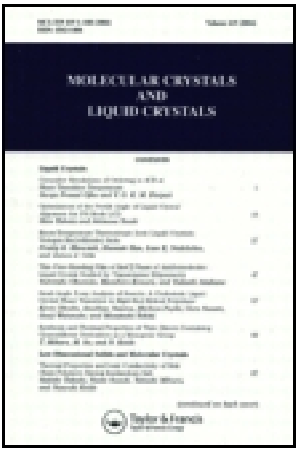

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New Insulating Layered Network 3D-Ferromagnets Composed of the Divalent Metal Perrhenates: $Fe(ReO_4)_2$, $Co(ReO_4)_2$ and $Ni(ReO_4)_2$

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NEW INSULATING LAYERED NETWORK 3D-FERROMAGNETS COMPOSED OF THE DIVALENT METAL PERRHENATES: $Fe(ReO_4)_2$, $Co(ReO_4)_2$ and $Ni(ReO_4)_2$

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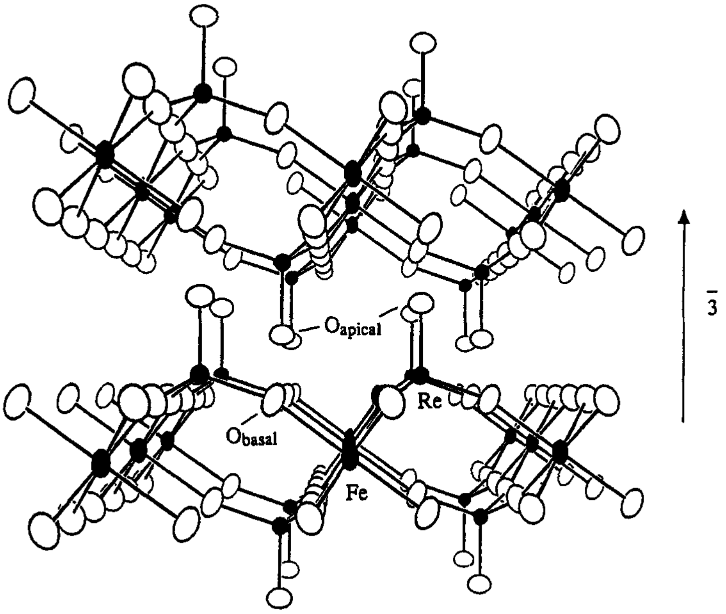
Abstract A variety of a.c. and d.c. magnetrometry data as well as iron-57 Mossbauer spectra show that the structurally layered divalent metal perrhenates: $M(ReO_4)_2$ (M = Ni, Fe, Co) have three dimensional ferromagnetic ground states with Curie temperatures of 12.5K, 8.5K and 4.7K respectively. The nickel compound exhibits a substantial coercivity (~0.26T) at 4.2K.

INTRODUCTION

The title compounds form an isomorphous series crystallizing in the trigonal space group $P\bar{3}m1$ such that the $\bar{3}$ axis is perpendicular to the layer planes (1). Herein, a combination of a.c. susceptibility data (strong imaginary components ($\chi''_m \neq 0$ near T_c), and d.c. magnetization measurements (observation of classical hysteresis, remenance decay with T increasing towards T_c and magnetization in very low applied field with T decreasing towards T_c) show that these compounds have genuine 3D-ferromagnetic ground states with

Curie temperatures: 12.5K(Ni), 8.5K(Fe) and 4.7K(Co). $Ni(ReO_4)_2$ is "hardest" of the group exhibiting a significant coercivity, ≈ 0.26T at 4.2K, while the hysteresis for the Fe and Co analogues is most obvious at <4.2K or for small (±25 Oe) field sweeps. The layer networks, formed of six coordinate Fe, Co or Ni bridged via tetrahedral ReO_4



Fe-O	2.084 Å (x6)	Fe-Fe (interlayer)	6.117 Å
Re-O_{basal}	1.713 Å (x3)	Fe-Fe (intralayer)	5.766 Å
Re-O_{apical}	1.689 Å (x1)	Re-Re (interlayer)	4.240 Å
O_{ap}-O_{ap} (interlayer)	3.413 Å	Fe-Re (intralayer)	3.759 Å
O_{ap}-O_{bas} (interlayer)	3.244 Å	Fe-O_{ap} (interlayer)	4.275 Å

