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Bond Distances and Thermal Motion in Ferrous Fluosilicate Hexahydrate: A Neutron Diffraction Study*

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The crystal structure of $FeSiF_6 . 6H_2O$ has been refined by single crystal neutron diffraction methods. The structure may be described as a slightly distorted cesium chloride structure composed of the two ions, SiF_6^{--} and $Fe(H_2O)_6^{++}$. A simple static disorder, involving rotation about the three-fold axis for both ions, must be postulated to explain the $R\bar{3}m$ symmetry found for the crystal. Each hydrogen atom participates in one O–H · · · F hydrogen bond at an O–F distance of 2·72 Å with an O–H · · · F angle of 168°; each fluorine atom is involved in two such bonds. The SiF_6^{--} octahedron is regular with a Si–F distance of 1·706 Å. The $Fe(H_2O)_6^{++}$ octahedron is stretched along the three-fold axis; the two distinct O · · · O distances across the octahedron differ by 0·07 Å. The water molecules are oriented such that the two-fold axis of each molecule is directed approximately toward the metal ion; the Fe–O distance is 2·146 Å. The thermal motions of the ions as determined by a general least-squares refinement can be described accurately in terms of rigid body translations and oscillations. The root mean square amplitude of translation is about 0·14 Å for both ions, and the root mean square amplitude of oscillation is 2·5° for the $Fe(H_2O)_6^{++}$ ion and 5·6° for the SiF_6^{--} ion. These motions are approximately isotropic.

Introduction

The transition metal fluosilicates crystallize as hexahydrates with a rhombohedrally distorted CsCl type of ionic packing (Wyckoff, 1960; Hassel, 1927; and Hassel & Salvesen, 1927). They are typical members of a large series of compounds $M^{+2}Y_6BX_6^{--}$ where M^{+2} is a metal ion, Y may be ammonia or water, X may be Cl or F, and B is a quadrivalent metal, typically Sn or Si. The only member of the series which has been the subject of an extensive crystallographic study is $Ni(H_2O)_6.SnCl_6$ (Pauling, 1930).† A structure was found with atoms in the following positions of $R\bar{3}$ (*International Tables for X-Ray Crystallography*, 1952):

Ni in (a): 0, 0, 0
Sn in (b): $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
6 H_2O in (f): $\pm(x, y, z;\ y, z, x;\ z, x, y)$
6 Cl in (f)

with the following parameter values:

H_2O: $x=0{\cdot}14,\ y=0{\cdot}31,\ z=0{\cdot}94$
Cl: $x=0{\cdot}64,\ y=0{\cdot}81,\ z=0{\cdot}44$.

In determining these parameters, the ions were assumed to be regular octahedra with dimensions fixed by the assumed ionic radii. Pauling (1930) also suggested that the other compounds of this type have similar parameter values.

The present investigation was undertaken to provide detailed information on the configuration of the water molecules in a typical member of the series as well as to obtain a more accurate description of the general structure than was possible thirty years ago.

Experimental

Ferrous fluosilicate hexahydrate was prepared by dissolving a slight excess of metallic iron powder in concentrated fluosilicic acid and evaporating slowly to dryness. Large, optically transparent single crystals were easily obtained on recrystallization from water by slow evaporation at room temperature.

The cell constants given by Hassel & Salvesen (1927) and the rhombohedral symmetry were confirmed by rotation and Weissenberg X-ray photographs taken about the (001) and (111) axes. The cell constants were further refined by use of a powder diffractometer and Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). The Laue symmetry appeared from the X-ray photographs to be $\bar{3}m$ rather than $\bar{3}$, and this was confirmed when the neutron data were collected.

A crystal $3{\cdot}5\times1{\cdot}6\times4{\cdot}7$ mm.^{3} was mounted with one of the rhombohedral axes (coincident with the long dimension of the crystal) vertical for the collection of neutron diffraction intensity data. The intensities of 90 ($hk0$)* reflections were measured to an estimated average accuracy of 5% on a single-crystal diffractometer at the Brookhaven reactor. These intensities were corrected for absorption ($\mu=2{\cdot}02$ cm.$^{-1}$)

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† A number of the AX_6BY_6 compounds with the NaCl structure have been studied. See Watanabe, Atoji & Okazaki (1950) and Atoji & Watanabe (1952).

* All parameters can be determined from this single projection.

and reduced to structure factors by a program (ESAF, available on request) written by the author for the IBM 704.

Crystal data

$FeSiF_6.6H_2O$: pale green rhombohedra, generally elongated along [111].

Rhombohedral cell constants:

$$a = 6{\cdot}418 \pm 0{\cdot}005\ \text{Å},\ \alpha = 97{\cdot}1 \pm 0{\cdot}1.$$

Hexagonal cell constants:

$$a = 9{\cdot}621 \pm 0{\cdot}008,\ c = 9{\cdot}648 \pm 0{\cdot}008\ \text{Å}.$$

One formula unit per unit cell. Space group $R\bar{3}m$.

