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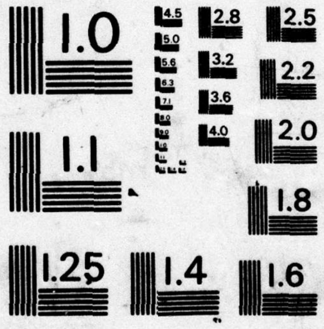
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THE STRUCTURE OF A MIXED-VALENCE IRON FLUORIDE, $Fe_2F_5 \cdot 2H_2O$

by

W. Hall, S. Kim, J. Zubieta, E. G. Walton and D. B. Brown

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The mixed valence iron compound, $Fe_2F_5 \cdot 2H_2O$, crystallizes in the orthorhombic system, space group Imma. The unit cell has dimensions a = 7.489(7)A, B = 10.897(8), and c = 6.671(6)A and contains four formula weights. The calculated and experimental densities are 2.96 g/cc and 2.94 g/cc, respectively, at 20 ± 1°. Measurements of diffracted intensities employed ~~θ-2θ scans~~ theta-2theta scans with filtered MoK +α radiation on a Picker diffractometer. A total of 250 reflections in the range 2 ≤ 2θ < 50° were retained as observed.

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20. Abstract (continued)

The structure was determined using the heavy-atom method and least-squares refinement. The final conventional discrepancy factor was 0.053. The non-molecular solid possesses a three dimensional network structure with distinct Fe(II) and Fe(III) coordination sites. The average Fe(II)-F and Fe(III)-F bond lengths are 2.060(6)Å and 1.941(6)Å, respectively. The aquo groups are coordinated to the iron (II) with Fe-O bond length of 2.13(1)Å .

Introduction

Fluoride complexes of the transition metals have been studied extensively in recent years, particularly by solid state scientists interested in cooperative phenomena. The interest in metal fluorides has several causes.[2] With most transition metals a variety of stoichiometries are possible, leading to a versatility of structures and physical properties. Metal fluorides are generally well behaved, with structures dependent largely on stereochemical factors. Furthermore, as a result of the high electronegativity of the fluoride ion, metal complexes are generally insulators or large band-gap semiconductors. The lack of electron delocalization leads to a certain simplicity in the interpretation of physical properties such as magnetism, and in consequence metal fluorides have often been studied as model systems.

In 1958, Brauer and Eichner[3] reported the preparation of the mixed-valence iron fluoride $Fe_2F_5 \cdot 7H_2O$. They further showed that this yellow heptahydrate could be dehydrated sequentially to a red trihydrate and a blue-gray anhydrous material. Because these materials appear (based on color) to span a range of mixed-valence classifications[4], they have generated significant interest in recent years. On the basis of various physical measurements, the heptahydrate has been formulated[5,6] as a Class I mixed-valence complex[4] having the ionic structure

$$[Fe(H_2O)_6{}^{+2}][FeF_5(H_2O)^{-2}].$$

The red material, initially formulated[3] as a trihydrate, has subsequently been shown[7,8] by thermoanalytical techniques to be a dihydrate, $Fe_2F_5 \cdot 2H_2O$. This complex has been investigated by Mossbauer spectroscopy[9,10], and we have shown[11], using Mossbauer and magnetic measurements, that the material orders ferrimagnetically at 48.5°K. In spite of the interest in this material, no detailed

structural information has been presented. This is undoubtedly a result of the typical method of preparation of this material, which involves the thermal dehydration of the heptahydrate and leads to non-crystalline products. We have succeeded in preparing single crystals of $Fe_2F_5 \cdot 2H_2O$ directly, and report here the structure as determined by X-ray diffraction[12]. A subsequent paper[11] will present the results of our studies of the magnetism and Mossbauer spectra of this material.

