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Proton Resonance in Paramagnetic and Antiferromagnetic $CoCl_2 \cdot 6H_2O$

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Preliminary measurements are reported for the proton resonance in $CoCl_2 \cdot 6H_2O$ in the paramagnetic and antiferromagnetic states. The data is not yet complete enough for accurate conclusions to be drawn about the proton positions. Effects associated with short range magnetic order are observed within the temperature region 0.07°K below the Neel temperature of 2.28°K.

Standard radio-frequency nuclear resonance spectroscopy techniques have been applied to study the fine structure of the proton resonance absorption line in single crystals of $CoCl_2 \cdot 6H_2O$. Cobaltous chloride undergoes a paramagnetic-antiferromagnetic phase transition at 2.28°K.

At room temperature the proton resonance at 12 Mc/sec in a field of 2.82 kilogauss consists of a single line about six gauss wide. A splitting of this line into a maximum of six components has been observed at 4.2°K. The maximum over-all separation at 4.2°K is about 110 gauss in an external field of 3.16 kilogauss.

A record of the spectrum as a function of crystal orientation is shown in Fig. 1 for H_0 in the *a-c* plane and for T=4.2°K. According to the crystal structure[1] of $CoCl_2 \cdot 6H_2O$, four water molecules and the two chlorine ions form a regular octahedron about a central cobalt ion. Assuming that (1) only the central cobalt ion contributes to the local field at the four octahedral water molecules (the other nearest neighbors contribute only about 10% to the local field), (2) that there are protons associated with these H_2O molecules "near" the oxygen sites, and (3) neglecting the proton-proton interaction, a curve for the proton resonance frequency as a function of external field orientation could be fitted closely to curve (1a) of Fig. 1. In Fig. 1, the axis

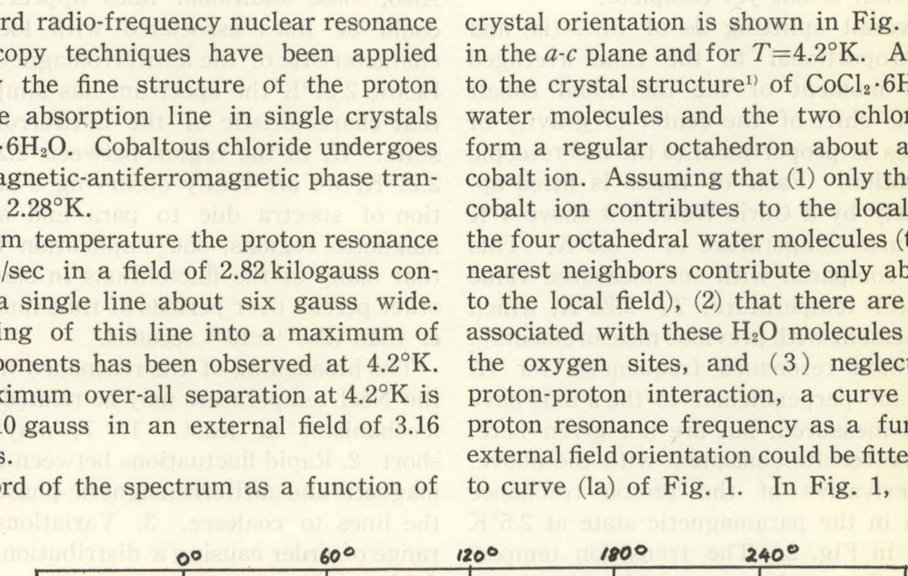

Fig. 1.

of rotation is in the plane containing the four octahedral oxygens so that these four positions are magnetically equivalent and would only give one line if the proton-proton interaction was neglected. The small separation of lines (1a) and (1b) may then be attributed to the proton-proton interaction within one H_2O molecule. The above argument would indicate that some of the eight protons lie very close to the plane of the 4 oxgens of the octahedron. Lines (1a) and (1b) account for approximately 1/7 of the total intensity. A detailed analysis of the rest of the spectrum is not yet complete.

The overall splitting $\Delta\omega$ of lines (1a) and (1b) is proportional to the time averaged magnetic moment of the individual cobalt ions. The shift of the center of gravity of these lines is proportional to the macroscopic magnetization. Each of these is fitted approximately by a Curie-Weiss law above 4°K with a Curie temperature of −3.8°K. This is to be compared with our measured value of the Néel temperature, $T_n=2.28$°K, which is in agreement with previous measurements[2].

The proton resonance frequencies for H_0 in the plane perpendicular to the a-axis have also been measured, but are not given here. They give results consistent with the above.

The derivative of the proton resonance spectrum in the paramagnetic state at 2.5°K is shown in Fig. 2. The transition temperature to the antiferromagnetic state was measured by observing the change in the signal of Fig. 2 at the maximum located at 13.320 Mc. A plot of this maximum versus temperature is shown Fig. 3. In the antiferromagnetic state (e. g. 2.21°K) there is zero signal at this point. Below about 2.28°K the signal gradually disapperas over a temperature range of 0.07°K. This spread of the transition indicates that short range order effects are present. These effects are being investigated in more detail.

