

# Pressure dependence of magnetic ordering temperature for decamethylferrocenium tetracyanoethanide

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It has been demonstrated that the linear-chain charge-transfer salt, decamethylferrocenium tetracyanoethanide (DMeFc)(TCNE), is a ferromagnet with a transition temperature of  $\sim 4.8$  K. This low-temperature 3D ordering has been attributed to a strong intrachain and a weak interchain interaction. To study these interactions, we have determined the  $T_c$  up to 20 kbar by measuring the ac susceptibility  $\chi$  at low frequency. Our results show that the  $T_c$  increases with pressure at a rate of  $\sim 0.22$  K/kbar, while the  $\chi$  peak indicative of the ferromagnetic transition continues to decrease rapidly. A small peak was also detected above the main transition at pressures above 3 kbar. This new peak persists even after the pressure is removed. The result from dc magnetization suggests that this corresponds to a metamagnetic state. For the first time, we have observed pressure-induced phase-transition in this material.

## I. INTRODUCTION

Studies of molecular and polymeric ferromagnetism are important to solid-state physics. Decamethylferrocenium tetracyanoethanide (DMeFc)(TCNE) is the first known molecular ferromagnet.<sup>1</sup> The (DMeFc)(TCNE) consists of stacks of alternate donors (DMeFc) $\cdot^+$  and acceptors (TCNE) $\cdot^-$ , each with spin  $S = \frac{1}{2}$ ,<sup>2,3</sup> dc susceptibility, magnetization, neutron diffraction, and specific-heat studies<sup>1,4,5</sup> show that the system becomes a 3D ferromagnet below the transition temperature  $T_c \sim 4.8$  K. At higher temperatures (17–300 K) the susceptibility can be fit well by a 1D Heisenberg model<sup>6</sup> with  $S = \frac{1}{2}$  and ferromagnetic coupling,  $J/k_B \sim 27$  K.<sup>1</sup> Specific-heat measurements show that  $\sim 4\%$  of the entropy is involved in the 3D ordering of the spins and most of the entropy is consumed during the 1D ferromagnetic ordering at much higher temperatures.<sup>5</sup> This suggests that strong intrachain coupling, with weak interchain coupling, is responsible for the observed ferromagnetic phase transition.

The mechanisms that govern the ferromagnetic coupling in this class of linear-chain systems are not firmly established. However, the admixing of a virtual triplet excited state with the ground model, originally proposed by McConnell,<sup>7</sup> offers an attractive explanation for ferromagnetic coupling in such a linear-chain system.<sup>8</sup> Although the ferromagnetic interaction in the chains (intrachain interaction) can be obtained qualitatively within the frame of such a model, the interchain interaction, which is very crucial for the 3D phase transition, is far more complicated. For example, the disproportionality of adjacent in-registry (DMeFc) $\cdot^+$ 's to form  $S = 1$  (DMeFc) $^{2+}$  and  $S = 0$  (DMeFc) $^0$  can lead to a ferromagnetic exchange interaction, whereas the disproportionality of adjacent in-registry (TCNE) $\cdot^-$ 's to form  $S = 0$  (TCNE) $^{2-}$  and  $S = 0$  (TCNE) $^0$  will lead an antiferromagnetic exchange interaction.<sup>8</sup> The competition between the ferro- and antiferro-

magnetic exchange interactions determines the ground state of a specific compound. The competition might be drastically changed under high pressure because (i) organic compounds are usually rather compressible and the magnetic interaction would depend on the distance between neighboring spins; and (ii) the charge transfer between donors and acceptors depends roughly on the Madelung energy at their positions.<sup>9</sup> Therefore, high pressure is useful in the exploration of the magnetic interaction in organic compounds. We report ac susceptibility studies under high pressure at 1.2–40 K and dc magnetization measurements in (DMeFc)(TCNE).

