

Neutron-Diffraction Study of Antiferromagnetic  $\text{FeCl}_3$ J. W. CABLE, M. K. WILKINSON, E. O. WOLLAN, AND W. C. KOEHLER  
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Neutron diffraction measurements were made on polycrystalline and single-crystal samples of anhydrous  $\text{FeCl}_3$  at sample temperatures from 298 to 1.3°K. Antiferromagnetic reflections were observed which indicate a complicated magnetic structure with a Néel temperature of  $15 \pm 2^\circ\text{K}$ . In this structure the magnetic moments of near-neighbor atoms in the  $c$ -axis direction are oppositely oriented, but superimposed on this order there is a modulation of the moment distribution in the  $[1450]$  direction. From the absence of satellite reflections other than first order and from the relative intensities of the first order satellites, it is concluded that the modulation is of the helical type in which the moments lie within  $(1450)$  planes and rotate by  $2\pi/15$  in successive planes along the  $[1450]$  direction. Absolute intensity measurements yield a moment of  $(4.3 \pm 0.4)\mu_B$  per  $\text{Fe}^{+3}$  ion, and indicate a slight distortion of the helix.

## INTRODUCTION

FERRIC chloride crystallizes in a hexagonal layer-type structure similar to that of  $\text{MnBr}_2$ . These materials also exhibit similar paramagnetic susceptibility behavior with moments which correspond to five unpaired electrons per metal ion.<sup>1</sup> Manganous bromide is known to be antiferromagnetic below  $2.16^\circ\text{K}$ ,<sup>2</sup> and it was expected that  $\text{FeCl}_3$  would also order magnetically at low temperatures. This investigation was undertaken to determine the existence and type of that magnetic order. It was anticipated that a comparison of these results with those for  $\text{MnBr}_2$  would contribute to an understanding of the magnetic interactions in these hexagonal layer-type crystals.

## EXPERIMENTAL RESULTS

## Polycrystalline Sample

The polycrystalline sample was prepared by vacuum sublimation of the anhydrous salt. An x-ray examination of this material gave lattice constants of  $a_0 = 6.065 \text{ \AA}$  and  $c_0 = 17.44 \text{ \AA}$  in agreement with values recently

reported by Gregory.<sup>3</sup> Neutron powder diffraction patterns were taken at several temperatures between 298 and 1.3°K. At 298 and 78°K no coherent magnetic scattering was observed, but at 43°K a broad, small angle peak appeared. This peak became sharper and more intense with decreasing temperature and attained a half-width comparable to the nuclear peaks below 15°K. The peak height intensity (background-corrected) is shown as a function of temperature in Fig. 1. The intensity in the vicinity of the Néel temperature ( $T_N$ ) has been resolved into its components by means of a Brillouin curve extrapolation of the data at lower temperatures. The dashed curve then represents the long-range order component, and the dotted curve shows the corresponding short-range order component in the temperature region just below  $T_N$ . This procedure is somewhat arbitrary and probably yields a high value for  $T_N$ . However, a value of  $T_N = 15 \pm 2^\circ\text{K}$  seems to encompass any plausible method of resolution.

Other peaks were observed in addition to the small angle peak and some of these are shown in Fig. 2. This is a temperature-difference pattern in which the scattering at 298°K has been subtracted from that at 4.2°K. Over the angular range shown, the temperature effects on the nuclear scattering are negligible so that only magnetic scattering is represented. The negative background shows the decrease in paramagnetic scattering on ordering and, to a first approximation, is proportional to the square of the ordered moment. If the experimental  $\text{Fe}^{+3}$  form factor<sup>4</sup> is used, then the background near  $2\theta = 10^\circ$  yields an ordered moment of  $(4.7 \pm 0.3)\mu_B$  per molecule. It is apparent that a large magnetic unit cell is required to account for the positions of the peaks in this pattern. The previous study of  $\text{MnBr}_2$  had shown the futility of structure analysis from powder data for such complex magnetic structures, so it was decided to extend the investigation to single-crystal samples.

