

AD-A035 714

VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY  
THE STRUCTURE OF A MIXED-VALENCE IRON FLUORIDE,  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O} \cdot (\text{U})$   
FEB 77 W HALL, S KIM, J ZUBIETA, E G WALTON N00014-75-C-0756

F/G 7/3

UNCLASSIFIED

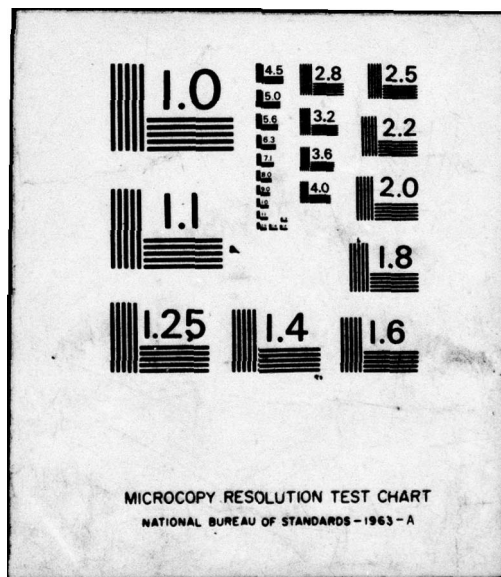
TR-4

NL

1 OF 1  
AD  
A035714



END  
DATE  
FILMED  
3-77



ADA035714

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0756

Project NR 356-593

TECHNICAL REPORT NO. 4

THE STRUCTURE OF A MIXED-VALENCE IRON FLUORIDE,  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$

by

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

Prepared for Publication

in

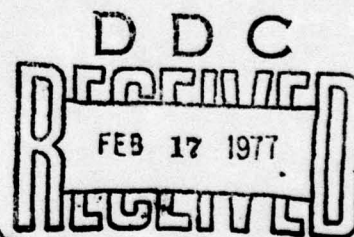
Inorganic Chemistry

University of Vermont

Department of Chemistry

Burlington, Vermont 05401

February 9, 1977



Reproduction in whole or in part is permitted for any purpose  
of the United States Government

Approved for Public Release: Distribution Unlimited.

COPY AVAILABLE TO DDC DOES NOT  
PERMIT FULLY LEGIBLE PRODUCTION

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER

2. JOINT ACCESSION NO.

3. PERFORMING ORGANIZATION'S CATALOG NUMBER

4. TITLE (and Subtitle)

THE STRUCTURE OF A MIXED-VALENCE IRON FLUORIDE,  
 $\text{Fe}_2\text{F}_{11}\cdot 2\text{H}_2\text{O}$ 

5. TYPE OF REPORT &amp; PERIOD COVERED

Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

W. Hall (SUNY Albany), S. Kim (NYS Department of Health), J. Zubieta (SUNY Albany), E. G. Walton, and D. B. Brown; University of Vermont

8. CONTRACT OR GRANT NUMBER(s)

N00014-75-C-0756

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Chemistry  
University of Vermont  
Burlington, Vermont 05401

10. PROGRAM ELEMENT, PROJECT, TASK AREA &amp; WORK UNIT NUMBERS

9 Feb 77

11. CONTROLLING OFFICE NAME AND ADDRESS

Office of Naval Research  
Department of the Navy  
Arlington, Virginia 22217

12. REPORT DATE

February 9, 1977

13. NUMBER OF PAGES

20

14. MONITORING AGENCY NAME &amp; ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (for the abstract entered in Block 20, if different from Report)

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

18. SUPPLEMENTARY NOTES

To be published in Inorganic Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Iron Fluorides, Mixed-Valence, Crystal Structure

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The mixed valence iron compound,  $\text{Fe}_2\text{F}_{11}\cdot 2\text{H}_2\text{O}$ , crystallizes in the orthorhombic system, space group Imma. The unit cell has dimensions  $a = 7.489(7)\text{\AA}$ ,  $b = 10.897(8)$ , and  $c = 6.671(6)\text{\AA}$  and contains four formula weights. The calculated and experimental densities are  $2.96\text{ g/cm}^3$  and  $2.94\text{ g/cm}^3$ , respectively, at  $20 \pm 1^\circ$ . Measurements of diffracted intensities employed  $\theta$ - $2\theta$  scans with filtered MoK $\alpha$  radiation on a Picker diffractometer. A total of 250 reflections in the range  $2 < 2\theta < 50^\circ$  were retained as observed.

Continued on next page.

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

408892

theta-2Theta scans

2

•  
↑

UNCLASSIFIED  
DATE 08-06-2009 BY SP8 BJS/BJS

UNANNOUNCED  
JUSTIFICATION.....

