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Neutron Diffraction Investigations of the Magnetic Ordering in $FeBr_2$, $CoBr_2$, $FeCl_2$, and $CoCl_2$

M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler
Oak Ridge National Laboratory, Oak Ridge, Tennessee

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Neutron diffraction experiments have been performed on anhydrous $FeBr_2$, $CoBr_2$, $FeCl_2$, and $CoCl_2$ at temperatures from 295°K to 4.2°K to investigate the existence of magnetic ordering in these hexagonal layer-type structures. All four compounds have an antiferromagnetic transition at low temperatures to structures in which the atomic magnetic moments within a metal layer form ferromagnetic sheets and the moments in adjacent layers are antiparallel. In the iron compounds the moments are oriented parallel to the hexagonal c axis and in the cobalt compounds the moment orientation is perpendicular to that axis. Values of the atomic magnetic moments are close to those expected for the divalent metallic ions if the orbital contribution is quenched. Small-angle scattering experiments on $FeCl_2$ and $CoCl_2$ have shown that the ferromagnetic coupling between moments within a layer is much stronger than the antiferromagnetic coupling between atoms in adjacent layers, and single-crystal investigations on these two compounds have determined the method by which large net magnetization values are obtained at temperatures below T_N in moderate magnetic fields.

INTRODUCTION

THE anhydrous dibromides and dichlorides of iron and cobalt are hexagonal layer-type structures which consist of layers of metal atoms separated by two layers of halide atoms. The specific crystal structures of the bromides are slightly different from those of the chlorides because there is a different stacking sequence of the MX_2 groups. Neutron diffraction investigations of the magnetic ordering in these four compounds were undertaken to determine the magnetic interactions which are important in layer-type structures. Since the chlorides have been the subject of numerous magnetic investigations that have led to conflicting opinions concerning their possible magnetic structures, many of the neutron diffraction measurements were directed toward a detailed understanding of the magnetic properties of these two compounds.

The unusual magnetic properties of $FeCl_2$ and $CoCl_2$ were first observed about forty years ago[1] and prompted many experiments.[2–6] More recent measurements by Starr, Bitter, and Kaufmann[7] have confirmed all these early investigations and elaborated on them. The magnetic susceptibilities of both compounds obey the Curie-Weiss law, $\chi=C/(T-\theta)$, from room temperature to about 75°K, and extrapolations of these results give positive values of the paramagnetic Curie temperature, θ. According to the Weiss theory, a positive value of θ corresponds to a positive molecular field and suggests the occurrence of a ferromagnetic transition. On the other hand, susceptibility measurements at lower temperatures exhibit maxima which occur at the same temperatures that λ-type anomalies are observed in the specific heat measurements,[8,9] thereby suggesting antiferromagnetic transitions. Values of the specific heat peaks, magnetic susceptibility maxima, and paramagnetic Curie temperatures are given in Table I together with magnetic susceptibility maxima observed in recent experiments[10,11] on the bromides. Susceptibility measurements on $FeCl_2$ and $CoCl_2$ in an external magnetic field at temperatures below the anomalies also do not have the characteristics usually associated with either antiferromagnetism or ferromagnetism. A large fraction of the expected saturation magnetization can be produced by magnetic fields that are much smaller than those usually associated with the exchange coupling in an antiferromagnetic structure which has a transition temperature of 25°K. Furthermore, the spontaneous magnetization exhibited by a ferromagnet is absent, and no big hysteresis effects are observed when the applied field is varied. In fact, the gross magnetic properties of these compounds were considered so unusual that Becquerel and van den Handel[12] suggested that they be considered as a special class of magnetic materials called "Metamagnetics." Because of these unusual properties, there has been considerable specula-

TABLE I. Values of paramagnetic Curie temperatures, and locations of magnetic susceptibility maxima and specific heat peaks.

Compound	θ (°K)	Temperature for maximum χ (°K)	Temperature for sp. ht. peak (°K)
$FeCl_2$	48.0	24	23.5
$CoCl_2$	38.1	25	24.9
$FeBr_2$		11	
$CoBr_2$		19	

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[1] B. Cabrera, J. chim. phys. **16**, 442 (1918).

[2] H. R. Woltzer, Leiden Comm. **173b** (1925).

[3] H. R. Woltzer and H. Kamerlingh Onnes, Leiden Comm. **173c** (1925).

[4] H. R. Woltzer and E. C. Wiersma, Leiden Comm. **201a** (1929).

[5] W. J. de Haas and B. H. Schultz, Leiden Comm. **256d** (1939).

[6] de Haas, Schultz, and Koolhaas, Leiden Comm. **259a** (1940).

[7] Starr, Bitter, and Kaufmann, Phys, Rev. **58**, 977 (1940).

[8] O. Trapeznikowa and L. Schubnikow, Physik Z. Sowjetunion **7**, 66 (1935).

[9] Trapeznikowa, Schubnikow, and Miljutin, Physik Z. Sowjetunion **9**, 237 (1936).

[10] Bizette, Terrier, and Tsai, Compt. rend. **245**, 507 (1957).

[11] Bizette, Terrier, and Tsai, Compt. rend. **246**, 251 (1958).

[12] J. Becquerel and J. van den Handel, J. phys. radium **10**, 10 (1939).

TABLE II. Lattice constants of the hexagonal chemical unit cells.

Compound	a(A)	c(A)	Molecules/unit cell
$FeCl_2$	3.603	17.536	3
$CoCl_2$	3.553	17.359	3
$FeBr_2$	3.772	6.223	1
$CoBr_2$	3.728	6.169	1

tion on the type of magnetic ordering at low temperatures and even on the existence of three-dimensional magnetic lattices. One of the earliest proposals was by Landau[13] who suggested that the temperature variation of the susceptibility of these compounds could be explained by a magnetic structure in which the atomic magnetic moments within a layer are aligned parallel and the moment directions in adjacent layers are antiparallel. Schultz[14] extended the application of this model to the low-temperature susceptibility measurements in an external field and showed that the experimental results can be explained qualitatively by a molecular-field model with a ferromagnetic interaction between ions within a plane and an antiferromagnetic interaction between ions in adjacent planes. However, Starr[15] has proposed a theory based on the ordering of small groups of moments, and more recently, Leech and Manuel[16,17] have attempted to explain the results by ferromagnetic order of the moments in the metal layers but no coupling between layers. Néel[18] did not limit his considerations to a specific magnetic structure, but he used the molecular field treatment to show that the experimental results are consistent with a two-sublattice antiferromagnetic model which has certain restrictions on the anisotropy energy and exchange energy.

The neutron diffraction investigations[19,20] were first made with powdered specimens of the compounds and the general characteristics of the antiferromagnetic structures were determined from these measurements. Single-crystal experiments were then performed on $FeCl_2$ and $CoCl_2$ to obtain additional details of the structures and to determine the method by which the atomic moments could be aligned parallel in relatively small magnetic fields.

