Specific heat of decamethylferrocenium tetracyanoethanide (DMeFc)(TCNE)

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We report the specific heat $C(T)$ of (DMeFc)(TCNE) for temperatures 3 K $< T <$ 50 K. We observe an anomaly at $T_c = 4.82$ K corresponding to a transition to a three-dimensional (3D) macroscopic ferromagnet. A broad maximum at ≈ 15 K corresponds to an exchange interaction of $J \approx 35$ K along the chain axis. We propose a generalized 1D Hubbard Hamiltonian to account for this feature. Below T_c results are consistent with the opening up of a gap of approximately 2 meV in the spin-wave spectrum due to the anisotropy in the exchange interaction within the 1D chains.

There has been considerable experimental and theoretical interest in the past decade in the physics of quasi-one-dimensional (quasi-1D) charge-transfer salts.[1] Stacks of alternate donors and acceptors are of interest particularly due to their magnetic properties.[2] Decamethylferrocenium tetracyanoethanide, (DMeFc)(TCNE), consisting of stacks of alternate donors (DMeFc)$^{.+}$ and acceptors (TCNE)$^{.-}$, is the first reported[3] molecular ferromagnet. Above the transition temperature $T_c = 4.82$ K, the system has been described[3,4] as having primarily 1D ferromagnetic interactions among the spin $S = \frac{1}{2}$ radicals along the chain axis. At T_c, magnetization and neutron studies[3,4] show that (DMeFc)(TCNE) undergoes a phase transition to a macroscopic 3D ferromagnet.

We report here the specific heat of (DMeFc)(TCNE) in the temperature range 3–50 K. The data show a cusp in the specific heat $C(T)$ at the 3D ferromagnetic transition temperature with a crossover to primarily 1D behavior at higher temperatures. There is a broad maximum in $C(T)$ at $T \approx 15$ K, in accord with a one-dimensional anisotropic Hesienberg exchange along the chain axis with a ferromagnetic $J \approx 35$ K. For T just above T_c the magnetic specific heat varies as $C_M \sim (T - T_c)^{-\alpha}$ with $\alpha = 0.1 \pm 0.02$. For $T < T_c$, C_M is proportional to $\exp(\Delta/k_B T)$ with $\Delta = 22$ K, which is consistent with the opening up of a gap of ≈ 2 meV at $q = 0$ in the spin-wave spectrum.

(DMeFc)(TCNE) crystalizes in an orthorhombic structure (space group $Cmca$) with stacks of alternating (DMeFc)$^{.+}$ and (TCNE)$^{.-}$ radical ions parallel to the long needle axis of the solution grown crystals.[5] Both cation and anion have spin $\frac{1}{2}$, with the highest occupied energy levels of the donor being degenerate and those of the acceptor nondegenerate.[5] The presence of the partly occupied degenerate orbital on the donor (DMeFc)$^{.+}$ has been proposed as the origin of the ferromagnetic intrastack and interstack exchange.[5,6]

The specific-heat measurements were performed in an adiabatic calorimeter. The samples were in pellet form with a mass of ≈ 0.5 g. The measurements between 3–11 K were performed using a drift method described earlier.[7,8] Measurements between 10 and 50 K were performed by loading the samples onto copper holders and then letting them drift down in temperature. The thermal links between the holders and the reservoir were calibrated separately. The drift method consisted of relating the specific heat to the time (t)-temperature (T) decay of the sample temperature ($dT/dt \approx 10$–20 mK/s). The carbon-chip sample thermometers were calibrated *in situ*.[9] We measured the specific heat of spinless (DMeCo)(C$_3$(CN)$_5$) to obtain an experimental measurement of the background lattice contribution and hence the magnetic contribution to the specific heat (C_M) in (DMeFc)(TCNE).

