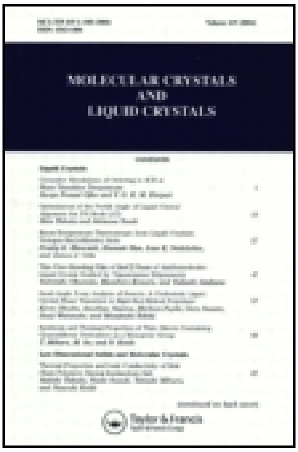

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On the Independent Cation and Anion Sub-Lattice Long Range Antifferomagnetic Orderings of Layered Ferricenium Tetra-Halo Ferrates: Effects of Highly Different Magnetic Symmetries

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ON THE INDEPENDENT CATION AND ANION SUB-LATTICE LONG RANGE ANTIFFEROMAGNETIC ORDERINGS OF LAYERED FERRICENIUM TETRA-HALO FERRATES: EFFECTS OF HIGHLY DIFFERENT MAGNETIC SYMMETRIES

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Abstract The anions and cations of the complex $[Fe(cp)_2][FeBr_4]$ (cp=h^5-cylopentadiene) behave as isolated non-interacting Heisenberg and Ising layers respectively. The S=1/2 cations order at ~ 2.5K while the S=5/2 anions order at ~ 12.5K. A variety of experimental data confirm independent 3D antiferromagnetic ground states for the component ions as opposed to the usual expectation of ferrimagnetism resulting from the collinear antiferromagnetic interaction of cation and anion sublattices of highly different spin in e.g., a simple two magnetic sublattice system.

INTRODUCTION

The layered magnet ferricenium tetrachloroferrate $[Fecp_2]FeCl_4]$, has recently (1) been shown to act as a composite material with separate cation and anion sublattice ordering temperatures through a combination of low field dc and ac susceptibility measurements as well as zero-field Mossbauer spectroscopy. While the anion sublattice orders near 4.2K, the cation sublattice remains paramagnetic to 3.8K, a relative shift of ordering temperature of nearly ten percent. Each sublattice orders in a three-dimensional antiferromagnetic ground state for which there is no absorbtion in the ac-susceptibility i.e., $\chi_m''=0$. $[Fe(cp)_2][FeCl_4]$ is an orthorhombic (Pmna) salt having the layered structure (2) shown in Figure 1.

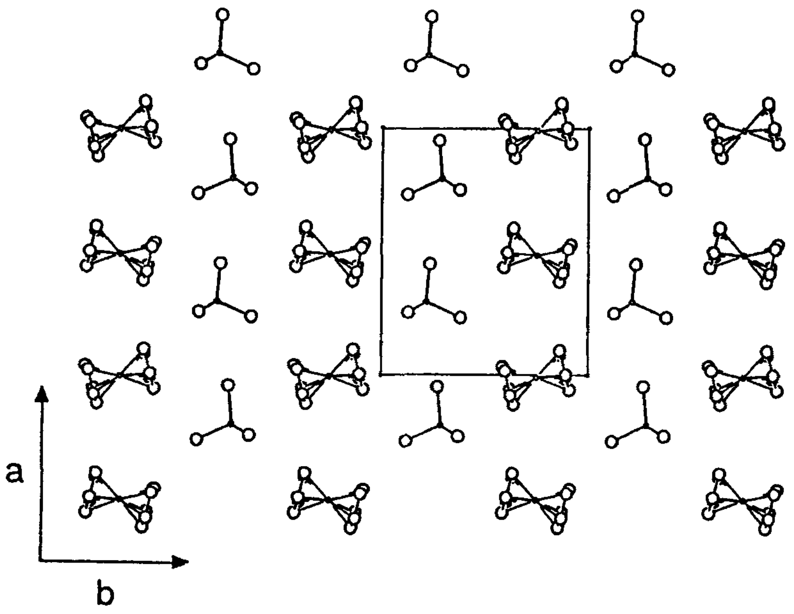


FIGURE 1 The layered orthorhombic structure of $[Fe(cp)_2]FeCl_4]$ after Paulus(2).

We have now extended these investigations to $[Fe(cp_2)][FeBr_4]$ which is like-wise orthorhombic (Pmna)(3). The extension is clearly not trivial! A similar but much more dramatic separation of the sublattice ordering temperatures is observed, i.e., $T_N(S=5/2$ anion$) \sim$ 12.5K, $T_N(S=1/2$ cation$) \sim$ 2.5K or $\Delta T \approx$ 10K! Again, there is no out of phase component (χ''_m) in high resolution a.c.-susceptibility measurements thus ruling out simple ferro- or ferri- magnetic ground states.