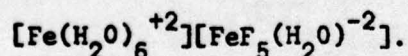
BY.....  
DISTRIBUTION/AVAILABILITY CODES

| ORIG. | SYMBOL | SERIAL |
|-------|--------|--------|
| A     |        |        |

## 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.<sup>2</sup> 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<sup>3</sup> reported the preparation of the mixed-valence iron fluoride  $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ . 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<sup>4</sup>, they have generated significant interest in recent years. On the basis of various physical measurements, the heptahydrate has been formulated<sup>5,6</sup> as a Class I mixed-valence complex<sup>4</sup> having the ionic structure



The red material, initially formulated<sup>3</sup> as a trihydrate, has subsequently been shown<sup>7,8</sup> by thermoanalytical techniques to be a dihydrate,  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ . This complex has been investigated by Mossbauer spectroscopy<sup>9,10</sup>, and we have shown<sup>11</sup>, using Mossbauer and magnetic measurements, that the material orders ferromagnetically 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  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  directly, and report here the structure as determined by X-ray diffraction<sup>12</sup>. A subsequent paper<sup>11</sup> will present the results of our studies of the magnetism and Mossbauer spectra of this material.

### Experimental Section

Pentafluorodiiron (II,III) dihydrate,  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ , was prepared by a modification of Brauer and Eichner's preparation of the heptahydrate<sup>3</sup>. 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  $\text{F}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  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  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ : Fe, 46.0; F, 39.1;  $\text{H}_2\text{O}$ , 14.9. Found: Fe, 45.1, F, 38.4;  $\text{H}_2\text{O}$ , 14.82.

Iron was determined by permanganate titration following  $\text{SnCl}_2$  reduction.

Fluoride was determined using an Orion 94-01 fluoride specific ion electrode.

Water analyses were performed by Schwarzkopf Microanalytical 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  $\phi$  axis of the goniometer.

Weissenberg and precession photographs of crystal taken with  $\text{CuK}_\alpha$  radiation showed them to be orthorhombic with extinctions for  $hkl$ ,  $h+k+1 = 2n+1$  and  $hk0$ ,  $h=2n+1$ , requiring a space group  $\text{Imma}$ . 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  $\chi$ ,  $\phi$  and  $2\theta$  for these reflections. The cell

parameters and relevant crystal data are presented in Table I.

Intensity data were collected on the Picker diffractometer using MoK $\alpha$  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  $2\theta$  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  $2^\circ < 2\theta < 50^\circ$ . 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 ( $\sim 20$ ) 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  $0.75 \text{ e}/\text{\AA}^3$ , on a scale where the average value for an oxygen atom is  $6 \text{ e}/\text{\AA}^3$ . 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  $(0, 1/2 - y, z)$ .

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  $\text{FeF}_6$ , whereas Fe1 coordination is characterized by trans -  $\text{FeF}_4(\text{H}_2\text{O})_2$  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<sup>4</sup>, in agreement with various physical probes<sup>5,10,11</sup>. The fluorine atoms of both types are doublybridging: 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  $\text{FeF}_6$  octahedra thus share all six vertices, and the  $\text{FeF}_4(\text{H}_2\text{O})_2$  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  $\text{FeF}_6$  octahedra, running parallel to the cell a axis. Each  $[\text{FeF}_n]^{2n+}$  chain is cross-linked to four adjacent chains through bridging  $\text{FeF}_4(\text{H}_2\text{O})_2$  octahedra to product an unusual three dimensional framework, diagrammed in Figure 3. Each  $\text{FeF}_4(\text{H}_2\text{O})_2$  octahedron connects two  $[\text{FeF}_n]^{2n+}$  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  $\text{FeF}_6$  octahedra, a characteristic shared by the Fe(III) octahedra in  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$ . The aquo groups function exclusively as terminal ligands, uninvolved in vertex sharing, in common with structures presently available.

In  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$  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  $\text{FeF}_6$  columns or in cross-linking Fe(III) and Fe(II) atoms and from the metal-fluoride bond lengths. The average Fe2-fluoride bond length,  $1.946\text{\AA}$ , is significantly shorter than the Fe1-fluoride bond length of  $2.060\text{\AA}$ ,

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  $2.06\text{\AA}$  for the Fe(II)-bridging fluoride distance and  $1.93\text{\AA}$  for Fe(III) bridge fluoride<sup>33</sup>. The average iron (III)-fluoride distances in the  $\text{FeF}_3$ <sup>17</sup>,  $\text{BaFeF}_5$ <sup>23</sup> and  $\text{FeF}_3(\text{H}_2\text{O})_3$ <sup>32</sup> structures, where the fluoride assumes a similar bridging function, are  $1.93\text{\AA}$ ,  $1.92\text{\AA}$  and  $1.94\text{\AA}$ , respectively. The iron(II)-fluoride distance in  $\text{FeF}_2$ <sup>29</sup> and  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$  of  $2.07\text{\AA}$  and  $2.06\text{\AA}$ , 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  $2.13\text{\AA}$  in  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$  may be compared to those found in  $\text{K}_2\text{FeF}_5(\text{H}_2\text{O})$ <sup>30</sup>,  $[\text{FeCl}_2(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}$ <sup>34</sup>, and the ammonium and potassium salts of  $\text{FeCl}_5(\text{H}_2\text{O})^{1-}$ <sup>35,36</sup> of  $2.07\text{\AA}$ ,  $2.07\text{\AA}$ , and  $2.10\text{\AA}$ , respectively, and to the calculated value of  $2.13\text{\AA}$ <sup>33</sup>.

