

## The crystal structure of ferberite, $\text{FeWO}_4$

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### Auszug

Die Kristallstruktur von  $\text{FeWO}_4$  wurde bestimmt und verfeinert aus  $hk0$ -Interferenzen bis  $R = 7,2\%$  und aus  $h0l$ -Interferenzen bis  $R = 5,4\%$ . Die Struktur ist aus W- und Fe-Oktaedern, die endlose zickzackförmige Ketten parallel zur  $c$ -Achse bilden, aufgebaut. Jede Kette enthält nur eine Kationenart, und jedes Oktaeder ist mit dem nächsten durch eine gemeinsame Kante verbunden. Durch gemeinsame Oktaederecken ist jede W-Kette an vier Fe-Ketten gebunden und jede Fe-Kette an vier W-Ketten. Die Atomkonfiguration ist danach anders als die für  $\text{MgWO}_4$  angegebene, in der die Kationen zwar die gleichen Lagen wie im  $\text{FeWO}_4$  einnehmen, aber die W-Atome tetraedrisch vom Sauerstoff umgeben sein sollen.

### Abstract

The crystal structure of ferberite has been determined and refined by projections to  $R$  values of  $7.2\%$  for  $hk0$  reflections and  $5.4\%$  for  $h0l$  reflections. The structure is based on W and Fe octahedra forming infinite zig-zag chains in the direction of the  $c$  axis. Each chain contains just one type of cation and each octahedron is joined to the next by a common edge. Each W-octahedral chain is attached by common corners to four Fe chains, and each Fe chain is also surrounded by four W chains. The atomic configuration is then different from the structure reported for  $\text{MgWO}_4$ , which was believed to be isostructural with the members of the wolframite group, even though the cation positions are proved to be correct.

### Introduction

Ferberite is an end member of the isomorphous series of the wolframites, whose chemical formula is  $(\text{Fe},\text{Mn})\text{WO}_4$ . The different names of the members of the series apply to the particular ranges of composition given on Table 1.

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Table 1. *Iron and manganese content in the wolframite series*

Name	Atomic per cent substitution		Corresponding weight percentages	
	Fe	Mn	FeO	MnO
Hübnerite	0 to 20	100 to 80	0 to 4.8	23.4 to 18.7
Wolframite	20 to 80	80 to 20	4.8 to 18.9	18.7 to 4.7
Ferberite	80 to 100	20 to 0	18.9 to 23.6	4.7 to 0

The minerals of the group are monoclinic, space group  $P2/c$  with two formula units per cell. The first x-ray study of these compounds was made by BROCH<sup>1</sup> in 1929 but the axial ratio and the monoclinic character had been reported by Des Cloizeaux<sup>2</sup> as early as 1850.

BROCH made an x-ray study of several tungstates of the wolframite-type structure and of the scheelite-type structure. He proved by x-ray methods that the isomorphism of the wolframites and  $MgWO_4$  found by optical methods by MACHATSCHKI<sup>3</sup> was correct. He determined the cation positions for  $MgWO_4$  and by comparison of the x-ray data he showed that the same structure was valid for the Zn, Mn, Fe, Co and Ni tungstates and for the minerals hübnerite, wolframite and ferberite. His results are resumed on Table 2.

BROCH made no assumptions on the oxygen positions, but in the *Strukturbericht*, Vol. II, page 85, the following approximate coordinates are suggested for the oxygen atoms:

$$\begin{aligned} x_1 &\sim 0.20 & ; & \quad x_2 \sim 0.20 \\ y_1 &\sim 0.04 & ; & \quad y_2 \sim 0.40 \\ z_1 &\sim 0.10 & ; & \quad z_2 \sim 0.40. \end{aligned}$$

These parameters yield  $WO_4$  tetrahedra in which  $W-O = 1.73 \text{ \AA}$ , and Mg in octahedral coordination with  $Mg-O = 2.24 \text{ \AA}$ .

Crystals of a wolframite from Liquinaste, Argentina<sup>4</sup>, were kindly provided by PABLO KITTL from the National Atomic Energy Comis-

<sup>1</sup> EINAR KLAUMANN BROCH, Untersuchungen über Kristallstrukturen des Wolframittypus und des Scheelittypus. *Norsk Akad., Oslo, Mat.-nat. Kl. Skrifter* No. 8 (1929) 4–61.