A combination of Mossbauer spectroscopy chemical isomer shifts, and iron-57 isotopic enrichment of the S=5/2 anion lattice clearly confirms that the latter orders at the higher temperature for each compound. This novel and to our knowledge unprecedented behavior is likely somehow a function of the magnetic symmetry extremes possible in these materials, namely Ising (S=1/2) vs Heisenberg (S=5/2). The behaviors of the per-methylated ferricenium systems (T_c's ranging ~0.6K to ~2.6K) are also of interest in the present context. In summary, the anions of $[Fe(cp)_2][FeBr_4]$ and $[Fe(cp^*)_2][FeBr_4]$ order at higher temperatures than the corresponding chlorides in part because of the higher polarizability of bromine thus leading to greater overall electron spin delocalization.

Results

Some specific results for $[Fe(cp)_2][FeBr_4]$ are given in Figures 2 and 4 and 5. In Figure 2, χ_m vs T (a.c. susceptibility data taken at H_o=1 Oe and 125 Hz), the separate antiferromagnetic transition for the anion lattice (with $\chi_m''=0$) is apparent at ~ 12.5K. Similar behavior (i.e., $\chi''_m=0$) is observed for the cation lattice at T ~ 2.5K.

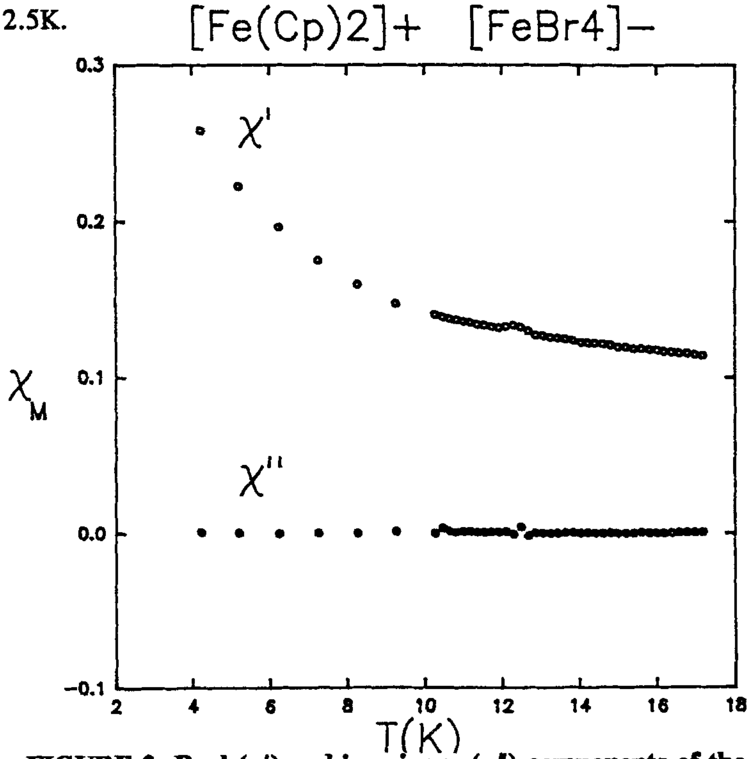
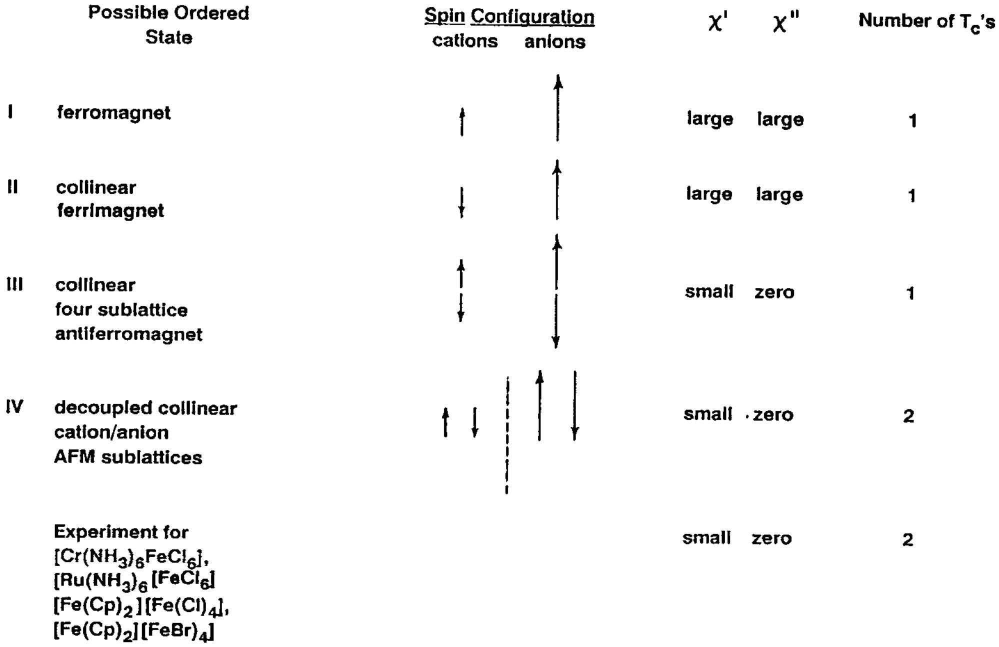


