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Mihai A. Gîrtu [a], Charles M. Wynn [a], Carmen R. Kmety [a], Jie Zhang [b], Joel S. Miller [b] & Arthur J. Epstein [a c]

[a] Department of Physics, The Ohio State University, Columbus, Ohio, 43210-1106

[b] Department of Chemistry, University of Utah, Salt Lake City, Utah, 84112-0850

[c] Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210-1106

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MIHAI A. GÎRŢU[a], CHARLES M. WYNN[a], CARMEN R. KMETY[a], JIE ZHANG[b], JOEL S. MILLER[b] and ARTHUR J. EPSTEIN[ac]

[a]*Department of Physics, The Ohio State University, Columbus, Ohio 43210–1106,* [b]*Department of Chemistry, University of Utah, Salt Lake City, Utah, 84112–0850 and* [c]*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210–1106*

We report and review studies of new partially crystalline members of the high-T_c molecule-based magnets family, $M(TCNE)_2 \cdot x(CH_2Cl_2)$, (M = Fe, Mn, TCNE = tetracyanoethylene). Remanent magnetization revealed high critical temperatures, T_c= 97 K for M = Fe and 75 K for M = Mn. Hysteresis curves for the Fe compound, for $5 \leq T \leq 80$ K, have a spin-flop shape, indicating ferrimagnetic behavior. Field-cooled and zero-field-cooled magnetization reveals magnetic irreversibilities below T_c for both compounds. Static and dynamic scaling analyses of the dc magnetization and ac susceptibility for M = Mn show a transition to a 3D ferrimagnetic state at T_c = 75 K, followed by a reentrant transition, to a spin glass state at T_g = 2.5 K. For M = Fe static scaling analyses are consistent with a high-T transition to a correlated sperimagnet, while below ~20 K there is a crossover to sperimagnetic behavior.

Keywords: organic-based magnets; TCNE; spin glass; sperimagnet

INTRODUCTION

The discovery of a spontaneous moment at room temperature in the $V(TCNE)_x \cdot y(CH_2Cl_2)$ molecule-based magnet[1] (TCNE = tetracyanoethylene), led to considerable interest in generating a broad class of hybrid organic/inorganic materials[2,3] displaying cooperative magnetic behavior at high temperature. The interest in these systems, for which a substantial

fraction of the spin is supplied by electrons in *p* orbitals, was stimulated in part by the possibility for some of these low-density room-temperature magnets to substitute for other magnets in various applications.[3]

Magnetic studies of $V(TCNE)_x \cdot y$(solvent) systems (solvent = acetonitrile, tetrahydrofuran, or dichloromethane) revealed[4] static critical behavior consistent with existing models for random anisotropy magnets (RAM), previously applied only for site-diluted and amorphous *f* and *d* electron systems.[5] It also was shown that the spinless organic solvent has a key role in resulting magnetic properties.[4]

Recently $M(TCNE)_2 \cdot x(CH_2Cl_2)$ (M = Mn, Fe) have been synthesized.[6] We review and report here results of new and recent extensive magnetic studies[7,8] of these two materials and compare and contrast with earlier studies[4] on $V(TCNE)_x \cdot y$(solvent). We also discuss the possible origins of their unusual magnetic behavior in the context of ferrimagnetism, reentrance, and double transition RAM, extending the concept of sperimagnetism, traditionally applied to rare-earth/transition-metal alloys with both ferrimagnetic and random anisotropy behavior,[5] to a molecule-based magnet.

EXPERIMENTAL

Materials

$M(TCNE)_2 \cdot y(CH_2Cl_2)$ (M = Mn, Fe) have unpaired spins on both the *d* orbitals of the transition metal ion and the π^* molecular orbital of the $[TCNE]^-$ bridging organic ion. The results of a Mössbauer spectroscopy study of $Fe(TCNE)_2 \cdot x(CH_2Cl_2)$ indicated that iron is present as high spin ($S = 2$) Fe^{II}.[6a] A study of the precursor of the $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ magnet, $Mn[C_4(CN)_8](CH_3CN)_2 \cdot (CH_2Cl_2)$, which has a Mn^{II} ion, suggested[6b] that Mn is present as $S = 5/2$ Mn^{II}. Based on infrared absorption measurements $[TCNE]^-$ is present. Elemental and thermogravimetric analyses of various samples from different batches lead to an estimation of the solvent content of $0.4 < x < 1.1$ for the Fe-based and similar values for the Mn-based compound.[6a] For the samples reported here the solvent content was $x \sim 0.7$ for M = Fe and $x \sim 0.8$ for M = Mn.