The distinct nature of the two iron sites, formally Fe(II) and Fe(III), in the  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$  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,  $\text{LiFe}_2\text{F}_6$ . This material, which crystallizes with a triputile structure,<sup>26</sup> 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<sup>37</sup>. The difference in the nature of exchange interactions in  $\text{LiFe}_2\text{F}_6$  and  $\text{Fe}_2\text{F}_5\cdot 2\text{H}_2\text{O}$ , a difference which arises in part from the structural variations, will be considered in a subsequent publication.<sup>11</sup>

Acknowledgment. Work performed at the University of Vermont was supported by the Office of Naval Research.

Supplementary Material Available: Listing of structure factor amplitudes (3 pages).

Ordering information is given on any current masthead page.

References and Notes

- (1) (a) State University of New York. (b) NYS Department of Health  
(c) The University of Vermont.
- (2) J. Portier, Angew. Chem. Int. Ed. Engl., **15**, 475 (1976).
- (3) G. Brauer and M. Eichner, Z. Anorg. Allg. Chem., **296**, 13 (1958).
- (4) M. B. Robin and P. Day, Adv. Inorg. and Radiochem., **10**, 247 (1967).
- (5) E. G. Walton, P. J. Corvan, D. B. Brown, and P. Day, Inorg. Chem., **15**, 1737 (1976).
- (6) T. Sakai and T. Tominaga, Bull. Chem. Soc. Jap., **48**, 3168 (1975).
- (7) P. Charpin and Y. Macheteau, C. R. Hebd. Seances, Acad. Sci., Ser. C., **280**, 61 (1975).
- (8) K. J. Gallagher and M. R. Ottaway, J. Chem. Soc., Dalton Trans., 978 (1975).
- (9) T. Sakai and T. Tominaga, Radioisotopes, **23**, 347 (1974).
- (10) P. Imbert, G. Jehanno, Y. Macheteau, and F. Varret, J. de Physique, **37**, 969 (1976).
- (11) E. G. Walton, D. B. Brown, H. Wong, W. M. Reiff, and J. Zubieta, to be submitted.
- (12) In their initial work<sup>3</sup>, Brauer and Eichner prepared crystalline material using a different route. The unit cell parameters which they determined are in agreement with our work. However, the improper formula used, and the apparently incorrect density of 2.43 g/ml. (determined pycnometrically in decalin) led to a value of 3 formula units in the unit cell. It should be noted that published powder pattern data for this compound contain several errors.<sup>13</sup>
- (13) G. Brauer, personal communication.
- (14) D. T. Cromer and J. T. Waber, Acta. Crystallogr., **18**, 104 (1965).
- (15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., **42**, 3175 (1965).
- (16) F. Eleat, Z. anorg. allgem. Chem., **196**, 395 (1931).
- (17) M. A. Hepworth, K. H. Jack, R. D. Peacock, G. J. Westland, Acta Cryst. **10**, 63 (1957).

- (18) A. M. Hardy, A. Hardy, and G. Ferey, Acta Cryst. B29, 1654 (1973).
- (19) K. Knox, Acta Cryst., 14, 583 (1961).
- (20) M. Kestigian, F. D. Leipzigen, W. J. Croft, and R. Guidoboni, Inorg. Chem., 5, 1462 (1966).
- (21) A. Tressaud, J. Portier, R. de Pape and P. Hagenmuller. J. Solid State Chem. 2, 269 (1970).
- (22) R. de Pape, Bull. Soc. Chim Fr., 12, 3489 (1965).
- (23) R. von der Muhll, S. Anderson, and J. Galy, Acta Cryst. B27, 2345 (1971).
- (24) K. Knox and S. Geller, Phys. Rev., 116, 771 (1958).
- (25) M. Vlasse, F. Menil, C. Moritiere, J. M. Dance, A. Tressaud, and J. Portier, J. Sol. State Chem., 17, 291 (1976).
- (26) J. Portier, A. Tressaud, R. dePape, and P. Hagenmuller, C. R. Hebd. Seances Acad. Sci., Ser. C., 267, 1711 (1968).
- (27) H. Bode, E. Voss, Z. anorg. allgem. Chem., 290, 1 (1957).
- (28) K. Knox and D. W. Mitchell, J. Inorg. Nucl. Chem. 21, 253 (1961).
- (29) W. H. Baur and A. A. Khan, Acta Cryst., B27, 2133 (1971).
- (30) A. J. Edwards, J. Chem. Soc., 816 (1972).
- (31) B. R. Penfold and M. R. Taylor, Acta Cryst., 13, 953 (1960).
- (32) G. Teufer, Acta Cryst., 17, 1480 (1964).
- (33) R. D. Shannon and C. T. Prewitt, Acta Cryst., B25, 925 (1969).
- (34) M. D. Lind, J. Chem. Phys., 47, 990 (1967).
- (35) I. Lindquist, Acta Chem. Scand., 2, 530 (1948).
- (36) A. Bellanca, Periodico Mineral (Rome), 17, 59 (1948).
- (37) N. N. Greenwood, A. T. Howe, and F. Ménil, J. Chem. Soc. A, 2218 (1971).