Experimental Section

Pentafluorodiiron (II,III) dihydrate, $Fe_2F_5 \cdot 2H_2O$, was prepared by a modification of Brauer and Eichner's preparation of the heptahydrate[3]. A large excess of metallic iron was heated to boiling in concentrated hydrofluoric acid. After decanting, the supernatant was heated at reflux temperatures until perhaps one half of the solution had boiled away. Small crystals of $F_2F_5 \cdot 2H_2O$ precipitated and continued to form so long as the solution was kept hot. (Allowing the solution to stand at room temperatures results in the formation of the yellow heptahydrate.) The product was filtered, washed with ethanol and ether, and air dried.

Anal. Calcd. for $Fe_2F_5 \cdot 2H_2O$: Fe, 46.0; F, 39.1; H_2O, 14.9. Found: Fe, 45.1, F, 38.4; H_2O, 14.82.

Iron was determined by permanganate titration following $SnCl_2$ reduction. Fluoride was determined using an Orion 94-01 fluoride specific ion electrode. Water analyses were performed by Schwarzkopf Microananlytical Laboratory, Woodside, N.Y.

Small but well-formed prismatic crystals for the diffraction study were obtained by this preparative route. As the compound is totally insoluble in all common solvents, the crystals were mounted without further purification. The red-brown opaque data crystal was mounted with [010] parallel to the ϕ axis of the goniometer.

Weissenberg and precession photographs of crystal taken with CuK_α radiation showed them to be orthorhombic with extinctions for hkl, h+k+l = 2n+1 and hk0, h=2n+1, requiring a space group Imma. Using the approximate cell dimensions obtained by film measurement, 20 reflections were accurately centered in the counter window of a Picker full-circle automated X-ray diffractometer. A least squares procedure was used to obtain a best fit between the observed and calculated values of χ,ϕ and 2θ for these reflections. The cell parameters and relevant crystal data are presented in Table I.

Intensity data were collected on the Picker diffractometer using MoKα radiation filtered through nickel foil. A scan speed of 1°/min was employed in measuring each reflection by the moving crystal-moving counter technique with a scan range in 2θ of 2°, plus an allowance for the splitting of the $K\alpha_1$ and $K\alpha_2$ radiation. The background for each reflection was determined by 10 sec stationary counts at each end of the scan range. A total of 248 unique reflections were collected in the limits $2° < 2\theta < 50°$. Three standard reflections were employed to monitor diffractometer and crystal stability. The variation in integrated intensities of the standards was that expected from counting statistics (1.5% of the mean.)

The observed intensities were corrected for background, Lorentz, polarization and absorption affects. The transmission factors range from 0.04 to 0.13. A Wilson plot yielded an approximate absolute scale factor. Scattering factors for iron, fluorine and oxygen were taken from Cromer and Waber (14). The anomalous dispersion corrections for iron were included. Scattering factors for the hydrogen atoms were those of Stewart, Davidson and Simpson (15). Only reflections with $I > 2.5\sigma(I)$ were included in the refinement, a total of 229 reflections. Although at the final stage of refinement the 040 reflection was excluded as it appeared to be seriously affected by extinction, no systematic attempt was made to correct the data for extinction effects.

Structure Determination

An initial Patterson map revealed the positions of all non-hydrogen atoms, and the small number of peaks (∿20) confirmed the choice of the centrosymmetric space group Imma. Refinement of the non-constrained positional parameters and individual isotropic temperature factors converged at a value of 0.11 for the conventional R factor. Assignment and refinement of anisotropic temperature factors reduced the residual to 0.053. A final difference Fourier map showed no excursions of electron density greater than 0.75 e/$\mathring{A}^3$, on a scale where the average value for an oxygen atom is 6e/$\mathring{A}^3$. The final positional and thermal parameters are presented in Table II. The pertinent bond lengths and angles are given in Table III. Figure 1 provides an atom labelling scheme while Figure 2 presents a stereo view of the molecular packing.