FIGURE 1 The layered structure of anhydrous divalent transition metal perrhenates, specifically $Fe(ReO_4)_2$

groups, are held together solely by van der Waals interactions between interleaving oxygen atoms as shown in Figure 1. Iron-57 Mossbauer spectra show that: $Fe(ReO_4)_2$ exhibits long range magnetic order with the easy axis of

magnetization in the layer planes, i.e., perpendicular to the $\bar{3}$ axis. In comparison, the important divalent metal hydroxides $M(OH)_2$ are also layered ($P\bar{3}m1$) compounds (*compressed* along $\bar{3}$) but 3D order as antiferromagnets (T_N = 26.6K (Ni), 24K (Fe) and 12.3K (Co)) exhibiting metamagnetism such that $H_{critical}$ is ~ 1.5 to 2.0T (Co) (2,3) and 5.5T (Ni) (2). The related $Co_2(NO_3)(OH)_3$ is likewise a 2D-layered ferromagnet (3) that nevertheless ultimately 3D orders as an anti-ferromagnet (T_N=9.8K) and with a critical field for its meta-magnetism of 0.17T, i.e., only about 10% of that for $Co(OH)_2$. To our knowledge and in this context, the field dependence of magnetization for $Fe(OH)_2$ has not been investigated. The easy axis of magnetization lies perpendicular to $\bar{3}$ for $Co(OH)_2$ and $Fe(OH)_2$ (on the basis of Mossbauer spectroscopy results (4)) and parallel to $\bar{3}$ for $Ni(OH)_2$. The substantially higher Néel temperatures for the preceding hydroxides and the cobaltous hydroxy-nitrate versus Curie temperatures for the corresponding perrhenates are likely the result of strong hydrogen bonded interlayer interactions in the former which are simply not possible for $M(ReO_4)_2$ systems.

A comparison of the Mossbauer spectra quadrupole splitting parameters for $Fe(ReO_4)_2$ and $Fe(OH)_2$ (4) clearly indicates an orbital doublet (^5E) single ion electronic ground state for the former and a singlet (^5A) for the latter. This is consistent with trigonal axis compression for the hydroxide and elongation for the perrhenate. The limiting (4.2K) internal hyperfine field for $Fe(ReO_4)_2$ is only ~ 10T while that for $Fe(OH)_2$ is ~ 20T suggesting a significantly greater orbital component to the hyperfine field of $Fe(ReO_4)_2$ as predicted for a ^5E ground state. The latter orbital contribution to the internal field opposes the Fermi contact term for the case of iron (5). The smaller internal field of $Fe(ReO_4)_2$ can not be the result of zero-point spin reduction in this material, a direct consequence (6) of an inherently low dimensional magnetic nature since this effect occurs only for 3D-AF ground states.

RESULTS

Some exemplary results bearing on the confirmation of three dimensional ferromagnetic ground states for the specific cases of $Ni(ReO_4)_2$ and $Fe(ReO_4)_2$ are given in Figures 2, 3 and 4 respectively.