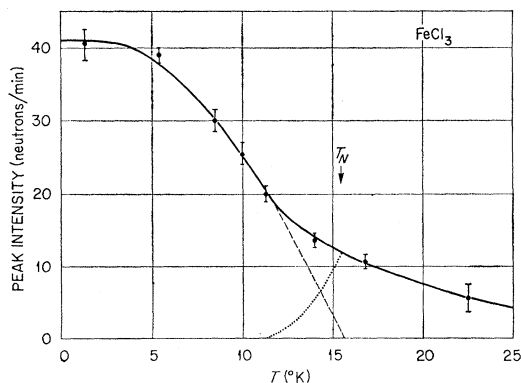


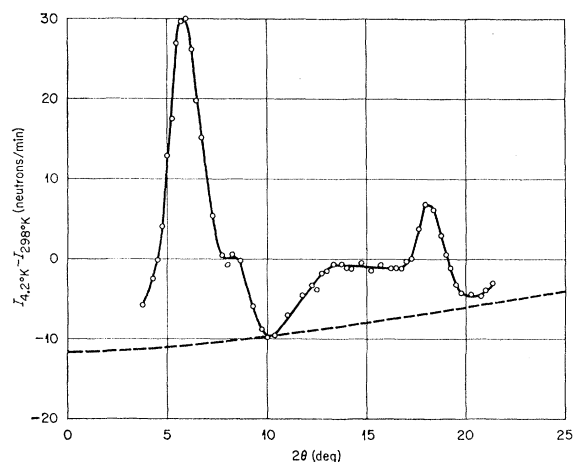
FIG. 1. Temperature dependence of the small-angle reflection of  $\text{FeCl}_3$ .

<sup>1</sup> C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Rev.* **58**, 977 (1940).

<sup>2</sup> E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, *Phys. Rev.* **110**, 638 (1958).

<sup>3</sup> N. W. Gregory, *J. Amer. Chem. Soc.* **73**, 472 (1951).

<sup>4</sup> B. N. Brockhouse, L. M. Corliss, and J. M. Hastings, *Phys. Rev.* **98**, 1721 (1955).

FIG. 2. Temperature-difference pattern of  $\text{FeCl}_3$ .

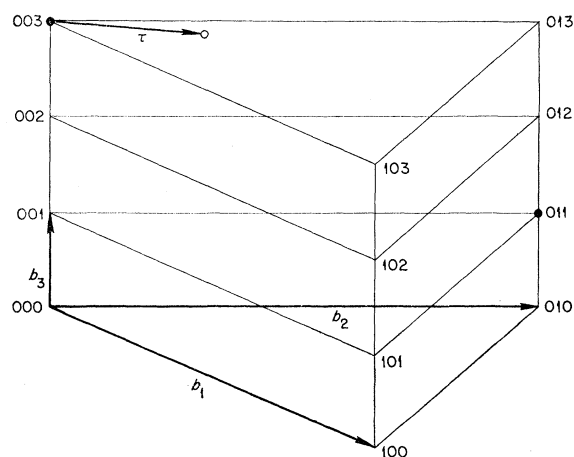
### Single-Crystal Sample

The single crystal of  $\text{FeCl}_3$  was grown from a melt of the anhydrous material. The sample was cut from the boule in the shape of a flat cylinder about  $\frac{1}{8}$ -in. high and of  $\frac{1}{4}$ -in. diam and mounted in the previously described<sup>2</sup> low-temperature goniometer with the  $c$  axis parallel to the horizontal rotation axis. The data were taken with the crystal immersed in the helium bath at 4.2°K. The magnetic reflections exhibited three- and sixfold symmetry about the  $c$  axis of the crystal. A magnetic field was applied to determine if this apparent symmetry was that of the magnetic unit cell or merely a domain growth property of the system. An externally applied magnetic field is useful in distinguishing between these two possibilities, since domain growth symmetry is more readily influenced by magnetic fields than is magnetic superlattice symmetry. It was found that a field of 12 kOe applied parallel to the scattering vector of one of the six equivalent small angle reflections was sufficient to increase the intensity of that reflection by a factor of 3. On removal of the field, about 90% of the enhanced intensity remained. The crystal was then rotated through 60° intervals about the  $c$  axis, and the intensities of the other five reflections observed. Four of these reflections were practically extinguished while the one 180° away from the direction of field application had increased by about a factor of 3. This behavior showed that the apparent symmetry was due to domain growth along three equivalent crystallographic axes, that one domain could be grown at the expense of the other two by the application of a magnetic field, and that the actual magnetic unit cell had twofold symmetry. These conclusions were borne out by further examination of the intensities of the magnetic reflections in both the virgin and remanent state. The intensities of all observed reflections were in agreement with the deduction that one-third of the crystal was contributing to a given reflection in the virgin state, and that 88%

of the crystal was contributing to the same reflection in the remanent state. Both sets of data were used in the structure analysis.