EXPERIMENTAL TECHNIQUES

Sample Preparation

Anhydrous $FeBr_2$ and $CoBr_2$ have the hexagonal structure characteristic of CdI_2 with one molecule per unit cell. The metal atom is located at (0,0,0), while the coordinates of the two bromine atoms are $\pm(\frac{1}{3},\frac{2}{3},u)$ with u equal to 0.25 ± 0.01. Anhydrous $FeCl_2$ and $CoCl_2$ are isomorphous with $CdCl_2$ and are rhombohedral structures with one molecule per unit cell, but in the present investigation it has been convenient to consider the larger hexagonal cell which contains three molecules. In this hexagonal cell, the metal atoms are located at (0,0,0) and $\pm(\frac{1}{3},\frac{2}{3},\frac{2}{3})$, and the six chlorine atoms have coordinates of $(0,0,\pm u)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3}\pm u)$, and $(\frac{2}{3},\frac{1}{3},\frac{1}{3}\pm u)$, where u has been previously determined to be 0.25 ± 0.01. Lattice constants for the hexagonal unit cells were obtained from x-ray measurements,[21] and these values are listed in Table II.

In layer structures of these types, the metal atoms are bonded tightly to the halide atoms in the planes on either side, but there are relatively weak forces which bond adjacent planes of halide atoms. Because of this weak bonding, stacking faults are easily produced in the structures, and the preparation of these compounds must be performed with extreme care in order to obtain crystallographically pure samples. Many methods of preparation were attempted, and most of the samples showed extra reflections which were apparently due to stacking faults in the structures. The best samples were prepared by sublimation of the anhydrous compounds which were obtained by dehydration of the hydrates. However, the method of sublimation was also found to be very important. The best bromide samples were prepared by sublimation in vacuum, but it was necessary to prepare the chlorides by sublimation in HCl. Large quantities of the compounds were sublimed so that there would be sufficient 100-mesh power without the necessity of grinding the large particles.

Single crystals of $CoCl_2$ and $FeCl_2$ were obtained by the Bridgman technique with the sublimed material sealed under vacuum in a quartz container lined with Aquadag. Large crystals were grown by this method, and smaller specimens were then cut from the boule. Similar attempts to obtain single crystals of $CoBr_2$ and $FeBr_2$ were unsuccessful in producing sufficiently large specimens that were not twinned.

EXPERIMENTAL PROCEDURE

In the experiments with powdered specimens, it was necessary to examine the scattering characteristics of these compounds at temperatures from room temperature to 4.2°K. These measurements were made with the samples enclosed in a double-jacketed vacuum cryostat at pressures below 10^{-6} mm Hg. The samples were contained in thin-walled aluminum cells and sealed in a helium atmosphere. These cells were suspended below the coolant container of the cryostat and a small heater was inserted so that the sample temperature could be raised with respect to that of the coolant. Temperatures were measured with a calibrated copper-constan-

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[13] L. Landau, Physik Z. Sowjetunion **4**, 675 (1933).

[14] B. H. Schultz, Physica **7**, 413 (1940).

[15] C. Starr, Phys. Rev. **58**, 984 (1940).

[16] J. W. Leech and A. J. Manuel, Proc. Phys. Soc. (London) **B69**, 210 (1956).

[17] J. W. Leech and A. J. Manuel, Proc. Phys. Soc. (London) **B69**, 220 (1956).

[18] L. Néel, Report to 10th Solway Congress, September (1954).

[19] M. K. Wilkinson and J. W. Cable, Bull. Am. Phys. Soc. Ser. II, **1**, 190 (1956).

[20] W. C. Koehler and E. O. Wollan, Bull. Am. Phys. Soc. Ser. II, **1**, 190 (1956).

[21] H. Yakel and R. M. Steele (private communication).

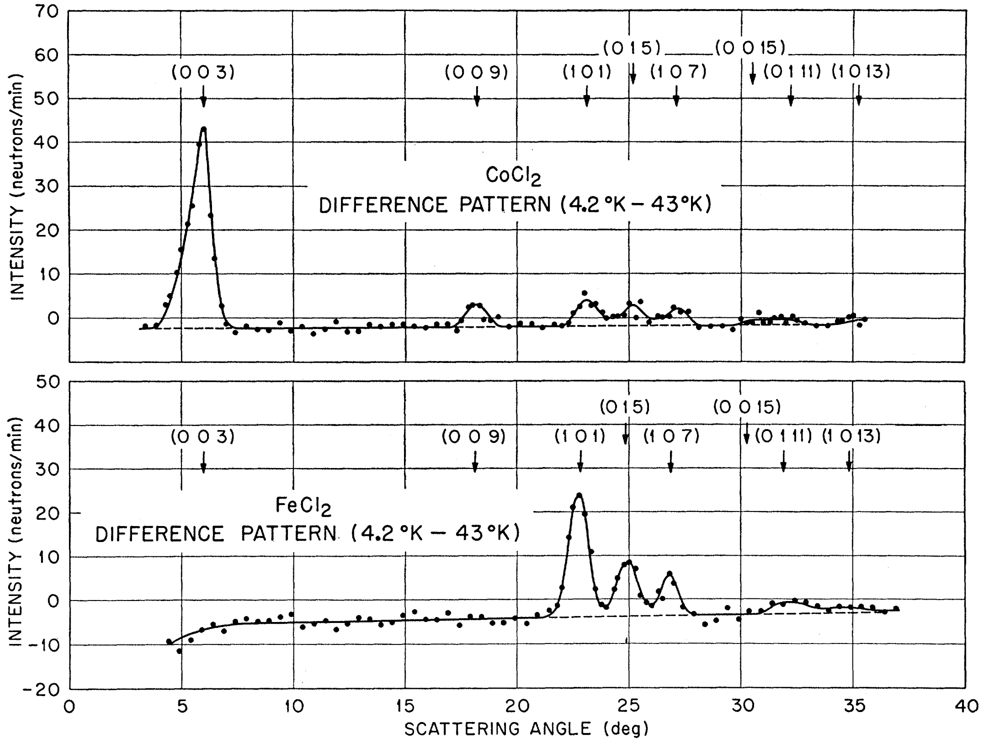

FIG. 1. Powder diffraction patterns for $CoCl_2$ and $FeCl_2$ showing the difference between data obtained at 4.2°K and 43°K.

tan thermocouple. In the magnetic structure determinations the samples were placed in cylindrical cells and the collimation of the scattered beam was effected by a Soller slit in front of the detector. In the small-angle scattering experiments, the samples were enclosed in flat cells and both incident and reflected beams were very well collimated to allow investigations into the small-angle region.

