

THE CRYSTAL STRUCTURE OF
POTASSIUM HEXATITANATE, $K_2Ti_6O_{13}$.

by

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Abstract

Crystals of potassium hexatitanate synthesized by melting TiO_2 and K_2CO_3 were used. Unit cell and space group were determined by means of precession, simple Weissenberg and precision Weissenberg photographs. The cell constants were adjusted by least-squares. The unit cell dimensions are:

$$\begin{aligned} a &= 15.582 \pm 0.006 \text{ \AA} \\ b &= 3.82 \pm 0.001 \text{ \AA} \\ c &= 9.112 \pm 0.001 \text{ \AA} \\ \beta &= 99^\circ 76' \pm 0.008^\circ \end{aligned}$$

The space group is $C2/m$, and the cell contains $2(K_2Ti_6O_{13})$.

Three-dimensional intensity data were recorded by means of a single-crystal geiger counter diffractometer and the intensities were corrected for Lorentz-polarization factor and absorption. In later stages of the structure determination the three Ti were corrected for anomalous scattering.

A three-dimensional Patterson synthesis suggested a structure based on Ti octahedra with their axes parallel to the 2-fold axis, and a trial model, which gave the correct number of oxygens in this symmetry, was tested by vector methods, which confirmed it.

This structure, consisting of chains of Ti octahedra sharing edges and corners, with some tunnels where the K ions occur, was refined primarily by successive three-dimensional Fourier syntheses and finally by least-squares methods, leading to a discrepancy factor R of 12.4% for all reflections. Individual temperature factors and interatomic distances are in agreement with reported values.

Thesis Supervisor: Martin J. Buerger

Title: Professor of Mineralogy and Crystallography

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Chapter I

Introduction

Potassium hexatitanate was synthesized for the first time in 1959 by the Central Research Department of the Experimental Station of E.I. du Pont de Nemours and Company, by Berry et al.⁹, who reported at the same time the x-ray powder data, the space group and the unit cell. A little later Anderson and Wadsley¹⁴ reported an unusual five-coordinated Ti in a compound of the same family, and this made the determination of the structure of potassium hexatitanate of great interest. Since it appeared to be of a reasonable complexity, it was thought that it could be solved by using vector methods such as an implication diagram and minimum functions⁴. It was found that, even though the interpretation of these turned out not to be so simple because of the strong substructure which made almost every peak multiple in the Patterson synthesis, these methods were still the most useful.

Recently Anderson and Wadsley¹⁶ published the structures of sodium and rubidium hexatitanate which are obviously isotypic with our potassium hexatitanate. A comparison between these structures is given at the end of this work.

Chapter II.

A. Unit cell and space group

Most of the crystals were prismatic with a good cleavage corresponding to (100), and elongated in the direction of the 2-fold axis. A thin prismatic crystal which gave a good extinction under the polarizing microscope was chosen and oriented in the optical goniometer.

Three Weissenberg photographs corresponding to the levels 0, 1 and 2 with the 2-fold axis as the rotation axis were taken, and the intensity distribution was found to correspond to the monoclinic symmetries $C 2/m$, Cm or $C2$. For the first stages of this determination it was assumed to be $C 2/m$, Fig. 1. This ambiguity is discussed further in the section on the refinement. Every reflection was indexed on the basis of a monoclinic cell of approximate dimensions $\underline{a} = 15.5 \text{ \AA}$, $\underline{b} = 3.82 \text{ \AA}$, $\underline{c} = 9.1 \text{ \AA}$ and $\beta = 99^{\circ}5'$.

More exact values of the \underline{a} and \underline{c} axes and the angle β were obtained from a precision back-reflection Weissenberg photograph using the technique described by Buerger¹. These results were adjusted by means of a least-squares calculation using a program written for the IBM 709 computer by Burnham^{15a}.

The value of the \underline{b} axis was obtained by averaging the measurements of one rotation photograph and two precession photographs, which corresponded to the zero levels of the \underline{a} and \underline{c} axes.

