

The crystal structure of triplite, $(\text{Mn,Fe})_2\text{FPO}_4$

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(Received 20 January 1969)

Auszug

Die Kristallstruktur des Minerals Triplit, $(\text{Mn,Fe,Mg,Ca})_2\text{FPO}_4$, wurde mit Hilfe von Minimumfunktionen bestimmt und nach der Methode der kleinsten Quadrate mit dreidimensionalen Daten bis zu einem R -Wert von 4,90% verfeinert. Die Struktur besteht aus isolierten PO_4 -Tetraedern, die über Ecken mit verzerrten MO_4F_2 -Oktaedern verknüpft sind. Diese Oktaeder sind über gemeinsame Kanten zu Ketten verbunden. Die M(1)-Oktaederketten verlaufen parallel zu b , die M(2)-Oktaederketten parallel zu a . Die F-Atome sind auf zwei jeweils halb besetzte Punktlagen, die voneinander einen Abstand von 0,62 Å haben, verteilt. In diesem Material aus dem Pegmatit von Mica Lode, Colorado, scheinen die Metallatome Mn, Fe, Mg und Ca grundsätzlich ungeordnet auf die beiden Metallpunktlagen verteilt zu sein.

Abstract

The crystal structure of triplite, $(\text{Mn,Fe,Mg,Ca})_2\text{FPO}_4$, has been determined using minimum-function methods. A three-dimensional, least-squares refinement reduced the discrepancy index R to 4.90%. The structure is composed of isolated PO_4 tetrahedra joined by vertices to distorted MO_4F_2 octahedra. These octahedra are linked into chains by shared edges. The chains of M(1) octahedra are parallel to b , those of M(2) octahedra parallel to a . The F atoms are distributed between two half-occupied sites, separated by 0.62 Å. In this material from the Mica Lode pegmatite, Colorado, the metal atoms Mn, Fe, Mg, Ca appear to be essentially disordered between the two metal sites.

Introduction

The minerals triplite, $(\text{Mn,Fe})_2\text{FPO}_4$, and triplidite, $(\text{Mn,Fe})_2(\text{OH})\text{PO}_4$, differ in composition by the substitution of F ions in one for OH ions in the other. Since the F and OH ions have approximately the same size and bonding characteristics, many such pairs of minerals or inorganic compounds are isotypic, like the well-known pair, fluorapatite and hydroxyapatite. An exception is found

in triplite and triploidite, since they have different space groups and cell dimensions.

Structure determinations of these interesting non-isotypic minerals were undertaken. The preliminary findings on triplite and triploidite have been published, WALDROP (1968*a,b*). This paper reports the results of the study of triplite.

Experimental data

Cell dimensions and space group

Translucent brown cleavage fragments from the pegmatite from Mica Lode, Fremont County, Colorado, were chosen for the structure determination of triplite. These were made available through the kindness of Professor CLIFFORD FRONDEL of Harvard University. A description of material from this locality was given by WOLFE and HEINRICH (1947). They reported a measured specific gravity of 3.64. HEINRICH (1951) gave the composition of crystals from Mica Lode as $\text{Mn}_{0.95}\text{Fe}_{0.25}\text{Mg}_{0.7}\text{Ca}_{0.1}\text{FPO}_4$.

Least-squares refinement of spacing values based on measurements of $0kl$ and $h0l$ back-reflection Weissenberg photographs gave the unit-cell dimensions

$$\begin{aligned} a &= 12.065 \pm 0.001 \text{ \AA}, \\ b &= 6.454 \pm 0.001 \text{ \AA}, \quad \beta = 107.093 \pm 0.006^\circ, \\ c &= 9.937 \pm 0.001 \text{ \AA}. \end{aligned}$$

These are in agreement with values reported by RICHMOND (1940) and WOLFE and HEINRICH (1947). There are eight formula units per cell.

Since there was a possibility that triplite might have a doubled b axis, like triploidite, several b -axis rotation photographs with $\text{CuK}\alpha$ radiation were taken with varying degrees of overexposure. There was no indication of additional layer lines.

Triplite was assigned the space group $P2_1/a$ by RICHMOND (1940). WOLFE and HEINRICH (1947) suggested $I2/m$. From complete sets of b - and c -axis precession photographs the following reflections were found to be present:

$$\begin{aligned} hkl: & h + k + l = 2n; \\ h0l: & h = 2n, l = 2n. \end{aligned}$$

Even on overexposed $h0l$ photographs no reflections could be found with h odd. These findings suggested one of the two space groups $I2/a$ or Ia .

Strong evidence pointed to the centrosymmetric space group $I2/a$. First, the Harker section at $y = 0$ had more strong peaks than other sections of the Patterson map. Also, refinement of the structure in space group Ia did not improve the discrepancy index R and gave atomic coordinates in agreement with those of the centrosymmetric model to within one standard deviation.

