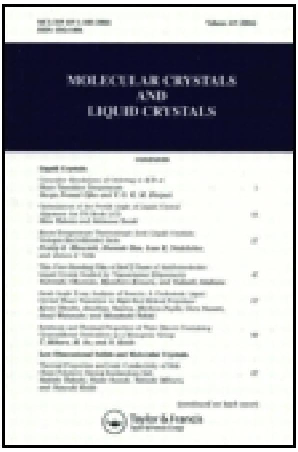

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ON THE MIXED VALENCE BEHAVIOR AND COOPERATIVE 3D ORDERING OF A SERIES OF TRIS-OXALATO FERRATES: $Bu_4N\{M\,Fe^{III}(ox)_3\}(M=Mn^{II}(A),Fe^{II}(B),\ Co^{II}(C),\ Ni^{II}(D)$ AND $\phi_4P\{Fe^{II}Fe^{III}(ox)_3\}(E)$: NEW FERRIMAGNETS

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Abstract A combination of a.c. susceptometry and Fe^{57} Mossbauer spectroscopy measurements confirm valence trapped 3D-ferrimagnetically ordered ground states for the title compounds save (A) that orders antiferromagnetically with a very broad maximum in χ'_m centered at ~50K. Their ground state magnetic behavior is contrasted with the previously demonstrated ferromagnetism of $Bu_4N\{Fe^{II}Cr^{III}(ox_3)\}$ and $\phi_4P\{Mn^{II}Cr^{III}(ox_3)\}$.

INTRODUCTION

As part of our continuing interest in dynamic mixed valence behavior, we have studied the title compounds using Fe^{57} Mossbauer spectroscopy and a.c. susceptometry over the range 4.2K to 300K. Unfortunately, we find that all of these materials are valence trapped on the Fe^{57} Mossbauer spectroscopy time scale (100ns) showing typical high-spin iron III spectra for (A), (C) and (D) and valence trapped high-spin Fe II and Fe III for (B) and (E). The initial studies (1) in this area focused on the $Bu_4N\{MCr(ox)_3\}$series, $M=Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} and $\phi_4P\{MnCr(ox)_3\}$(F), (2), all of which were found to be genuine bulk 3D ferromagnets, albeit, with low T_c's ($\leq$14K) with the butyl systems assumed to have 3D-network structures.

RESULTS

For the present systems we observe interesting ferrimagnetic behavior for (B), (C) and (D), and $\phi_4P\{Fe^{II}Fe^{III}(ox)_3\}$(E) with high critical temperatures: 44K, 30K, 28K and 37K respectively and antiferro-magnetism for (A). Our powder x-ray diffractometry studies show (E) isomorphous with (F) whose single crystal x-ray study confirms a layered structure. The ferrimagnetism of the present systems is accompanied by strong out of phase absorption ($\chi_m'' \neq 0$) and is clearly complex for (C) and (E) with multiple transitions in evidence for χ_m' and χ_m'' in the vicinity of $T_{Critical}$ suggesting possible changes of magnetic structure (spin reorientation) just below the initial ordering temperature. The a.c. susceptibility for the case of (B) is shown in Figure 1.

