only recently been observed in molecular materials. We present here a summary of the ferromagnetic phenomena observed in the molecular charge transfer salt, decamethylferrocenium tetracyanoethanide (DMeFc)(TCNE), and related compounds. A spontaneous magnetization is observed in this material for $T < 4.8$ K, with a saturation moment in agreement with alignment of individual spins localized on the DMeFc$^{+\cdot}$ and TCNE$^{-\cdot}$ ions. A comparison of these results with analogous charge transfer salts is presented. Models for the magnetic interaction in the charge transfer salts and the preparation of other molecular and/or polymeric materials with ferromagnetic exchange are presented.

I. INTRODUCTION

Molecular, organic, and polymeric materials constitute a broad class of solids that until recently, were characterized by the absence of ferromagnetic behavior. The earliest studied molecular, organic and polymeric materials were diamagnetic, spin paired insulating compounds. The preparation of radical anion tetracyanoquinodomethane (TCNQ) salts[1] opened the opportunity to study the interaction among open shell molecules and polymers in the solid state. For nearly three decades, interest has focussed on segregated linear chain charge transfer salts. The overlap of the orbitals of like molecules in the segregated stacks enables the formation of the metallic energy bands. There has been intensive study of the broad range of phenomena present in these low-dimensional metals. For example, these materials often are metallic with transitions to a Pieries semiconducting ground state at low temperature and several of the donor based (e.g., tetramethyltetraselofulvalene) segregated stack charge transfer salts become superconducting below 8 K.[2]

Study of mixed-stack charge transfer salts where the donor molecule alternates with the acceptor molecule has received comparatively less emphasis. Interaction among the unpaired electrons in such systems generally has lead to antiferromagnetic exchange interactions.[3] Recently, we reported[4,5] the existence of a ferromagnetic ground state in the decamethylferrocenium tetracyanoethanide (DMeFc) (TCNE). The discovery of ferromagnetism in this system together with the systematic study of the magnetic phenomena in related salts opens the opportunity to investigate the origins of ferromagnetic exchange and to probe the magnetic phenomena in these low-dimensional materials and the extension of ferromagnetic phenomena to polymeric materials.

We present here a summary of the results on the magnetism in this class of materials. Emphasis is given to DMeFc TCNE which shows a crossover from a dominance of one-dimensional ferromagnetic exchange interaction to the 3D mean-field-like behavior at ~ 16 K and becomes 3D ordered for $T_C = 4.8$ K. The critical exponents are in agreement with mean field behavior. Section II presents our experimental techniques. Section III summarizes the experimental data for (DMeFc) (TCNE) and other related compounds. Models for the magnetic behavior and the origins of ferromagnetic exchange are outlined in Sec. IV. The results are summarized in Sec. V together with an outline of future research directions.

II. EXPERIMENTAL TECHNIQUES

Samples of (DMeFc) (TCNE) and related materials were grown from acetonitrile and tetrahydrofuran solutions.[5,6] The magnetization M and susceptibility χ were measured using oriented single crystals or randomly oriented powders by the Faraday technique. Data were recorded for fields up to 80 kG and variable field gradients. The contributions of aluminum sample holders and sample core diamagnetism[7] were subtracted out. Neutron diffraction on powdered samples have been underway at the High Flux Beam Reactor of Brookhaven National Laboratory.

III. DMeFc TCNE AND RELATED COMPOUNDS

The solid-state structure of (DMeFc) (TCNE) consists of parallel stacks of alternating (DMeFc) $[(C_5(CH_3)_5)_2Fe]$ and (TCNE) $[C_2(CN)_4]$ radical ions, although disorder in the anion positions[5] has prevented refinement of the orthorhombic structure. The crystal structure includes neighboring stacks that are both in and out of registry. An example of part of the crystal structure is indicated in Fig. 1.