The positions of the magnetic reflections are indicated in Fig. 3. This shows a portion of the reciprocal lattice of  $\text{FeCl}_3$  for which the  $c$  axis of the chemical cell has been doubled. The enlarged lattice sites (003 and 011) correspond to the positions of allowed reflections for an antiferromagnetic structure of the  $\text{CrCl}_3$  type<sup>5</sup> in which the magnetic moments in adjacent (001) planes are oppositely directed. Reflections were not observed in these positions, but rather in positions indicated by the open circle and the vector  $\tau$ . This was found throughout the region of reciprocal space in which observations were made; the magnetic reflections were observed displaced by  $\pm\tau$  from the reciprocal lattice sites of the allowed reflections from the above described antiferromagnetic cell. Such reflections have been commonly referred to as satellite reflections and their scattering vectors are represented by  $\epsilon_{hkl} = B_{hkl} \pm \tau$ , in which  $B_{hkl}$  is the reciprocal lattice vector of the unmodulated reference lattice and  $\tau$  is the modulation wave vector. From the displacement of the satellites it was determined that  $\tau = (b_1 + 4b_2)/15$  so that the modulation is parallel to the  $[14\bar{5}0]$  direction with a wavelength of 15  $(14\bar{5}0)$   $d$  spacings.

The modulation direction and wavelength are obtained directly from the positions of the satellite reflections, but the type of modulation must be deduced from other considerations. One such consideration is the presence or absence of higher order satellites, there being one pair of satellites for each harmonic in the modulated wave. Thus, the absence of higher order satellites shows that the modulation is sinusoidal. In practice these absences are difficult to establish but,

FIG. 3. Reciprocal lattice of  $\text{FeCl}_3$  showing the allowed reflections for a  $\text{CrCl}_3$  type of magnetic structure (003 and 011) and the position of an observed magnetic reflection (open circle).

<sup>5</sup> J. W. Cable, M. K. Wilkinson, and E. O. Wollan, J. Phys. Chem. Solids **19**, 29 (1961).

in the present case, no higher order satellites were observed to the extent of 1% of the intensity of the primary satellite. Another consideration is that of the relative intensities of the primary satellites. For any model with a single magnetic axis (such as the oscillating component structure reported for erbium<sup>6</sup>) the intensities are proportional to  $(q_{hkl})^2 = 1 - (\mathbf{e}_{hkl} \cdot \mathbf{\kappa})^2$ , in which  $\mathbf{e}_{hkl}$  is the unit scattering vector and  $\mathbf{\kappa}$  is a unit vector parallel to the magnetic axis. Regardless of the direction that  $\mathbf{\kappa}$  assumes there will be reflections for which the scattering vectors make small angles with  $\mathbf{\kappa}$  and which will consequently have very low intensities. This is not the case for multidirectional magnetic axis structures. For example, with a helical model the intensities are proportional to  $(1 + \cos^2 \Theta)/2$ , where  $\Theta$  is the angle between the scattering vector and the axis of constant projection of the moments.<sup>7</sup> The intensities can therefore vary by only a factor of 2 (aside from geometrical structure factor and form factor variations) regardless of the direction of scattering. In the present case, the observed relative intensities fall within these limits of a factor of 2 and, furthermore, exclude any single magnetic axis structure. These considerations suggest a helical model for this material. However, the most stringent test of any model is that of the absolute-intensity measurements, and we shall see that these indicate a slight departure from a simple helical moment configuration.

The absolute intensities were obtained by internal calibration with the intensities of the nuclear reflections. Absorption corrections, which vary a maximum of 10% among the observed reflections, were neglected. Extinction effects were minimized by use of only those weak nuclear reflections with structure factors comparable in magnitude to those of the magnetic reflections. In order to obtain the calibration constant it was necessary to determine the positional parameters of the atoms. Wooster<sup>8</sup> reported the probable space group as  $R\bar{3}$  with 6 Fe atoms at  $(000, \frac{1}{3}, \frac{2}{3}, \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) \pm 00u$  and 18 Cl atoms at  $(000, \frac{1}{3}, \frac{2}{3}, \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) \pm (xyz; \bar{y}, x-y, z; y-x, \bar{x}, z)$  in the hexagonal unit cell. The parameters reported were  $u = \frac{1}{3}$ ,  $x = \frac{2}{3}$ ,  $y = 0$ , and  $z = 0.077$ . In this investigation a least squares fit of 25 reflections gave the parameters  $u = \frac{1}{3}$ ,  $x = 0.653$ ,  $y = 0$ , and  $z = 0.076$  with an average intensity deviation of 8%. (These pertain to the 4.2°K data; the room temperature data yield  $z = 0.077$  in agreement with Wooster's value.) With these parameters and the corresponding calibration constant the absolute intensities of the magnetic reflections were obtained. These are given in column two of Table I. In column three are the calculated intensities for the simple helical model in which the magnetic moments lie within the (1450) planes and rotate by  $2\pi/15$  in

TABLE I. Observed and calculated intensities for FeCl<sub>3</sub>.