Determination of the structure

It was immediately obvious from the neutron intensities $(I(hk0) = I(kh0))$ that the space group must be $R\bar{3}m$ rather than $R\bar{3}$. As the general position in $R\bar{3}m$ is twelve-fold, and as there are only six F and six O atoms per unit cell, these atoms must either lie in the mirror planes, or there must be some disorder. A Patterson function calculated from the $(hk0)$ neutron F^2 values as well as a three-dimensional Fourier synthesis calculated from a set of rather inaccurate X-ray data* left no doubt that the disorder hypothesis was correct. There were in both the Patterson and the Fourier twelve resolved peaks instead of the six that would be expected for the Fe–F vectors or F atoms, respectively. The peaks in the Patterson corresponding to Fe–O vectors were single, but elongated in a direction perpendicular to the mirror plane; the oxygen peaks in the Fourier, although not completely resolved, did have double maxima.

It was therefore decided to refine the structure as a superposition of two structures, each having $R\bar{3}$ symmetry and related to each other by the mirror plane, i.e., a half-atom corresponding to each of F, O, H_1, and H_2 was placed in a set of general pointions in $R\bar{3}m$:

$$\pm (x, y, z;\ y, z, x;\ z, x, y;\ y, x, z;\ x, z, y;\ z, y, x)\ .$$

Starting with trial parameters from the neutron Patterson projection and X-ray Fourier, a series of anisotropic least-squares refinements (using the complete least-squares matrix, of course) led to the parameter values in Table 1. Good agreement could also be obtained by assuming the O atoms to be fixed in the mirror planes, but this assumption led to unrealistic values for the thermal vibration parameters for this atom alone.

Although there is of course an ambiguity in the assignment of the half-peaks to the individual molecules, the parameters given in Table 1 may fortunately be taken as the parameters of *one* of the structures in $R\bar{3}$. The other possible choices lead to either unreasonable configurations for the water molecule or unreasonable hydrogen bond distances (or both). Thus the disorder does not complicate the calculation

Table 1. *Positional and thermal parameters in* $FeSiF_6.6H_2O$

The thermal parameters are defined such that the Debye–Waller factor is expressed as

$$\exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)\right].$$

The errors are expressed as estimated standard deviations

Fe: $x = y = z = 0$
$b_{ii} = 0{\cdot}0102 \pm 0{\cdot}0007 \quad i = 1, 2, 3$
$b_{ij} = 0{\cdot}0013 \pm 0{\cdot}0008 \quad i \neq j$

Si: $x = y = z = \frac{1}{2}$
$b_{ii} = 0{\cdot}0080 \pm 0{\cdot}0013 \quad i = 1, 2, 3$
$b_{ij} = 0{\cdot}0019 \pm 0{\cdot}0019 \quad i \neq j$

F	x	0·2595 ± 0·0012	H_1	x	0·2909 ± 0·0118
	y	0·3899 ± 0·0015		y	0·3432 ± 0·0126
	z	0·5460 ± 0·0012		z	0·0245 ± 0·0026
	b_{11}	0·0115 ± 0·0016		b_{11}	0·0435 ± 0·0197
	b_{22}	0·0183 ± 0·0024		b_{22}	0·0407 ± 0·0179
	b_{33}	0·0189 ± 0·0018		b_{33}	0·0279 ± 0·0041
	b_{12}	0·0007 ± 0·0021		b_{12}	−0·0101 ± 0·0180
	b_{13}	0·0058 ± 0·0019		b_{13}	0·0066 ± 0·0077
	b_{23}	0·0022 ± 0·0024		b_{23}	0·0069 ± 0·0078
O	x	0·2055 ± 0·0018	H_2	x	0·2311 ± 0·0033
	y	0·2614 ± 0·0021		y	0·2875 ± 0·0031
	z	−0·0736 ± 0·0013		z	−0·2060 ± 0·0027
	b_{11}	0·0135 ± 0·0024		b_{11}	0·0153 ± 0·0050
	b_{22}	0·0136 ± 0·0022		b_{22}	0·0141 ± 0·0039
	b_{33}	0·0154 ± 0·0012		b_{33}	0·0235 ± 0·0034
	b_{12}	0·0004 ± 0·0029		b_{12}	0·0017 ± 0·0040
	b_{13}	0·0035 ± 0·0017		b_{13}	0·0044 ± 0·0046
	b_{23}	0·0032 ± 0·0019		b_{23}	0·0055 ± 0·0037

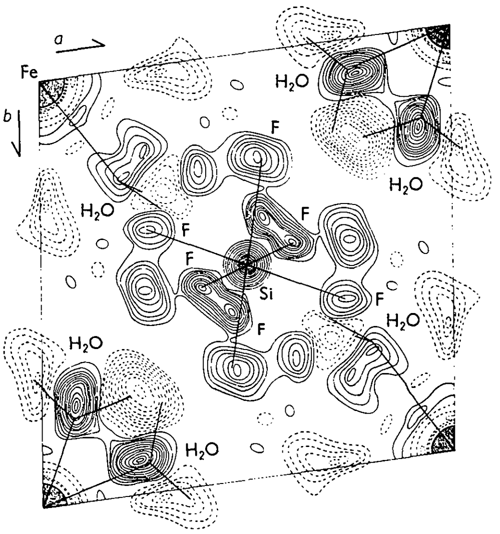

Fig. 1. Fourier projection of the structure on (001). Only the zero contour is omitted. Two formula units superimposed by the disorder discussed in the text are seen. The solid lines indicate the bonds for one of the two configurations only. The bad overlap of the hydrogen atoms makes it clear that large estimated errors in the thermal parameters for these atoms is to be expected.

