

## MAGNETIC BEHAVIOUR OF A 3-DIMENSIONAL HYBRID ORGANIC/INORGANIC MAGNET

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Magnetic studies of a hybrid organic/inorganic compound,  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  (TCNE = tetracyano-ethylene), with a relatively high critical temperature of 97 K are reviewed and report. Below  $T_c$  a complex behavior is observed, as revealed by static and dynamic magnetic measurements and scaling analyses. The magnetization measurements indicate the presence of a net magnetic moment, while the field-cooled and zero-field-cooled magnetization measurements suggest low-temperature irreversibilities below 20 K. The possible origin of the unusual magnetic behavior of this compound is discussed in the context of ferrimagnetism and double transition random magnetic anisotropy, extending the concept of sperimagnetism, traditionally applied to rare-earth/transition-metal alloys with both ferrimagnetic and random anisotropy behavior, to a hybrid organic/inorganic magnet.

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### 1. Introduction

Magnetic ordering in hybrid organic/inorganic compounds has been a topic of intense research after the discovery in 1991 of a spontaneous moment at room temperature in the  $\text{V}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  magnet (TCNE = tetracyanoethylene) [i]. The interest in these molecule-based magnets [ii], for which a substantial fraction of the spin is supplied by electrons in  $p$  orbitals, was stimulated by the possibility for some of these low-density room-temperature magnets to substitute for ferrites or other materials in various applications [iii]. We discuss here such a hybrid organic/inorganic compound  $\text{Fe}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$  in the context of nontraditional magnetic ordering mechanisms.

Traditionally, magnetic ordering in solids was an orderly subject that considered orderly systems with identical magnetic ions distributed throughout a regular crystalline lattice on equivalent atomic sites [iv]. Five types of magnetic behavior were distinguished and they were diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism [iv]. The subject of magnetic ordering in solids was upset by theoretical and experimental studies of two related types of systems: amorphous solids (in which no two atomic sites are equivalent) and disordered solids (in which different atoms occupy randomly the sites in a regular lattice). These studies lead to new types of ordering, which received new and unusual designations such as: speromagnetism and sperimagnetism, to name just the two of interest in this paper [v, vi].

To provide a framework for our discussion, consider the following hamiltonian [vii]:

$$H = -2 \sum_{i,j} J_{ij} \vec{S}_i \vec{S}_j - \sum_i D_i S_{i,z} \quad (1)$$

where  $J_{ij}$  is the exchange coupling constant between the spins at sites  $i$  and  $j$ , while  $D_i$  is the constant describing the crystal field (the single ion anisotropy term at site  $i$ ), and may have a distribution of

values in magnitude and may vary randomly in orientation. When the exchange term is much stronger than the anisotropy term and if the exchange is random but of the same sign a ferromagnetic or an antiferromagnetic ground state is achieved for positive or negative coupling constants, respectively. If the exchange term dominates and  $J_{ij}$  has both positive and negative random values one gets various types of spin-glass systems [viii]. If, however, the second term is dominant a random anisotropy magnet is obtained. The state in which the spins in a domain are frozen into more or less random orientations, with average correlations over at most one-two interatomic distances, in an isotropic fashion, was called speromagnetic [v,vi]. If the correlation length is longer due to stronger exchange interactions (the anisotropy remaining dominant) a correlated speromagnet is obtained [ix].

When the system consists of two different types of spin sites as in rare-earth/transition-metal alloys the Hamiltonian is more complicated:

$$H = -2\sum_{i,j} J_{ij} \vec{S}_i \vec{S}_j - 2\sum_{i,j} J_{ij} \bar{s}_i \bar{s}_j - 2\sum_{i,j} J_{ij} \vec{S}_i \bar{s}_j - \sum_i D_i S_{i,z} - \sum_i D_i \bar{s}_{i,z} \quad (2)$$

a distinction having to be made between the two spins, their anisotropies, and the interactions between them. The cases of special interest are those in which the third term has a negative coupling constant leading to antiferromagnetic interactions. If the exchange terms dominate the anisotropy terms and if the randomness in exchange is small a ferrimagnetic state is achieved while if the random anisotropy prevails a sperimagnet is obtained. A sperimagnet comprises two (or more) magnetic species with the moments of at least one frozen in random directions [v,vi].

Depending on the strength of the random exchange (RE) and of the random anisotropy (RA) energies, as compared to temperature ( $T$ ), one can get various types of transitions on lowering  $T$ : In the random anisotropy plane the system can go from a paramagnet (PM) to a correlated speromagnet (CSM) at small anisotropies, or from a PM to a speromagnet (SM) at large anisotropies [ix]. When the random anisotropy varies with temperature there is also the possibility for double transition, from PM to CSM to SM, as marked by the arrow labeled 1. In the random exchange plane, at small randomness of the exchange integral, the transition is from a PM to a ferromagnet (FM) while at strong randomness (both positive and negative  $J_s$ ) from a PM to a spin glass (SG). Reentrance is possible when the system undergoes two transitions, from PM to FM, followed at lower  $T$  by a second transition to a mixed phase (M), in which some or all components of the spin are frozen but a net magnetic moment is still achieved (see arrow 2).

