# PROTON MAGNETIC RESONANCE IN PARAMAGNETIC

AND ANTIFERROMAGNETIC CoCl<sub>2</sub>.6H<sub>2</sub>O

by

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B.Sc., University of British Columbia, 1958 M.Sc., University of British Columbia, 1960

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### PROTON MAGNETIC RESONANCE IN PARAMAGNETIC AND ANTIFERROMAGNETIC CoCl<sub>2</sub>·6H<sub>2</sub>O

#### ABSTRACT

The work reported here is a detailed study of the proton magnetic resonance in single crystals of CoCl<sub>2</sub>. 6H<sub>2</sub>O. This substance is paramagnetic at high temperatures and becomes antiferromagnetic at about 2.25°K. The proton resonance frequency is a measure of the total magnetic field at the positions of the protons, which is the vector sum of the applied magnetic field with the internal field produced by the surrounding magnetic ions.

At room temperature a single line about 6 gauss wide is observed. This line splits into a number of components at liquid helium temperatures. The position and number of lines strongly depend on temperature and on the direction of the externally applied magnetic field. The maximum overall splitting at 4.2°K is about 150 gauss in a field of 5000 gauss. At 2.1°K the maximum splitting observed is about 2500 gauss. From the resonance lines in the paramagnetic phase it was possible to calculate the direction cosines of one proton-proton vector. The resonance spectra in both phases were found to agree well with the theory predicting the positions of the resonance lines and their dependence on crystal orientation.

The transition temperature  $T_N$  was measured as a function of applied field and crystal orientation using the proton resonance lines, since they are very sensitive functions of temperature near  $T_N$ .  $T_N$  is found to be a complicated function of the applied field and crystal orientation, which cannot be described by  $T_N({\rm H},)$  = T(0) - const. H<sup>2</sup>, as predicted by the Weiss Molecular field theory.

The transition takes place over a temperature region of about  $10^{-2}$  °K, and effects due to short range order are observed just above  $T_N$ .

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The magnetic susceptibility in zero field was measured along the preferred axis of antiferromagnetic alignment. This, together with specific heat data from published literature, was used to show a mutual consistency between thermodynamic variables and  $T_{\rm N}$  obtained by NMR.

The sublattice magnetization in the antiferromagnetic phase was measured as a function of temperature. It is found to depend logarithmically on  $T_N$  - T, but is independent of applied field and crystal orientation.

Further experiments are suggested, which would add greatly to the understanding of the magnetic behaviour of  $CoCl_2 \cdot 6H_2O$ .

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#### CHAPTER I

#### INTRODUCTION

The nuclear magnetic resonance technique provides a powerful method of studying the interactions between atomic nuclei and their magnetic environment. The steady state branch of this technique is particularly suited for the investigation of internal magnetic fields, because the nuclear resonance frequency is a measure of the magnetic field at the nucleus under investigation. In the field of solid state physics, the importance of nuclear magnetic resonance (NMR) is now well recognized, and valuable contributions have been made to the understanding of many different classes of materials, among them paramagnetic and antiferromagnetic substances.

In this work we are concerned with the proton magnetic resonance in single crystals of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  both in the paramagnetic and antiferromagnetic phases of this substance. The proton resonance in both phases is profoundly influenced by the electronic magnetic moments of the cobalt ions and by the protons themselves and may thus be used to study the internal magnetic properties of the crystal.

In general, if a system of non-interacting protons with spin I = 1/2 is placed in a uniform magnetic field  $\overrightarrow{H}$ , each proton can assume either of two orientations with respect to this field  $\vec{H}$  corresponding to two energy levels  ${}^{\pm}\mathcal{M}_{p}\mathcal{H}$ , where  $\mathcal{M}_{p}$  is the magnetic moment of the protons. The difference in energy between the two levels is thus  $2\mathcal{M}_{p}\mathcal{H}$ . Transitions between the two levels may be induced by applying electromagnetic radiation, which is circularly polarized with the magnetic vector rotating in a plane perpendicular to the static magnetic field  $\vec{H}$ . The frequency of this radiation must be equal to the classical larmor frequency

$$\omega_{\rm c} = 2 \,\mu_{\rm p} H/\hbar = \delta_{\rm p} H$$

where  $\delta_p = 2.675 \times 10^4$  rad/sec-gauss is the gyromagnetic ratio for protons. In a typical field of 5,000 gauss, the proton resonance frequency is 21.297 Mc/sec.

The simple picture of non-interacting protons outlined above is never strictly true, since interactions with neighbouring magnetic moments are always present, although in liquids and gases these interactions are averaged considerably due to thermal motion of the atoms and molecules. In crystalline solids the nuclei occupy, except for thermal vibrations, fixed positions, and each nucleus experiences, in addition to the externally applied static magnetic field  $\overrightarrow{H}_{0}$  and the small r-f field  $\overrightarrow{H}_{1}$ , an inhomogeneous internal magnetic field due to the neighbouring magnetic dipoles. The proton resonance frequency is a measure of the total magnetic field at the positions of the protons, which is the vector sum of the applied field  $\vec{H}_{o}$  with the internal field  $\vec{H}_{int}$ , i.e.  $\vec{H}_{loc} = \vec{H}_{o} + \vec{H}_{int}$  (1.1)

and the resonance frequency is  $\omega = \delta H_{loc}$ .

If the crystal contains paramagnetic ions, as is the case in  $CoCl_2 \cdot 6H_20$ , the internal magnetic field  $\vec{H}_{int}$  may be of the order of 1000 gauss, whereas internal fields due to non-paramagnetic ions are usually not larger than 20 gauss. Since the magnetic moment of the paramagnetic ions may be oriented in (2S + 1) different directions ( S = effective spin of the paramagnetic ion), the internal field produced by the neighboring ions at the positions of different protons in a unit cell of the crystal may vary between approximately  $\pm$  1000 gauss. This range of internal fields should give rise to a spread of resonance frequencies, and we would expect very broad proton resonance lines in paramagnetic substances. However, it can be shown<sup>1)</sup> that if exchange interactions between the magnetic ions are present, this broadening action of the magnetic ions is considerably reduced. From the exchange interaction and the Zeeman energy of the cobalt ions in the external field  $\overline{H}_{0}$  the time averaged magnetic moment  $\left< \overline{\mathcal{U}_{\mathcal{O}}} \right>$  is obtained to a first approximation<sup>2)</sup> in the paramagnetic phase

 $\langle \vec{\mu}_{co} \rangle = \beta^2 \tilde{g} \cdot (\tilde{g} \cdot \tilde{H}_o) S(s+1) / 3k(T - \Theta)^{(1.2)}$ 

where  $\beta$  is the Bohr magneton,  $\tilde{g}$  is the anisotropic g-tensor, and  $\boldsymbol{\varTheta}$  is the Curie temperature of the substance. This mean magnetic moment gives rise to a time averaged internal field which depends strongly on the spatial coordinates and on the orientation of the crystal with respect to the external magnetic field  $\overline{H}_{0}$ . The energy levels of the proton magnetic moments are determined by the vector sum of this internal field with  $\overrightarrow{H}_{o}$ , and non-equivalent protons in a unit cell have different resonance frequencies. Assuming that  $\vec{H}_{o}$  is constant over the sample, the local field will be the same for equivalent protons in the unit cells and the proton resonance will split into a number of component lines, provided the local fields are sufficiently different at non-equivalent protons. To resolve a pair of lines the difference in local fields must be greater than the proton line widths which are typically of order 5 to 10 gauss for hydrated salts of the transition elements. Since the internal field has roughly an inverse temperature dependence, the separation between component lines increases with decreasing temperature. Thus the number of component lines observed in any particular applied field depends on the sample temperature, on the number of water molecules per unit cell, and on the degree of symmetry of the crystal.

The internal field at a proton due to a paramagnetic ion at a distance r is of the order of magnitude  $\langle \mathcal{U} \rangle / r^3$ . The field therefore falls off rapidly with increasing r , so

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that only the nearest neighbours make important contributions to  $H_{local}$ . Taking  $r = 2 \times 10^{-8}$  cm and  $H_0 = 5,000$ gauss, the splitting in  $CoCl_2 \cdot 6H_2O$  at  $300^{\circ}K$  is about 2 gauss, at  $78^{\circ}K$  about 7 gauss, and at  $4^{\circ}K$  about 120 gauss. We therefore do not expect any resolution of the proton resonance line at room temperature, and only partial resolution at  $78^{\circ}K$  and  $4^{\circ}K$ . Experimentally a single line about 5 gauss wide is observed at room temperature. The maximum splitting at  $78^{\circ}K$  is about 35 gauss and at  $4.2^{\circ}K$  about 170 gauss in good agreement with the above order of magnitude arguments, since r was chosen arbitrarily as  $2^{\circ}A$ .

The work to be described in the following chapters of this thesis is an extensive study of the proton magnetic resonance in CoCl<sub>2</sub>. 6H<sub>2</sub>O as a function of temperature, crystal orientation and applied field. A summary of the theory describing the positions of the component lines as a function of temperature, orientation, and applied field is presented in chapter III, for both the paramagnetic and antiferromagnetic phases. In the paramagnetic phase the internal field due to the cobalt ions is found to be proportional to

 $\langle \vec{\mathcal{U}}_{G} \rangle (1 - 3 \cos^2 \Theta_{ik}) r_{ik}^{-3}$ , where  $r_{ik}$  is the magnitude of the radius vector between the i<sup>th</sup> proton and the k<sup>th</sup> cobalt ion, and  $\Theta_{ik}$  is the angle between  $\vec{H}_{o}$  and  $\vec{Y}_{ik}$ . This implies that the resonance lines in the paramagnetic phase behave like sine functions with a period of 180°. In

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addition to the internal field due to cobalt ions, a proton in one water molecule experiences a field proportional to  $\int_{12}^{2} \hbar^{2} \left( 3 \cos^{2} \Theta_{12} - I \right) \gamma_{12}^{-3}$  due to the other proton in the same water molecule. This field is much smaller than that due to the cobalt ions, but nevertheless gives rise to an additional splitting of component lines which is independent of the magnitude of the applied magnetic field. The maximum observed proton-proton splitting at 4.2°K was found to be 15 gauss. From the proton-proton splitting as a function of orientation it was possible to find the direction cosines for the line joining one pair of protons. The 180° periodicity of the resonance curves in the paramagnetic phase was verified experimentally. The antiferromagnetic phase is characterized by a spontaneous alignment of the cobalt magnetic moments, independent of the applied field  $\vec{H}_{o}$ , provided  $H_0$  is not too large. This spontaneous antiparallel alignment gives rise to an internal field of the form

$$\vec{H}_{int} = \langle \vec{\mu}_{co} \rangle \cos(\alpha + \alpha_{o})$$

where  $\checkmark$  is the angle between  $\langle \mathcal{M}_{0} \rangle$  and  $\mathcal{H}_{0}$  and  $\checkmark_{0}$  is a phase angle depending on the orientation of  $\langle \mathcal{M}_{0} \rangle$  with respect to the crystal axes and on the spatial coordinates. Thus the resonance curves are found to behave like sine functions with a period of 360° instead of 180° as in the paramagnetic phase. The number of resonance lines effectively doubles when we pass from the paramagnetic to the

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antiferromagnetic phase due to the fact that we now have two sublattices, i.e.,  $\langle \mathcal{U}_{CO} \rangle$  can point in a + direction or in a -direction. The resonance diagrams in the antiferromagnetic phase are thus symmetrical about a central frequency which is determined by  $\overrightarrow{H}_{O}$ . The splittings in the antiferromagnetic phase are much larger than in the paramagnetic phase. Splittings of the order of 2,500 gauss were observed at 2.1° K. It was verified experimentally that  $\langle \mathcal{U}_{CO} \rangle$  in the antiferromagnetic phase is independent of the applied field in the range of fields used in this experiment.

The phase transition or Néel temperature  $T_N$  is treated in chapter V. It is found that the transition is not sharp, but takes place over a temperature range of a few millidegrees indicated by an overlap of both types of spectra in this range. The resonance line amplitudes decrease sharply as  $T_N$  is approached, whereas the line widths show an anomalous peak at  $T_N$ . This behaviour together with the anomalous peak in the specific heat at  $T_N$  is very suggestive of a  $\lambda$ -type transition as observed in liquid helium. The transition temperature was studied as a function of crystal orientation and applied field. The orientation dependence could be described by a function of the type

 $\left\{T_{N}(\varphi)\right\}_{H_{o}} = A(H_{o}) + B(H_{o}) \sin^{2} \varphi$ ,

where  $\varphi$  is the angle between  $\widehat{H}_{o}$  and the preferred axis of

antiferromagnetic alignment. From the field dependence of  $T_N$  it is found that  $B(H_0)$  is nearly a linear function of  $H_0$ . The dependence of  $T_N$  on  $H_0$  and  $\varphi$  is inconsistent with molecular field theory. Extrapolating to  $H_0 = 0$ ,  $T_N$  was found to be equal to  $2.27^{\circ}$ K. When  $\vec{H}_0$  is applied perpendicular to the preferred (c) axis,  $T_N$  is found to have a broad minimum at about 3000 gauss and a maximum at 5000 gauss. This type of behaviour is not found in other phase transitions, where the line separating two phases is usually a monotonic function of the intensive thermodynamic coordinate. No explanation has been given for this behaviour of  $T_N$ .

The magnetic susceptibility parallel to the preferred (c) axis in zero applied field was measured as a function of temperature by measuring the self-inductance of a coil containing a sample of  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 O$  as a core. These measurements were found to be in good agreement with previous susceptibility measurements<sup>3</sup> using an inductance bridge. The present measurements together with specific heat data are used to show the mutual consistency between the thermodynamic properties and the slope of the transition temperature near zero field as obtained with NMR.

The temperature dependence of the resonance frequencies in the antiferromagnetic phase was studied in various applied fields and at several crystal orientations. In chapter VI we shall see that the resonance frequency is

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a measure of the sublattice magnetization  $\vec{M}$ . It was found, regardless of  $H_0$  and orientation, that  $\vec{M}$  depends logarithmically on  $(T_N - T)$  over the whole temperature range studied. This behaviour must, of course, break down near  $T_N$ . The logarithmic behaviour was found to hold to within about 20 millidegrees of  $T_N$ . It is interesting to note that this behaviour is qualitatively similar to the behaviour of the specific heat, which also depends logarithmically on  $(T_N - T)$  near the transition temperature.