Results and Discussion

As indicated by the unit cell composition a number of atoms must sit at special positions in the unit cell. The eight iron atoms in the cell are located in two distinct sites:

Fe1 at the Wyckoff positions *a* of 2/m symmetry and fourfold multiplicity, (0,0,0), (0,1/2,0) and the set generated by the center of symmetry at (1/2, 1/2, 1/2)

Fe2 at the Wyckoff positions *C* of 2/m symmetry and fourfold multiplicity, (1/4, 1/4, 1/4) and (3/4, 1/4, 1/4)

F2 at the Wyckoff positions *e* of mm symmetry and fourfold multiplicity, (0, 1/4, z) and (0, 3/4, z)

O1 at the Wyckoff positions *h* with m point symmetry and eightfold multiplicity, (0, y, z), (0, $\bar{y}$, $\bar{z}$), (0, 1/2 + y, $\bar{z}$) , and (o, 1/2 - y, z).

Only atoms of the type F1 sit at the general positions of sixteen-fold multiplicity.

A significant feature of the structure is the distinct nature of the two unique iron sites. The Fe2 sites consist of vertex-sharing octahedra FeF_6, whereas Fe1 coordination is characterized by *trans* - $FeF_4(H_2O)_2$ octahedra with vertex sharing in the equatorial fluorine plane. Coupled with the observed bond distances (vide infra), it is clear that the Fe2 atoms are thus formally Fe(III) while the Fe1 sites are characterized as Fe(II). The existence of discrete Fe(II) and Fe(III) coordination environments demonstrates that this is a Class II mixed-valence species[4], in agreement with various physical probes [5,10,11]. The fluorine atoms of both types are doubly bridging: F2 participating solely in coordination to iron atoms of type Fe2, while F1 serves to link iron atoms of types Fe1 and Fe2 as indicated in Figure 1. The aquo groups are terminal, participating in coordination to type Fe1 iron only. The axially distorted FeF_6 octahedra thus share all six vertices, and the $FeF_4(H_2O)$ polyhedra share four equatorial fluorine positions.

The overall structure may be described in terms of zig-zag chains of Fe2-F2 groups, formed by trans vertex sharing of the FeF_6 octahedra, running parallel to the cell a axis. Each $[FeF]_n^{2n+}$ chain is cross-linked to four adjacent chains through bridging $FeF_4(H_2O)_2$ octahedra to product an unusual three dimensional framework, diagrammed in Figure 3. Each $FeF_4(H_2O)_2$ octahedron connects two $[FeF]_n^{2n+}$ chains, and, since the structure is built up through vertex sharing exclusively, each Fe1 atom is associated with four Fe2 atoms via the fluorine bridges.

The three dimensional structure is significantly different from those previously reported for iron-fluoride and iron-fluoride hydrate phases. The structures common to simple iron-fluoride systems are described in Table IV in terms of the edge or vertex sharing characteristics of the iron octahedra, and the relevant bond distances are listed. A feature common to a number of non-molecular Fe(III) fluoride lattices is the trans-vertex sharing or columnar arrangement of the FeF_6 octahedra, a characteristic shared by the Fe(III) octahedra in $Fe_2F_5 2H_2O$. The aquo groups function exclusively as terminal ligands, uninvolved in vertex sharing, in common with structures presently available.

In $Fe_2F_5 \cdot 2H_2O$ there are two different types of fluoride bridges, which may be recognized from their respective roles in bridging two Fe(III) groups in the trans vertex sharing FeF_6 columns or in cross-linking Fe(III) and Fe(II) atoms and from the metal-fluoride bond lengths. The average Fe2-fluoride bond length, 1.946Å, is significantly shorter than the Fe1-fluoride bond length of 2.060Å, in accord with the formal oxidation state assignments of Fe(III) and Fe(II), respectively. These observed bond lengths compare quite favorably with the values calculated from the effective ionic radii compiled by Shannon and Prewitt of 2.06Å for the Fe(II)-bridging fluoride distance and 1.93Å for Fe(III) bridge fluoride[33]. The average iron (III)-fluoride distances in the FeF_3[17], $BaFeF_5$[23] and $FeF_3(H_2O)_3$[32] structures, where the fluoride assumes a similar bridging function, are 1.93Å, 1.92Å and 1.94Å, respectively. The iron(II)-fluoride distance in FeF_2[29] and $Fe_2F_5 2H_2O$ of 2.07Å and 2.06Å, respectively, are significantly longer and show a trend that follows the expected expansion in the metal ionic radii, Fe(II)>Fe(III). The iron (II)-aquo oxygen distance of 2.13Å in $Fe_2F_5 \cdot 2H_2O$ may be compared to those found in $K_2FeF_5(H_2O)$[30], $[FeCl_2(H_2O)_4]Cl \cdot 2H_2O$[34], and the ammonium and potassium salts of $FeCl_5(H_2O)^{1-}$[35,36], of 2.07Å, 2.07Å, and 2.10Å, respectively, and to the calculated value of 2.13Å[33].