Figure 1 shows the specific heat of both (DMeFc)-(TCNE) and (DMeCo)(C$_3$(CN)$_5$) in the range 3–11 K. A cusp in the specific heat is clearly seen at $T = 4.82$ K for (DMeFc)(TCNE). This confirms previous magnetization,[3-5] neutron diffraction,[4] and Mossbauer results[5] that the system becomes a ferromagnet below 4.82 K. Careful examination of the data also reveals a small anomaly at $T \approx 6.1$ K. The inset in Fig. 1 shows the specific heat of the above compounds in the range 10–50 K. The magnetic contribution to the specific heat of (DMeFc)(TCNE), C_M, obtained by subtracting the lattice term is plotted in Fig. 2 in units of $(C/3Nk_B)$ vs $(k_B T/J)$, with $J = 35$ K. Also depicted in Fig. 2 are the exact solutions for the 1D Ising and isotropic Heisenberg chains[10] with ferromagnetic exchange.

The magnetic entropy, $S_m(T) = \int_0^T [C_M(T)/T] dT$, is plotted in Fig. 3. The entropy saturates to $3R \ln 2$. (DMeFc)(TCNE) consists of two spin $\frac{1}{2}$'s, one each on the donor and the acceptor. Hence it is expected that the entropy would saturate to $2R \ln 2$ instead of $3R \ln 2$. We plotted C_M in units of $C/3Nk_B$ in Fig. 2, to facilitate com-
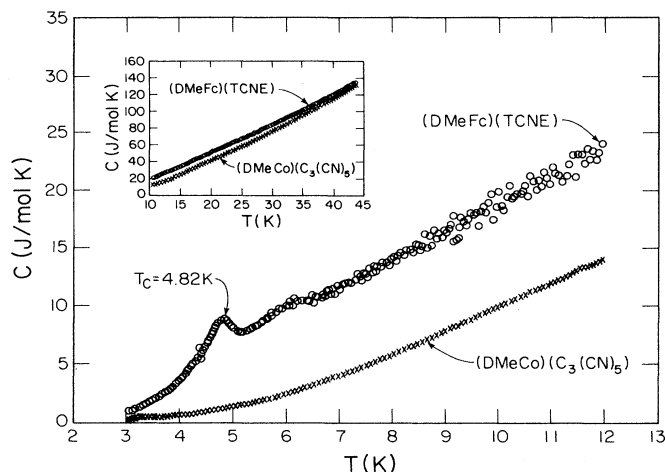
FIG. 1. Specific heat vs T for (DMeFc)(TCNE) and (DMeCo)$(C_3(CN)_5)$ from 3 to 11 K. Inset shows specific heat from 10 to 50 K.

parison with the model-Ising and the Heisenberg-chain predictions.

We consider these data in the context of a generalized Hubbard Hamiltonian with only near-neighbor interactions along the stack and accounting for the orientational dependence of the (DMeFc)$^{\cdot+}$ moment:

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

$$J' > 0.$$

Here J' is the ferromagnetic exchange expected in a Hubbard model for sites with a partially occupied degenerate level.[6] Using $g_\parallel^{DMeFc} \approx 4.0$, $g_\perp^{DMeFc} \approx 1.3$ (Ref. 11) and $g^{TCNE} = 2.0$:

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

$$J > 0, \gamma \approx 0.35,$$

where $J = 4J'$. It is emphasized that the anisotropy in the Hamiltonian arises from the fact that g is anisotropic at the (DMeFc)$^{\cdot+}$ site. Hence, even though the intrachain
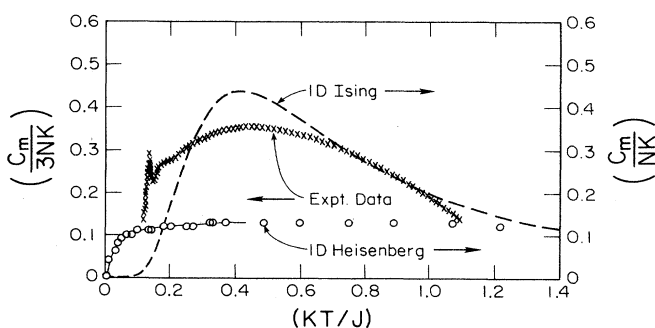