<sup>2</sup> A. DES CLOIZEAUX, Sur les formes cristallines du wolfram. *Ann. chim. physique* [3] 28 (1850).

<sup>3</sup> FELIX MACHATSCHKI, Über die Kristallgestalt des Magnesiumwolframates. *Z. Kristallogr.* 67 (1928) 163–165.

<sup>4</sup> ERWIN KITTL, Sobre la Wolframita de Liquinaste, Jujuy. *Revista Minera* 20 (1951) 56–61.

sion, Buenos Aires, Argentina, to be used in a study of two varieties of the mineral with very different specific gravities<sup>5-7</sup>. This material which turned out to be ferberite was used for the complete revision of the crystal structure.

### Unit cell and space group

A large single crystal 4 to 5 cm long was used for a chemical analysis and for measurements of the specific gravity. From it was also detached a small crystal to be used for cell-parameter determination and intensity measurement.

Table 2. *The wolframite-type-structure tungstates*

Substance	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>d</i>
MnWO <sub>4</sub>	4.85 Å	5.77 Å	4.98 Å	89° 7'	7.18 g/cm <sup>3</sup>
Hübnerite	4.83	5.77	4.98	89° 7'	7.25
Wolframite	4.79	5.74	4.99	89° 34'	7.34
Ferberite	4.72	5.70	4.96	90°	7.58
FeWO <sub>4</sub>	4.71	5.70	4.94	90°	7.61
ZnWO <sub>4</sub>	4.69	5.74	4.96	89° 30'	7.79
CoWO <sub>4</sub>	4.67	5.69	4.94	90°	7.76
MgWO <sub>4</sub>	4.69	5.67	4.94	89° 40'	6.88
NiWO <sub>4</sub>	4.69	5.67	4.94	89° 40'	7.78

Space group: monoclinic  $P2/c$

Number of formulas per cell: 2

Atomic positions:

2 wolfram atoms in  $\pm [0 u_1 \frac{1}{4}]$ ;  $u_1 = 0.182 \pm 0.003$

2 divalent cations in  $\pm [\frac{1}{2} u_2 \frac{1}{4}]$ ;  $u_2 = 0.68$

8 oxygen atoms in  $\pm [xyz]$ ,  $\pm [\bar{x}, y, \frac{1}{2} - z]$

The estimated errors are 0.02 Å for the cell edges, and 8' for the angle.

The crystal was oriented on the precession camera with the *a* axis as the spindle axis. The cell parameters and the space group were obtained from two precession photographs, levels 0 and 1, using *b* as the precessing axis, and two photographs, also levels 0 and 1 using *c* as

<sup>5</sup> PABLO KITTL, Sobre la Wolframita liviana de Liquinaste, Jujuy. *Revista Minera* 25 (1960) 3-7.

<sup>6</sup> ERWIN KITTL und PAUL KITTL, Der leichte Wolframit von Liquinaste, Jujuy in Argentinien. *Aufschluß* 16 (1965) 52-54.

<sup>7</sup> CARMEN ESCOBAR and HILDA CID-DRESDNER, The relation between "light wolframite" and common wolframite. [In preparation.]

the precessing axis. The space group is  $P2/c$  and the cell parameters are:

$$a = 4.750 \text{ \AA}, \quad b = 5.720 \text{ \AA}, \quad c = 4.970 \text{ \AA}, \quad \beta = 90^\circ 10'$$

in good agreement with BROCH's results for ferberite given in Table 2.

These cell parameters and the chemical analysis given on Table 3 together with a measured value of  $7.40 \text{ g/cm}^3$  for the specific gravity were used to determine the unit-cell contents.