## II. EXPERIMENT

The preparation of polycrystalline samples of (DMeFc)(TCNE) is described in Ref. 2. The hydrostatic pressure environment was provided by a Be-Cu high-pressure clamp with a Teflon cell using 3M fluorinert liquid as the pressure medium.<sup>10</sup> The pressure was determined by a superconducting Pb-manometer. The real part of ac susceptibility was measured with an ac mutual-inductance bridge operating at 16 Hz and a constant excitation current ranging from 0.1 to 10 mA. The primary coil (1000 turns) was built in the pressure clamp. The secondary coils were wound on a quartz tube with 2 mm i.d., 3 mm o.d., and 9 mm long. Each of the two coils was 450 turns and about 3 mm long. A  $\sim 2$  mg sample of the material was put into one of the secondary coils. Then the secondary coils were placed inside the Teflon cell. The temperature was measured with a Ge thermometer in the range of 1.2–40 K. dc magnetization at different fields and temperatures was carried out in a Quantum Design superconducting quantum interference device Magnetometer.

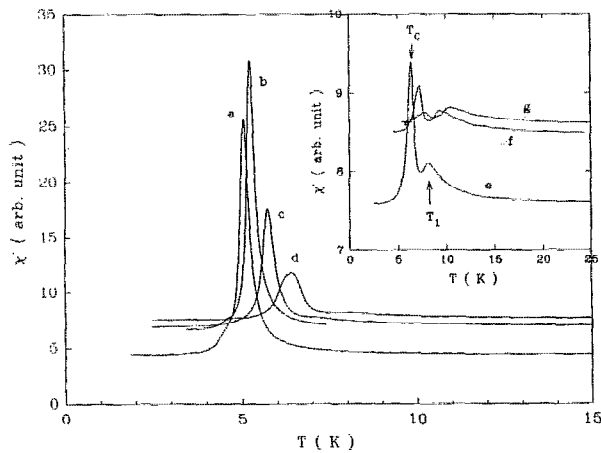


FIG. 1. ac susceptibility as a function of  $T$  under several pressures:  $a=0.24$  kbar,  $b=0.89$  kbar,  $c=2.69$  kbar,  $d=5.30$  kbar,  $e=5.49$  kbar,  $f=10.63$  kbar,  $g=13.81$  kbar. (Insert: The definition of  $T_c$  and  $T_1$ .)

### III. RESULTS AND DISCUSSION

Figure 1 shows a typical  $\chi'$ - $T$  curve, which is similar to that observed by Narayan *et al.*<sup>11</sup> The sharp maximum is attributed to the 3D ferromagnetic phase transition. Under pressure,  $T_c$  increases linearly with pressure at a rate of 0.21 K/kbar (Fig. 2). The change in  $T_c$  under pressure is reversible within our experimental resolution. In the fresh sample, the amplitude of this ferromagnetic peak increases slightly with pressure, then decreases drastically with pressure at relative low pressures ( $\sim 2$  kbar) and in a narrow pressure region (from 2 to 5 kbar). Above 2 kbar, the change is not reversible and the amplitude is significantly reduced when the pressure is removed. Above the drastic-change region, the amplitude decreases slowly with pressure. After the first pressure cycle, the amplitude becomes reversible with a much smaller amplitude compared with the fresh sample. The drastic decrease in the amplitude is accompanied by the appearance of a new peak at a temperature  $T_1$  higher than  $T_c$ . The  $T_1$  also increases linearly

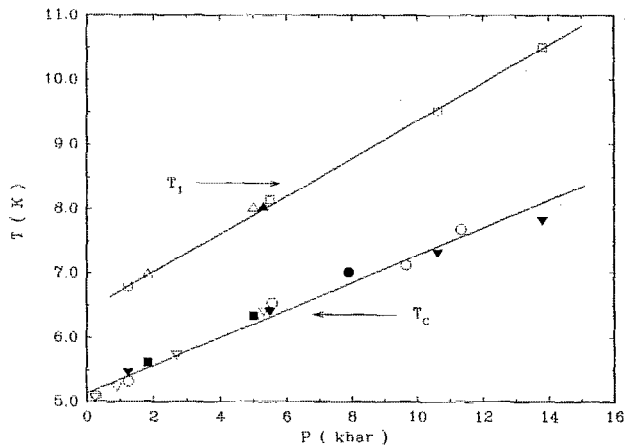


FIG. 2.  $T_c$  and  $T_1$  as a function of pressure. First sample:  $\circ$  (pressure increasing),  $\bullet$  (pressure decreasing); second sample:  $\nabla$ ,  $\blacktriangle$  (first run);  $\square$ ,  $\blacktriangledown$  (second run);  $\blacksquare$ ,  $\triangle$  (third run).