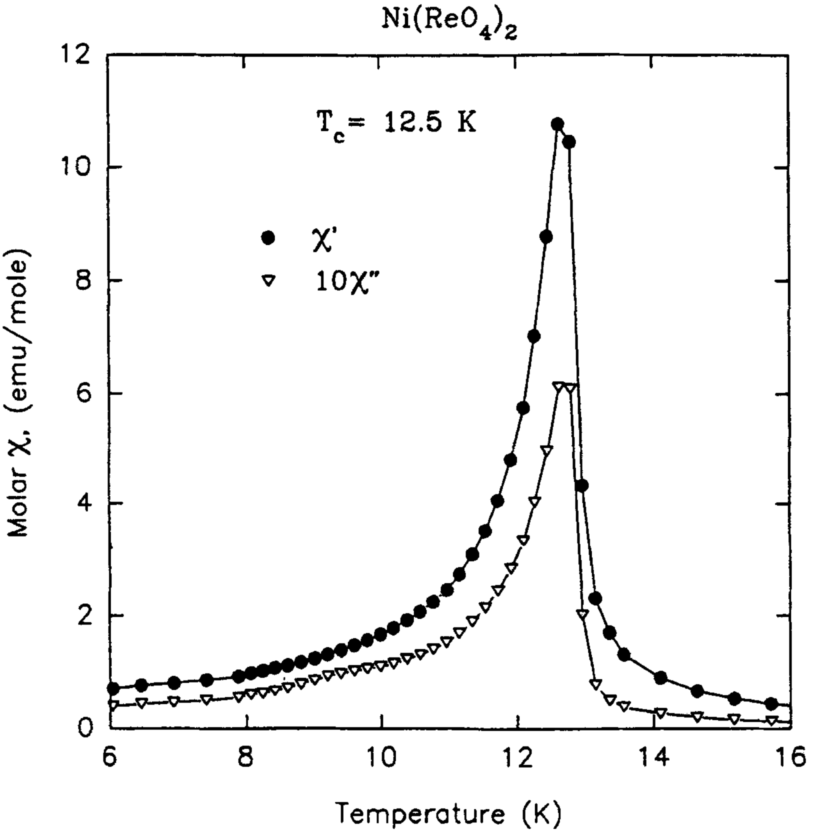


FIGURE 2 Real (χ'_m) and imaginary (χ''_m) components of the a.c. susceptibility of $Ni(ReO_4)_2$

The expected out of phase signal ($\chi''_m \neq 0$) at T_{Curie} is evident in Figure 2 while hysteresis is apparent in Figure 3.

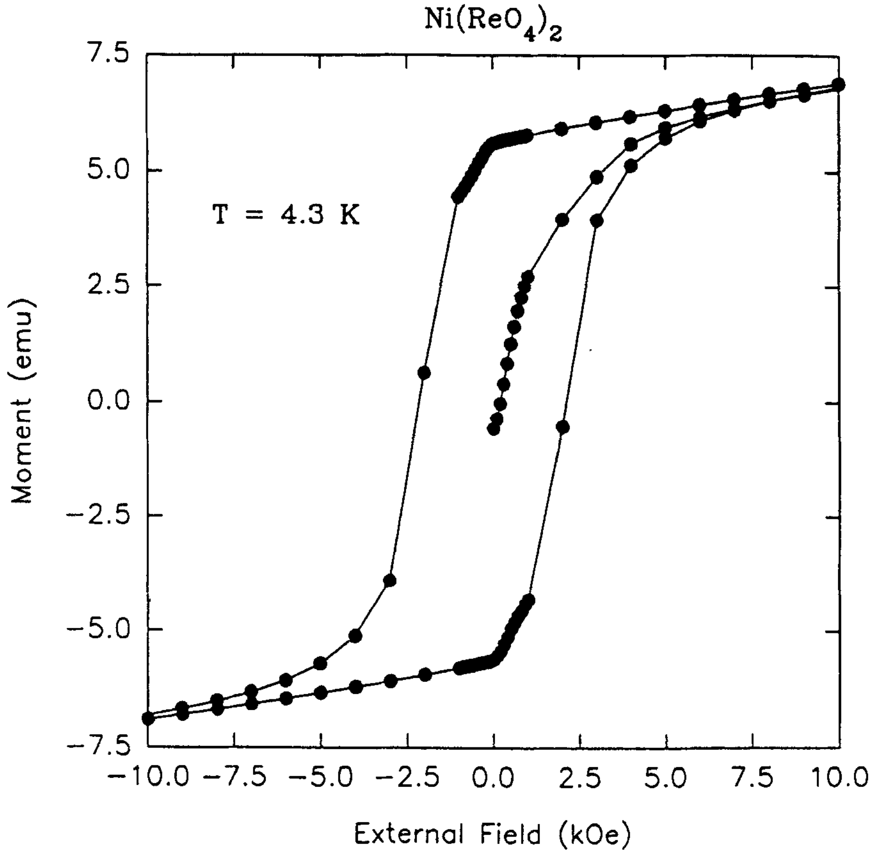


FIGURE 3 **Field dependence of magnetization for $Ni(ReO_4)_2$**

Finally, in Figure 4 the temperature dependence of (1G applied d.c. field) spontaneous magnetization and remanence for $Fe(ReO_4)_2$ suggest $T_{Curie} \approx 8.0K$ consistent with $T_{Curie} \approx 8.5K$ from a.c. susceptometry at 1 Oe and 125 Hz and zero field Mossbauer spectroscopy results.