Table 3. *The wolframite from Liquinaste, Argentina*

Analysis of the mineral	Same recalculated for $(\text{Fe,Mn,Mg})\text{O} \cdot \text{WO}_3$	Unit-cell contents normalized to 8 oxygen atoms
$\text{WO}_3$ : 73.60%	$\text{WO}_3$ : 76.76%	W 2.0
$\text{FeO}$ : 20.28%	$\text{FeO}$ : 21.12%	Fe 1.77
$\text{MnO}$ : 1.21%	$\text{MnO}$ : 1.26%	Mn 0.11
$\text{MgO}$ : 0.82%	$\text{MgO}$ : 0.85%	Mg 0.12
$\text{H}_2\text{O}$ : 0.05%		O 8.0
$\text{ZnO}$ : 0.01%		
$\text{SiO}_2$ : 0.22%		
$(\text{Nb,Ta})_2\text{O}_5 + \text{SnO}_2$ : 3.65%		

The chemical analysis corresponds to a ferberite, of ideal composition  $\text{FeWO}_4$ , with two formula units per cell. The corresponding calculated density is  $7.55 \text{ g/cm}^3$ .

#### Intensity measurement

Since the cell dimensions were favorable for two-dimensional study, only the intensities for the  $hk0$  and  $h0l$  reflections were obtained. Mo radiation and a Zr filter were used for all measurements.

A small crystal of prismatic shape and dimensions  $0.18 \times 0.08 \times 0.06 \text{ mm}$  was used for intensity measurement. The crystal was elongated in the  $a$ -axis direction and it was mounted on the precession camera with this direction parallel to the spindle axis.

The intensities were measured by means of a microdensitometer Kipp from two integrated precession photographs for each reciprocal plane. In order to keep the intensity of the x-ray diffraction spots within the linearity range of the film, a three-cycle integrating precession photograph was used to measure the intense spots and a six-cycle photograph for the weak spots.

The weak and intense reflections were set to a common scale, by comparing the values of the medium-size reflections in both films.

The set of relative intensities were corrected for the Lorentz and polarization factors but not for absorption. It was found that for the dimensions of the crystal the absorption correction would amount to a factor smaller than the reproducibility of our measurements (5 to 7<sup>0</sup>/<sub>0</sub>).

46 *hk0* reflections of which five were less than the minimum observable, and 37 *h0l* reflections were used in the structure determination.

#### Determination and refinement of the structure

Patterson functions  $P(xy)$  and  $P(xz)$  were calculated on a "Lorentz" General Electric computer by means of a two-dimensional Fourier summation program<sup>8</sup> written in ALGOL. The program is set for triclinic symmetry of space group  $P\bar{1}$ .

Space group  $P2/c$  restricts the location of the two W and the two Fe to the special positions *e* and *f*. According to BROCH<sup>1</sup>, the wolframium atoms are located in position *e* of coordinates  $\pm [0y\frac{1}{4}]$  and the Fe atoms are in position *f*:  $\pm [\frac{1}{2}y\frac{1}{4}]$ . This implies that in the *h0l* projection, the W and Fe atoms are fixed, and that in the *hk0* projection only the *y* coordinate of the cations need to be determined.

Atomic scattering curves for W, O and Fe<sup>+2</sup> were used<sup>9</sup> in all structure-factor calculations together with individual isotropic-temperature factors. The initial values of *B* were 0.15 for W<sup>10</sup>, 0.30 for Fe<sup>11</sup> and 0.6 for O<sup>12</sup>.

#### Study of the projection $\rho(xz)$

A structure-factor calculation for the *h0l* reflections based on the position of the W and Fe atoms only (which are fixed) gave an *R* factor

<sup>8</sup> PATRICIO RIVERA, Centro de Computación, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile. [Personal communication, 1966.]

<sup>9</sup> International tables for x-ray crystallography, Vol. III (1962).

<sup>10</sup> R. D. BURBANK, Absolute integrated intensity measurement. Application to CaWO<sub>4</sub> and comparison of several refinements. Acta Crystallogr. **18** (1965) 88–97.

<sup>11</sup> P. COPPENS and M. EIBSCHÜTZ, Determination of the crystal structure of yttrium orthoferrite and refinement of gadolinium orthoferrite. Acta Crystallogr. **19** (1965) 524–531.

<sup>12</sup> HILDA CID-DRESDNER, Determination and refinement of the crystal structure of turquoise, CuAl<sub>6</sub>(PO<sub>4</sub>)<sub>4</sub>(OH)<sub>8</sub> · 4H<sub>2</sub>O. Z. Kristallogr. **121** (1965) 87–113.