## CHAPTER II

## APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental data in this thesis was obtained with a standard steady state nuclear resonance spectrometer. A block diagram of the apparatus is shown in figure 1. Circuit diagrams of the more common units are given in Appendix A, together with some notes on the operation and construction of the various units. Details of the low temperature system are also given in Appendix A. Only modifications, original designs, and the experimental procedure shall be described in this chapter.

The oscillating detector was a slightly modified version of a circuit by Watkins and Pound<sup>4</sup>. We have substituted a voltage sensitive capacitor, (varicap), for the mechanically variable capacitor in the tuned circuit in order to minimize incidental noise and to eliminate sudden frequency changes during very slow sweeps due to irregularities in the mechanical drive (see figure 1A in the Appendix). These modifications, together with the linear voltage sweep described below, proved very convenient and time saving.

The sawtooth voltage required to sweep the frequency of the oscillating detector by means of a varicap voltage sensitive capacitor is derived from a modified Tektronix type



Fig. 1 Block Diagram of Apparatus

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162 Waveform Generator. Part of this generator is shown in figure 2 (permission for reproduction of schematic granted by Tektronix Inc., May 11, 1962), the modifications being indicated by dashed enclosures. The basic operation of the Tektronix 162 Waveform Generator is fully described in the Tektronix 160 Series Instruction Manual. The modifications are described below.

Changing the values of the timing resistors and timing capacitors<sup>5)</sup> as indicated in figure 2 provides a variable sawtooth voltage rundown from 6000 volts per hour to as slow as 8 volts per hour. When SW6 is closed, V2B is at cut-off and the plate of V4 rises to maximum voltage, causing the timing capacitor to quickly recharge and a new cycle may be started by opening SW6. Thus, SW6 provides a means of starting a new cycle during any part of the voltage rundown. The starting voltage is preset by means of R7A and the cathode follower V7A. Any voltage between 50V and 150V may be selected, producing a sawtooth output at the cathode of V5B decreasing uniformly from the preset voltage to positive 20V.

The voltage sensitive capacitors used in this experiment are rated at 100V maximum and are most sensitive at low voltages. In order to obtain a sawtooth voltage varying uniformly between 100V and OV, the cathode of V5B is connected to the grid of V7B, and the cathode of V7B is returned to the -170 volt supply through a 50V Zener diode and a 33K

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resistor. The voltage appearing at the cathode of the Zener diode is 50V lower than that at the cathode of V5B. Thus we now have a sawtooth voltage of maximum range between positive 100V and negative 30V. The negative tail is eliminated by means of diode F4 and R7B. The final output is a uniformly decreasing voltage adjustable between 100V and OV.

Thus, with the modifications described above, any range and slope of the voltage rundown may be selected to sweep the frequency of the oscillating detector. The change in oscillator frequency corresponding to this voltage sweep depends on the type and number of varicaps used and on the inductance of the oscillator coil. Various combinations of varicaps were used, and it was possible to obtain frequency sweep rates from a few hundred Kc/sec to a few cycles per second.

A circuit diagram of the 30cps source and its accompanying phase shifting networks is shown in figure 3. The frequency of this source is locked to the frequency of the A.C. mains by means of a bistable multivibrator V2 which is triggered by the 60cps mains voltage. This arrangement minimizes interference from the A.C. mains via field modulation and detector output amplification. A 30cps sinusoidal voltage is obtained from the multivibrator square wave by means of two filters tuned to 30cps. The remainder of the network of the 30cps source is selfexplanatory from the schematic of figure 3.

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Fig. 3 30 cps Source and Modulation Signal Output



Fig. 3 cont'd. Phase Shifter, Audio, and Reference Voltage Outputs

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The magnet current was derived from a power supply adapted from a circuit by R. L. Garwin<sup>6)</sup>. Since the magnet used in this work has a considerably higher impedance than that used by Garwin, it was necessary to increase the reference resistor to 0.1 ohms. Resistance variations in the reference resistor were minimized by means of a water cooled oil bath. It was also found that the performance of this circuit improves greatly if the signal transistors are water-cooled. A circuit diagram of the existing regulator is shown in figure 5A.

The remainder of the apparatus in figure 1 is standard equipment and shall not be described here, except for its uses in this work. Circuit diagrams of the units not mentioned here are shown in Appendix A.

The external field  $H_0$  is supplied by an air-cooled iron-core electromagnet (manufactured by Newport Instruments Ltd., Ser. No. 6010/3) with four inch diameter plane pole tips and adjustable air-gap. With an air-gap of 3.2 cm an inhomogeneity of about 0.3 gauss per cm exists near the center of the pole faces at a field of 5.0 Kgauss. The magnet is mounted on a rotating table provided with a graduated scale so that any field orientation relative to the sample in the plane of rotation can be obtained. Field modulation is achieved by means of a pair of flat coils glued to the pole faces in order to minimize modulation interference in the magnet power supply and at the same time to minimize the pole face separation. The modulation current is supplied by a Williamson type power amplifier driven by the 30cps source (see figures 1 and 3). With maximum input from the 30cps source, a modulation field of 100 gauss can be achieved.

The proton resonance line widths in  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 \operatorname{O}$  are of the order of 5 gauss or larger. To observe the derivative of the true line shape with a recording milliameter, the modulation amplitude should not exceed about 1/4 the line width and so a modulation of about 1 gauss was used when recording the derivatives of the resonance lines.

With the above-mentioned current regulator field stabilities of the order of 1 part in  $10^5$  can be easily obtained. The magnetic field was measured before and after each run, and in some experiments several times during each run with the aid of a second oscillating detector by measuring the frequency of the proton resonance in a sample of water doped with approximately 2% of  $CusO_4 \cdot SH_2O$ . The field was obtained from  $\omega = \delta H_o$ , where  $\delta$  is well known for protons in water.

Single crystals of  $CoCl_2 \cdot 6H_2O$  were grown from aqueous solutions and found to be of the same type described by P. Groth<sup>7)</sup>.  $CoCl_2 \cdot 6H_2O$  crystals grow very rapidly, but tend to form multi-oriented, polycrystalline blocks. Several growing methods were employed with varying degrees of success. The most successful arrangement is shown in Fig.4a.





4b

Fig. 4a. Crystal Growing Vessel Fig. 4b. Crystal Holder

A temperature gradient of 1 or 2 degrees between the top and the bottom of the solution is maintained by means of the heater coil. A few irregular pieces of crystalline  $CoCl_2 \cdot 6H_2O$  are placed in the tail of the vessel, and the solution surrounding these pieces is more concentrated and slightly warmer than the top layers of the solution. Thus a continuous upward current of a more concentrated solution is maintained. As this solution current reaches the upper layers it cools and some of the excess solute is deposited on the seed suspended with a thin nylon thread. With this method it was possible to obtain good single crystals with dimensions roughly up to 3 x 2 x 2 cm.

Cylinders 8 mm in diameter and about 2 cm long were cut from the grown crystals, taking great care to insure that a particular crystal axis was parallel to the cylinder axis. These cylinders were placed in a thin-walled (0.5 mm) "Teflon" tube which is attached to a 3/8 inch stainless steel tube in the manner shown in figure 4b. The stainless steel tube with the Teflon holder was mounted vertically so that the field  $\vec{H}_0$  would be perpendicular to the cylinder axis ( $\vec{H}_0$  is adjusted to be horizontal). It is estimated that the error in orientation did not exceed 5 degrees in the various mountings. With this arrangement different crystal cylinders could be investigated under identical conditions since the same sample holder could be used for different crystals.

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The low temperatures were achieved with the aid of an ordinary double dewar glass cryostat. A schematic of the low temperature system is shown in figure 6A. Temperatures lower than 4.2°K were obtained by pumping on the helium vapour and were maintained constant by regulating the rate of pumping with a manostat. The temperature was measured by observing the vapour pressure with a meniscus type cathetometer. The lowest temperature obtained was about 1.25°K.

It was feared that the Teflon holder would prevent rapid temperature equilibrium between the sample and the helium bath, but extensive investigations showed that this was not the case. All temperature sensitive properties of  $CoCl_2 \cdot 6H_2O$  investigated in this work were rechecked against various rates of temperature change and were found to follow the temperature (vapour pressure) very closely. When raising the temperature, a strong light was directed into the liquid helium bath and maintained there until the helium boiled violently to insure proper stirring of the liquid. The tips of both dewars were unsilvered, providing a path for radiation into the helium. It was found that the temperature of the sample could be raised by  $0.1^{\circ}$  K in a few seconds by placing a common 100 watt light bulb near the dewar tips.

Whenever measuring a temperature dependent quantity by continuously following the temperature (vapour pressure), the measurement was always made at decreasing temperatures,

and even then at a slower rate than previously found permissible. When measuring the transition temperature by following the signal amplitude as a function of vapour pressure (hence temperature), the temperature variation was often stopped at some arbitrary temperature, and it was found that the signal amplitude remained at whatever value the temperature variation was stopped, indicating that the sample temperature followed closely the vapour pressure. If there were not a continuous equilibrium, the signal amplitude should continue to change, as it is a very sensitive function of temperature near the Néel temperature. It was found that this continuous temperature equilibrium was even true for increasing temperatures, because enough light from the room in general could get into the dewars providing a continuous heat source. However, all measurements were made at decreasing temperatures.

Frequency measurements were made with a Hewlett Packard Model 524C Electronic Counter coupled to a Model 561B Digital Recorder. In the antiferromagnetic phase where the separation between lines is very large (up to 15 Mc/sec. at 2.1<sup>°</sup> K) the signal was merely brought onto an oscilloscope screen and the resonance frequency recorded. In the paramagnetic phase and in experiments near the Néel temperature all signals were recorded on a recording milliameter. A marker on the recording milliameter was coupled to the digital recorder in order to correlate the numbers from the

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digital recorder to positions on the recording charts.

The usual method of phase-sensitive detection was employed to record the derivatives of the actual resonance lines. In all cases, the frequency of the oscillator rather than the magnitude of the external field was varied. The rate of sweep was adjusted in each case to avoid distortion of the signal by integration through the relatively long time constant in the phase sensitive detector.

#### CHAPTER III

#### THEORY OF THE POSITIONS OF THE RESONANCE LINES

In this chapter a brief summary of the theory describing the positions of the proton magnetic resonance lines as a function of the externally applied magnetic field in hydrated single crystals containing paramagnetic ions is presented. The calculations which follow below were developed by N. Bloembergen<sup>2</sup>) in connection with similar measurements in  $CuSo_4 \cdot 5H_2O_*$ .

The position and width of each resonance line are complicated functions of the direction and magnitude of the applied magnetic field  $H_o$ , and of the internal structure of the crystal. For each direction of the applied field the separation between the lines increases with The character of the resonance decreasing temperature. spectrum changes drastically as we pass from the paramagnetic phase  $(T > T_N)$  to the antiferromagnetic phase  $(T < T_N)$ . Theoretical formulae for the positions of the component lines are developed by considering the proton two-spin system within a water molecule of hydration acted upon by the externally applied field  $\vec{H}_0$  and the inhomogeneous timeaveraged field arising from the electronic magnetic moments of the cobalt ions. The dipolar interactions with the protons in neighbouring water molecules and with other nuclei

are assumed to contribute only to a broadening of the resonance lines.

We consider a crystal containing paramagnetic ions and one or more water molecules of hydration. Except for the positions of the protons, the crystal structure is generally known. At each point in the crystal there will be, in addition to the applied field, a time-varying inhomogeneous internal field contributed by the electronic magnetic moments of the paramagnetic ions with spin S. There is also a weaker field due to the neighbouring proton magnetic moments with spin I = 1/2. The magnitude and direction of this internal field at any given point depend on the orientation and separation of the magnetic moments at that time. The Hamiltonian describing this system may be written in the form

$$\mathcal{H} = -\sum_{k} \beta \vec{S}_{k} \cdot \vec{g}_{k} \cdot \vec{H}_{o} + \mathcal{H}_{SS} + \mathcal{H}_{ex}^{S} \qquad (3.1)$$
$$+ \mathcal{H}_{SI} + \mathcal{H}_{II} - \sum_{i} \delta_{i} \hbar \vec{I}_{i} \cdot \vec{H}_{o}$$

where  $\beta$  is the nuclear Bohr magneton and  $\widetilde{g}_k$  is the anisotropic g-factor in the tensor form. The first and last terms in (3.1) are the Zeeman energies of the cobalt ions and protons in the externally applied field  $\widetilde{H}_0$  respectively.  $\mathcal{H}_{SS}$  is the magnetic interaction between the cobalt ions, and  $\mathcal{H}_{e_X}^S$  the exchange energy between them. The term  $\mathcal{H}_{SI}$  represents the magnetic interaction between the cobalt ions and proton moments, and  $\mathcal{H}_{II}$  is the magnetic interaction

between the protons themselves.

Since we consider the proton spin system immersed in the homogeneous applied field  $H_{o}$  and the inhomogeneous fluctuating field produced by the neighbouring magnetic moments, it is convenient to divide the Hamiltonian (3.1) (a) HC, from which the internal field is into two parts: calculated and (b) the Hamiltonian for the proton spin system subjected to the total local field at the proton sites. In considering the cobalt ions we shall neglect  $\mathcal{H}_{\texttt{SI}}$ , since the effect of the protons on the system of cobalt spins is very small as compared to  $\mathcal{R}^{S}_{ex}$  and the magnetic energy of the cobalt spins in the field  $\hat{H}_{o}$ . This term, however, is of great importance in the Hamiltonian for the proton spin system to be discussed below. The term  $\mathcal{H}_{SS}$  may also safely be neglected in comparison with  $\mathcal{H}_{ex}^{5}$  , since the exchange energy is roughly 100 times greater than the magnetic energy between two cobalt ions. Thus, the Hamiltonian of the cobalt spin system, using the standard notation for the exchange interaction, is:

$$\mathcal{H}_{C_0} = -\sum_{k} \beta \vec{S}_k \cdot \vec{g}_k \cdot \vec{H}_0 - 2 \sum_{j>k} \sum_{k} A_{jk} \vec{S}_j \cdot \vec{S}_k \qquad (3.2)$$

where  $A_{jk}$  is the so-called exchange integral between the cobalt spins.

