Ferromagnetic behavior and magnetic excitations in a molecular-based alternating-spin chain: Decamethylchromocenium tetracyanoethanide

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We report the study of magnetic properties of a molecular-based alternating-spin chain: metallocenium electron-transfer salt decamethylchromocenium tetracyanoethanide, $[CrCp_2^*]$ [TCNE]. We give a modified spin-wave theory for the Heisenberg alternating-spin chains. The low-field susceptibility and magnetization data agree with the theoretical results indicating that one-dimensional linear magnon excitations dominate the magnetic behavior above the three-dimensional ordering temperature. Strong ferromagnetic intrachain coupling, $J \simeq 9$ K, is found. Unusual critical phenomena associated with lattice dimensional crossover are discussed.

Low-dimensional magnetism continues to be of interest, especially with the possibility of studying phenomena such as mixed-spin linear-chain systems.[1] The recent availability of a new class of quasi-one-dimensional (quasi-1D) magnetic systems based on donor and acceptor electron-transfer salts enables the preparation of new magnetic systems.[2,3] In addition to determining the magnetic phenomena in these systems, it is currently challenging to determine the mechanism for magnetic exchange in molecular-based systems.[4,5] We present the results here of high- and low-field studies of the magnetization (M) and susceptibility (χ) of the metallocene electron-transfer salt decamethylchromocenium tetracyanoethanide, $[CrCp_2^*][TCNE]$.[6-8] This material differs from the earlier studied ferromagnetic decamethylferrocenium TCNE,[9] $[FeCp_2^*]$ [TCNE], in that the donor $[CrCp_2^*]^+$ has a spin of $\frac{3}{2}$ with essentially isotropic $g = 2.00$, while $[FeCp_2^*]^+$ has a spin of $\frac{1}{2}$ with an anisotropic $g_\parallel \simeq 4$ and $g_\perp \simeq 1.3$. It also differs from a third member of this class, decamethylmanganocenium TCNE, $[MnCp_2^*][TCNE]$, in that $[MnCp_2^*]^+$ has spin 1. We develop a modified spin-wave theory for the Heisenberg ferromagnetic mixed-spin chains. Comparing with the experimental data, we found that the low-temperature magnetization and susceptibility of this system are mainly determined by 1D linear magnons. A strong field dependence of the critical isotherm (with a very small value of the critical exponent $\delta \sim 1.85$) is found; this indicates that the transition observed at T_c is indeed composed of a lattice dimensional crossover. Long-range order occurs for $T \leq T_c$ due to the presence of a weak interchain ex-

change, J'.

The crystal structure[6] of $[CrCp_2^*]^+ [TCNE]^-$ is similar to (but not isomorphic with) that of $[FeCp_2^*]^+ [TCNE]^-$. The low-field magnetic field magnetic data of the former compound indicates a ferromagnetic transition with 3D mean-field-like critical exponents[7] $\beta \simeq 0.5$ and $\gamma \simeq 1.21$, nearly identical to the values for the latter compound.[9] The high-field magnetization and dc susceptibility of the powdered samples reported here were measured using a Faraday balance magnetometer.[9] Figure 1 shows the dc
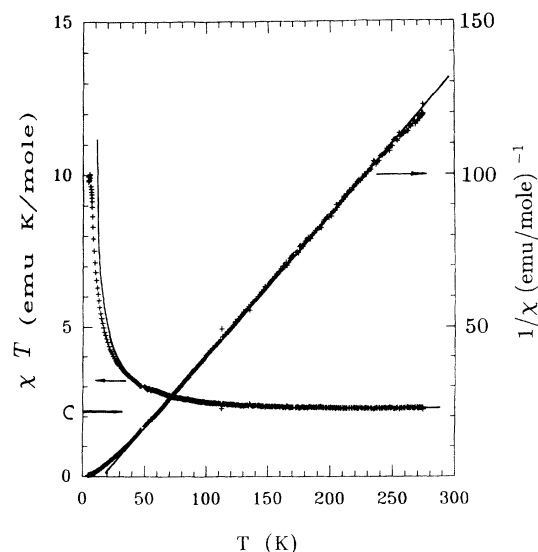

FIG. 1. χT vs T and $1/\chi$ vs T. Solid line is theoretical result with $J \simeq 9.0$ K.

