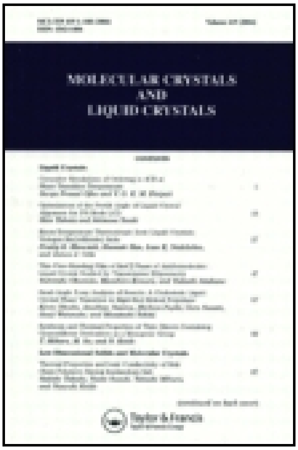

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FERROMAGNETISM IN DECAMETHYLFERROCENIUM TETRACYANOETHANIDE, $[\mathrm{DMeFc}]^{\cdot +}[\mathrm{TCNE}]$

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Abstract The three-dimensionally ordered ferromagnetic ground state of decamethylferrocenium tetracyanoethanide, $[\mathrm{DMeFc}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$, and its development from the paramagnetic state have been extensively studied utilizing a wide variety of techniques. The magnetic susceptibility for magnetic fields oriented parallel and perpendicular to the stacking axis is consistent with Heisenberg-like behavior, though the apparent exchange interaction differs for magnetic fields oriented parallel and perpendicular to the stacking axis. Neutron diffraction studies show the presence of increasing order below the Curie temperature, $T_C = 4.8$K. Specific heat experiments show a transition to the order state at 4.8K and reveal the dominance of one-dimensional interactions for $T \gg T_C$. AC susceptibility studies confirm the transition and reveal the presence of unusual loss mechanisms in the ferromagnetic state. Together these experiments lead to a prospective of a transition from predominately one-dimensional interactions for $T \gg T_C$ to three-dimensional ordering at T_C, to an anisotropic ferromagnetic state for $T \ll T_C$. Numerous critical constants have been estimated for these systems and show that the behavior is intermediate between Heisenberg and Ising-like as the material approaches the 3-D ferromagnetic transition.

INTRODUCTION

In recent years there has been increasing interests in the magnetic properties of novel materials [1]. Linear chain inorganic or covalently bonded one-dimensional chains with ferromagnetic and antiferromagnetic interactions have been extensively studied [2]. In contrast, quasi-one-dimensional molecular charge transfer salts have largely been examined in terms of their segregated stack structures leading to the metallic state [3]. Mixed stack systems where the donor molecule alternates with the acceptor molecule were less studied. Unpaired electrons on the donors and acceptors generally lead to antiferromagnetic exchange [4, 5]. The discovery of a ferromagnetic ground state in the mixed stack molecular charge transfer salt, decamethylferrocenium tetracyanoethanide $[\mathrm{DMeFc}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$ enabled the study of the ferromagnetic state in highly anisotropic molecular charge transfer salts as well as to probe the origins of ferromagnetic exchange (as opposed to antiferromagnetic exchange) in molecular based systems [4, 6, 7-9].

In this review we summarize the extensive magnetic, neutron diffraction, and specific heat experiments which give insight into the formation of a ferromagnetic state in $[\mathrm{DMeFc}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$. The results together reveal a strong one-dimensional ferromagnetic exchange in the direction parallel to the segregated stacks with a crossover to three-dimensional interactions below 16K. The spins on individual sites develop a spontaneous magnetic magnetization for $T \leqq 4.8$K. These detailed experiments, together with examination of critical exponents as T_c is approached both from below and above suggest a behavior intermediate between Ising and Heiseberg-like, as may be expected given the anisotropic g values [10] for the $[\mathrm{DMeFc}]^{\cdot +}$ unit.

CRYSTAL STRUCTURE

Crystallization of $[\mathrm{DMeFc}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$ from tetrahydrofuran enables the isolation of crystals with one-dimensional structure motif with chains made up of alternating cation donors and anion acceptors [6]. The orthorhombic unit cell consists of three distinct parallel stacks of radical ions. Two pairs of near-neighbor stacks have anions approximately opposite cations, Fig. 1a. Other near-neighbor stacks have radical cations opposite radical cations and radical anion opposite radical anions, Fig. 1b. Extensive studies of model compounds replacing $[\mathrm{DMeFc}]^{\cdot +}$ with the spinless cation donor, $[\mathrm{DMeCo}]^{+}$, and replacing $[\mathrm{TCNE}]^{\cdot -}$ with the spinless anion acceptor, $[\mathrm{C_3(CN)_5}]^{-}$, demonstrates that it is essential that both donor and acceptor be radicals in order for significant magnetic exchange to be present [4, 6, 9].