The single-crystal measurements were made on a neutron spectrometer equipped with a cryostat and magnet, and the specimens were mounted on the low-temperature single-crystal goniometer in the same manner which has been described previously.[22] The crystals were flat cylinders with the axes of the cylinders parallel to the hexagonal c axis of the crystals, and specimens of different size were used to determine the effects of extinction. While the volume of the samples varied by about a factor of ten, the average specimen was about $\frac{1}{4}$ in. in diameter and $\frac{1}{16}$ in. in thickness. Measurements were made at room temperature and 4.2°K, and to ensure temperature equilibrium at 4.2°K, the samples were immersed within the liquid helium. The position of the magnet pole pieces limited observations to reflections which occurred at relatively small values of the scattering angle, and the geometry of the apparatus limited the magnetic field to a direction closely parallel to the scattering vector of the scattering planes under observation.

EXPERIMENTAL RESULTS

Results from Powdered Samples

Determinations of the Magnetic Structures

The diffraction patterns from all four compounds at 4.2°K showed additional reflections which were caused by the development of an antiferromagnetic lattice. Since many of the magnetic reflections were nearly superimposed on nuclear reflections, their angular positions and intensities were obtained from difference patterns representing a point-by-point subtraction of data taken above and below the transition temperature. Results for $FeCl_2$ and $CoCl_2$ are shown in Fig. 1, where the difference patterns were obtained from results at 4.2°K and 43°K. The reflections in these patterns are representative of the ordered magnetic lattices at 4.2°K, and the negative backgrounds represent the diffuse paramagnetic scattering at 43°K. The choice of these two temperatures essentially eliminated effects from temperature-dependent nuclear scattering, but the patterns at 43° showed the presence of some short-range order of the magnetic moments. The decrease in background at low angles in the difference pattern for $FeCl_2$ was caused by this magnetic-short-range order.

The indices for the antiferromagnetic reflections in Fig. 1 are based on an hexagonal magnetic unit cell in which the c axis is twice the c axis of the hexagonal chemical unit cell and the a axis is identical to that of the chemical cell. This magnetic cell, therefore, represents an antiferromagnetic structure in which the atomic

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[22] Wollan, Koehler, and Wilkinson, Phys. Rev. **110**, 638 (1958).

moments are aligned parallel within each hexagonal layer, and the moments of adjacent layers are aligned antiparallel. This is exactly the structure suggested for these compounds in 1933 by Landau. The absence of magnetic (00*l*) reflections from $FeCl_2$ restricts the moment orientation in this compound to a direction parallel to the *c* axis, and the relative magnetic intensities from $CoCl_2$ suggest a moment orientation closely parallel to the layers of moments. Although the diffraction patterns were taken with Soller slits limiting the horizontal divergence of the scattered radiation, there was considerable vertical divergence, and the asymmetry of the magnetic (003) reflection from $CoCl_2$ is probably the result of this divergence.

Similar diffraction patterns were obtained from powdered $FeBr_2$ and $CoBr_2$, and identical conclusions were obtained. The magnetic structures consist of ferromagnetic sheets of moments within the metal layers, and adjacent sheets have the magnetic moments directed antiparallel. In $FeBr_2$ the moments are oriented parallel to the hexagonal *c* axis, while in $CoBr_2$ they are nearly perpendicular to that axis.

The relative saturation of the ordered magnetic lattices at 4.2°K and values for the transition temperatures were obtained from measurements of the temperature dependence of the magnetic reflections. Figure 2 shows this variation for the (003) magnetic reflection from $CoCl_2$ as the sample was warmed slowly from 4.2°K. The magnetic intensity follows a Brillouin-type curve to background and indicates a Néel temperature of 25°K in excellent agreement with the anomalies observed in measurements of the specific heat and magnetic susceptibility. Similar measurements were made on magnetic reflections from the other compounds, and the transition temperatures were found to agree satisfactorily with the specific heat and magnetic susceptibility data listed in Table I.

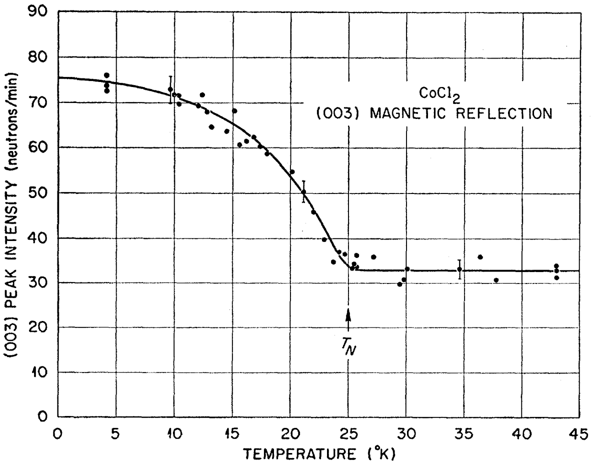

FIG. 2. Temperature variation of the intensity of the (003) antiferromagnetic reflection from $CoCl_2$.

The diffracted intensity in a Bragg reflection is proportional to the differential scattering cross section. For incident unpolarized neutrons on an ordered magnetic lattice in which the atomic moments are aligned along only one axis, this cross section is given by[23]

$$F^2 = b^2 + q^2 p^2, \tag{1}$$

in which *b* and *p* are the nuclear and magnetic scattering amplitudes and

$$q^2 = 1 - (\mathbf{e} \cdot \boldsymbol{\kappa})^2, \tag{2}$$

where **e** is the unit scattering vector and **κ** is a unit vector parallel to the atomic magnetic moment. The magnetic scattering amplitude is equal to

$$p = (e^2\gamma/2mc^2)\mu f, \tag{3}$$

where γ is the neutron magnetic moment, μ is the projection of the atomic magnetic moment on its axis of quantization, and *f* is the form factor representative of the magnetic electrons.

Powder patterns for all four compounds were analyzed in terms of the ferromagnetic sheet structures which have been described. Temperature corrections were applied using the Debye theory of independent oscillators, and intensities were adjusted to include the lack of saturation of the magnetic lattices at 4.2°K. The plate-like structure of the small particles caused considerable preferred orientation in the powdered samples. This preferred orientation together with the small number of observed magnetic reflections made it impossible to determine the proper Fe^{++} and Co^{++} magnetic form factors or the exact orientation of the moments in the cobalt compounds. The experimentally determined Fe^{++} form factor[24] was used for all compounds, and the atomic moments in $CoBr_2$ and $CoCl_2$ were assumed to be within the plane of the layers and directed with equal probability along three equivalent hexagonal directions. The average values of the moments as determined from the largest magnetic reflections are listed in Table III, and the errors are estimates based on considerations of preferred particle orientation, structure defects due to stacking faults, and the intensity determinations.

