

TEMPERATURE DEPENDENCE OF THE MAGNETIC PHASE
TRANSITIONS OF $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$

Marian A. LOWE* †

*Department of Chemistry
Boston University, Boston, Mass., USA*

C. R. ABELEDO †

*Department of Chemistry
Brandeis University, Waltham, Mass., USA*

and

A. A. MISETICH**

*Gerencia de Investigaciones, Comision Nacional de
Energia Atomica, Buenos Aires, Argentina*

*and
Francis Bitter National Magnet Laboratory**
Massachusetts Institute of Technology, Cambridge, Mass., USA*

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The H - T phase diagram for the antiferromagnet $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ has been measured. The two metamagnetic transitions are observed to meet at a triple point at 8.8 K and 38.5 kG. A molecular field calculation is in good agreement with experiment.

Cobalt chloride dihydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, is an interesting magnetic system which has attracted considerable theoretical and experimental attention [1-5]. The crystal is monoclinic, space group $C2/m$ [6]. Chlorine bridged ($-\text{CoCl}_2-$) chain run parallel to the c axis; chains are held together by hydrogen bonds. Below $T_N = 17.3$ K, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ orders as a two sublattice antiferromagnet. The nature of the magnetic interactions is such that it may be considered as a one-dimensional antiferromagnet with strongly coupled linear chains of Co^{2+} ions along the crystallographic c axis. The ordering along the chains is ferromagnetic with Ising-like interactions; that is, the interaction along the chain, J_0 , is highly anisotropic ($J_0^z \gg J_0^{x,y}$). The interchain ordering is antiferromagnetic with much weaker coupling. To show the interchain interactions, the projection of the magnetic structure on the a - b plane in zero applied field is shown in fig. 1(a). The

ferromagnetically ordered chains are perpendicular to the a - b plane. Interchain interactions involve three constants: J_1 , J_2 and J_3 and the spins align along the b axis.

If an external magnetic field is applied along b at 4.2 K, two magnetic phase transitions take place, from an antiferromagnetic (AF) to a ferrimagnetic phase (FI) at $H_1 = 32$ kG and from the ferrimagnetic to a paramagnetic phase (FP) at $H_2 = 45$ kG [1, 2]. The magnetic structures of these phases are shown in figs. 1(b) and 1 (c). Note that ordering along the chains remains ferromagnetic in all three phases. Due to the large magnetic anisotropy, the first transition is to a ferrimagnetic phase rather than to a "spin flopped" phase.

There have been several determinations of the exchange parameters reported in the literature. From the values of the critical fields, H_1 and H_2 , at 4.2 K, the exchange constants $J_1^z = -3.25 \text{ cm}^{-1}$ and $J_2^z = 0.7 \text{ cm}^{-1}$ have been calculated by Torrance and Tinkham [6]. Values determined by Narath [2,3] are similar. From far infrared measurements, Torrance and Tinkham have given values of $J_0 = 12.7 \text{ cm}^{-1}$ and $J_3 = 0.09 \text{ cm}^{-1}$. From susceptibility data, Narath reports

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† Visiting Scientist, Francis Bitter National Magnet Laboratory.

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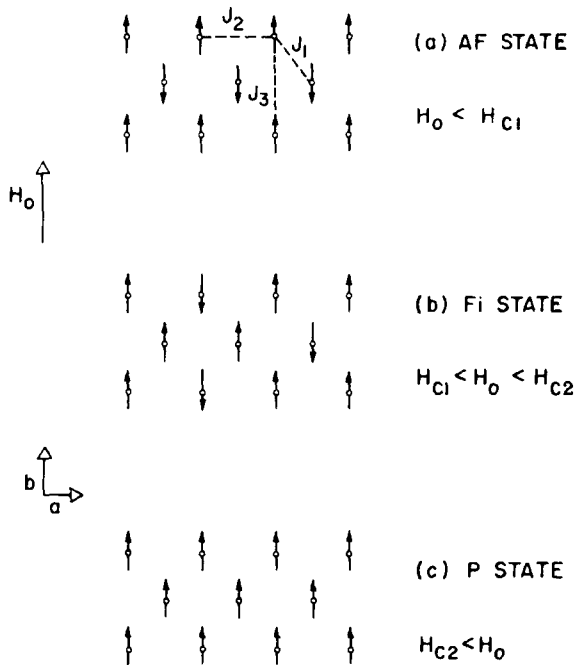


Fig. 1. Projections on the a - b plane of the spin structures of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. (a) Antiferromagnetic phase; (b) ferrimagnetic phase; and (c) paramagnetic phase.

