The Crystal Structure of a Disordered Form of Iron(II) Fluoride Tetrahydrate

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The crystal structure of a disordered form of iron(II) fluoride tetrahydrate has been determined by means of electron-density projections (including generalized projections) down two crystallographic axes. Atomic parameters have been refined by least-squares treatment of limited three-dimensional diffraction data. The crystals are trigonal, space group $R\bar{3}m$, with $a = 9\cdot50$, $c = 4\cdot82$ Å for the disordered hexagonal cell. The structure may be described as an assemblage of discrete $Fe(H_2O)_4F_2$ octahedral groups randomly oriented over 12 possible sites for H_2O and F. Each of these sites is occupied on the average by $\frac{2}{3}O + \frac{1}{3}F (=X)$. The distance $Fe-X$ is $1\cdot955 \pm 0\cdot007$ Å. The groups are connected by hydrogen bonds of length $2\cdot52$ and $2\cdot67$ Å.

1. Introduction

In a recent paper (Penfold & Grigor, 1959) the structure of iron(II) chloride tetrahydrate, obtained by X-ray analysis, has been described. Iron(II) fluoride also forms a tetrahydrate (Poulenc, 1894). Its crystal structure was examined as part of a program of investigation of the hydrates of iron halides but with the particular object of making a comparison with the chloride. The results of this structure analysis were reported by us at the 1959 Cornell meeting of the American Crystallographic Association.

2. Experimental

A pale green solution of iron(II) fluoride was obtained by dissolving iron in warm HF. The tetrahydrate was precipitated from this solution in a white microcrystalline form by addition of ethyl alcohol, as described by Biltz & Rahlfs (1927). On dissolving the precipitate in water containing a little HF and allowing evaporation at room temperature, white crystals of two distinct habits were obtained, rhombohedra (form *A*) and acicular hexagonal prisms (form *B*). The compositions of both the initial precipitate and the two forms of large crystals were confirmed as $FeF_2 . 4H_2O$ by ignition to Fe_2O_3. The crystals oxidize readily in moist air, becoming coated with a brown deposit which was identified by its X-ray powder diagram as $FeF_3 . 4\frac{1}{2}H_2O$, reported by Hanawalt, Rinn & Frevel (1938). For X-ray examination the single crystals were sealed in Lindemann glass capillaries, where they remained stable for several weeks.

Crystallographic data

From layer line spacings on rotation photographs about the *c* (hexagonal) axis, the length of *c* was determined to be approximately 9·5 Å for form *B*.

The even-order layer lines of form *A* appeared with the same spacing as in *B*, but in place of the odd-order layer lines there appeared weak, diffuse streaks, indicating a disordered structure with a halved *c* axis. Accurate unit-cell parameters for form *A* were determined from powder photographs using Fe $K\alpha$ radiation ($\lambda = 1\cdot937$ Å). From inspection of rotation photographs, it is deduced that the hexagonal cells of *A* and *B* are related, at least to a first approximation, so that $c(B) = 2c(A)$ and $a(B) = a(A)$.

The following account refers to form *A*. Hexagonal cell: $a = 9\cdot50 \pm 0\cdot01$, $c = 4\cdot82 \pm 0\cdot01$ Å. Rhombohedral cell: $a = 5\cdot71 \pm 0\cdot01$ Å, $\alpha = 112° 45' \pm 15'$. Density observed (by flotation) $2\cdot20 \pm 0\cdot02$ g.cm.$^{-3}$; calculated for three units of $FeF_2 . 4H_2O$ per hexagonal cell, $2\cdot19$ g.cm.$^{-3}$. Linear absorption coefficient for Mo $K\alpha$ radiation, $30\cdot5$ cm.$^{-1}$.

The only absent spectra were $hkil$ for $-h+k+l \neq 3n$, indicating a rhombohedral type lattice. Further, the diffraction symmetry was observed from Weissenberg photographs to be $\bar{3}m$, indicating one of the space groups $R32$, $R3m$ or $R\bar{3}m$. The presence of a center of symmetry was indicated by the rhombohedral habit of the crystals, so the space group was determined as $R\bar{3}m$, which was confirmed by the subsequent structure analysis.

