

## The Crystal Structure of Ferric Chloride $FeCl_3$ .

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With one figure.

Crystals of ferric chloride in the form of small thin hexagonal plates are easily prepared by heating clean iron wire in a fast stream of chlorine. The crystals deliquesce instantaneously on coming into contact with the air.

Several attempts were made to enclose crystals prepared in this way in thin-walled capillary glass tubes. A dessicator designed so that the operator could handle the contents through rubber gloves let into the sides proved impossible to dry sufficiently, even by phosphorus pentoxide acting over several days. More successful was an attempt to transfer the crystals at low temperatures. A room maintained at  $-40^{\circ}C$  was kindly placed at my disposal by Dr. Callow in the Low Temperature Research Station. A tube, containing some excellent crystals, and the capillaries were put in the cold room for an hour, and then an attempt was made to seal up some of the crystals separately. The deliquescence slowed down so much that it would have been possible to do this but for the acute discomfort of working at such low temperatures. Freezing the apparatus only, and working at room temperature was only half successful, the crystal becoming hydrated in the process of transference.

A really satisfactory method was ultimately devised. Into each end of a test tube a short length of glass tube was sealed, and one piece was drawn down to a capillary. A stream of dry carbon dioxide was passed through this capillary and the apparatus warmed. When it was dry, and while the gas was still passing some lumps of commercial ferric chloride were dropped into the tube, and then the tube through which they had been introduced was sealed off at the far end. The apparatus was connected through the capillary to a "Hyvac" pump, and evacuated. It was sealed off at the capillary while still evacuated. The tube was placed in an inclined position in an air oven, and kept at a temperature of  $196^{\circ}C$  for about five hours. At the end of this period some fine crystals had

sublimed. Some were very thin, more or less hexagonal plates, growing perpendicular to the glass walls; these tended to form at the top of the tube. Others were small thick plates, apparently rhombohedra with well developed (111) faces. Only a few of these grew out from the walls. The others which were curved through growing parallel to the walls were considered unsuitable for X-ray investigation. Keeping the tube upright, to prevent the dross which remained at the bottom of the tube from coming into contact with the crystals, a scratch was made on the lower narrow tube as near to the seal as possible. A piece of rubber tubing connected to the supply of carbon dioxide, was then slipped over this tube until it gripped the wide tubing firmly. The tube was then broken off at the scratch. Thus the apparatus was filled with dry carbon dioxide. The broken glass and the dross were then worked down the rubber until a sufficient length was free to be clipped. The rest of the tube was then cut off. A piece of lithium borosilicate glass tube was carefully dried and drawn down to a capillary at one end. While dry carbon dioxide was passed through this, the wide end was fitted into the piece of rubber tubing beyond the clip. The end of the capillary was then sealed off. The clip was removed and a piece of stout wire pushed through the rubber was used to dislodge any particular crystal that was required. Being perfectly dry it dropped straight into the capillary without sticking anywhere. When the crystals were too small to fit the capillary they moved about inside. To prevent this it was found necessary to draw the capillary down to a taper. With care it was found possible to draw the tubes down after the crystal had been sealed up.

In this way several perfect crystals were obtained, permanently protected from deliquescence and mounted in a convenient way for X-ray and optical work.

#### Double refraction.

A fine plate shaped like a triangle with the corners cut off was so thin that by transmitted light it was a brilliant ruby red. It measured about 0.4 cm across, and from 0.0054 to 0.0049 cm in thickness. The plate was fairly uniform in thickness but it was impossible to determine this more accurately owing to irregularities at the edge of the plate. Examined in convergent polarised light it showed a negative uniaxial figure with five rings. The semi-angles subtended by these in air were  $19^{\circ}30'$ ,  $28^{\circ}0'$ ,  $35^{\circ}30'$ ,  $42^{\circ}0'$  and  $48^{\circ}30'$  respectively. The approximate formula  $\mu_e - \mu_o = \frac{\lambda \cdot n}{d^2 c^2}$  was used, where  $\mu_e$  and  $\mu_o$  are the extraordinary and ordinary refractive indices,  $\lambda$  the wave-length of light,  $d$  the thickness

of the plate,  $n$  the number of the ring, and  $\phi = \text{sine semi-angle}$ : mean refractive index. Taking the thickness as the mean of the above figures, viz. 0.0038 cm, the double refraction is 0.34, assuming the mean refractive index to be 1.6. In spite of its probable inaccuracy this measurement shows that the double refraction is very high — a result in accordance with the proposed structure which is a layer-lattice.

