

Spin dilution in a ferromagnetic chain

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We have systematically introduced spinless defects in the quasi-one-dimensional ferromagnetic system decamethylferrocenium tetracyanoethanide, $[\text{FeCp}_2^*][\text{TCNE}]$. The three-dimensional ordering temperature T_c decreases rapidly with the concentration of spinless sites. The rate of decrease of T_c with concentration is in the order of the exchange spatial anisotropy (i.e., $J_{\text{interchain}}/J_{\text{intra-chain}}$) of the parent system in accordance with long-standing theoretical predictions.

Despite the apparent simplicity of the problem of a site-diluted one-dimensional (1D) ferromagnet, i.e., a magnetic system in which some magnetic spin sites are replaced by nonmagnetic spinless sites in increasing amounts, little experimental information is available. This may be attributed in part to the difficulty in finding magnetic compounds that can be diluted without drastic changes in the lattice symmetry or in the lattice parameters, leading to strong variations in the magnetic exchange interactions. The *magnetic dilution problem* is a particularly simple form of the more general *percolation or connectivity problem*, which encompasses widely different phenomena such as branching processes, electrical networks, polymerization of chemical monomer units, clustering of lattice defects, etc.¹ Since the magnetic systems can be investigated by a variety of different experiments, the various aspects of the percolation problem, in principle, can be advantageously studied in diluted magnets. In parallel, there is increasing interest in 1D magnetic chains, especially molecular-based systems.²

Molecular electron transfer salts based on alternating metallocene donors and planar organic acceptors form a convenient system to study the effects of magnetic and nonmagnetic defects in a quasi-1D system. A variety of isomorphous donors with differing spin configurations are available enabling a parent compound to be doped through donor substitutions, thus making possible a systematic study of changes in the magnetic phenomena. Using the molecular ferromagnetic compound $[\text{FeCp}_2^*][\text{TCNE}]$ as the parent compound, we have determined the effects of dilution in a low-dimensional magnetic system. We find that the three-dimensional ordering temperature decreases with increasing defect concentration at a rate that is of the order of the spatial anisotropy of the system. Though site dilution has been studied for quasi-1D ferromagnetic systems where the interchain interaction is antiferromagnetic,³ here we study the site dilution in a quasi-1D ferromagnetic system where the interchain interaction is ferromagnetic.

$[\text{FeCp}_2^*][\text{TCNE}]$, which consists of $S = \frac{1}{2} [\text{FeCp}_2^*]^+$ donors and $S = \frac{1}{2} [\text{TCNE}]^-$ acceptors, crystallizes with stacks of alternating cations and anions parallel to the long needle axis of the solution-grown crystals.⁴ The donor $[\text{FeCp}_2^*]^+$ consists of two $\text{C}_5(\text{CH}_3)_5$ rings π bonded to a Fe^{III} ion. The acceptor $[\text{TCNE}]^-$ is essentially planar. The Landé g factors for $[\text{FeCp}_2^*]^+$ are $g_{\parallel} \sim 4.0$ and $g_{\perp} \sim 1.3$, where the g_{\parallel} and g_{\perp} refer to the g factor obtained for magnetic fields (H) parallel and perpendicular to the molecular axis.^{6,7} In contrast, the $[\text{TCNE}]^-$ has $g = 2$ and is isotropic. The dc susceptibility (χ), magnetization (M), specific heat (C), and neutron diffraction studies show that the system is a three-dimensional ferromagnet below the transition temperature $T_c \approx 4.8$ K.⁵⁻⁷ The M -vs- H hysteresis curves at 2.0 K indicate that the material is a hard ferromagnet with a coercive field of ~ 1 kG.⁶ The temperature-dependent specific heat has a cusp at the 3D ferromagnetic transition temperature with a crossover to primarily 1D behavior at higher temperatures.⁷

The magnetic properties of the individual chains have been described by a Heisenberg form spin Hamiltonian with a near-neighbor interaction and an orientational dependence of the $[\text{FeCp}_2^*]^+$ moment:^{6,7}

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

where $g^{[\text{TCNE}]} = 2.0$ and is isotropic, and $g_{\parallel}^{[\text{FeCp}_2^*]} = 3.9$ and $g_{\perp}^{[\text{FeCp}_2^*]} = 1.3$. Substituting these values, the Hamiltonian can be rewritten as

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

where $\gamma \sim 0.35$. Hence even though $J_{\text{intra-chain}}$ is isotropic in spin space, the final Hamiltonian is anisotropic. Utilizing $J_{\text{intra-chain}} = 25$ K from fits of $T > 50$ K data to 1D Heisenberg models,⁸ we estimate the value of $J_{\text{interchain}}$, which is responsible for 3D ferromagnetic ordering, using

a simplified mean-field-theory result:⁹ $T_c \sim 1.5 (J_{\text{intrachain}} J_{\text{interchain}})^{1/2}$, i.e., $J_{\text{interchain}}/J_{\text{intrachain}} \sim 1/60$.