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* Almost all signs are positive.

Table 2. *Observed and calculated* (*hk*0) *structure factors*

The calculated values are derived from the parameters in Table 1 and the following neutron scattering lengths: Fe, 0·96; Si, 0·40; F, 0·55; O, 0·58; and H, $-0{\cdot}378 \times 10^{-12}$ cm. They have also been multiplied by a scale factor of $70{\cdot}9 \times 10^{12}$

h	k	$\|F_o\|$	F_c	h	k	$\|F_o\|$	F_c	h	k	$\|F_o\|$	F_c
0	1	29	−27	3	5	70	71	2	−6	52	51
0	2	138	143	3	6	88	88	2	−7	76	76
0	3	74	−70	3	7	37	35	2	−8	120	110
0	4	90	88	3	8	8	5	2	−9	36	34
0	5	19	39	3	9	53	49	2	−10	45	49
0	6	87	−88	4	4	29	21	3	−3	141	140
0	7	13	−7	4	5	89	89	3	−4	158	158
0	8	68	70	4	6	25	27	3	−5	73	69
0	9	11	−22	4	7	8	−20	3	−6	24	−28
0	10	10	9	4	8	20	28	3	−7	114	120
1	1	195	193	5	5	81	83	3	−8	12	−13
1	2	35	39	5	6	45	−34	3	−9	49	51
1	3	211	218	5	7	18	28	3	−10	38	15
1	4	148	157	5	8	48	32	4	−4	11	−8
1	5	151	151	6	6	77	77	4	−5	7	−11
1	6	8	7	6	7	61	68	4	−6	49	40
1	7	81	79	1	−1	210	223	4	−7	22	−13
1	8	20	−23	1	−2	41	42	4	−8	41	39
1	9	56	51	1	−3	130	−116	4	−9	11	−16
1	10	26	14	1	−4	51	−51	5	−5	11	−22
2	2	15	−3	1	−5	34	35	5	−6	42	43
2	3	13	1	1	−6	101	99	5	−7	77	77
2	4	174	177	1	−7	18	−20	5	−8	8	18
2	5	58	49	1	−8	8	14	5	−9	24	24
2	6	98	97	1	−9	65	66	6	−6	81	81
2	7	46	41	1	−10	37	40	6	−7	11	−23
2	8	83	82	2	−2	136	−132	6	−8	73	74
2	9	9	4	2	−3	95	99	6	−9	48	47
3	3	106	−111	2	−4	190	193	7	−7	110	111
3	4	90	−88	2	−5	109	101	7	−8	10	−14

of bond distances and thermal motion parameters. It does of course limit the accuracy with which the structure parameters, particularly the hydrogen atom thermal parameters, can be determined.

The observed and the calculated structure factors are presented in Table 2. The agreement ratio $R = (\Sigma w|F_o - F_c|^2/\Sigma w F_o^2)^{\frac{1}{2}}$ has the value 0·057. This is about three times the value which would have been expected from weights derived from the counting statistics, and it is hoped that any additional errors also are random.*

An (*hk*0) Fourier projection for the observed neutron data is shown in Fig. 1. The contours are drawn, as the data demands, for the superposition of the two configurations. The heavy straight lines connect the atoms of one configuration only. The other configuration is related to the first by reflection in the mirror planes (110) and $(1\bar{1}0)$. Note that there is considerable overlap between the hydrogen, oxygen, and fluorine atoms lying nearest the line $x = y$.

Nature of the disorder

Although the Fourier projection in Fig. 1 gives some picture of the nature of the disorder, a clearer picture can be obtained by looking at the structure down the three-fold axis. Fig. 2 presents such a view; the $Fe(H_2O)_6^{++}$ octahedron in the center is surrounded by eight SiF_6^{--} octahedra approximately at the corners of a cube. (The one directly above and the one directly below are not shown.) The $Fe(H_2O)_6^{++}$ octahedron is shown in an average position, with the two heavy dots indicating the two actual positions related by the mirror plane for one of the apex oxygen atoms. Only one set of the SiF_6^{--} octahedra is shown. The alternate positions are obtained by reflection in the

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* The referee has remarked that the conventional R factor is 4·6% for the reflections with $h+k=2n$ and 13% for those with $h+k=2n+1$; this apparent discrepancy suggests that the description of the disorder might be inadequate. That the discrepancy is only apparent may be seen at once by an examination of the weighted sum of the squared residuals. The value of this sum is 369·41 for the 43 reflections with $h+k$ even and 411·15 for the 47 reflections with $h+k$ odd. The average weighted squared residuals are thus 8·59 and 8·74; the difference is insignificant. The agreement for the two groups of reflections *is* essentially the same despite the large difference in the conventional R factors. This difference is to be expected from the fact that the relative errors in the small reflections are larger; the mean value of the structure factors for the reflections with $h+k$ odd is 44, that for $h+k$ even, 81.

The referee also pointed out that twenty of the ninety reflections have residuals greater than or equal to $\frac{1}{2}F_o$. Here again, examination of the weighted sum of squares is of interest. The sum is 205·51; the average value of 10·27 is not unusual, considering that the reflections with large residuals have been deliberately selected. A histogram of the weighted residuals indicates nothing unusual in the distribution of errors.

mirror planes or, equivalently, by rotating approximately 54°. Note that the $Fe(H_2O)_6^{++}$ octahedron must be rotated by only 18° to reach the mirrored configuration.