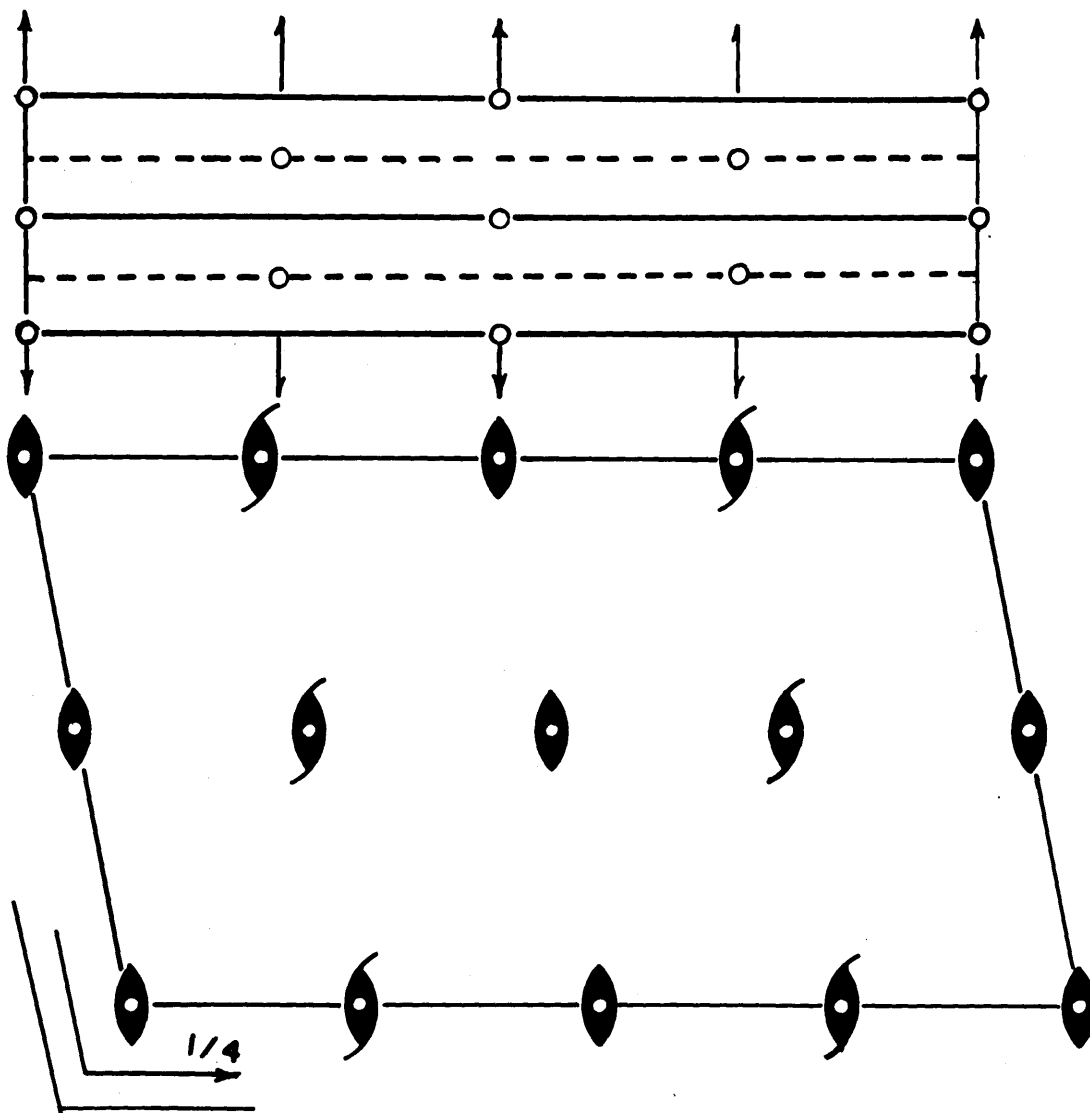


Fig. 1.
Space group $C 2/m$.

These results as well as those reported by Berry et al.⁹ are listed in Table 1.

B. Cell content

The volume of the unit cell is given by

$$V = a b c \sin \beta = 534.86 \text{ \AA}^3$$

The mass of one $\text{K}_2\text{Ti}_6\text{O}_{13}$ formula is

$$M = 1.915 \times 10^{-21} \text{ gr.},$$

and using the reported density,⁹ $\rho_o = 3.58 \text{ gm/cm}^3$, the number of formulae per cell is $\underline{n} = \frac{V\rho}{m} = 2.05 \approx 2$. If $\underline{n} = 2$ is accepted, the value of the calculated density turns out to be $\rho_c = 3.581 \text{ gr/cc}$.