FIG. 2. Magnetic specific heat (C_M) vs $(k_B T/J)$ of (DMeFc)(TCNE) (×). The experimental data are plotted with $J = 35$ K. Also shown are 1D Ising and Heisenberg (isotropic) results.
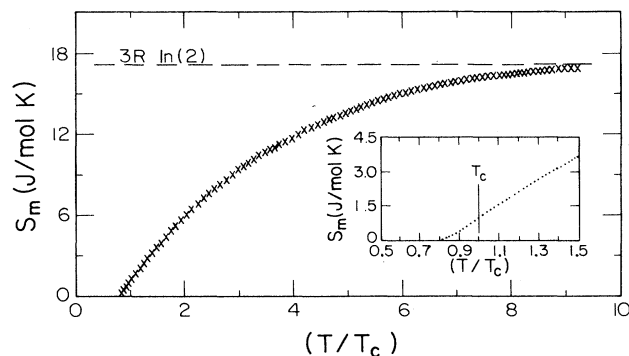
coupling J is isotropic (spin space) the final Hamiltonain is anisotropic. The above Hamiltonian does not distinguish between g and J anisotropy. Comparison of the experimental $C_M(T)$, Fig. 2, with the limiting model predictions, indeed shows that the specific-heat data are between $\gamma = 0$ (isotropic Heisenberg) and $\gamma = 1$ (Ising) limits, for $T > T_c$. The entropy (S_m) as a function of the reduced temperature T/T_c, Fig. 3, shows little change at T_c, in contrast with other 1D systems like $CoCl_2 \cdot 2H_2O$ which is an Ising chain with $T_c = 3.15$ K.[10] The inset in Fig. 3 shows the entropy gained in the vicinity of T_c. Approximately only 4% of the total entropy is involved in the 3D ordering, in accord with the specific-heat peak being so small. The vast majority of the spin entropy is involved in the 1D correlations evident in the broad peak at ~ 15 K, Fig. 2.

At T_c when the system undergoes a phase transition, $C \approx |\epsilon|^{-\alpha, -\alpha'}$, where $\epsilon = (T - T_c)/T_c$ and α, α' are the critical exponents above and below T_c. To determine α, $\ln(C_M)$ vs $\ln(T - T_c)$ is plotted in Fig. 4, for T between 4.82 and 5.12 K which corresponds to $0 < \epsilon < 0.06$. The small magnitude of the peak makes a good determination of the critical exponent difficult. Noting that our data spans a little more than one decade in ϵ, we obtain $\alpha = 0.10 \pm 0.02$, close to the value predicted for an Ising system,[12] as might be expected in a material with anisotropic J.

Below T_c we were unable to determine the exponent α'. The plot of $\ln(C_M)$ vs $\ln(T_c - T)$ did not yield a straight line. Instead C_M varies as $\exp(\Delta/k_B T)$ below T_c from our lowest temperature to the transition temperature of 4.82 K. The failure to obtain α' below T_c is likely due to the fact that the specific heat below T_c shows an activation behavior all the way up to T_c. Attempts to force a fit to the data below T_c as a power law yielded an exponent of ≈ 5 which is unrealistic. One should note that for a 3D Heisenberg ferromagnet $C_M \approx T^{3/2}$ for T below T_c. Instead $\ln(C_M)$ vs $1/T$, Fig. 5, yields a gap $\Delta = 22$ K in the spin-wave spectrum. The likely origin of Δ lies in the presence of 1D chains in this material. The anisotropy in the exchange interaction along the chains causes a gap to open up at $q = 0$, for T below T_c. It is conceivable that multimagnon states as well as nonlinear excitations (soli-
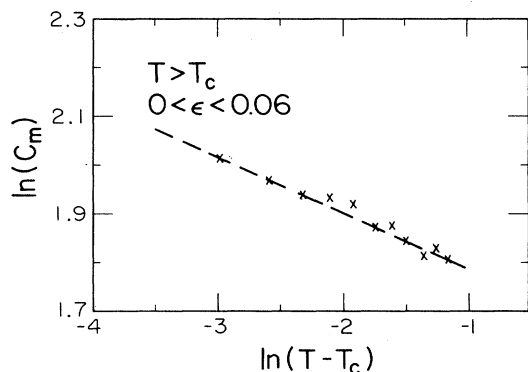

FIG. 3. Entropy vs reduced temperature T/T_c for (DMeFc)(TCNE). Inset shows entropy vs T/T_c in the vicinity of T_c.