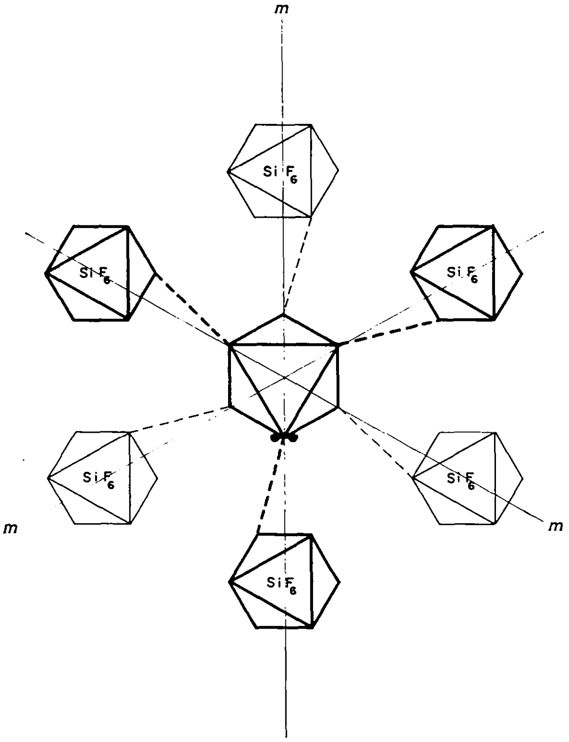

Fig. 2. View of idealized ions, looking down the three-fold inversion axis. In the center is the $Fe(H_2O)_6$ octahedron, drawn in an average position. It should be rotated clockwise by 9° to have the configuration relative to the fluosilicate ions used for the calculation of interionic bond angles and distances in the text. In addition to the six fluosilicate octahedra shown, two more, above and below the central group, complete the coordination number of eight. These ions are shown in only one of the disordered positions; the other is obtained by reflection in the mirror planes.

Additional support for the disorder on a microscopic basis was given by the observation that a satisfactory fit to the data could not be obtained on the assumption that the individual crystallites were well-ordered in one of the two configurations but that there was disorder on a macroscopic scale. That is, there appeared to be no question but that it was necessary to average the F's rather than the intensities for the two configurations to obtain a satisfactory fit to the data. An additional hypothesis that could explain the apparent disorder is that the size of the unit cell might be doubled in the directions of the hexagonal **a** and **b** axes. This is perhaps suggested by the observation of Hassel & Salvesen (1927) that X-ray photographs of manganese fluosilicate exhibit additional reflections which could be accounted for only on the basis of a doubled unit cell. Such reflections were not observed by these authors in the other fluosilicates, even for quite long exposures. An attempt was made to observe extra neutron reflections at positions which would be predicted by such a hypothesis, but none was observed. Thus the disorder would appear to be completely random rather than giving rise to a superstructure of the hypothesized kind.

There have been reports that some of the fluosilicates exhibit specific heat anomalies at temperatures well above that of boiling nitrogen. It was suggested to the author by Dr E. Kanda that these anomalies might be associated with an ordering transition which removes the disorder found in this investigation. Accordingly, several reflections which are equivalent in $R\bar{3}m$ but which would not be equivalent in $R\bar{3}$ were measured at about 90 °K. Reflections were chosen which should have very large differences of intensity if ordering does take place and if the positional parameters remain the same. No changes in intensity other than a general enhancement due to the lower temperature were observed, and it may be concluded that any transition that does occur in ferrous fluosilicate apparently does not affect the nature of the disorder described here. It may be noted that magnetic ordering in these materials occurs only at temperatures well below 1 °K. (Kanda, 1960).

The disorder is remarkably similar to the rotational disorder found in $FeF_2(H_2O)_6$ by Penfold & Taylor (1960). In the latter structure there is of course only one type of ion, and there is additional disorder due to apparent equivalence of F and H_2O.

Interatomic distances and bond angles

The interatomic distances and bond angles calculated from the final parameters are presented in Tables 3 and 4. The errors quoted are the standard deviations obtained from the least-squares variance-covariance matrix by the usual formulas for the propagation of error and thus include the effects of all correlations between parameters. (See Busing & Levy, 1959). Also presented are the bond distances only corrected for thermal motion by the method suggested by Busing & Levy (1959, 1960). For this purpose, it was assumed that the lighter atoms are 'riding' on the heavier, so that the apparent thermal motion of the light atom is a convolution of the thermal motion of the heavy atom and the distribution function for the bond length. It will be noted that these corrections are quite small except for one of the O–H distances. The assumption of riding would seem to be reasonable for the Fe–O, Si–F and O–H bonds in the present case. In the absence of any certain knowledge regarding the proper correction in the case of the non-bonded distances, it was felt that it would be better to make no correction at all.*

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* Calculations of the maximum correction, that based on assumed independent motion, were small for all distances not involving H.