FIGURE 2 Real (χ') and imaginary (χ'') components of the a.c. susceptibility data for $[Fe(cp)_2]FeBr_4]$ above 4.2K

The fact that $\chi_m''=0$ and χ_m' is small is inconsistent with any type of 3D ferro, collinear ferri or anti-ferromagnetic ground state that one can readily envision for this system as summarized in figure (3) save choice IV.



	Possible Ordered State	Spin Configuration cations	Spin Configuration anions	χ'	χ''	Number of T_c's
I	ferromagnet	↑	↑	large	large	1
II	collinear ferrimagnet	↓	↑	large	large	1
III	collinear four sublattice antiferromagnet	↑ ↓	↑ ↓	small	zero	1
IV	decoupled collinear cation/anion AFM sublattices	↑ ↓	↑ ↓	small	zero	2
	Experiment for $[Cr(NH_3)_6FeCl_6]$, $[Ru(NH_3)_6[FeCl_6]$ $[Fe(Cp)_2][Fe(Cl)_4]$, $[Fe(Cp)_2][FeBr)_4]$			small	zero	2

FIGURE 3 Some possible magnetic ground-states for collinear cation-anion spin arrangements

On the other hand, in relatively small applied d.c. fields as in Figure 4(d.c. squid magnetometry results at $H_0=100$ Gauss), the anion sublattice moments are apparently essentially totally decoupled leading to a high moment state while the cation lattice is still AF-ordered at low T.

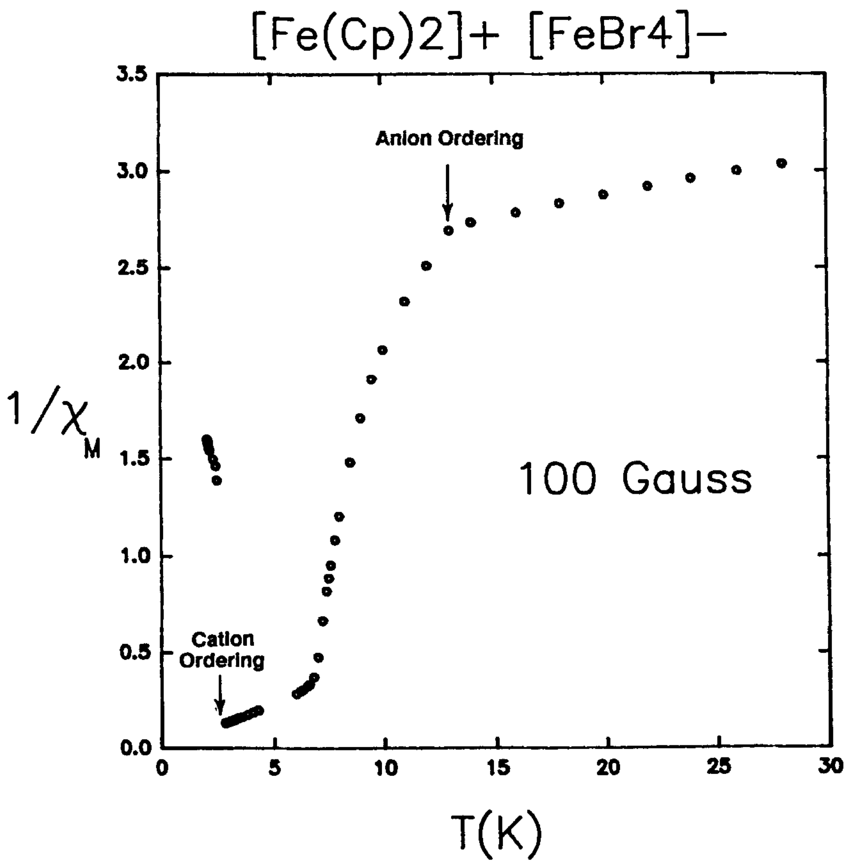


FIGURE 4 Reciprocal susceptibility of [Fe(cp)$_2$]FeBr$_4$] at 100 Gauss

These states are reflected in the reciprocal susceptibility data of Figure 4 wherein a large drop in χ_m^{-1} is observed between 12 and 13K and then χ_m^{-1} abruptly rises below ~ 2.5K. Finally we refer to sample (zero field) iron-57 Mossbauer spectroscopy results in Figure 5.