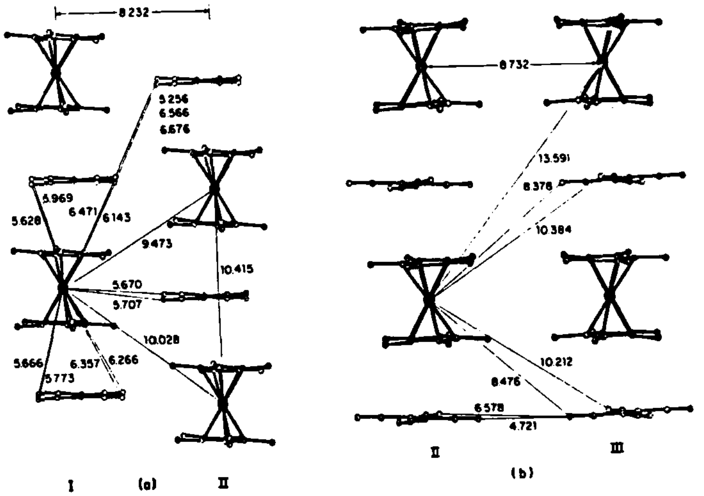

FIGURE 1. In-registry chains I-II (a) and out-of-registry chains II-III (b) with the intra- and interchain Fe-N,N-N, and Fe-Fe distances [from [6]].

STATIC MAGNETIC MEASUREMENTS

The magnetization, M, and susceptibility, χ, were measured on single crystals of [DMeFc]$^{\cdot+}$[TCNE]$^{\cdot-}$ utilizing a Faraday technique [7]. Independent control of the applied magnetic field and field gradients enable the measurement of the magnetic response in approximately zero field. The reciprocal of the experimental measured spin susceptibility for applied magnetic field parallel to the stacking axis, $\chi_{\|}$, defined here as M/H, is plotted versus temperature, T, in Fig. 2.

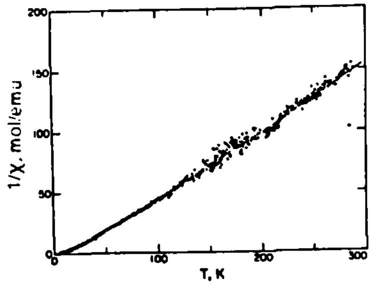

FIGURE 2. $(\chi^{spin})^{-1}$ vs. T for [DMeFc]$^{\cdot+}$[TCNE]$^{\cdot-}$. The data for T>30K were taken at 65kG, those for T<30K at 2.0kG. The solid curve is a fit by a 1D Heisenberg S-1/2 ferromagnetic chain [from [7]].

The behavior as the temperature approaches the critical temperature, $T_C = 4.8$K, is shown in Fig. 3.

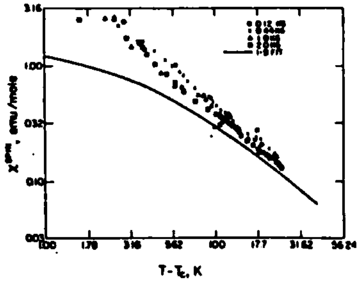

FIGURE 3. logχ^{spin} vs log(T-T_C) with T_C = 4.8K at fields of 0.12, 0.44, 1.0, and 2.0kG. The solid line is a continuation of the fit by the 1-D model shown in Fig. 2 [from[7]].

The magnetic susceptibility for fields parallel to the stacking axis, at room temperature, 6.67x10^{-3} emu/mol, is in agreement with the calculated susceptibility for [DMeFc]$^{\cdot +}$ (for parallel molecular axis) and [TCNE]$^{\cdot -}$, 6.46x10^{-3} emu/mol. The magnetic susceptibility for magnetic field perpendicular to the applied field [11] is show in Fig. 4.

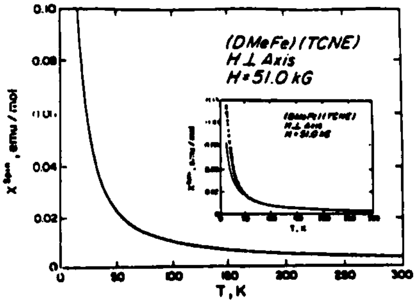

FIGURE 4. A plot of χ^{spin} vs. T for a single crystal oriented with needle axis approximately perpendicular to the applied field. The solid line is fit to a 1-D Heisenberg ferromagnetic chain [from [11]].

The absolute value of $\chi_\perp$ is somewhat larger than expected given $g_\perp$~1.3 for [DMeFc]$^{\cdot +}$ [10] indicating a small misalignment of the perpendicular oriented crystal. The temperature dependence of the $\chi_\|$(T) is well fit by a Padé series expansion for the S = ½ Heisenberg model using an exchange interaction J = 27.4K (19cm^{-1}) and assuming that all spins are identical (not taking into account that [DMeFc]$^{\cdot+}$[TCNE]$^{\cdot-}$ is an alternating $g = 4$ and $g = 2$ system). A solid line in Figs. 2 and 3 represents the predictions of this Heisenberg spin $\frac{1}{2}$ model. It is noted that there are substantial deviations from the model for temperatures less than 10K above T_C, i.e., $T < 16K$, indicating the increasing role of three-dimensional interactions in the build-up of magnetic order as the temperature is further decreased.