The replacement of some $S = \frac{1}{2} [\text{FeCp}_2^*]^+$ sites by $S = 0 [\text{CoCp}_2^*]^+$ sites in a chain causes substantial changes in the magnetic properties. $[\text{FeCp}_2^*]_x [\text{CoCp}_2^*]_{(1-x)} [\text{TCNE}]$ forms an isostructural dilution series. Samples with compositions $(1-x) = 0, 0.045, 0.077, 0.085, 0.145$ were obtained in form of needlelike crystals.¹⁰ The ratios of the Fe and Co in these samples were further verified using the Rutherford backscattering technique.

The dc susceptibility and magnetization measurements were performed using a modified version of the Faraday technique where the field gradient varies between $+(dH/dz)$ and $-(dH/dz)$ and the change in force is monitored for cycles typically of 40-sec duration. The magnetometer has an absolute sensitivity of 10^{-11} emu. The measurements were carried out from 2.2 to 300 K. In order to confirm our experimental observations, we measured the ac susceptibility of these compounds using a mutual inductance bridge technique. For these experiments an alternating magnetic field is applied to a sample by means of a primary coil. Two oppositely wound secondary coils connected in series are used to detect a flux variation created when the sample is positioned in one of the secondary coils. A phase-sensitive detector analyzes the resulting signal obtained via a highly sensitive mutual inductance bridge, and produces an output voltage proportional to the susceptibility of the sample. The mutual inductance bridge employs operational amplifiers and a Kelvin-Varley divider in a configuration providing high precision and low noise. The experimental setup was modified in order to be accommodated in a dilution refrigerator to achieve low temperatures down to 25 mK.

That ferromagnetic interactions dominate at low temperatures for all the doped samples is demonstrated by the magnetic moment, which grows larger as the temperature decreases. The reciprocal of the experimentally measured spin susceptibility χ^{spin} , for the highest and lowest doped samples, is plotted vs T in Fig. 1. To estimate a value for the intrachain exchange integral $J_{\text{intrachain}}$ we fit the high-temperature data ($T > 30$ K) to the high-temperature Padé series expansion for the $S = \frac{1}{2}$ Heisenberg model.⁸ The value of $J_{\text{intrachain}}$ obtained from the fit (Fig. 1) is approximately 23 K for the $(1-x) = 0.045$ compound, essentially the same as that of the undoped sample. The high-temperature series-expansion results for the infinite chain become less valid for the higher doping levels, and deviation from the predicted behavior is observed. The values obtained for $J_{\text{intrachain}}$ is not substantially different from that of the pure system.

As the temperature is decreased the onset of spontaneous magnetization, i.e., magnetization at zero applied magnetic field, is observed for $(1-x) = 0.045, 0.077, 0.085$ at temperatures 4.4, 3.8, and 2.75 K, respectively; see Fig. 2. The zero-field magnetization for $(1-x) = 0.045$ is fit well to a curve $M = (T_c - T)^\beta$, where β is the critical exponent. It is noted that the value of $\beta \approx 0.35 \pm 0.015$ obtained for a T_c of 4.4 K lies between

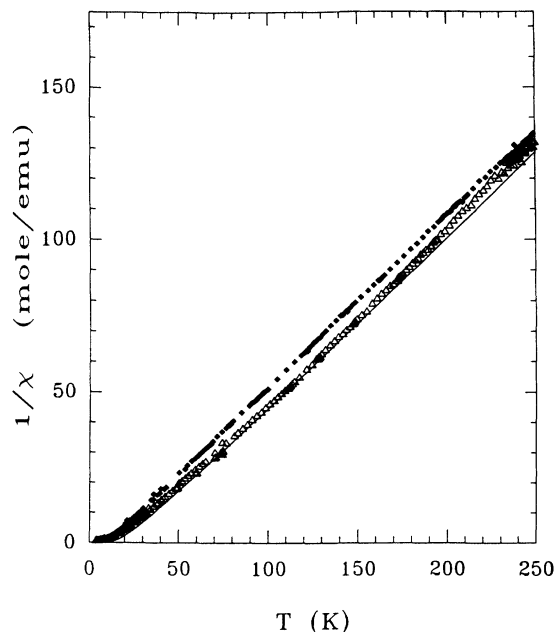


FIG. 1. Inverse molar spin susceptibility of $[\text{FeCp}_2^*]_x [\text{CoCp}_2^*]_{(1-x)} [\text{TCNE}]$ as a function of temperature, for $(1-x) = 0.045$ \triangle and $(1-x) = 0.145$ \blacklozenge . The solid curve is a fit to the high-temperature series expansion (Ref. 8) for $(1-x) = 0.045$ using $g_{\parallel}^{\text{FeCp}_2^*} = 3.9$ and $g^{\text{TCNE}} = 2.0$.

