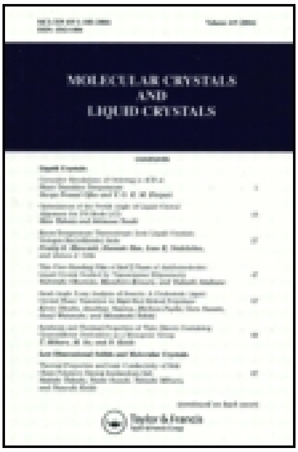

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Ferromagnetism in a New Structural, Phase of $[Fe(C_5Me_5)_2]$ [TCNQ]

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FERROMAGNETISM IN A NEW STRUCTURAL PHASE OF $[Fe(C_5Me_5)_2][TCNQ]$

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Abstract

The five integrated-stack charge-transfer salts $[M(C_5Me_5)_2][TCNQ]$ (M=Mn, Cr) and $[M(C_5Me_5)_2][TCNE]$ (M=Fe, Mn, Cr) are bulk ferromagnets, whereas $[Fe(C_5Me_5)_2][TCNQ]$ was reported to exist as two different phases, a metamagnet and a paramagnet. We now report that with careful control of the crystallization conditions, it is possible to isolate a new structural phase of $[Fe(C_5Me_5)_2][TCNQ]$ which is a bulk 3-D ferromagnet with $T_c = 3.1$ K. Thus $[Fe(C_5Me_5)_2][TCNQ]$ is the first example of a single compound giving rise to three distinctly different magnetic phenomena, a finding that will permit an assessment of the subtle structural features that control magnetic ordering in this class of materials.

The search for molecular based magnetic materials[1] gained great impetus from the realization of bulk 3-D ferromagnetism in the integrated-stack charge-transfer (CT) donor-acceptor (D^+-A^-) salts containing decamethylmetallocenium cations and organic radical anions (Table 1). This class of ferromagnets was discovered in 1987 with the synthesis of $[Fe(C_5Me_5)_2]^+[TCNE]^-$, with a critical temperature, $T_c = 4.8$K.[3] Subsequent demonstration that the $[Mn(C_5Me_5)_2]^+$ [5] and $[Cr(C_5Me_5)_2]^+$ [7]analogues as well as $[Mn(C_5Me_5)_2]^+[TCNQ]^-$ [4] and $[Cr(C_5Me_5)_2]^+[TCNQ]^-$ [6] are also ferromagnets not only demonstrated the generality of ferromagnetic ordering in this class of materials,

TABLE 1. Chronology of magnetically ordered integrated-stack CT salts

Compound	D^+ spin	type	T_c (K)	Date	Reference
$[Fe(C_5Me_5)_2][TCNQ]$	1/2	metamagnet	T_N= 2.55	1979	2
$[Fe(C_5Me_5)_2][TCNE]$	1/2	ferromagnet	4.8	1987	3
$[Mn(C_5Me_5)_2][TCNQ]$	1	ferromagnet	6.2	1990	4
$[Mn(C_5Me_5)_2][TCNE]$	1	ferromagnet	8.8	1991	5
$[Cr(C_5Me_5)_2][TCNQ]$	3/2	ferromagnet	3.1	1991	6
$[Cr(C_5Me_5)_2][TCNE]$	3/2	ferromagnet	4.0	1993	7

but also resulted in a better understanding of the intrastack interactions responsible for ferromagnetic coupling.

When examining the group, it appears anomalous that $[Fe(C_5Me_5)_2]^+[TCNQ]^-$, the first magnetically ordered material of this class, is a metamagnet, where antiferromagnetic *inter*chain couplings dominate at low applied fields. This suggested that a study of the binary solid solutions $[Fe_xMn_{1-x}(C_5Me_5)_2]^+ [TCNQ]^-$ might lead to a better understanding of the relevant interstack interactions. However, for values of x ranging from 0.1 to 0.9, no deviation from ferromagnetism was discovered, only a monotonic increase in the T_c with increasing Mn content.[8] Thus we were led to reinvestigate the pure phase, $[Fe(C_5Me_5)_2]^+[TCNQ]^-$; we find that, in addition to the previously reported paramagnetic and metamagnetic phases, there exists a third distinct phase - a bulk 3-D ferromagnet.

Bulk $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ is prepared by addition of a THF solution of $Fe(C_5Me_5)_2$ to a THF solution of TCNQ. Careful control of the crystallization conditions permits us to obtain either green metamagnetic phase II or purple parallelepipeds of the new ferromagnetic phase III. Phase III is isostructural to $[Mn(C_5Me_5)_2]^+[TCNQ]^-$ and different from the paramagnetic phase I and metamagnetic phase II of $[Fe(C_5Me_5)_2]^+[TCNQ]^-$. While phase I contains isolated $D^+A^-A^-D^+$ dimeric units, phases II and III consist of $\cdots D^+A^-D^+A^-\cdots$ integrated stacks. However, there are clear structural differences between the latter two phases, the most obvious being the conformation of the C_5Me_5 rings, which are staggered in phase II and eclipsed in phase III.