TABLE I. Experimental Summary

Crystal Data for  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ 

|                                                  |                                                 |
|--------------------------------------------------|-------------------------------------------------|
| $F_{\omega} = 242.72$                            | Orthorhombic                                    |
| $a = 7.489(7)\text{\AA}$                         | Systematic absences: $hkl, h+k+l =$             |
| $b = 10.897(8)\text{\AA}$                        | $2n+1; hk0, h=2n+1$                             |
| $c = 6.671(6)\text{\AA}$                         | Space group $\text{Imma}$                       |
| $\alpha=\beta=\gamma=90.00^\circ$                | $Z = 4$                                         |
| $\rho_{\text{calc}} = 2.96\text{ g cm}^{-3}$     | $F(000) = 468$                                  |
| $\rho_{\text{found}} = 2.94(2)\text{ g cm}^{-3}$ | $\lambda(\text{Mo}): K\alpha, 0.7107\text{\AA}$ |
| (flotation in dibromoethylene)                   |                                                 |

## Data Collection

Crystal dimensions:  $0.352 \times 0.340 \times 0.325\text{ mm}$  $\mu(\text{MoK}\alpha) = 55.1\text{ cm}^{-1}$ 248 symmetry-independent reflections for  $2 < 2\theta < 50^\circ$

Table II. Final Positional and Anisotropic Thermal Parameters<sup>a,b</sup>

| 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)   |

<sup>a</sup>Estimated standard deviations are given in parentheses.

<sup>b</sup> $U_{ij} \times 10^4$ . The vibrational coefficients relate to the expression:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}k1a^{*}c^{*} + 2U_{23}k1b^{*}c^{*})].$$

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

(i) Interatomic distances in Å<sup>a,b</sup>

|           |          |         |                     |
|-----------|----------|---------|---------------------|
| 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

|       |          |
|-------|----------|
| F1-F1 | 2.793(9) |
| F1-O1 | 2.89(1)  |
|       | 2.87(1)  |

## Fe2 Polyhedron

|       |          |
|-------|----------|
| F2-F1 | 2.720(8) |
|       | 2.78(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) |

<sup>a</sup>The number of equivalent bonds of a given type is indicated in parentheses.

<sup>b</sup>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, Å <sup>a</sup>                      | Ref.     |
|-------------------------------------------------------------|---------------------------------------------------|----------------------------------------------|---------------------------------------------------|----------|
| FeF <sub>3</sub>                                            | 6 vertices                                        | 3-dimensional network                        | FeF: 1.926                                        | 16, 17   |
| K <sub>0.6</sub> FeF <sub>3</sub>                           | 6 vertices                                        | 3-dimensional tungsten-bronze network        | FeF: 1.93-2.11                                    | 18       |
| KFeF <sub>3</sub> ,<br>RbFeF <sub>3</sub>                   | 6 vertices                                        | 3-dimensional, perovskite network            | FeF: 2.06                                         | 19, 20   |
| KFeF <sub>4</sub> ,<br>K <sub>2</sub> FeF <sub>4</sub>      | 4 vertices                                        | Single <u>cis</u> -layer                     | a                                                 | 21<br>22 |
| BaFeF <sub>5</sub>                                          | 4 and 2 vertices                                  | ramified chain and linear <u>trans</u> chain | FeF: 1.92(4), av.                                 | 23       |
| K <sub>3</sub> Fe <sub>2</sub> F <sub>7</sub>               | 5 vertices                                        | Double octahedral layer                      | a                                                 | 22       |
| Na <sub>5</sub> Fe <sub>3</sub> F <sub>14</sub>             | 2 and 4 vertices                                  | Layer                                        | a                                                 | 24       |
| γ-Na <sub>5</sub> Fe <sub>3</sub> F <sub>14</sub>           | 2 and 4 vertices                                  | Layer                                        | FeF: 1.76-2.02                                    | 25       |
| Rb <sub>2</sub> Fe <sub>5</sub> F <sub>17</sub>             | 5 and 6 vertices                                  | Multiple layer                               | a                                                 | 21       |
| K <sub>2</sub> FeF <sub>5</sub>                             | 2 vertices                                        | Chain                                        | a                                                 | 21       |
| LiFe <sub>2</sub> F <sub>6</sub>                            | 2 edge, 2 vertices                                | trirutile structure                          | a                                                 | 26       |
| Rb <sub>3</sub> FeF <sub>6</sub>                            | 0                                                 | Isolated Octahedra                           | a                                                 | 27       |
| K <sub>2</sub> NaFeF <sub>6</sub>                           | 0                                                 | Isolated Octahedra                           | FeF: 1.910(3)                                     | 28       |
| FeF <sub>2</sub>                                            | 2 edge, 2 vertices                                | 3-dimensional, rutile structure              | FeF: 2.118(4)<br>1.998(6)                         | 29       |
| K <sub>2</sub> FeF <sub>5</sub> (H <sub>2</sub> O) 0        |                                                   | Isolated Octahedra                           | FeF: 1.92(1)<br>FeO: 2.07(1)                      | 30       |
| FeF <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> 0          |                                                   | Isolated                                     | FeF: 1.96,b                                       | 31       |
| FeF <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> 2 vertices |                                                   | <u>trans</u> -chain                          | FeF: 1.951,<br>1.926<br>FeF <sub>0</sub> :1.937,b | 32       |

