

**METAMAGNETIC BEHAVIOR OF LINEAR CHAIN PYRIDINE COMPOUNDS:
Co(PYRIDINE)₂Cl₂, Fe(PYRIDINE)₂Cl₂, Fe(PYRIDINE)₂(NCS)₂ AND Ni(PYRIDINE)₂Cl₂**

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Magnetic phase transitions in the pyridine (pyr) compounds Co(pyr)₂Cl₂, Fe(pyr)₂Cl₂, Fe(pyr)₂(NCS)₂ and Ni(pyr)₂Cl₂ have been observed at applied magnetic fields of ~0.7, 0.7, 1.1 and 2.7 kG respectively. These low field phase transitions are observed in the Fe and Ni compounds at $T = 4.2$ K, and in the Co compound at $T < 3$ K, and are consistent with metamagnetic behavior. Magnetic saturation is not achieved in any of these compounds for fields of 60 kG, reflecting high anisotropy.

FEW magnetically ordered compounds show metamagnetic phase transitions. Here we report the observation of low field, apparently metamagnetic, transitions in the pyridine (pyr) compounds Co(pyr)₂Cl₂,¹ Fe(pyr)₂Cl₂,² Fe(pyr)₂(NCS)₂,³ and Ni(pyr)₂Cl₂. These compounds as well as Mn(pyr)₂Cl₂⁴ and Cu(pyr)₂Cl₂^{1,5,6} have linear chain structures with strong exchange interactions along the chains, and relatively weak exchange interactions between chains. The Mn and Cu compounds have intrachain anti-

ferromagnetic exchange, whereas the other four compounds exhibit ferromagnetic intrachain interactions.

The temperature dependence of the magnetic susceptibility of Co(pyr)₂Cl₂ has been studied¹ in low applied fields (0.1–40 Oe) and the compound was shown to order antiferromagnetically with $T_N = 3.17$ K and with a paramagnetic Curie temperature $\theta \approx +5$ K. A theoretical fit¹ of the susceptibility with a ferromagnetic Ising model yielded an intrachain interaction $J/k = 11.7$ K. In Fig. 1(a) we plot the magnetic moment, σ , as a function of applied magnetic field, H_0 , for several selected temperatures both above and below the previously reported¹ value of $T_N = 3.17$ K. The magnetic moment data were obtained with a vibrating sample magnetometer adapted to a superconducting solenoid. The data in Fig. 1(a) cover the range where the onset of long range

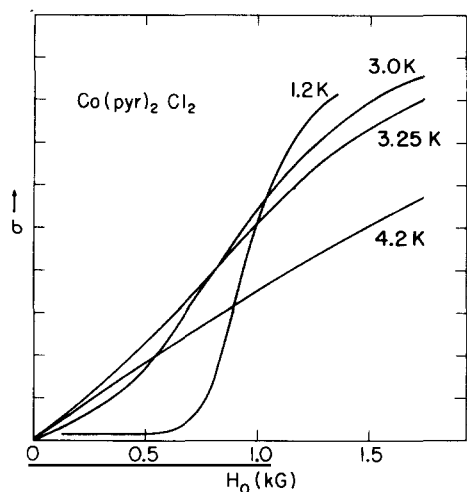


FIG. 1. (a) Relative magnetic moment, σ , vs applied magnetic field, H_0 , for $\text{Co}(\text{pyr})_2\text{Cl}_2$ for several temperatures. At 1.2 K and 1.5 kG, $\sigma = 31$ e.m.u./g ($1.6\mu_B/\text{Co}$ atom). At 4.2 K and 48 kG, $\sigma = 47$ e.m.u./g ($2.4\mu_B/\text{Co}$ atom).

order occurs. At low temperatures the magnetic data show a rapidly increasing moment with increasing field, reflecting a first order phase transition. Because the sample is an irregularly shaped (and presumed randomly oriented) polycrystalline powder compact, the detailed shape of the observed transitions reflects demagnetization and anisotropic contributions in addition to the intrinsic phase transitions. The transition field increases slightly as T is decreased to 1.2 K. This behavior is expected for a metamagnetic transition, whereas for a spin-flop transition we would expect the transition field to decrease with decreasing temperature. For fields above the knee of the σ vs H_0 data, the magnetization increases gradually and is not saturated even at the highest field.