A complete set of b -axis precession photographs was also made with an iron-rich triplite from Zwiesel, Bavaria. This material, sometimes referred to as zwieselite, has been shown by OTTO (1935) to have an Fe:Mn ratio of 2.3:1. A careful visual, layer-by-layer comparison of these photographs with the corresponding ones for triplite showed the reflection intensities to be identical.

Intensity measurements

For intensity measurements a single crystal of triplite was ground to a sphere of radius 0.13₉ mm. Integrated intensities for 348 reflections were measured by the fixed-counter, rotating-crystal method on an equi-inclination diffractometer. A xenon-filled proportional counter with associated pulse-height analysis circuitry was used as a detector. Manganese-filtered $FeK\alpha$ radiation was employed. After the intensities were corrected for absorption, Lorentz and polarization effects, they were converted to F_o , which were put on an absolute scale by the WILSON (1942) method.

Determination and refinement of the structure

Structure determination

Since the triplite formula contains Mn, one might expect to solve the structure by the heavy-atom method. But in crystals from the Mica Lode pegmatite, Mg substitutes for some of the Mn so that the average scattering power of the metal is roughly equivalent to that of Ca.

A powerful alternative approach for unraveling the Patterson is through image seeking using the minimum function, as suggested by BUEGER (1959). In some cases one can begin by finding a single-weight inversion peak in the Patterson function, but in triplite, single-weight inversion peaks and double-weight rotation peaks are submerged in the background. A careful study of the Patterson reveals a different way to get a beginning image.

In the $P(x0z)$ section of the Patterson function, given as Fig. 1, an interpretation can be suggested for the peaks labeled A , B and C . Since the distance from the origin is 1.6 \AA for peak A and 2.0 \AA for peak B , it seems unlikely that they are Harker peaks. Peak C is 2.0 \AA from A and 1.6 \AA from B . The heights of the three peaks also suggest that A , B and C are multiple peaks associated with P—O, M—O and M—P vectors respectively; since triplite crystals from various localities differ in composition, a general designation of M is used here for the metal atom. So it appears likely that the three atoms, M, P and O, have the same y coordinate with relative locations given by the triangle having the origin, A and C as vertices.

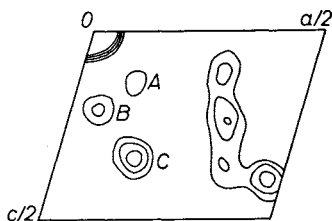


Fig.1. $P(x0z)$ section of the Patterson function for triplite

Using the triangle of peaks, origin, A , C , as an image, a three-dimensional minimum-function $M_3(xyz)$ was computed. The $M_3(xyz)$ function suggested three possible locations for the triangle of atoms. Since only one of the three sites was consistent with information contained in the Harker section and the Harker line of the Patterson function, this location was accepted; thus the coordinates for the atoms M(2), P, O(2) were determined. Now the peaks which were symmetry-equivalent to the original three peaks could be added to the image to give an image of twenty-four peaks. The new minimum-function map $M_{24}(xyz)$ gave the positions of two more oxygen atoms.

From interatomic-distance considerations it seemed likely that several badly distorted peaks represented the other missing atoms. However, only the five atom positions which appeared certain were used to calculate structure-factor signs. A Fourier synthesis based on all the observed F 's and these signs confirmed the positions of the missing M, O and F atoms. Using $B = 0.8 \text{ \AA}^2$ for all atoms, this model gave a discrepancy index R of 30%.

Refinement

A full-matrix, least-squares refinement was carried out using the program SFLSQ3, written by CHARLES PREWITT. Each cycle made use of corrections for anomalous scattering. All reflections were included except five which had large extinction effects. With equal weights for all reflections, three cycles of refinement of scale factor and coordinates, followed by two cycles of refinement of isotropic temperature factors, reduced the R to 8.20%.

At this point the weighting scheme proposed by WUENSCH (1964) was adopted. First the value of R was calculated as a function of F_o . Then a weighting function was computed in which the product of weight and R is constant for all F_o .

The model was acceptable except for some aspects of its representation of the F atom. The isotropic B value for F was 4.2 Å². Of the four M—F distances, 2.06, 2.57, 2.44 and 2.03 Å, two were somewhat larger than normal. Also, WALDROP (1968*a,b*) has shown that the atomic positions of triploidite and triplite are approximately the same, except for the splitting of one OH site into two in triploidite. Thus it appeared desirable to investigate the effect of splitting the F site into two sites, each of which could be considered to be half-filled on the average. The two half-filled sites adopted were derived from the OH positions found in triploidite.

Three cycles of scale-factor and coordinate refinement, followed by a cycle of isotropic B refinement of this adapted model, reduced the R value to 5.50%. The B 's for the two half-filled sites were lowered to 1.4 Å². In addition, the M—F distances were improved, as will be discussed later in more detail. The separation of the two F sites is 0.62 Å.

Ordering of metal atoms

This improved model gave isotropic B values of 0.4 Å² and 1.1 Å² for the two metal sites. Thus it was likely that some order was present among the four metals Mn, Fe, Mg, Ca.