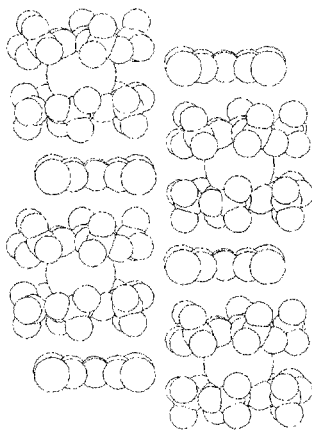The [DMeFc]$^{+\cdot}$ cation has three electrons occupying

FIG. 1. Example of one type of stacking arrangement of donor and acceptor molecules for out of registry chains of the compound (DMeFc) (TCNE).

the highest-energy (doubly degenerate) e_{2g} ($d_{x^2-y^2}/d_{xy}$) orbitals[9] while the TCNE anion has one electron in the highest-lying b_{3g} (p_z) orbital.[10] As a result, both the donor and the acceptor have a spin $S = \frac{1}{2}$ although the (DMeFc) has an anisotropic g value ($g_{\parallel} \simeq 4$ and $g_{\perp} \simeq 1.3$) (Refs. 8 and 11) while the TCNE has a nearly isotropic $g = 2$.[10,12]

Powder x-ray diffraction experiments indicate that the (DMeFc)$^+$ (C$_3$(CN)$_5$)$^-$ and the (DMeCo)$^+$ (TCNE)$^-$ are isostructural while the former one has spin only on the donor molecules the latter has spin only on the acceptor molecules, enabling a comparison with the ferromagnetic (DMeFc)$^+$ (TCNE)$^-$. Substitution of Ni or Cr for Fe and C$_6$(CH$_3$)$_6$ for C$_5$(CH$_3$)$_5$ enables systematic study of this class of compounds although the existence of more than one stable structure and/or stoichiometry complicates the investigations.

Figure 2 shows a plot of the effective magnetic moment μ_{eff} [defined as $2.8279(\chi T)^{1/2}$ (Ref. 13)] for (DMeFc) (TCNE), (DMeFc)(C$_3$(CN)$_5$), and (DMeCo) (TCNE) as a function of temperature. The data for the latter two compounds can be fit to a Curie–Weiss expression, i.e., $\chi = C/T - \theta$, with $\theta \sim -1$ K. In general, compositions with spin only on the donor or the acceptor sites (but not both sites) showed only weak antiferromagnetic exchange. In contrast, above 60 K the data for the (DMeFc) (TCNE) salt followed the Curie–Weiss expression with a ferromagnetic θ of 30 K. The preparation of single crystals of macroscopic size enabled the quantitative study of the magnetism in this system. The susceptibility data for a 1.35-mg needle-shaped sample is shown in Fig. 3 for the magnetic field parallel to the long axis (parallel to the stacks of molecules).

The experimental $\chi_{\parallel}^{\text{spin}}$ (290 K) $= 6.67 \times 10^{-3}$ emu/mol is in rough agreement with a χ of 6.4×10^{-3} emu/mol calculated for independent spins, although the T behavior reported in Fig. 3 is not a simple Curie or Curie–Weiss type. For $T \ll T_C$ the saturation moment M^{sat} can similarly be compared to the sum expected for independent spins:

$$M^{\text{sat}} = N (g_{\parallel}^{\text{DMeFc}} + g^{\text{TCNE}}) S \mu_B. \qquad (1)$$

The experimental value of 1.63×10^4 emu G/mol, Fig. 6, is in very good agreement with the 1.675×10^4 emu G/mol which is calculated using $g_{\parallel}^{\text{DMeFc}} = 4$ and $g^{\text{TCNE}} = 2$.
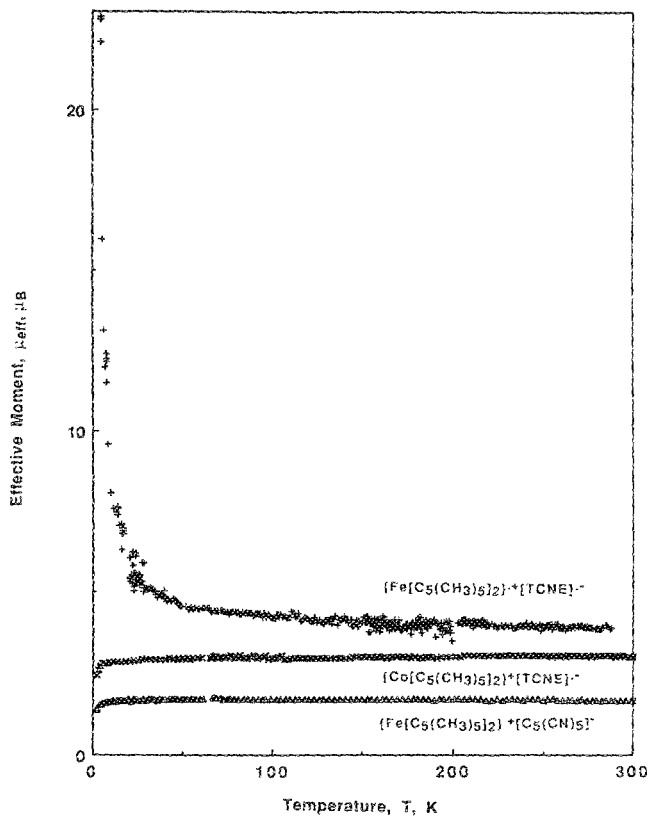

