

Ferromagnetic behavior of decamethylchromocenium tetracyanoethanide [CrCp₂^{*}][TCNE]

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Studies on the magnetic properties of decamethylchromocenium tetracyanoethanide, [CrCp₂^{*}][TCNE] are reported herein. Near-zero field ($H=150$ mG) data indicates a ferromagnetic transition with $T_c=3.65$ K. The temperature dependence below T_c can be fit to a mean-field result $M=M_0(1-T/T_c)^{1/2}$, and the data above T_c gives a critical exponent $\gamma=1.2$ for the dc magnetic susceptibility. Data at higher temperature indicates a strong 1-D ferromagnetic behavior. Magnetizations at different H and T at low temperature can be scaled to a universal function with $M=f(H/T^{3.2})$. The reduction in T_c in [CrCp₂^{*}][TCNE] compared with [FeCp₂^{*}][TCNE] indicates a competition between the coupling constants and the residing spins.

The excitement generated in the discoveries of 3-D ordered molecular magnets has attracted a lot of attention in the past few years.¹⁻⁶ One focus has been on the understanding of the mechanisms of magnetic interaction and thus to facilitate the design and engineering of new materials. The first reported ferromagnetically ordered molecular-based magnet, decamethylferrocenium tetracyanoethanide, [FeCp₂^{*}][TCNE], has a Curie temperature of 4.8 K.⁷ By replacing [FeCp₂^{*}]⁺ ($S=1/2$) with [MnCp₂^{*}]⁺ ($S=1$) to form [MnCp₂^{*}][TCNE], the ferromagnetic transition temperature is increased to 8.8 K.⁸ A mean-field theory gives a quantitative agreement by predicting $T_c([\text{MnCp}_2^*][\text{TCNE}])/T_c([\text{FeCp}_2^*][\text{TCNE}]) \approx 1.63$.⁹ We report here experimental magnetic studies on [CrCp₂^{*}][TCNE] where [CrCp₂^{*}]⁺ ($S=3/2$) is substituted for [FeCp₂^{*}]⁺ ($S=1/2$). Rather than an increase in T_c , a substantial decrease is observed.

[CrCp₂^{*}][TCNE] crystallizes with 1-D chains of alternating [CrCp₂^{*}]⁺ and [TCNE]⁻ ions parallel to the long needle axis.¹ The magnetization was measured with a quantum design superconducting quantum interference device (SQUID) which has a low field capability. The data was taken on a polycrystalline sample sealed inside a quartz sample holder. The sample holder has a negligible contribution to the magnetic susceptibility which was corrected by measuring a similar quartz holder. The inhomogeneity of the magnetic field in the sample space is less than 5 mG. The lowest field used in the experiments was 150 mG. We have measured the magnetization as a function of scan length ($4.0 < L < 6.0$ cm), and no observable changes were found in our experiments.

The high temperature magnetic susceptibility ($60 < T < 300$ K) data¹⁰ were fit to the Curie-Weiss form $\chi=\chi_0+C/(T-\theta)$. The effective moment, $\mu_{\text{eff}}=[(3\chi T)^{1/2}]$ is about $(4.22 \pm 0.02)\mu_B$, very close to the expected value of

$4.24 \mu_B$. This is consistent with a spin system with an isotropic g value of $g=2.0$ for the $S=3/2$ and $1/2$ ions. The Curie-Weiss temperature θ obtained is about 22 ± 1 K. The positive value of θ indicates ferromagnetic interactions at high temperature among the spins. At lower temperature, the magnetization susceptibility deviates from the Curie-Weiss form and strongly depends on temperature. For $T > 25$ K, the susceptibility data can be fit to a 1-D Heisenberg model, with an intrachain exchange $J=9.0$ K. For $T < 25$ K, the susceptibility increases more rapidly suggesting a small ferromagnetic interchain exchange.¹¹

The low temperature (SQUID) magnetization was measured after aligning the sample in high field at low T . Samples not aligned at high field and low temperature showed only a gradual magnetic transition. Figure 1 shows a plot of the magnetization M per mole versus T at $H=150$ mG. The sample was aligned at 2 K with an applied field of