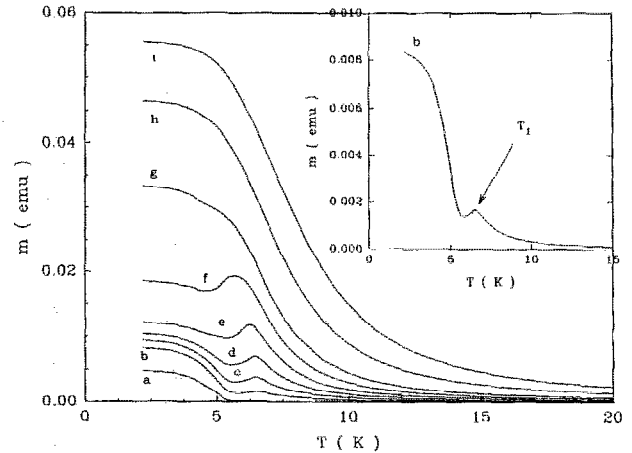


FIG. 3. Field-cooled dc magnetization as a function of  $T$  at different fields:  $a, 0.002$  T;  $b, 0.01$  T;  $c, 0.02$  T;  $d, 0.03$  T;  $e, 0.05$  T;  $f, 0.07$  T;  $g, 0.1$  T;  $h, 0.2$  T;  $i, 0.3$  T.

with pressure at a rate of 0.29 K/kbar, which is slightly higher than that of  $T_c$  (Fig. 2). Above 13 kbar, the peak height at  $T_1$  is larger than that at  $T_c$ . The new peak is reversible both in temperature and amplitude with the change of pressure and persists even after the pressure is removed, once the sample is through the first pressure cycle. The irreversible phenomena suggest that a structural transformation was induced by the pressure or due to chemical reaction with the pressure medium. However, the reversibility after the first pressure cycle demonstrates that the new phase is stable. To determine whether this structural transformation is induced by high pressure or due to chemical reaction with the pressure medium, a fresh sample was mixed with the pressure medium for 5 days at room temperature and ambient pressure, then dc magnetization measurements were made. Our results show no change in the magnetic susceptibility above  $T_c$ . We also monitored the weight before and after application of high pressure and found no difference, within our experimental error. This implies that no significant amount of the pressure medium was left in the pressed sample. All of these observations suggest that the structural transformation cannot be caused by chemical reaction with the pressure medium.

To further study the properties of the pressure-induced phase, we raised the pressure on the sample to 15 kbar, released it, and then measured the dc magnetization at ambient pressure. Figure 3 shows a typical field-cooled magnetization as a function of temperature at several fields. Clearly, at low fields, a local maximum (indicated as  $T_1$ ) appears above the ferromagnetic phase transition, which is consistent with our ac susceptibility measurements. This local maximum does not exist in the fresh sample. Further measurements reveal that  $T_1$  decreases with increased magnetic field and disappears at fields above 0.1 T, then becomes ferromagneticlike, i.e., the field-cooled magnetization saturates below a certain temperature. This suggests that  $T_1$  may correspond to a metamagnetic phase transition.<sup>12</sup> A two-step-like behavior in  $M$  vs  $H$  is ob-