Relative intensities of 132 $hki0$, $hki1$, $hki2$ and $h0\bar{h}l$ reflections out to a $\sin \theta/\lambda$ value of $1\cdot20$ were determined by visual estimation of Weissenberg photographs using Mo $K\alpha$ radiation. The crystals used measured not more than 0·2 mm. in any direction.

3. The structure

The three iron atoms in the hexagonal unit cell must occupy positions *a* or *b* (see *International Tables for X-ray Crystallography*, Vol. I) of point symmetry $3m$. By choosing set *a*, we make the unit cell origin coincide with one of the iron atoms, the other two iron atoms

being found at the two centering points of the unit cell, $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$, and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$. The signs of structure factors for nearly all X-ray reflections will be positive and the Patterson function will closely resemble the electron-density distribution. A projection of the Patterson function on (0001) revealed 36 equivalent peaks in three groups of twelve surrounding large peaks at the origin and the two lattice centering positions. This indicated that the two fluoride ions and four water molecules in each group were distributed over twelve equivalent positions, and a subsequent electron-density projection showed that each of the small peaks had a content of approximately half an oxygen atom. Subsequent $hki1$ and $hki2$ generalized electron-density projections down the c axis and an electron-density projection down the a axis revealed the approximate positions in space of the small peaks.

The structure possesses disorder of two kinds. It may be described as an assemblage of discrete octahedral groups Fe(H₂O)₄F₂ in all possible orientations, so that the group symmetry averaged over the whole crystal is $\bar{3}$. In other words, water molecules and fluoride ions cannot be differentiated in this crystal. Then further, for every such orientation there is a second orientation related to the first by the set of mirror planes parallel to the three-fold axis of the crystal. The six fluoride ions and twelve water molecules in the unit cell, therefore, occupy one set of 36-fold positions, each site containing on the average $\frac{1}{6}F^- + \frac{1}{3}O\,(=X)$. Views of the structure down c and a axes are shown in Fig. 1.

All positional and thermal parameters for Fe and X were refined by a three-dimensional least-squares treatment of all reflections in the monoclinic sub-group $C2/m$ (the least-squares program for the UNIVAC 1103 digital computer as described by Rossmann et al. (1959) being unable to handle hexagonal coordinates). There are three independent sets of monoclinic coordinates for X, giving three independent values for the hexagonal coordinates x, y, z. These three sets were averaged, giving fractional coordinates

$$x = 0\cdot185_5, \quad y = 0\cdot044_5, \quad z = 0\cdot235 .$$

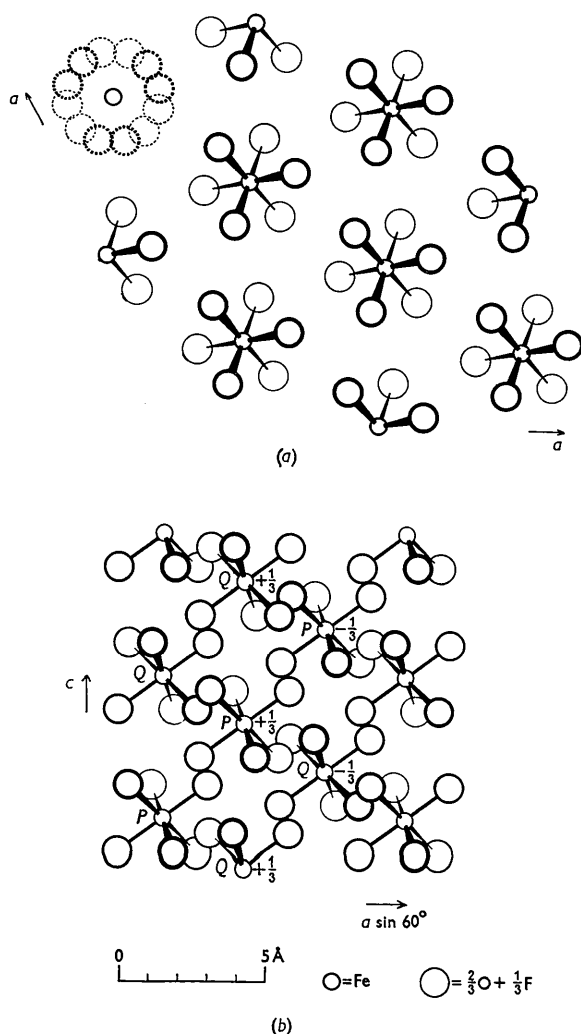The mean deviation from these values of the three

Fig. 1. (a) View of crystal structure down the c axis, only one orientation, P, being shown for all but one of the octahedral groups. (b) View of crystal structure down the a axis, only one orientation, P or Q, being shown for each octahedral group.