the 3D Heisenberg value of 0.37 and the 3D Ising value of 0.31. The deviation of $M(T)$ below $0.9T_c$ is not proportional to a simple $T^{3/2}$ behavior as predicted by spin-wave theory for a classical ferromagnet with lattice impurities.¹¹ The different anisotropies and internal fields in the system have to be taken into account to predict the

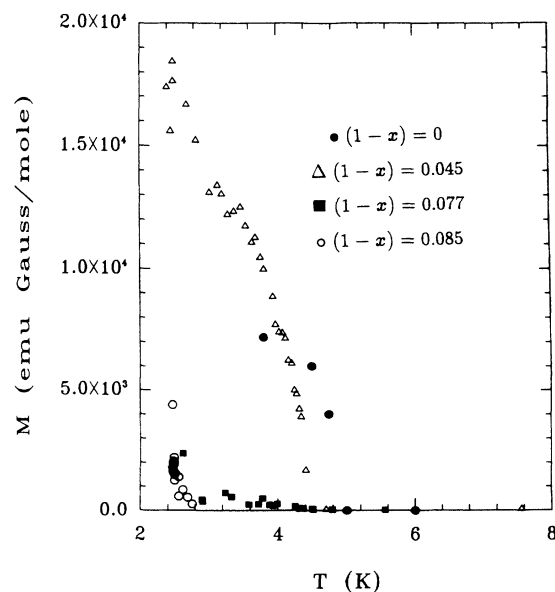


FIG. 2. Spontaneous magnetization of $[\text{FeCp}_2^*]_x [\text{CoCp}_2^*]_{(1-x)} [\text{TCNE}]$ as a function of temperature.

correct behavior. The $M(H)$ curves for $(1-x)=0.045, 0.077, 0.085$ samples show substantial hysteresis at 2.3 K, characteristic of a hard ferromagnet. Hysteresis was not observed for the $(1-x)=0.145$ sample at 2.3 K.

The ac $\chi(100 \text{ Hz})$ for $(1-x)=0, 0.045$, and 0.145 has a maximum at the ferromagnetic transition at 4.9, 4.4, and 0.75 K, respectively; see Fig. 3. The decrease in the dynamic susceptibility below T_c is attributed to the hardness of the ferromagnet. These results are in agreement with the results of the dc susceptibility experiment.

The dependence of T_c on the defect concentration is directly related to the dependence of the correlation lengths on temperature and the defect concentration. It follows that in such quasi-1D systems the nonmagnetic ions will break up the chains in finite segments and effectively reduce the correlation length, thereby reducing T_c . The variation of T_c with x has been studied for different lattice models and interaction Hamiltonians by such methods as Monte Carlo simulations, closed-form approximations (cluster methods), series expansions, and renormalization-group techniques.¹² These theories have a similar quantitative estimation of the decrease in the transition temperature at low impurity concentration levels. The common features of these theories are as follows.¹³

(i) For low concentration levels the $T_c(x)$ curve depends on the spatial anisotropy (1D, 2D, or 3D) as well as the spin dimensionality (Ising, XY, or Heisenberg).

(ii) The initial decrease of T_c with increasing x is linear in x with the slope $\approx (J_{\text{intra}}/J_{\text{inter}})$.

(iii) The critical concentration for x_c , where $T_c=0$ is independent of the anisotropy and spin dimensionality, in contrast to feature (i), for 3D lattices coincides with the percolation limit, which is a purely geometric quantity,

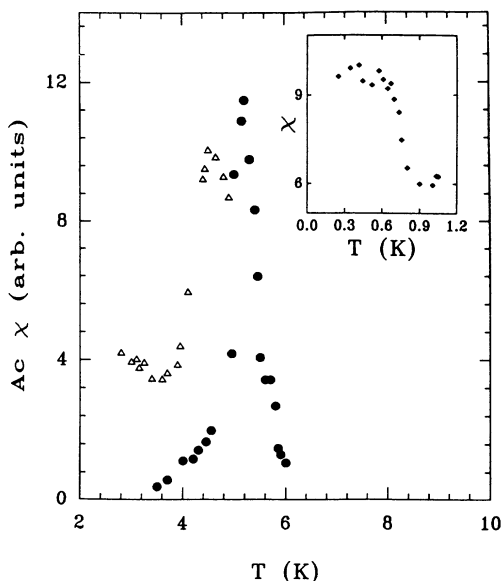


FIG. 3. ac susceptibility of $[\text{FeCp}_2^*]_x[\text{CoCp}_2^*]_{(1-x)}[\text{TCNE}]$ vs temperature for $(1-x)=0.0$ ●, 0.045 △, and $(1-x)=0.145$ ◆ (inset).

and the value of x_c is thus determined by the topology of the underlying lattice only.