The distinct nature of the two iron sites, formally Fe(II) and Fe(III), in the $Fe_2F_5 \cdot 2H_2O$ species is supported by considerations of the overall polyhedron geometries and individual bond lengths. This may be contrasted with another stoichiometric mixed-valence iron (II, III) fluoride, $LiFe_2F_6$. This material, which crystallizes with a trirutile structure,[26] has Fe(II) and Fe(III) sites which are indistinguishable crystallographically. Such a result would be compatible with either Class III mixed-valence behavior (e.g., non-integral valence) or else a disordered structure. Mossbauer spectroscopy, however, clearly demonstrates Class II behavior (e.g., trapped valences) and suggests an ordered structure[37]. The difference in the nature of exchange interactions in $LiFe_2F_6$ and $Fe_2F_5 \cdot 2H_2O$, a difference which arises in part from the structural variations, will be considered in a subsequent publication.[11]

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Supplementary Material Available: Listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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TABLE I. Experimental Summary

Crystal Data for $Fe_2F_5 \cdot 2H_2O$

F_ω = 242.72

a = 7.489(7)Å

b = 10.897(8)Å

c = 6.671(6)Å

$\alpha=\beta-\gamma=90.00°$

ρcalc = 2.96g cm^{-3}

ρfound = 2.94(2)g cm^{-3}

(flotation in dibromoethylene)

Orthorhombic

Systematic absences: hkl,h+k+l = 2n+1; hk0, h=2n+1

Space group Imma

Z = 4

F(000) = 468

λ(Mo): $K\bar{\alpha}$, 0.7107Å

Data Collection

Crystal dimensions: 0.352 x 0.340 x 0.325 mm

$\mu(MoK\alpha) = 55.1\ cm^{-1}$

248 symmetry-independent reflections for $2<2\theta\leq50°$

Table II. Final Positional and Anisotropic Thermal Parameters[a,b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	.0000	.0000	.0000	67(18)	77(17)	152(20	0	0	-20(15)
Fe2	.2500	.2500	.2500	51(16)	49(16)	140(19)	0	3(1)	0
F1	.2022(9)	.1239(6)	.05838(10)	142(40)	125(32)	208(41)	-20(20)	-5(2)	-15(20)
F2	.0000	.2500	.3368(22)	59(60)	114(66)	199(80)	0	0	0
O1	.5000	.5640(13)	.1974(22)	160(70)	365(80)	266(90)	0	0	20(60)

[a] Estimated standard deviations are given in parentheses.

[b] $U_{ij} \times 10^4$. The vibrational coefficients relate to the expression:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}kla^*c^* + 2U_{23}klb^*c^*)].$$

Table III. Internuclear Distances, Polyhedral Edge Lengths, and Bond Angles

(i) Interatomic distances in Å^{a,b}

Fe1-F1(4)	2.060(6)	Fe1-Fe1	5.558(2) , 5.015(2)
Fe1-O1(2)	2.13(1)	Fe1-Fe2	3.702(2)
Fe2-F1(4)	1.932(7)	Fe2-Fe2	3.744(2)
Fe2-F2(2)	1.960(4)		

(ii) Polyhedral edge distances

Fe1 Polyhedron		Fe2 Polyhedron	
F1-F1	2.793(9)	F2-F1	2.720(8)
F1-O1	2.89(1)		2.78(1)
	2.87(1)	F1-F1	2.749(9)
			2.714(9)

(iii) Bond Angles, °

F1-Fe1-F1	85.4(3)	F1-Fe2-F2	88.7(4)
	94.6(3)		91.3(4)
F1-Fe1-O1	92.8(3)	F1-Fe2-F1	89.3(3)
	87.2(3)		90.7(3)
Fe1-F1-Fe2	136.1(4)	Fe2-F1-Fe2	145.7(8)

[a] The number of equivalent bonds of a given type is indicated in parentheses.

