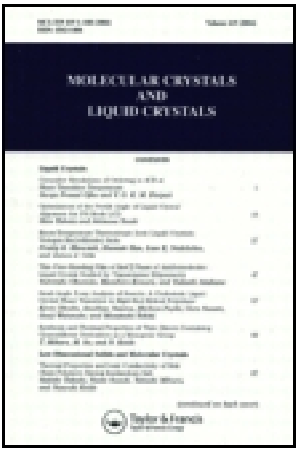

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Reductive Topotactic Metal Ion Insertion Chemistry of Trivalent Iron III Networks as an Approach to New Magnetic Materials

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REDUCTIVE TOPOTACTIC METAL ION INSERTION CHEMISTRY OF TRIVALENT IRON III NETWORKS AS AN APPROACH TO NEW MAGNETIC MATERIALS

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Abstract The basic magnetism of new magnetic materials obtained by the mild condition metal ion insertion chemistry of inorganic high-spin iron III networks is highlighted.

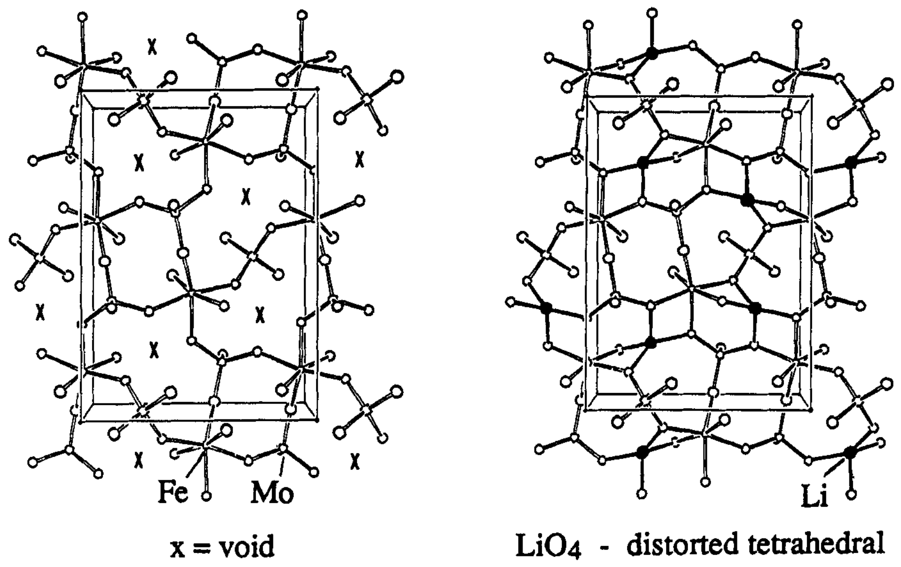
INTRODUCTION

Interesting new magnetic materials are readily obtained via mild condition, heterogeneous, reductive lithium and proton insertion reactions of classical high-spin ferric inorganic networks such as anhydrous monoclinic $Fe_2(SO_4)_3$ and $Fe_2(MoO_4)_3$. Some typical syntheses are:

$$2\ LiI(SOLN) + Fe_2^{III}(SO_4)_3(S) \xrightarrow[\underline{\text{slurry}}]{CH_3CN} \underset{(A)}{Li_2Fe_2^{II}(SO_4)_3(S)} + I_2(SOLN)$$

$$2HI(G) + Fe_2^{III}(SO_4)_3(S) \xrightarrow[\underline{\text{slurry}}]{CH_3CN} \underset{(B)}{H_2Fe_2^{II}(SO_4)_3(S)} + I_2(SOLN)$$

Previous x-ray and neutron diffraction investigations show that these new high-spin ferrous materials e.g., $Li_2Fe_2^{II}(MoO_4)_3$ (C) from $Fe^{III}_2(MoO_4)_3$ (1,2) and $LiFe^{II}Cl(MoO_4)$ (D) from $Fe^{III}Cl(MoO_4)$ (2) are formed topotactically with lithium cations occupying oxygen coordinated voids of the unreduced precursor networks. This insertion process is seen in Figure 1 where the lithium ion locations (as tetrahedral LiO_4 chromophores) were ascertained via Rietveld refinement procedures of powder neutron diffraction data (2).



