METAMAGNETISM IN SINGLE CRYSTAL γ-Co(PYRIDINE)$_2$Cl$_2$

S. Foner and R.B. Frankel
Francis Bitter National Magnet Laboratory,† MIT, Cambridge, Mass. 02139
W.M. Reiff* and H. Wong
Northeastern University, Boston, Mass. 02115
G.J. Long**
University of Missouri-Rolla, Rolla, Missouri 65401

ABSTRACT

Small (≤ 1 mg) single crystals of γ-Co(pyr)$_2$Cl$_2$ have been grown and measurements of magnetic moment vs applied field H and temperature have been made for $0 \le H \le 54$ kG and $1.25\,K \le T \le 4.2\,K$. At 1.25 K, metamagnetic transitions are observed along the a-axis at ~700 G; along the b-axis at both ~800 and ~1500 G; and along the c-axis at ~4 kG. The low field susceptibilities show a maximum at T ≃ 3.4 K for each orientation. Magnetic saturation is not achieved at 54 kG; about 2.5 μ_B is achieved along the a*- or b-axes, whereas a lower moment is achieved along the c-axis. Along the b-axis, the low field moment change is 1/2 the higher field moment change, suggesting a six-sublattice magnetic structure.

INTRODUCTION

Previously[1,2] we reported on magnetic measurements on polycrystalline samples of Co(pyr)$_2$Cl$_2$, Fe(pyr)$_2$Cl$_2$, Fe(pyr)$_2$(NCS)$_2$ and Ni(pyr)$_2$Cl$_2$ where (pyr) is pyridine. These materials all have linear chain structures with ferromagnetic interactions along the chain and relatively weak interactions between chains. The temperature dependence of the low field data indicated metamagnetic behavior for all these linear chain systems. Another feature of the data was that the magnetic moment at high field was not saturated in fields to 200 kG. At that time we noted that detailed characteristics of the relatively low field transitions required measurements in single crystals. In this paper we present magnetic data obtained on single crystal γ-Co(pyr)$_2$Cl$_2$ which is isomorphous[3] with Cu(pyr)$_2$Cl$_2$. The results confirm the metamagnetic behavior at low field observed in the powder material.

EXPERIMENTAL DETAILS

The experimental results were obtained with a vibrating sample magnetometer adapted to a superconducting solenoid. The Co(pyr)$_2$Cl$_2$ crystals were grown from absolute ethanol solution.

The single crystals were each nominally < 1 mg in weight. In order to obtain relatively large signals, samples composed of 2 to 3 oriented crystals were used. Individual crystal measurements were also made to guarantee that the composite samples reflected the single crystal behavior. There was a tendency for the crystallites to deteriorate or fracture with repeated measurements because the high temperature α phase transforms to the low temperature γ phase and so the major part of the data was obtained for each orientation by cooling each batch of crystals only once.

EXPERIMENTAL RESULTS

General Features

The main features of the magnetic moment vs applied field, σ(H), for single crystal Co(pyr)$_2$Cl$_2$ are illustrated in Fig. 1. Figure 1a shows σ(H) at 1.25 K for H parallel to the a*-axis. There is a single low-field transition and saturation is not achieved in fields of 50 kG. A more complex

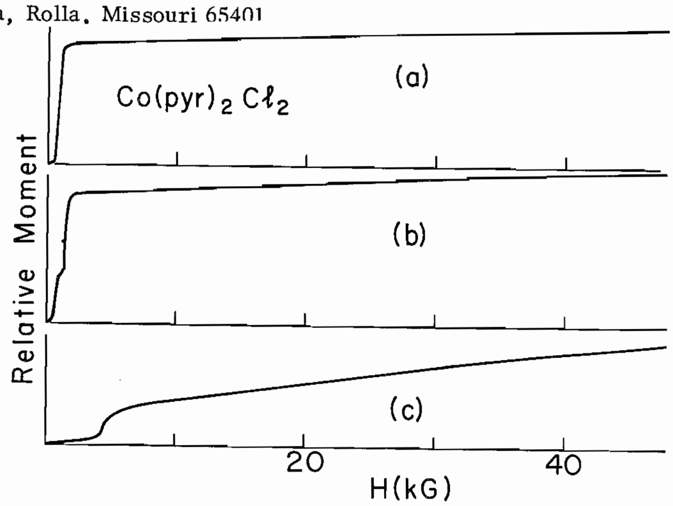

Fig. 1. Relative magnetic moment σ versus applied field H at 1.25 K: a) H||a*-axis; b) H||b-axis; c) H||c-axis. The moments at H = 52 kG are ~ 2.5 μ_B/Co atom for (a) and (b), and ~1.1 μ_B/Co atom for (c).

behavior is observed for H parallel to the b-axis (Fig. 1b); σ(H) shows two sharp metamagnetic transitions with a rapid rise at low field which is approximately one-half the rapid rise at higher field. Again the high-field region shows a gradual increase of σ up to 50 kG. The σ(H) for H along the c-axis is shown in Fig. 1c; for this orientation there is a single transition, but the field at which this transition takes place is considerably higher than those for the a*- or b-axes. Furthermore, the magnetic moment at ~50 kG is much less than for H along the a*- or b-axis.