$hkl^\pm$	$F^2$ (obs)	$F^2$ (calc) <sup>a</sup>	$hkl^\pm$	$F^2$ (obs)	$F^2$ (calc) <sup>a</sup>
003 <sup>+</sup>	0.38	0.37	011 <sup>+</sup>	0.07	0.11
003 <sup>-</sup>	0.36	0.37	011 <sup>-</sup>	0.16	0.12
113 <sup>+</sup>	0.30	0.26	101 <sup>+</sup>	0.05	0.07
113 <sup>-</sup>	0.24	0.26	101 <sup>-</sup>	0.10	0.09
113 <sup>+</sup>	0.35	0.30	111 <sup>+</sup>	0.04	0.06
113 <sup>-</sup>	0.27	0.30	111 <sup>-</sup>	0.10	0.08
213 <sup>+</sup>	0.15	0.17	105 <sup>+</sup>	0.10	0.07
213 <sup>-</sup>	0.17	0.17	105 <sup>-</sup>	0.04	0.06
213 <sup>+</sup>	0.15	0.16	115 <sup>+</sup>	0.06	0.06
213 <sup>-</sup>	0.17	0.16	115 <sup>-</sup>	0.04	0.06
123 <sup>+</sup>	0.31	0.23	015 <sup>+</sup>	0.09	0.08
123 <sup>-</sup>	0.21	0.23	015 <sup>-</sup>	0.06	0.08
123 <sup>+</sup>	0.27	0.23	017 <sup>+</sup>	0.05	0.07
123 <sup>-</sup>	0.22	0.23	017 <sup>-</sup>	0.08	0.06
			107 <sup>+</sup>	0.03	0.05
			107 <sup>-</sup>	0.07	0.06
			117 <sup>+</sup>	0.03	0.05
			117 <sup>-</sup>	0.08	0.05

<sup>a</sup> Assuming  $4.3\mu_B/\text{Fe}^{+3}$ , the  $\text{Fe}^{+3}$  form factor, and that the plane containing the moments is normal to the helical axis.

successive planes along the [1450] direction. The experimental  $\text{Fe}^{+3}$  form factor<sup>4</sup> was also used in this calculation. The agreement is reasonably good and yields a moment value of  $(4.3 \pm 0.4)\mu_B$  per  $\text{Fe}^{+3}$  ion. This should be compared with the average ordered moment of  $(4.7 \pm 0.3)\mu_B$  obtained from the change in the paramagnetic scattering and which is independent of the actual moment configuration. The observed ordered moment is less than the value of  $5\mu_B$  expected on the basis of the paramagnetic susceptibility measurements and indicates that some disorder remains in the spin system at temperatures below which sublattice saturation has been attained. It should be realized that a helical model is a very special case in which two transverse oscillations are perfectly phased to yield the maximum coherent scattering in the primary satellites. Any distortion, either in amplitude or in phase angle, will reduce this scattering. Such distortions may account for the low moment value observed for this material.

### Magnetic Field Effect

The effect of a magnetic field in transforming the domains was described earlier. In that case the field was applied parallel to the scattering vector of the (003<sup>+</sup>) reflection so that the scattered neutron intensity could be conveniently monitored as the field was applied. Of more interest is the determination of the most effective direction of field application since this is related to the direction of spontaneous moment alignment in the crystal. For this determination, use was made of the large remanence in the domain transformations. The field was applied in the desired direction, then removed and the crystal examined in the remanent state. The first experiment was designed to find the most effective field direction relative to the  $c$  axis. In order to start with the crystal in the same condition before each measurement the domain under

<sup>6</sup> J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, J. Appl. Phys. **32**, 49S (1961).

<sup>7</sup> W. C. Koehler, Acta. Cryst. **14**, 535 (1961).