Corner-sharing FeO6 (octahedral) and MoO4 (tetrahedral) framework.

FIGURE 1 The $Fe_2(MoO_4)_3$ network structure before (left) and after (right) lithiation showing FeO_6, MoO_4, and LiO_4 units.

Mossbauer spectroscopy and d.c. magnetometry confirm complete reduction to ferrous and long range magnetic order. The synthetic reduction sequence and long range magnetic order are highlighted by the Mossbauer spectra of Figures 2 and 3 respectively for the specific case of compound (B).

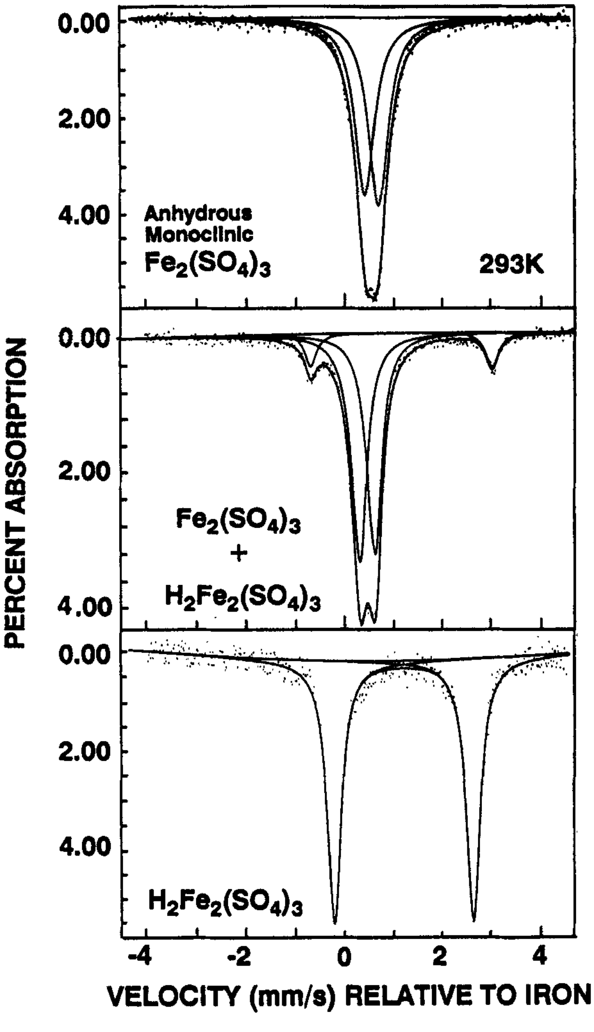


FIGURE 2 Some ambient temperature Mossbauer spectra showing the conversion of $Fe_2(SO_4)_3$ to $H_2Fe_2(SO_4)_3$.