Analyses were also made of the magnetic diffuse scattering by comparing the paramagnetic diffuse scattering at room temperature to the diffuse scattering at 4.2°K. To a first approximation[25] this difference is proportional to μ^2, and determinations of moment values by this method are independent of preferred particle orientation in the samples. The analyses were made at small values of the scattering angle where the results are insensitive to the choice of the form factor, and the moment values obtained by this procedure are

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[23] O. Halpern and M. H. Johnson, Phys. Rev. **55**, 898 (1939).

[24] C. G. Shull and E. O. Wollan in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. II, p. 210.

[25] G. T. Trammell (private communication).

TABLE III. Antiferromagnetic structures determined from neutron diffraction powder patterns.

		Atomic magnetic moment values (Bohr magnetons)	
Compound	Structure	Coherent scattering determination	Diffuse scattering determination
$FeCl_2$	Ferromagnetic layers ($\mu \| c$ axis)	4.5 ± 0.7	4.3 ± 0.6
$CoCl_2$	Ferromagnetic layers ($\mu \perp c$ axis)	3.0 ± 0.6	3.2 ± 0.5
$FeBr_2$	Ferromagnetic layers ($\mu \| c$ axis)	4.4 ± 0.7	4.5 ± 0.6
$CoBr_2$	Ferromagnetic layers ($\mu \perp c$ axis)	2.8 ± 0.6	3.1 ± 0.6

also listed in Table III. Within experimental error, values by the two methods are in agreement, and all values are fairly close to those for atomic magnetic moments in which the orbital contributions are quenched.

Small-Angle Scattering

The most logical interpretation of the magnetic susceptibility measurements on $CoCl_2$ and $FeCl_2$ in terms of the known magnetic structures is that the ferromagnetic interaction between magnetic moments within the layer is much larger than the antiferromagnetic interaction between moments in adjacent layers. Moreover, molecular-field calculations on layer structures of this type show that positive values of θ can be obtained from susceptibility measurements if such interactions exist.

Neutron diffraction investigations of the diffuse scattering at sample temperatures near the magnetic ordering transition provide a method of checking this interpretation.[26] A ferromagnetic interaction between magnetic moments enhances the small-angle scattering above the paramagnetic level, while an antiferromagnetic interaction causes this scattering to be lower than the paramagnetic value. Therefore, if both types of interactions are present in a magnetic substance, an examination of the small-angle scattering can frequently determine the relative strengths of these interactions.

Both the incident and reflected neutron beams were very well collimated to allow investigations into the small-angle region, and scattering data at small angles were obtained for fixed sample temperatures in the vicinity of the Néel transitions. The results for $FeCl_2$ are shown in Fig. 3(a), where the curves represent the scattered intensities at the various temperatures in excess of that at 4.2°K. Since measurements of the temperature dependence of the magnetic reflections from $FeCl_2$ had shown that the magnetic lattice is almost completely ordered at 4.2°K, these curves represent the magnetic scattering that results from the disruption of the ordered lattice. The cross-section scale at the right of the figure gives the absolute intensity of this scattering. The data at 295°K which correspond to a completely disordered magnetic lattice were analyzed by the method mentioned previously and were found to be in good agreement with those expected from a spin-only value for the Fe^{++} magnetic moment. As the sample temperature was lowered below 295°K, increased small-angle scattering was observed, and the intensity of this small-angle scattering reached a maximum at sample temperatures near the Néel transition. The temperature variation of this scattering is more apparent in Fig. 3(b), where the difference in intensity at scattering angles of 2 degrees and 16 degrees is plotted as a function of temperature. This ferromagnetic type of small-angle scattering is observed at temperatures well above the Néel temperature and confirms the interpretation that the decrease in background at small angles in the difference pattern for $FeCl_2$ in Fig. 1 is caused by short-range magnetic order at 43°K.

A theoretical treatment of the neutron scattering from ferromagnetic materials near their Curie transitions has been given by Van Hove,[27] and the scattering has been termed critical magnetic scattering. This critical scattering, which is caused by the presence of large fluctuations in the magnetic scattering density, has been observed at small angles in experiments on iron[28] and has been analyzed[29] according to the Van Hove treatment. For ferromagnetic materials, a maximum in the intensity of the small-angle scattering is expected at the Curie temperature, since the regions in which there is a correlation between atomic moments are largest at this temperature. No quantitative anal-

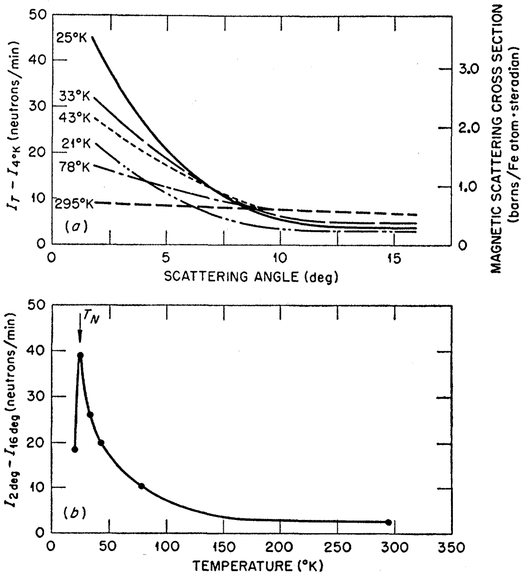

FIG. 3. (a) Small-angle scattering from $FeCl_2$. (b) Temperature variation of the small-angle scattering from $FeCl_2$.

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[26] M. Slotnick, Phys. Rev. **83**, 1226 (1951).

[27] L. Van Hove, Phys. Rev. **95**, 1374 (1954).

[28] M. K. Wilkinson and C. G. Shull, Phys. Rev. **103**, 516 (1956).

[29] Gersch, Shull, and Wilkinson, Phys. Rev. **103**, 525 (1956).

ysis has been made on the small-angle scattering from $FeCl_2$ since the data are not sufficiently accurate to warrant it, but the maximum at the Néel temperature is undoubtedly associated with a maximum in the size of the regions with correlated magnetic moments. An estimate of the dimensions of these regions has been obtained by the application of small-angle scattering theory to the data shown in Fig. 3(a). The angular distribution of the curve at 25°K can be explained on the basis of clusters of magnetic moments that have effective diameters ranging roughly between 10 A and 20 A.

Similar small-angle scattering experiments were also performed on $CoCl_2$. While the presence of the (003) magnetic reflection made these experiments somewhat more difficult, small-angle scattering was definitely observed from this compound, and it reached a maximum intensity in the vicinity of the Néel temperature. No experiments were performed to investigate this type of scattering from $FeBr_2$ and $CoBr_2$, but powder diffraction patterns used in the structure determinations indicated the existence of small-angle scattering from both compounds at 43°K.