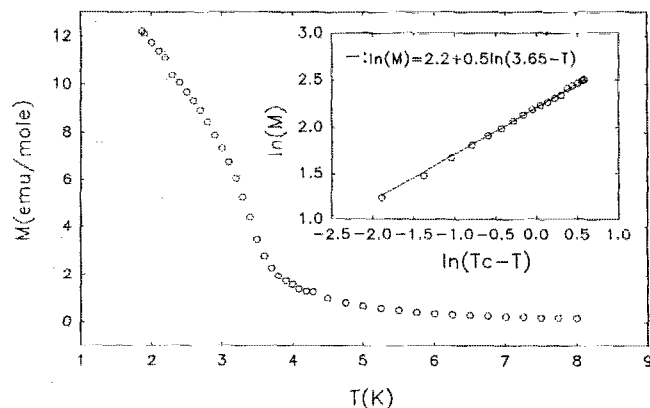


FIG. 1. Magnetization vs temperature at $H=150$ mG at low temperature. The inset is a plot of $\ln M$ vs $\ln(T_c - T)$, and the solid line is a fit to $\ln M=2.21+0.51 \ln(3.65-T)$.

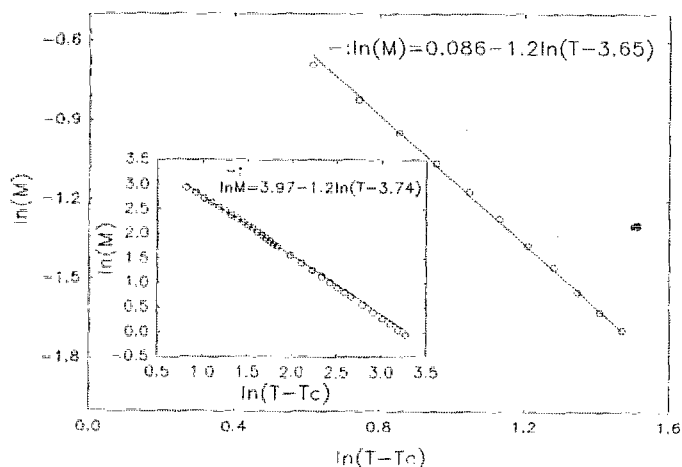


FIG. 2. $\ln M$ vs $\ln(T - T_c)$ for $T > T_c$ at $H = 150$ mG, the fitted line is a linear extrapolation of $\ln M = 0.086 - 1.21 \ln(T - 3.65)$. The inset is $\ln M$ vs $\ln(T - T_c)$ for a different applied field $H = 8.68$ G, and the line is a fit to $\ln M = 3.97 - 1.20 \ln(T - 3.74)$.

2 kG. The temperature was then raised to $T = 10$ K, and a very small magnetic field of 150 mG was applied so that near-zero field magnetization could be observed. A magnetic transition is indicated by a very sharp increase in M observed below 4 K. A plot of $\ln M$ vs $\ln(T_c - T)$ is shown in the inset of Fig. 1. The solid line is a fit to $\ln M = 2.21 + 0.51 \ln(T_c - T)$ with $T_c = 3.65 \pm 0.05$ K. The T_c is chosen such that the slope has the largest magnitude at that point. The near-zero field experimental results show that the critical exponent β as defined in $M \propto (1 - t)^\beta$ with $t = T/T_c$ is 0.51. This is consistent with a classical mean-field result.¹² Shown in Fig. 2 is a plot of $\ln M$ vs $\ln(T - T_c)$ for $T > T_c$. The solid line is a linear fit to the data with the slope being 1.21 ± 0.01 . Thus the critical exponent γ defined in $\chi \propto (t - 1)^{-\gamma}$ is equal to $\gamma = 1.21 \pm 0.01$. The exponents obtained are almost exactly the same as found in the $[\text{FeCp}_2^*][\text{TCNE}]$ system where $T_c = 4.8$ K.⁷ The deviation from critical behavior is shown in the inset of Fig. 2. The data was taken with an applied magnetic field of 8.68 G, and the fit is given by $\ln M = 3.97 - 1.20 \ln(T - T_c)$ with $T_c = 3.74$. The slight increase in the value of T_c is due to a larger applied field. The deviation from the line at around $T = 12$ K is indicative of dimensional crossover from primarily 3-D to 1-D correlations.