A typical phase diagram of $T_c(x)$ using position-space renormalization-group technique for an Ising-like chain system shows that the T_c drops drastically to a small value as one approaches one dimensionality, i.e., as $J_{\text{interchain}}/J_{\text{intra-chain}}$ tends to 0.^{12,14} $T_c(x)$ eventually vanishes at the percolation concentration x_c^d for the dimensionality corresponding to that of the coupled chains. In other words, the transition temperature decreases rapidly with increasing defect concentration when 1D correlations dominate, crossing over to a lesser variation with x at higher concentration of defects when the 3D couplings dominate.¹²

The experimental curve of $T_c(x)$ obtained for $[\text{FeCp}_2^*]_x[\text{CoCp}_2^*]_{(1-x)}[\text{TCNE}]$, Fig. 4, follows the trend predicted for diluted quasi-1D magnets. (For comparison, the inset of Fig. 4 shows the typical predictions¹⁴ for Ising systems of different spatial anisotropies.) We obtain an average slope of ≈ 7.0 for the experimental curve, implying (noting that there are two spins per $[\text{FeCp}_2^*][\text{TCNE}]$ repeat unit) $J_{\text{interchain}}/J_{\text{intra-chain}} \sim 1/14$. This value is in good agreement with the value of $J_{\text{interchain}}/J_{\text{intra-chain}}$ obtained from the knowledge of T_c and $J_{\text{intra-chain}}$ of the undoped $[\text{FeCp}_2^*][\text{TCNE}]$. The reduced value obtained from the slope of $T_c(x)/T_c(0)$ is expected in accord with the calculations.¹⁴ A dimensionality crossover to a 3D percolation behavior is not observed as the $[\text{FeCp}_2^*]^+$ ion concentration is decreased to $x=0.855$. A higher spinless site concentration may be

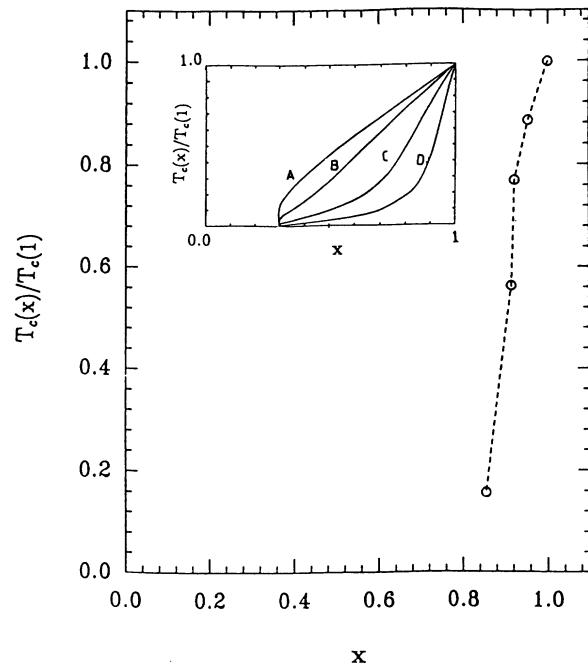


FIG. 4. $T_c(x)/T_c(1)$ vs x for $[\text{FeCp}_2^*]_x[\text{CoCp}_2^*]_{(1-x)}[\text{TCNE}]$. The inset shows the typical theoretical calculation assuming Ising-spin nature for different spatial anisotropies and values of γ . The ratio of interchain to intrachain coupling is 1 (A), 0.1 (B), 0.02 (C), and 0.005 (D) (Ref. 14).

necessary to observe the onset of the crossover, which will be indicated by a change of slope in $T_c(x)$.

These experiments illustrate and confirm the long-standing theoretical predictions concerning effects of spin dilution in quasi-1D molecular ferromagnets. These results are in accord with the absence of 3D magnetism in high spin-oligomeric systems.¹⁵ Systems with small ($J_{\text{interchain}}/J_{\text{intra-chain}}$) need to have long chains and few

spinless defects to observe intrinsic T_c .

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