Results from Single Crystals of $FeCl_2$ and $CoCl_2$

Investigations of the Magnetic Structures

The small number of magnetic reflections in the powder diffraction patterns and the preferred particle orientation in the samples prevented accurate determinations of the size and orientation of the atomic magnetic moments. Therefore, single-crystal investigations were performed, but these were limited to the chloride compounds since no satisfactory single-crystal specimens of the bromides were available.

The measurements were analyzed by the method used in the single-crystal neutron diffraction investigations of Peterson and Levy.[30] In such investigations the entire crystal is irradiated by the neutron beam, and the integrated intensities, E_{hkl}, of the Bragg reflections are given by

$$E_{hkl}=(KI_0F_{hkl}^2/\sin 2\theta)A_{hkl}, \tag{4}$$

where I_0 is the incident intensity, F_{hkl} the structure amplitude, θ the Bragg angle, A_{hkl} the absorption factor, and for a particular experiment, K is a constant of the experiment. In order to normalize the magnetic intensities so that values could be obtained for the atomic magnetic moments, it was necessary to determine the scale factor, KI_0. This determination was made from measurements of the intensities of nuclear reflections where the structure amplitudes could be calculated from known values of the nuclear coherent scattering cross sections of Fe, Co, and Cl. Absorption coefficients were calculated by the procedure established by Busing and Levy.[31] The inherent imperfection of these crystals allowed the use of fairly large specimens without involving appreciable extinction corrections, but the effects of extinction were investigated by examination of the relative intensities of strong and weak reflections from crystals of different size.

Although the parameter, u, designating the coordinates of the chlorine atoms had been previously determined to be 0.25 ± 0.01, an analysis of the calculated structure amplitudes showed that the intensities of many weak nuclear reflections were very sensitive to the value of this parameter within the listed limit of accuracy. Hence, it was necessary to establish a more accurate value of u at the same time that a determination was made of the scale factor. Both results were obtained from a plot of the experimentally determined values of KI_0 for several nuclear reflections as a function of u. A typical plot is shown in Fig. 4 which repre-

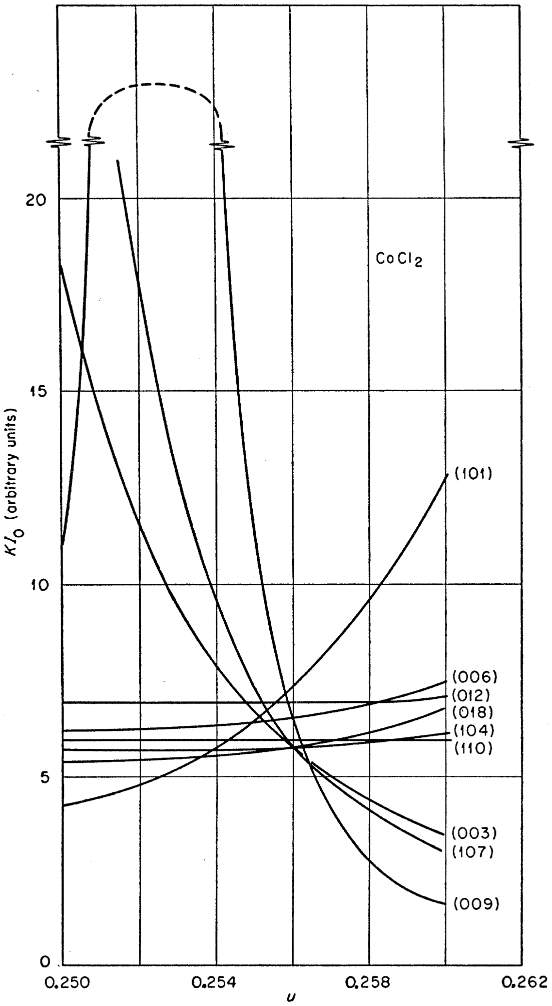

FIG. 4. Determination of the scale factor, KI_0, and chlorine parameter, u, in $CoCl_2$ from single-crystal nuclear reflections.

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[30] S. W. Peterson and H. A. Levy, J. Chem. Phys. **20**, 704 (1952).

[31] W. R. Busing and H. A. Levy, Acta. Cryst. **10**, 180 (1957).

sents data from one of the $CoCl_2$ crystals and lists the nuclear reflections on the basis of the hexagonal chemical unit cell. The reflections can be divided into one group which have intensities that are sensitive to the value of the parameter and another in which the intensities are parameter insensitive. The intensities of the (101), (003), (009), and (107) reflections vary considerably with u and all are quite weak, while the intensities from the other reflections are very much stronger. Since both groups of reflections give nearly the same average values of KI_0, extinction effects in this crystal must be relatively unimportant. The value of the chlorine parameter in $CoCl_2$ was determined from these results to be 0.2558±0.0007. A similar determination on the basis of eleven nuclear reflections from $FeCl_2$ gave a value of 0.2543±0.0005 for u.

With the scale factors obtained by this procedure, an analysis was made of the magnetic reflections which occurred at sufficiently small scattering angles that they were not affected by the magnet pole pieces. In the determination of the integrated intensities of antiferromagnetic reflections, it is necessary to consider the possibility of antiferromagnetic domains in which the axis of antiferromagnetism can be oriented along equivalent crystallographic directions. In $CoCl_2$ the presence of such domains was actually observed by the variation in intensities of equivalent magnetic (hkl) reflections. Such intensity differences, of course, indicate that the crystal was not divided equally into regions with different antiferromagnetic axes. Measurements on $FeCl_2$ where the axis of antiferromagnetism is directed along the unique c axis of the hexagonal cell did not show any variation in intensities from equivalent magnetic reflections. The determinations of the magnetic structures of $FeCl_2$ and $CoCl_2$ were made from average values of the integrated intensities obtained from all reflections with equivalent indices. This method cancels any effect due to an inequality in the distribution of atomic moments between antiferromagnetic domains.

The observed magnetic intensities definitely confirmed the magnetic structures which had been determined from the powder diffraction patterns. The atomic moments in $CoCl_2$ were found to be directed parallel to the plane of the layers, and, as will be discussed later, experiments with an external magnetic field determined the exact orientation to be along the $\langle 210 \rangle$ directions.

In the determinations of the atomic magnetic moments in these ordered antiferromagnetic lattices, attempts were also made to obtain the best magnetic form factor from the experimental data. The results for $FeCl_2$ agreed very satisfactorily with the experimental Fe^{++} form factor determined previously, and the magnetic moment calculated on this basis was 4.35±0.40 Bohr magnetons. The form factor which gave the best fit to the experimental data from $CoCl_2$ was one which was slightly higher than the Fe^{++} form factor at the largest values of the scattering angle (about 10% higher at $\sin\theta/\lambda = 0.25$), and the value for the atomic magnetic moment was determined to be 3.30±0.30 Bohr magnetons. Both moment values are therefore in good agreement with those obtained from the powder analyses.