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susceptibility measured under an applied field of 5000 Oe. To estimate the ferromagnetic exchange constant between $[CrCp_2^*]^+$ ($S = \frac{3}{2}$) and $[TCNE]^-$ ($S = \frac{1}{2}$) along the chain, we adopt a classical treatment for a Heisenberg linear chain with alternating spins, $\hat{H} = -2J\sum_i \mathbf{S}_1^i \cdot \mathbf{S}_2^{i+1}$, where S_1 and S_2 denote the spin operators for $[CrCp_2^*]^+$ and $TCNE^-$, respectively. The expression for the susceptibility may be written as[10]

$$\chi_{1D} = \frac{N_A\mu_B^2}{3k_BT}\left[g_+^2\frac{1+F(\beta\tilde{J})}{1-F(\beta\tilde{J})}+g_-^2\frac{1-F(\beta\tilde{J})}{1+F(\beta\tilde{J})}\right]$$

where $F(\beta\tilde{J})=\coth(\beta\tilde{J})-(\beta\tilde{J})^{-1}$, $g_+=\frac{1}{2}(\tilde{g}_1+\tilde{g}_2)$, $g_-=\frac{1}{2}(\tilde{g}_1-\tilde{g}_2)$, $\tilde{g}_{1,2}=g_{1,2}[S_{1,2}(S_{1,2}+1)]^{1/2}$, $\tilde{J}=2J[S_1(S_1+1)S_2(S_2+1)]^{1/2}$, and g_1 and g_2 represent the values of the isotropic g factor for spin site S_1 and S_2, respectively. Fitting the data for $300\ K > T > 30$ K, we find $J=9.0$ K, $g_1=1.95$, and $g_2=2.00$.[11] This result is shown as the solid line in Fig. 1. Due to the finite field effect, the expression for χ_{1D} does not fit to the high-field data (5000 Oe) below ~ 30 K. With a mean-field correction for the interchain exchange coupling J' the susceptibility takes the form[12] $\chi_{3D} = \chi_{1D}/[1-(2zJ'/C)\chi_{1D}]$. Using the same values of J, g_1, and g_2 obtained above, we fit the low-field (0.15 Oe) susceptibility data with $zJ' \simeq 0.06$ K.

Since the ground state is ordered, one may expect that low-energy properties are governed by ferromagnetic spin waves (magnons). An isolated chain cannot have true long-range order at any finite temperature, but the correlation length diverges as $\xi(T) \propto T^{-1}$ in the low-temperature regime.[13] Spin waves are well defined for excitations of length scales shorter than $\xi(T)$. We show that there indeed exists a temperature window above T_c where it is possible to describe the system with quantitative accuracy in terms of 1D self-consistent magnons. When 1D correlation length $\xi(T)$ becomes large enough, small interchain coupling J' drives the chains into a 3D ordered state at a critical temperature which should approximately scale[14] as $T_c \propto (J')^{1/2}$.

We rewrite the isotropic 1D Heisenberg Hamiltonian as $H = -2J\sum_i[S_i^zS_{i+1}^z+1/2(S_i^+S_{i+1}^-+S_i^-S_{i+1}^+)]$. Spins on even sites (sublattice 1) have magnitude $S_1=\frac{3}{2}$, while those on odd sites (sublattice 2) have $S_2=\frac{1}{2}$. We then apply Dyson-Maleev (DM) transformation[15] for spin operators (r is a site label and $\alpha=1,2$ is a sublattice label): $S_\alpha^+(r)=(2S_\alpha)^{1/2}a_\alpha^\dagger(r)$, $S_\alpha^-(r)=(2S_\alpha)^{1/2}[1-(2S_\alpha)^{-1/2}a_\alpha^\dagger(r)a_\alpha(r)]a_\alpha(r)$, and $S_\alpha^z(r)=-S_\alpha+a_\alpha^\dagger(r)a_\alpha(r)$, to obtain an equivalent boson Hamiltonian: $H_{DM}=H_2+H_4+H_\mu$, with

$$H_2=2J\sum_{r,\delta=\pm1}\{S_2a_1^\dagger(r)a_1(r)+S_1a_2^\dagger(r+\delta)a_2(r+\delta)-\sqrt{(S_1S_2)}[a_1^\dagger(r)a_2(r+\delta)+a_2^\dagger(r+\delta)a_1(r)]\} ,$$

$$H_\mu=-\sum_{r,\delta=\pm1}[\mu_1a_1^\dagger(r)a_1(r)+\mu_2a_2^\dagger(r+\delta)a_2(r+\delta)] ,$$

$$H_4=J\sum_{r,\delta=\pm1}[\sqrt{(S_1/S_2)}a_1^\dagger(r)a_2^\dagger(r+\delta)a_2(r+\delta)a_2(r+\delta)+\sqrt{(S_2/S_1)}a_1^\dagger(r)a_2^\dagger(r+\delta)a_1(r)a_1(r)] .$$

Here H_2 describes noninteracting magnons, while H_4 describes magnon interactions. We have also introduced the chemical potential H_μ, to control the average number of magnons.