Table 1. *Observed and calculated structure factors*

h	k	ℓ	F_{obs}	F_{calc}
0	0	0		252
0	0	3	44	50
0	0	6	*	9
1	0	1	155	158
1	0	4	98	97
1	0	7	*	13
2	0	2	113	110
2	0	5	43	50
3	0	0	26	32
3	0	3	29	33
3	0	6	35	38
4	0	1	165	164
4	0	4	28	31
4	0	7	*	13
5	0	2	44	49
5	0	5	35	40
6	0	0	107	106
6	0	3	47	50
6	0	6	16	14
7	0	1	47	50
7	0	4	29	34
8	0	2	53	58
8	0	5	22	25
9	0	0	23	22
9	0	3	14	13
9	0	6	22	20
10	0	1	40	43
10	0	4	17	11
11	0	2	22	24
12	0	0	19	16
12	0	3	22	24
$\bar{1}$	0	2	23	13−
$\bar{1}$	0	5	47	51
$\bar{1}$	0	8	14	17
$\bar{2}$	0	1	57	62
$\bar{2}$	0	4	56	60
$\bar{2}$	0	7	25	22
$\bar{3}$	0	3	125	124
$\bar{3}$	0	6	26	29
$\bar{4}$	0	2	95	93
$\bar{4}$	0	5	16	19
$\bar{5}$	0	1	65	67
$\bar{5}$	0	4	49	53
$\bar{5}$	0	7	11	14
$\bar{6}$	0	3	28	29
$\bar{6}$	0	6	14	17
$\bar{7}$	0	2	44	44
$\bar{7}$	0	5	27	29

h	k	ℓ	F_{obs}	F_{calc}
$\bar{8}$	0	1	24	26
$\bar{8}$	0	4	22	25
$\bar{9}$	0	3	49	50
$\bar{10}$	0	2	28	29
$\bar{11}$	0	1	25	28
1	1	0	179	176
1	4	0	95	97
1	7	0	44	43
1	10	0	34	29
2	2	0	29	32
2	5	0	88	88
2	8	0	35	34
2	11	0	25	21
3	3	0	89	97
3	6	0	36	37
3	9	0	40	40
3	12	0	14	10
4	4	0	52	55
4	7	0	37	37
4	10	0	22	20
5	5	0	29	28
5	8	0	28	26
6	6	0	29	28
6	9	0	14	11
7	7	0	16	13
7	10	0	11	10
8	8	0	14	11
1	3	1	27	27
1	6	1	81	83
1	9	1	17	13
1	12	1	26	25
2	1	1	168	153
2	4	1	87	83
2	7	1	44	47
2	10	1	27	27
3	2	1	105	102
3	5	1	78	78
3	8	1	29	32
3	11	1	25	16
4	3	1	50	52
4	6	1	50	51
4	9	1	22	22
5	1	1	64	64

h	k	ℓ	F_{obs}	F_{calc}
5	4	1	32	35
5	7	1	31	30
6	2	1	28	30
6	5	1	29	29
6	8	1	17	16
7	3	1	27	30
7	6	1	24	22
8	1	1	55	59
8	4	1	26	25
9	2	1	34	35
9	5	1	20	20
10	3	1	22	19
11	1	1	17	13
1	2	2	142	136
1	5	2	38	37
1	8	2	47	46
1	11	2	19	20
2	3	2	89	85
2	6	2	52	52
2	9	2	22	19
2	12	2	19	16
3	1	2	133	133
3	4	2	47	46
3	7	2	41	40
3	10	2	15	11
4	2	2	49	46
4	5	2	57	56
4	8	2	18	15
5	3	2	47	46
5	6	2	34	34
5	9	2	17	14
6	1	2	38	30
6	4	2	43	41
6	7	2	22	22
7	2	2	52	48
7	5	2	20	22
7	8	2	20	18
8	3	2	23	20
8	6	2	19	21
9	1	2	40	38
9	4	2	19	11
10	2	2	19	13
10	5	2	24	16
11	3	2	20	13
12	1	2	25	17

* Unobserved reflection.