[b] Standard deviations, in parentheses, occur in the last significant figure for each parameter.

Table IV. Iron-Fluoride Lattices

Compound	Number of Octahedral Vertices and/or Edges Shared	Description of Overall Structure	Bond Lengths, A°	Ref.
FeF_3	6 vertices	3-dimensional network	FeF: 1.926	16, 17
$K_{0.6}FeF_3$	6 vertices	3-dimensional tungsten-bronze network	FeF: 1.93-2.11	18
$KFeF_3$, $RbFeF_3$	6 vertices	3-dimensional, perovskite network	FeF: 2.06	19, 20
$KFeF_4$, K_2FeF_4	4 vertices	Single *cis*-layer	a	21 22
$BaFeF_5$	4 and 2 vertices	ramified chain and linear *trans* chain	FeF: 1.92(4), av.	23
$K_3Fe_2F_7$	5 vertices	Double octahedral layer	a	22
$Na_5Fe_3F_{14}$	2 and 4 vertices	Layer	a	24
γ-$Na_5Fe_3F_{14}$	2 and 4 vertices	Layer	FeF: 1.76-2.02	25
$Rb_2Fe_5F_{17}$	5 and 6 vertices	Multiple layer	a	21
K_2FeF_5	2 vertices	Chain	a	21
$LiFe_2F_6$	2 edge, 2 vertices	trirutile structure	a	26
Rb_3FeF_6	0	Isolated Octahedra	a	27
K_2NaFeF_6	0	Isolated Octahedra	FeF: 1.910(3)	28
FeF_2	2 edge, 2 vertices	3-dimensional, rutile structure	FeF: 2.118(4) 1.998(6)	29
$K_2FeF_5(H_2O)$	0	Isolated Octahedra	FeF: 1.92(1) FeO: 2.07(1)	30
$FeF_2(H_2O)_4$	0	Isolated	FeF: 1.96,b	31
$FeF_3(H_2O)_3$	2 vertices	*trans*-chain	FeF: 1.951, 1.926 FeF,O:1.937,b	32

[a] Unit cell dimensions are listed, but no structural details are available.

[b] Statistically disordered structures.