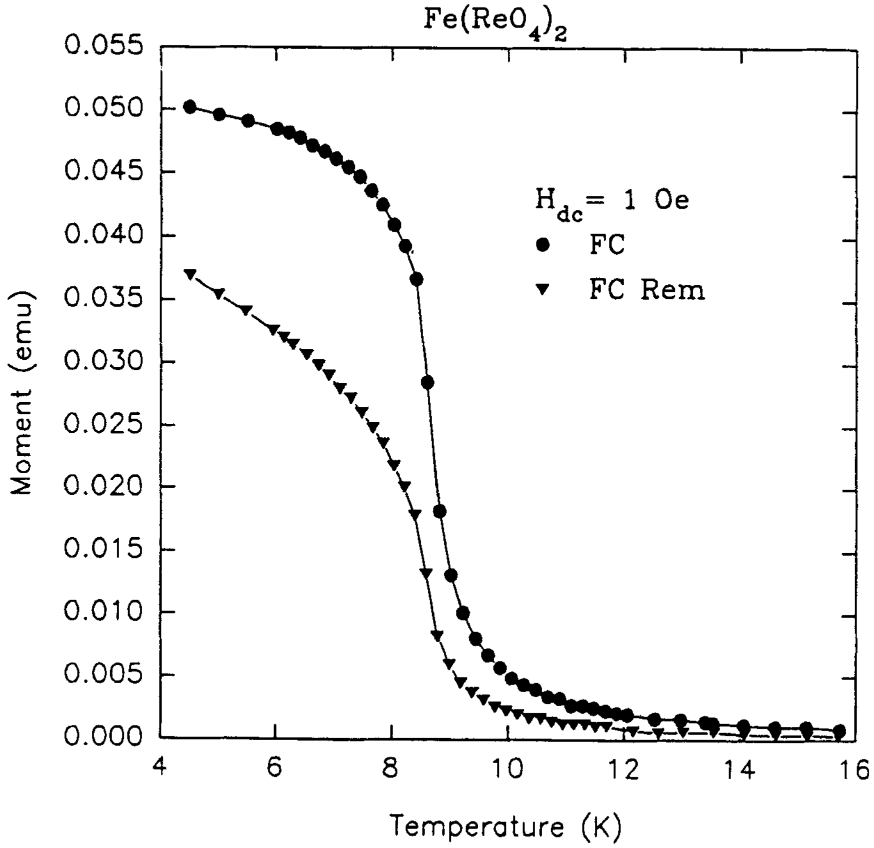


FIGURE 4 **Temperature dependence of spontaneous magnetization and remanence for Fe(ReO$_4$)$_2$ indicating T_{Curie}= 8.5K.**

All three of the perrhenates exhibit a sharp decrease of χ'_m for T < T_c as in Figure 2 indicating single domain ferromagnetism (7).

SUMMARY

In closing, we cite recent interesting studies by Stumpf et al (8) strongly suggesting that high coercivity bi-metallic molecular magnets require incorporation of magnetic centers with substantial unquenched orbital angular momentum. The present study of homo-metallic layered perrhenates appears to follow the reverse trend. That is, $Ni(ReO_4)_2$ with its $L \approx 0$ $^3A_{2g}$ ground state (save for spin-orbit coupling to $L \neq 0$ $^3T_{2g}$ and $^3T_{1g}$ excited states) is hard while the cobaltous and ferrous analogues (nominal $^4T_{1g}$ and $^5T_{2g}$ ground states respectively) are "soft". The reason(s) for these opposite behaviors are worthy of further study. The complete details of the x-ray structure, Mossbauer spectra, a.c. and d.c. susceptibility and field dependence of magnetization for these perrhenates including extension to the divalent manganese and copper analogues will be published subsequently elsewhere. Suffice it to conclude for now by stating that preliminary results for $Mn(ReO_4)_2$ indicate antiferromagnetic interactions while $Cu(ReO_4)_2$ exhibits ferromagnetic behavior. (*Supported by the NSF Division of Materials Research).

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