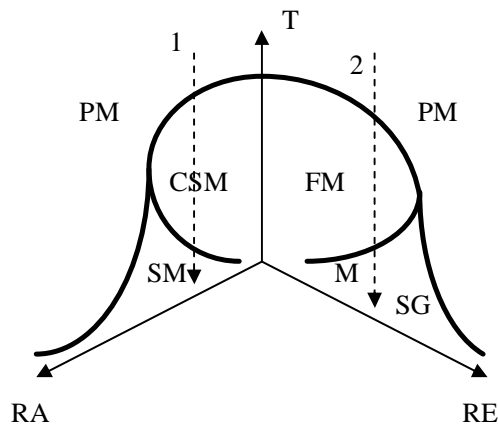


Fig. 1. Schematic phase diagram of possible magnetic states in the presence of random exchange (RE) and random anisotropy (RA): paramagnet (PM), ferromagnet (FM), speromagnet (SM), correlated speromagnet (CSM), spin-glass (SG) and mixed FM & SG (M). (see text.)

We note in the end of this introduction that if the exchange constant is negative and the system

consists of two species of magnetic ions the double transition marked with arrow 1 is from a paramagnet to a correlated sperimagnet and then to a sperimagnet. Such transitions have been observed experimentally and reported for rare-earth/transition-metal alloys [ix]. The theoretical explanation was later proposed [x] and dealt with temperature dependent random anisotropy.

Magnetic studies of  $V(\text{TCNE})_{x,y}(\text{solvent})$  systems (solvent = acetonitrile, tetrahydrofuran, or dichloromethane) revealed [xi] 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 [ix]. It was also shown that the spinless organic solvent has a key role in determining magnetic properties [xi]. Recently  $M(\text{TCNE})_{2,x}(\text{CH}_2\text{Cl}_2)$  ( $M = \text{Mn}, \text{Fe}$ ) have been synthesized [xii].  $\text{Mn}(\text{TCNE})_{x,y}(\text{CH}_2\text{Cl}_2)$  was found to be a reentrant spin glass with successful data collapse in the static scaling at the higher temperature transition and in the dynamic scaling at the low  $T$  transition [xiii]. In the following we discuss the case of  $\text{Fe}(\text{TCNE})_{x,y}(\text{CH}_2\text{Cl}_2)$  and compare and contrast with earlier studies on  $M(\text{TCNE})_{x,y}(\text{solvent})$  ( $M = \text{V}, \text{Mn}$ ).

## 2. Experimental

All magnetic data were taken on polycrystalline samples that had been handled under argon and sealed in quartz EPR tubes, under vacuum, to avoid possible degradation in air. 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. Static magnetization data were collected using a Quantum Design MPMS-5 SQUID magnetometer with a 5.5 T superconducting solenoid. Dynamic susceptibility data at various frequencies ( $5 \leq f \leq 10000$  Hz) were recorded on a Lake Shore 7225 ac susceptometer with a 5 T superconducting coil.

## 3. Results and discussion

$\text{Fe}(\text{TCNE})_{2,y}(\text{CH}_2\text{Cl}_2)$  has unpaired spins on both the  $d$  orbitals of the transition metal ion and the  $\pi^*$  molecular orbital of the [TCNE] bridging organic ion. The results of a Mössbauer spectroscopy study of  $\text{Fe}(\text{TCNE})_{2,x}(\text{CH}_2\text{Cl}_2)$  indicated that iron is present as high spin ( $S = 2$ )  $\text{Fe}^{\text{II}}$  [xii]. Based on infrared absorption measurements it was concluded the cyanocarbon acceptor is present as the [TCNE] anion and has a net spin of 1/2 [xii]. Elemental and thermogravimetric analyses of various samples from different batches lead to an estimation of the solvent content of  $0.4 < x < 1.1$  [xii]. For the samples reported here the solvent content was estimated to  $x = 0.7$ . Also, unlike the reentrant  $V(\text{TCNE})_{x,y}(\text{solvent})$ , for which the structural correlation length is short (less than 25 Å [xi]), but similar to  $\text{Mn}(\text{TCNE})_{2,y}(\text{CH}_2\text{Cl}_2)$ , the diffraction patterns for  $\text{Fe}(\text{TCNE})_{2,x}(\text{CH}_2\text{Cl}_2)$  exhibit sharp X-ray diffraction lines indicating partially crystalline, much less disordered structures [xii].