Many authors have pointed out that the scattering curve for a site occupied by two different cations can be expressed as the weighted average of the curves for the two individual cations. Expanding this concept to sites occupied by three cations, one can consider the scattering curves $f_{M(1)}$ and $f_{M(2)}$ for metal atoms in the two sites to be

$$f_{M(1)} = c_a f_{Mn, Fe} + c_b f_{Ca} + (1 - c_a - c_b) f_{Mg}$$

and

$$f_{M(2)} = c_c f_{Mn, Fe} + c_a f_{Ca} + (1 - c_c - c_a) f_{Mg}$$

where f_{Ca} , f_{Mg} , $f_{Mn, Fe}$ are the scattering curves of Ca, Mg and averaged Mn, Fe respectively and c_a , c_b , c_c , c_d are refinable parameters. Actually only c_a and c_b are refined since their values fix those of c_c and c_d respectively, because $c_a + c_c$ represents the amount of Mn, Fe present per formula unit and $c_b + c_d$ represents the corresponding amount of Ca present.

A correlation matrix was computed for the scale factor, c_a , c_b and all the isotropic B 's. As suspected, the correlations were quite high among c_a , c_b and the B 's for the metal sites, $B_{M(1)}$, $B_{M(2)}$. Since high correlation between refined parameters can sometimes cause meaningless results, two precautions were taken. First, in order to prevent the interaction of the four correlated parameters, each refinement step was divided into four parts:

1. refinement of c_a , scale factor, coordinates,
2. refinement of c_b , scale factor, coordinates,
3. refinement of all B 's, except $B_{M(1)}$,
4. refinement of all B 's, except $B_{M(2)}$.

The second precaution was to carry out the refinement of the metal-site occupancy twice; two different sets of beginning values for c_a , c_b , $B_{M(1)}$, $B_{M(2)}$ were refined to convergence.

The first model of metal-site occupancy began with an equal distribution of atoms in the two sites and with the B 's established in earlier cycles: $c_a = 0.6$, $c_b = 0.05$, $B_{M(1)} = 0.4 \text{ \AA}^2$, $B_{M(2)} = 1.1 \text{ \AA}^2$. The refinement slowly converged to the following values: $c_a = 0.696 \pm 0.007$, $c_b = 0.051 \pm 0.007$, $B_{M(1)} = 0.67 \pm 0.03 \text{ \AA}^2$, $B_{M(2)} = 0.77 \pm 0.04 \text{ \AA}^2$.

The second beginning model of metal-site occupancy was deliberately chosen to test the sensitivity of the refinement to the starting position. The new c_a value of 0.40 was below the disorder value of 0.6, in contrast to the value of 0.7 just obtained. To make certain that the final value of c_a had not resulted from the original unequal values for $B_{M(1)}$, $B_{M(2)}$, the $B_{M(1)}$, $B_{M(2)}$ values were both set at 0.5 \AA^2 in this second model. The starting values were $c_a = 0.40$, $c_b = 0.05$, $B_{M(1)} = 0.5 \text{ \AA}^2$, $B_{M(2)} = 0.5 \text{ \AA}^2$. Although these values were somewhat different from those of the first model, the final parameters were

similar, specifically $c_a = 0.717 \pm 0.007$, $c_b = 0.052 \pm 0.007$, $B_{M(1)} = 0.66 \pm 0.03 \text{ \AA}^2$, $B_{M(2)} = 0.62 \pm 0.04 \text{ \AA}^2$.

Thus, in spite of the high correlation, both refinements of the metal-site occupancy converged to approximately the same values of c_a , c_b , $B_{M(1)}$, $B_{M(2)}$. Average values are $c_a = 0.71$, $c_b = 0.05$, $B_{M(1)} = 0.66 \text{ \AA}^2$, $B_{M(2)} = 0.69 \text{ \AA}^2$; so

$$\text{Metal site 1} = 0.71 (\text{Mn, Fe}) + 0.05 \text{ Ca} + 0.24 \text{ Mg},$$

$$\text{Metal site 2} = 0.49 (\text{Mn, Fe}) + 0.05 \text{ Ca} + 0.46 \text{ Mg}.$$

Although the values of c_a and c_b are probably not as reliable as the standard deviations given above would indicate, one can safely assume for the Mica Lode material that there is only a small degree of metal ordering and that metal site 1 contains slightly less Mg than site 2.