Low Field Transitions

For H along the a*-, b- or c-axis, the initial susceptibility versus T shows a maximum at T ≃ 3.4 K for each orientation, and a rapid decrease below 3.4 K. For each orientation there is a maximum in susceptibility in the range of 3.2 to 3.4 K, and the maximum change in susceptibility occurs in the region of about 3.2 K. The values of T_c are therefore in good agreement with earlier measurements in polycrystalline samples.[2] The average susceptibilities for intermediate field regions are strongly dependent on H and T. As an example, σ(H) for different fixed temperatures with H along the b-axis is shown in Fig. 2. Measurements for other orientations will be presented elsewhere.

The critical field H_c was determined as in Refs. 1 and 2. We find that H_c increases as T is decreased for all the low field transitions. At 1.25 K, H_c = ~700, ~800 and ~1500, and ~4 kG for the a*-, b-, and c-axis respectively, and in some cases H_c exhibits hysteresis.

High Field Results

Saturation is not achieved by 50 kG, but the magnetic moment for H along the c-axis is considerably smaller than

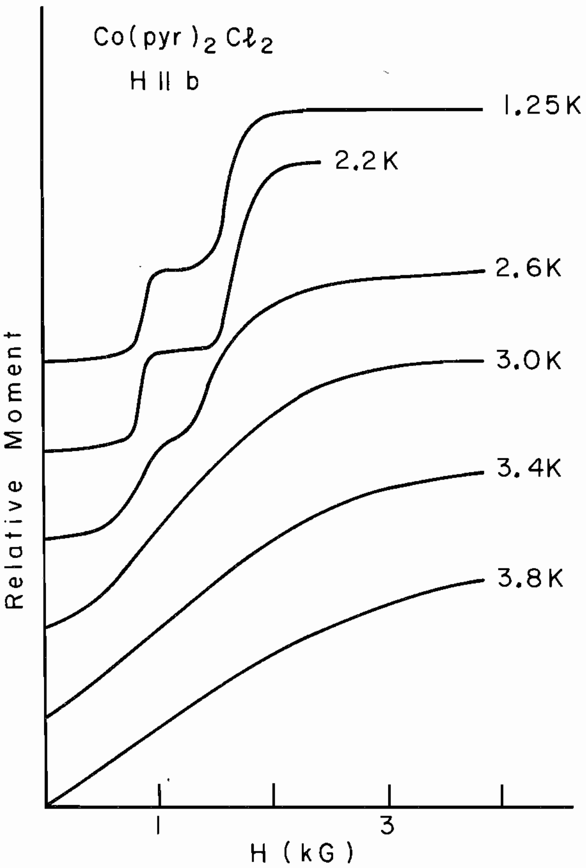

Fig. 2. Relative moment σ versus applied field H for $1.25 \leq T \leq 3.8$ K. The curves are displaced along the ordinate for clarity.

that along the other two axes. These results are consistent with the data presented earlier[2] for polycrystalline samples for fields of over 200 kG. The earlier polycrystalline data showed only one transition, which can be understood in terms of broadening introduced by the randomly oriented crystallites; the a*- and b-axis transitions occur at almost the same field and the second transition for the b-axis occurs over a relatively narrow angular orientation.

DISCUSSION OF RESULTS

The σ(H,T) data for single crystal $Co(pyr)_2Cl_2$ presented here may be compared to the results reported by Narath[4] for $Co(H_2O)_2Cl_2$. Because of the bulky pyridine ligands, the interchain interactions are considerably reduced compared to the dihydrate and the transitions occur at fields more than one order of magnitude lower. There is no possibility for exchange via hydrogen bonding as in the case of the dihydrate.[5]

In the dihydrate case, the spins are ferromagnetically coupled along the c-axis, the b-axis is the easy magnetic axis, and external fields along b induce metamagnetic transitions at ~31 kG and ~46 kG. A six sublattice model describes the intermediate spin structure.[4] In the present case, the spins, which also are ferromagnetically coupled along the c-axis, appear to order antiferromagnetically along the b-axis as well. For H||b, one again observes two transitions. For H||a* a single metamagnetic transition occurs to a state with the spins aligned parallel to a*. The slightly lower H_c for H||a* compared to H||b is consistent with our observed susceptibilities $\chi_a^* > \chi_b$.

REFERENCES

Supported by the National Science Foundation.
Work supported by NSF Grant No. GH39010 and in part by Grant No. PP07143, Department of Health, Education and Welfare.
Supported by National Science Foundation Grant GP8653.

1. S. Foner, R.B. Frankel, W.M. Reiff, B.F. Little and G.J. Long, Solid State Commun. 16, 159 (1975).
2. S. Foner, R.B. Frankel, E.J. McNiff, Jr., W.M. Reiff, B.F. Little and G.J. Long, AIP Conf. Proc. 24, 363 (1975).
3. P.J. Clarke and H.J. Milledge Acta. Cryst. B31, 1543 1554 (1975).
4. A. Narath, J. Phys. Soc. Japan 19, 2244 (1964); Phys. Rev. 136, A766 (1964).
5. J.N. McElearney, S. Merchant and R.L. Carlin, Inorganic Chem. 12, 906 (1973).