Table 3. *Interatomic distances*

(A) Bonded distances (Å)

	Uncorrected	Lighter atom 'riding' on heavier
Fe–O	2·140 ± 0·013	2·146 ± 0·012
Si–F	1·692 ± 0·008	1·706 ± 0·009
$O–H_1$	0·857 ± 0·023	0·924 ± 0·050
$O–H_2$	0·916 ± 0·020	0·920 ± 0·025

(B) Distances involved in hydrogen bonds (Å)

$O–F_{111}$	2·681 ± 0·013	$H_1–F_{111}$	1·857 ± 0·038
$O–F_{\perp}$	2·720 ± 0·013	$H_2–F_{\perp}$	1·817 ± 0·018

(C) Other distances (Å)

$O_1–O_1$	related by $\underline{3}$	2·991 ± 0·019	$\Delta r = 0·072 \pm 0·018$
$O_1–O_2$	related by $\bar{3}$	3·063 ± 0·021	
$F_1–F_1$	related by $\underline{3}$	2·390 ± 0·015	$\Delta r = 0·007 \pm 0·017$
$F_1–F_2$	related by $\bar{3}$	2·396 ± 0·014	
$Fe–H_1$		2·681 ± 0·026	$\Delta r = 0·105 \pm 0·034$
$Fe–H_2$		2·787 ± 0·016	
$H_1–H_2$	no correction	1·469 ± 0·025	
	corrected for independent motion	1·548 ± 0·036	

Table 4. *Bond angles in degrees*

All uncorrected for thermal motion

Angle	Value	
$H_1–O–H_2$	111·9 ± 1·6	
$O_1–Fe–O_1$	88·6 ± 0·3	
$O_1–Fe–O_2$	91·4 ± 0·3	
Difference	2·8 ± 0·7	Probably significant
$F_1–Si–F_1$	89·8 ± 0·4	
$F_1–Si–F_2$	90·2 ± 0·4	
Difference	0·4 ± 0·8	Not significant
$Fe–O–H_1$	120·7 ± 1·9	
$Fe–O–H_2$	126·7 ± 1·1	
Difference	6·0 ± 2·5	Possibly significant
$O–H_1 \cdots F$	160·7 ± 9·4	Bond approximately parallel to $\bar{3}$ axis
$O–H_2 \cdots F$	168·1 ± 1·5	Bond approximately perpendicular to $\bar{3}$ axis
Mean value	167·9 ± 1·5	Difference not significant

Sum of bond angles around oxygen
359·2 ± 1·2

Dihedral angle between the planes defined by $Fe–O–H_1$ and $Fe–O–H_2$
10·9 ± 8·2

Thus the $Fe(H_2O)$ group is planar

The SiF_6^{--} octahedron is quite regular with a Si–F distance of 1·706 ± 0·009 Å if the small correction for thermal motion is made. This is in excellent agreement with older values for the bond length. This distance was first determined in ammonium fluosilicate by Bozorth (1922) to be 1·72 Å. A redetermination of the cell constant by Ketelaar (1935), who also determined the structures of the K, Rb, Cs, and Tl salts, led to a value of 1·706 in the ammonium salt and an average value of 1·71 ± 0·03 for the entire isomorphous series. A value of 1·71 in the double salt $(NH_4)_2SiF_6.NH_4F$ has been reported (Hoard & Williams, 1942).

There is less consistent information on $Fe–(H_2O)$ distances. Wyckoff (1960) lists many hydrates of the transition metals with $M–H_2O$ distances largely in the range 1·9–2·2 Å. Some of the more recent values for $Fe–H_2O$ distances are presented in Table 5. Although the metal ion in most of the compounds listed in Table 5 is octahedrally coordinated, the present determination of 2·15 Å for the Fe–O distance is the only one in which the coordination is to six water molecules in a relatively undistorted octahedron. The agreement with the sum of the Pauling (1940) radii for Fe^{++} and O^{--}: 2·15 Å is perhaps not remarkable, despite the fact that we are dealing here with a water molecule rather than an oxygen ion.

Table 5. *Recent determinations of* Fe–O *distances in hydrates of iron salts*

Compound	Distances (Å)	Reference
Ludlamite, $Fe_3(PO_4)_2.4H_2O$	2·17	Ito & Mori, 1951
Symplesite, $Fe_3(AsO_4)_2.8H_2O$	2·00–2·02	Mori & Ito, 1950
Scorodite, $FeAsO_4.2H_2O$	2·13, 2·26	Hiriyama & Sakurai, 1949
$K_2FeCl_5.H_2O$	2·05	Bellanca, 1947, 1948
$(NH_4)_2FeCl_5.H_2O$	2·08	Lindquist, 1947
$Fe_3Br_8.16H_2O$	2·01, 2·18	Zvonkova, 1954
$FeCl_2.4H_2O$	2·09, 2·59	Penfold & Grigor, 1959
$FeF_2.4H_2O$	1·94–1·97	Penfold & Taylor, 1960
$Fe(H_2O)_6SiF_6$	2·146	Present investigation

The difference between the distinct intraionic O–O distances is four times the corresponding standard deviation and indicates a significant, although small, stretching of the ion along the three-fold axis. This is in disagreement with an interpretation of the optical spectra at liquid nitrogen temperature (Jackson, 1959) which indicates that the octahedron is squashed. Although the results are not strictly comparable because of the differing temperatures at which the two experiments were done, the interpretation of the neutron diffraction experiment would appear to be more straightforward.