The magnetic moment data at 4.2 K for $\text{Fe}(\text{pyr})_2\text{Cl}_2$ and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ are shown in Fig. 2(a). The transition fields for $\text{Co}(\text{pyr})_2\text{Cl}_2$, $\text{Fe}(\text{pyr})_2\text{Cl}_2$ and $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ occur at approximately 0.7, 0.7 and 1.1 kG respectively in Figs. 1 and 2. Here we define the transition field as the extrapolation of the linear portion of σ vs H_0 to the $\sigma = 0$ axis. As in the Co compound, magnetic saturation is not achieved in fields up to 50 kOe, as illustrated in Fig. 2(b) for $\text{Fe}(\text{pyr})_2\text{Cl}_2$ at 4.2 K. Data at lower temperature similarly show no saturation, consistent with large anisotropic interactions for the compounds studied here.

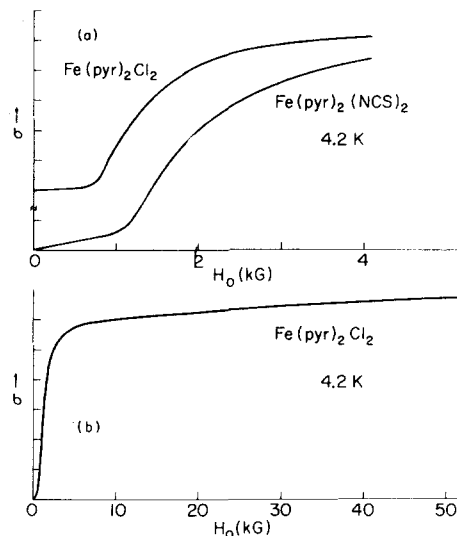


FIG. 2. Relative magnetic moment, σ , vs applied field, H_0 , at 4.2 K. (a) Low field data. Note the break in ordinate axis and that the relative moment scale differs for the two sets of data. For the $\text{Fe}(\text{pyr})_2\text{Cl}_2$ data, $\sigma = 27$ e.m.u./g ($1.4\mu_B/\text{Fe}$ atom) at 3.9 kG; for the $\text{Fe}(\text{pyr})_2(\text{NCS})_2$ data, $\sigma = 34$ e.m.u./g ($2.0\mu_B/\text{Fe}$ atom) at 4.2 kG. (b) High field data showing that saturation is not achieved in the powder material. For the $\text{Fe}(\text{pyr})_2\text{Cl}_2$, $\sigma = 51$ e.m.u./g ($2.6\mu_B/\text{Fe}$ atom) at 55 kG.

In $\text{Ni}(\text{pyr})_2\text{Cl}_2$ the transition is observed at 2.7 kG at 4.2 K, and the high field magnetic behavior is similar to that reported above for the Co and Fe compounds. Recent low temperature specific heat measurements⁷ point to a large single-ion anisotropy.

The crystal structures of $\text{Co}(\text{pyr})_2\text{Cl}_2$ and $\text{Co}(\text{pyr})_2(\text{NCS})_2$ are monoclinic^{8,9} and the iron analogues are isomorphous^{2,3} at room temperature. The structures are basically linear chains formed by aggregation of $M\text{Cl}_2$ or $M(\text{NCS})_2$ units with six-coordination completed by trans-pyridine moieties. They are quite similar to the analogous $M\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ compounds ($M = \text{Co}, \text{Fe}$) in that the *intrachain* metal-metal distance for the pyridine and hydrate systems¹⁰ are both ~ 3.6 Å. However, for $M\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ the *interchain* metal distances are ~ 5.5 Å whereas for the $M(\text{pyr})_2\text{Cl}_2$ and $M(\text{pyr})_2(\text{NCS})_2$ they are ~ 9 Å.