Unlike the reentrant $V(TCNE)_x \cdot y$(solvent), for which the structural correlation length is short and depends upon the solvent used (e.g., ~10, 15, and 25 Å, when the solvent is acetonitrile, tetrahydrofuran, and dichloromethane, respectively[4]), the diffraction patterns for

$M(TCNE)_2 \cdot x(CH_2Cl_2)$ (M = Mn, Fe) exhibit sharp X-ray diffraction lines indicating partially crystalline much less disordered structures.[6a] The same study indicated that the diffraction patterns for the Fe and the Mn-based compounds are almost identical suggesting the two are isomorphous.[6a]

The high spin $3d^5$ Mn^{II} ions in an octahedral environment has a nondegenerate orbital ground state ($^6A_{1g}$), the orbital momentum being quenched. The single-ion anisotropy, arising from small distortions of the octahedral environment and the mixing of low-lying excited states through spin-orbit interaction, is very small, and the Landé g-factor is expected to be close to the spin only value.[9] The $3d^6$ Fe^{II} ion in an octahedral crystal field, in contrast has $^5T_{2g}$ ground state, with unquenched orbital momentum, leading to large deviations of the Landé g-factor from the spin only value. A small distortion from the octahedral symmetry (very common for such systems with T ground states) together with the spin-orbit interaction will remove some or all of the orbital degeneracy and introduce magnetic anisotropies with large zero-field splittings, which will affect the overall magnetic behavior of the compound.[9]

Magnetic data were taken on polycrystalline samples that were handled under argon and sealed in quartz EPR tubes, under vacuum, to avoid possible degradation. Multiple samples from different batches reproducibly show similar overall behavior. The quantitative variations from sample to sample mentioned throughout the paper are attributed to the differences in solvent content, leading to variations in the local environment around the metal ions.

Experimental Techniques

Static magnetization data were collected using a Quantum Design MPMS-5 SQUID magnetometer with a continuous-flow cryostat and a 5.5 T superconducting solenoid. Dynamic susceptibility data as well as second and third harmonics of the susceptibility at various frequencies ($5 \leq f \leq 10000$ Hz) were recorded on a Lake Shore 7225 ac susceptometer/dc magnetometer with an exchange cryostat and 5.0 T superconducting solenoid.

RESULTS AND DISCUSSION

The remanent magnetization measured on warming, in zero (±0.05 Oe) applied dc magnetic field, after cooling in small fields ($5 \leq H \leq 50$ Oe) has a similar shape for both compounds. For $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$, Fig. 1, upon

increasing the temperature (T) the remanent magnetization decreases sharply until ~10 K, then decreases slowly as T is increased to ~70 K, and vanishes at ~75 K. Similarly, in the case[8] of $Fe(TCNE)_2 \cdot x(CH_2Cl_2)$ the remanent magnetization has the initial strong decrease until ~20 K and it vanishes at ~97 K.

Based on similar results obtained on various ferrites,[10] the unusual shape of the remanent magnetization was attributed,[7,8] to the ferrimagnetic nature of these compounds, in particular, to the presence (at least locally) of various sublattices with different exchange coupling and different temperature dependencies of the sublattice magnetizations. The interactions between the spins on the transition metal ion and on the cyanocarbon ligand are expected to be antiferromagnetic, as kinetic exchange (virtual reverse electron transfer from $[TCNE]^-$ to Fe^{II}) is generally dominant in such compounds.[1,4,7,8] Antiferromagnetic interactions have been reported[11] for quasi-one-dimensional systems with similar orbital overlap between Mn^{III} and $[TCNE]^-$. Assuming that the remanent magnetization is a good measure of the spontaneous magnetization, which is the order parameter for a ferromagnetic (FM) or ferromagnetic-like material, the T where it vanishes is a good