The water molecules are hydrogen bonded to fluorine, each hydrogen atom participating in an $O–H \cdots F$ hydrogen bond (see Fig. 3). The $O \cdots F$ distances are 2·68 and 2·72 Å. The difference between the two is barely significant. Correction for thermal motion of the hydrogen atoms would increase these lengths by a maximum of 0·02 Å. The average $O–H \cdots F$ angle is 168 ± 1·5°, a departure from linearity of 12°, which seems to be not unusual in H-bonded crystals. There is no evidence that the O–H distances are lengthened from the normal 0·96 Å in the water molecule, but distances of 1·0 Å, in view

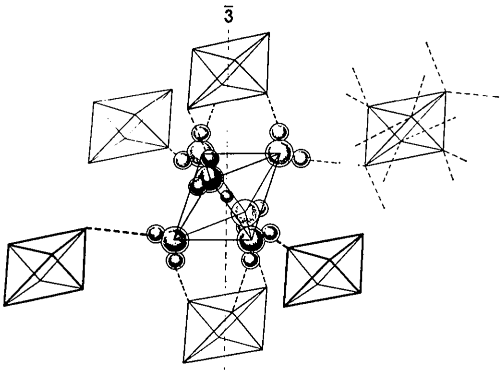

Fig. 3. Perspective view of the structure, illustrating the hydrogen bonding system. Two of the SiF_6^{--} octahedra are omitted for clarity. The position of these is obvious from the three-fold symmetry. Each $Fe(H_2O)_6^{++}$ octahedron has three hydrogen bonds to the SiF_6^{--} ions immediately above and below and one hydrogen bond to each of the other six SiF_6^{--} ions. Each F atom is involved in two hydrogen bonds, as can be seen from the single SiF_6^{--} octahedron which has all H-bonds sketched in. The six H-bonds approximately parallel to $\bar{3}$ are crystallographically equivalent, as are the other six.

of the lack of knowledge of the proper motional corrections, should be considered compatible with the data. Unfortunately, the accuracy of the data, particularly because of the overlap of the hydrogen atoms caused by the disorder, is not sufficient to obtain either the hydrogen position parameters or the thermal parameters with sufficient accuracy to get really good O–H distances.*

The inter-hydrogen distance of 1·481 together with the short O–H bond distances leads to a satisfactory bond angle of 112°. Correction for thermal motion can increase the H–H distance to as much as 1·548 ± 0·036 in satisfactory agreement with the range of 1·56 to 1·61 Å found by McGrath & Silvidi (1961) in other solid hydrated compounds. Correction of the angle for thermal motion results in values ranging from 103·5 to 114·2°, again emphasizing the importance of precise knowledge of the thermal motion in determining structural parameters for molecules involving hydrogen.

The quantitative features of hydrogen bonding are in good agreement with those found by Abrahams (1960) in $CuF_2.2H_2O$. In the latter compound the length of the O–H · · · F hydrogen bond is 2·645 ± 0·006 Å, the O–H · · · F angle is 165 ± 1° and the bond length of O–H is 0·98 ± 0·007. The H–H distance is appreciably greater: 1·654 ± 0·009. The O–H · · · F distances in $Fe(H_2O)_4F_2$ were found to be 2·52 and 2·67 by Penfold & Taylor (1960), in good agreement both with the present results and those of Abrahams (1960).

Description of the thermal motion

The lengths and directions of the principal axes of the ellipsoid of thermal motion were derived for each atom; the root-mean-square components of thermal motion along these axes are presented in Table 6. The errors in these numbers as well as in all others quoted in this section were calculated by the usual formula for the propagation of error, including all off-diagonal terms in the error matrix. The directions of the principal axes for the Si and Fe atoms are fixed by symmetry, principal axis 3 lying along the three-fold axis, while the other two of equal length lie in the plane perpendicular to this axis. There is no significant anisotropy for these two atoms.

Table 6. *Root-mean-square thermal displacements in Å in directions of principal axes*

The directions of the principal axes are discussed in the text

Atom	Axis 1	Axis 2	Axis 3
Silicon	0·12 ± 0·02	0·12 ± 0·02	0·14 ± 0·02
Iron	0·14 ± 0·01	0·14 ± 0·01	0·14 ± 0·01
Fluorine	0·14 ± 0·02	0·19 ± 0·02	0·20 ± 0·01
Oxygen	0·15 ± 0·02	0·18 ± 0·03	0·18 ± 0·01
Hydrogen 1	0·35 ± 0·12	0·25 ± 0·02	0·22 ± 0·04
Hydrogen 2	0·22 ± 0·02	0·18 ± 0·04	0·16 ± 0·03

The short principal axis of the fluorine vibrational ellipsoid makes an angle of 15 ± 12° with the Si–F bond, and the short axis of the oxygen ellipsoid makes an angle of 12 ± 15° with the Fe–O bond. Thus, these short axes may be considered to lie along the bonds. In each case, the components approximately perpendicular to the bond are nearly equal, and the directions of these axes are hence rather indeterminate. The directions of all the axes for the hydrogen atoms are poorly defined, the standard errors in the directions being on the order of 30°. As will be shown, however, the axes found for the hydrogen atoms are consistent with the description of the ionic motion that follows.