The major effect of dilution by the organic ligand is to lower the interchain interaction, and consequently T_N , as well as the metamagnetic transition field. For example, in FeCl_2 , which has planes of Fe atoms

coupled antiferromagnetically, a metamagnetic transition occurs at 11 kOe at 4.2 K.¹¹ The linear chain type structures of $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ are characterized by antiferromagnetic to ferrimagnetic to paramagnetic phase transitions¹² which occur at 39 and 45 kOe, and 32 and 46 kOe respectively. The effect of substituting NCS for Cl as the bridging ligand in the chain of the iron compounds presumably alters the intrachain exchange, and may alter the interchain exchange as well. According to a simple Ising model¹² with an intrachain and two interchain exchange constants, the metamagnetic transition fields in the present compounds are proportional to the interchain exchange constants and inversely proportional to the single ion g -factors. However, Mössbauer studies^{3,13} in the iron compounds reveal significant differences in the ground state magnetic properties, so that at present it is not possible directly to compare the interchain exchange constants except to note that they are of the same order of magnitude.

The magnetic data presented here for the four linear chain compounds point to the existence of tricritical points in the magnetic phase diagrams at relatively low temperatures and low magnetic fields. Despite the low magnetic transition fields, these compounds have large anisotropic contributions which

make it difficult to achieve magnetic saturation in high magnetic fields for powdered materials. For instance, the magnetic moment of $\text{Fe}(\text{pyr})_2\text{Cl}_2$ powdered material is $\sigma = 52 \text{ e.m.u./g}$ at 55 kG, which corresponds to $2.6\mu_B/\text{Fe atom}$ [see Fig. 2(b)]. One advantage of the Co pyridine compound discussed here is that the entire phase diagram can be studied at relatively low magnetic fields in the liquid He⁴ temperature range. However, a complete elucidation of the magnetic properties of the Co compound as well as the Fe compounds, will require measurements in single crystals. Further work on these chain compounds will be presented elsewhere.

It should be noted that the low field magnetic phase transitions reported here may be elusive when conventional magnetic measurements are made. Zero-field differential susceptibility measurements will not show evidence of this transition. Susceptibility measurements above $\sim 1 \text{ kG}$ will suggest evidence of a magnetic phase transition indirectly by showing an average susceptibility which is larger than that expected. Only a careful scan of the magnetic moment or differential susceptibility vs H_0 in the low field range will clearly show evidence of this low field transition as demonstrated in Figs. 1 and 2.

REFERENCES

1. TAKEDA K., MATSUKAWA S. and HASEDA T., *J. Phys. Soc. Japan* **30**, 1330 (1971).
2. LONG G.J., WHITNEY D.L. and KENNEDY J.E., *Inorg. Chem.* **10**, 1406 (1971).
3. REIFF W.M., FRANKEL R.B., LITTLE B.F. and LONG G.J., *Inorg. Chem.* **13**, 2153 (1974).
4. RICHARDS P.M., QUINN R.K. and MOROSIN B., *J. Chem. Phys.* **59**, 4474 (1973).
5. TAKEDA K., YAMAMATO Y. and HASEDA T., *Phys. Lett.* **45A**, 419 (1973).
6. ENDOH Y., SHIRANE G., BIRGENAU R.J., RICHARDS P.M. and HOLT S.L., *Phys. Rev. Lett.* **32**, 170 (1974).
7. KLAAIJSEN F.W., BLÖTE H.W.J. and DOKOUPIL Z., *Solid State Commun.* **14**, 607 (1974).
8. DUNITZ J., *Acta Cryst.* **10**, 207 (1957).
9. PORAI-KOSHITS M.A. and TISHCHENKO G.M., *Sov. Phys. Crystallogr.* **4**, 216 (1959).
10. HARKER D., *Z. Krist.* **93**, 136 (1936).
11. WILKINSON W.K., CABLE J.W., WOLLAN E.O. and KOEHLER W.C., *Phys. Rev.* **113**, 497 (1959).
12. NARATH A., *Phys. Rev.* **139**, A1221 (1965).
13. REIFF W.M., FRANKEL R.B., LITTLE B.F. and LONG G.J., *Chem. Phys. Lett.* **28**, 68 (1974).