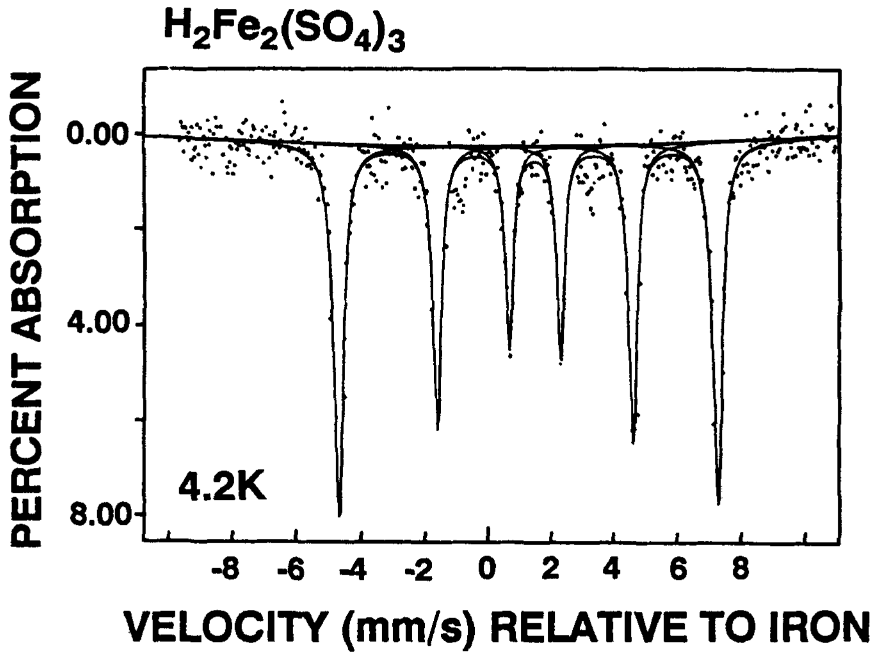


FIGURE 3 Mossbauer spectrum of $H_2Fe_2(SO_4)_3$ at 4.2K (compound (B))

In passing we note that insertion compound **(C)** is weakly ferromagnetic (1) - T_N = 13K and that **(D)** is anti-ferromagnetic (3) - T_N = 68.5K.

Results

Herein, a.c. susceptometry is used to further characterize the three dimensional magnetic ground state of some of these new iron II phases. Thus **(A)** and **(B)** order near 14K (actually two sharp transitions ~ 13.5K and 16K) and 28K respectively. Very strong out of phase absorption ($\chi''_m \neq 0$) for **(A)** suggests ferrimagnetic order (16K) and spin reorientation (13.5K) consistent with *two iron II environments observed in its Mossbauer spectra*. On the other hand, a single transition in χ_m with $\chi''_m = 0$ for **(B)** indicates a 3-D antiferromagnetic ground state although $\theta \approx +30K$ suggests dominant ferromagnetic interactions. In accord with the latter, σ vs H for (B) exhibits a sharp, low field (<50 Oe) metamagnetic transition to a high moment state. The precursor material, anhydrous monoclinic $Fe_2(SO_4)_3$, orders three dimensionally as an L-type ferrimagnet at 28.6K with two Fe III sites apparent in the Mossbauer spectrum corresponding to the ordered state (4).

The a.c. susceptometry data for compound (B) are shown in Figure 4 where a sharp a.f. ordering transition is obvious at ~28K in excellent agreement with $T_{Neél}$ suggested by a study of temperature dependence of the Mossbauer spectra (~30K) for (B).

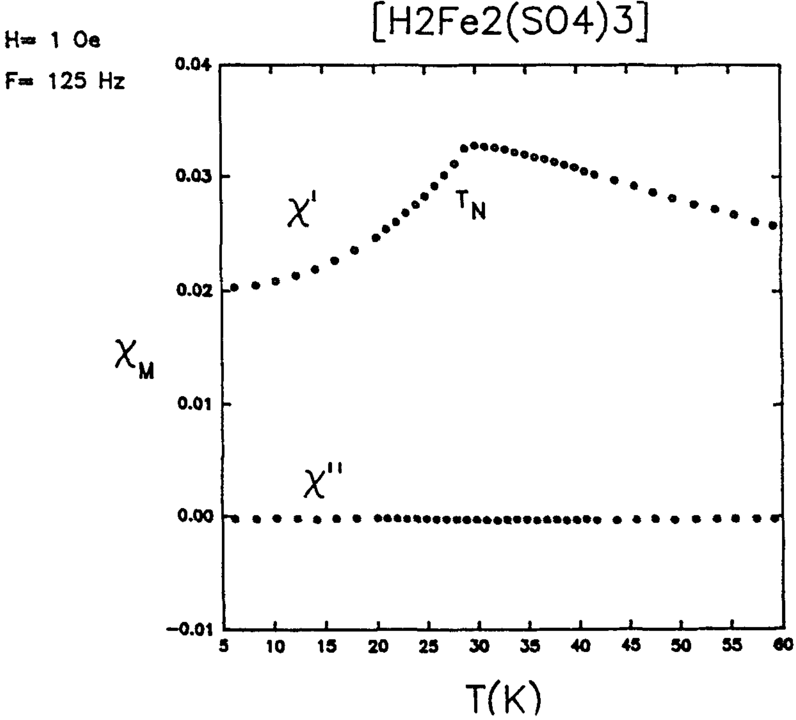


FIGURE 4 The real (χ'_m) and imaginary (χ''_m) components of the a.c. susceptibility of $H_2Fe_2(SO_4)_3$.