FIG. 2. Effective magnetic moment vs T for the compounds (DMeFc) (TCNE), (DMeCo) (TCNE) and (DMeFc)(C$_5$(CN)$_5$).

The linear chain crystal structure together with the deviation from the three-dimensional mean-field Curie–Weiss behavior at temperatures an order of magnitude larger than the three-dimensional ordering temperature $T_C = 4.8$ K lead to the examination of several models for 1D magnetic chains, including Ising for $S = \frac{1}{2}$ (Ref. 14) and Heisenberg for $S = \frac{1}{2}$ (Refs. 15–17). The experimental data can be fit by a Pade[15] series expansion for the $S = \frac{1}{2}$ Heisenberg model,
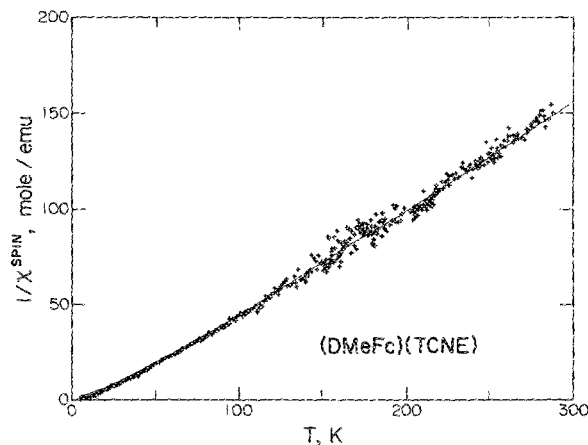

FIG. 3. ($\chi_{\parallel}^{\text{spin}}$)$^{-1}$ vs T for (DMeFc) (TCNE) for the magnetic field parallel to the stacking axis. The data for $T > 30$ K were taken at 65 kG, those for $T < 30$ K at 2.0 kG. The solid curve is a fit to a 1D Heisenberg $S = \frac{1}{2}$ ferromagnetic chain [see Eq. (2) in text].

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

where $K = J/2k_B T$, k_B is the Boltzmann's constant, and $J/k_B = 27.4$ K, despite the assumption that all spins are identical (not identical: $g = 4$ and $g = 2$).

The crossover from predominately one-dimensionally coupled spins to the three-dimensional ordered state is of fundamental interest. Figure 4 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 16 K, χ^{spin} increases much more rapidly than predicted by the 1D Heisenberg model, increasing as $(T - T_C)^{-\gamma}$, with $\gamma \simeq 1.22 \pm 0.02$. $\gamma \simeq 1.2$ is typical of 3D Heisenberg ferromagnets,[18] for example, the insulator $CrBr_3$.[18] An attempt to model the susceptibility in the crossover regime (4.8 K $< T <$ 16 K) as $\chi\alpha \exp(bt^n)$ with $t = (T - T_C)/T_C$ and b and n constants of order 2.5 and 0.5, respectively, was unsuccessful, indicating the absence of an intermediate temperature regime where ferromagnetic interactions in two dimensions[19] dominate. The temperature variation of the magnetization at constant applied field was examined for fields of 1.0 kG $< H <$ 76 kG. A critical temperature in the presence of the applied field, $T_C(H)$, was defined as the maximum dM/dT at constant H. A plot of $T_C(H)$ vs H is a smooth, monotonically increasing function, demonstrating the absence of an easy plane of magnetization[20] perpendicular to the crystalline stacking axis.