<sup>a</sup>Unit cell dimensions are listed, but no structural details are available.

<sup>b</sup>Statistically disordered structures.

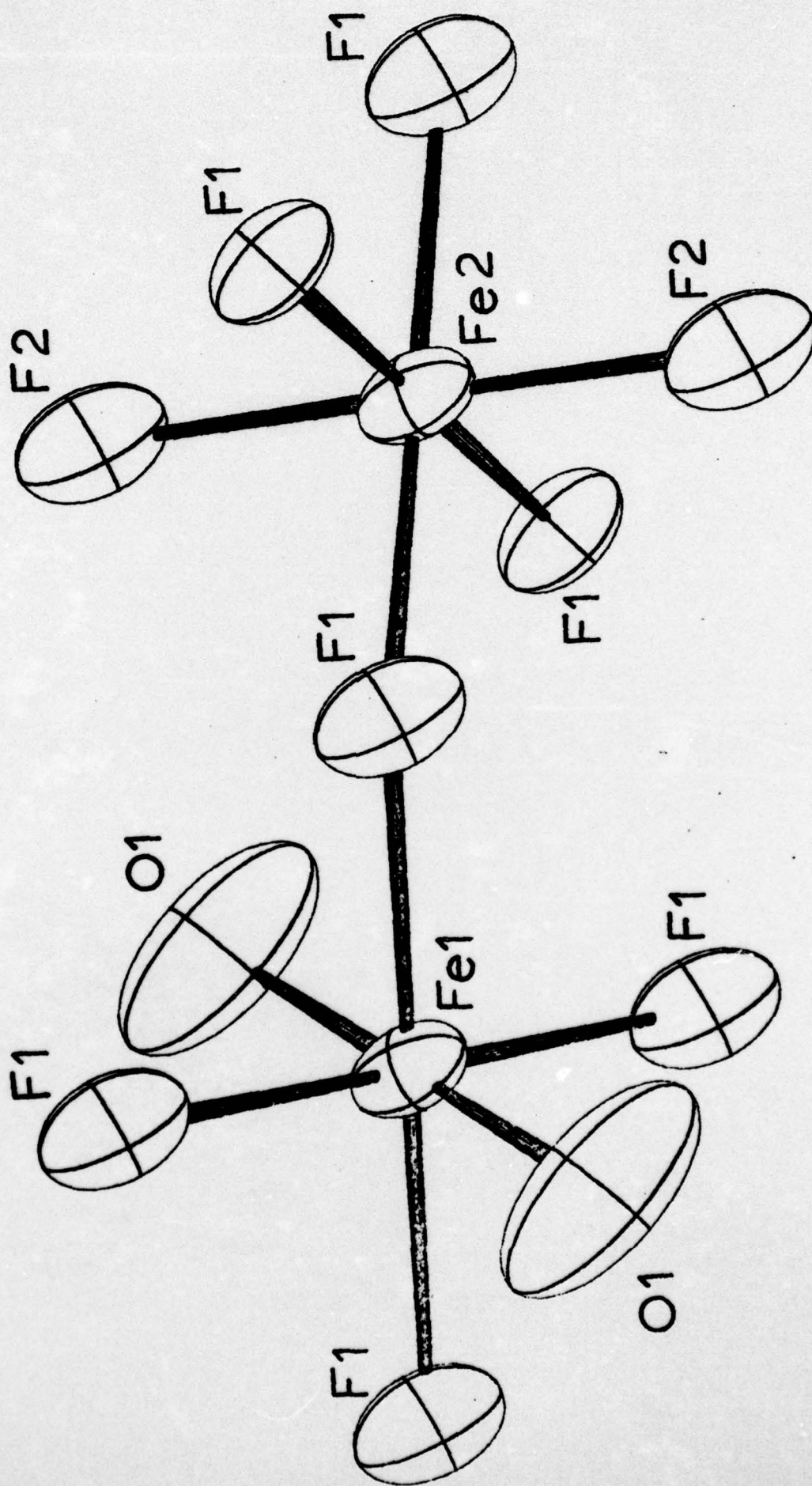
### Captions to Figures:

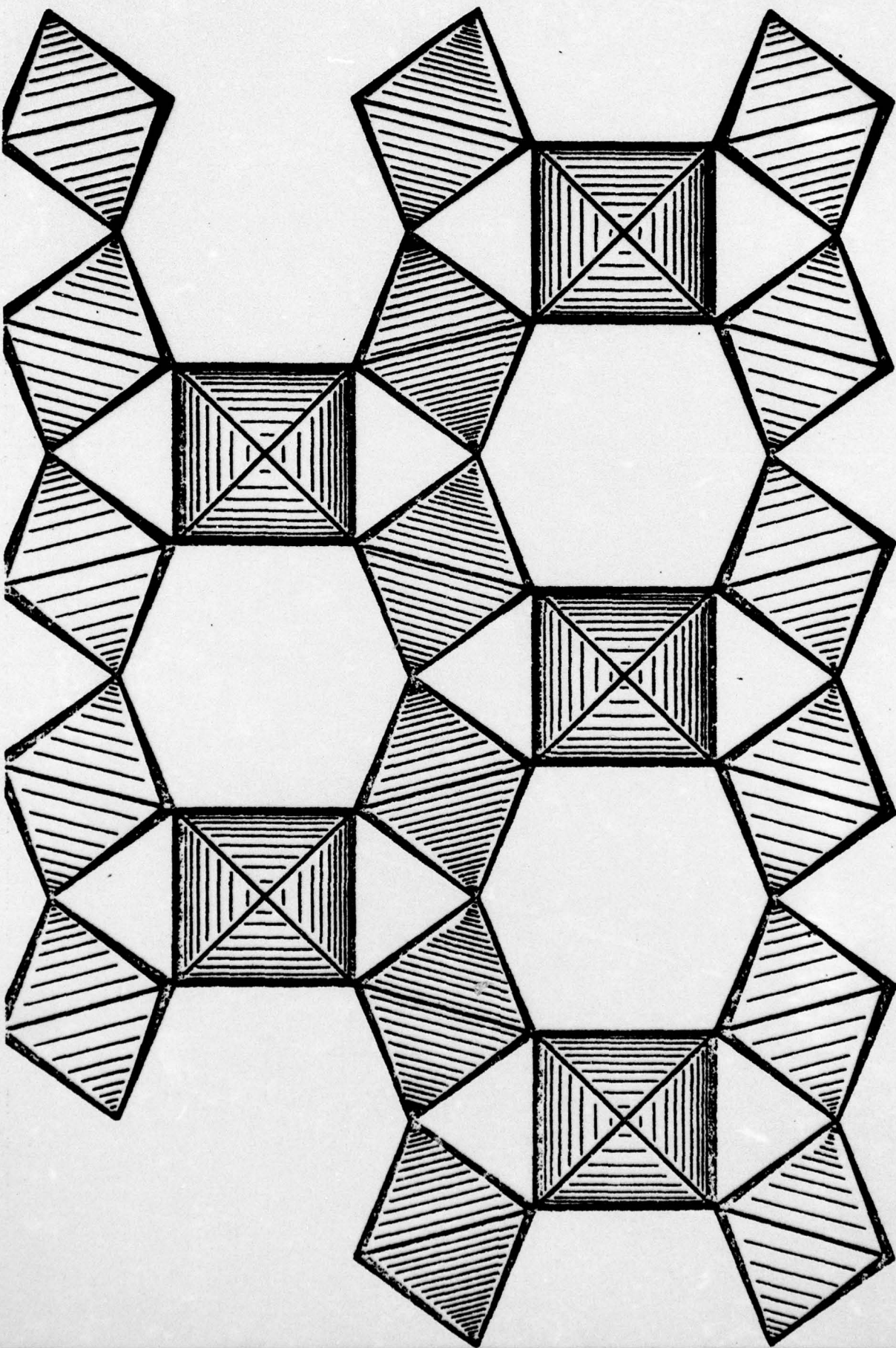
Figure 1: Perspective view of an isolated fragment of the three-dimensional network structure of  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  showing the 50% probability ellipsoids and the atom-labelling scheme.

Figure 2: A stereoscopic view of the packing of the non-molecular phase  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  in the unit cell.