Though the distribution of metal atoms in the Mica Lode triplite appears to be nearly random, this may not be true of crystals from all localities. HAAPALA and OJANPERÄ (1969) point out that triplite from Eurajoki, Southwestern Finland, exhibits diffraction symmetry compatible with the space groups $I2/m$, Im , $I2$. The $h0l$ reflections display a pronounced pseudo $I2/a$ or Ia symmetry, but weak reflections with h odd show the true symmetry to be $I2/m$, Im , $I2$. These additional reflections in the Eurajoki material probably result from

Table 1. *Final positional parameters and isotropic temperature factors of triplite*

Atom	Set of equivalent positions		x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
	Designation	Occupancy								
M(1)*	8f		0.1927	0.0002	0.9815	0.0003	0.1921	0.0002	0.66 \AA^2	0.03 \AA^2
M(2)*	8f		0.0931	0.0002	0.1442	0.0003	0.4503	0.0002	0.69	0.04
P	8f		0.0743	0.0002	0.6546	0.0004	0.3798	0.0002	0.50	0.04
O(1)	8f		0.0556	0.0004	0.8301	0.0009	0.4752	0.0005	0.72	0.10
O(2)	8f		0.9606	0.0004	0.6066	0.0009	0.2666	0.0005	0.77	0.10
O(3)	8f		0.1673	0.0004	0.7124	0.0009	0.3091	0.0005	0.82	0.10
O(4)	8f		0.1165	0.0004	0.4630	0.0009	0.4739	0.0005	0.59	0.10
F(1)	8f	$\frac{1}{2}$	0.2591	0.0008	0.1227	0.0016	0.3947	0.0010	1.36	0.18
F(2)	8f	$\frac{1}{2}$	0.2786	0.0008	0.1694	0.0017	0.3521	0.0010	1.43	0.18

* In the Mica Lode triplite, M(1) represents $(\text{Mn, Fe})_{5.7}\text{Ca}_{0.4}\text{Mg}_{1.9}$ and M(2) represents $(\text{Mn, Fe})_{3.9}\text{Ca}_{0.4}\text{Mg}_{3.7}$.

Table 2. Observed and calculated structure amplitudes
Unobserved reflections are designated *. In brackets: reflections suffering from extinction