The critical exponents β and δ were also estimated. $M(H)$ was measured at constant T for $T \simeq T_C$. The results for $T \simeq 4.82 \pm 0.02$ K plotted on a logarithmic scale are detailed in the inset in Fig. 5. For modest fields, 96 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 $CrBr_3$ though larger than the $\delta = 3$ obtained from mean-field theory.[18] The zero-field magnetization increases rapidly as T is decreased below T_C. The solid curve in Fig. 5 is the fit to $M = M_0(T_C - T)^\beta$ with $\beta \simeq 0.5$, $T_C = 4.8$ K, and
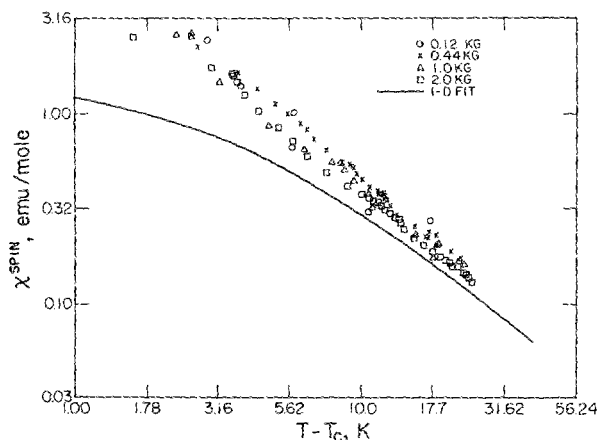
$M_0 = 8000$ emu G/mol. Though $\beta = 0.5$ is the mean-field result[17] it is larger than that usually observed for 3D magnetic systems. The value of M is less than the saturation moment in the presence of the applied field, 1.64×10^4 emu G/mol, consistent with ferromagnetic domain formation.

Figure 6 shows the magnetization as a function of applied field for $T < T_C$, the loops are increasingly well defined as T decreases. For $T = 4.7$ K, a hysterisis 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 hysterisis loop is recorded, with a sizeable coercive field (parallel to the stacking axis) of $H_c = 1$ kG. Preliminary neutron diffraction experiments show the development of the ferromagnetic spin lattice at temperatures less than the ordering temperature T_C.[21]

IV. MODELS FOR FERROMAGNETISM

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 chargetransfer salts composed of identical molecules with nondegenerate highest-energy occupied orbitals, each with one electron in them, can be accounted for within 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[3,22]:

FIG. 4. $\log \chi_\parallel^{spin}$ 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 shown in Fig. 3.
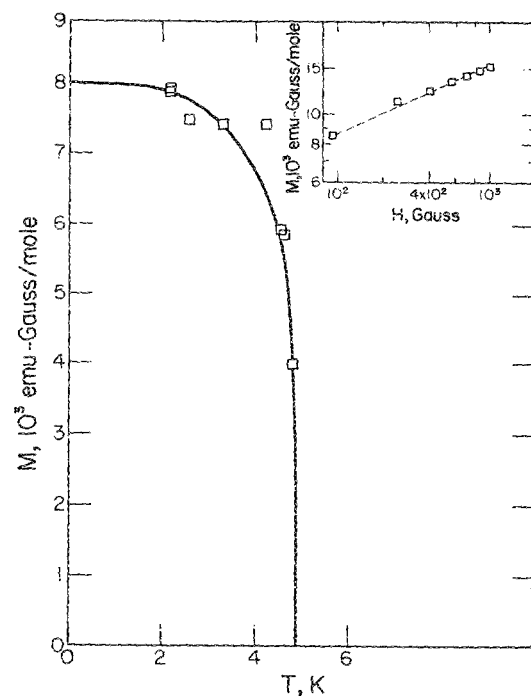

FIG. 5. Magnetization M vs T showing spontaneous magnetization. Solid curve is a fit to $M_0(T_C - T)^{0.5}$. Inset: $\log M$ vs $\log H$ at $T = 4.8$ K. The solid line is a fit to $M \propto H^{1/4.4}$.