Table 1
Unit cell dimensions of potassium hexa-
titanate

	Berry et al.	Least squares values
a	15.60 Å	15.582 ± 0.006 Å
b	3.80	3.82 ± 0.01
c	9.13	9.112 ± 0.001
β	99.6°	99.764° ± 0.008°

Chapter III.

Intensity measurement

Selection of the sample. In choosing the crystal the primary consideration was the behavior of the crystal under the polarizing microscope. Since a new program for correcting absorption in prismatic crystals^{15b} is now available in this laboratory, it was not absolutely necessary to obtain an approximately cylindrically-shaped crystal, to simplify the absorption correction.

The dimensions of the crystal finally chosen were 0.0923 × 0.0213 mm., and 0.2272 mm. The elongated direction corresponded to the 2-fold axis which was designated as the b axis. The crystal had two well developed (100) faces, and it was easily oriented optically. The orientation was corrected by means of precession photographs.

Intensity measurement. The collection of the intensities was made with a Buerger¹² single-crystal diffractometer operated with a Philips generator, using an argon-filled geiger counter as the detector. CuK α radiation (Ni filter) was used, and the generator was run uniformly at 35 kV and 15 ma. Six hundred reflections, corresponding to the levels 0, 1, 2, 3 and 4 perpendicular to the b axis, were collected.

In order to keep the measurements within the linearity range of the counter, two aluminum foils of different thicknesses were used to cut down the strongest reflections. Rather than trying to calculate

the absorption factor of each foil accurately, these were calculated roughly, and instead three different scale factors were used: scale factor 1 being used for all reflections without aluminum foil; scale factor 2 for all reflections measured with the less absorbent of the foils, and scale factor 3 for those measured with the thicker foil.

The ϕ and Υ values for all reflections were computed on the IBM 709 computer using a program written by Prewitt⁸ which also computes the Lorentz-polarization factor $1/l_p$.

The uniformity of the x-ray beam was checked according to the technique described by Burnham^{15d} and the white-radiation effect¹³ was found to be negligible.

The technique used was as follows: for each peak, the background was counted for a fixed point on each side of the peak; the counts per second were averaged and subtracted from the total number of counts per second for the scanned peak. Reflections where zero or a "negative" number of counts per second were found were set to a value equal to $1/3$ times the value of the smallest non-zero reflection found^{15c}. The integrated intensities were corrected for Lorentz-polarization factor and for absorption. The absorption correction for a prismatic crystal for which the equations of the crystal faces are known and which has no re-entrant angles has been described^{15b}. The approximate error when 64 integration points inside the crystal are used has been estimated at 3.8%.

It was relatively simple to establish these equations, since

this crystal had only six faces. On the other hand, if a cylindrical approximation for this particular crystal had been used, the error in the zero-level reflections could have been as large as 63%^{15b}, due to the shape of the crystal and the high absorption coefficient, $\mu = 389.39\text{cm}^{-1}$, which it has. That this absorption correction was accurate was proved by the fact that it was possible to use a single scale factor for the reflections of the different levels which were measured without aluminum foil.

The values of the integrated intensities, corrected as described above, were used as the F_{obs}^2 coefficients for a two-dimensional Patterson synthesis.

Chapter IV.

Structure determination

Four facts lead to the formulation of the trial model which proved to be the correct structure of potassium hexatitanate:

1. The length of the b axis is just equal to the height of a titanium octahedron in the rutile structures;
2. Strong substructure reflections outline a sublattice repeating itself three times along the c axis (Fig. 2);
3. The number of oxygens (13 in the structural unit) drastically restricts the packing of the octahedra;
4. The large ionic radius of the K cations, together with the symmetry restrictions, sets up definitely the positions of the potassium atoms.