The term in equation (3.1) connecting the two spin systems is  $\mathcal{H}_{ST}$  and may be written
$$\mathcal{H}_{SI} = \sum_{ik} \left\{ \frac{\delta_i \hbar \vec{I}_i \cdot \vec{\mathcal{U}}_k}{Y_{ik}^3} - \frac{3\delta_i \hbar \left(\vec{I}_i \cdot \vec{Y}_{ik}\right) \left(\vec{\mathcal{U}}_k \cdot \vec{Y}_{ik}\right)}{Y_{ik}^5} \right\} (3.3)$$

where  $\mathcal{I}_{k}$  is the magnetic moment of the k<sup>th</sup> cobalt ion and  $\gamma_{ik}$  is the radius vector connecting the i<sup>th</sup> proton and the  $k^{th}$  cobalt ion. As pointed out before,  $\widetilde{\mu_k}$  varies rapidly with time due to the exchange coupling between the cobalt ions. The exchange interaction causes a pair of antiparallel cobalt spins to change direction simultaneously, so that there is no energy involved, but the magnetic field due to  $\mathcal{I}_k$  changes direction in the neighbourhood of a pair of cobalt spins. The exchange frequency is approximately given by  $\hbar \omega_{ex} \simeq k T_N$ where  $T_N$  is the paramagnetic-antiferromagnetic phase transition temperature. For  $CoCl_2 \cdot 6H_2O$  T<sub>N</sub> = 2<sup>O</sup>K, so that  $V_{ex} = 5 \times 10^{10} \text{cps}$ . The Larmor frequency of protons in the internal fields of magnetic crystals never exceeds 107cps, so that the protons cannot follow the rapid variations of the internal field. The proton spins react only to the time-averaged field of the cobalt ions. We therefore can use the time-average  $\langle \mathcal{U}_k \rangle$  of  $\mathcal{J}_k$  in (3.3), i.e., the operator  $\mathcal{M}_k$  in equation (3.3) is replaced by a number,  $\langle \mathcal{M}_k \rangle$ The time-averaged magnetic moment  $\langle \mathcal{I} \mathcal{I} \rangle$  of the cobalt ion spins can now be calculated in principle from the reduced Hamiltonian (3.2) of the cobalt ion spin system by the

diagonal sum method described by Van Vleck<sup>8)</sup>, since the time averaged  $\langle \mathcal{A}_{k} \rangle$  should be the same as the statistical mechanical average for the equilibrium state of the  $C_{0}^{++}$  spin system.  $\langle \mathcal{A}_{k} \rangle$  is proportional to the magnetization  $\overrightarrow{M}$  in the paramagnetic phase (T > T<sub>N</sub>) and to the so-called sub-lattice magnetization in the antiferromagnetic phase (T  $\langle$  T<sub>N</sub>).

The effect of the time-averaged magnetic moment  $\langle \mathcal{M}_{k} \rangle$  on the proton spin system is now obtained from the Hamiltonian of the protons:

$$\begin{aligned} \mathcal{H}_{p} &= -\sum_{i} \chi_{i} \hbar \vec{I}_{i} \cdot \vec{H}_{o} \\ &+ \sum_{ik} \left\{ \chi_{i} \hbar \left[ \frac{\vec{I}_{i} \cdot \langle \vec{u}_{k} \rangle}{r_{ik}^{3}} - \frac{3(\vec{I}_{i} \cdot \vec{r}_{ik})\langle \langle \vec{u}_{k} \rangle \cdot \vec{r}_{ik}}{r_{ik}^{5}} \right] \right\} \quad (3.4) \\ &+ \sum_{ij} \left\{ \chi_{i} \hbar \left[ \frac{\vec{I}_{i} \cdot \vec{I}_{j}}{r_{ij}^{3}} - \frac{3(\vec{I}_{i} \cdot \vec{r}_{ij})(\vec{I}_{j} \cdot \vec{r}_{ij})}{r_{ij}^{5}} \right] \right\} \end{aligned}$$

Since the dipole-dipole interaction is proportional to  $1/r^3$ , only the nearest neighbours will contribute appreciably to this interaction. We therefore consider only interactions between the two protons in the same water molecule in the last term of (3.4). The interactions with other protons in the crystal and with the time dependent part of the field produced by the cobalt ions contribute only to the width of the resonance lines. We now have the relatively simple system of two interacting protons immersed in the homogeneous external field  $\overrightarrow{H}_{O}$  plus the static inhomogeneous internal field produced by the neighbouring cobalt ions, i.e. the protons are subjected to a field

$$\vec{H}_{loc} = \vec{H}_{int} + \vec{H}_{o}.$$

To find the resonance frequencies, (3.4) must be solved for its eigenvalues which give the energy levels of the two-proton system. We here present the results of N. Bloembergen<sup>2)</sup>, who obtains for the energy levels of the two protons in one water molecule to first order perturbation theory:

$$E_{1} = -8\pi H_{0} + a + d$$

$$E_{2} = -d + \sqrt{b^{2} + d^{2}}$$

$$E_{3} = -d - \sqrt{b^{2} + d^{2}}$$

$$E_{4} = 8\pi H_{0} - a + d$$
(3.5)

where

$$a = \frac{1}{2} \delta \hbar \left( H_{z}^{1} + H_{z}^{2} \right)$$

$$b = \frac{1}{2} \delta \hbar \left( H_{z}^{1} - H_{z}^{2} \right)$$

$$d = -\frac{1}{4} \delta^{2} \hbar^{2} \left( 1 - 3 \cos^{2} \theta_{12} \right) r_{12}^{-3}$$

$$H_{z}^{i} = \sum_{k} \langle \mathcal{M}_{k} \rangle \left( 1 - 3 \cos^{2} \theta_{ik} \right) r_{ik}^{-3} ; i = 1, 2.$$

and  $H_z^{1}$  and  $H_z^{2}$  are the z-components of the field produced by the cobalt ions at protons 1 and 2 respectively when the z-direction is chosen parallel to  $\overline{H_0}$ . The quantities a and b are functions of temperature by virtue of  $H_z^{1}$  and  $H_z^{2}$  which are calculated from  $\mathcal{H}_{SI}$  with  $\overline{\mathcal{M}_k}$  replaced by  $\langle \overline{\mathcal{M}_k} \rangle$ . The energy levels in (3.5) give rise to four transition frequencies as follows:

$$hv_{1} = 8\hbar H_{0} - a + 2d + \sqrt{b^{2} + d^{2}} = 8\hbar H_{loc_{1}}$$

$$hv_{2} = 8\hbar H_{0} - a - 2d - \sqrt{b^{2} + d^{2}} = 8\hbar H_{loc_{2}}$$

$$hv_{3} = 8\hbar H_{0} - a + 2d - \sqrt{b^{2} + d^{2}} = 8\hbar H_{loc_{3}}$$

$$hv_{4} = 8\hbar H_{0} - a - 2d + \sqrt{b^{2} + d^{2}} = 8\hbar H_{loc_{4}}$$
(3.7)

with corresponding intensities arbitrarily normalized to 4

$$I_{1} = I_{2} = \frac{\left(b - d - \sqrt{b^{2} + d^{2}}\right)^{2}}{b^{2} + d^{2} - b\sqrt{b^{2} + d^{2}}}$$

$$I_{3} = I_{4} = \frac{\left(b - d + \sqrt{b^{2} + d^{2}}\right)^{2}}{b^{2} + d^{2} + b\sqrt{b^{2} + d^{2}}}$$
(3.8)

Thus, with the approximations made in the preceding paragraphs, each water molecule of hydration in principle gives rise to four resonance lines. In the absence of the magnetic ions a = b = 0, and the problem has the solution given by Pake<sup>9)</sup> for the water molecule in gypsum. If, in the present case, a, b  $\ll$  d, which is certainly true at room temperature,

then the influence of the cobalt ions may be partly ignored and Pake's solution still holds. However, in  $CoCl_2 \cdot 6H_2O$  the number of protons per unit cell is large and the cobalt magnetic moment is not completely negligible even at room temperatures and we do not observe any resolved lines at room temperature, but a single line about six gauss wide. At helium temperatures, none of the terms in (3.6) are necessarily negligible, and each water molecule should give rise to four lines in two pairs of two. In CoCl, 6H,0 the positions of the protons are not known. However, if we assume that the protons in each water molecule in the unit cell are magnetically nonequivalent, then the six different water molecules of hydration should lead to 24 lines in six groups of four. At low temperatures we can safely assume that  $b \gg d$ , since the field of the cobalt ions is much larger than that of the protons. Then we have four lines of equal intensity consisting of two pairs, the centres of which are separated by a distance 2b, and the separation between the two lines in a pair is 4d. From (3.6) we see that for some particular configuration b may be equal to zero and only half of the maximum number of lines will be observed. Also, when the sums of the terms in the resonance frequencies in (3.7) containing the geometrical factors are equal, the resonance frequencies for the protons in different water molecules will coincide. It is thus expected that the number of resonance lines observed depends on the orientation of the

crystal relative to the external magnetic field  $\overrightarrow{H}_{O}$  and on the temperature of the system.

The distinguishing characteristic of the resonance diagrams in the paramagnetic phase is the periodicity of the resonance curves. From  $H_{Z}^{i}$  in (3.6) we see that the resonance curves are sine functions with a period of 180 degrees. In the next section we shall see that this periodicity changes to 360 degrees in the antiferromagnetic phase. These points will be discussed in detail in the next chapter in connection with the proton resonance measurements in paramagnetic and antiferromagnetic  $CoCl_{2} \cdot 6H_{2}O$ . All the above arguments apply to the paramagnetic state of the crystal where  $\langle \mathcal{M}_{k} \rangle \prec \overline{H}_{O}/(T + \Theta)$  to a first approximation, where  $\Theta$  is the Curie temperature.

The antiferromagnetic phase (T <  $T_N$ ) is characterized by a spontaneous alignment of the cobalt ion spins. The exchange integral  $A_{jk}$  in (3.2) may be positive or negative. If it is positive, then we have an ordinary ferromagnet with all the spins aligned in one direction. If  $A_{jk}$  is negative, adjacent spins will align in opposite directions giving rise in the simplest case to two ferromagnetic <u>sublattices</u> pointing in opposite directions. The bulk magnetic moment of the sample is still zero in the absence of an applied field, but inside the crystal there now exists a strong internal field alternating in direction from cobalt ion to cobalt ion. Recently it has been suggested<sup>10</sup> that there may exist more than two directions of alignment in some substances. A discussion of this possibility in  $CoCl_2 \cdot 6H_2O$  is postponed to a later chapter. For the purpose of describing the main features of the proton resonance curves in antiferromagnetic  $CoCl_2 \cdot 6H_2O$  it will suffice to assume a two-sublattice system.

The spontaneous alignment of the cobalt ion moments along some preferred direction in the crystal at a very low temperature is an inherent property of the system and persists even in the presence of an applied field. Therefore, in calculating the positions of the resonance lines in the antiferromagnetic phase, the arguments applied to the paramagnetic phase must be slightly modified.

In considering the local field at the proton positions we must take into account the fact that the cobalt spins have fixed directions and that adjacent cobalt ion spins point in opposite directions. The total magnetic field at a proton position is the vector sum of  $\vec{H}_0$  with the internal field due to the cobalt ions. In order to calculate the position of each resonance line as a function of the direction of the external field  $\vec{H}_0$ , we need consider only the component of the internal field parallel to  $\vec{H}_0$ . The perpendicular component will be discussed later. For simplicity consider one water molecule in the vicinity of a single cobalt ion magnetic moment  $\vec{H}_0$  and assume that  $\vec{H}_{c_0}$  is in the plane of rotation of  $\vec{H}_0$ . The magnetic field due to the cobalt ion at the position of proton i obtained from (3.3) by factoring out  $\delta_i \hbar \vec{I}_i$ , is given by

$$\vec{H}_{c_0} = \sum_{k} \left( \frac{\langle \vec{\mathcal{U}}_k \rangle}{r_{ik}^3} - \frac{3(\langle \vec{\mathcal{U}}_k \rangle \cdot \vec{\mathcal{V}}_{ik}) \vec{\mathcal{V}}_{ik}}{r_{ik}^5} \right)$$
(3.9)

The component of this internal field parallel to the applied field  $\overrightarrow{H_0}$  is then

$$H_{int \parallel H_0} = \vec{H}_{c_0} \cdot \frac{\vec{H}_o}{H_o}$$

and may be written in the form

$$H_{int \parallel H_{o}} = \sum_{k} \left\langle \mathcal{M}_{k} \right\rangle \left[ \cos \alpha - 3 \cos \theta_{ik} \cos \left( \alpha + \theta_{ik} \right) \right]^{(3.10)}$$

where  $\Theta_{ik}$  is the fixed angle between  $\langle \vec{\mathcal{U}}_k \rangle$  and  $\vec{\mathcal{V}}_{ik}$ , since we assume that  $\langle \mathcal{U}_k \rangle$  is coupled tightly to the crystal lattice, and  $\prec$  is the angle between  $\langle \vec{\mathcal{U}}_k \rangle$  and  $\vec{H}_0$ . Equation (3.10) may be rewritten in the more convenient form

$$H_{int || H_0} = \sum_{k} \langle \mathcal{M}_k \rangle A_k \cos(\alpha + \alpha_0)$$
<sup>(3.11)</sup>

where

$$A_{k} = \left[ \left( 1 - 3\cos^{2}\theta_{ik} \right)^{2} + \left( \frac{3}{2} \sin 2\theta_{ik} \right)^{2} \right]^{1/2}$$

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$$\tan d_0 = \frac{3/2 \sin 2\theta_{ik}}{1 - 3\cos^2 \theta_{ik}}$$

 $A_k$  and  $\prec_o$  are constants of the crystal lattice, and Both the variation of  $\vec{H}_{int} \| \vec{H}_{o}$ with orientation is determined Therefore, to determine the positions of the by & alone. proton resonance lines in the antiferromagnetic phase, the term  $H_z^{i}$  in (3.6) must be replaced by (3.11). It should be noted that in (3.11)  $\langle \vec{\mathcal{U}}_k \rangle$  belonging to one sublattice is positive, while  $\langle \mathcal{I}_k \rangle$  belonging to the other sublattice is Thus, the internal field is oriented in opposite negative. directions for corresponding protons in adjacent unit cells, and the number of resonance lines should double as we pass from the paramagnetic to the antiferromagnetic phase. Also. for each resonance line displaced in one direction due to Hint || Ho there will be another resonance line displaced an equal amount in the opposite direction due to  $H_{int} \| \overrightarrow{H_o} \|$ The resonance curve diagram will therefore be symmetric about the centre of gravity of the lines. In addition to the displacement of the resonance lines due to the parallel component of  $\overline{H}_{int}$ , there is also a contribution of the perpendicular component, which causes a slight lack of symmetry of the resonance curves about the centre of gravity of the resonance diagram.