$$H = \sum_i \Delta E n_{i\uparrow} n_{i\downarrow} - \sum_{i,j,\sigma} t_{ij} (C^\dagger_{i\sigma} C_{j\sigma} + C^\dagger_{j\sigma} C_{i\sigma}) . \qquad (3)$$

Here $C^\dagger_{i\sigma}$ and $C_{j\sigma}$ are, respectively, creation and annihilation operators for an electron spin σ on the ith and jth sites and $n_{i\sigma}$ is the number of electrons of spin σ in the ith site. For $\Delta E \gg t_{ij}$ and $\Delta E \gg k_B T$ the Hamiltonian in Eq. (3) reduces to the Heisenberg form,

$$H_{\text{eff}} = \sum_{ij} J_{ij} S_i \cdot S_j \qquad (4)$$

with $J_{ij} = t^2_{ij}/\Delta E$. If sites i and j are not identical ΔE depends upon the direction of the charge transfer: $J^i_{ij} = t^2_{ij}/\Delta E_i$ for change transfer from j to i and $J^j_{ij} = t^2_{ij}/\Delta E_j$ 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 the (TCNE)$^-$ has a single electron (spin) in the highest occupied b_{3g} 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 the (TCNE)$^-$ to the (DMeFc)$^+$ leads to antiferromagnetic exchange,

$$|J^{\text{DMeFc}}_{ij}| \simeq t^2_{ij}/\Delta E_{\text{DMeFc}} .$$

However, a virtual transition from DMeFc$^+$ to TCNE$^-$ to form the doubly ionized excited state will lead to a ferromagnetic exchange[23]

$$|J^{\text{TCNE}}_{ij}| \simeq t^2_{ij}/\Delta E_{\text{TCNE}} ;$$

thus the total exchange along a chain, $J_{ij} = J^{\text{TCNE}}_{ij} + J^{\text{DMeFc}}_{ij}$, can be ferromagnetic.[24] Similarly, the exchange interaction among spins in parallel chains will be antiferro-magnetic between pairs in (TCNE)$^-$ ions but can be ferromagnetic between (DMeFc)$^+$ pairs and (DMeFc)$^+$-(TCNE)$^-$ pairs, resulting in a net ferromagnetic exchange.

The electron configurations that stabilize the ferromagnetic state through either forward or retro charge transfer have been identified and tabulated for singly, doubly, or triply degenerate partially occupied molecular orbitals.[25] Assuming virtual charge transfer involves only the partly occupied molecular orbitals, within this model the ferromagnetic state requires a stable radical with a degenerate non-half-filled partly occupied molecular orbital.

V. SUMMARY

A wide range of magnetic phenomena have now been observed in molecular charge transfer salts. The first molecular based ferromagnet has been synthesized and studied. The results obtained have led to the development of a detailed model for ferromagnetic exchange and a set of predictions as to the likelihood of ferromagnetism in a wide variety of molecular materials. These predictions are currently being tested[26] and the concepts extended[27] to purely organic and polymeric materials.
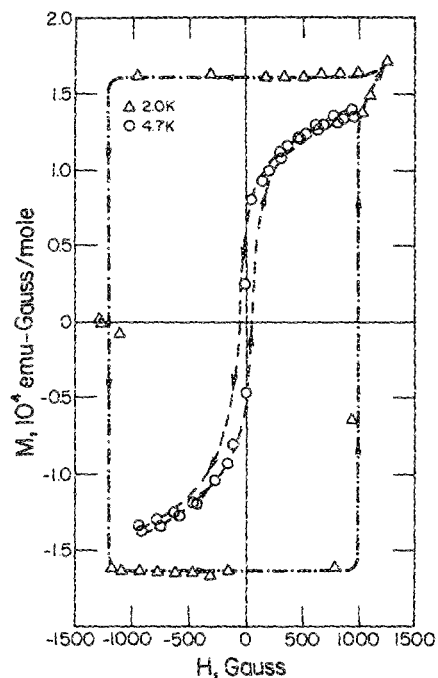
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FIG. 6. Magnetization M vs applied magnetic field . Open circle: 4.7 K; open triangle: 2.0 K.

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2955   J. Appl. Phys., Vol. 63, No. 8, 15 April 1988

Epstein *et al.*   2955

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