Magnetic Field Investigations

Recent magnetic susceptibility measurements by Bizette, Terrier, and Tsai[32,33] on single crystals of $FeCl_2$ and $CoCl_2$ are in good qualitative agreement with the earlier powder susceptibility results in which large magnetization values were obtained at low temperatures with moderate external fields. Moreover, these single-crystal results indicate that such magnetization values can be achieved only when the field is applied parallel to the c axis of $FeCl_2$ and perpendicular to the c axis of $CoCl_2$. Neutron diffraction investigations were performed in external magnetic fields to determine the procedure by which the atomic moments became aligned parallel. Furthermore, it was of interest to examine the behavior of antiferromagnetic domains in these compounds and to determine the specific orientation of the magnetic moments within the layers in $CoCl_2$.

(*a*) *Effects of a magnetic field on the magnetic structure of* $CoCl_2$.—The single-crystal measurements on $CoCl_2$ in zero magnetic field had suggested the existence of antiferromagnetic domains in this compound, and this interpretation was confirmed when a field was applied to the sample. Figure 5 shows the change in intensity of the hexagonal (113) magnetic reflection when a magnetic field was applied parallel to the scattering vector. This intensity variation is associated with changes in the effective value of q^2 in Eq. (2) as the atomic magnetic moments were reoriented by the field, and the diagrams within the figure explain the results according to the domain behavior. Before the field was applied, the intensities of equivalent reflections of this type, such as the (113), $(1\bar{2}3)$, and $(\bar{2}13)$ reflections,

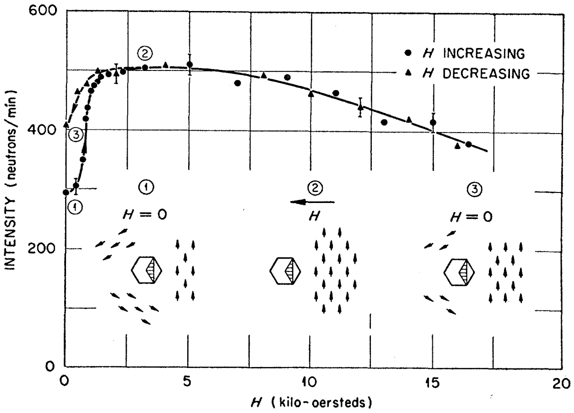

FIG. 5. Variation of the intensity of the (113) antiferromagnetic reflection from $CoCl_2$ in an external magnetic field.

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[32] Bizette, Terrier, and Tsai, Compt. rend. **243**, 895 (1956).
[33] Bizette, Terrier, and Tsai, Compt. rend. **243**, 1295 (1956).

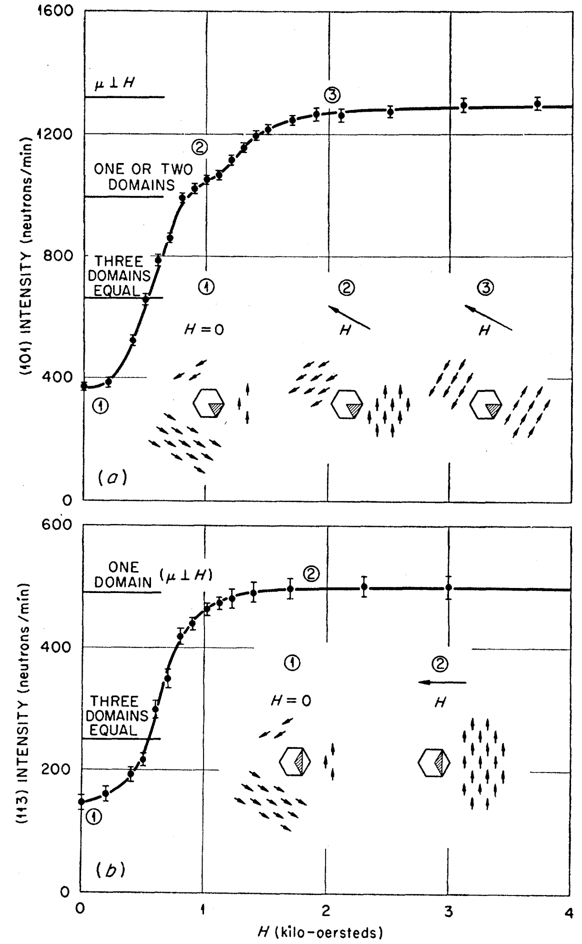

FIG. 6. Comparison of the field dependence of the (113) and (101) magnetic reflections from $CoCl_2$.

varied about 30%, and this variation is represented in the diagram by slightly unequal numbers of moments pointing along the three equivalent hexagonal directions. In an external field the moment orientation perpendicular to the field direction is the most stable, and the domain pattern changed with applied field until with about 1.2 kilo-oersteds the entire crystal was transformed into one domain direction. When the field was removed, the intensity remained considerably higher than the original zero-field value, indicating that much of the domain transformation had remained. This was confirmed by intensity measurements of the (1$\bar{2}$3) and ($\bar{2}$13) reflections, because these intensities were much smaller than the original values.

The decrease in intensity of the (113) reflection at high fields is associated with the production of a net magnetization in the crystal. After all of the moments are oriented perpendicular to the direction of the field, larger fields rotate these moments into the field direction thereby producing a net magnetic moment per unit volume. Magnetization data as a function of the field are not given in the single-crystal susceptibility measurements on $CoCl_2$, but the powder measurements show a magnetization at low fields which increases almost linearly with the field. The diffraction data of Fig. 5 might appear to be inconsistent with these results since no positive effects are observed until reasonably large field values. However, since the change in intensity is proportional to $(\mu \cos\varphi)^2$, where φ is the angle between the atomic moment μ and the field direction, the experiment is not sensitive to small rotations of the moments. Rough calculations based on the magnetization values in the powder susceptibility measurements show that the intensity should be about 5% below the maximum at 10 kilo-oersteds and about 20% below it at 16.5 kilo-oersteds. The results in Fig. 5 are in good agreement with these predictions.