A two-dimensional Patterson synthesis, Fig. 3, of the crystal showed a square arrangement of peaks which confirmed that the structure was based on Ti octahedra with their axes parallel to the b axis. Now, in the symmetry $C 2/m$, this fact implies that the basic structure will have to be a sort of layer structure, with atoms only at the values zero and $\frac{1}{2}$ for the y coordinate. A three-dimensional Patterson synthesis proved that within the error limits there were peaks only in the y = 0 and y = $\frac{1}{2}$ sections. Both sections were identical but displaced $\frac{a}{2}$ in the a direction, as required for the face-centered cell. Therefore the three-dimensional work required in the

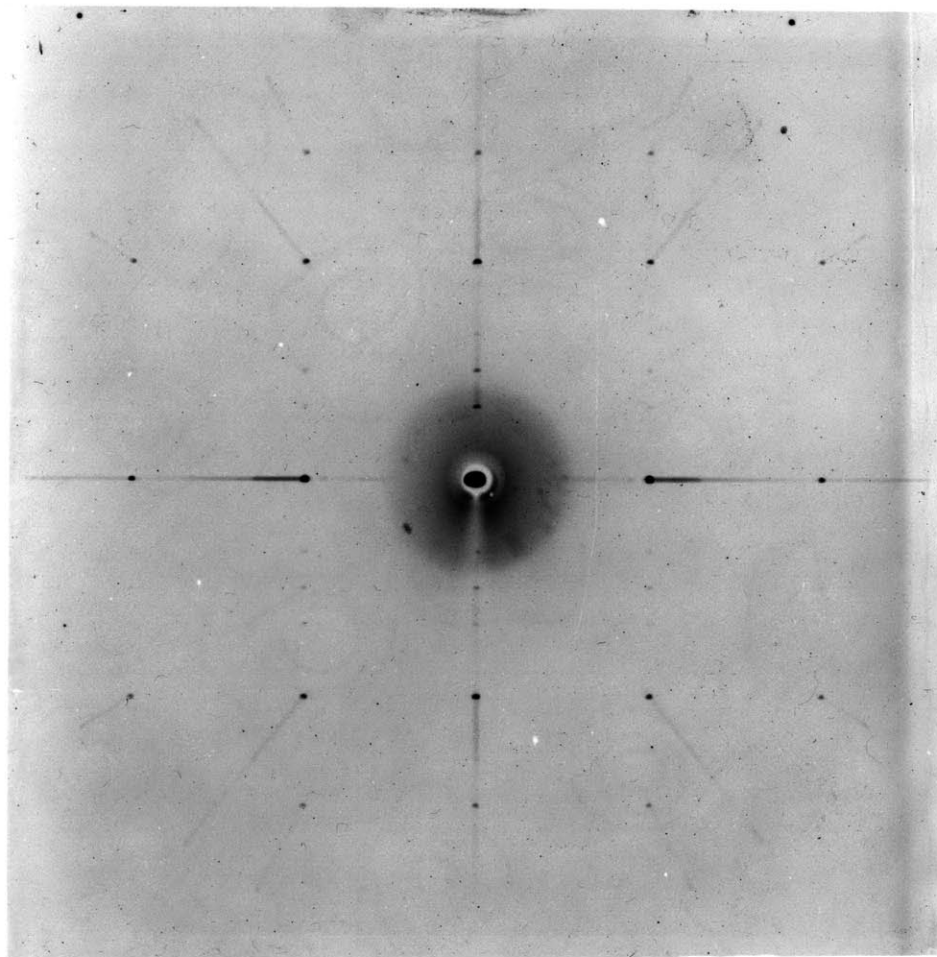


Fig. 2.

Zero-level precession photograph, a axis

(c^* is vertical)