The limiting low temperature Mossbauer spectrum Figure 3 confirms only one type of iron II site consistent with a simple two sublattic 3D-A.F. ground state and the temperature variation of B's magnetic moment, Figure 5.

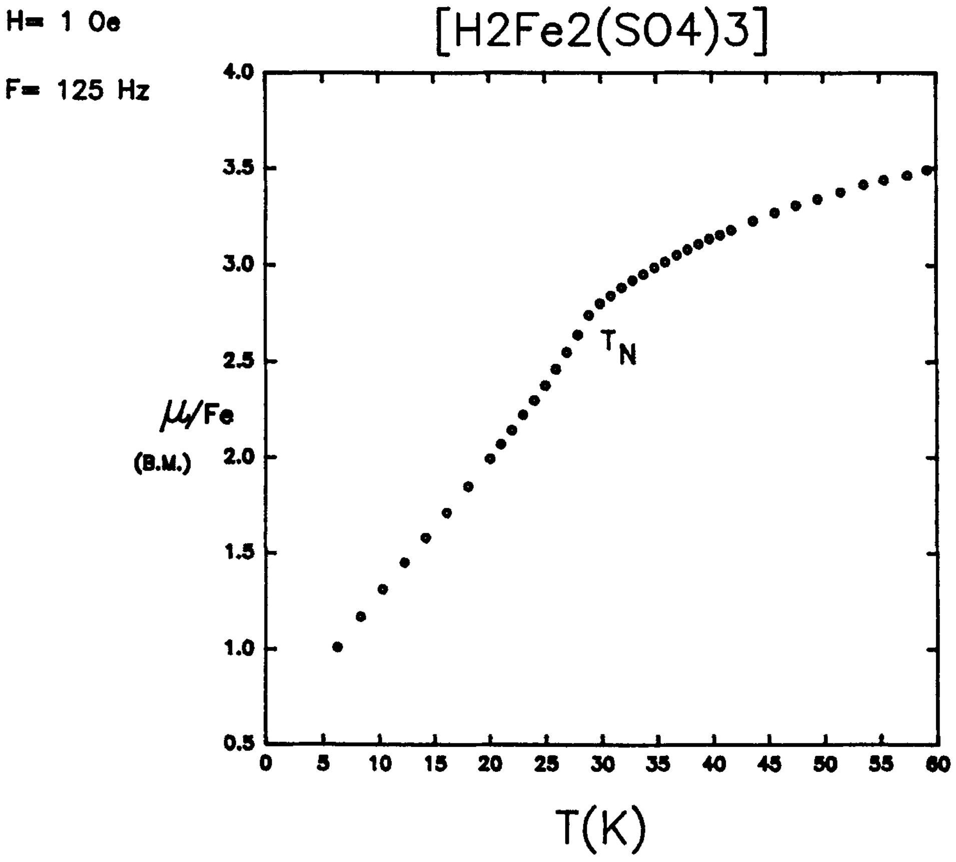


FIGURE 5 The temperature dependence of the magnetic moment of $H_2Fe_2(SO_4)_3$, H_{ac}=1 Oe.

Summary

Further studies of the present and other host materials (e.g., $Fe_2(WO_4)_3$) (5) are envisioned. One of our primary goals is the discovery and characterization of new, mild condition synthons in the present context that will ensure topotactic insertions and relatively defect free products. The latter will have potential application as fast ion conductors and as new battery materials. In addition, such insertion products are undoubtedly of interest from a basic magnetism point of view in the context of the present international conference. *Supported by the NSF Division of Materials Research.

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