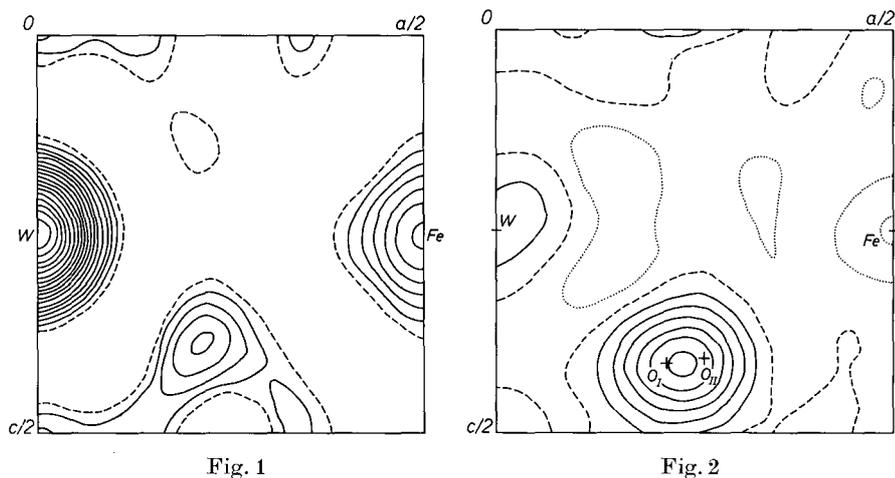


Fig. 1. Electron-density projection  $\rho(xz)$ , based on the signs determined by the W and Fe ions only

Fig. 2. Difference Fourier synthesis  $\Delta\rho_1(xz)$ , calculated with  $(F_o - F_c)$  as coefficients and the signs determined by the W and Fe ions

of 13.9%. The plot of the electron-density function  $\rho(xz)$  based on the signs determined by the two cations only is shown in Fig. 1. There is only one extra peak that could correspond to the positions of  $O_I$  and  $O_{II}$ . A difference Fourier synthesis using as coefficients  $(F_o - F_c)$  with the signs determined by the cations only also showed just one peak, of a height approximately double the expected height of an oxygen atom (Fig. 2). When  $O_I$  and  $O_{II}$  were located within that peak, the  $R$  factor dropped to 5.4%.

#### Study of the projection $\rho(xy)$

In order to determine the  $y$  coordinate of the cations in this projection, a minimum function  $M_2(xy)$  was made, based on a W—Fe peak. The peak was not single due to the strong superstructure of the compound, but the location of the cations was certain from the minimum function. A structure-factor calculation based on the coordinates of the W and Fe only (Fig. 3), with  $y_W = 0.1912$  and  $y_{Fe} = 0.6875$  gave an  $R$  factor of 34%. Three cycles of Fourier refinement (using difference synthesis followed by structure-factor calculations) reduced the  $R$  index to 14%. Only at this stage the coordinates for the oxygen atoms  $O_I$  and  $O_{II}$  shown on the difference

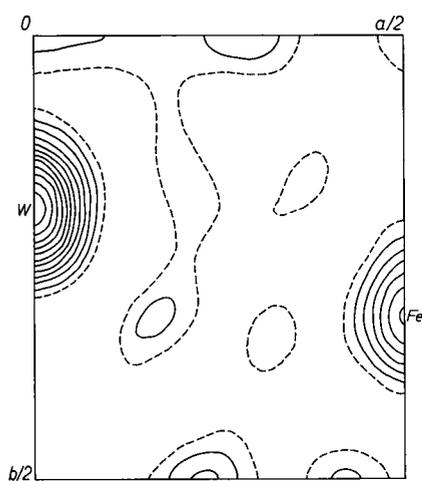


Fig. 3

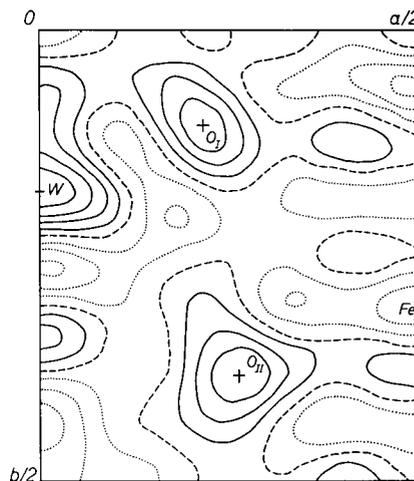


Fig. 4

Fig. 3. Electron-density projection  $\rho(xy)$  based on the signs determined by the W and Fe positions only