#### X-ray investigation.

A Laue photograph taken normal to a flat plate showed no symmetry except a triad axis. It is reproduced in fig. 4. There are pseudo planes

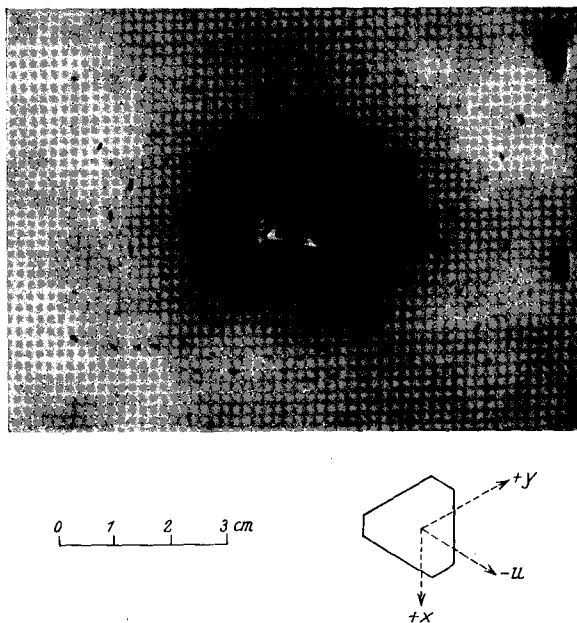


Fig. 4. Laue photograph of  $FeCl_3$ . X-rays perpendicular to the basal plane. Distance of crystal from plate 3 cm. The outline of the crystal and the orientation of the axes are shown in the right-hand corner.

of symmetry but the evidence against their being true planes is indubitable.

Weissenberg photographs were taken with a small equably developed crystal about 0.3 mm across and a small flat plate 1.5 mm across, rotating first parallel and then perpendicular to one of the hexagonal edges. A Weissenberg goniometer by Seemann, and a Philips sealed copper "Crossfoc" tube were used.

**Cell size.**

The cell size was obtained from orders of the basal plane and the  $\{30\bar{3}l\}$  planes. The results are tabulated in table I. Hence  $c = 17.26 \pm .02$ ,  $a = 5.92 \pm .02$  Å.U. if the hexagonal cell is considered, or  $a = 6.69$  Å.U. and  $\alpha = 52^\circ 30'$  for the rhombohedral cell.

Table I.

Index	$d$ observed	$d$ calculated
000 3	5.753	5.753
000 6	2.863	2.877
000 9	1.918	1.918
000 12	1.439	1.439
000 15	1.151	1.151
000 18	0.959	0.959
$30\bar{3} 0$	1.710	1.709
$30\bar{3} 3$	1.637	1.638
$30\bar{3} 6$	1.469	1.469
$30\bar{3} 12$	1.099	1.100
$30\bar{3} 15$	0.956	0.954

**Number of molecules per cell.**

Assuming the density obtained by W. Biltz and E. Birk<sup>1)</sup> to be 2.898, there are six molecules in the hexagonal cell. The density appears to be too low, the calculated density being 3.04.

**Lattice class and space-group.**

The indices of the planes which reflect are all such that  $(2H + K + L)$  is divisible by three, hence the underlying lattice is rhombohedral. The symmetry shown by the Laue photograph is compatible with  $C_3$  or  $C_{3i}$ . The crystals have not been tested for pyroelectricity. The space-group is therefore either  $C_{3i}^2$  or  $C_3^4$ , ( $R\bar{3}$  or  $R3$ ). In the absence of any evidence for the lack of a centre of symmetry the former is assumed to be the space-group.

**Arrangement of atoms.**

In the hexagonal cell there are six iron and eighteen chlorine ions to place. Since the volume of the cell is 524 cubic Å.U. and the volume of eighteen close-packed chlorine ions of radius 1.81 Å.U. is 603 cubic Å.U., it follows that the chlorines must be close-packed. Since there are six layers, and the packing is rhombohedral the close packing must be

1) Z. anorg. Ch. **134**, 132. 1924.

hexagonal. The ratio of the radii of iron and chlorine ions (.67 : 1.81) is .37, which, considering the degree of close-packing of the chlorines, suggests octahedral coordination. The irons may therefore be expected to occupy octahedral positions, arranged in pairs in three layers up the cell. This layer lattice is of the type found for bismuth triiodide by H. Braekken<sup>1</sup>).