A more interesting description of the thermal motion may be had in terms of rigid body motions. (See, for example, Cruickshank, 1956.) Each ion can be treated as if it were a rigid body undergoing oscillations about axes through the center of mass and translations. If these motions are to satisfy the symmetry of the crystal in this case, the description is greatly simplified, there being for each XY_6 ion four independent thermal parameters, namely,

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* In order to be sure that the refinement had not converged to a false minimum, five cycles of refinement were run, starting with all the parameters as found above but setting the hydrogen atoms at positions corresponding to bond lengths of 0·98 and a normal H–O–H angle. This refinement converged again to the identical values found in the initial refinement. This was tried both by refining the H atoms only and by refining all parameters together.

$T_{11}^{1/2}$, root-mean-square translation perpendicular to $\bar{3}$,
$T_{33}^{1/2}$, root-mean-square translation along $\bar{3}$,
$\omega_{11}^{1/2}$, root-mean-square oscillation around axes perpendicular to $\bar{3}$,
$\omega_{33}^{1/2}$, root-mean-square oscillation around the $\bar{3}$ axis.

These quantities were evaluated for the two ions by a least-squares method, as suggested by Cruickshank (1956). A non-diagonal weight matrix was used in a least-squares program for the IBM 704 computer written by the author. The estimated errors thus include the effects of all off-diagonal terms in the original least-squares refinement. There were for each of the ions ($Fe(H_2O)_6^{++}$ and SiF_6^{--}) eight thermal parameters to be explained in terms of the four quantities above. (The hydrogen atoms were omitted from this stage of the analysis.) The results are presented in Table 7.

Table 7. *Rigid body motions derived from the anisotropic thermal parameters*

	SiF_6^{--}	$Fe(H_2O)_6^{++}$
$T_{11}^{1/2}$	0·12 ± 0·01 Å	0·14 ± 0·01 Å
$T_{33}^{1/2}$	0·14 ± 0·02 Å	0·15 ± 0·01 Å
$\omega_{11}^{1/2}$	4·6 ± 0·6°	2·8 ± 0·3°
$\omega_{33}^{1/2}$	6·5 ± 1·0°	2·3 ± 1·9°

The weighted sum of squares of residuals to this least-squares fit was about 0·25 as opposed to an expected value of 1·00. The fit to this model must be considered extremely satisfactory. The estimated standard deviations in Table 7 are based on the input weights and are thus twice the estimates which would be obtained from the goodness of fit.

The hydrogen atoms were omitted from the estimation of the rigid body motions because they are much more likely to exhibit the effects of intra-group vibrations. In order to assess the importance or significance of these intra-group vibrations, a comparison was made between the observed hydrogen vibration tensors and those to be expected from the rigid body motions calculated above. The results of this comparison are presented in Table 8. The differences between the observed values and the calculated values, although occasionally of the size to be expected for vibrations of a water molecule, are in only one or two instances possibly significant. We may thus conclude, if the heavy atom motions are described largely by rigid-body motions, that the original data are not accurate enough to provide any information whatsoever about the intra-molecular vibrations. The hydrogen atom thermal parameters would have to be determined to at least one more order of magnitude of accuracy for one to be able to derive vibrational frequencies, for example, with any certainty. *A fortiori*, the corrections to the bond distances due to thermal motion are but poorly known, and the O–H bond distances quoted above are to be taken as lower limits.

Table 8. *Hydrogen atom thermal vibration tensors relative to orthohexagonal axes of unit length defined by*

$$\mathbf{a}_0 = \begin{pmatrix} 0{\cdot}1039 & -0{\cdot}1039 & 0{\cdot}0000 \\ 0{\cdot}0600 & 0{\cdot}0600 & -0{\cdot}1200 \\ 0{\cdot}1037 & 0{\cdot}1037 & 0{\cdot}1037 \end{pmatrix} \mathbf{a}_R \,.$$

The units are Å²

U_o is derived from the data in Table 1 by the appropriate transformation. U_c is derived from the rigid body motions fit to the Fe and O atoms only. The estimated errors include all pertinent correlations from both the least-squares treatment used in the original refinement and the least-squares treatment used to determine the T and ω tensors. It may be concluded from this table that little can be said about the intra-ionic motions of the hydrogen atoms

H_1 at $(x, y, z) = (-0{\cdot}2517, 1{\cdot}6242, 2{\cdot}1167)$

i, j	U_o^{ij}	U_c^{ij}	$U_o^{ij} - U_c^{ij}$	σ of difference
11	0·122	0·036	0·087	0·081
22	0·048	0·032	0·016	0·017
33	0·062	0·028	0·035	0·015
12	0·002	0·001	0·002	0·018
13	0·002	0·001	0·001	0·016
23	−0·002	−0·008	0·006	0·008

H_2 at $(x, y, z) = (-0{\cdot}2714, 2{\cdot}5833, 1{\cdot}0047)$

i, j	U_o^{ij}	U_c^{ij}	$U_o^{ij} - U_c^{ij}$	σ of difference
11	0·031	0·034	−0·003	0·018
22	0·034	0·023	0·011	0·009
33	0·040	0·037	0·003	0·012
12	0·002	0·001	0·001	0·005
13	0·000	0·001	−0·001	0·006
23	−0·011	−0·006	−0·005	0·006

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References

ABRAHAMS, S. C. (1960). *Acta Cryst.* **13**, 1110 and private communication.