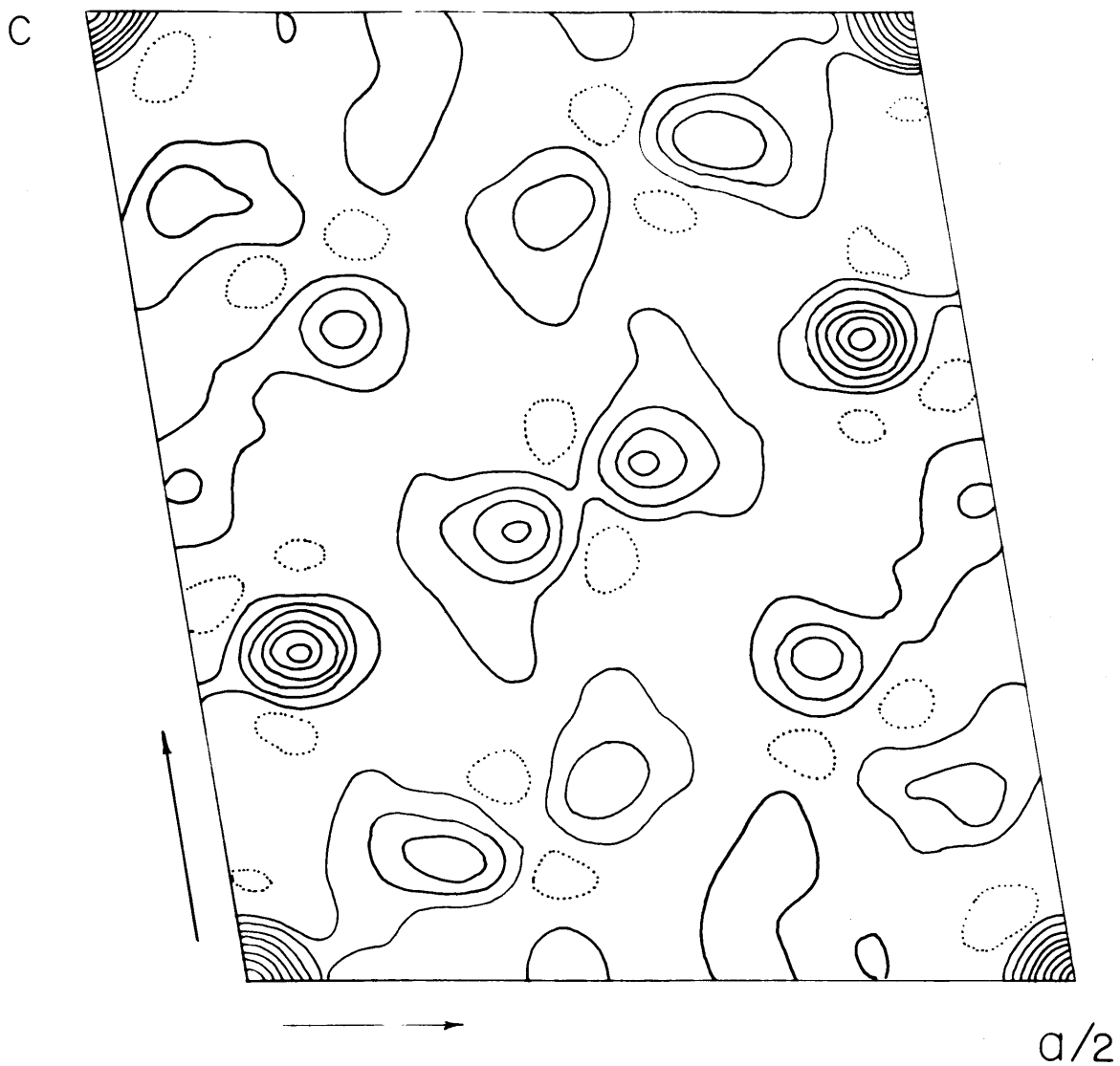


Fig. 3.

Patterson synthesis $P(xz)$.

(Contours at equal but arbitrary intervals)

use of vector methods was reduced to the study of the section $\underline{P(x0z)}$, Fig. 4.

Minimum functions based on different peaks of $\underline{P(x0z)}$ were built up, and although these did not give an unambiguous result (because the peaks turned out to be multiple peaks) they all agreed in giving three strong peaks in a line which made a small angle with the \underline{c} axis, Fig. 5. These peaks were identified with the Ti atoms. Although not all the oxygens were obtained, there was sufficient evidence to prove that the basic unit was three octahedra sharing edges, as outlined in Fig. 5. This choice agreed with the fact that the substructure reflections previously mentioned indicated a motif repeated three times along the \underline{c} axis.

