LINEAR CHAIN COMPOUNDS: METAMAGNETISM IN
 $\text{Co}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ AND $\text{Ni}(\text{pyr})_2\text{Cl}_2$

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ABSTRACT

We report the observation of low field metamagnetic behavior in powder samples of $\text{Co}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ and $\text{Ni}(\text{pyr})_2\text{Cl}_2$ where pyr=pyridine. These materials have linear chain structures with strong ferromagnetic interactions along the chains, and relatively weak antiferromagnetic interactions between chains. In all four compounds the transitions were observed as a rapid increase in the magnetic moment with increasing magnetic field. In $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$, and $\text{Ni}(\text{pyr})_2\text{Cl}_2$, the transitions at 4.2 K were observed at 0.7 kG, 1.1 kG and 2.7 kG respectively. In the Co compound the transition (at ~ 0.7 kG) was observed for $T < 3\text{ K}$ ($T_N = 3.17\text{ K}$). Differential magnetic moment measurements in $\text{Fe}(\text{pyr})_2\text{Cl}_2$ and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ are presented. Above the low field transitions the magnetic moment continues to increase and saturation is not achieved for applied fields up to 200 kG. High field Mössbauer data consistent with these results are discussed.

INTRODUCTION

The magnetic properties of $\text{Co}(\text{pyr})_2\text{Cl}_2$, where pyr=pyridine, have the characteristics of Ising linear chains.⁽¹⁾ Because of the current interest in nearly one-dimensional systems, studies of the susceptibility, specific heat, crystal structure and related properties have recently been reported for this and similar linear chain magnetic structures. In this work we discuss the magnetic properties of $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$, $\text{Ni}(\text{pyr})_2\text{Cl}_2$ and $\text{Co}(\text{pyr})_2\text{Cl}_2$. These compounds have strong ferromagnetic interactions along the chains and relatively weak antiferromagnetic interactions between the chains. We will show that their magnetic properties are quite similar.

EXPERIMENTAL DETAILS

The experimental results reported here involve static magnetic moment measurements made in fields to 60 kG with a vibrating sample magnetometer⁽²⁾ adapted to a superconducting solenoid and measurements in dc fields to 210 kG in water-cooled Bitter solenoids with a very low frequency VSM.⁽³⁾ Differential magnetic moment (DMM) measurements were made in a small balanced coil system at zero field and low fields with small amounts of material ($\sim 1\text{ mg}$) as described elsewhere.⁽⁴⁾ The materials examined were powders; single crystals were not available.

EXPERIMENTAL RESULTS

A. Low Field Transitions

In all the compounds we find that below the ordering temperature, T_N , the magnetic moment remains small at very low field, shows a rapid increase at relatively low fields and above a few kG shows a gradual increase in moment up to the highest dc fields we have available (see Figs. 1 and 2). This behavior is consistent with the occurrence of a low field metamagnetic phase transition when the antiferromagnetic coupling between chains is overcome.⁽⁵⁾

Generally measurements have been made in such systems at zero field so that a large anomaly in susceptibility is observed. When conventional susceptibility measurements are made one should observe a relatively large value of suscep-

Fig. 1. Differential magnetic moment versus temperature, T , at $B_0 = 0$ for $\text{Fe}(\text{pyr})_2\text{Cl}_2$ and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$. The ac field is less than 10 G.

Fig. 2. Magnetic moment, σ , versus applied field, B_0 , for several pyridine compounds. The insert shows example of low field transition for $\text{Fe}(\text{pyr})_2\text{Cl}_2$.

tibility below T_N because the applied fields are usually much greater than the transition fields. Examples of DMM results for $\text{Fe}(\text{pyr})_2\text{Cl}_2$ and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ are shown in Fig. 1. It should be noted that the transitions are quite sharp. The accuracy of the data is estimated to be better than 1 K, and the position of the transition depends on whether one defines it as the maximum or the most rapid increase in χ vs T . The value of $T_N = (7 \pm 0.5) \text{ K}$ for the $\text{Fe}(\text{pyr})_2\text{Cl}_2$ compares to 10.5 K reported by Sanchez et al.⁽⁶⁾ For the $\text{Fe}(\text{pyr})_2(\text{NCS})_2$, $T_N = (6 \pm 0.5) \text{ K}$. It should be noted that for both of these materials the metamagnetic behavior is observed at 4.2 K.

The evidence for apparent metamagnetic behavior for these systems is not unambiguous because these are powder samples. There is thus the possibility that we are observing one of several possible low field transitions, e.g., a spin-flop transition. However, for a spin-flop transition we would expect that the transition field H_C would decrease rapidly with decreasing temperature because $\chi_{\parallel}(T)$ is rapidly decreasing. We observe a slight increase in H_C as T decreases, consistent with metamagnetic behavior. Furthermore, the systems are similar to $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ (the pyr are replaced by H_2O) where single crystal data shows two metamagnetic transitions for this six-sublattice system.⁽⁷⁾ For the pyr materials $T_N \leq 7 \text{ K}$ whereas for the dihydrate materials $T_N \sim 17 \text{ K}$ so that the interchain antiferromagnetic exchange field is smaller in the former. In addition, the spin-flop transition

occurs when $H_A \ll H_A^{\text{ex}}$ whereas metamagnetic transitions are expected for highly anisotropic systems (such as expected for these linear chain systems) where $H_A > H_A^{\text{ex}}$. The magnitude of the moment change at the low field transition does not correspond to complete alignment of the atomic moments, however, as expected for a polycrystalline aggregate. If these systems are similar to the dihydrate material we might expect two transitions versus field. Possible reasons for not observing two are: a) the second transition occurs at very low fields in which case it would be observed at low temperatures, b) it occurs at higher fields and may be averaged out; c) the relative exchange constants are such that the pyridine materials are effectively two-sublattice systems.