ATOJI, M. & WATANABE, T. (1952). *J. Chem. Phys.* **20**, 1045.

BELLANCA, A. (1947). *Ric. Sci. Ricostruz.* **17**, 1360.

BELLANCA, A. (1948). *Period. Miner.* **17**, 59.

BOZORTH, R. M. (1922). *J. Amer. Chem. Soc.* **44**, 1066.

BUSING, W. R. & LEVY, H. A. (1959). Oak Ridge National Laboratory Report 59-12-3.

BUSING, W. R. & LEVY, H. A. (1960). Abstracts of Washington, D. C. meeting of ACA, p. 9.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.

HASSEL, O. (1927). *Z. Phys. Chem.* **126**, 118.

HASSEL, O. & SALVESEN, J. R. (1927). *Z. Phys. Chem.* **128**, 345.

HIRIYAMA, R. & SAKURAI, K. (1949). *X-rays*, **5**, 85.

HOARD, J. L. & WILLIAMS, M. B. (1942). *J. Amer. Chem. Soc.* **64**, 633.

International Tables for X-ray Crystallography (1952). Vol. 1. Birmingham: Kynoch Press.

ITO, T. & MORI, H. (1951). *Acta Cryst.* **4**, 212.
JACKSON, L. C. (1959). *Phil. Mag.* **4**, 269.
KANDA, E. (1960). Paper presented at Conference on Magnetism and Magnetic Materials, New York, November 1960.
KETELAAR, J. A. A. (1935). *Z. Kristallogr.* **92**, 155.
LINDQUIST, I. (1947). *Ark. Kemi, Min. Geol.* A, **24**, 1, 1.
MCGRATH, J. W. & SILVIDI, A. A. (1961). *J. Chem. Phys.* **34**, 322.
MORI, H. & ITO, T. (1950). *Acta Cryst.* **3**, 1.
PAULING, L. (1930). *Z. Kristallogr.* **72**, 482.
PAULING, L. (1940). *Nature of the Chemical Bond*, p. 350, 2nd Ed. Ithaca: Cornell University Press.
PENFOLD, B. R. & GRIGOR, J. A. (1959). *Acta Cryst.* **12**, 850.
PENFOLD, B. R. & TAYLOR, M. R. (1960). *Acta Cryst.* **13**, 953.
WATANABE, T., ATOJI, M. & OKAZAKI, C. (1950). *Acta Cryst.* **3**, 405.
WYCKOFF, R. W. G. (1960). *Crystal Structures*. Chapter X. New York: Interscience.
ZVONKOVA, Z. V. (1954). *Zhur. Fiz. Khim.* **28**, 453.

Acta Cryst. (1962). **15**, 360

The Crystal Structure of β-Iodine Monochloride

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β-ICl is monoclinic, $P2_1/c$, with $a = 8{\cdot}883$, $b = 8{\cdot}400$, $c = 7{\cdot}568$ Å, $\beta = 91{\cdot}35°$ and 8 molecules per cell. In β-ICl, as in α-ICl reported by Boswijk *et al.* (1956), the molecules are arranged in zig-zag chains; the bond lengths are I–Cl = 2·35 and 2·44 Å in the two independent molecules. Within chains the I · · · I distance is 3·06 and the I · · · Cl distance is 2·94 Å; between chains the distances are much longer. These short distances indicate interactions between molecules in one chain strong enough to be called weak bonds.

Introduction

In order to gain further understanding of the intermolecular forces which operate in halogen crystals, the structure of β-iodine monochloride has been determined for comparison with that of α-iodine monochloride (Boswijk, van der Heide, Vos & Wiebenga, 1956). The α forms melts at 27, the β form at 14 °C. It was hoped that a study of the two structures would help to reveal the factors most significant for determining the packing of the molecules in these crystals.

Experimental

The experimental part of this investigation is described more fully by Richards (1959).

Iodine monochloride, prepared by union of the elements at dry ice temperature and subsequent fractional crystallization, was sealed into Pyrex capillaries. Crystals were grown and preserved in these capillaries by cooling with a stream of cold nitrogen. Either the α or the β form could be grown by variation of the procedure. In both cases crystallization was initiated by touching the capillary lightly with a piece of dry ice. If the cooling gas was flowing while this was done, the α form resulted; if the cooling stream was started immediately after crystallization began, the β form was usually obtained. Subsequent partial melting and slow refreezing produced satisfactory crystals. (If a small portion re-froze, separated from the main body of material in the capillary, it usually produced a long needle of the α form; when this touched some of the β form, it was quickly converted to the more stable α form.) The two forms were readily distinguished under the microscope by slight differences in color and texture.

A series of multiple-film rotation and Weissenberg photographs was prepared about [001] and [011], the only orientations which were obtained along the capillary axis. The temperature was held at −15 to −20 °C. during these exposures. Zr-filtered Mo $K\alpha$ radiation was used. Intensities were estimated visually from multiple films by comparison with a set of standard intensities, and relative structure factor magnitudes were extracted in the usual way. A correction was made for differences in absorption among the three crystals used for intensities, based on cylindrical-sample absorption. Results from various photographs were then correlated by the method of Dickerson (1959). Eventually, when refinement of the structure was nearly complete, a rough correction for extinction and remaining absorption errors was applied to 25 intense reflections at small angles, by

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