The main difference between the paramagnetic phase

and the antiferromagnetic phase is the periodicity of the respective resonance curves. In the paramagnetic phase the resonance curves were sine functions with a period of 180 degrees rotation of the applied field  $\overrightarrow{H}_{0}$ . Equation (3.11) shows that this periodicity has now been changed to 360 degrees in the antiferromagnetic phase due to the  $\cos(\not \leftarrow + \not \sim_{0})$  factor in  $H^{i}_{z}$ . Also, since in this case the spins align spontaneously in their respective directions, the internal fields will be much larger in the antiferromagnetic phase than they are in the paramagnetic phase. This means that the resonance lines will be displaced much greater distances from the centre of gravity. In the next chapter we shall see how well these points are borne out by experiment.

In this chapter we have described the magnetic field at nuclear positions in terms of the applied field  $\vec{H}_{o}$  plus the internal field produced by the surrounding magnetic moments at the nuclear positions. We have thus neglected the contribution to the average magnetic field due to the average macroscopic magnetization  $\vec{M}$  per unit volume. In the next chapter we shall see that contributions of this type amount to about 40 gauss at  $4.2^{\circ}$  K. If we want to take this extra field into account, the external field  $\vec{H}_{o}$  should everywhere be replaced by  $\vec{Bo} = \vec{H}_{o} + (4\pi - N)\vec{M}$ , where N, the demagnetization factor for the crystal, must be calculated from the geometry of the sample<sup>11</sup>. Only if the sample is in the form of an ellipsoid will  $\overrightarrow{M}$  be uniform over the whole sample. For any other configuration,  $\overrightarrow{M}$  will be a function of position in the crystal and this non-uniformity of  $\overrightarrow{M}$  is equivalent to an inhomogeneity in the applied field in that it will contribute to the nuclear resonance line width.

### CHAPTER IV

THE PROTON RESONANCE IN CoCl<sub>2</sub>·6H<sub>2</sub>O

#### AT CONSTANT TEMPERATURE

## A. THE CoCl<sub>2</sub>.6H<sub>2</sub>O CRYSTAL

 $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 0$  forms dark purple monoclinic crystals of the type described by P. Groth<sup>7)</sup>. The unit cell edges are a:b:c = 1.4788:1:0.9452 with  $\beta = 122^{\circ}19'$ . Perfect cleavage occurs along the C(001) face. J. Mizuno et al<sup>12)</sup> have analyzed single crystals of  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 0$  by the X-ray method and report two formula units per unit cell with space group  $\operatorname{C}_{2h}^3 - \operatorname{C}_2^2/m$  with a = 10.34A°, b = 7.06A°, and c = 6.67A°. The atomic positions, except for the protons, are given in the following table:

Type of atom	Position	x	<u>y</u>	<u>Z</u>
Co	origin	0	0	0
Cl	4(1)	.278	0	.175
oı	8(j)	.0288	221	.255
OII	4(j)	.275	0	•700

The proton positions cannot be found by the X-ray diffraction method.

According to the authors of reference<sup>12)</sup>, two Cl<sup>-</sup> ions from 4(i) and four water molecules from 8(j) form an octahedron with the  $\text{Co}^{++}$  ion at the center to form the group  $(\text{CoCl}_2 \cdot 4\text{H}_2\text{O})$ . The octahedral plane contains the  $\text{Co}^{++}$  ion and the four water molecules, and the two Cl<sup>-</sup> ions are at the apexes of the octahedron. The other two water molecules of the formula unit are located at somewhat greater distances from the cobalt ions. The groups seem to be joined with one another by hydrogen bonds  $O_{I} \cdot \cdot \cdot \text{H} - O_{II} - \text{H} \cdot \cdot \cdot O_{I}$  and  $O_{T} - \text{H} \cdot \cdot \cdot \text{Cl}$  in the plane parallel to (OOl), the a-b plane.

## B. RESULTS AND DISCUSSIONS

In this chapter measurements at two fixed temperatures,  $T = 4.2^{\circ}$ K in the paramagnetic phase and  $T = 2.1^{\circ}$ K in the antiferromagnetic phase are discussed. The temperature dependence of the proton resonance, including a detailed discussion of the results near the Néel temperature  $T_{\rm N} = 2.275^{\circ}$ K, will be presented in the next chapter.

In making these measurements the crystal was kept fixed in the laboratory reference frame while the orientation of  $\overrightarrow{H}_{o}$  was changed by rotating the magnet. In one set of measurements  $\overrightarrow{H}_{o}$  was oriented in the a-c plane of the crystal, while in another set it was oriented in the a'-b plane, where a' lies in the a-c plane and is mutually perpendicular to the b and c axes, i.e., a' makes an angle of  $32^{\circ}19'$  with the a-axis. The angle between  $\overrightarrow{H}_{o}$  and the a'-axis is designated by  $\cancel{\varphi}$ . In subsequent discussions  $\cancel{\varphi} = 0$  shall refer to  $\overrightarrow{H}_{o}$  parallel to the a'-axis in both rotations. The measurements were made with the magnitude of  $\dot{H}_{O}$  kept constant, while the oscillator frequency was swept through the resonance spectrum at a rate slow enough to avoid distortion of the line shape.

When the separation between the component lines was small (1 Mc/sec or less), as is the case in the paramagnetic phase, the derivatives of the resonance lines were recorded using a phase sensitive detector and a recording milliameter. The oscillator frequency was marked directly on the recording chart with an automatic "event marker" at approximately 5 Kc/sec intervals. The resonance frequencies were then established by observing the lst, 3rd, 5th, etc. null in the derivative of the resonance spectrum. In this way permanent records of the spectra were obtained which could be used to study the line shapes and intensities of the individual lines. A sample recording is shown in Figure 5.

In the case of large line separations, as in the antiferromagnetic phase, the lines were not recorded on a recording chart. The different resonance lines were brought into the centre of an oscilloscope screen by adjusting the oscillator frequency manually, and the resonance frequency was read directly from the frequency counter. Derivatives were recorded only when the line widths were desired.

(i) The proton resonance in the paramagnetic phase at  $4.2^{\circ}$ K.

The results of the measurements in the paramagnetic phase are shown in Figures 6 to 9. Each set of points

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Fig. 5 Derivative of the Resonance Spectrum with H<sub>o</sub> in the a-b plane. H<sub>o</sub>=5000 gauss,  $\varphi = 100^{\circ}$ , T = 4.2<sup>°°</sup> K

parallel to the frequency scale was obtained from a recording of the type shown in Figure 5. In each of the Figures 6 to 9 the proton resonance frequency in water is indicated by a vertical line and the positions of the crystal axes are marked on the "orientation scale". The measured resonance frequencies are indicated by solid points. Solid lines are then drawn through the experimental points. In places where the resonance lines overlap, the null in the derivative is not a true measure of the peak resonance frequency, since the peak is slightly shifted due to the overlap. No corrections were made for such shifts, since the line shape is not known. Figure 6 shows the resonance diagram for the  $\overrightarrow{H_{o}}$  rotating in the a-c plane with  $H_0 = 5000$  gauss and the sample temperature  $T = 78^{\circ}$  K. Figures 7 and 8 are the resonance diagrams for  $\vec{H}_{0}$ rotating in the a-c plane at  $4.2^{\circ}$ K with H<sub>o</sub> = 3005 and  $H_{o} = 4970$  gauss respectively. Figure 9 shows the resonance diagram for  $\overrightarrow{H}_{O}$  rotating in the a'-b plane with  $H_{O} = 4990$ gauss and  $T = 4.2^{\circ}K$ .

As pointed out in chapters I and III, the separation between component lines depends on the temperature of the sample and on the applied field. The different resonance lines in Figure 6 were never completely resolved and only a maximum number of six lines could be observed. However, the resonance diagram of Figure 6 is basically similar to the diagrams of Figures 7 and 8, since all three diagrams were obtained with  $\overrightarrow{H_0}$  rotating in the a-c plane. The resolution

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Fig. 6. Resonance Diagram for H<sub>o</sub> in a-c plane. H<sub>o</sub> = 5000 gauss. T =  $77^{\circ}$  K

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Fig. 7 Resonance Diagram for H<sub>o</sub> in a-c plane. H<sub>o</sub> = 3005 gauss. T =  $4.2^{\circ}$  K

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Fig. 8 Resonance Diagram for  $H_0$  in a-c plane.  $H_0 = 4970$  gauss.  $T = 4.2^{\circ}$  K

**4**5



Fig. 9 Resonance Diagram for H<sub>o</sub> a'-b plane. H<sub>o</sub> = 4990 gauss. T =  $4.2^{\circ}$  K

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in Figures 7 to 9 is much better, and in some orientations completely resolved lines could be observed. All four diagrams are characteristic of the paramagnetic phase as outlined in chapter III. Each curve in the resonance diagrams behaves to a first approximation like a sine function with a period of 180 degrees due to the factor  $(3 \cos^2 \theta - 1)$ in the internal fields. This is in good agreement with the theory in chapter III. The resonance diagram for the a'-b rotation (Figure 9) is symmetric with respect to the a'-axis and the b-axis, in agreement with the space group  $C^2/m$ . The symmetry about the a'-axis is due to a' lying in the mirror plane m, the a-c plane; and the symmetry about the b-axis is due to b being a two-fold axis perpendicular to the mirror plane m.

In each of the resonance diagrams the centre of gravity of the lines is shifted from the proton frequency in water, indicating the need for the ideas put forth at the end of chapter III. The amount by which the lines are shifted from the proton frequency in water, due to the average bulk magnetization  $\overrightarrow{M}$ , can be calculated if theoretical resonance diagrams are available, but these can be obtained only if the proton positions are known. However, approximate shifts can be obtained by assuming the protons are situated at the oxygen positions. These ideas have been used<sup>13)</sup> in connection with earlier measurements to determine the ratios  $M(\overline{T_1})/M(\overline{T_2})$  and  $\langle u(\overline{T_2}) \rangle/\langle u(\overline{T_2}) \rangle$ . The two ratios

were found to be the same; as they should be, since  $\overrightarrow{M}$ , the <u>space</u> average magnetization, and  $\langle \overrightarrow{\mathcal{I}} \rangle$ , the <u>time</u> average magnetic moment of a given magnetic ion, should have the same temperature dependence.

The theoretical number of 24 lines was never observed. At most, eight lines were present, suggesting that some of the protons have the same local fields, thus giving rise to identical resonance frequencies. To determine which of the protons are magnetically equivalent requires a knowledge of the proton positions. Figures 7 and 8 show that the eight lines appear in four pairs (indicated by la, lb; etc.).

The spectrum in the a-c rotation for  $\mathcal{Q}$  = 115° at 4.2°K has been investigated as a function of the applied field  $H_0$ . In Figure 10 are shown plots of  $f_{4b}^{}$  -  $f_{4a}^{}$  and  $f_{4b}^{}$  -  $f_{2a}^{}$  as a function of the magnitude of the applied field. The separation  $\Delta f = f_{4b} - f_{4a}$  is seen to be independent of the applied field and must thus be due to the proton dipole-dipole interaction in one of the water mole-The separation  $f_{4b} - f_{2a}$  is a linear function of  $H_0$ cules. and is due to the internal field produced by the cobalt ions, which is proportional to the applied field. We could now apply the method of Pake<sup>9)</sup> to calculate the proton-proton r from the splitting of the line pair 4. However, distance the measured splittings are reliable only in the vicinity of arphi = 115°. For  $arphi\lesssim$  70° and  $arphi\gtrsim$  130° the splitting in line pair 4 cannot be measured accurately since

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Fig. 10 The Frequency Difference  $(f_{4a} - f_{4b})$  and  $(f_{4a} - f_{2a})$  vs applied Field H<sub>0</sub>. The Orientation is at IlO<sup>0</sup> w.r.t. Fig. 8. T =  $4.2^{\circ}$ K

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there is too much overlapping of lines.

J. W. McGrath and A. A. Silvidi<sup>14)</sup> have found that the proton-proton distance r in water molecules of hydration is nearly constant for a great variety of substances with an average value of  $r = 1.595 \pm 0.003$  Å, assuming that the proton-oxygen distance is always 0.97 Å. With these values the average H-O-H angle is  $100 \pm 5$  degrees. If we assume that these values also hold for  $CoCl_2 \cdot 6H_2O$ , the direction of the proton-proton vector  $\vec{r}$  due to the two protons giving rise to line pair 4 can be found.

Due to the large magnetic moment of the cobalt ions we can safely assume that b  $\gg$  d in (3.7), and the separation between lines 4a and 4b is

$$\Delta H = 4d = \frac{\gamma^2 \hbar^2}{\gamma^3} (3\cos^2 \theta_{12} - 1)$$
 (4.1)

where  $\theta_{2}$  is the angle between  $\overrightarrow{H}_{0}$  and  $\overrightarrow{r}$ . Expressed in terms of frequency (4.1) becomes

$$\Delta f = \frac{\delta \hbar^2}{2\pi r^3} \left( 3 \cos^2 \Theta_{12} - 1 \right) \tag{4.2}$$

The term  $\cos^2 \Theta_{R}$  is conveniently expressed in terms of the direction cosines of  $\vec{r}$  and  $\vec{H}_0$ . The direction cosines of  $\vec{r}$  and  $\vec{H}_0$  respectively are defined, using Figure 11 as

and 
$$\alpha' = \cos A$$
,  $\beta' = \cos B$ ,  $\gamma' = \cos C$   
 $\alpha'' = \cos \varphi$ ,  $\beta'' = 0$ ,  $\gamma'' = -\sin \varphi$ 

$$(4.3)$$



Figure 11. Definition of the direction angles of  $\vec{r}$  and  $\vec{H_0}$ . Equation (4.2) can now be rewritten in the form

$$\Delta f = a \left[ 3 (\alpha' \cos \varphi - \gamma' \sin \varphi)^2 - 1 \right]$$
<sup>(4.4)</sup>

where

$$a = \frac{th^2}{2\pi r^3} = 29.58 \times 10^3 \text{ cps}$$

when r is chosen to be equal to 1.595  $A^{O}$ .