The spectrum at 2.25°K (not shown here) shows that the paramagnetic lines have been broadened somewhat but are still recognizable. Also, some additional lines appear. These could be lines associated with local fields characteristic of the antiferromagnetic phase. Below 2.21°K the spectrum has simplified to that characteristic of the antiferromagnetic state. If, in the region between 2.28°K and 2.21°K, we are really observing a superposition of spectra due to para and antiferromagnetic regions, one implication would be that many of the fluctuations in short range order persist over periods of time much greater than $(\Delta\omega)^{-1}\simeq10^{-6}$ seconds.

The broadening of the resonance lines near the Néel temperature may be related to three mechanisms at least. 1. T_1 may become short. 2. Rapid fluctuations between the paramagnetic and antiferromagnetic phase causing the lines to coalesce. 3. Variations in the range of order causing a distribution of local fields.

Preliminary measurements in the antiferro-

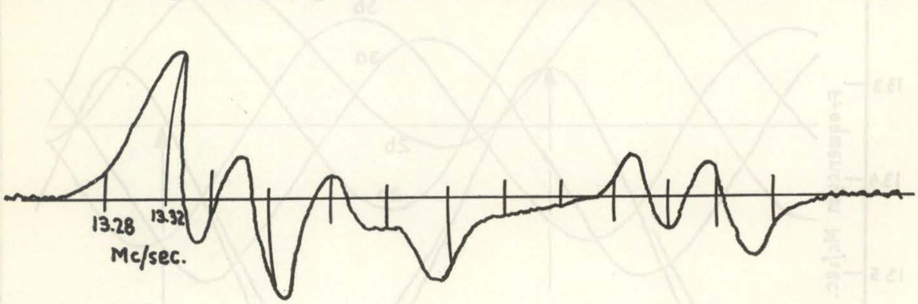

Fig. 2.

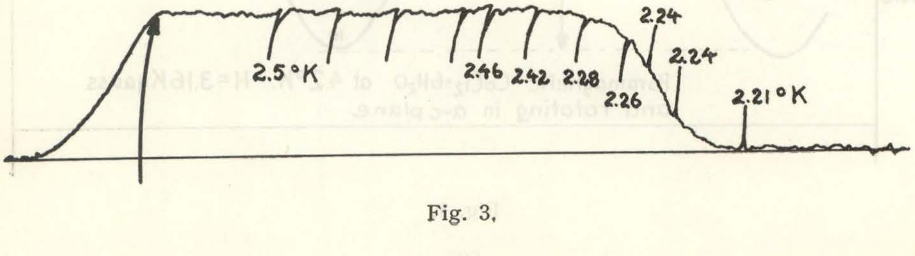

Fig. 3.

magnetic state in the *a-c* plane agree with those of T. Sugawara[3] except for a strong central line at almost exactly the free proton frequency which seems completely independent of crystal-orientation. This discrepancy may be due to the faulty crystal alignment and should resolve itself with further investigation.

References

1 J. Mizuno, K. Ukei and T. Sugawara: J. Phys. Soc. Japan **14** (1959) 383.

2 W. K. Robinson and S. A. Friedberg: Phys. Rev. **117** (1960) 402.

3 T. Sugawara: J. Phys. Soc. Japan **14** (1959) 1248.

DISCUSSION

N. J. POULIS: In Leiden myself and Dr. Spence in Michigan found in azurite the existence of two states (paramagnetic as well as antiferromagnetic) at one temperature. There exists a linear decrease of the proton resonance line over a temperature range from 2.1°K to 1.84°K. The lines for the antiferromagnetic state are sharp in a region of 0.1°K and have a strong temperature dependence. Above 1.95°K the lines for the antiferromagnetic state broaden and are independent on temperature.

As far as we could find out there are no hysteresis effects. There can be no faults in the temperature readings because the crystals are directly immersed in liquid helium and experiments were carried out with increasing and decreasing temperature.

R. J. ELLIOTT: It seems very unreasonable that the paramagnetic and antiferromagnetic phases should co-exist in the same part of the sample. Even in critical neutron scattering where slowing of the fluctuations is observed, it is only slow on this scale over a minute temperature range.

It would be interesting to measure the line width in the paramagnetic phase. F in MnF_2 shows a broadening near T_c but Co in CoO does not and the difference is not understood.

K. TOMITA: Concerning the distinction between various mechanisms which Dr. Bloom mentioned in the last part of his talk, the following points are quite relevant.

1. Have you observed any shift in frequency of the antiferromagnetic components in the coexistence range?

2. Have you noticed any change in line shape in the same temperature range?

M. BLOOM: The line shapes have not yet been investigated in detail, but the paramagnetic lines were broadened. Some lines were broadened more than others.

N.J. POULIS: Above 1.84°K, for azurite the antiferromagnetic components still follow a certain dependence of magnetization on temperature. They don't stay at one place, but they really displace as a function of temperature. They broaden also.

DE GENNES: Is it possible to saturate the paramagnetic line and observe the antiferromagnetic lines? This might be a good test of the sample homogeneity.

M. BLOOM: We are planning to do pulse experiments on this system. Under certain conditions one might expect nuclear spin polarization to be transferred rapidly between a paramagnetic line and the antiferromagnetic line for the same proton.