We ignore the kinematic interactions and solve this Hamiltonian within the Hartree-Fock (HF) approximation.[16,17] This amounts to a decoupling of the interaction terms and after transforming to the Fourier variables, we obtain a quadratic effective HF Hamiltonian in momentum space:

$$H_{HF}=\sum_{k,\alpha,\beta}a_\alpha(k)A_{\alpha\beta}(k)a_\beta(k) , \qquad (1)$$

with

$$A_{11}(k)=2JZS_2[1-\mu_1/JZS_2-N_2/S_2+(S_1S_2)^{-1/2}\eta] ,$$

$$A_{22}(k)=2JZS_1[1-\mu_2/JZS_1-N_1/S_1+(S_1S_2)^{-1/2}\eta] ,$$

$$A_{12}(k)=-2JZ(S_1S_2)^{1/2}(1-N_1/S_1+\eta)\gamma(k) ,$$

$$A_{21}(k)=-2J(S_1S_2)^{1/2}(1-N_2/S_2+\eta)\gamma(k) ,$$

$$\gamma(k)=\frac{1}{Z}\sum_\delta e^{ik\delta} ,$$

$$N_1=\langle a_1^\dagger(r)a_1(r)\rangle=\frac{2}{N}\sum_k\langle a_1^\dagger(k)a_1(k)\rangle$$

$$=\frac{2}{N}\sum_k n_1(k) , \qquad (2)$$

$$N_2=\langle a_2^\dagger(r)a_2(r)\rangle=\frac{2}{N}\sum_k\langle a_2^\dagger(k)a_2(k)\rangle=\frac{2}{N}\sum_k n_2(k) , \qquad (3)$$

$$\eta=\eta^*=\langle a_1^\dagger(r)a_2(r+\delta)\rangle=\frac{2}{N}\sum_k\langle a_1^\dagger(k)a_2(k)\rangle , \qquad (4)$$

where the averages N_1, N_2, and η must be determined self-consistently. The HF Hamiltonian is diagonalized, by the Bogoliubov transformation: $H_{HF}=\sum_{k,\alpha}b_\alpha(k)E_\alpha(k)b_\alpha(k)$ where $b_\alpha(k)$ are rotated magnon operators $b_\alpha(k)=\sum_\beta U_{\alpha\beta}a_\beta(k)$. The rotation matrices are $U_{11}(k)=U_{22}(k)=\cos(\theta(k))$ and $U_{12}(k)=-U_{21}(k)=-\sin(\theta(k))$, and the rotation angle is $\tan(2\theta(k))=-[A_{12}(k)+A_{21}(k)]/[A_{22}(k)-A_{11}(k)]$. $E_\alpha(k)$ are the excitation energies of the two magnon branches: $E_{1,2}(k)=\frac{1}{2}(A_{11}(k)+A_{22}(k)\pm\{[A_{22}(k)-A_{11}(k)]^2+4A_{12}(k)A_{21}(k)\}^{1/2})$.

Within the HF approximation, sublattice magnetizations are given by

$$M_1 = S_1 - \frac{2}{N} \sum_k [u(k)n_1(k) + v(k)n_2(k)] , \qquad (5)$$

$$M_2 = S_2 - \frac{2}{N} \sum_k [v(k)n_1(k) + u(k)n_2(k)] , \qquad (6)$$

where $u(k) = \cos^2(\theta(k))$, $v(k) = \sin^2(\theta(k))$ and $n_\alpha(k) = (e^{\beta E_\alpha(k)} - 1)^{-1}$ are magnon occupation numbers. We will enforce rotational symmetry above T_c by tuning the chemical potentials so that the average sublattice magnetizations M_1 and M_2 vanish.[13] Equations (1)–(6) then constitute a set of coupled integral equations, which are solved numerically to obtain $\mu(T)$.