Some simple algebraic manipulation in (4.4) leads to:

$$\Delta f/a = 3/2 \left( {\alpha'}^2 - {\beta'}^2 \right) - 1 \qquad (4.5)$$

$$+ 3/2 \left( {\alpha'}^2 - {\beta'}^2 \right) \cos 2 \left( \varphi + \varphi_0 \right)$$

where 🖇 is defined by

$$\tan 2\varphi_{0} = \frac{\chi' \beta'}{\chi'^{2} - \gamma'^{2}}$$
<sup>(4.6)</sup>

Equation (4.5) describes the proton-proton splitting when  $\overrightarrow{H}_{o}$  rotates in the a-c plane. Since the maximum splitting  $(\Delta f/a)$  max occurs at  $\varphi$  = 115° in line pair 4 in the a-c rotation, we have that

$$\cos 2(115^\circ + \varphi) = 1$$

and therefore

$$q_0 = -115^\circ$$
 or  $q_0 = \pi - 115^\circ = 65^\circ$   
from (4.6)

so that, from (4.6)

$$\mathcal{L}' f' = 0.5959 \left( {\gamma'}^2 - {\mathcal{L}'}^2 \right) \tag{4.7}$$

In Figure 12 equation (4.5) has been fitted to the experimental splitting  $\Delta f$  (solid points) in the vicinity of  $\varphi = 115^{\circ}$ . The maximum splitting at  $\varphi = 115^{\circ}$  is

$$(\Delta f/a)_{max} = 2.00 \pm 0.06$$

which leads to

$${\lambda'}^2 + {\gamma'}^2 \simeq 1$$

This implies that  $\beta' = 0$ , so that  $\vec{r}$  is in a plane parallel to the a-c plane. From Figure 12 and equation (4.7) the values of  ${\alpha'}^2$  and  ${\beta'}^2$  are found to be

$$\mathcal{L}^{2} = 0.1778$$
$${\gamma}^{2} = 0.8178.$$



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One set of solutions obtained from these values for the angles A and C is eliminated using the fact that  $\overrightarrow{H}_0$  must be parallel to the  $p_1 - p_2$  line when  $\Delta f$  is a maximum, and one obtains

A = 
$$65^{\circ}$$
 and C =  $25^{\circ}$ 

Thus the direction of  $\overrightarrow{\mathbf{r}}$  for the two protons giving rise to line pair 4 has been fixed. Since the two protons in each water molecule should give rise to two pairs of lines, each pair being split by an amount 4d, there should be a pair of lines in Figures 7 and 8 whose splitting is in phase with line pair 4. Line pair 2 satisfies this requirement. However, it is difficult to establish experimentally whether this pair of lines is really the counterpart of pair 4, since line pair 2 is never completely separated from the rest of the spectrum.

Applying equation (4.2) in the a'- b rotation for the direction of  $\vec{r}$  obtained from line pair 4, the splitting  $\Delta f$  is -13.8 Kc/sec when  $\vec{H}_0$  is parallel to the a'-axis and -29.6 Kc/sec when  $\vec{H}_0$  is parallel to the b-axis. In Figure 9 the measured separation in line pair 1 is about 25 Kc/sec when  $\vec{H}_0$  is parallel to the b-axis, and less when  $\vec{H}_0$  is in any other direction. When two lines are so close to one another that they overlap, as is the case in line pair 1 in Figure 9, the measured peak frequencies are not the true resonance frequencies, since the peaks are shifted towards

one another due to the overlap. In line pair 1 of Figure 9 the measured peak separation is approximately equal to the line width of each line. We may therefore assume that line pair 1 in Figure 9 is produced by the same protons as line pair 4 in Figure 8, and line pair 2 in Figure 9 is then the counterpart of line pair 1.

The intensity of line pair 4 in Figure 8 is approximately 1/6 of the total intensity of the spectrum in the a-c rotation. The intensity of line pair 1 in Figure 9 is also about 1/6 of the intensity of the spectrum in the a'-b rotation. In the a-c rotation the protons associated with the  $O_I$ are magnetically equivalent, since  $\widehat{H}_0$  rotates in the mirror plane of the crystal. The two line pairs discussed above must thus originate from protons associated with the  $O_{II}$ , since one proton from each of the  $O_{II}$  water molecules comprises 1/6 of the total number of protons in the unit cell.

In the a'-b rotation (Figure 9) six line pairs are observed. This may now be explained by the fact that in this rotation only the  $O_{I}$  water molecules situated diagonally opposite from the cobalt ion are magnetically equivalent. There are thus a total of three magnetically equivalent groups of water molecules in the unit cell, two associated with the octahedron about a cobalt ion, and the  $O_{II}$  group. Each group gives rise to two pairs of lines, thus accounting for the six pairs of lines in Figure 9.

At present it is not possible to uniquely determine

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the proton positions in  $CoCl_2 \cdot 6H_2O$  from the proton resonance measurements due to the relatively large number of lines and their extensive overlapping. A solution to the problem should become feasible when the present measurements are repeated at much higher fields and a third rotation in the b-c plane is completed, and accurate relative intensity measurements are made. Since a crystallographic analysis was not the goal of this work, these measurements were not pursued to the fullest possible extent.

# (ii) The proton resonance in the antiferromagnetic phase at $2.1^{\circ}$ K.

Measurements similar to those mentioned in the preceding section have been made in the antiferromagnetic phase (T < T<sub>N</sub>) at T = 2.1<sup>o</sup>K. The results are shown in the resonance diagrams of Figures 13 and 14 respectively for  $\overrightarrow{H_o}$  rotating in the a-c plane and for  $\overrightarrow{H_o}$  rotating in the a'-b plane. These results exhibit some features strikingly different from the measurements in the paramagnetic temperature region.

The characteristic features of the rotations in the antiferromagnetic phase are: (1) Each curve in Figures 13 and 14 behaves like a sine function with a period of  $360^{\circ}$  instead of  $180^{\circ}$  as in the paramagnetic phase. (2) The resonance diagrams are symmetric with respect to a central frequency which is about 200 Kc/sec higher than the proton frequency in water, i.e. for each line displaced by an amount



Fig. 13 Resonance Diagram for H<sub>o</sub> in the a-c plane. H<sub>o</sub> = 5000 gauss. T =  $2.11^{\circ}$  K Proton frequency in water at 21.28 Mc/sec



Resonance frequency Mc/sec

Fig. 14 Resonance Diagram for H<sub>o</sub> in a'-b plane.

 $H_0 = 5000 \text{ gauss.} T = 2.11^{\circ} \text{ K.}$ 

Proton frequency in water at 21.28 Mc/sec

 $+\delta f$  from the central frequency there is an identical line displaced by an equal and opposite amount  $-\delta f$  from the central frequency. (3) In general the lines are much broader than in the paramagnetic phase. (4) The maximum number of lines observed is again 8, but there is no evidence of a proton-proton splitting. (5) The maximum separation between lines is of the order of 10 Mc/sec instead of 600 Kc/sec as in the paramagnetic phase. (6) In the a'-b rotation (Figure 14) the resonance diagram is again symmetric with respect to the a'-axis and the b-axis in agreement with space group C2/m. These points are in good agreement with theory as outlined in chapter III.

In connection with (3.11) of chapter III it was pointed out that the number of lines should double when passing from the paramagnetic to the antiferromagnetic phase. Experimentally only eight lines are observed. However, the separation between any pair of lines is much too large to be attributed to a proton dipole-dipole interaction. We therefore conclude that each of the curves in Figures 13 and 14 consists of two resonance lines, the splitting between them being too small to be observed since the lines in general are quite broad as compared to the line widths in the paramagnetic phase. Thus we can say that the number of lines in fact has doubled.

The fact that six line pairs were observed in the a'-b rotation in the paramagnetic phase does not contradict

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the above arguments in regard to Figure 14, since in the antiferromagnetic phase the cobalt spins are coupled to the crystal axes and lie in the a-c (mirror) plane independent of the applied field. The four O<sub>I</sub> water molecules associated with the octahedron are thus magnetically equivalent even in the a'-b rotation in the antiferromagnetic phase. Therefore, only two groups of magnetically non-equivalent water molecules are present, and only eight lines are expected in the antiferromagnetic phase in the a'-b rotation.

The spectrum at  $\varphi = 133^{\circ}$  in the a-c rotation has been investigated as a function of the applied field at  $T = 1.14^{\circ}$  K. The results are shown in Figure 15, where we have plotted the entire spectrum as a function of  $H_{o}$ . These measurements show that the separation between the various lines is independent of the applied field. This result proves that the magnetic moment  $\mathcal{M}_{G}$  of the cobalt ions in the antiferromagnetic phase is independent of the applied field as long as it is not too large. The shape of the resonance diagrams is determined by the vector sum of of  $\overline{H}_{o}$  with the internal field due to the antiferromagnetic cobalt ions  $\langle \mathcal{M}_{Co} \rangle$ . The small demagnetization field merely adds to the applied field.

No attempt has been made to give theoretical formulae for the resonance curves in Figures 13 and 14 since the proton positions are not yet known and since it



Fig. 15 Plot of Resonance Frequencies 2 to 7 of Fig. 13 as a function of the applied field.  $\varphi$  = 133°. T = 1.14°K

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is not known what the sublattice arrangement of the cobalt ion magnetic moments is in the antiferromagnetic phase. In a later chapter we shall see that there is some evidence that more than two sublattices are present in antiferromagnetic  $CoCl_2 \cdot 6H_2O$ .

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#### CHAPTER V

# THE PARAMAGNETIC-ANTIFERROMAGNETIC PHASE TRANSITION

The proton magnetic resonance technique provides a simple but accurate method for investigating the paramagnetic-antiferromagnetic phase transition in hydrated salts. In chapters III and IV it was pointed out that the character of the resonance spectrum changes drastically when the sample temperature is lowered from the paramagnetic to the antiferromagnetic temperature region. This change in character of the resonance spectra can be used to determine the transition temperature  $T_N$  as a function of the applied field, and the crystal orientation relative to the applied field.

The transition temperature of  $CoCl_2 \cdot 6H_2O$  in zero applied field has previously been determined by Sugawara<sup>15)</sup>  $(T_N = 2.35 \pm .05^{\circ}K)$  from proton magnetic resonance experiments; by Robinson and Friedberg<sup>16)</sup>  $(T_N = 2.29^{\circ}K)$ ; and by Miss Voorhoeve and Dokoupil<sup>17)</sup>  $(T_N = 2.28^{\circ}K)$  from the  $\lambda$ -transition in the specific heat, and by Van der Lugt and Poulis<sup>18)</sup>  $(T_N = 2.275 \pm .01^{\circ}K)$  from proton magnetic resonance experiments similar to those to be described in the following paragraphs. We have essentially duplicated and extended the measurements of Van der Lugt and Poulis with improved accuracy. Our results are in good agreement with theirs, but additional details have been brought out not reported by these authors.

The transition from the paramagnetic phase into the antiferromagnetic phase is characterized by a broadening and decrease in amplitude of the resonance lines in the paramagnetic phase. In Figure 16 a plot of the signal amplitude of the resonance lines 1a, 2a, and 4b of Figure 8 for  $\varphi = 130^{\circ}$  and  $H_{o} = 5000$  gauss is shown as a function of temperatures. The amplitudes given here are differences between maximum and minimum values of the first derivative. Figure 16 shows that the amplitudes of the resonance lines increase slightly as the Néel temperature is approached and drop very rapidly near the transition temperature. However, the rate of change of the amplitude is different for different lines. Similar graphs were obtained for other values of  $\varphi$  and  $\hat{H}_{o}$ , and in each case the general behaviour is similar to that of Figure 16.

The region near the transition temperature is of particular interest. Figure 17 is a magnification of the region near  $T = 2.2^{\circ}K$ , including part of the antiferromagnetic temperature region. Over a small temperature region, approximately 7 millidegrees in Figure 17, lines from both phases are present simultaneously. As we shall see in a later paragraph, the lines associated with the paramagnetic phase broaden rapidly as the transition temperature is





• paramagnetic phase,  $\triangle$  antiferromagnetic phase.

approached. Thus very broad lines of low amplitude begin to overlap and eventually it becomes impossible to identify any single line. Also, the lines associated with the antiferromagnetic phase first appear near the proton frequency in water so that these lines also overlap with one another and with the lines from the paramagnetic phase very near the transition temperature. It is thus impossible to analyze this region quantitatively from the existing data and to determine the exact range of coexistence. The range of coexistence seems to be independent of  $\mathscr{Q}$  . If there is any variation in this range with arphi , then it is beyond the accuracy of this experiment. Measurements for  $H_0 = 3000$ gauss indicate that the coexistence range increases with decreasing Ho. At 3000 gauss the temperature range over which both spectra exist simultaneously is of the order of 15 millidegrees. Such regions of coexistence have also been observed in Azurite<sup>19)</sup> (about 160 millidegrees) and in 20) (about 25 millidegrees). MnF,

On first sight one might attribute this coexistence region to lattice imperfections in the crystal or to "supercooling" and "superheating", i.e. hysterisis. Lattice imperfections are ruled out by the fact that the same range was always present for different samples and that the range is field dependent. We have eliminated the possibility of hysterisis by varying the temperature within the coexistence range and were able to reproduce any particular set of lines over several hours. We thus tentatively attribute the region of coexistence of both types of spectra to short range order. It would be interesting to test this conjecture experimentally.

The line widths also show an anomalous change near the transition temperature. In Figure 18 a plot of the line width of line 5 of Figure 9 (paramagnetic) and of line 8 of Figure 14 (antiferromagnetic) is presented as a function of temperature with  $H_0 = 5000$  gauss at  $q^2 = 120^{\circ}$ . This graph is very suggestive of a  $\lambda$ -type transition. It has been pointed out by Nakamura (private communication) that superexchange interactions between the protons via the cobalt ions, or between protons and paramagnetic impurities at the cobalt ion positions, could produce a line broadening of this type.