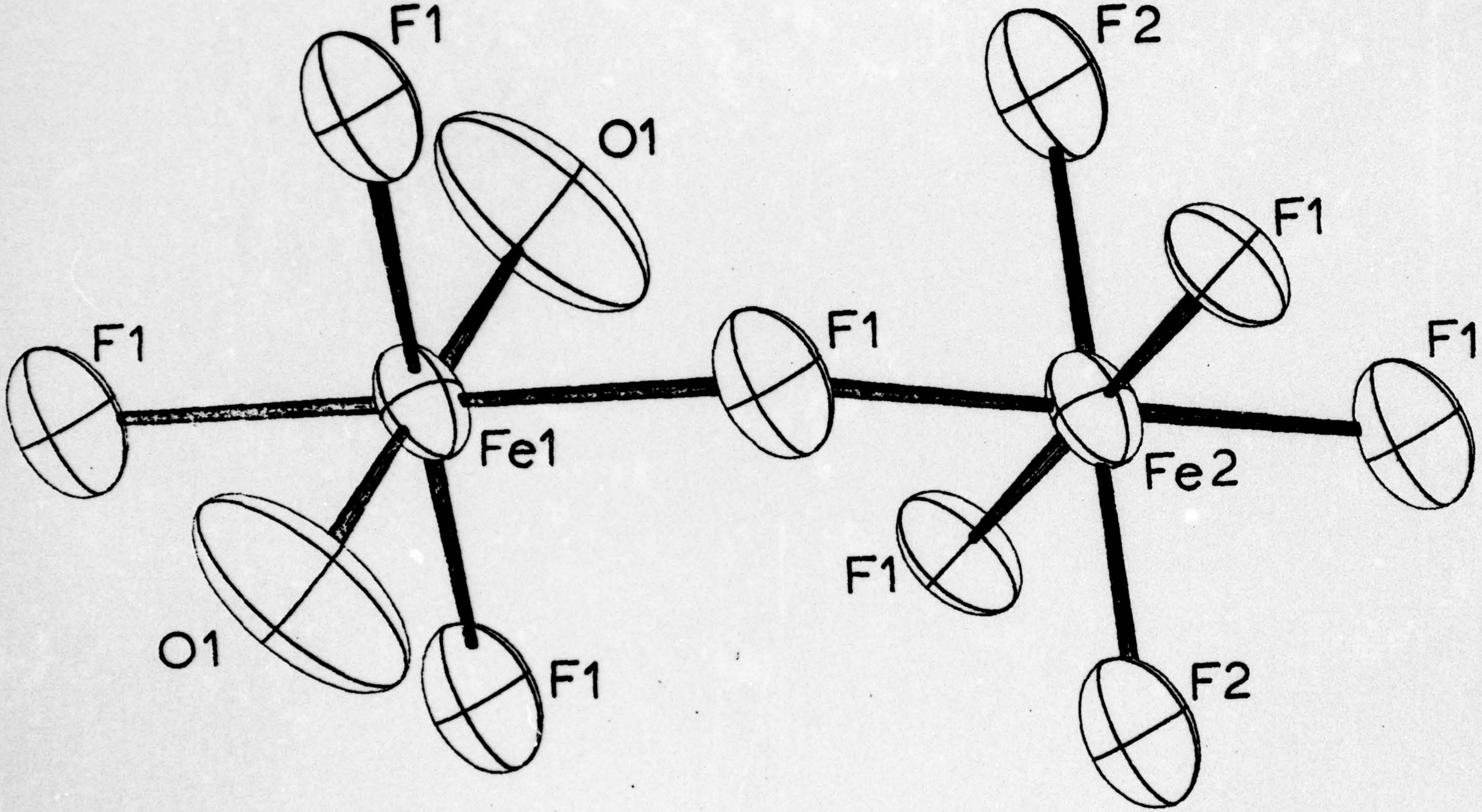
Captions to Figures:

Figure 1: Perspective view of an isolated fragment of the three-dimensional network structure of $Fe_2F_5 \cdot 2H_2O$ showing the 50% probability ellipsoids and the atom-labelling scheme.

Figure 2: A stereoscopic view of the packing of the non-molecular phase $Fe_2F_5 \cdot 2H_2O$ in the unit cell.

Figure 3: a) Diagrammatic representation of the $Fe_2F_5 \cdot 2H_2O$ structure viewed parallel to the a cell axis. The squares represent columns of trans-vertex sharing FeF_6 octahedra and the rhombi represent the cross-linking $FeF_4(H_2O)_2$ polyhedra.