Fig. 4. Difference Fourier synthesis  $\Delta\rho_1(xy)$ , calculated with the  $(F_o - F_e)$  coefficients and signs determined by the W and Fe positions for  $R = 14.0\%$

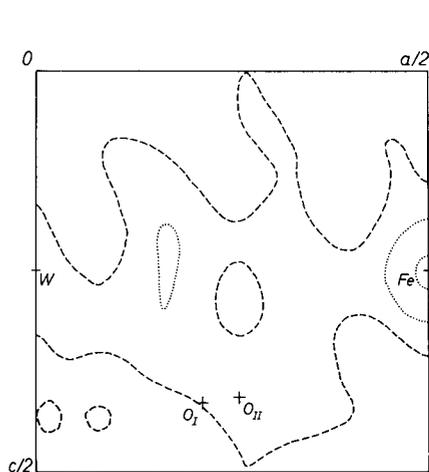


Fig. 5

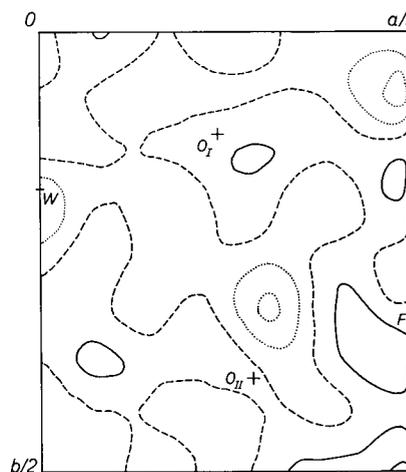


Fig. 6

Fig. 5. Final difference Fourier synthesis,  $\Delta\rho_2(xz)$  for  $R = 5.40\%$

Fig. 6. Final difference Fourier synthesis,  $\Delta\rho_2(xy)$  for  $R = 7.20\%$

Fourier synthesis of Fig. 4 were introduced, maintaining the  $x$  coordinates obtained from the  $\rho(xz)$  projection. A final structure-factor calculation gave an  $R$  value of 7.20% for the  $hk0$  reflections. No further refinement was intended, since the precision of our intensity measurements is not better than 7.0%. Figures 5 and 6 are the difference Fourier projections  $\Delta\rho(xz)$  and  $\Delta\rho(xy)$  calculated after the refinement was completed.

### Description and discussion of the structure

The final atomic coordinates and isotropic temperature factors for the ferberite structure are listed in Table 4. A comparison of the observed and calculated structure factors for the refined structure is given in Table 5.

Table 4. *Final atomic coordinates of ferberite*

Atom	$x_j$	$y_j$	$z_j$	$B_j$
W	0	0.1808	1/4	0.20
Fe	1/2	0.3215	3/4	0.40
O <sub>I</sub>	0.2158	0.1068	0.5833	0.6
O <sub>II</sub>	0.2623	0.3850	0.0912	0.6