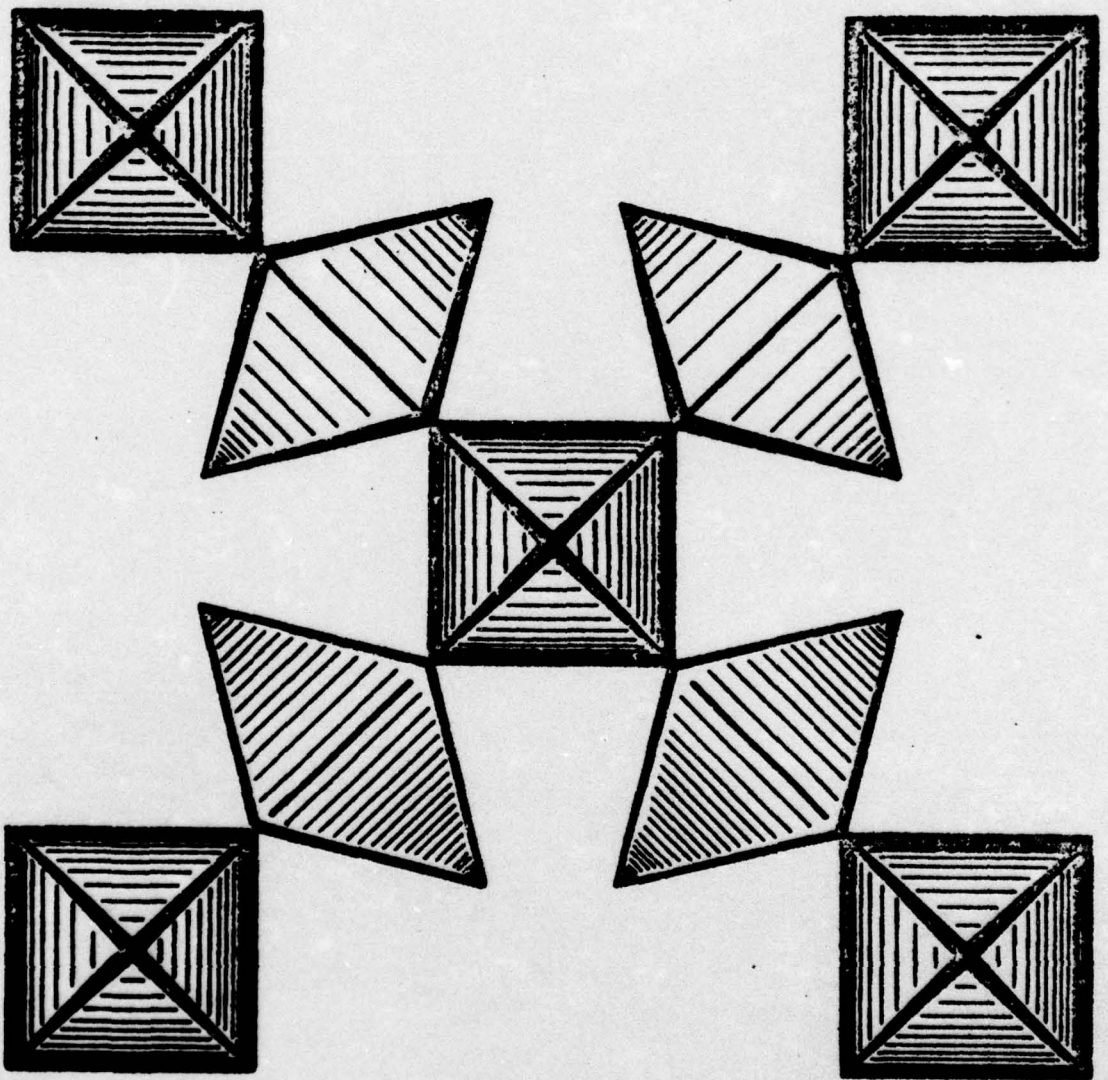
Figure 3: a) Diagrammatic representation of the  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  structure viewed parallel to the a cell axis. The squares represent columns of trans-vertex sharing  $\text{FeF}_6$  octahedra and the rhombi represent the cross-linking  $\text{FeF}_4(\text{H}_2\text{O})_2$  polyhedra.

b) Diagrammatic representation of the  $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$  structure viewed parallel to the b cell axis. The squares represent cross-linking  $\text{FeF}_4(\text{H}_2\text{O})_2$  polyhedra, and the rhombi represent the trans-vertex sharing  $\text{FeF}_6$  octahedra.