FIG. 4. $\ln(C_M)$ vs $\ln(T - T_c)$ for $T > T_c$. The data are plotted for $0 < \epsilon < 0.06$, where $\epsilon = (T - T_c)/T_c$.

FIG. 5. $\ln(C_M)$ vs $1/T$; $T < T_c$ for $(1/4.82 \text{ K}) < 1/T < (1/3.0 \text{ K})$. Inset shows a soliton/antisoliton pair along the chain.

tons) exist in this system. Soliton pairs created in the form of a pair of spin flips along the length of a chain, are depicted in the inset of Fig. 5. One should note that both multimagnon states as well as solitons have been known to exist in 1D ferromagnetic chains.[13,14] Further experiments like far-infrared spectroscopy and inelastic neutron diffraction may elucidate these features. The origin of the small 6.1 K anomaly in $C_M(T)$ is elusive. The limiting value of $3R \ln 2$ for $S_m(T)$, instead of the expected $2R \ln 2$, may lie in an additional degree of freedom in (DMeFc)-(TCNE).

In summary, we have reported the specific heat of (DMeFc)(TCNE). This system exhibits one dimen-
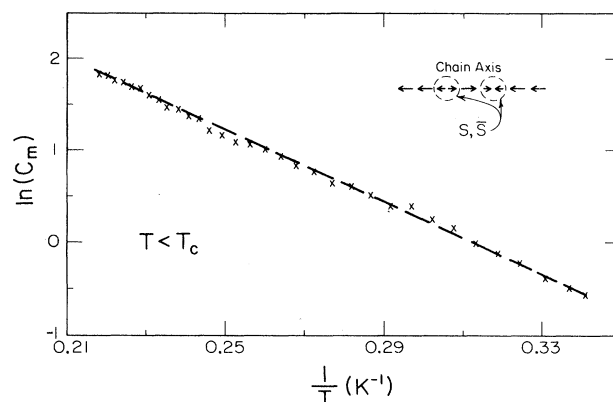
sionality both below and above T_c in its magnetic properties. We confirm that the system undergoes a phase transition at T_c to a long-range ferromagnetic ordered state. The spin-wave spectrum below T_c is dominated by the one-dimensional chains. This is the first known molecular ferromagnet to illustrate these features.

[1]For recent results, see Proceedings of the International Conference on Science and Technology of Synthetic Metals, Santa Fe, NM, 1988 [Synth. Met. 27 (1988); ibid. 28–29 (1989)].

[2]Z. G. Soos, in The Physics and Chemistry of Low Dimensional Solids, edited by L. Alcacer (Reidel, Dordrecht, Holland, 1980), p. 143; J. S. Miller, A. J. Epstein, and W. M. Reiff, Chem. Rev. 88, 201 (1988).

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

[4]S. Chittepeddi, M. A. Selover, A. J. Epstein, D. M. O'Hare, J. Manriquez, and Joel S. Miller, Synth. Met. 27, B417 (1988).

[5]J. 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).

[6]J. S. Miller and A. J. Epstein, J. Am. Chem. Soc. 109, 3850 (1987).

[7]W. N. Lawless, C. F. Clark, and R. W. Arenz, Rev. Sci. Instrum. 53, 1647 (1982).

[8]A. Chakraborty, A. J. Epstein, D. L. Cox, E. M. McCarron, and W. E. Farneth, Phys. Rev. B 39, 12 267 (1989).

[9]W. N. Lawless, S. K. Hampton, and C. F. Clark, Rev. Sci. Instrum. 59, 2505 (1988).

[10]L. J. De Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).

[11]D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, Inorg. Chem. 10, 1559 (1971).

[12]H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Oxford Univ. Press, Oxford, 1971).

[13]J. B. Torrance and M. Tinkham, Phys. Rev. 187, 595 (1969).

[14]M. Steiner, K. Kakurai, and W. Knop, Solid State Commun. 41, 329 (1982).