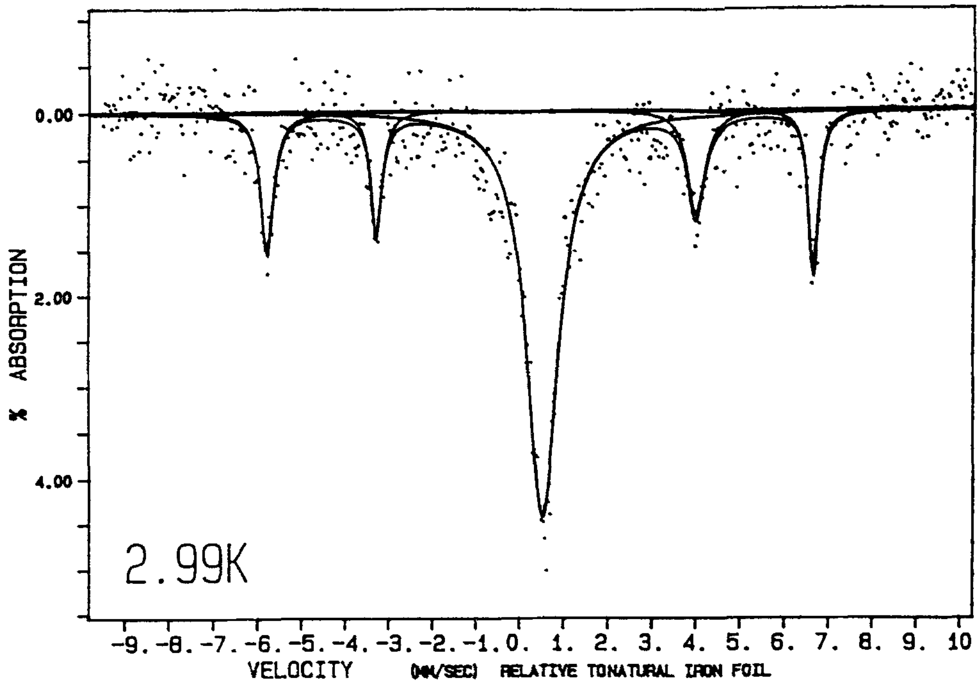


FIGURE 5 **Zero field Mossbauer spectrum of [Fe(cp)$_2$]FeBr$_4$] at 2.9K**

At 2.9K,only the S=5/2 FeBr$^-_4$ sublattic is ordered. This corresponds to the Zeeman split background pattern in the figure for which the internal hyperfine field is ~380 kOe. This result is some ~ 7 to 8T less than values typical (3) of S=5/2 FeBr$^-_4$ anions and suggests that the anion lattice is not magnetically saturated at this temperature. The intense singlet near the center of the spectral pattern reflects the ferricenium cations still in their rapidly relaxing paramagnetic state at this temperature. The center shift of this component is 0.50 mm/sec relative to iron metal, a value typical (3) of Fe(cp)$_2^+$ cations. As expected, in view of the susceptibility data, the latter intense singlet component hyperfine splits below 2.5K corresponding to its long range ordering.

Summary

Complete details for this system, and the related [Fe(cp)$_2$] [FeCl$_4$], [Fe(cp*)$_2$][FeCl$_4$],[Fe(cp*)$_2$] [FeBr$_4$] complexes including x-ray structure determinations, field and temperature dependence of Mossbauer spectra and magnetic susceptibility will be published subsequently elsewhere (4).

In conclusion, the unprecedented magnetic behavior observed herein, i.e., independent 3D-AF orderings of intimately associated paramagnetic layer sublattices appears to occur for another rather different class of compounds, namely "rock salt like" structures such as $[Cr(NH_3)_6][FeCl_6]$ and $[Ru(NH_3)_6][FeCl_6]$. This work is considered in another contribution (5) to these proceedings. *Supported by the Div of Materials Research †Current Address: Xavier University.

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5. See W.M. Reiff and W.E. Hatfield, in these proceedings.