The transition fields at 4.2 K for $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$, and $\text{Ni}(\text{pyr})_2\text{Cl}_2$ are $\sim 0.7 \text{ kG}$, 1.1 kG , and 2.7 kG respectively; and for $\text{Co}(\text{pyr})_2\text{Cl}_2$ at 1.2 K the transition field is $\sim 0.7 \text{ kG}$. Here the transition fields are defined as the extrapolation of the linear portion of the σ versus B_0 curve (see insert of Fig. 2) to the $\sigma = 0$ axis.

B. High Field Results

The high field approach to saturation for these materials is shown in Fig. 2. It should be noted that: a) the $\text{Co}(\text{pyr})_2\text{Cl}_2$ compound is not ordered at 4.2 K ($T_N \approx 3.17 \text{ K}$),⁽¹⁾ so that the σ versus B_0 data reflects paramagnetic behavior; b) none of the systems are completely saturated at 200 kG. This is consistent with high anisotropy as expected. The moments at 200 kG are given in Table I. If the low field transition reflected a spin-flop transition, we would expect a nearly linear increase in σ versus B_0 up to $\approx 2 H_A^{\text{ex}}$ at which point the system would be saturated. For the low T_N 's of these materials this would occur at $\leq 100 \text{ kG}$ (see, e.g., Ref. 4). Extrapolation from the low field transition would indicate that saturation should occur at $\leq 20 \text{ kG}$ if this transition were a spin-flop transition. Thus the high field behavior is inconsistent with a low field spin-flop transition.

Table I. High Field Magnetic Moments of Pyridine Compounds

Compound	200 kG Moment (μ_B)	Spin-Only Moment (μ_B)
$\text{Fe}(\text{pyr})_2\text{Cl}_2$	3.3	4
$\text{Fe}(\text{pyr})_2(\text{NCS})_2$	4.3*	4
$\text{Co}(\text{pyr})_2\text{Cl}_2$	2.8	3
$\text{Ni}(\text{pyr})_2\text{Cl}_2$	2.2	2

* Mössbauer measurements showed evidence of some Fe^{3+} so that this value may be slightly high.

C. Mössbauer Measurements

Mössbauer measurements have been reported in $\text{Fe}(\text{pyr})_2\text{Cl}_2$ ^(6,8) and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$.⁽⁹⁾ The spectrum of the latter consists of a quadrupole doublet with splitting $\Delta E_Q = 3.03 \text{ mm/sec}$ above T_N , and a magnetic hyperfine pattern below T_N , with $H_h = -280 \text{ kOe}$. Measurements in longitudinal external magnetic fields up to 80 kOe show that the electronic moments tend to align parallel to the external field, but the polarization is incomplete at the highest field, as is also seen in the high field magnetization measurements. The low field metamagnetic transition cannot be seen in powder samples by Mössbauer effect.

$\text{Fe}(\text{pyr})_2\text{Cl}_2$ is isomorphous with $\text{Co}(\text{pyr})_2\text{Cl}_2$ at room temperature and undergoes a transition at 250 K⁽⁶⁾ which has been postulated⁽⁸⁾ to be a form which is isomorphous with $\text{Cu}(\text{pyr})_2\text{Cl}_2$ below 250 K. For $250 \text{ K} > T > T_N$, the spectrum consists of a quadrupole doublet with $\Delta E_Q = 1.26 \text{ mm/sec}$.

Below T_N , a magnetic hyperfine field is observed. External magnetic field measurements up to 80 kOe show that the iron moments tend to polarize along the field direction, but that the polarization is incomplete at 80 kOe, again consistent with the high field magnetization results. The overall splitting of the spectrum increases with increasing B_0 , indicating that the hyperfine field has a positive sign. The smaller quadrupole splitting and effective magnetic field below T_N in the chloride compared to the thiocyanate suggest less complete quenching of the orbital angular momentum in the chloride, and hence considerable orbital admixture in the ground state. This should be reflected in larger magnetic anisotropy of the chloride compared to the thiocyanate, and is indeed consistent with the data presented in Fig. 2 and Table I.

CONCLUSION

We have shown that the linear chain materials $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2(\text{NCS})_2$, $\text{Co}(\text{pyr})_2\text{Cl}_2$ and $\text{Ni}(\text{pyr})_2\text{Cl}_2$ are antiferromagnetic at low temperature and undergo metamagnetic transitions in low external fields. The high anisotropy of these materials is demonstrated in the high field magnetization and Mössbauer data. Further elucidation of the magnetic properties of these materials will be possible when single crystals become available. More detailed results will be presented elsewhere.

REFERENCES

1. K. Takeda, S. Matsukawa and T. Haseda, J. Phys. Soc. Japan, **30**, 1330 (1971).
2. S. Foner, Rev. Sci. Instr. **30**, 548 (1959).
3. S. Foner and E.J. McNiff, Jr., Rev. Sci. Instr. **39**, 171 (1968).
4. N.F. Oliveira, Jr., S. Foner, and Y. Shapira, Phys. Rev. **5**, B 2634 (1972).
5. A preliminary report of the low field behavior is given by S. Foner, R.B. Frankel, W.M. Reiff, B.F. Little and G.J. Long, Solid State Comm. (in press).
6. J.P. Sanchez, I. Asch, and J.M. Freidt, Chem. Phys. Letters **18**, 250 (1973).
7. A. Narath, Phys. Rev. **139**, A 1221 (1965).
8. W.M. Reiff, R.B. Frankel, B.F. Little, and G.J. Long, Chem. Phys. Letters **28**, 68 (1974).
9. W.M. Reiff, R.B. Frankel, B.F. Little, and G.J. Long, Inorganic Chem. **13**, 2153 (1974).

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