The number of oxygens, 26 in the complete cell, required that at least one should be placed at a symmetry center, and this was therefore placed at the origin. It was then found that the three octahedra sharing edges contained all the required information: the symmetry elements of the space group $C 2/m$ produced the other three octahedra to complete a set having composition $K_2Ti_6O_{13}$. A picture of the idealized projection of the structure along the \underline{b} axis is shown in Fig. 6. Fig. 7 is a clinographic projection of the structural unit.

The only thing necessary to complete the model now was to fix the position of the K ions. As a rough approximation the side of the square section of the Ti octahedra was 3 \AA ; when four oxygens were placed one at each corner, a void was left of $3.2 - 2 \times 1.4 =$

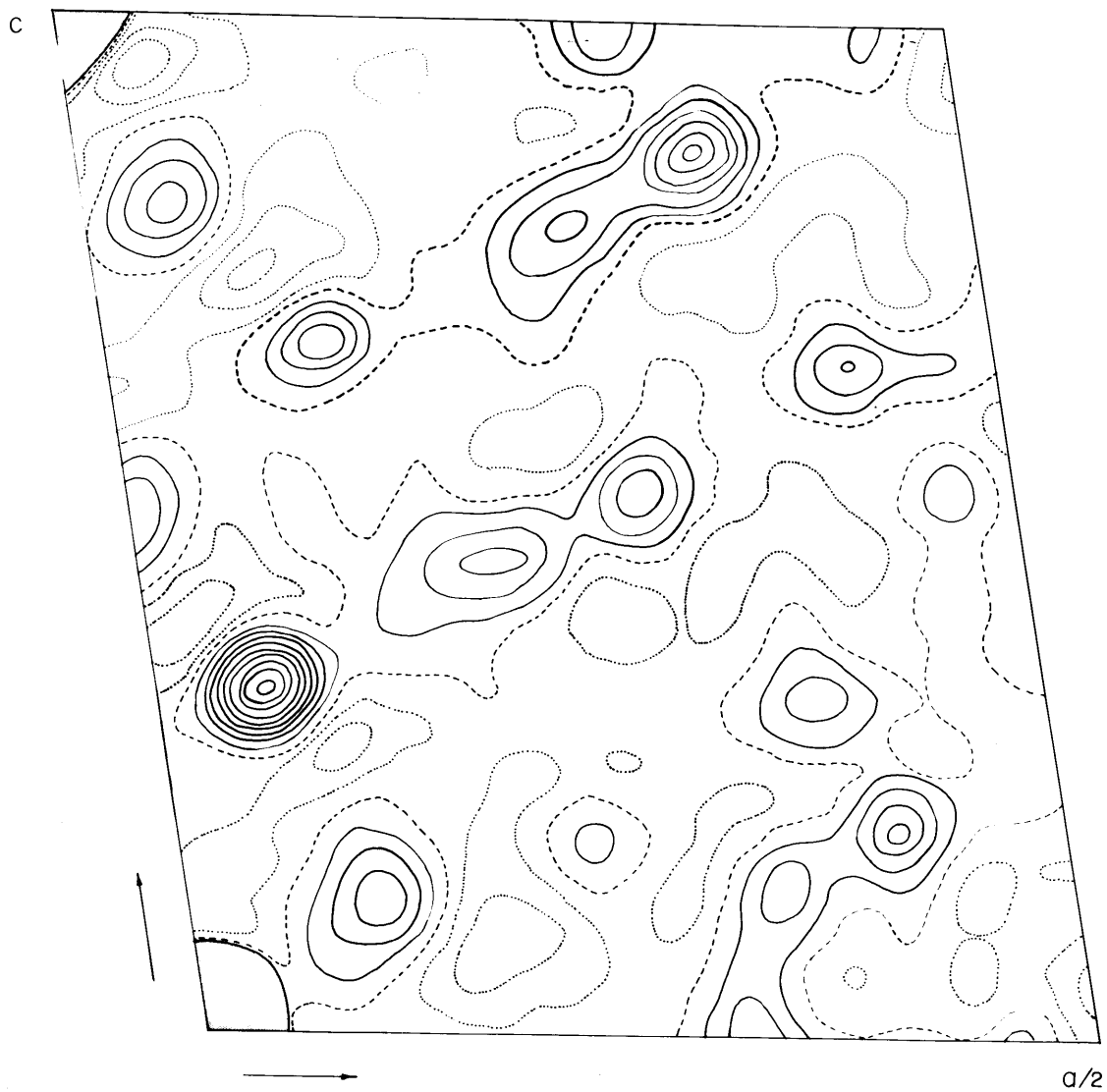


Fig. 4.
Three dimensional Patterson synthesis
section $P(x_0z)$.
(Contours at equal but arbitrary intervals).