h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $	h k l	$ F_o $	$ F_c $								
0 0 4	55.4	50.3	3 1 8	66.4	71.7	2 2 0	85.6	85.8	1 3 0	55.1	63.2	2 4 -4	9.0	2.4								
0 0 2	40.2	41.7	4 1 -9	25.4	25.6	2 2 2	81.1	80.1	2 2 2	15.3	14.5	4 1 -2	126.8	124.1								
0 0 4	32.4	31.2	-7	52.4	50.0	4 4 0	68.0	67.5	4 4 0	8.3	4.6	0 129.1	122.5									
2 0 -8	11.4	13.2	-5	111.4	111.8	6 6 0	56.1	57.5	6 6 0	54.2	52.7	2 50.0	44.4									
-6	92.1	95.4	-5	25.3	26.6	8 8 0	66.7	62.9	2 3 -7	66.7	62.9	4 48.2	43.7									
-4	118.6	121.4	-1	105.0	106.3	3 2 -9	11.4	10.9	-5	154.6	151.3	6 29.0	27.0									
-2	9.4	9.4	1	38.9	40.2	-7	57.3	59.0	-3	86.1	84.2	3 4 -7	57.9	56.9								
2 [199.9]	242.0	3 27.8	28.0	-5	87.3	86.9	-1	74.7	69.5	-1	74.7	69.5	-5	45.1	40.7							
4 [198.8]	214.0	5 62.9	64.7	-5	18.1	17.1	-3	18.1	17.1	1	98.3	99.9	-3	7.1	5.3							
6 43.0	41.1	6 43.0	41.1	-1	106.8	105.9	3	183.0	183.4	3	183.0	183.4	-1	9.8	6.8							
8 115.0	124.0	5 1 -8	82.6	85.7	1 11.7	11.3	5 152.6	153.9	5 152.6	153.9	1 111.2	107.7										
4 0 -8	9.8	10.9	-6	93.4	97.0	3 32.7	32.7	7 43.9	40.7	3 37.1	37.1											
-6	52.2	50.3	-4	21.9	22.6	5 40.1	53.0	3 3 -8	24.9	23.8	5 7.1	5.6										
-4	80.5	81.0	-2	106.5	105.2	7 19.1	19.9	-6	43.5	44.4	4 4 -6	54.6	53.5									
-2 [262.1]	327.8	0 21.8	18.8	2 46.4	44.3	4 2 -8*	2.9	1.7	-4	113.7	109.2	-4	94.6	91.6								
0 69.3	69.1	2 46.4	44.3	-6	89.7	92.1	-2	42.0	39.6	-2	42.0	39.6	-2	73.7	66.7							
2 82.3	85.8	4 57.5	56.2	-4	112.8	113.1	0	63.1	60.4	0 13.2	9.1											
4 9.2	1.5	6 58.8	61.6	-2	89.3	85.8	-2	57.9	53.9	2 23.4	13.2											
6 20.6	19.5	6 1 -9	68.9	70.2	0 12.4	11.0	4 21.1	19.7	4 92.4	92.3												
-8	73.9	73.9	-7*	3.6	1.0	2 8.2	9.0	6 41.5	43.0	5 4 -7	25.3	23.1										
-6	155.5	159.9	-5	97.5	96.2	4 114.9	118.5	4 3 -7	131.7	134.5	-5	64.9	63.2									
-4	12.2	10.1	-6	86.2	84.1	6 51.0	52.2	-5	100.1	96.9	-5	115.9	109.7									
-2	92.7	91.1	-1	136.8	135.6	5 2 -9*	1.9	1.5	-3	55.0	49.5	-1	7.1	5.0								
0 112.9	117.3	1 31.6	28.2	-7	17.8	17.9	-1	127.9	122.6	1 10.4	5.1											
2 [195.7]	212.5	3 51.8	51.3	-5	103.6	101.4	3 157.2	154.0	3 157.2	154.0	3 18.2	21.8										
4 94.5	95.1	5 31.8	32.9	-3	135.2	135.2	-3	135.2	135.2	6 4 -6	14.5	12.4										
6 29.9	30.7	7 1 -2	32.4	34.4	-1	27.4	26.2	4 82.8	82.8	4 11.3	7.2											
8 0 -8	32.1	29.4	-6	104.0	106.0	1 107.8	109.5	5 3 -8	15.8	15.5	-2	48.0	42.1									
-6	17.5	11.9	-4	10.8	14.1	3 62.3	61.3	-6	50.0	48.8	0 144.9	143.8										
-4	124.5	123.9	-2	8.7	7.8	5 45.0	62.1	-4	50.0	50.6	2 16.4	14.2										
-2	111.5	107.5	0 94.0	94.1	6 2 -8*	2.6	3.1	-2	7.2	5.9	7 4 -5*	2.2	3.2									
0 135.6	135.2	2 90.2	93.6	-6	66.3	66.6	0 15.0	12.1	-0	15.0	12.1	-3	50.7	50.7								
2 35.0	29.6	4 4.1	10.8	-2	59.7	56.3	2 21.8	63.3	2 21.8	63.3	1 78.2	77.5										
4 52.6	55.5	8 1 -7	28.5	27.1	-2	64.3	63.9	4 71.3	69.1	1 25.1	23.1											
-6	30.9	28.6	-5	44.7	44.8	0 67.5	65.9	6 3 -7	67.6	70.0	8 4 -4	24.3	24.6									
-4	35.7	32.7	-3	118.2	113.7	2 56.2	52.3	-5	55.7	53.4	-2	8.1	4.9									
-2	92.1	91.6	-1	18.2	14.7	4 22.8	21.3	-3	76.2	73.5	0 11.3	3.0										
0 57.2	59.4	1 31.2	28.0	7 2 -2	55.3	55.5	-1	45.3	42.2	0 5 1	40.7	40.4										
2 61.1	60.2	3 101.3	105.0	-5	15.2	12.3	1 107.1	106.7	1 107.1	106.7	3 51.8	54.7										
0 1 1	30.9	28.5	9 1 -8	70.2	73.6	-3	104.4	101.4	3 103.5	104.1	5 33.1	33.3										
3 147.7	152.0	-6	38.2	39.1	-1	99.6	96.8	5 5 5	5.8	7.1	1 5 -4	41.1	40.2									
5 102.5	102.7	1 39.3	28.4	4 4.8	6.7	1 34.9	36.8	7 3 -6	35.9	36.0	-2	64.6	66.7									
7 12.7	13.5	-2	7.3	2.8	5 27.1	28.6	-4*	3.3	3.4	0 48.5	47.1											
9 48.3	51.6	0 34.0	29.6	5 23.6	23.5	-2	41.3	42.5	-2	41.3	42.5	2 20.6	16.7									
1 1 -8	18.8	20.6	2 74.9	78.8	8 2 -8	60.0	64.0	0 26.4	24.2	4 20.0	15.5											
-6	33.5	36.2	10 1 -7	65.4	64.6	-6	10.1	8.8	2 51.6	48.2	2 5 -5	60.1	62.0									
-4	73.4	69.4	2 21.0	20.1	-4	16.3	15.2	4 8.1	6.5	-3	22.7	24.4										
-2*	2.8	1.2	-3	45.4	44.4	-2	69.3	66.7	8 3 -7	100.3	102.3	-1	26.3	25.8								
0 3.1	4.3	-1	9.6	5.7	0 10.2	7.4	-5	18.6	17.1	1 20.8	22.1											
2 118.5	126.2	1 12.7	10.6	2 74.3	73.0	-3	23.5	23.5	-3	23.5	23.5	3 45.7	46.7									
4 55.5	55.9	11 1 -4	14.0	17.8	4 4.8	6.7	-1	13.9	11.4	3 5 -4	35.1	30.9										
6 87.5	87.5	-3	26.9	26.3	1 34.9	36.8	9 2 -7	62.1	62.2	0 38.1	37.0											
8 34.2	35.5	0 66.2	67.8	-5	55.7	54.3	3 12.9	14.5	3 12.9	14.5	0 58.1	59.0										
2 1 -9*	2.5	2.5	0 2 2	66.2	63.8	-3	28.1	26.7	9 3 -6	6.9	9.1	2 18.2	16.8									
-7	107.8	110.7	4 56.5	54.7	-1	119.3	119.4	-4	24.7	20.9	4 84.7	81.8										
-5	49.5	50.4	6 29.6	30.3	1 36.9	40.2	-2	34.5	31.4	4 5 -5	21.2	21.4										
-3	41.7	45.5	8 44.4	43.7	3 9.7	4.7	0 34.0	33.0	0 34.0	33.0	-3	15.8	17.5									
-1	44.1	45.6	1 2 -9	15.8	16.5	10 2 -6	21.5	19.8	10 3 -3	37.6	32.8	-1	68.9	67.6								
3 87.3	88.4	-7	46.8	49.3	-4	36.2	34.9	-1	10.0	9.2	1 32.9	33.7										
5 54.6	52.6	-5	8.3	3.5	-2	91.6	88.6	0 4 2	95.5	92.8	3 24.4	23.7										
7 134.0	137.7	-3	26.9	26.3	0 58.4	55.3	4 37.5	36.0	4 37.5	36.0	5 5 -4	24.7	25.9									
9 23.7	22.4	-1 [206.2]	218.4	1 7.7	7.2	11 2 -5	110.3	112.8	6 73.1	73.8	-2	74.0	51.2									
3 1 -8	93.0	95.9	3 119.0	121.8	3 70.9	64.9	5 118.4	116.7	1 4 -7	17.9	18.2	0 35.5	31.7									
-6	40.7	39.9	5 57.4	56.7	5 118.4	116.7	-5	36.1	33.8	-5	36.1	33.8	2 15.3	15.7								
-4	56.9	60.4	7 29.2	27.6	7 51.9	51.4	-1	93.8	87.0	6 5 -3	26.0	24.8										
-2	14.9	15.5	2 2 -8	9.5	6.1	1 3 -8	29.3	29.3	1 10.7	2.0	-1	17.3	16.7									
0 33.5	36.0	-6	20.4	19.7	-6	31.9	32.5	3 49.6	44.8	7 3 -2	10.8	8.5										
2 7.2	8.1	-4	86.5	86.1	-4	42.8	38.5	5 9.4	9.3													
4 133.4	140.0	-2	109.8	108.2	-2	56.5	51.7	2 4 -6	15.9	10.9												
6 9.9	9.6																					