Table 5. *Calculated and observed structure factors of ferberite*

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
0	0	2	119.7	-140.4	3	0	0	71.3	67.2	0	1	0	46.6	40.2
4			106.4	105.5	2			58.0	-51.6	2			95.0	-98.3
6			95.0	-100.5	-2			95.0	-88.5	3			71.3	-71.6
1	0	0	101.7	96.6	4			70.3	70.9	4			58.0	-47.3
			108.3	-114.5	-4			52.3	47.6	5			54.2	-52.3
			59.4	-43.5	6			40.1	-47.6	6			85.5	78.5
			52.3	47.5	-6			45.6	43.7	7			0	-9.0
			81.7	80.5	4	0	0	131.1	131.6	8			50.4	-64.6
			52.3	-50.7	-2			94.1	-98.5	1	0	0	101.7	96.6
			56.1	-53.9	-2			107.4	-103.9	1			89.3	80.5
2	0	0	123.5	117.9	4			85.5	88.7	2			54.2	-53.1
			156.8	-158.5	-4			78.9	81.1	3			129.2	-139.5
			155.4	-149.1	5	0	0	66.5	60.8	4			0	-11.3
			114.0	118.8	2			57.0	-61.7	5			86.5	87.3
			118.8	121.3	-2			40.1	-43.7	6			50.4	47.0
			71.3	-74.2	4			39.9	41.9	7			0	-6.5
			73.2	-72.6	-4			54.2	53.1	2	0	0	123.5	117.9
					6	0	0	70.3	78.1	1			43.7	33.8
					2			75.1	-87.3	2			102.6	-97.7
					-2			76.7	-81.2	3			75.1	-70.4
										4			0	-2.2
										5			54.2	50.2
										6			89.3	87.8
										7			0	-4.6
										3			46.6	39.0
										5			46.6	38.0
										6	0	0	70.3	78.1
										1			24.7	23.5
										2			46.6	-53.7
										3			39.0	-47.7

The structure can be described in terms of infinite zig-zag chains of octahedral groups of oxygen atoms around the cations. The octahedral chains follow the direction of the  $c$  axis and are formed by either W octahedra only, or Fe octahedra only (Figs. 7 and 8). Each W octahedron shares two edges with two other W octahedra and shares four corners with four Fe octahedra which belong to four different Fe zig-zag chains.

The arrangement and environment of the Fe octahedra in the structure is similar to that described for the W octahedra (Fig.9). This type of structure leaves open channels in the  $c$  direction.

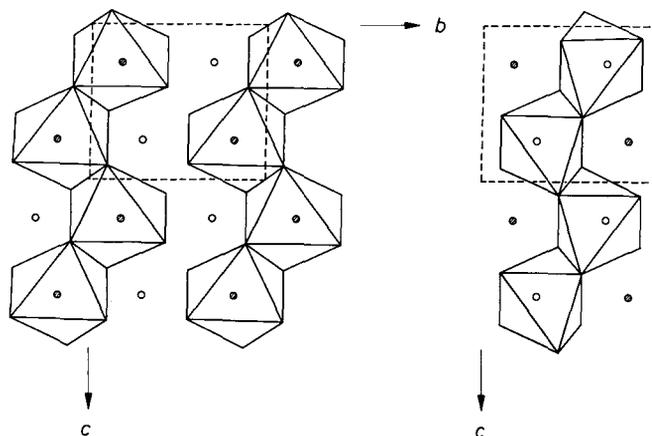


Fig.7. The W and Fe octahedral chains in the ferberite structure projected on the (100) plane. Black circles represent W atoms and white circles, Fe atoms. The W and Fe zig-zag chains are shown separately to simplify the drawing

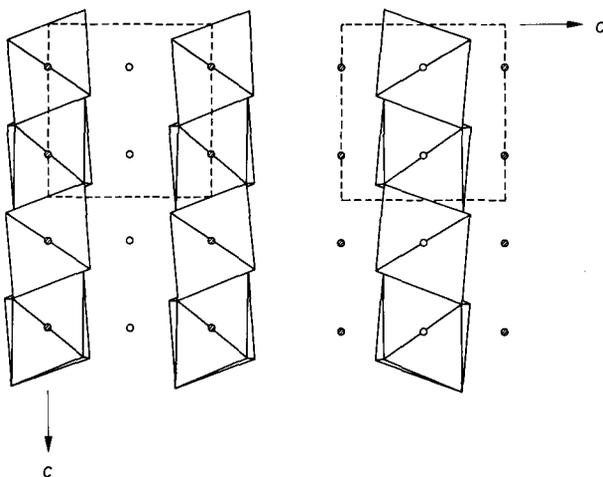


Fig.8. Same as Fig.7 projected on the (010) plane

Table 6 and Table 7 list the principal interatomic distances in the structure and the octahedral angles, respectively. The average Fe—O

Table 6. *Principal interatomic distances in ferberite*

Atom pair	Multiplicity	Distance	Atom pair	Multiplicity	Distance
W octahedron			Fe octahedron		
W—O <sub>I</sub> (1)	2	1.99 Å	Fe—O <sub>I</sub> (1')	2	1.95 Å
W—O <sub>I</sub> (2)	2	2.11	Fe—O <sub>II</sub> (1)	2	2.17
W—O <sub>II</sub> (1)	2	2.08	Fe—O <sub>II</sub> (2)	2	2.02