Strictly speaking, the two branches of the line widths in Figure 18 should cross over near 2.24°K, since some lines associated with the antiferromagnetic phase appear before those of the paramagnetic phase have vanished. No attempt has been made to measure line widths throughout the transition region, since here most of the lines overlap, making accurate line-width determination impossible, especially in view of the very small amplitudes. As pointed out previously, hysterisis is absent in this transition. Indeed, the fact that some of the change occurs even before the transition region is reached shows that there is no choice



і 69 of paths for the transition. The new phase is established gradually rather than at one single temperature.

Figure 17 points out some ambiguity in the definition of the transition temperature. Strictly speaking, there is a small range of temperature over which the transition takes place. We have investigated the transition temperature as a function of the applied field and crystal orientation. These measurements were performed by continuously monitoring the amplitude of one of the lines associated with the paramagnetic phase, and  ${\rm T}_{\rm N}$  was chosen as that temperature at which this amplitude had decreased to the noise level. Thus the lower values of the transition range were obtained. These measurements are possible, since each resonance frequency is independent of temperature in the paramagnetic phase, except for the last 10 or 15 millidegrees where the frequencies are shifted towards the proton frequency in water. These shifts, however, are at most 50 Kc/sec whereas the line widths in the transition region are usually much greater, so that the amplitude measurements are only slightly affected. A graph of  ${\rm T}_{\rm N}$  as a function of the applied field in the a-c plane for three values of  $\psi$  is shown in Figure 19. T<sub>N</sub> is independent of orientation in the a'-b plane. The arphi-dependence of T $_{
m N}$  has been investigated for several values of H and  $\mathbf{T}_{\mathbf{N}}(arphi)$  is found to behave like a sine function with a period of 180 degrees. This behaviour of  $\mathrm{T}_{\mathrm{N}}(\mathcal{O})$  can be expressed in the form



Fig. 19 Paramagnetic-antiferromagnetic phase to transition temperature as a function of the applied field for  $\varphi = 0^{\circ}$ , 45°, and 90°.

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$$\left\{T_{N}\left(\varphi\right)\right\}_{H_{o}} = A(H_{o}) + B(H_{o})\cos^{2}\varphi \qquad (5.1)$$

where  $A(H_0)$  and  $B(H_0)$  are functions of  $H_0$ . In Figure 20 a plot of  $T_N(\varphi)$  is shown for  $H_0 = 5000$  gauss and rotating in the a-c plane. For this value of  $H_0$  the best fit for (5.1) is obtained with

$$A(H_0) = 2.162^{\circ}K$$
 (5.2)  
 $B(H_0) = 0.078^{\circ}K$ 

and from Figure 19,  $B(H_0)$  is found to be nearly linear in  $H_0$  as shown in Figure 21 with

$$B(H_0) = (1.45.10^{-5} \times H_0)^{\circ}K.$$

We cannot attribute this anisotropy of  $T_N$  to the anisotropic g-factor in  $CoCl_2 \cdot 6H_2O$ . The principal values of the g-factor have been measured by Hased<sup>3</sup>, 21)</sup> in connection with paramagnetic susceptibility measurements and by  $Date^{22}$ ) in connection with paramagnetic and antiferromagnetic resonance experiments. The values given by Haseda are  $g_a$ , = 2.7,  $g_b = 4.9$ , and  $g_c = 4.9$ . Date's values are only slightly different. Thus, the g-tensor varies identically in the a'-c plane as in the a'-b plane, yet  $T_N$  is independent of orientation when  $\overrightarrow{H}_0$  rotates in the a'-b plane. Therefore, the variation of  $T_N$  with  $\mathcal{P}$  in the a-c plane cannot be a direct consequence of the variation in the g-tensor.





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Nagamiya, Yosida and Kubo<sup>23)</sup> have established a theory describing the variation of  $T_N$  with applied field on the basis of the Weiss molecular field approximation. A summary of this theory with minor modifications to conform with  $CoCl_2 \cdot 6H_2O$  is presented in Appendix B. The results by Nagamiya et al show that  $T_N$  may be expressed in the form

$$T_{N}(H_{0}) = T_{N}(0) - C \times H_{0}^{2} + \cdots$$
<sup>(5.3)</sup>

to a first approximation in  $H_0$ , when the exchange interactions are assumed to be isotropic. The quantity C depends on the orientation of  $\overline{H}_0$ . Date<sup>24)</sup> has found it necessary to introduce additional anisotropic exchange interactions to explain his antiferromagnetic microwave resonance experiments in CoCl<sub>2</sub>.6H<sub>2</sub>O. These additional terms, however, only change the field independent quantity C in (5.3), but not the nature of the field dependence. Such a behaviour, however, does not agree with the present measurements, since this implies that  $dT_N/dH_o = 0$  for  $H_o = 0$ . Experimentally it is found that  $T_{N}(H_{O})$  has a finite slope at  $H_{O} = 0$ , and none of the curves in Figure 19 can be approximated by a quadratic function in  $H_0$ . In particular, the term  $B(H_0)$  in (5.1) was found to be linear in  $H_0$ , which completely rules out an  $H_0^2$  dependence of  $T_N(H_0)$  on  $H_0$ . Equation (5.3) implies that  $T_N(H_0 \perp c)$  decreases monotonically with increasing  $H_0$ , whereas experimentally we observe a minimum at about 3000 gauss and a maximum at 5000 gauss. This cannot be explained by any existing theories. The

present theory does, however, agree with the general trend of this experiment, namely, that the transition temperature in zero field is always greater than that in a finite field.

Similar measurements have been performed in CuCl<sub>2</sub>·2H<sub>2</sub>O<sup>25)</sup>. However, the available data is not suffi-sufficiently accurate to really test the present theory.

It is not surprising that this theory does not agree with the present measurements, since these were obtained very accurately, and the theory is based on a crude approximation, not including any details of the antiferromagnetic sublattice arrangements.

#### CHAPTER VI

#### THERMODYNAMICS OF THE PHASE TRANSITION

In this chapter we shall discuss some thermodynamic aspects of the paramagnetic-antiferromagnetic phase transitions.

As is seen in Figure 18, the proton resonance line widths exhibit a lambda-shaped anomalous peak near the transition temperature  ${\rm T}_{\rm N},$  i.e. they increase anomalously as  $T \twoheadrightarrow T_N$  either from below or above  $T_N.$  This type of behaviour has also been observed in  $M_n F_2^{20}$ . Also, the specific heat in CoCl<sub>2</sub>.6H<sub>2</sub>O has been measured by Robinson and Friedberg<sup>16)</sup> as a function of temperature between about 1°K and 20°K in zero applied field. These measurements show that the specific heat also has an anomalous peak at 2.29°K. The peak is identified with a cooperative order-disorder transition and the temperature at which the peak occurs is the transition temperature. Robinson and Friedberg found that the behaviour of the magnetic contribution to the specific heat near the transition temperature could be described by a logarithmic function of the form log  $(T-T_N)$ , which is also characteristic of the anomaly in the  $\lambda$ -transition of liquid helium. Such a singularity is integrable, giving a finite enthalpy and entropy and no latent heat. We can therefore follow the method used by Buckingham and Fairbank<sup>26)</sup> in their analysis of the liquid helium  $\lambda$ -transition to discuss some

thermodynamic aspects of the magnetic phase transition in  $CoCl_2 \cdot 6H_2O$ . We confine ourselves to the case  $\left[T_N(H_0)\right]_{H_0||C}$ , since here the slope  $\frac{dH}{dT_N}$  of the  $\lambda$ -line  $T_N(H_0)$  is always finite. The case where  $\frac{dH}{dT_N}$  becomes infinite will be discussed later.

Using the identity

$$\left(\frac{\partial W}{\partial X}\right)_{Y} = \left(\frac{\partial W}{\partial X}\right)_{Z} - \left(\frac{\partial W}{\partial Y}\right)_{X} \left(\frac{\partial W}{\partial X}\right)_{Z}$$

$$(6.1)$$

where W, X, Y, Z are functions of state with two independent variables; and the Maxwell relations, we have

$$\begin{pmatrix} \frac{\partial T}{\partial H} \end{pmatrix}_{S} = \begin{pmatrix} \frac{\partial T}{\partial H} \end{pmatrix}_{C_{H}} - \begin{pmatrix} \frac{\partial T}{\partial S} \end{pmatrix}_{H} \begin{pmatrix} \frac{\partial T}{\partial H} \end{pmatrix}_{C_{H}}$$

$$(6.2)$$

anđ

$$\left( \frac{\partial T}{\partial H} \right)_{M} = \left( \frac{\partial T}{\partial H} \right)_{C_{H}} - \left( \frac{\partial T}{\partial M} \right)_{H} \left( \frac{\partial M}{\partial H} \right)_{C_{H}}$$
 (6.3)

Since  $C_H \longrightarrow \infty$  as  $T \longrightarrow T_N \left( C_H = T \left( \frac{\partial S}{\partial T} \right)_H \right)$ 

we have from (6.2) that

$$\left(\frac{\partial T}{\partial H}\right)_{S} = \left(\frac{\partial T}{\partial H}\right)_{C_{H}} = \frac{dT_{N}}{dH} \text{ at } T = T_{N}$$
 (6.4)

and from (6.3) that

$$\left(\frac{\partial T}{\partial H}\right)_{M} = \frac{dT_{N}}{dH}$$
(6.5)

The latter can easily be shown by using the relation

$$\left(\frac{\partial T}{\partial S}\right)_{H} = -\left(\frac{\partial T}{\partial M}\right)_{H} \left(\frac{\partial T}{\partial H}\right)_{S}$$
<sup>(6.6)</sup>

The left-hand side in (6.6) vanishes on the  $\lambda$ -line and  $\begin{pmatrix} \partial T \\ \partial H \end{pmatrix}_{S}$  is finite and equal to the slope of the  $\lambda$ -line at T = T<sub>N</sub>, so that  $\begin{pmatrix} \partial T \\ \partial M \end{pmatrix}_{H}$  must vanish. Using this fact in (6.3) immediately gives (6.5). In the above relations H denotes the applied magnetic field.

In order to study the variation of thermodynamic properties near the transition temperature Buckingham and Fairbank introduce a new variable, the "neighbourhood temperature" t, a function of state defined by

$$t = T - T_N(H)$$
. (6.7)

The line t = 0 is the  $\lambda$ -line and a line t = t<sub>o</sub>(constant) is a line parallel to the  $\lambda$ -line in the phase diagram.

Using (6.1) and the new variable we have

$$\frac{C_{H}}{T} = \left(\frac{\partial S}{\partial T}\right)_{t} - \left(\frac{dH}{dT_{N}}\right) \left(\frac{\partial M}{\partial T}\right)_{T}$$
(6.8)

and

$$\left(\frac{\partial M}{\partial T}\right)_{H} = \left(\frac{\partial M}{\partial T}\right)_{t} - \left(\frac{d H}{d T_{W}}\right) \left(\frac{\partial M}{\partial H}\right)_{T}$$
(6.9)

Combining (6.8) and (6.9) gives

$$\frac{C_{H}}{T} = \left(\frac{dH}{dT_{N}}\right)^{2} \left(\frac{\partial M}{\partial H}\right)_{T} + \left(\frac{\partial S}{\partial T}\right)_{t} - \left(\frac{dH}{dT_{N}}\right) \left(\frac{\partial M}{\partial T}\right)_{t}$$
(6.10)

Buckingham and Fairbank argue that the quantity  $\begin{pmatrix} \partial S \\ \partial T \end{pmatrix}_t$  varies relatively little over a small temperature range in the neighbourhood of the transition, although it has an infinite temperature derivative at the transition temperature itself. This can be seen from the following argument: Near the transition line we could write

$$S = S(T_N) + A(H)f(t)$$

where A(H) is a function of the applied field H and the function f(t) has an infinite derivative at t = 0. Then

$$\left(\frac{\partial S}{\partial T}\right)_{t} = \left(\frac{\partial S}{\partial T}\right)_{T} = T_{N} + \left(\frac{dH}{dT_{N}}\right) \left(\frac{dA}{dH}\right) f(t)$$

so that  $\begin{pmatrix} \partial S \\ \partial T \end{pmatrix}_t$  depends on t in a manner similar to the t dependence of S itself. Therefore, even though  $\begin{pmatrix} \partial S \\ \partial T \end{pmatrix}_t$  has an infinite temperature derivative at  $T_N$ , its total variation over a small temperature range near  $T_N$  will nevertheless be small. Similar arguments may be applied to the

quantity  $\left(\frac{\partial M}{\partial T}\right)_t$ . Therefore, a plot of  $\frac{C_H}{T}$  versus  $\left(\frac{\partial M}{\partial H}\right)_T$  should be linear near  $T_N$  with a slope  $\left(\frac{dH}{dT_N}\right)_t^2$ .

The specific heat  $C_{H}$  of CoCl<sub>2</sub>.6H<sub>2</sub>O as a function of temperature has been measured in zero field by Robinson and Friedberg<sup>16)</sup>. Flippen and Friedberg<sup>3)</sup> have measured the adiabatic susceptibility  $\left(\frac{\partial M}{\partial H}\right)_{S}$  "near"  $H_{O} = 0$  (the measurements involve a small oscillatory field). We have repeated some of the susceptibility measurements with an improved accuracy. Our measurements were made by measuring the self-inductance of a coil containing a sample of CoCl, •6H20. The coil formed part of the tuned circuit of the same Pound-Knight-Watkins oscillator used to perform the NMR measurements discussed in the preceding chapters, and the changes in self-inductance were calculated from the changes in the oscillator frequency. The oscillator frequency at 4.2°K was set to 21 Mc/sec and the total change in frequency was found to be approximately 60 Kc/sec as the temperature changed from 4.2°K to about 1.3°K. We have calibrated our measurements against those of Flippen and Friedberg at 1.5°K. The results of these measurements for zero field are shown in Figure 22, where the crosses (x) indicate the points published by Flippen and Friedberg. The two sets of measurements are in good agreement, but in the present measurements many more points were obtained, especially near the transition temperature. The transition temperature is clearly indicated by a discontinuity in the



 slope of the susceptibility, and this method could actually be used to measure the transition temperature.