b) Diagrammatic representation of the $Fe_2F_5 \cdot 2H_2O$ structure viewed parallel to the b cell axis. The squares represent cross-linking $FeF_4(H_2O)_2$ polyhedra, and the rhombi represent the trans-vertex sharing FeF_6 octahedra.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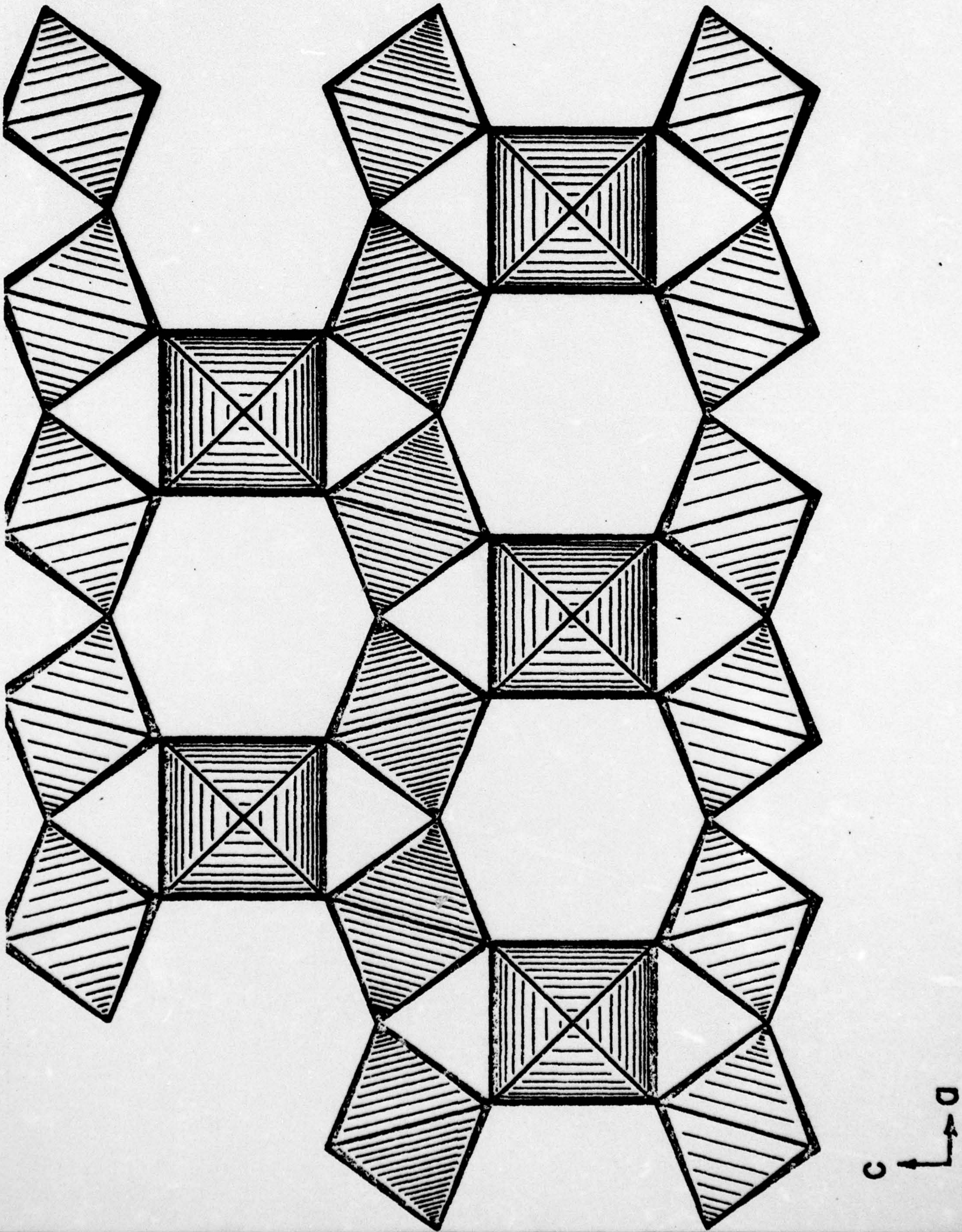
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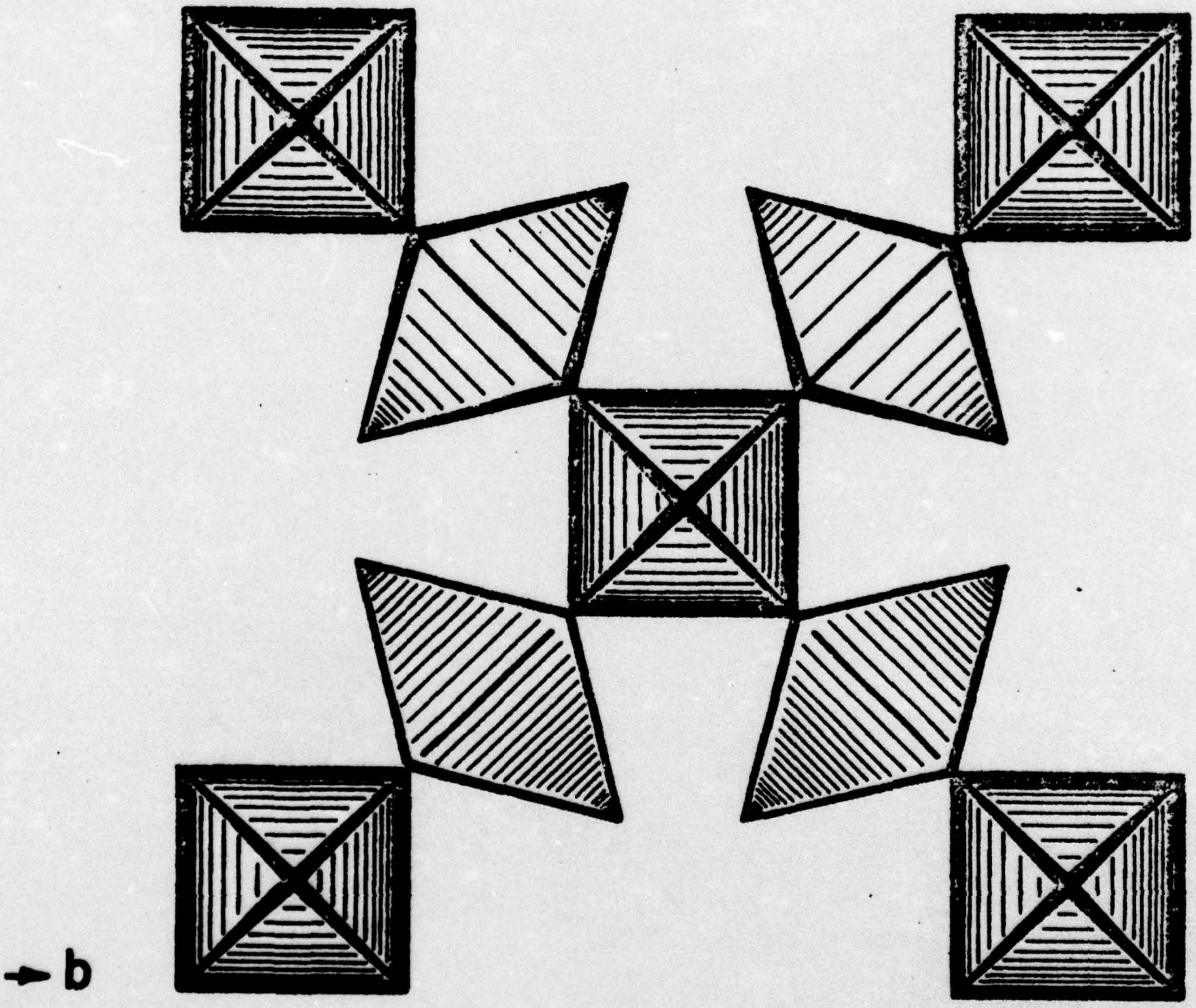
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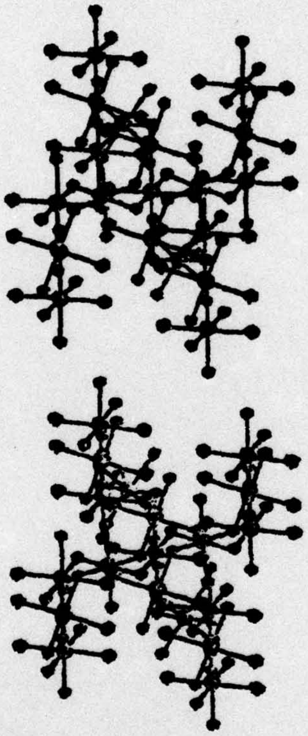

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