Table 7. *Octahedral bond angles in the ferberite structure*

Atoms	Multiplicity	Angle	Atoms	Multiplicity	Angle
W octahedron			Fe octahedron		
O <sub>I</sub> (1)—W(1)—O <sub>I</sub> (4)	1	155° 40'	O <sub>II</sub> (1)—Fe(1)—O <sub>II</sub> (4)	1	139° 10'
O <sub>II</sub> (4)—W(1)—O <sub>I</sub> (2)	2	176° 40'	O <sub>II</sub> (3)—Fe(1)—O <sub>I</sub> (1')	2	167° 30'
O <sub>II</sub> (1)—W(1)—O <sub>I</sub> (2)	2	96° 20'	O <sub>I</sub> (1')—Fe(1)—O <sub>I</sub> (4)	1	109°
O <sub>I</sub> (2)—W(1)—O <sub>I</sub> (3)	1	77° 20'	O <sub>II</sub> (1)—Fe(1)—O <sub>II</sub> (3)	2	74° 10'
O <sub>II</sub> (1)—W(1)—O <sub>II</sub> (4)	1	90° 10'	O <sub>II</sub> (2)—Fe(1)—O <sub>II</sub> (3)	1	98°
O <sub>I</sub> (1)—W(1)—O <sub>I</sub> (2)	2	84° 50'	O <sub>II</sub> (2)—Fe(1)—O <sub>II</sub> (1)	2	76°
O <sub>I</sub> (1)—W(1)—O <sub>I</sub> (3)	2	76°	O <sub>II</sub> (1)—Fe(1)—O <sub>II</sub> (1')	2	100° 10'
O <sub>I</sub> (1)—W(1)—O <sub>I</sub> (4)	2	99° 10'	O <sub>II</sub> (4)—Fe(1)—O <sub>I</sub> (1')	2	103° 20'
O <sub>I</sub> (1)—W(1)—O <sub>II</sub> (4)	2	98° 20'	O <sub>II</sub> (2)—Fe(1)—O <sub>I</sub> (1')	2	82° 30'

distance is 2.05 Å, much shorter than the 2.14 and 2.17 Å average values reported for the Fe<sup>+2</sup>—O bond in ludlamite<sup>13,14</sup>.

The W—O distances in the W octahedron range from 1.99 to 2.11 Å. The only well-refined structure, we could find, which reported a wolfram atom octahedrally coordinated is the WO<sub>3</sub> structure done with neutron-diffraction data<sup>15</sup>. The minimum and maximum values for the W—O bond are 1.73 and 2.17 Å respectively; the ferberite values fall within this range.

In the ferberite structure both cations are located on two fold axes, so that all octahedra show a two fold symmetry. The distortion of the W and Fe octahedra can be better appreciated from the deviation from the ideal values of the angles listed on Table 7. The Fe octahedron is the more distorted; the value of 139° 10' found for the

<sup>13</sup> S. C. ABRAHAMS and J. L. BERNSTEIN, Crystal structure of paramagnetic ludlamite, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O, at 298°K. *J. Chem. Physics* **44** (1966) 2223—2229.

<sup>14</sup> S. C. ABRAHAMS, Ferromagnetic and crystal structure of ludlamite, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O, at 4.2°K. *J. Chem. Physics* **44** (1966) 2230—2237.

<sup>15</sup> B. O. LOOPSTRA and P. BOLDRINI (1966), Neutron diffraction investigation of WO<sub>3</sub>. *Acta Crystallogr.* **21** (1966) 158—162.

$\text{O}_{\text{II}}(1)\text{—Fe}(1)\text{—O}_{\text{II}}(4)$  angle differs almost  $41^\circ$  from the ideal  $180^\circ$  value. Unfortunately it was not possible to compare this value with others, since most of the literature on iron compounds do not give this type of data.