the ordering of metal atoms so that all sites of the eight-fold equi-point of space group $I2/a$ are not equivalent. In this way the symmetry can easily be reduced to space group $I2$, while all the coordinates remain the same.

During the refinement of metal occupancy, c_a , c_b , $B_{M(1)}$ and $B_{M(2)}$ were the only parameters with significant changes. The final coordinates and B values are given in Table 1. All atoms occupy the general position $8f$. The coordinates here can be shifted by $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ for comparison with those given for space group $I2/c$ by WALDROP (1968a).

The final model is given with isotropic temperature coefficients. The reason for this is twofold. Since the reflections are those contained in the $\text{FeK}\alpha$ sphere, the ratio of the number of reflections to the number of refined parameters is small; so it appears unlikely that meaningful improvement could come from introducing anisotropic temperature factors into the refinement. Actually anisotropic refinement is not required since the difference map, using this model with isotropic B 's, gives no indication of anisotropic motion.

Table 2 gives the observed and calculated structure amplitudes. In computing the structure factor F_o for unobserved reflections, an intensity of one-third the minimum observable intensity has been assigned, as suggested by HAMILTON (1955). The unweighted R value is 4.9% for all 348 reflections but only 4.3% if the 5 reflections which suffer from large extinction effects are removed. The weighted R is 3.6%.

Description of the structure

Interatomic distances and their standard deviations are given in Tables 3 and 4. Table 3 displays cation-oxygen distances. In Table 4 the distances between M and the half-filled sites F(1), F(2) are given. Also shown are the distances from M to the average position F(av)

Table 3. *Interatomic distances in triplite*

The primed atoms are labeled in Fig. 3. For M—F distances see Table 4

Atoms	Distance	σ
P tetrahedron		
P—O(1)	1.536 Å	0.006 Å
P—O(2)	1.529	0.005
P—O(3)	1.535	0.006
P—O(4)	1.543	0.006
M(1) octahedron		
M(1)—O(2)'	2.164	0.005
M(1)—O(3)	2.161	0.006
M(1)—O(3)'	2.105	0.006
M(1)—O(4)'	2.123	0.005
M(2) octahedron		
M(2)—O(1)	2.107	0.006
M(2)—O(1)'	2.138	0.005
M(2)—O(2)'	2.075	0.005
M(2)—O(4)	2.081	0.006

Table 4. Distances between *M* and *F* sites

The half-filled sites, separated by 0.62 Å, are symbolized F(1), F(2). The average position for each F(1), F(2) pair is denoted F(av)

Atoms	Distance	σ	Atoms	Distance
M(1)—F(1)	2.139 Å	0.010 Å	M(1)—F(av)	2.060 Å
M(1)—F(2)	2.026	0.010	M(1)—F(av)'	2.568
M(1)—F(1)'	2.811	0.010	M(2)—F(av)	2.456
M(1)—F(2)'	2.341	0.011	M(2)—F(av)''	2.032
M(2)—F(1)	2.234	0.010		
M(2)—F(2)	2.697	0.010		
M(2)—F(1)''	1.989	0.010		
M(2)—F(2)''	2.119	0.010		

for each F(1), F(2) pair; i.e., the probable M—F distance if F were not split between two half-filled sites.