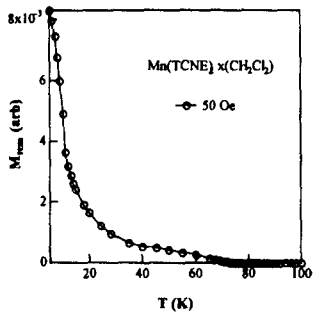

FIGURE 1: Remanent magnetization versus temperature for $Mn(TCNE)_2x(CH_2Cl_2)$. (From Ref. 7. Copyright The American Physical Society, 1998.)

indication of the critical temperature, T_C. Critical analysis of the remanent magnetization based on the power law behavior $M \sim |t|^{\beta}$, where $t = (T - T_c)/T_c$ is the reduced T, provided $T_C = 75$ K, $\beta = 0.35$ for M = Mn,[7] and $T_C = 97$ K, $\beta = 0.45$ for M = Fe.[8] These exponents suggest transitions to a three-dimensional (3D) ferrimagnet for the Mn-based compound[7] and to a

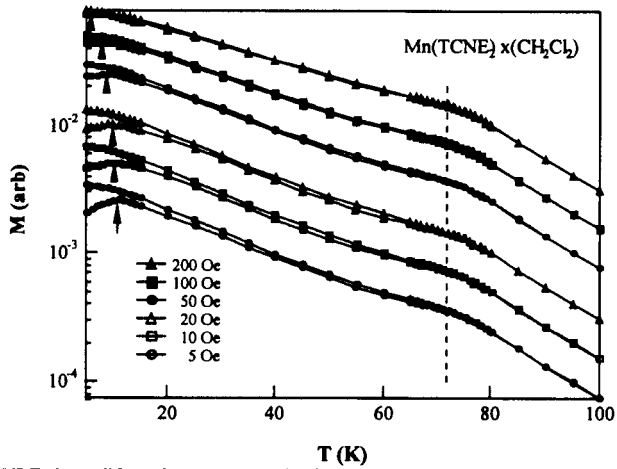

FIGURE 2: FC and ZFC magnetization versus T for Mn(TCNE)$_2$·x(CH$_2$Cl$_2$). (Ref. 7. Copyright The American Physical Society, 1998.)

correlated sperimagnet for the Fe-based material.[8]

Antiferromagnetic interactions also were revealed for Fe(TCNE)$_2$·x(CH$_2$Cl$_2$) by the hysteresis curves, based on the constricted shape with an inflection point indicating a field induced spin-flop transition.[8] Spin-flop behavior consistent with the hysteresis curves also was observed in the ac susceptibility data taken in the presence of various additional dc fields.[8]

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization data, were collected on warming in various applied dc fields. For Mn(TCNE)$_2$·x(CH$_2$Cl$_2$), Fig. 2, a small field independent bifurcation of the FC and ZFC curves is observed near ~72 K. These irreversibilities become more pronounced near ~10 K, when a field dependent peak is observed in the ZFC curves. In the case of Fe(TCNE)$_2$·x(CH$_2$Cl$_2$) a sizeable difference between FC and ZFC magnetizations occurs below ~97 K and these irreversibilities become more pronounced below ~20 K.[8] Strong irreversibilities (in which the ZFC magnetization decreases rapidly with decreasing T below the bifurcation, leading to large differences between the FC and ZFC magnetizations), with a field dependence of the bifurcation point (such that the bifurcation temperature decreases[12] with increasing H) are indicative of glassy behavior.[12,13] In the case of a typical FM without disorder

such irreversibilities are not expected or are small.[13] According to these criteria, it was suggested[7] that $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ has a reentrant behavior, with a high-T paramagnet (PM) to ferrimagnet transition and a low-T ferrimagnet to spin glass (SG) transition. Correspondingly, it was argued[8] that upon decreasing T $Fe(TCNE)_2 \cdot x(CH_2Cl_2)$ has a first transition from PM to