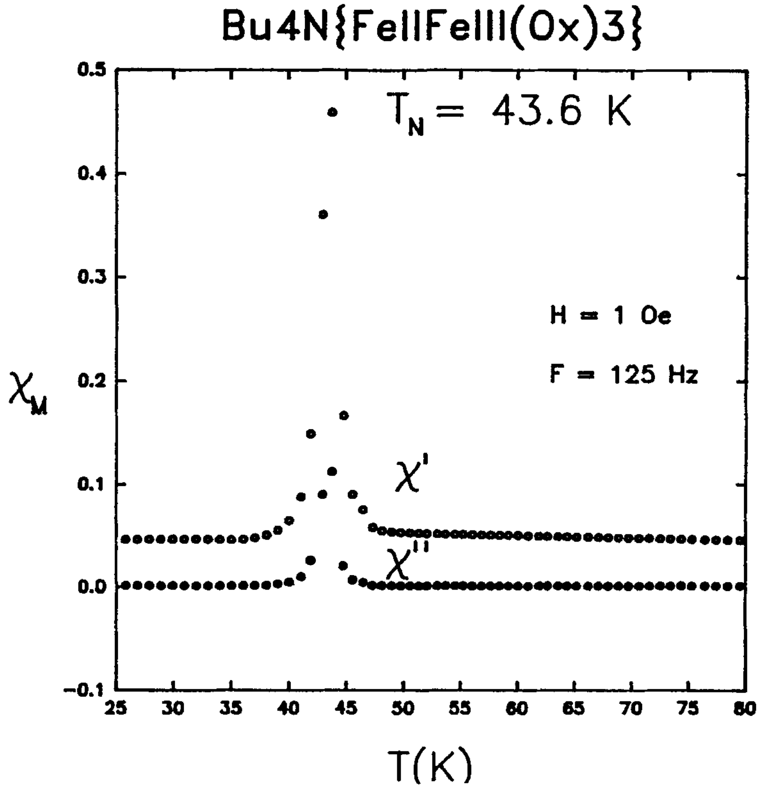

FIGURE 1 Real (χ'_m) and imaginary χ''_m components of the a.c. susceptibility of $Bu_4N\{FeII\ FeIII(Ox)3\}$

The 4.2K Mossbauer spectrum of $Bu_4N\{Fe^{II}Cr^{III}(ox)_3\}$ (G) corresponds to the perturbation scheme ΔE(quadrupole) > > H(internal) i.e., a low velocity doublet and high velocity triplet indicating that V_{zz} (the principal component of the electric field gradient tensor) is negative at the ferrous sites (3). This was useful in the deconvolution of the spectra of (B) and (E) whose high spin ferric component exhibits an additional classical six line pattern (i.e., H(internal) > > ΔE(quadrupole), with H(internal) ≈ 53T vs only ~ 4T for the Fe^{II} as seen in Figure 2.

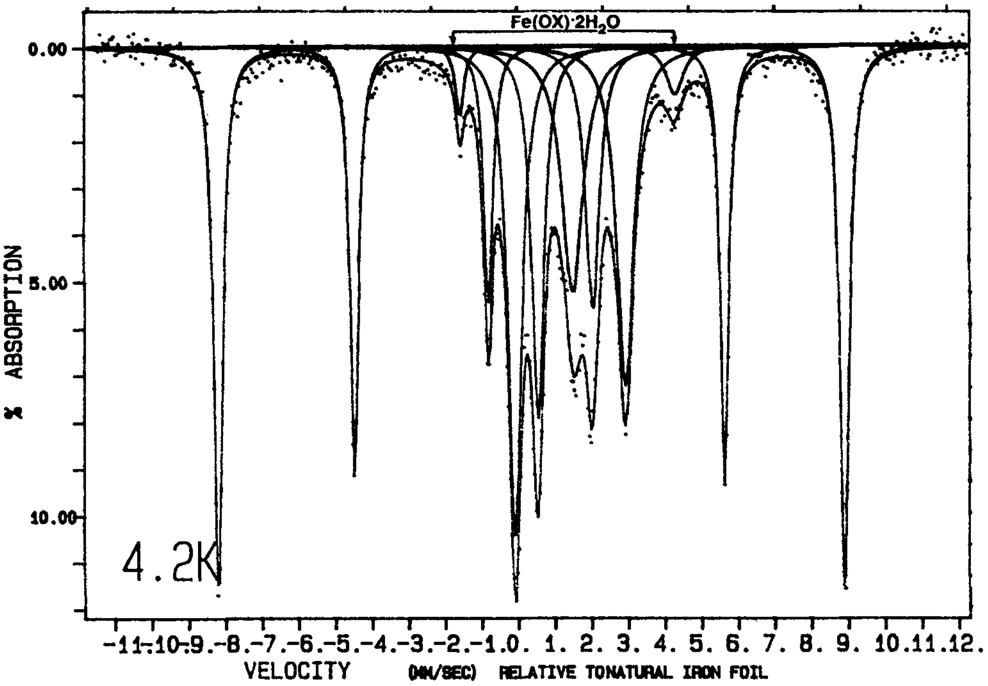

FIGURE 2 Iron-57 Mossbauer spectrum of Bu_4N {FeII FeIII $(ox)_3$} at 4.20K, arrows indicate $Fe(ox)\cdot 2H_2O$ contamination

At low temperatures, Figure 3, a single high spin Fe^{III} environment is apparent for compounds (A) and (C) with H(internal) ≈ 52T.