The magnetic moments in the diagrams are shown directed along the equivalent hexagonal ⟨210⟩ directions. This moment orientation was indicated by experiments which investigated the intensity changes of several magnetic reflections after the field was applied at various angles parallel to the hexagonal layer and then removed. Since these experiments involve the repopulation of domains when the field is removed, the interpretation was not completely unambiguous. However, the moment direction appears to be confirmed by close examination of the intensity changes of the (101) and (113) magnetic reflections when small fields are applied parallel to the scattering vectors of those planes. The results are shown in Fig. 6 and the diagrams within the figure represent an interpretation of the intensity changes. The variation of the (113) intensity with an external field shown in Fig. 6(b) involves merely a domain transformation as previously discussed. However, when the field is applied along the scattering vector of the (101) reflection, the intensity variation seems to involve two processes. First, there is a domain transformation in which all of the moments become oriented in the two domains which have the axes of antiferromagnetism most closely perpendicular to the field direction. The results do not permit a determination of the relative population of the two domains. This transformation is completed at about the same field value[34] that is required when the field is applied along the scattering vector of the (113) planes. However, as the external field is increased further, a critical field is exceeded and the moments flip from the preferred crystallographic direction to one perpendicular to the field. This process is completed with a field of about 2 kilo-oersteds. Since the intensities at zero field depend on previous applications of the magnetic field, these experiments were started for both reflections with a domain population which minimized the intensities of the reflections which were studied. The intensities which should have been observed for these

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[34] Because of the relative orientation of the field and the moment directions in the two experiments, the field required for a domain transformation should be slightly larger when applied along the scattering vector of the (101) planes.

reflections if there had been equal population of the domains are shown on the figures. These two values are experimental determinations of the average intensities of all reflections which are equivalent to the (113) and the (101) reflections. These experimental values representing equal domain population were then used to calculate the intensities expected for the various moment orientations that were suggested by the intensity variation with applied field. These calculated values are also shown on the figures, and the experimental measurements are in good agreement. Although the results are not shown, higher fields along the (101) scattering vector also rotated the moments to produce a net magnetization, and the (101) intensity decreased in the same manner as that of the (113) reflection shown in Fig. 5.

Fields applied along scattering vectors of the (101) and (113) planes make angles of about 85° and 81°, respectively, with the c axis, and these experiments thereby show that reasonably small fields applied parallel to the layers produce a net magnetization in $CoCl_2$. An examination of the (003) magnetic reflection with the field applied parallel to the scattering vector and hence parallel to the c axis showed no intensity change from zero field to 16.5 kilo-oersteds. No intensity increase would be expected, of course, since q^2 is equal to one for this reflection regardless of the domain population. The absence of an intensity decrease for higher fields confirms the single-crystal susceptibility results which had indicated that large magnetization values cannot be obtained with moderate fields if they are applied in this direction.

(*b*) *Effects of a magnetic field on the magnetic structure of* $FeCl_2$.—In an antiferromagnetic material such as $FeCl_2$ where the axis of antiferromagnetism is along a unique crystallographic direction, effects on neutron diffraction intensities due to domains would not be expected, and they were not observed. Measurements of the intensities of three antiferromagnetic reflections in an external magnetic field are shown in Fig. 7, and the only variation is the intensity decrease at high fields which is associated with the parallel alignment of the atomic moments. Figure 7(b) represents data obtained with the magnetic field applied either parallel or nearly parallel to the scattering vectors of the reflecting planes, and Fig. 7(a) shows the same data plotted against the component of magnetic field parallel to the c axis of the crystal. These results confirm the single-crystal susceptibility measurements which showed that large magnetization values can be obtained in $FeCl_2$ with moderate fields only if the fields are applied parallel to the c axis. The numerical values of the critical field required to produce this condition in the two experiments are also in satisfactory agreement.

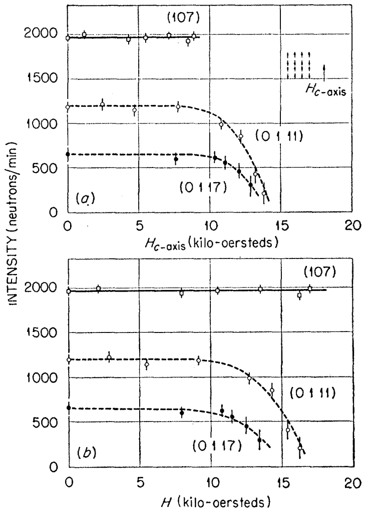

FIG. 7. Variations of the intensities of antiferromagnetic reflections from $FeCl_2$ in an external magnetic field.

Previous investigations of this effect which were made on another crystal showed that the crystal can be seriously damaged in an experiment of this type. If the component of the applied field parallel to the c axis exceeds the critical value required for parallel alignment of the moments, and simultaneously, there is a large field component perpendicular to the c axis, the magnetic forces can be sufficiently strong to fracture the crystal. Such a fracture, of course, causes a sudden decrease in the intensity of the reflections, but both magnetic and nuclear reflections are affected, and the process is irreversible. For the investigations of the (0 1 11) and (0 1 17) reflections shown in Fig. 7, the field was applied as closely parallel to the c axis as permitted by the apparatus, and it made angles of 14° and 18°, respectively, with the scattering vectors of the planes. The effects were completely reproducible as the intensity of the magnetic field was varied, and no effects were observed on nuclear reflections studied under similar conditions. For investigations of the (107) reflection, the field was applied parallel to the scattering vector, and the critical field along the c axis was not exceeded with applied fields up to 17 kilo-oersteds. This result is in quantitative disagreement with the difficult experiment by Herpin and Mériel[35] who studied the intensity variation of the (107) reflection from a powdered sample when an external field was applied parallel to the scattering vector.

In $CoCl_2$ small magnetic fields first flip the axis of antiferromagnetism perpendicular to the field after which larger fields rotate the moments into the field direction. If this process also occurred in $FeCl_2$, strong hexagonal $(00l)$ antiferromagnetic reflections would be observed at the first indication of a net magnetization in the sample. The angular position corresponding to the (003) antiferromagnetic reflection was scanned carefully as the magnetic field was applied parallel to the c axis, and no reflection was observed for fields up to 17 kilo-oersteds. Since this field is considerably higher than the critical field of about 11 kilo-oersteds required to start the parallel alignment, the moments

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[35] A. Herpin and P. Mériel, Compt. rend. **245**, 650 (1957).

do not flip to an alignment perpendicular to the field. Instead of this procedure, those moments which are antiparallel to the direction of the field must undergo a complete reversal in direction. Since this type of transformation involves a sudden disruption of the antiferromagnetic lattice, the intensities of the antiferromagnetic reflections decrease rapidly with changes in the moment orientation as shown in Fig. 7.