Following Ref. 18, the uniform magnetic susceptibility is computed as a rotationally invariant average:

$$\frac{3\chi(T)T}{\mu_B^2} = \frac{2}{N} \sum_{\alpha\beta} \sum_{rr'} g_\alpha S_\alpha(r) g_\beta S_\beta(r')$$

$$= \frac{2}{N} \sum_k \sum_{\alpha\beta} n_\alpha(k) n_\beta(k) G_{\alpha\beta}(k) + g_1^2 S_1 + g_2^2 S_2 ,$$

where $G_{11}(k) = [g_1 u(k) + g_2 v(k)]^2$, $G_{22}(k) = [g_1 v(k) + g_2 u(k)]^2$, $G_{12}(k) = G_{21}(k) = u(k)v(k)(g_1 - g_2)^2$.

To extend the applicability of the theory to lower temperatures, again we treated interchain correlations in a mean-field-like fashion. The agreement between theory and experiment is quite good even close to T_c. The unknown exchange couplings J and J' and g factors were treated as variational parameters and are adjusted to give the best agreement with experimental results, χ and M. The values obtained within spin-wave theory ($J \simeq 9.0$ K, $zJ' \simeq 0.03$ J) agree very well with the estimates derived from the classical treatment. The results for susceptibility are shown in Fig. 2. The agreement between two opposite temperature regimes confirms that the essential physics is captured by the Heisenberg model. The application of a uniform external magnetic field H amounts to a shift in the self-consistently determined chemical poten-

tials: $\mu_\alpha \rightarrow \mu_\alpha + g_\alpha \mu_B H$. This *shifted* chemical potential is then used in (5) and (6) to compute the magnetization $M(H) = g_1 \mu_B M_1 + g_2 \mu_B M_2$. In Fig. 3(a) we compare the experimental results with spin-wave theory prediction.

In a pure 1D system, in addition to the thermally activated spin-diffusion processes, nonlinear excitations, like bound magnons,[19,20] solitons,[21] and large-size mobile clusters[22] may become important at low magnetic fields. However, given that the measured magnetization at low fields is higher than that expected from spin-wave theory alone, and that the agreement is better further above T_c, this is highly unlikely here. This discrepancy between 1D theory and experiment is easily explained by a larger effective magnetic field and spin stiffness (which is important at low external fields), due to development of interchain correlations near T_c, resulting in a smaller number of thermally excited spin waves. Figure 3(a) shows the isothermal magnetization data at low temperatures, but above T_c. Even at $T = 2.5T_c = 9$ K the 1D spin-wave model describes well the magnetic data. It is noted, however, that for [FeCp$_2^*$][TCNE] with large effective spin stiffness due to significant Ising character, the 1D model only fits down to $3.3T_c$.[9]
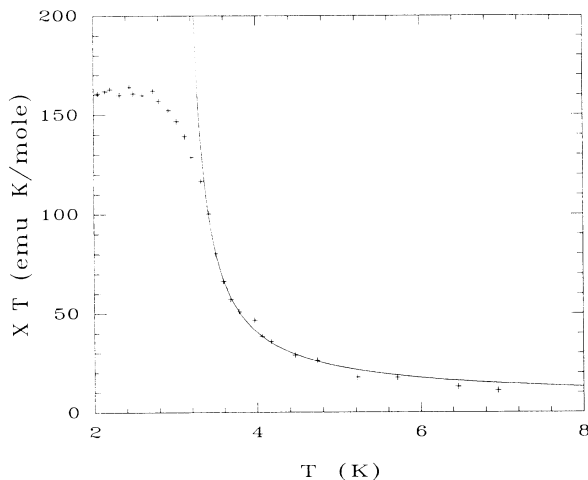