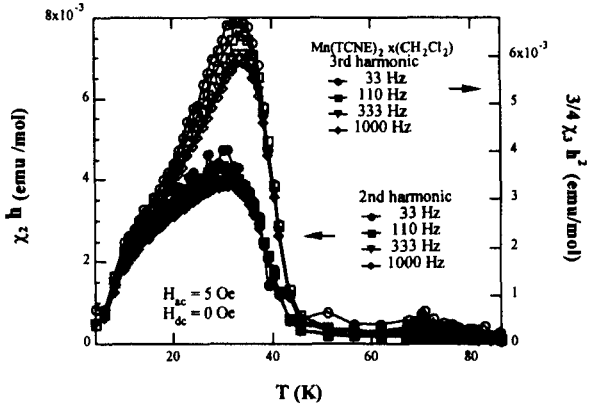

FIGURE 3: Second (left axis, filled symbols) and third (right axis, empty symbols) harmonics of the ac susceptibility versus temperature for $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ in zero dc field and an ac field of amplitude 5 Oe and various frequencies.

a correlated sperimagnet (CSM) followed by one to a sperimagnet (SM). These suggestions were based on the assumption of the dominance of random exchange for M = Mn and random anisotropy for M = Fe.

The in-phase, χ', and out-of-phase, χ'', components of the ac susceptibility were measured on warming in zero applied dc magnetic field and various ac frequencies for both compounds.[7,8] For M = Mn the frequency dependence of χ' and χ'' was observed[7] only below ~30 K and especially below ~10 K, while for M = Fe the frequency behavior was modest, occurring especially in χ'' below ~20 K.[8] Generally, the frequency dependence of the ac susceptibility is indicative of slow relaxation processes, typical for spin glasses[13] or spin glass-like materials such as RAM.[5] (Typical FMs display frequency dependence due to domain wall pinning only at microwave frequencies, outside the range of the ac susceptibility measurements.[13]) Consequently, the ac susceptibility data are consistent with the suggestions based on the FC/ZFC magnetization studies that $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ has a

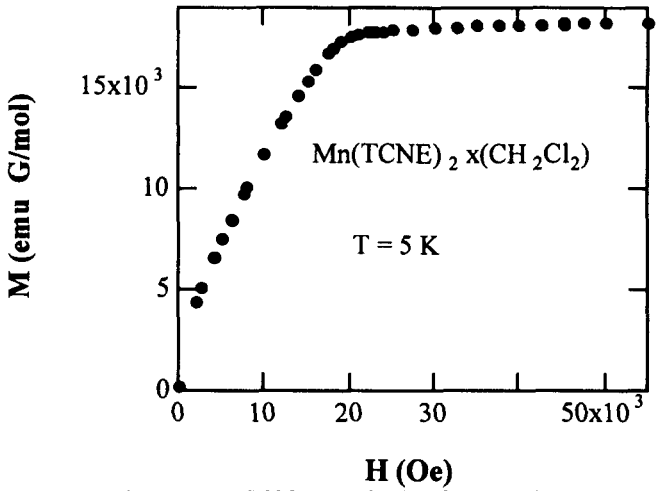

FIGURE 4: Magnetization versus field for $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ at 5 K.

reentrant SG behavior[7] while $Fe(TCNE)_2 \cdot x(CH_2Cl_2)$ has a double transition RAM behavior.[8]

The second, χ_2, and third, χ_3, harmonics of the ac susceptibility for $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$, Fig. 3, reveal a strong peak just below 40 K that extends to low T. The peak in the second harmonic is indicative of a spontaneous moment,[14] consistent with ferrimagnetic behavior. It is puzzling, however, that the harmonics do not peak at the ferrimagnetic transition, but at a temperature intermediate between the two transitions. Also, although the second harmonic decreases abruptly at $T < 10$ K, where the irreversibilities increase, the shoulder observed suggests that the spontaneous moment does not vanish completely, consistent with the remanent magnetization data of Fig. 1. We were unable to clearly observe similar behavior in the Fe-based compound using similar experimental conditions.

The low-T approach to saturation in the magnetization data suggested[8] for M = Fe RAM behavior, in the high anisotropy limit. The approach to saturation, $M(H)$, at 5 K for M = Mn, Fig, 4, reveals an unusual behavior, inconsistent with either the $H^{1/2}$ or H^2 dependencies expected[5] for a 3D RAM.