$J_0 = 6.5 \text{ cm}^{-1}$. A similar value was obtained by Oguchi [5] by fitting the Néel temperature with a Green function calculation.

We have investigated the temperature dependence of the phase transitions. The magnetic field versus temperature phase diagram thus obtained is analyzed within the framework of the molecular field model using previously reported exchange constants. We studied the location of the phase transitions in the H - T plane with strain gages*. At each phase transition there is a change in lattice constants which can be detected easily with a strain gage. Strain gages were cemented to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ single crystals so as to detect variations in length along the b direction. The resistance of the strain gage was measured at constant temperature as a function of applied field (H_0/b). To compensate for the effect of magnetic field on the strain gage we included strain gages on two arms of a DC resistance bridge. One of these - a reference gage - was placed in the dewar next to the strain gage which was cemented to the crystal. The magnetic field was swept upfield and downfield at rates of about 5 kG per minute.

* Model SR-4 from Baldwin-Lima-Hamilton, Waltham, Mass.

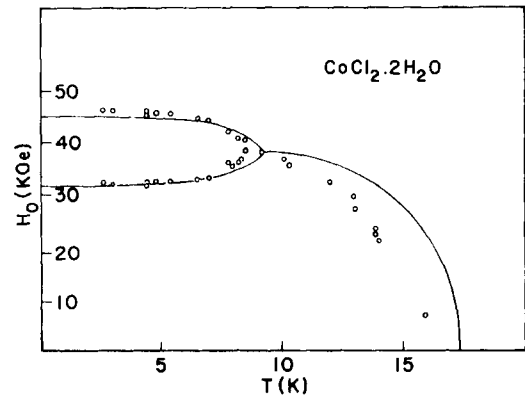


Fig. 2. Magnet field versus temperature phase diagram $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. Circles: experimental points. Solid line: calculated phase boundaries obtained with $J_0 = 6.2 \text{ cm}^{-1}$, $J_1 = 3.25 \text{ cm}^{-1}$, $J_2 = 0.7 \text{ cm}^{-1}$ and $J_3 = 0.09 \text{ cm}^{-1}$.

At 4.2 K we observe two sharp transitions at nearly the values of applied field reported previously**. The differences from the reported values appear to be due to misalignment. A small hysteresis (a few tenths of a kG at 4.2 K) was observed which was found to be rate independent below about 15 kG per minute. As the temperature is increased, the separation between the two phase transitions decreases until they meet at triple point at $T = 8.8 \text{ K}$ and $H = 38.4 \text{ kG}$. The transitions become broader as the temperature is raised, and the behavior of the measured quantity, the change in lattice parameter, becomes more complicated. A complete phase diagram is shown in fig. 2. (The points have been corrected for misalignment.) The uncertainty in the measurements increases as the temperature is increased due to the width of the transition. The shape of the transitions and the hysteresis effects will be discussed in a later publication.

Calculations using the molecular field model were carried out [8]. We calculate the free energy as a function of magnetic field at constant temperature for each phase and find points at which the free energy curves cross. Our molecular field calculations do not show the presence of a ferromagnetic state above H_2 but indicate only the existence of the paramagnetic state. The phase diagram obtained using the exchange constants and g value of 6.8 reported by Torrance and

** The lattice parameter along the b axis increases as one goes from the AF to the FI phase and also from the FI to the FP state ($\Delta l/l_b$ is about 10^{-4}).

Tinkham reproduces the qualitative features of the experimental phase diagram, but the calculated values of the triple point (19 K) and for T_N (26 K) are too high. Since there are serious discrepancies in the reported values of the dominant exchange constant J_0 , calculations were made in which this constant was varied. A fit to the reported Néel temperature of 17.3 K gives $J_0 = 6.2$. The calculated phase diagram with $J_0 = 6.2$, shown in fig. 2, has a triple point at $T = 9.3$ K and $H = 38$ kG. As mentioned above the uncertainty in locating the phase transition increase with temperature. Because of this we show the result of a molecular field calculation that fits the reported $T_N = 17.3$ K rather than our higher temperature data. If the value of J_0 is chosen to fit the temperature at the triple point, $J_0 = 5.9$, the triple point is at 8.8 K and 38.5 kG and the Néel temperature is 16.3 K. These values of J_0 are very close to that reported by Narath and by Oguchi. It can be seen that the

molecular field model with reasonable values of the exchange parameters reproduces the main features of the magnetic phase diagram for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ quite well.

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