There is no doubt that the structure determined for ferberite is also the structure of the whole wolframite group. It is very likely that this is also the structure of  $\text{MgWO}_4$  which BROCH<sup>1</sup> showed to be

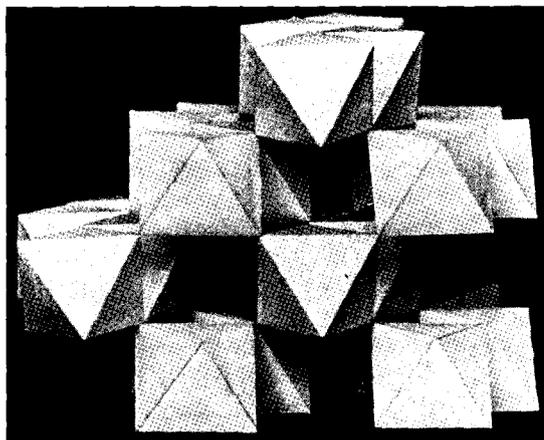


Fig. 9. Polyhedral representation of an idealized ferberite structure viewed along the  $c$  axis. The  $b$  axis is set horizontally and the  $a$  axis is in the vertical position

isostructural with the wolframites, which was reported with the W ion tetrahedrally coordinated to the oxygen atoms. A revision of the  $\text{MgWO}_4$  structure is actually in progress.

#### Acknowledgements

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*Note added in proof:* At the same time this paper was sent for publication, D. ÜLKÜ's paper "Zur Kristallstruktur und magnetischen Struktur des Fer-

berits" appeared<sup>16</sup>. There are some differences between his results and the results of this work. At first glance, one could attempt to explain these differences from the fact that ÜLKÜ used three-dimensional data and performed least-squares refinement, compared to the two-dimensional data and Fourier refinement of this work. The intensity measurements are comparable, so ÜLKÜ's results should be more accurate.

There is however a fact in ÜLKÜ's work which makes necessary some discussion. A comparison of the  $R$  values obtained in both cases considering only the Fe and W atoms in the cell is shown below:

	ÜLKÜ's work	This work
$R_{h0l}$	11.5 <sup>0</sup> / <sub>0</sub>	13.9 <sup>0</sup> / <sub>0</sub>
$R_{hko}$	9.8 <sup>0</sup> / <sub>0</sub>	14 <sup>0</sup> / <sub>0</sub>
$R_{0kl}$	7.2 <sup>0</sup> / <sub>0</sub>	—

The results are similar only on the  $(h0l)$  projection, in which the W and Fe atoms have coordinates fixed by the space group. This projection (where the coordinates cannot be wrong) yields the highest  $R$  value in ÜLKÜ's work. Unless his x-ray data for the  $(h0l)$  projection were considered to be less reliable, one should accept the possibility that there has been some problem in the refinement. The structure could be "over refined", due, for example, to interactions among those parameters allowed to vary at the same time in the refinement procedure. (A study of the Geller matrix<sup>17</sup> searching for high interactions is not mentioned in ÜLKÜ's work).

In order to check the degree of refinement of the present structure, a calculation of structure factors was made using ÜLKÜ's atomic coordinates and our x-ray data. Had the results reported here needed more refinement, this calculation should have yielded a lower  $R$  factor. The results obtained were  $R_{h0l} = 7.1^0/0$  and  $R_{hko} = 7.1^0/0$ , as compared to  $R_{h0l} = 5.4^0/0$  and  $R_{hko} = 7.2^0/0$  referred to above.

There existed still the possibility of errors in the atomic positions reported here due to superpositions of atoms on the projections  $(h0l)$  or  $(hk0)$  used. A structure-factors calculation performed with ÜLKÜ's  $(0kl)$  x-ray data and the atomic coordinates of Table 4 yielded  $R_{0kl} = 4^0/0$ . This was considered to be an evidence of the good state of refinement of our structure and of the fact that the data used was sufficient to determine it.

<sup>16</sup> DİNÇER ÜLKÜ (1967), Untersuchungen zur Kristallstruktur und magnetischen Struktur des Ferberits  $\text{FeWO}_4$ . Z. Kristallogr. **124**, 192–219.

<sup>17</sup> S. GELLER (1961), Parameter interaction in least squares refinement. Acta Crystallogr. **14**, 1026–1035.