Plotted in Fig. 3 is an overlay of zero-field cooled magnetization versus magnetic field scaled by $1/T^{3.2}$. The isothermal magnetizations were taken at $T = 4.00, 3.75, 3.50, 3.00, 2.75$ K, as shown in the inset of Fig. 3. We did not find the critical behavior in $M(H)$ at $T = T_c$, where $M \propto H^{1/5}$, as was observed in the data on single crystal of $[\text{FeCp}_2^*][\text{TCNE}]$. It is likely due to the fact that the sample is polycrystalline. A gradual increase in $M(H)$ for fields up to $H = 1$ kG at $T = 2.75$ K is consistent with this picture. The scaling of magnetization at different T and H (< 1000 G) with $H/T^{3.2}$ to a universal function of $M(T, H) = f(H/T^{3.2})$, also reflects the interplay between tempera-

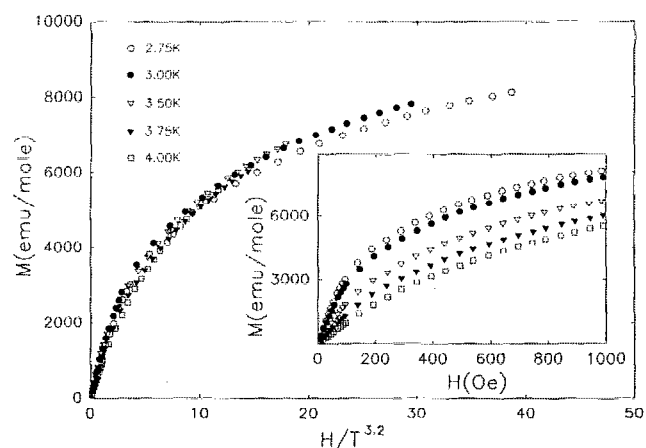


FIG. 3. An overlay of magnetization at different temperatures vs scaled field ($H/T^{3.2}$). The inset is a direct overlay of magnetization vs field at different temperatures. The 4.00 K data is at the bottom of the inset and the data is presented in the sequence of reducing temperature.

ture and field on the polycrystalline sample near the critical temperature.

The temperature and field dependence of magnetization for the $[\text{CrCp}_2^*][\text{TCNE}]$ is indicative of a ferromagnetic transition with the Curie temperature at 3.65 K for $H = 150$ mG. The curvature in $1/\chi$ above T_c , the temperature dependence of the susceptibility, and the saturation moment support the notion that the intrachain and interchain couplings are all ferromagnetic. Measurements of $[\text{CrCp}_2^*][\text{TCNE}]$ with fields up to 8 T,¹⁰ and of the similar $[\text{CrCp}_2^*][\text{TCNQ}]$ (TCNQ = tetracyanoquinodimethane) with fields up to 5 T (Ref. 13) show a tendency toward complete ferromagnetic saturation. Work on a single crystal sample of this material is needed to understand the dynamics of magnetic domains in this system.

The observed decrease in T_c rather than an increase in this compound due to an increase of the spin S of the cation presents a puzzle in understanding the roles of spin and exchange. In a mean-field theory, T_c is proportional to $[S_D(S_D + 1) \cdot S_A(S_A + 1)]^{1/2}$ for isostructural systems. Metallocene charge transfer salts are well suited to test this model. Indeed, the T_c increases from 4.8 to 8.8 K from $[\text{FeCp}_2^*][\text{TCNE}]$ to $[\text{MnCp}_2^*][\text{TCNE}]$, consistent with an increase of S_D from 1/2 to 1. Hence, one would expect $T_c \approx 11$ K for the $[\text{CrCp}_2^*][\text{TCNE}]$ where $S_D = 3/2$. The experimental results reported here indicate the inadequacy of applying the mean-field model to this system, though small differences among the crystal structures must also be accounted for. The spin dependence of T_c , the intrachain and interchain exchange interactions, and the competition between the interactions must be considered in order to understand the magnetic behavior in the metallocenium-based magnets.

In summary, we report an experimental result on the temperature and field dependence of magnetization in the $[\text{CrCp}_2^*][\text{TCNE}]$ system. Our data clearly indicates a magnetic transition at 3.65 K. For well aligned samples, the near zero-field data for $T < T_c$ can be fit to a mean-field

result with the exponent $\beta=0.51$. Above T_c , critical behavior is observed with $\gamma=1.21\pm 0.01$, and the dimensional crossover from 1D to 3D is around $T=12$ K. The field and temperature dependence around T_c can be scaled to a universal function $M(T,H)=f(H/T^{3.2})$. The decrease in T_c in $[\text{CrCp}_2^*][\text{TCNE}]$ conflicts with the simple model. More systematic studies are in progress on the metallocenium electron transfer salts in order to gain a better understanding of the origins of couplings among spins.

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