One notes that P is surrounded by four O atoms at an average distance of 1.536 Å. The coordination of anions around M(1) and M(2) is probably best described as distorted octahedral with four O and three half-filled F sites at a normal distance, and one more-distant,

Table 5. Interatomic angles in triplite

Atoms	Angle	σ	Atoms	Angle	σ
O(1)—P—O(2)	109.9°	0.3°	O(1)—M(2)—O(1)'	78.6°	0.3°
O(1)—P—O(3)	111.3	0.3	O(1)—M(2)—O(2)'	89.8	0.2
O(1)—P—O(4)	107.4	0.3	O(1)—M(2)—O(4)	164.8	0.2
O(2)—P—O(3)	109.4	0.3	O(1)—M(2)—F(av)	106.0	0.3
O(2)—P—O(4)	110.4	0.3	O(1)—M(2)—F(av)''	93.1	0.3
O(3)—P—O(4)	108.4	0.3	O(1)'—M(2)—O(2)'	109.4	0.2
O(2)'—M(1)—O(3)	86.2	0.2	O(1)'—M(2)—O(4)	89.1	0.2
O(2)'—M(1)—O(3)'	162.7	0.2	O(1)'—M(2)—F(av)	174.8	0.3
O(2)'—M(1)—O(4)'	89.6	0.2	O(1)'—M(2)—F(av)''	105.1	0.3
O(2)'—M(1)—F(av)	80.1	0.3	O(2)'—M(2)—O(4)	102.9	0.2
O(2)'—M(1)—F(av)'	85.8	0.3	O(2)'—M(2)—F(av)	73.2	0.3
O(3)—M(1)—O(3)'	76.5	0.3	O(2)'—M(2)—F(av)''	145.4	0.3
O(3)—M(1)—O(4)'	126.7	0.2	O(4)—M(2)—F(av)	85.9	0.3
O(3)—M(1)—F(av)	92.4	0.3	O(4)—M(2)—F(av)''	81.2	0.3
O(3)—M(1)—F(av)'	162.4	0.3	F(av)—M(2)—F(av)''	72.8	0.5
O(3)'—M(1)—O(4)'	101.6	0.2			
O(3)'—M(1)—F(av)	99.2	0.3			
O(3)'—M(1)—F(av)'	110.5	0.3			
O(4)'—M(1)—F(av)	139.0	0.3			
O(4)'—M(1)—F(av)'	68.8	0.3			
F(av)—M(1)—F(av)'	70.8	0.5			

half-filled F site. For the M(1) octahedra the average distances are 2.138 Å for M(1)—O, 2.169 Å for M(1)—F (near) and 2.811 Å for M(1)—F (distant). For M(2) octahedra they are 2.100 Å for M(2)—O, 2.114 Å for M(2)—F (near) and 2.697 Å for M(2)—F (distant). Overall averages of both types of octahedra are 2.119 Å for M—O, 2.142 Å for M—F (near), 2.754 Å for M—F (distant).

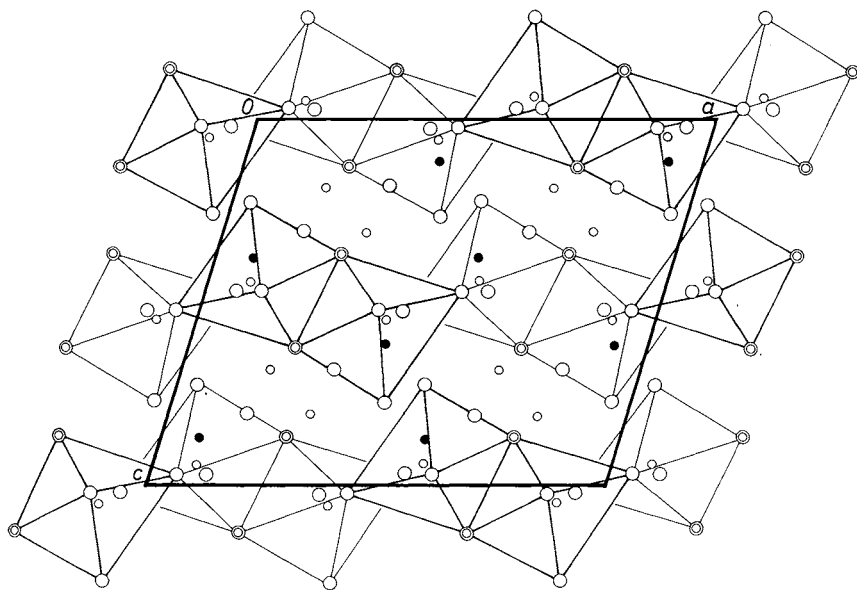


Fig.2. The chains of M(2) octahedra projected along b . The locations are represented by small circles for M, shaded circles for P, large circles for O and double circles for F

Interatomic angles are given in Table 5. For simplicity in describing the angles within octahedra, the F atoms are assigned to the position F(av).