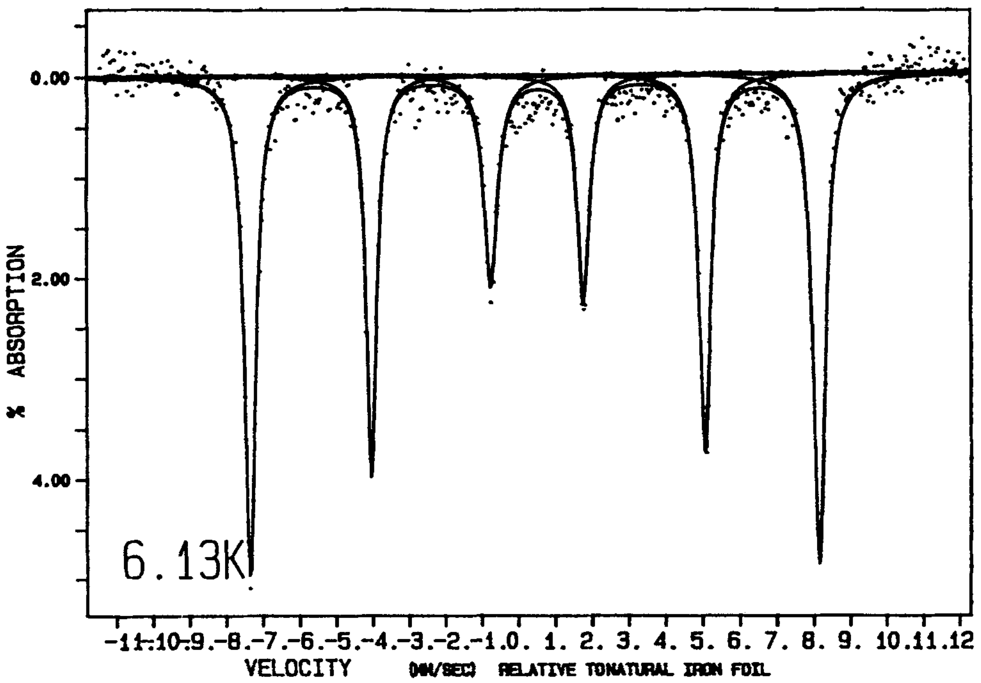

FIGURE 3 **Mossbauer spectrum of $Bu_4N\{MnIIFeIII(ox)_3\}$ at 6.13K**

The values for the Curie temperatures of (F) and (G) as determined via a.c. susceptometry are 5.6K and 12K in good agreement with those found (5.9K and 12K) using d.c. magnetometry (1, 2). The near zero field a.c. measurements with $\chi''_m \neq 0$ Figures 4 and 5 further confirm the 3D ferromagnetic ground states of these materials and eliminate any possibility of some type of field induced (metamagnetic) behavior in the original studies of these materials, (1) and (2) at 0.1 and 0.2T respectively.

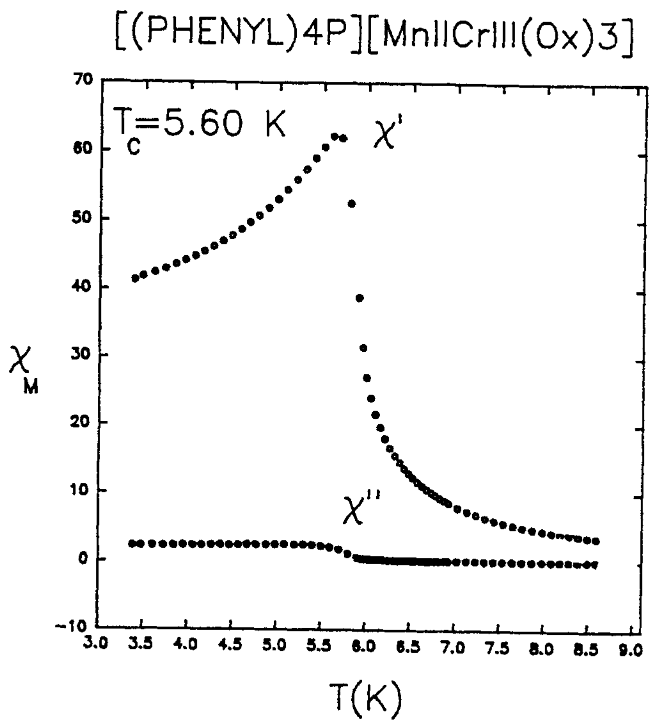

FIGURE 4 The real (χ'_M) and imaginary (χ''_M) components of the a.c. susceptibility of $\phi_4P\{MnIICrIII(ox)_3\}$