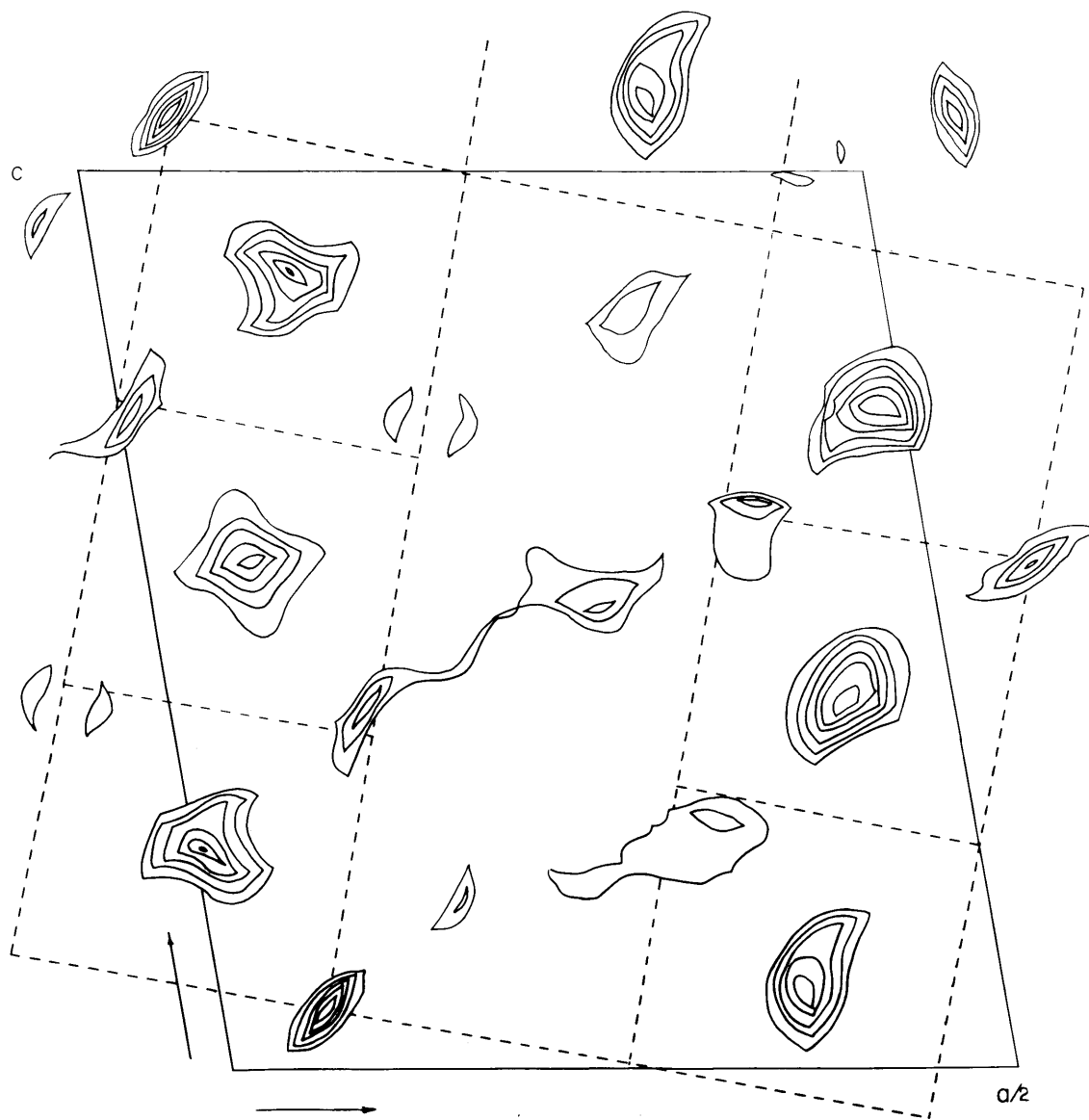


Fig. 5.
Minimum function $M(x_0z)$, based
on an O-O peak.