It is shown in table II that the relative intensities of the orders of the basal plane and  $\{30\bar{3}l\}$  are markedly similar, which suggests that the ions are arranged in vertical columns<sup>2</sup>). Thus there are vertical planes of symmetry, which cannot be dispelled by vertical parameters either of the irons or chlorines, but there are no planes of symmetry to be seen in the Laue photograph. The fact that the vapour of ferric chloride is composed of  $Fe_2Cl_6$  molecules also suggests that a small parameter should be given to the irons tending to associate them in pairs. The proposed structure however, which is admittedly approximate, neglects this distortion, though the author hopes to find time subsequently to evaluate it. The suggested coordinates of the ions are:

$$\begin{array}{l} \text{Iron:} \quad \pm \frac{1}{3}, \frac{1}{3}, 0; \quad \pm \frac{1}{3}, \frac{1}{3}, \frac{1}{3}; \quad \pm 0, 0, \frac{1}{3} \\ \text{Chlorine} \quad \pm \frac{1}{3}, 0, z; \quad \pm \frac{1}{3}, 0, \frac{1}{3} + z; \quad \pm \frac{1}{3}, 0, \frac{2}{3} + z; \\ \quad \pm 0, \frac{1}{3}, z; \quad \pm 0, \frac{1}{3}, \frac{1}{3} + z; \quad \pm 0, \frac{1}{3}, \frac{2}{3} + z; \\ \quad \pm \frac{1}{3}, \frac{1}{3}, z; \quad \pm \frac{1}{3}, \frac{1}{3}, \frac{1}{3} + z; \quad \pm \frac{1}{3}, \frac{1}{3}, \frac{2}{3} + z. \end{array}$$

The structure factor is

$$\left[ 2F_{Fe} \left\{ \cos 2\pi \left( \frac{h-k}{3} \right) + \cos 2\pi \left( \frac{h-k+l}{3} \right) + \cos 2\pi \left( \frac{l}{3} \right) \right\} \right. \\ \left. + 2F_{Cl} \left( 2 \cos 2\pi \frac{l}{3} + 1 \right) \left\{ \cos 2\pi \left( \frac{h}{3} + zl \right) \right. \right. \\ \left. \left. + \cos 2\pi \left( \frac{k}{3} + zl \right) + \cos 2\pi \left( \frac{h+k}{3} - zl \right) \right\} \right]^2.$$

#### Determination of the parameter $z$ .

The parameter  $z$  has been obtained from the relative intensity of reflection of the orders of  $\{000l\}$ ,  $\{11\bar{2}l\}$ ,  $\{30\bar{3}l\}$ . The values are given in table II. The calculated structure factors have been corrected for polarisation. The most satisfactory value for the parameter is thus between  $27^\circ 30'$  and  $28^\circ 0'$ . The agreement of the calculated and observed intensities for other reflections observed in the Weissenberg photographs is shown in table III. The  $z$ -parameter used is  $27^\circ 45'$ . The intensities were judged by eye, comparing them with the intensities of planes in their

1) Z. Krist. **74**, 67. 1930.

2) W. L. Bragg, C. Gottfried and J. West, Z. Krist. **77**, 262. 1931.

own zone, and with the basal planes which were present on all the Weissenberg photographs. A certain amount of uncertainty is introduced by the glass tube, but by comparing photographs taken with different crystals

Table II.

Index	Observed intensity	Structure factors for $z$			
		= 26° 30'	= 27° 0'	= 27° 30'	= 28° 0'
000 3	vvs	263	244	225	205.5
000 6	vs	30.0	32.5	35.0	36.7
000 9	w	0	.3	1.4	3.2
000 12	vs	50.7	54.8	60.4	64.4
000 15	ms	33.9	29.5	25.4	20.4
000 18	vw	0.0	0.4	1.9	2.3
11 $\bar{2}$ 3	ms	22.7	21.7	20.7	20.0
11 $\bar{2}$ 6	s	36.1	41.7	47.7	53.9
11 $\bar{2}$ 9	vs	102.6	102.6	102.0	100.5
11 $\bar{2}$ 12	m	12.5	10.1	6.9	3.1
11 $\bar{2}$ 15	mw	3.1	3.9	4.3	4.6
11 $\bar{2}$ 18	a	0.0	0.1	0.8	2.2
11 $\bar{2}$ $\bar{3}$	vs	197	222.5	228.0	232.0
11 $\bar{2}$ $\bar{6}$	s	130.6	124.0	115.6	112
11 $\bar{2}$ $\bar{9}$	a	0.0	0.0	0.1	0.8
11 $\bar{2}$ $\bar{12}$	a	5.0	4.2	3.3	2.3
11 $\bar{2}$ $\bar{15}$	ms	7.7	11.1	15.0	19.2
11 $\bar{2}$ $\bar{18}$	ms	33.8	33.6	33.3	30.5
30 $\bar{3}$ 3	m	23.1	20.8	20.3	17.8
30 $\bar{3}$ 6	vw	5.4	5.8	6.2	6.6
30 $\bar{3}$ 9	a	0.0	0.1	0.4	1.0
30 $\bar{3}$ 12	s	28.7	31.8	34.6	37.0
30 $\bar{3}$ 15	ms	26.2	22.8	19.2	15.5