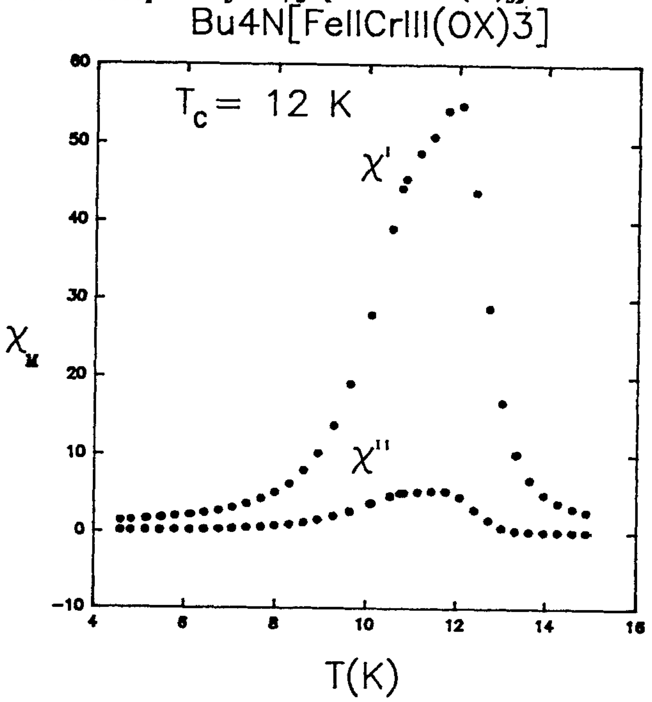

FIGURE 5 Real (χ'_M) and imaginary (χ''_M) components of the a.c. susceptibility of $Bu_4N\{FeII\ CrIII(ox)_3\}$

The shapes of the susceptibility curves (particularly χ_m') for (F) and (G) are quite different. The a.c. response of (G) appears to suggest essentially single domain behavior below low T_c while the behavior of (F) is more reminiscent of a multi-domain material (4). Perhaps this difference reflects a fundamental difference in molecular structures, although the similarity of T_c for the Bu_4N^+ and ϕ_4P^+ $Mn^{II}Cr^{III}$ analogues has been used (2) to suggest a 2D structure for the former.

Summary

Finally, we point out that chemical analyses and Mossbauer spectra indicate a small degree of contamination from (~ 2% to 8%) (for compounds (B), (C) and (D)) with the well known chain polymer $Fe(ox){\cdot}2H_2O$. That is, some reduction of the tris-oxalato ferrate III apparently occurs during the preparative stage. This in turn is likely related to photo-sensitivity of $K_3[M^{III}(ox)_3]$ core systems in general as previously suggested (5) specifically for $K_3[Co(ox)_3]{\cdot}3H_2O$. In any event, the presence of a few percent $Fe(ox){\cdot}2H_2O$ should have no measurable effect on the magnetic properties of the systems reported on herein and in references (1) and (2). Its ground state is 3D antiferromagnetic ($T_N=11.7K$) (6,7). Moreover, it is a highly 1D a.f. chain with strong intra-chain exchange ($T_\chi(max) \sim 40K$). Thus in the temperature range of relevance (30K to 45K), the present (Co and Ni) ferrimagnets exhibit molar susceptibilities 25 to 50 times greater than that of any $Fe(ox){\cdot}2H_2O$ impurity.

REFERENCES

* Author to whom correspondence should be addressed, supported by the NSF Division of Materials Research

1. H. Tamaki, Z.J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, J. Am. Chem. Soc., 114, 6974, (1992)
2. S. Decurtins, H.W. Schmalle, H.R. Oswald, A. Linden, J. Ensling, P. Gütlich and A. Hauser, Inorganica Chimica Acta, 65 216, (1994)
3. W.M. Reiff, Coord.Chem.Rev., 2, 10, 37 (1973)
4. D.W. Carnegie, Jr., C.J. Tranchita, and H. Claus, J. Appl. Phys., 50 (1979)
5. J.C. Bailar and E.M. Jones, Inorganic Syntheses, in H.S. Booth (ed.), (Vol. 1, McGraw-Hill, New York), 37, (1939),
6. S. Simizu, J.Y. Chen, S.A. Friedberg, J. Martinez and G. Shirane, J. Appl. Phys. 61, (1987)
7. J.Y. Chen, S. Simizu and S.A. Friedberg, J. Appl. Phys., 57, (1985)