Similar analysis have been performed for $\chi_\perp$. The data are seen to diverge more rapidly than is predicted for a one-dimensional Ising $S = \frac{1}{2}$ chain as T approaches T_C. A better fit to the data is obtained for the 1-D Heisenberg model, although the value of J obtained is $J_\perp = 8.1K$. The difference in $J_\parallel$ and $J_\perp$ reflects the nonideal Heisenberg nature of the system. Below ~16K, the $\chi_\perp$ also diverges more rapidly than predicted for the one-dimensional Heisenberg model.

Below T_C there is a spontaneous magnetization that develops. Measurement of magnetization as a function of applied field for $T < T_C$ and H parallel to the stacking axis, Fig. 5, shows increasingly well-defined hysteresis loops as T decreases. For $T = 4.7K$ a coercive field of ~30G is observed. At lower temperatures, well-defined remnant magnetization nearly equals the saturation moment is seen. As T is decreased to 2.0K a rectangular hysteresis loop, with a sizable coercive field of $H_C = 1000G$ is recorded. For magnetic fields perpendicular to the stacking axis and $T < T_C$, partial hysteresis loops are observed, Fig. 6.

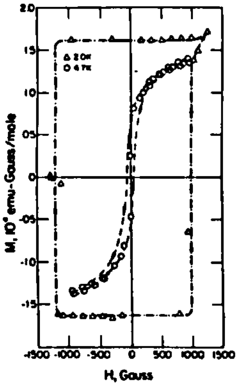

FIGURE 5. Magnetization M vs magnetic field applied parallel to the stacking axis, circles, 4.7K; triangles 2.0K [from [7]].

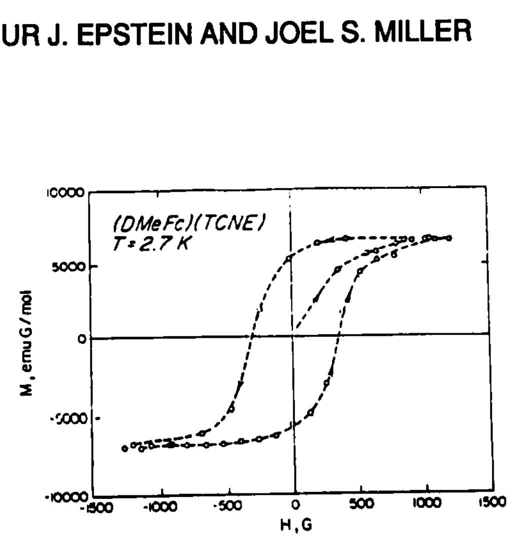

FIGURE 6. A partial hysteresis look for a single crystal oriented perpendicular to the applied magnetic field [from [11]].

AC SUSCEPTIBILITY

The ac susceptibility is measured using a mutual inductance bridge. Phase sensitive detection gives a measure of both the real part, χ', and imaginative part, χ'', of the susceptibility [12]. The temperature dependence of the χ' at frequencies of 80-1000Hz is similar to that of dc susceptibility for $T>T_c$. Below T_c, χ' decreases indicating the hardness of the ferromagnet. The out-of-phase component, χ'', also peaks at T_c with a frequency dependent width to the peak. Assuming that the relaxation processes occurring within the $[\mathrm{DMeFc}]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ can be characterized by single relaxation constant, a simple Debye model can be used to study the frequency dependent susceptibility:

$$\chi' = \chi_0 / (1 + \omega^2\tau^2)\cdot \qquad \chi'' = \omega\tau\chi_0 / (1 + \omega^2\tau^2)$$

for $H = H_0 e^{i\omega t}$ where χ_0 is the static susceptibility , ω the angular frequency and τ the relaxation time. For temperatures substantially less than $T_{c,}$, τ is seen to be activitated with an activation energy of approximately 35K [12].

NEUTRON DIFFRACTION

An excellent direct probe of magnetic ordering is the use of neutron diffraction which determines the additional magnetic scattering that occurs due to ordering of the spins. The samples of $[\mathrm{DMeFc}]^{\cdot+}[\mathrm{TCNE}]^{\cdot-}$ were deuterated to reduce the incoherent background scattering which would arise due to the hydrogen content of the samples [13]. Neutron diffraction measurements were made on the H4S triple axis spectrometer at the Brookhaven High Flux Beam Reactor using 14.7meV neutrons [11]. The variation of intensity, I, as a function of scattering angle, 2θ, is shown for temperatures above and below the ordering temperature, Fig. 7. The enhancement of the scattering below 4.8K can been assumed to be entirely magnetic in origin. There is clearly no doubling of the unit cell as would be expected for antiferromagnetic order, rather an increase in enhancement to the Bragg scattering as expected for ferromagnetic ordering in the solid. To confirm that the excess scattering is indeed of magnetic origin, the temperature dependence of the excess magnetic scattering is recorded as a function temperature at Fig. 8. The absence of excess scattering above 4.8K confirms that the excess scattering in Fig. 7 is due to the magnetic ordering in the sample.