Isothermal magnetization data,  $M(H)$ , were collected for scaling analyses at various  $T$  by zero-field cooling and measuring from 0 to 5.5 T for both compounds. The traditional approach to scaling for systems with the spontaneous magnetization as order parameter [xiv] is to measure  $M(H,T)$  near  $T_c$  and attempt to collapse the data onto two universal curves (corresponding to data above and below  $T_c$ ) by plotting either on logarithmic axes  $M/t^\beta$  versus  $H/t^{\beta\delta}$  or on linear axes  $(M/t^\beta)^2$  versus  $H/(M t^\gamma)$ , Fig. 2. For  $\text{Mn}(\text{TCNE})_{2,x}(\text{CH}_2\text{Cl}_2)$  it is found that  $T_c = 75$ ,  $\beta = 0.35$ , and  $\delta = 3.86$  while the range of reduced temperature was  $0.005 \leq |t| \leq 0.18$  [xiii]. In the case of  $\text{Fe}(\text{TCNE})_{2,x}(\text{CH}_2\text{Cl}_2)$  the corresponding values are  $T_c = 97$  K,  $\beta = 0.45$ , and  $\delta = 2.5$ , with  $0.001 \leq |t| \leq 0.23$ .

The remanent magnetization, measured on warming, in zero applied dc magnetic field, after cooling in small fields, was shown to have a similar shape for both compounds [xiii,xv]. In both cases it has a sharp decrease upon increasing the temperature, followed by a slow decrease up to  $T_c$ . Beyond those temperatures the remanent magnetization vanishes. Based on similar results obtained on various ferrites [xvi], the unusual shape of the remanent magnetization was attributed [xiii,xv], to the ferromagnetic 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 high spin  $3d^5$   $\text{Mn}^{\text{II}}$  ions in an octahedral environment has a nondegenerate orbital ground

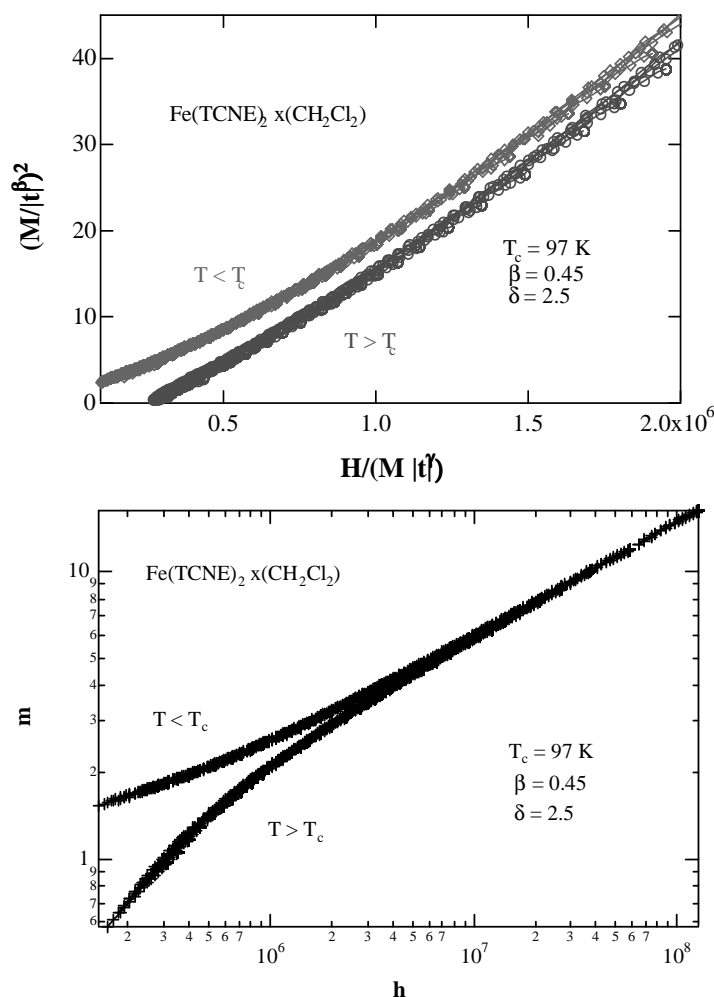


Fig. 2. Ferromagnetic-like scaling analyses with data collapse on linear axes (above) and logarithmic axes (below) for  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ .

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 in this case, and the Landé  $g$ -factor is expected to be close to the spin only value [xvii]. In the case of the  $3d^6$   $\text{Fe}^{\text{II}}$  ion in an octahedral crystal field the ground state is an orbital triplet ( ${}^5T_{2g}$ ), with the orbital momentum being only partially quenched, leading to large deviations of the Landé  $g$ -factor from the spin only value. Any small distortion from the octahedral symmetry together with the spin-orbit interaction will remove some or all of the orbital degeneracy and introduce magnetic anisotropies with large zero-field splitting, affecting the overall magnetic behavior of the compound [xvii]. In the case of  $\text{V}(\text{TCNE})_x \cdot y(\text{solvent})$ , an ideal octahedral environment for  $\text{V}^{\text{II}}$  ( $3d^3$ ) is expected to cause no single-ion anisotropy; however, structural disorder leads to distortions of the octahedral environment and, likely, to random anisotropy [xi].

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization data (collected on warming in various applied dc fields) revealed a bifurcation of the FC and ZFC curves near the high  $T$  transition and strong irreversibilities that are more pronounced near the low temperature transition. Strong irreversibilities (showing large differences between the FC and ZFC magnetizations), with a field

dependence of the bifurcation point (the bifurcation temperature decreases [xviii] with increasing  $H$ ) are indicative of glassy behavior [xviii,viii], while for a typical magnet without disorder such irreversibilities are not expected or should be small [viii,xviii]. According to these criteria and based on the assumption of the dominance of random exchange for  $M = \text{Mn}$  and random anisotropy for  $M = \text{Fe}$ , it was suggested [xiii] that  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  has a reentrant behavior, (paramagnet to ferrimagnet to spin glass), while  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  has a double transition RAM behavior [xv].

The in-phase  $\chi'$  and out-of-phase  $\chi''$  components of the ac susceptibility were measured on

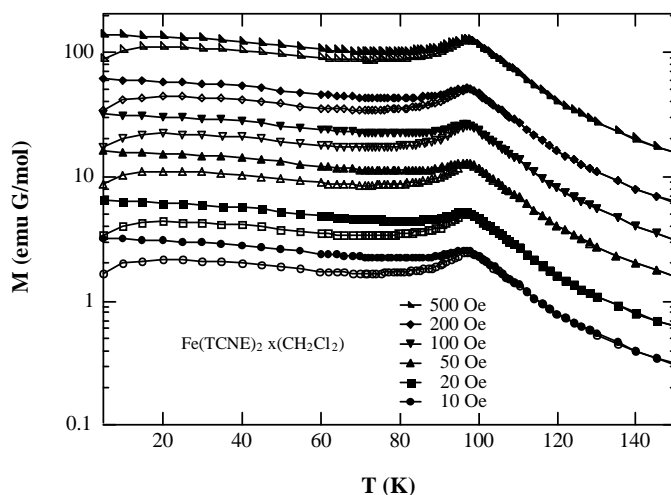


Fig. 3. FC and ZFC magnetization versus  $T$  for  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  at various applied dc magnetic fields.

warming in zero applied dc magnetic field and various ac frequencies for both compounds [xiii,xv]. For  $M = \text{Mn}$  the frequency dependence of  $\chi'$  and  $\chi''$  was observed only below  $\sim 30$  K and especially below  $\sim 10$  K, while for  $M = \text{Fe}$  the frequency behavior was modest, occurring especially in  $\chi''$  below  $\sim 20$  K. Generally, the frequency dependence of the ac susceptibility is indicative of slow relaxation processes, typical for spin glasses or spin glass-like materials such as RAM [viii,ix]. (Typical FM display frequency dependence due to domain wall pinning only at microwave frequencies, outside the range of the ac susceptibility measurements [viii].) Consequently, the ac susceptibility data are consistent with the suggestions based on the FC/ZFC magnetization studies that  $\text{Mn}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  has a reentrant SG behavior while  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$  has a double transition RAM behavior.

For both Fe-based and Mn-based compounds the irreversibilities and the increase of the magnetic moment appear to occur simultaneously, which leads us to speculate that there may be a connection between ferrimagnetism and the formation of the magnetically disordered state. Given the partial crystallinity of these compounds 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 various exchange interactions between sublattices may lead at low  $T$  to canted spin configurations. We further speculate 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. We can, therefore, extend the concept of sperimagnetism, traditionally applied to rare-earth/transition-metal alloys with both ferrimagnetic and random anisotropy behavior [ix], to  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ . In our case the role of the rare-earth and of the transition-metal ions are played by  $\text{Fe}^{2+}$  and [TCNE] respectively. Hence, we note once again the importance of the organic component (especially through the spin in the  $\pi^*$  molecular orbital) of this hybrid organic/inorganic molecule based magnet.

#### 4. Conclusion

We reported and reviewed magnetic studies of  $\text{Fe}(\text{TCNE})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ , a high  $T_c$  molecule-based

magnet. 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  $T$  irreversibilities, indicated reentrant behavior. Scaling analyses revealed successive transitions to a correlated sperimagnet ( $\sim 97$  K) and a sperrimagnet ( $< 20$  K) for  $M = \text{Fe}$ .

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