The data in Tables 3, 4 and 5 indicate that the PO_4 tetrahedra depart only slightly from perfect regularity. On the other hand, the MO_4F_2 octahedra are quite distorted.

In viewing the triplite structure it is convenient to consider the M(1) and M(2) octahedra separately; the final refined structure can be regarded as a composite of the polyhedra given in two drawings, Figs.2 and 3. To make the structure easier to visualize, each F(1), F(2) pair is represented by a double circle at the site F(av).

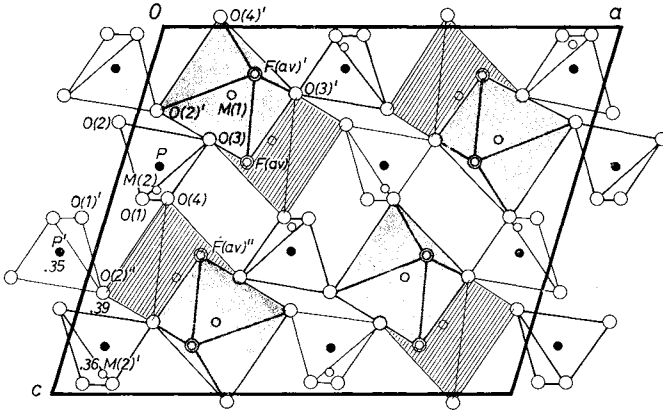


Fig.3. A projection along b of the P tetrahedra and the chains of M(1) octahedra

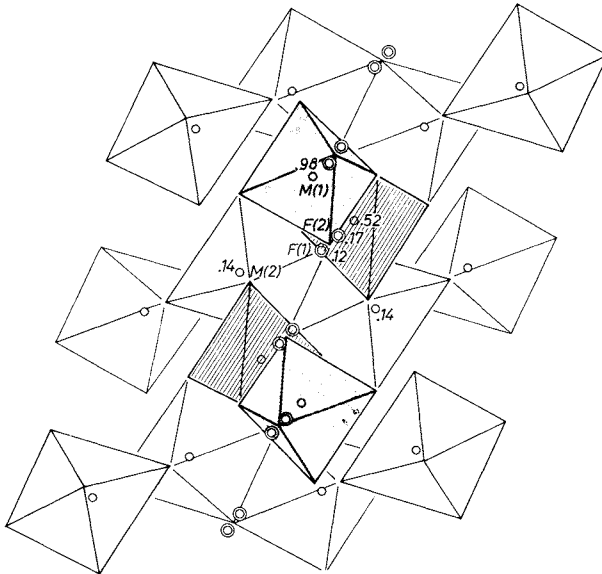


Fig.4. Interweaving of chains of M(1) octahedra (shaded) and chains of M(2) octahedra (unshaded) as seen projected along b . The orientation is identical with that in Figs. 2 and 3

The M(2) octahedra share edges to form zigzag chains parallel to a , as emphasized in Fig.2. These chains are connected by the sharing of edges with M(1) octahedra and vertices with isolated

P tetrahedra. The framework of M(1) octahedra and P tetrahedra is shown in Fig. 3.

Of interest in Fig. 3 are the atoms labeled P', O(2)'', M(2)' in the lower left corner of the projection. These three atoms contribute to the triangle of Patterson peaks used in solving the structure by image-seeking.

The M(1) octahedra share edges to form chains parallel to *b*. Figure 4, a composite of M octahedra from Figs. 2 and 3, illustrates the interweaving of chains of M(1) octahedra (shaded) and chains of M(2) octahedra (unshaded). Again the projection is along *b*.

It is interesting to consider the M—F interaction as seen in Fig. 4. An F(av) site is shown as an octahedral vertex between a pair of F(1), F(2) sites, represented by double circles. Two M(1) atoms (within shaded octahedra) and two M(2) atoms (within unshaded octahedra) would compete for each atom in an F(av) site. The competition between M atoms for F is somewhat reduced by splitting the F(av) site into F(1), F(2) half-filled sites so that each F atom can be at a normal distance from three M neighbors, instead of only two.

Acknowledgements

I gratefully acknowledge the advice and support given by Professor MARTIN J. BUERGER during this investigation. Drs. PETER SÜSSE, HERBERT THURN and FELIX TROJER have contributed to this work through many helpful discussions. I am also thankful to Dr. ILMARI HAAPALA for his letter describing the diffraction symmetry of Eurajoki triplite and for allowing me to see both his *h0l* precession photograph and the manuscript of the article that he and PENTTI OJANPERÄ had submitted for publication. Professor CLIFFORD FRONDEL supplied the specimens of triplite and zwieselite. This research was supported by a grant from the National Science Foundation GA-1308. The computations were carried out at the M.I.T. Information Processing Center.

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