These results, together with Figure 19, can now be used to show the mutual consistency of the heat capacity  $C_H$ as a function of temperature and field derivatives of the magnetization in the vicinity of  $T_N$  in zero applied field. In doing so we assume that the difference between the adiabatic and isothermal susceptibilities is negligible in very small fields which is reasonable in the absence of an applied field. We therefore use the adiabatic susceptibility  $\left(\frac{\partial M}{\partial H}\right)_T$  to obtain  $\left(\frac{dH}{dT_N}\right)^2$ , since the error introduced in this change will be negligible. A plot of  $\frac{C_H}{T}$  versus  $\left(\frac{\partial M}{\partial H}\right)_S$  is shown in Figure 23 for both T < T<sub>N</sub> and T > T<sub>N</sub>. The neighborhood temperature t = T - T<sub>N</sub> is indicated by the arrows.

A linear plot is obtained over the entire temperature range studied for  $T < T_N$ . The value of  $\begin{pmatrix} dH \\ dT_N \end{pmatrix}$  thus obtained is 1.71 x 10<sup>4</sup> gauss/<sup>O</sup>K and is shown as a dotted line in Figure 19, and is seen to be in agreement with the  $T_N(H)$  curve obtained using proton resonance for  $\vec{H}_0$  parallel to the c-axis. The proton resonance data at low fields are rather poor, because at such low frequencies the oscillator sensitivity has greatly decreased, so that it would be interesting to make plots similar to those of Figure 23 for large applied fields. Unfortunately, no heat capacity measurements have been made so far in the presence of large d.c. fields.



For  $T > T_N$  we do not get a linear relationship between  $\frac{C_H}{T}$  and  $(\partial M/\partial H)_S$  except for the region  $t \ge 0.1^{\circ}$ K. If one identified the magnitude of the slope of the curve in this region with  $(\frac{dH}{dT_N})^2$ , one obtains  $\frac{dH}{dT_N} \simeq 1.85 \times 10^4$ gauss / °K which is in agreement with the value for  $T < T_N$ within experimental error. However, there is a difficulty in this assignment, because the slope of the  $\frac{C_H}{T}$  versus  $(\frac{\partial M}{\partial H})_S$  curve for  $t > 0.1^{\circ}$ K is negative. This is clearly impossible since  $(\frac{dH}{dT_N})^2$  must be positive. Since no way out of this dilemma has been found, it appears that the numerical agreement mentioned above may be fortuitous and that one may anticipate  $(\frac{\partial M}{\partial H})_S$  going through a minimum as the Néel temperature is approached from above for  $t < 0.06^{\circ}$ K.

There are two pieces of evidence which support this conjecture. Firstly, extrapolation of  $\begin{array}{c} C_{H} \\ T \end{array}$  versus  $\left( \frac{\partial M}{\partial H} \right)_{S}$  to zero  $\left( \begin{array}{c} \frac{\partial M}{\partial H} \right)_{S}$  should give the same value for  $T > T_{N}$  and  $T < T_{N}$ , namely  $\left( \begin{array}{c} \frac{\partial S}{\partial T} \right)_{T_{N}} - \frac{dH}{dT_{N}} \left( \frac{\partial M}{\partial T} \right)_{T}$  as seen from equation (6.10). The straight line obtained for  $T < T_{N}$  extrapolates to approximately -0.125 cal  $/ \left( {}^{O}K \right)^{2}$  - mole for this quantity. In order to obtain a negative value for this quantity for  $T > T_{N}$ ,  $\left( \frac{\partial M}{\partial H} \right)_{S}$  must go through a minimum or  $\begin{array}{c} C_{H} \\ T \end{array}$  through a maximum.

More conclusive evidence that  $\left(\frac{\partial M}{\partial H}\right)_{S}$  goes through a minimum in zero field is that we have observed that this does happen for  $H_{O} \ge 2000$  gauss. This is seen in Figure 24, which is a plot of oscillator frequency versus temperature



Fig. 24 Oscillator frequency vs Temperature

for various applied fields. The curve for  $H_0 = 0$  is the one from which the susceptibilities in Figure 23 were obtained. In order to make use of careful measurements of  $\left(\frac{\partial M}{\partial H}\right)_S$  for t<0.06°K, the specific heat measurements would also have to be made closer to  $T_N$ . Since there are no specific heat measurements available for  $H_0 \neq 0$ , we are unable to make quantitative use of our data of Figure 24 except for the  $H_0 = 0$  curve.

It would also be desirable to do measurements of susceptibility for the case of  $\overrightarrow{H_0}$  perpendicular to the preferred axis since  $\frac{dH}{dT_N}$  is infinite for two values of field in that orientation. These measurements have not been carried out yet, but one may anticipate that the nature of the phase transition may change drastically above 3000 gauss.

Finally, the anomalous increase of  $\left(\frac{\partial M}{\partial H}\right)_5$  (decrease of frequency) at low temperatures for  $H_0 = 6,700$ , and  $H_0 = 7,000$  gauss in Figure 24 is a manifestation of the lowering of the critical field with decreasing temperature for the "flop-over" antiferromagnetic phase transition as discussed by Van der Lugt and Poulis<sup>18</sup>.

#### CHAPTER VII

# THE SUBLATTICE MAGNETIZATION BELOW $T_{N}$

In this chapter sublattice magnetization measurements as a function of temperature for  $T < T_N$  are discussed. It will be interesting to note an empirical relation between the sublattice magnetization in the antiferromagnetic state and the experimentally observed logarithmic dependence of the heat capacity on  $|T - T_N|$ .

The results were obtained by measuring the proton resonance frequencies as a function of temperature at constant external field and a given orientation. Measurements were performed at two fields and about a dozen different orientations. A representative set of measurements is shown in Figure 25, where  $H_0 = 5,260$  gauss was in the a-c plane at  $\varphi = 0$ . Each set of points parallel to the frequency scale was obtained by holding the temperature constant and recording the frequency at which resonance occurs. The measurements were usually terminated when the transition region was approached, since here too many lines overlap, making accurate measurements impossible.

As stated before, the resonance frequencies are determined by the local field at the positions of the different protons, where  $\overrightarrow{H}_{loc} = \overrightarrow{H_{o}} + \overrightarrow{H}_{int}$ . The quantity  $\overrightarrow{H}_{int}$  denotes the internal magnetic field at the proton



 $H_0 = 5.26$  Kgauss,  $H_0$  c-axis.

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positions produced by the neighbouring magnetic ions. It is now convenient to define the scalar quantity

$$h(H_o,T) = \left| \overrightarrow{H}_{loc} \right| - \left| \overrightarrow{H}_o \right| = \left| \overrightarrow{H}_o + \overrightarrow{H}_{int} \right| - \left| \overrightarrow{H}_o \right|$$
(7.1)

For  $H_0 \gg H_{int}$ , a condition satisfied in most of the experiments, h is the component of  $\overrightarrow{H}_{int}$  along the applied field  $\overrightarrow{H}_0$ .

In chapter III we saw that the component of the internal field along  $\overrightarrow{H}_0$  is proportional to the sum of the time-averaged magnetic moments  $\langle \overrightarrow{\mathcal{M}}_k \rangle$ . In the antiferromagnetic phase the magnetic moments of one sublattice all point in one direction, so that the sum of the magnetic moments over one sublattice gives the sublattice magnetization. Thus a measure of  $h(H_0, T)$  gives a measure of the sublattice magnetization as a function of temperature. Since  $\omega = 2\widetilde{\mathcal{M}}_f = \chi H_{loc}$  (7.1) may be rewritten in terms of frequency:

$$f(H_{o},T) = f_{res}(H_{loc},T) - f_{o}$$

where  $2\pi f \cdot \ell h$  and  $f_{res}$  is the measured resonance frequency of a given line at a temperature T, and  $f_0$  is the proton resonance frequency in water at an external field  $H_0$ . To avoid the contribution to  $H_{loc}$  from the bulk magnetization of the sample, it is convenient to measure the difference in frequency of a pair of resonance lines, rather than the actual frequency. This difference is then roughly proportional to the difference in sublattice magnetization. Thus, the temperature dependence of the sublattice magnetization may be obtained by measuring

$$\Delta f_{ij} = f_i(H_{o,T}) - f_j(H_{o,T}) = f_{res} - f_{res} j$$

which is independent of  $\overline{H}_0$  and the bulk magnetization of the sample.

The rapid variation of  $\Delta f_{ij}$  near  $T_N$  (Figure 25) suggests a logarithmic dependence of  $\Delta f_{ij}$  on  $|T - T_N|$ . Plots of  $\Delta f_{ij}$  versus  $\log(T_N - T)$  were prepared, and it was found that all the proton resonance lines give the following result, which is independent of  $H_0$  and crystal orientation

$$\frac{\Delta f_{ij}(H_{0,0})}{\Delta f_{ij}(H_{0,0})} = n \ln (T_{N} - T) + const., n \approx 0.13 \pm 108 \quad (7.2)$$

where  $\Delta f_{ij}(H_0,0)$  was obtained by extrapolating the plots of  $\Delta f_{ij}$  versus  $\log(T_N - T)$  to  $(T_N - T) = T_N$ , i.e. to T = 0. A plot  $\Delta f_{ij}$  versus  $\log (T_N - T)$  corresponding to the results of Figure 25 is shown in Figure 26. The individual values of n are indicated for each pair of lines. A similar plot (not shown) was prepared for  $H_0 = 0$ , using the curve published by Van der Lugt and Poulis<sup>18)</sup>, and the same relationship was found to hold.

The above results suggest that the sublattice magnetization has the form



$$\frac{M(T)}{M(o)} = n \ln \frac{T_N - T}{T_N} + 1. \qquad (7.3)$$

Equation (7.3) must, of course, break down as T approaches  $T_N$ . No evidence of this was observed to within about 20 millidegrees of  $T_N$ . We therefore conclude that the break-down occurs within the transition region.

Similar measurements have been performed in  $M_n F_2$ <sup>20)</sup>, and there it was found that  $M(T) \sim (T_N - T)^{1/3}$  near  $T_N$ . It is thus not at all clear whether the sublattice magnetization in different substances can be described by the same function.

The shape of the curve given by (7.3) differs considerably from the dependence of M(T) given by the Weiss molecular field approximation<sup>18</sup>). No explanation is given here for the behaviour of M(T) in CoCl<sub>2</sub>.6H<sub>2</sub>O. An attempt to understand it could be made following Dzialoshinskii's method<sup>27)</sup>, but the magnetic space groups of CoCl<sub>2</sub>.6H<sub>2</sub>O are not known. Neutron diffraction experiments would, therefore, be desirable, but so far there are very few neutron diffraction data on hydrated salts of the transition elements. A group theoretical analysis<sup>28</sup> of the proton resonances in the antiferromagnetic state may be successful however, and is being pursued in this department.

In connection with the possible sublattice structure of CoCl<sub>2</sub>•6H<sub>2</sub>O two experimental results should be mentioned: 1)) Daniels and Griffith (to be published) have studied the angular dependence of  $\delta$ -radiation from single crystals of  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 O$ , where the cobalt ions in the surface layers of the crystal were replaced by  $\operatorname{Mn}^{54}$  ions. It was found that the distribution of  $\delta$ -radiation could not be explained on the basis of a two-sublattice model. Although no sublattice structure could be given from these measurements, indications were that a more complicated sublattice structure than the two-sublattice model exists in  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 O$ .

2)) Measurements by Flippen and Friedberg show that the susceptibility parallel to the preferred axis does not approach zero at T = 0, which is incompatible with a two-sublattice model, since such a model requires that  $\chi_{\parallel} = 0$  at T = 0.

#### CHAPTER VIII

#### SUGGESTIONS FOR FURTHER EXPERIMENTS

The present measurements and others mentioned in the foregoing chapters indicate the need for more extensive and varied experiments in CoCl<sub>2</sub>.6H<sub>2</sub>O to fully explain the physical properties of this substance. The following experiments would be fruitful:

1) Measurements in the paramagnetic phase should be repeated at much higher fields than those employed in the present experiments. Such measurements would greatly improve the resolution of resonance lines and enable a complete crystallographic analysis.

2) A thorough study of the proton resonance line shapes and line intensities would provide information as to how many protons contribute to a particular resonance line. This information will be particularly useful in the proposed magnetic space group analysis using the resonance diagrams of the antiferromagnetic phase.

3) The transition region should be investigated in detail. An exact knowledge of the range of the transition and its field and orientation dependence could lead to a fuller understanding of the nature of the transition. In this region double-resonance experiments would be of particular interest. The effect, if any, on resonance lines in the antiferromagnetic phase when a line of the paramagnetic phase is saturated would immediately tell if the transition takes place by a gradual build-up of domains, or if individual magnetic moments fluctuate between the two phases.

4) NMR experiments on deuterated samples of  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 0$ might prove very useful. For instance, it would be very interesting to see what effect the replacement of protons by deuterons would have on the transition temperature. Since deuterated samples should give resonance diagrams very similar to those presented in chapter IV, such samples could be used for the high field experiments without the difficulty of obtaining high enough oscillator frequencies. Some other very useful experiments would be:

5) A study of the specific heat as a function of an externally applied field including the region very close to  $T_{\rm N}$ . As pointed out before, such experiments could immediately be used to check some of the ideas put forth in chapter VI. It would be most interesting to see if such measurements give the same phase diagram as obtained with NMR measurements.

6) Susceptibility measurements should be made in the presence of an applied field for the three principal orientations.

7) As pointed out before, neutron diffraction experiments would be most useful. These would determine the magnetic space group of antiferromagnetic CoCl<sub>2</sub>.6H<sub>2</sub>O and probably the nature of the sublattice structure.

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# APPENDIX A

### CONSTRUCTION HINTS

## AND

#### OPERATING INSTRUCTIONS

1) Oscillating detector (Figure 1A).

The oscillating detector was constructed in a box made of 1/8 inch brass sheet. The H.T. and filament supplies and their accompanying components are housed in a "false bottom", and the leads from this compartment to the tubes are kept as short as possible. Faraday shields are placed between the oscillator (6J6) and the r-f amplifier (3 x 40B3), between the r-f amplifier and the detector (6AL5), and between the detector and the audi-output tubes (2 x 6C4). This type of construction minimizes microphonic pick-up and undesirable r-f leakage between the various sections.