FIG. 2. Low-field susceptibility data at $H = 150 \times 10^{-3}$ Oe. The solid line is a result from the spin-wave theory with $J \simeq 9.0$ K and $zJ' \simeq 0.03$ J.
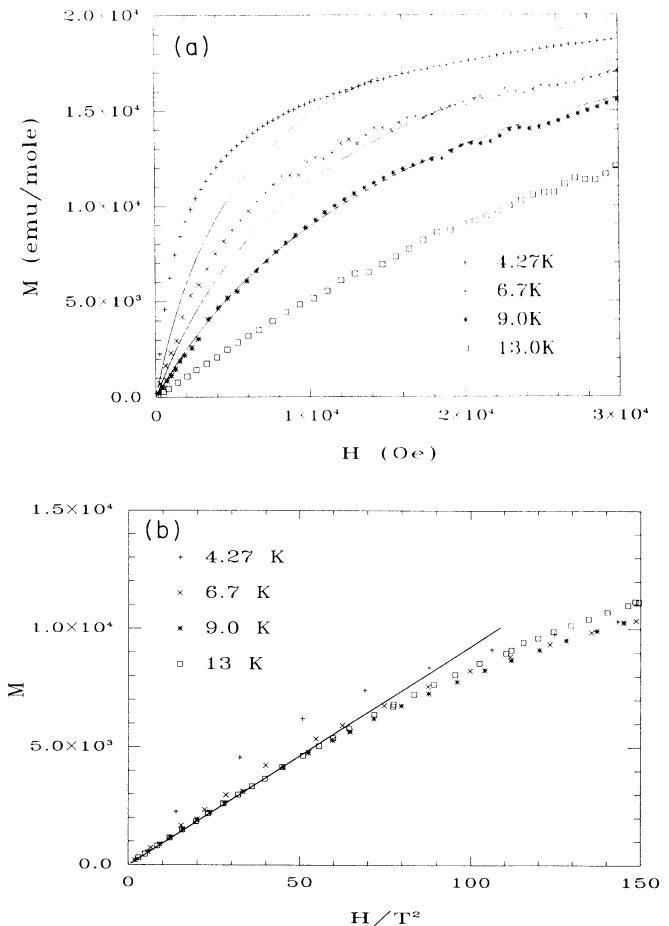

FIG. 3. (a) Isothermal data above T_c. The solid lines are the calculated results from the spin-wave theory with the same values of the parameters ($J' = 0$). (b) A scaling plot of M vs H/T^2.

In the regime governed by 1D correlations, the susceptibility is expected[13] to diverge as $\chi(T) \propto \xi^2 \propto T^{-2}$. This suggests that for small fields, the magnetization should be a universal function of H/T^2. In Fig. 3(b) we replot the isothermal data [Fig. 3(a)] in terms of M vs H/T^2, and found that at low fields the data are scaled fairly well as a linear function of H/T^2 except for the isotherm at 4.27 K splaying away, which signifies crossover to the regime governed by the exponents of the 3D transition. Within the crossover regime (near T_c), low-field isothermal magnetization behaves[7] as a universal function of $H/T^{3.2}$ instead of H/T^2. We found that the data seem to fit a "quasicritical isotherm" $M = A(H/T^{3.2})^{1/\delta}$, with $\delta = 1.85$ and $A = 1500$ (emu/mole) $(K^{3.2}/Oe)^{1/1.85}$. For the usual 3D ferromagnets, the critical isotherm is described as $M = CH^{1/\delta}$ with a constant critical amplitude. Here we may introduce a concept of effective critical amplitude, $C(T)$, i.e., that C is slightly dependent on the temperature near T_c. We then have $C(T) = A/T^{3.2/\delta} = 1500/T^{1.73}$ emu/(mole $Oe^{1/1.85}$). As an interesting result, we found that critical exponent $\delta \simeq 1.85$ is substantially smaller than that of usual 3D ferromagnets ($\delta \geq 5$) even though we obtained[7] 3D-like exponent $\beta \simeq 0.51$ and $\gamma \simeq 1.21$. Again, these contrast with the more usual value of $\delta = 4.4$ obtained for [FeCp$_2^*$][TCNE].[9] This implies that Widom's scaling relation $\gamma = \beta(\delta - 1)$ does not hold for the [CrCp$_2^*$][TCNE] system. Thus, our data may permit an interpretation in terms of a magnetic transition composed of a lattice dimensional crossover (from 1D to 3D ordering). *Above and near T_c*, the spins along the chains are strongly coupled.

Within this regime, although there is no long-range order, the system is not described as a usual paramagnetic phase because the thermal excited energy does not yet overcome the exchange energy along the chain. The 1D linear magnon excitations dominate the magnetization and give rise to a strong field dependence of isotherms (small value of δ). The quasicritical isotherm described here pronounces the crossover from 1D to 3D magnetic ordering in contrast to the usual transition in a uniform 3D system.

In summary, we have described the low-temperature susceptibility and magnetization of ferromagnetic alternating-spin chain in terms of spin-wave excitations. There is indeed a temperature window above T_c where the magnetic correlation length still obeys $\xi \propto T^{-1}$ and spin waves are well defined for excitations of length scales within $\xi(T)$. We have shown that the magnetization and low-field susceptibility of [CrCp$_2^*$][TCNE] are well described by 1D self-consistent magnons above T_c. Although some qualitative arguments need to be further justified, we have tried to provide a consistent picture for an understanding of excitations in a spin alternating chain. A sophisticated theory describing critical behavior of quasi-1D systems indeed is needed to give a quantitatively comprehensive view of a lattice-dimensional crossover.

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