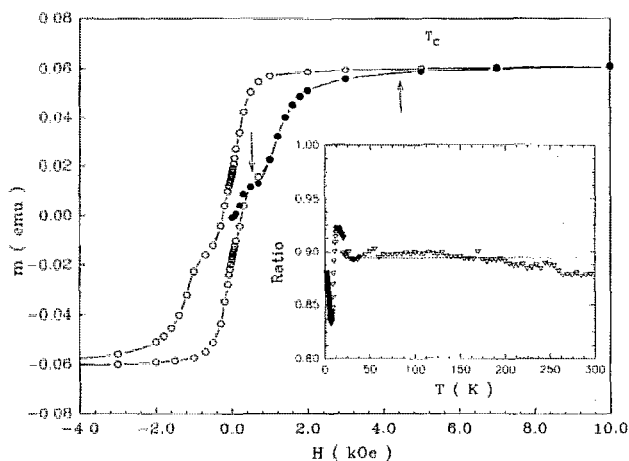


FIG. 4. dc magnetization  $m$  as a function of field  $H$  for pressured sample at 2.2 K. The arrows indicate the steps (see text): ● (initial magnetization), ○ (hysteresis loop). [Insert: The ratio of  $\chi$  (pressed sample) vs  $\chi$  (fresh sample) as a function of  $T$  at  $H=1$  T.]

served below  $T_1$  but not above (Fig. 4). Such an observation is clear evidence of the existence of a metamagnetic phase below  $T_1$ .<sup>12</sup> Details of the phase diagram will be discussed later.

The field-cooled magnetization at low fields shows a rapid increase below  $T_c$ , which is about the same as that of the fresh sample, then saturation at even lower temperatures. However, the saturation moment is smaller (about 10%–20%) than that of a fresh sample. Below  $T_c$ , the M-H shows two-step behavior. The saturation field for the first step is very close to that of the fresh sample. This suggests that the sample becomes inhomogeneous under high pressures. The observed ferromagnetic transition at low field might be due to the fact that some of the sample retains its original structure. From the decomposition of the M-H curve, this roughly accounts for about 15% of the original sample. The high-temperature susceptibility of the pressed sample is about 10% smaller than that of the fresh sample (Fig. 4). The difference might be attributed to the anisotropy. Although the susceptibility changes by a factor of 10 from 20 to 300 K, the ratio between the pressed and fresh samples is almost constant (Fig. 4). Since the  $T$  dependence of the susceptibility for the fresh sample at high temperatures is dominated by the 1D properties along the chains, our result suggests that the 1D chain in the new phase has not been altered significantly by pressure. Because the intrachain interaction is ferromagnetic, the observed metamagnetic phase below  $T_1$  suggests that some antiferromagnetic interactions might exist between the chains. In other words, the interchain interaction should include some antiferromagnetic couplings. It is not difficult to find the possible origin of the antiferromagnetic interaction between two neighboring chains. For example, the disproportionality of adjacent in-registry (TCNE)  $\cdot^-$ 's to

form  $S=0$  (TCNE)<sup>2-</sup> and  $S=0$  (TCNE)<sup>0</sup> will lead to an antiferromagnetic exchange interaction.<sup>8</sup> Since the 1D properties of the chains were not significantly altered by high pressure and the ferromagnetic  $T_c$  increases with pressure, it seems that the antiferromagnetic interaction cannot be caused by a simple reduction of the distance between the chains. One possible cause might be that the out-registry chains were shifted by  $\frac{1}{2}$  lattice spacing along the chain axis and all became in-registry chains. This structural transformation could be irreversible. Such an explanation can also account for the observed irreversible phenomena, such as the height of the main transition and the appearance of the new transition. This might also account for the observed small 6.1 K anomaly in the specific-heat measurement<sup>5</sup> if one assumes a small amount of the new phase exists in the original materials. If such a speculation is true, the interaction between neighboring spins in this system becomes more complicated than what has been proposed. A metamagnetic state in other linear-chain systems was also reported<sup>13</sup> and attributed to both the strong intrachain ferromagnetic interaction and the weak interchain antiferromagnetic interaction. We also noticed that the residual moment is very small in our case, which differs from the results reported in other systems.<sup>13</sup> This might suggest that a long-lived metastable phase does not exist in the system studied here.

In summary, we have measured the ac susceptibility under high pressures and dc magnetization for molecular ferromagnet (DMeFc) (TCNE). Our results show that the ferromagnetic interaction increases under pressure. In addition, a new phase induced by high pressure was also observed. This new phase is metamagnetic, resulting from a ferromagnetic intrachain interaction and an antiferromagnetic interchain interaction.

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