Table III.

Index	Observed intensity	Structure factor	Index	Observed intensity	Structure factor
11 $\bar{2}$ 0	a	0	33 $\bar{6}$ 0	m	40.0
22 $\bar{4}$ 0	a	0	10 $\bar{1}$ 1	m	28.4
22 $\bar{4}$ 3	w	4.7	10 $\bar{1}$ 2	m	23.6
22 $\bar{4}$ 6	ms	16.9	10 $\bar{1}$ 4	w	14.2
22 $\bar{4}$ 9	s	15.8	20 $\bar{2}$ 1	w	8.2
22 $\bar{4}$ 12	w	3.5	20 $\bar{2}$ 2	w	7.8
22 $\bar{4}$ 15	a	4.1	20 $\bar{2}$ 4	w	6.3
22 $\bar{4}$ $\bar{3}$	s	55.2	20 $\bar{2}$ 5	w	4.5
22 $\bar{4}$ $\bar{6}$	s	38.2	40 $\bar{4}$ 1	vw	1.6
22 $\bar{4}$ $\bar{9}$	a	0.3	40 $\bar{4}$ 2	vw	1.5
22 $\bar{4}$ $\bar{12}$	a	2.1	30 $\bar{3}$ 0	vvs	114.0
22 $\bar{4}$ $\bar{15}$	m	13.4			

this has probably been rendered of little importance. The observed intensities agree satisfactorily with the calculated values.

#### Distance apart of the ions.

Assuming the  $z$ -parameter of the chlorines to be  $27^\circ 45'$ , the distance of the centre of the iron to the centre of the chlorine ion is 2.38 Å.U.; the distances between two chlorines in an octahedron are 3.31 and 3.42 Å.U. and between two chlorines in adjacent layers 3.67 Å.U. The distances to be expected on the basis of Goldschmidt's ionic radii are 2.48 and 3.60 Å.U. respectively. Consequently the assumption of the ionic state of the crystal is justified.

#### Summary.

The crystal structure of ferric chloride,  $FeCl_3$ , has been investigated by means of Laue and Weissenberg photographs. It is shown to be built up on a rhombohedral lattice, the unit rhombohedral cell being  $a = 6.69$  Å.U.,  $\alpha = 52^\circ 30'$ , or the hexagonal cell  $a = 5.92$  Å.U.,  $c = 17.26$  Å.U. There are two molecules to the rhombohedral, or six to the hexagonal cell. The space-group is either  $C_3^4$  or  $C_{3i}^2$ ,  $R3$  or  $R\bar{3}$ , probably the latter. The structure is a layer lattice, and is isomorphous with that of bismuth triiodide. The chlorine parameter  $z$  is  $27^\circ 45'$  or .077.

#### Acknowledgments.

It is with great pleasure that I record my indebtedness to my brother, Mr. A. J. P. Martin, who cooperated with me in devising the technique for preparing and mounting the crystals. It is no exaggeration to say that without his skilful help the material would never have been available in such perfect crystals, nor so ideally mounted. I also wish to thank my husband for measuring the double refraction and Mr. J. D. Bernal for his helpful interest.

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#### The Absorption Spectrum of anhydrous Ferric Chloride.

By F. I. G. Rawlins and C. P. Snow.

We have examined the absorption spectrum of one of Mrs. Wooster's crystals of  $FeCl_3$  with a micro-spectrograph in the visible region. In addition to the general absorption starting around 5000 Å. U., there is a sharp absorption band of width 50—100 Å. U., at  $\lambda = 6200$  Å. U. This is the first case, so far as we know, of a discontinuous absorption definitely due to an ionic transition in any elements other than the rare earths. One must assume the transition to be  $^4X - ^2Y$  in the  $Fe^{+++}$ -ion.

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