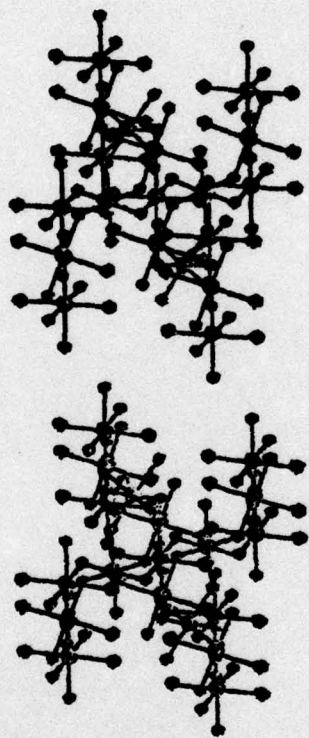




040



→ b



# TECHNICAL REPORT DISTRIBUTION LIST

|                                                                                                                               | <u>No. of Copies</u> |                                                                                                                                     | <u>No. Copies</u> |
|-------------------------------------------------------------------------------------------------------------------------------|----------------------|-------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| Office of Naval Research<br>Arlington, Virginia 22217<br>Attn: Code 472                                                       | 2                    | Defense Documentation Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314                                           | 12                |
| Office of Naval Research<br>Arlington, Virginia 22217<br>Attn: Code 102IP                                                     | 6                    | U. S. Army Research Office<br>P. O. Box 12211<br>Research Triangle Park,<br>North Carolina 27709<br>Attn: CRD-AA-IP                 |                   |
| ONR Branch Office<br>536 S. Clark Street<br>Chicago, Illinois 60605<br>Attn: Dr. George Sandoz                                | 1                    | Commander<br>Naval Undersea Research &<br>Development Center<br>San Diego, California 92132<br>Attn: Technical Library,<br>Code 133 | 1                 |
| ONR Branch Office<br>715 Broadway<br>New York, New York 10003<br>Attn: Scientific Dept.                                       | 1                    | Naval Weapons Center<br>China Lake, California 93555<br>Attn: Head, Chemistry Division                                              | 1                 |
| ONR Branch Office<br>1030 East Green Street<br>Pasadena, California 91106<br>Attn: Dr. R. J. Marcus                           | 1                    | Naval Civil Engineering Laboratory<br>Port Hueneme, California 93041<br>Attn: Mr. W. S. Haynes                                      | 1                 |
| ONR Branch Office<br>760 Market Street, Rm. 447<br>San Francisco, California 94102<br>Attn: Dr. P. A. Miller                  | 1                    | Professor O. Heinz<br>Department of Physics & Chemistry<br>Naval Postgraduate School<br>Monterey, California 93940                  |                   |
| ONR Branch Office<br>495 Summer Street<br>Boston, Massachusetts 02210<br>Attn: Dr. L. H. Peebles                              | 1                    | Dr. A. L. Slafkosky<br>Scientific Advisor<br>Commandant of the Marine Corps<br>(Code RD-1)<br>Washington, D. C. 20380               | 1                 |
| Director, Naval Research Laboratory<br>Washington, D. C. 20390<br>Attn: Library, Code 2029 (ONRL)                             | 6                    |                                                                                                                                     |                   |
| Technical Info. Div.                                                                                                          | 1                    |                                                                                                                                     |                   |
| Code 6100, 6170                                                                                                               | 1                    |                                                                                                                                     |                   |
| The Asst. Secretary of the Navy (R&D)<br>Department of the Navy<br>Room 4E736, Pentagon<br>Washington, D. C. 20350            | 1                    |                                                                                                                                     |                   |
| Commander, Naval Air Systems Command<br>Department of the Navy<br>Washington, D. C. 20360<br>Attn: Code 310C (H. Rosenwasser) | 1                    |                                                                                                                                     |                   |

TECHNICAL REPORT DISTRIBUTION LIST

|                                                                                                                           | <u>No. Copies</u> |                                                                                                                             | <u>No. Copies</u> |
|---------------------------------------------------------------------------------------------------------------------------|-------------------|-----------------------------------------------------------------------------------------------------------------------------|-------------------|
| Dr. W. N. Lipscomb<br>Department of Chemistry<br>Harvard University<br>Cambridge, Massachusetts<br>02138                  | 1                 | Dr. A. Cowley<br>University of Texas<br>Department of Chemistry<br>Austin, Texas 78712                                      | 1                 |
| Dr. R. M. Grimes<br>Department of Chemistry<br>University of Virginia<br>Charlottesville, Virginia<br>22903               | 1                 | Dr. W. Hatfield<br>University of North Carolina<br>Department of Chemistry<br>Chapel Hill, North Carolina<br>27514          | 1                 |
| Dr. M. Tsutsui<br>Department of Chemistry<br>Texas A&M University<br>College Station, Texas 77843                         | 1                 | Dr. D. Seyferth<br>Massachusetts Institute of<br>Technology<br>Department of Chemistry<br>Cambridge, Massachusetts<br>02139 | 1                 |
| Dr. C. Quicksall<br>Department of Chemistry<br>Georgetown University<br>37th & O Streets<br>Washington, D. C. 20007       | 1                 | Dr. M. H. Chisholm<br>Princeton University<br>Department of Chemistry<br>Princeton, New Jersey 08540                        | 1                 |
| Dr. M. F. Hawthorne<br>Department of Chemistry<br>University of California<br>Los Angeles, California 90024               | 1                 | Dr. B. Foxman<br>Department of Chemistry<br>Brandeis University<br>Waltham, Massachusetts 02154                             | 1                 |
| Dr. Alan Siedle<br>National Bureau of Standards<br>Department of Commerce<br>Chemistry Section<br>Washington, D. C. 20375 | 1                 |                                                                                                                             |                   |
| Dr. W. B. Fox<br>Naval Research Laboratory<br>Chemistry Division<br>Code 6130<br>Washington, D. C. 20375                  | 1                 |                                                                                                                             |                   |
| Dr. R. J. Lagow<br>University of Texas<br>Department of Chemistry<br>Austin, Texas 78712                                  |                   |                                                                                                                             |                   |