Table 2. *Interatomic distances in hydrated halides, together with sums of ionic radii*

Data for anhydrous salts are in parenthesis

	M–OH$_2$	*$R^+ + R^-$	M–X	$R^+ + R^-$	O–H $\cdots$ X	Ref.
Fe(H$_2$O)$_4$F$_2$	1·96 Å	2·15 Å	1·96 (1·99, 2·12) Å	2·10 Å	2·52, 2·67 Å	(a), (b)
Fe(H$_2$O)$_4$Cl$_2$	2·09, 2·59	2·15	2·38 (2·53)	2·55	3·07–3·45	(c), (d)
Cu(H$_2$O)$_2$F$_2$	1·93	2·00	1·89, 2·47 (1·93, 2·27)	1·95	2·66	(e), (f)
Cu(H$_2$O)$_2$Cl$_2$	1·93	2·00	2·28 (2·30)	2·40	3·20	(g), (h)

* Quoted values of ionic radii (R^+ and R^-) are those of Pauling (1940).

(a) This analysis; (b) Baur (1958); (c) Penfold & Grigor (1959); (d) Ferrari *et al.* (1929); (e) Geller & Bond (1958); (f) Billy & Haendler (1957); (g) Petersen & Levy (1957); (h) Wells (1947).

independent sets was 0·004 Å. The X atoms were treated as anisotropic vibrators but no detailed analysis was made of the final anisotropic parameters. The amplitude of vibration is greater in a direction normal to the Fe–X linkages than parallel to them. The anisotropy is not pronounced, however, and to a first approximation the thermal vibration may be considered isotropic with parameter B equal to 2·9. For Fe^{++}, B is 1·87. Atomic scattering factors used in structure factor calculations were, for iron, those listed for Fe^{++} by Thomas & Umeda (1957), and for fluorine (F$^-$) and oxygen (O), those of Berghuis *et al.* (1955). In all calculations, X was assumed to be $\frac{1}{6}$F$^- + \frac{1}{3}$O. In Table 1, observed and calculated structure factors are compared, the calculated values listed being averages of the independent monoclinic values, hydrogen atoms being ignored. For all listed reflections, values of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $r = \Sigma w (F_o^2 - F_c^2)^2 / \Sigma w F_o^4$ are 0·066 and 0·027, respectively. The standard deviation of the position of X, as determined from the least-squares data, is 0·007 Å, and the distance Fe–X is observed as 1·955 Å.

4. Discussion

One interpretation of the greater apparent temperature factor of X as compared with Fe is that the $\frac{1}{6}$F$^-$ and $\frac{1}{3}$O components of X are slightly separated. An approximate analysis of electron distributions shows that the maximum separations to be expected of these components (having the same temperature factor as Fe) are 0·35 Å and 0·20 Å normal and parallel, respectively, to the Fe–X direction. On this basis the observed Fe–O and Fe–F distances are within the range 1·94–1·97 Å. All interatomic distances quoted in the later discussion are for the case where the two components of X have the same coordinates. In Table 2 are listed the observed interatomic distances in this and a number of similar hydrates, together with sums of ionic radii.

The relative orientation of adjacent Fe(H$_2$O)$_4$F$_2$ (or Fe(2X)$_6$) groups must now be considered. The two possible orientations of Fe(2X)$_6$ (because of the operation of the set of mirror planes) are related by a rotation of 33° 24′ about the c axis. They will be designated P and Q. The c axis rotation photographs indicate that the whole structure is based on a sequence $PQPQ\ldots$ parallel to c (giving a repeat of 9·64 Å)