2) Williamson Power Amplifier (Figure 2A).

Best results are obtained with this circuit if the following adjustments are made when the input is grounded:

a) Adjust  $R_{25}$  to equal  $1200 \times \sqrt{10}$  ad impedance.

b) Connect a suitable ma meter in the lead to the center-tap of the output transformer primary and set the total current to 125 ma by means of  $R_{21}$ .

c) Connect a moving coil voltmeter (0 - 10V) across the whole of the output transformer primary and adjust  $R_{17}$ 

until the meter reads <u>zero</u> volts indicating proper balance. Ignore small random fluctuations in this adjustment since they are due to the A.C. mains and fluctuations in tube characteristics.

3) Magnet power supply (Figure 4A).

The power transistors (2N278's) are all mounted on a 1/4 inch copper plate soldered to a 1/2 inch O.D. copper tube for water cooling. The reference resistor is made from a 1 inch manganin strip and immersed in an oil bath which is maintained at a constant temperature by means of a cold water jacket. The reference voltage supply is imbedded in styrofoam to avoid voltage fluctuations due to temperature variations.

Operation: Switch on the reference voltage and set the helipot to some arbitrary value. The meter on the Honeywell Null Detector will indicate a negative reading. Now increase the A.C. voltage by means of the variac until the detector meter reads zero and the voltage drop across the power transistors is approximately 4 volts. The null detector will "hunt" momentarily, but should soon settle at <u>zero</u>. To obtain the desired magnet current, slowly vary the reference voltage and the A.C. supply voltage until the desired magnet current is reached, always keeping the drop across the power transistors at approximately 4 volts.
4) Low temperature system (Figure 6A).

Except for the manometers and dewars, which are made of glass, the low temperature system is made of copper and stainless steel tubing.

To "pre-cool": Insert the syphon into the dewar, close the free end, and evacuate the syphon jacket. Evacuate the inner dewar and then fill it with He gas to 1 atm. pressure. Evacuate the inner dewar jacket to approximately 4 cm Hg, and then fill the outer dewar with liquid nitrogen. From time to time add He gas to the inner dewar to keep the pressure at approximately 1 atm. Keep the nitrogen level in the outer dewar as high as possible at all times. When the pressure in the inner dewar has settled to a constant reading (approximately 90 min.), the system has reached liquid nitrogen temperature and is ready for a He transfer.

To transfer: Completely evacuate the inner dewar jacket and be sure to close stopcock A. Open the free end of the syphon and insert it into the liquid He vessel. Open valve 5 to allow the He gas to return to the storage vessel. Apply 4 to 6 cm Hg pressure to the liquid He can by means of the compressed He gas cylinder, effecting a transfer of liquid He into the inner dewar.

Temperatures lower than 4.2°K: Open values 1c, 2, 3, 4, and 14 fully. Close 5 and immediately begin to open 1a and then 1b if necessary. When the desired pressure

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has been reached, close 1c and 4. The pressure in the bellows B is now fixed and any change in the rate of pumping will be corrected by the expansion or contraction of the bellows. To change the temperature, valve 4 is opened and the pressure in the bellows is adjusted to the desired value.

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Fig. 1A Oscillating Detector

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Fig. 2A Narrow Band and Broad Band Amplifier



Fig. 3A Phase Sensitive Detector



Fig. 4A Williamson Power Amplifier

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Fig. 5A Transistor Magnet Current Regulator

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Fig. 6A Schematic of low temperature system

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## APPENDIX B

## THE NAGAMIYA, YOSIDA AND KUBO THEORY FOR T<sub>N</sub>(H) APPLIED TO CoCl<sub>2</sub>.6H<sub>2</sub>O

The exchange interaction between two ionic spins, responsible for the spontaneous alignment of neighboring spins in ferromagnetism and antiferromagnetism, is equivalent to an interatomic potential

$$V_{ij} = -\frac{1}{2} J (1 + 4 \vec{s}_i \cdot \vec{s}_j)$$

where  $\vec{S}_i$  and  $\vec{S}_j$  are the spin angular momentum vectors of atoms i and j respectively, and J is the exchange integral, which is negative for antiferromagnetic substances. In the simplest form of the molecular field model, one assumes that J is the same for all interacting neighbors and we replace  $\sum \vec{S}_j$  by  $z \langle \vec{S}_j \rangle$ , where  $\langle \vec{S}_j \rangle$  is the statistical average of  $\vec{S}_j$  over the sublattice to which j belongs. The potential energy of atom i in the field produced by the sublattice j is, apart from an additive constant, given by

$$V_i = \sum_{j} V_{ij} = -2J\langle \vec{S}_j \rangle \cdot \vec{S}_i = -\vec{H}_{ej} \cdot \vec{\mathcal{I}}_i \qquad (B.1)$$

where  $\mathcal{H}_{i}$  is the magnetic moment of an individual atom of spin  $\vec{S}_{i}$  and  $\vec{H}_{ej}$  is the exchange magnetic field produced by the sublattice j and acting on atom i. We now make the basic assumption that the whole antiferromagnetic crystal is divided into two similar sublattices, one with its spins pointing in the positive direction and the other with its spins pointing in the negative direction. The exchange field acting on each spin of the positive sublattice results from the spins of the negative sublattice and also from the other spins of the positive sublattice. If we define  $\overrightarrow{M}^+ = N/2 \langle \overrightarrow{\mathcal{U}}^+ \rangle$  and  $\overrightarrow{M}^- = N/2 \langle \overrightarrow{\mathcal{U}}^- \rangle$ where N is the number of magnetic ions per unit volume, then the exchange fields on the positive and negative sublattice are, respectively, from (B.1)

$$\vec{H}_{e}^{\dagger} = -A\vec{M}^{\dagger} - \vec{\Gamma}\vec{M}^{\dagger}$$

$$\vec{H}_{e}^{\dagger} = -A\vec{M}^{\dagger} - \vec{\Gamma}\vec{M}^{\dagger}$$
(B.2)

where A and  $\Gamma$ , containing the exchange integral J, are the isotropic molecular field constants of the crystal. Date<sup>24)</sup> has found it necessary to introduce additional anisotropic molecular field tensors  $\widetilde{A}'$  and  $\widetilde{\Gamma}'$  to explain his antiferromagnetic microwave resonance experiments in  $\operatorname{CoCl}_2 \cdot \operatorname{6H}_2 O$ .  $\widetilde{A}'$  and  $\widetilde{\Gamma}'$  are 3x3 matrices having zero traces and identical principal axes which determine the principal axes of the antiferromagnetic state. Equations analogous to (B.2) may now be written as

$$\vec{H}_{e}^{+} = -(A + \widetilde{A}')\vec{M}^{-} - (\Gamma + \widetilde{\Gamma}')\vec{M}^{+}$$

$$\vec{H}_{e}^{-} = -(A + \widetilde{A}')\vec{M}^{+} - (\Gamma + \widetilde{\Gamma}')\vec{M}^{-}$$
(B.3)

The total effective field acting on a sublattice is found by adding  $\overrightarrow{H}_0$ , the external field, to  $\overrightarrow{H}_0$ . To take into account the anisotropy of the g-factor of the magnetic ions, it is convenient to introduce the fictitious field  $\overrightarrow{H}'$ , which is defined in terms of the principal values of  $\widetilde{g}$  by its components as follows:

$$g_1 H_1 = g H_1', g_2 H_2 = g H_2', g_3 H_3 = g H_3'$$
 (B.4)

Since the principal axes of  $\widetilde{g}$  coincide with the principal axes of the antiferromagnetic state in  $CoCl_2 \cdot 6H_2O$ , the total effective field may now be written

$$\vec{H}_{eff}^{\pm} = \vec{H}' + \vec{H}_{e}^{\pm}$$
(B.5)

where  $H_{e}^{\pm}$  is given in (B.3).  $\overrightarrow{H}_{eff}^{\pm}$  is the total field at the position of an ion belonging to the positive ore negative sublattice, depending on whether the plus or minus sign is used. We may now proceed in the usual way to find the equilibrium values of  $\overrightarrow{M}^{\pm}$ . After some algebraic manipulation we obtain the familiar expression

 $(B_{\bullet}6)$ 

$$M^{\pm} = Ng\beta/2 SB_{S}(y^{\pm})$$

where  $B_{S}(y^{\pm})$  is the Brillouin function for a spin S with

$$y^{\pm} = |\vec{H} + \vec{H}e^{\pm}| sg\beta/kT$$

It has been found appropriate to use S = 1/2 for CoCl<sub>2</sub>·6H<sub>2</sub>O, in which case

$$\left[B_{s}(y^{t})\right]_{s=1/2} = tanh(y^{t})$$

Let the principal values of A' and  $\Gamma'$  be, respectively,  $A'_x$ ,  $A'_y$ ,  $A'_z$  and  $\Gamma'_x$ ,  $\Gamma'_y$ ,  $\Gamma'_z$ , where x, y, z correspond to the crystal axes c, b, and a'.

In the absence of an applied field we may write  $M^+ = M^- = M_0$  and (B.6) becomes

$$M_{o} = M_{oo} \tanh\left\{\frac{\left[(A + \widetilde{A}'_{:}) - (\Gamma + \widetilde{\Gamma}')\right]g_{\beta}M_{o}}{2\,\text{kT}}\right\}$$
(B.7)

where  $M_{00} = Ng\beta/4$ 

In the limit of  $T \rightarrow T_N(0)$ , the transition temperature in zero field,  $M_0 \rightarrow 0$  and  $tanh(Y_0) \rightarrow Y_0$  where  $Y_0$  is the quantity in the square brackets in (B.7). Substituting these values in (B.7) and solving for T we obtain

$$T_{N}(0) = M_{00} g\beta \left[ \left( A + \widetilde{A}' \right) - \left( \Gamma + \widetilde{\Gamma}' \right) \right], \qquad (B.8)$$

the transition temperature in zero applied field. In order to find the paramagnetic-antiferromagnetic phase transition temperature in the presence of an applied field, we may proceed as follows:

a) 
$$H_0$$
 parallel to the preferred (x) axis. Let  $A_x = A + A'_x$  and  $\Gamma'_x = \Gamma + \Gamma'_x$ , then  $M^{\pm}$  becomes

$$M^{\pm} = M_{oo} \tanh\left(\frac{H' - A_{X}M^{\mp} - \Gamma_{X}M^{\pm}}{2kT}g\beta\right)$$
(B.9)

Rewriting (B.9), we have

$$tanh^{-1}\left(\frac{M^{+}}{M_{00}}\right) - tanh^{-1}\left(\frac{M^{-}}{M_{00}}\right) = \frac{(A_{x} - \Gamma_{x})(M^{+} - M^{-})g\beta}{2kT}$$
(B.10)

In the limit of  $T \rightarrow T_N$ , the magnetization  $M^+ \rightarrow M^-$ , so that

$$\frac{d}{dM^{+}} \tanh^{-1}\left(\frac{M^{+}}{M_{oo}}\right) = \frac{(A_{x} - \Gamma_{x})g\beta}{2kT}M_{oo} \tag{B.11}$$

When  $T = T_N$ , we have that  $M^+ = M^-$ , so that (B.9) becomes

$$M^{+} = M_{oo} tanh\left[\frac{\left(H' - \left(A_{x} + \Gamma_{x}\right)M^{+}\right)g\beta}{2kT}\right]$$
(B.12)

Substituting (B.12) into (B.11) we obtain

$$\frac{2kT}{(A_x - \Gamma_x)M_{\infty}g\beta} = \frac{T}{T_N(0)} = 1 - tanh^2 \left[ \frac{(H' - (A_x + \Gamma_x)M^*)g\beta}{2kT} \right] \quad (B.13)$$

The solution of (B.13) for T gives  $T_N(H_0)$ . Since  $T_N(H_0)$  varies only by a relatively small amount with  $H_0$ , we are interested in small corrections to  $T_N(0)$ , and can thus use  $M + T_N(0)$  in (B.13) as a first approximation to find  $T_N(H)$ . We may also note that

$$M^{+}(T_{N}(0)) = \frac{1}{2} \chi_{x}(T_{N}(0)) H_{0}$$

$$A_{x} + \Gamma_{x} = \frac{1}{\chi_{x}(\Theta)}$$
(B.14)

so that (B.13) becomes

$$\frac{T_{N}(H_{0}) - T_{N}(0)}{T_{N}(0)} \cong \tanh^{2} \left[ \left( \frac{g_{x}}{g} - \frac{i}{2} \frac{\chi_{x}(T_{N}(0))}{\chi_{x}(0)} \right) \frac{g_{B}H}{2kT_{N}(0)} \right] \quad (B.15)$$

Equation (B.15) gives  $T_N$  as a function of the applied field  $H_0$  in a first approximation and becomes exact as  $T_N(H_0) \rightarrow T_N(0)$ , i.e. when  $H_0 \rightarrow 0$ . For small values of  $H_0$  (B.15)

becomes

$$\frac{T_{N}(H_{o}) - T_{N}(0)}{T_{N}(0)} \cong -\left[\left(\frac{g_{x}}{g} - \frac{1}{2}\frac{\chi_{x}(T_{N}(0))}{\chi_{x}(\Theta)}\right)\frac{g\beta}{2kT_{N}(0)}\right]^{2} H_{o}^{2} (B.16)$$

b)  $H_0$  perpendicular to the preferred axis; (i.e.  $H_0$  parallel to the y axis). In this case the antiferromagnetic spins are no longer parallel with  $\overline{H}_0$ . In general,  $\overline{M}^+$  and  $\overline{M}$  lie in the x-y plane and make equal angles with  $\overline{H}_0$ , and  $M = M^-$ . The derivation of  $T_N(H_0)$  in this case is more complicated than in the case discussed above, because the angle between  $\overline{H}_0$  and  $\overline{M}$  must be taken into account. The calculations give the following result:

$$\frac{T_{N}(H_{o}) - T_{N}(O)}{T_{N}(O)} \cong \frac{1}{3} \left[ \frac{g\beta}{2kT_{N}(O)} \frac{g_{y}(A_{x} - \Gamma_{x})}{(A_{x} - \Gamma_{x}) + (A_{y} + \Gamma_{y})} \right]^{2} H_{o}^{2} \qquad (B.17)$$

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