The magnetic susceptibility of phases II and III were measured with a Quantum Design MPMS SQUID magnetometer (DC susceptibility) and a LakeShore model 7110 AC Susceptometer (AC susceptibility). Magnetization data for phase III taken at an applied field of 5000 G for T > 50 K can be fit to the Curie-Weiss law, $\chi = C/(T-\theta)$, with $C=1.26\ \text{cm}^3\ \text{K mol}^{-1}$ and $\theta = +3$ K, with the positive θ suggesting dominant ferromagnetic interactions. Figure 1 shows the magnetization for phase III at low field (15 G) plotted as M vs. T for T<10 K, and an abrupt ferromagnetic transition is clearly present, corresponding to a critical temperature of 3.1K. Figure 2 shows the AC susceptibility for phase III. Both the real (χ') and imaginary (χ'') components show maxima at $T_c = 3.0$ K, as expected for a bulk ferromagnetic material. The identification of phase III as a ferromagnet was confirmed by investigation of the field dependence of the magnetization. While phase II clearly shows an inflection in M at $H \approx 1500$ G, indicating the transition from antiferromagnetic coupling to ferromagnetic coupling that is characteristic of a metamagnet, phase III shows a sharp rise in the magnetization at low fields, reaching a value of 7500 $\text{cm}^3\ \text{G mol}^{-1}$ at only 1000 G, followed by a gradual increase to a value of M =11,600 $\text{cm}^3\ \text{G mol}^{-1}$ at 50000 G. This value approaches the saturation magnetization of $M_{sat} = 12{,}100\ \text{cm}^3\ \text{G mol}^{-1}$ expected for a material with $S_A=S_B=1/2$, $g_A = 2.0$, $g_B = 2.33$.[9]

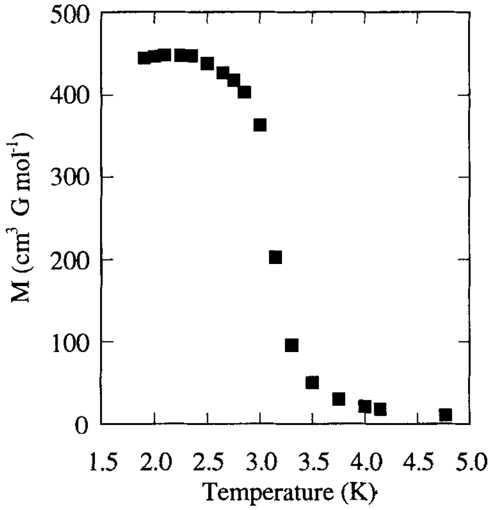

FIGURE 1 Magnetization for phase III of $[Fe(C_5Me_5)_2]^+[TCNQ]^-$ at 15 G

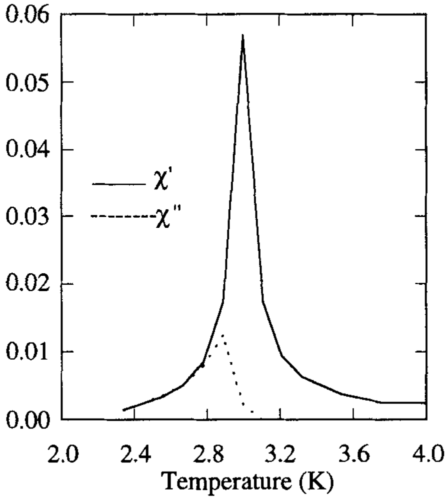

FIGURE 2 AC Susceptibility for phase III of $[Fe(C_5Me_5)_2]^+[TCNQ]^-$

Thus the reaction of $Fe(C_5Me_5)_2$ with TCNQ produces three distinct 1:1 charge-transfer salts: a paramagnet,[10] a metamagnet,[2] and a ferromagnet. To our knowledge, this is the first example of a single stoichiometry that crystallizes in three forms displaying distinctly different magnetic phenomena. Although the metamagnetic phase II and the ferromagnetic phase III have very similar structures, there are differences both in the juxtaposition of the C_5Me_5 rings and in the relative interstack approach of the donor and acceptor molecules. Such differences are certainly responsible for the change in sign of the interstack coupling which results in the shift from metamagnetism to ferromagnetism. We are currently engaged in a detailed structural analysis to determine the interchain interactions which control the magnetic behavior.

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