but that as many columns of groups at a particular level commence with P as with Q. Consideration of possible inter-group hydrogen bonding indicates further that the preferred arrangement is that in which all the neighboring groups of one central P group have orientation Q, and vice versa. A portion of this arrangement is shown in Fig. 1(b). There are two strong hydrogen bonds per O or F atom of lengths 2·52 Å (between groups in adjacent columns which differ in height by $\frac{1}{3}c$) and 2·67 Å (between successive groups in the same column). This may be regarded as an idealized arrangement which persists over small regions, the actual structure being derived by random displacement parallel to c of adjacent small regions. Hydrogen bonds of types O–H $\cdots$ O and O–H $\cdots$ F are possible, and if all close inter-group contacts are hydrogen bonds, all hydrogen atoms will be used if both types of bonds occur in equal numbers. This assignment of hydrogen bonds was supported qualitatively by a difference electron-density projection down the a axis, but subsequent inclusion of hydrogen atoms in structure-factor calculations led to only a barely significant decrease in the values of R and r.
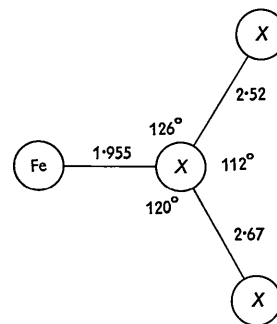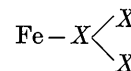

Fig. 2. Dimensions of the group FeX_3, where X may be F$^-$ or O. Both X–X linkages represent hydrogen bonds.

The tetrahedral charge environment for H$_2$O is well satisfied, as shown in Fig. 2, the Fe^{++} ion being assumed opposite the two negative regions of the water tetrahedron. The whole group

$$\mathrm{Fe} - X \Big\langle {{X}\atop{X}}$$

is very close to planar, the sum of the angles about the central atom being 358°.

The main feature of difference between the discrete groups in this structure and those of the corresponding hydrated chloride (Penfold & Grigor, 1959) is the equivalence of all water molecules in the fluoride, making individual groups much more closely octahedral. This is likely to be a consequence partly of the greater ionic character of the bonds in the fluoride, and also of the much greater similarity in size of fluoride ion (radius 1·35 Å) and oxygen atom (1·4 Å), as compared with chloride ion (1·8 Å) and oxygen atom.

5. The structure of form B

The diffraction symmetry of form B is $\bar{3}m$, indicating that, provided there is a center of symmetry as in A, the space group is $R\bar{3}m$. The intensity distribution of $hki0$ and $hki2$ reflections is similar but not identical to the distribution in $hki0$ and $hki1$ reflections of form A. It appears, therefore, that the major difference between the two forms concerns the nature of the P, Q sequence, discussed above for form A. The only quantitative intensity data at present available for form B are from Cu $K\alpha$ radiation for $hki0$ and $hki1$ reflections, and a detailed examination of this slightly less disordered form must await the accumulation of more data.

The final refinement of this structure was completed by one of us (B. R. P.) at the University of Minnesota during an appointment supported by the International Cooperation Administration under the Visiting Re-search Scientists Program administered by the National Academy of Sciences of the United States of America. We are greatly indebted to Prof. W. N. Lipscomb for research facilities made available and for his critical reading of the manuscript, and we acknowledge support in part by the Office of Naval Research.

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The perovskite-type structures of DyAlO$_3$, DyFeO$_3$, and some related lanthanon mixed oxides.

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1. Introduction

The perovskite-type structures of selected lanthanon mixed oxides ($LnBO_3$) have been investigated in an attempt to elucidate the factors that influence their distortion. Lanthanum, neodymium, gadolinium and dysprosium, which have a suitable range of ionic radii, were chosen for the tripositive Ln ions. Aluminium, iron and gallium, which have tripositive ions with an inert-gas, half-filled d-shell and eighteen-electron configuration, respectively, were chosen as B ions that would demonstrate the influence of partial covalent character of B–O linkages on the distortion. The definitive work of Geller and his colleagues (Geller, 1956; Geller & Wood, 1956; Geller & Bala, 1956; Gilleo, 1957; Geller, 1957) on crystals of many $LnBO_3$ perovskites has already been reported. In this note, therefore, brief reference only is made to the X-ray powder studies by which, as far as possible, these data were confirmed. The orthorhombic structures of DyAlO$_3$ and DyFeO$_3$, which have not been reported before, are described in more detail.

2. Experimental

Hundred-milligram quantities of the lanthanon mixed oxides were prepared from 'Specpure' grade materials