Isothermal magnetization data, $M(H)$, were collected for scaling analyses at various T by zero-field cooling and measuring from 0 to 55 kOe for both

compounds. For $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ $T_C = 75$, $\beta = 0.35$, and $\delta = 3.86$ with $0.005 = |t| = 0.18$. For $Fe(TCNE)_2 \cdot x(CH_2Cl_2)$ $T_C = 97$ K, $\beta = 0.45$, and $\delta = 2.5$, with $0.001 = |t| = 0.23$. Moreover, for $Mn(TCNE)_2 \cdot x(CH_2Cl_2)$ accurate χ'' data allowed[7] dynamic scaling analyses, the best collapse of the dynamic data (for $T < 20$ K) being obtained for the spin glass transition temperature $T_g = 2.5$ K.

Reentrance in $V(TCNE)_x \cdot y$(solvent) and $M(TCNE)_2 \cdot x(CH_2Cl_2)$ (M = Mn, Fe), suggests a generality of the phenomenon for this class of materials. For V and Fe materials (both with significant single-ion anisotropy[15]) the reentrant behavior was attributed[4,8] to randomness in the anisotropy likely due to random dilution of $[TCNE]^-$ by the nonmagnetic solvent. In contrast, for the Mn compound (with very small anisotropy) it was argued[7] that random exchange rather than random anisotropy was responsible for reentrance. In all these cases, the ability of $[TCNE]^-$ to bind in different orientations (at the same crystal sites) may contribute to disorder and glassiness, similar to the previously studied manganese-porphyrin compounds.[11]

Also, noting that for both Fe-based and Mn-based magnets glassiness and the increase of the magnetic moment appear to occur simultaneously (as observed in both ac susceptibility and FC/ZFC magnetization studies), we speculate that there may be a connection between ferrimagnetism and the formation of the glassy state. Given the partial crystallinity of these materials it is likely that a magnetic lattice exists, at least locally, and it consists of various sublattices, (made up of M^{2+}, and the two $[TCNE]^-$). The magnetic moment could increase, with decreasing T due to the difference between the exchange coupling between the various sublattices and the different temperature variation of the sublattice moments, as was previously shown for ferrites.[10] The various exchange interactions between sublattices may lead to canted spin configurations at low T, which would increase the magnetic moment as the spins are no longer antiparallel. Simultaneously, competing interactions may arise between the various sublattices for M = Mn, while increased anisotropy may occur due to the additional "stiffness" induced by canting caused by the exchange interactions (which at low T may favor only specific spin orientations) for M = Fe.

CONCLUSION

We reported and reviewed magnetic studies of $M(TCNE)_2 \cdot x(CH_2Cl_2)$ (M = Mn, Fe), high T_C molecule-based magnets. Remanent magnetization, hysteresis and ac susceptibility in a dc field studies suggested ferrimagnetic behavior, while the zero dc field ac susceptibility and FC/ZFC magnetization data showed increased low T irriversibilities, indicated reentrant behavior. Scaling analyses revealed successive transitions to a 3D ferrimagnet (T_C = 75 K, β = 0.35, δ = 3.86) and a spin glass (below ~10 K) for M = Mn, and to a correlated sperimagnet (T_C = 97, β = 0.45, δ = 2.5) and a sperrimagnet (below ~20 K) for M = Fe.

We speculated that the unusual increase of the magnetic moment at the low T transition may be due to the presence (at least locally) of various sublattices with different exchange coupling and different temperature dependencies of the sublattice magnetizations, likely resulting in canted spin configurations. We further speculated that at low temperature a disorder enhanced competition between the various sublattices, leading to spin frustration, may occur for the Mn-based compound, and an increase in spin stiffness and, hence, random anisotropy, may arise in the Fe-based compound. Reentrant behavior, either due to random anisotropy or random exchange has been observed in all the compounds of the $M(TCNE)_x \cdot y$(solvent) family studied extensively thus far (M = V, Mn, Fe).

Acknowledgments

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[15] It is noted that in an ideal octahedral environment [not the case for disordered $V(TCNE)_x \cdot y(solvent)$], V^{II} is expected to have no single-ion anisotropy.