DISCUSSION

The neutron diffraction results show that all of these iron and cobalt halides undergo magnetic ordering at low temperatures to antiferromagnetic structures in which the magnetic moments within the layers of metal atoms are coupled ferromagnetically and adjacent layers have the moments oriented antiparallel. Small-angle scattering experiments on $FeCl_2$ and $CoCl_2$ have shown that the ferromagnetic interaction within the hexagonal layer is much stronger than the antiferromagnetic interaction between layers, and similar conclusions were indicated in powder diffraction patterns from $FeBr_2$ and $CoBr_2$. Although the antiferromagnetic structures and the relative strengths of the coupling interactions in these compounds are known, the specific coupling mechanisms which produce the interactions are not understood. The ferromagnetic coupling between moments within a metal layer may be caused by a direct exchange interaction between the *3d* electrons of two neighboring magnetic atoms or by an indirect exchange mechanism through halide ions in the adjacent layers. The distance between these metal atoms is considerably larger than that usually associated with direct exchange, but even though the intralayer interaction is the strongest one in these compounds, it is relatively very weak when compared to known ferromagnetic interactions such as those which exist in the ferromagnetic metals. Of course, the distance between metal atoms in adjacent layers is sufficiently large that any exchange coupling between magnetic moments of these atoms must be indirect via the intervening halide ions. Furthermore, in $FeBr_2$ and $FeCl_2$ these exchange forces must exist, since the configurations are unstable with respect to dipole forces. In the bromides, there is a nearly straight-line path through two bromine atoms connecting metal atoms in adjacent layers, and experiments[22] on $MnBr_2$ have suggested that an antiferromagnetic coupling exists through this linkage. In the chlorides there is no straight-line path between metal atoms in adjacent layers through overlapping chlorine atoms, and the coupling must be more complex. An indication of the strength of the exchange interaction between moments in adjacent layers can be obtained for the chloride compounds from the magnetic fields required to produce parallel moment alignment. Although the field required to accomplish this condition in $CoCl_2$ is about twice as large as that necessary in $FeCl_2$, an exchange energy corresponding to a transition temperature of about 6°K is obtained for both compounds when dipole forces are considered. These forces help stabilize the magnetic structure of $CoCl_2$, but tend to make that of $FeCl_2$ unstable.

The large net magnetization values which are produced in $FeCl_2$ and $CoCl_2$ with moderate fields at temperatures below T_N are undoubtedly achieved by overcoming only the weak interaction which exists between magnetic moments in adjacent layers. This procedure would require that the moments within a particular layer are always aligned parallel and turn simultaneously with the application of the field. The procedures by which parallel moment alignment is accomplished are in good qualitative agreement with those predicted by Néel[18] from his molecular-field calculations based on a two-sublattice model of an antiferromagnet. The moments in $CoCl_2$ first undergo a domain transformation to the domain in which the antiferromagnetic axis is favored by the field direction, after which they flip to an alignment perpendicular to the field and are then rotated into parallel alignment. In $FeCl_2$ the moments never become perpendicular to the field direction, but the moments antiparallel to the field merely become reversed when a critical field is exceeded. According to Néel's treatment, both mechanisms are predicted depending on the ratio of the anisotropy energy to the exchange energy, and the moments will become perpendicular to the field direction only if this ratio is small. Since the magnetic interactions in these compounds are similar, their different behavior in an external field can be explained by the differences in the anisotropy energy. In $CoCl_2$, the anisotropy energy which must be overcome in rotating the moments to an alignment perpendicular to the field direction is the small value associated with the preferred crystallographic direction within the layer. Conversely, for $FeCl_2$ it is the large value which would be required to vary the moment direction with respect to the unique crystal axis. Therefore, although expressions based on a two-sublattice model may not be directly applicable to these magnetic structures, they certainly predict the observed behavior. It should be mentioned that Néel's calculations give an incorrect value for the anisotropy constant of $CoCl_2$. This value resulted from his interpretation of the magnetic susceptibility measurements that about 10 kilo-oersteds were required to align the moments perpendicular to the field. The neutron diffraction results show that this condition is achieved with only about 2 kilo-oersteds applied in a direction perpendicular to the *c* axis, so that the anisotropy constant within the hexagonal layer is considerably lower than Néel's value. These experiments do not give any information concerning the anisotropy energy associated with the unique crystal axis in $CoCl_2$.

The various diffraction experiments have given values for the atomic magnetic moments in these compounds which are not greatly different from moments corresponding to the ground state of the free metallic ions in which there is no contribution from the orbital currents. In both $FeCl_2$ and $CoCl_2$, there is good agreement between the values obtained from powdered specimens and single crystals, and the moments are about 10% higher than those expected for complete orbital quenching. This agreement with a spin-only value may be fortuitous, since in certain diluted cobalt salts at low temperatures a similar accidental agreement has been observed previously. An accurate measurement of the magnetic form factor at large values of $\sin\theta/\lambda$ should determine whether an orbital contribution exists, but this measurement was not possible in the present investigation. The value for the moment in $FeCl_2$ is in satisfactory agreement with the neutron diffraction observations of Herpin and Mériel, but it is considerably lower than the value which Bizette, Terrier, and Tsai obtained from the single-crystal magnetic susceptibility measurements. This disagreement between values obtained in the two types of investigations, which suggests that there is a different amount of orbital quenching in zero magnetic field and fields of only about 20 kilo-oersteds, is not understood.

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Hall Effect for Electrons in Silver Chloride*

Koichi Kobayashi† and Frederick C. Brown
Department of Physics, University of Illinois, Urbana, Illinois

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The Hall mobility of photoelectrons has been measured down to 5°K in single crystals of silver chloride. The experiment was carried out with a pulse technique which overcomes the difficulties of space charge and high impedance common to such measurements on insulating crystals. Results show that the electron Hall mobility rises to high values, 6000 cm^2/volt-sec. at very low temperature. On the other hand, drift mobility is strongly influenced by multiple trapping and is not characteristic of microscopic mobility in these crystals at low temperature. Comparison with mobility theory indicates that electrons are scattered by both the optical and acoustical modes of lattice vibration depending upon the range of temperature. Evidence for a structure-dependent scattering such as would be produced by impurities is found below 20°K. Magnetoresistance effects begin to become important at high values of mobility and magnetic field in qualitative agreement with the theory of electronic conductivity for a cubic crystal with simple energy bands and nondegenerate statistics.

I. INTRODUCTION

THE drift mobility of electrons in single-crystal silver chloride has been investigated over a wide temperature range by means of transit-time techniques.[1–3] Results of these measurements are in reasonable agreement with the theory of electron mobility in polar crystals[4,5] down to about 80°K but show a wide discrepancy at lower temperatures. Drift mobility has been found to decrease sharply below a maximum in the vicinity of 60 to 100°K depending upon the sample preparation. The present experiments on Hall effect were carried out to determine whether the decrease in drift mobility is due to scattering by imperfections or to multiple-trapping effects, and to extend mobility data into the very low-temperature range. It is well known that microscopic mobility is more closely related to Hall mobility than to drift mobility when shallow traps are present.

The new results on AgCl show that the Hall mobility for electrons released by light rises to very high values at low temperature, indicating samples of high perfection. Drift mobility is apparently influenced by multiple-trapping effects. Holes are found to make little contribution, if any, to Hall effect in the crystals studied which is in agreement with separate experiments on transient photoconductivity. It is found that electrons are scattered by both acoustical and optical vibrations depending upon the range of temperature. Magnetoresistance effects begin to become important

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† Present address: Department of Physics, Faculty of Science, Tohoku University, Sendai, Japan.

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