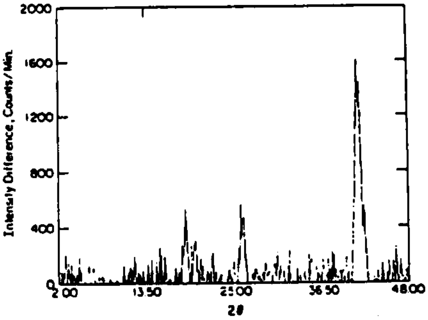

FIGURE 7. A plot of the intensity difference vs. scattering angle, 2θ, showing the difference in intensities between data sets obtained at 1.5 and 7.5K [from [11]].

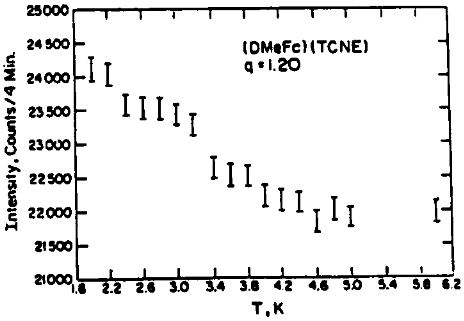

FIGURE 8. A plot of the intensity, I as a function of the temperature T for 2θ = 26.2° [from [11]].

SPECIFIC HEAT

Specific heat measurements [14] were performed in an adiabatic calorimeter using a drift technique [15]. A small cusp in the specific heat is clearly visible at T = 4.82K with the magnetic specific heat continuing to increase with increasing temperature until a broad maximum is reached in the vicinity of ~15K [14]. The magnetic entropy can be obtained from the specific heat. Most of the entropy in the disordering of the spins with increasing temperature occurs at several times T_c. Only about four percent of the entropy is involved in the ordering at T_c. Below T_c the magnetic specific heat decreases exponentially with decreasing temperature with an activation energy of ~20K. This is in contrast to the usual expectations of the spin wave theory which gives a specific heat proportional to $T^{3/2}$. The origin of the gap in the specific heat is of fundamental interest. A likely cause is the anisotropy in J leading to a gap in the spin wave spectrum. The activation energy measured may then reflect an effective gap to allow spin excitations or, possibly, the excitation of magnetic solitons within the effective gap.

CRITICAL EXPONENTS

There is particular interest in determining the divergance in the measurable parameters at a magnetic system as the critical temperature is approached both from above and below T_c [16]. We have been able to obtain a first measure of several of the critical exponents, including:

$C_H \propto (T-T_c)^{-\alpha}$ $T>T_c$: Utilizing our specific heat data we are able to estimate $\alpha = 0.1 \pm 0.02$ [14].

$M \propto (T_c-T)^{\beta}$ $T<T_c$: The experimental M(T, H = 0) β allows only the comment that $\beta = 0.5$ is within the experimental error [7].

$\chi \propto (T-T_c)^{-\gamma}$ $T>T_c$: γ has been measured for magnetic fields parallel and perpendicular to the stacking axis. For $\chi_{\parallel}$, $\gamma_{\parallel} = 1.21$ [7], while for $\chi_{\perp}$, $\gamma_{\perp} = 1.20$ [11]. An estimation of γ of a powder sample using ac susceptibility leads to a somewhat larger value of γ.

$M \propto H^{1/\delta}$ $T \approx T_c$: We observe $\delta = 4.42 \pm 0.06$ for magnetic field parallel to the stacking axis [7].

The behavior for $[DMeFc]^{\cdot +}[TCNE]^{\cdot -}$ in general lies intermediate between that of a Heisenberg system and that of a Ising system.

SUMMARY

The $[DMeFc]^{\cdot +}[TCNE]^{\cdot -}$ system is a mixed stack charge salt with strong magnetic exchange along the stack and weaker magnetic exchange between stacks. Within a single stack, the magnetic exchange is Heisenberg-like though with an anisotropy in the J value for fields parallel and perpendicular to the chain. As temperature is decreased below 16K three-dimensional interactions become increasingly important until full 3-D ordering occurs at 4.8K. Only a small fraction of the entropy is involved in this low temperature ordering. Below T_c the order parameter continues to grow with decreasing temperature. A gap appears in the excitation spectrum, likely associated with the anisotropy of the J values in the system.

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