<sup>8</sup> N. Wooster, Z. Krist **83**, 35 (1932).

study (domain 1) was extinguished by enhancing one of the other two domains. The remanent intensity in the  $(003^+)$  reflection of domain 1 was studied as the angle between the applied field direction and the  $c$  axis was varied. The results are shown in Fig. 4. There was no domain transformation up to 16 kOe with the field applied parallel to the  $c$  axis. For other directions, critical field type curves were obtained and two of these are shown. Several other curves were obtained and the results showed that the direction of field application most effective in domain transformation was  $90^\circ \pm 10^\circ$  to the  $c$  axis. After this was established another series of measurements was made to determine the most effective direction within the  $(00l)$  plane. In this experiment, a field of 9 kOe was applied at various angles within the  $(00l)$  plane. After the field was applied and removed, the  $(003^+)$  reflections of the three domains were examined in the remanent condition. In this case the crystal was not in the same domain condition before each measurement, but instead the angle ( $\phi$ ) between the field direction and the  $\tau$  vector of domain 1 was varied in successive increments and the crystal was left in the domain condition of the previous measurement. Each domain was found to be favored for one-third of a revolution. The favored regions consisted of two  $60^\circ$  intervals for each domain; however, the position of these angular intervals depended on whether the angular increments were being increased or decreased. For example, with increasing angles domain 1 was favored from  $\phi = 0^\circ$  to  $\phi = 50^\circ$  at which point domain 2 became favored. After this transformation had occurred, the angles were decreased and domain 1 did not reappear until  $\phi$  reached  $20^\circ$ . This  $30^\circ$  lag in the domain transformation apparently favors the domain already present at the time of the measurement. If this phase lag is taken into account, the favored region for a given domain consists of two  $60^\circ$  angular intervals approximately centered about the plus and minus  $\tau$  vectors of that domain.

For an antiferromagnet an applied magnetic field favors that domain in which the moments are most nearly perpendicular to the field. Within the experimental error of about  $10^\circ$  the most effective directions in  $\text{FeCl}_3$  are parallel to the  $\tau$  vectors, which indicates that the magnetic moments lie in planes perpendicular to those  $\tau$  vectors. The field effects are then consistent with the helical model previously introduced to account for the intensity measurements.

### CONCLUSIONS

The neutron diffraction measurements on  $\text{FeCl}_3$  show that the magnetic moments of near neighbor atoms in the  $c$ -axis direction are oppositely oriented and that

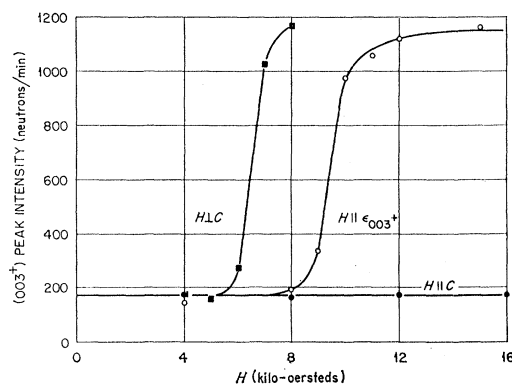


Fig. 4. Field dependence of the  $(003^+)$  intensity for various field application directions.

there is a superimposed modulation in the  $[14\bar{5}0]$  direction. They also establish the absence of higher order harmonics (to 1% of the intensity of the first order satellite), which indicates that the modulation is sinusoidal or nearly so. The intensity distribution of the primary satellites precludes any single magnetic axis model, but is consistent with a helical type of model in which the magnetic moments lie within the  $(14\bar{5}0)$  planes and rotate by  $2\pi/15$  in successive planes along the  $[14\bar{5}0]$  direction. This model is supported by the field induced domain transformations, for which the most effective field application direction is parallel to  $[14\bar{5}0]$ .

Helical structures have been proposed to account for the neutron diffraction observations on a variety of materials including salts, intermetallics, and metals. It has been shown that three interactions are necessary for the occurrence of a helical structure and the stability regions have been defined in terms of the exchange integral ratios for certain crystal systems.<sup>9,10</sup> In this case, the only near-neighbor interaction that can be readily visualized is the antiferromagnetic interaction between near neighbors along the  $c$  axis. The other important interactions are obscured by the unusual modulation direction, so it is not clear just what interactions are responsible for the antiferromagnetic order in this material.

### ACKNOWLEDGMENTS

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<sup>9</sup> A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959).

<sup>10</sup> J. Villain, J. Phys. Chem. Solids 11, 303 (1959).