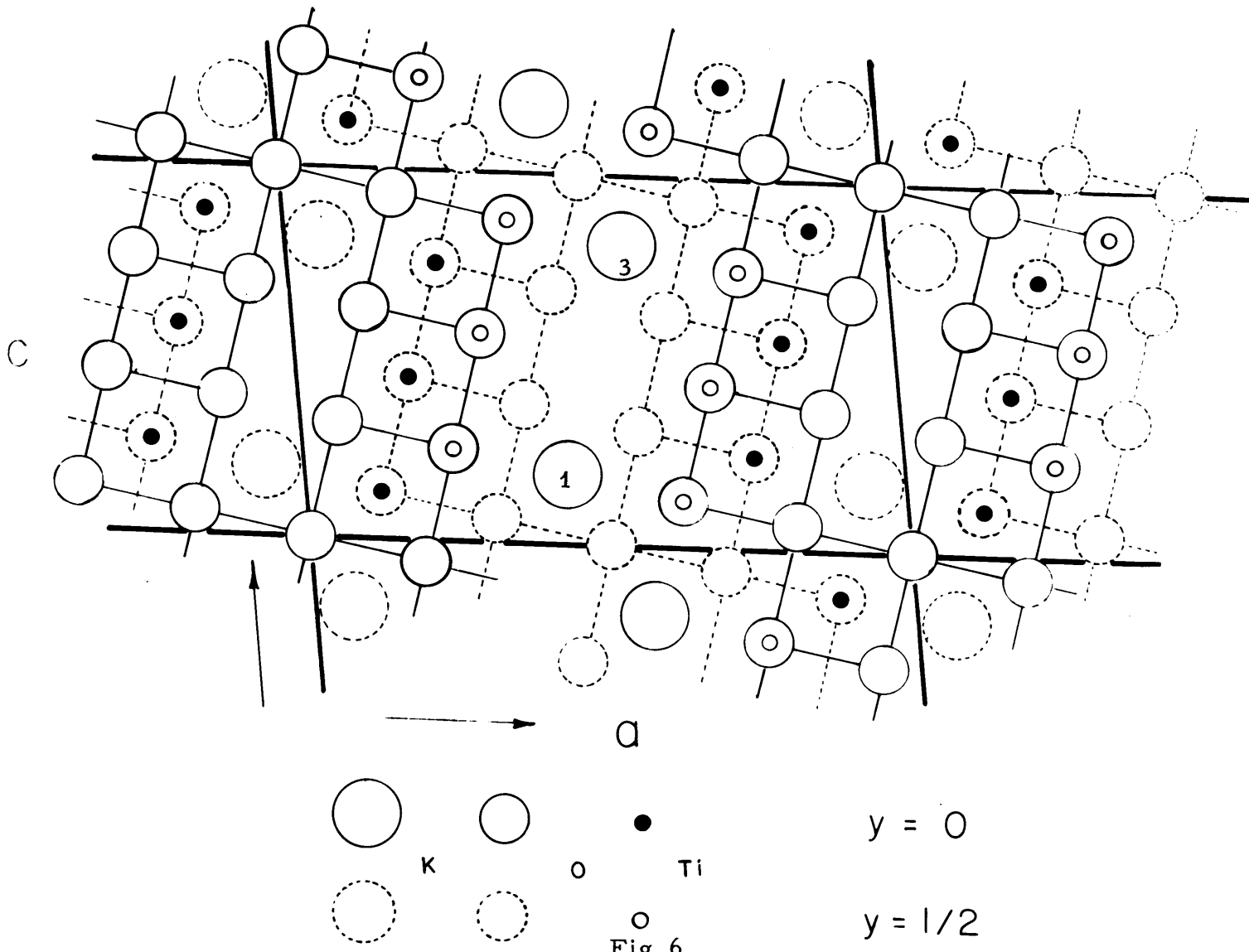


Fig. 6
 Idealized projection of the model structure of $K_2Ti_6O_{13}$ along the b axis.

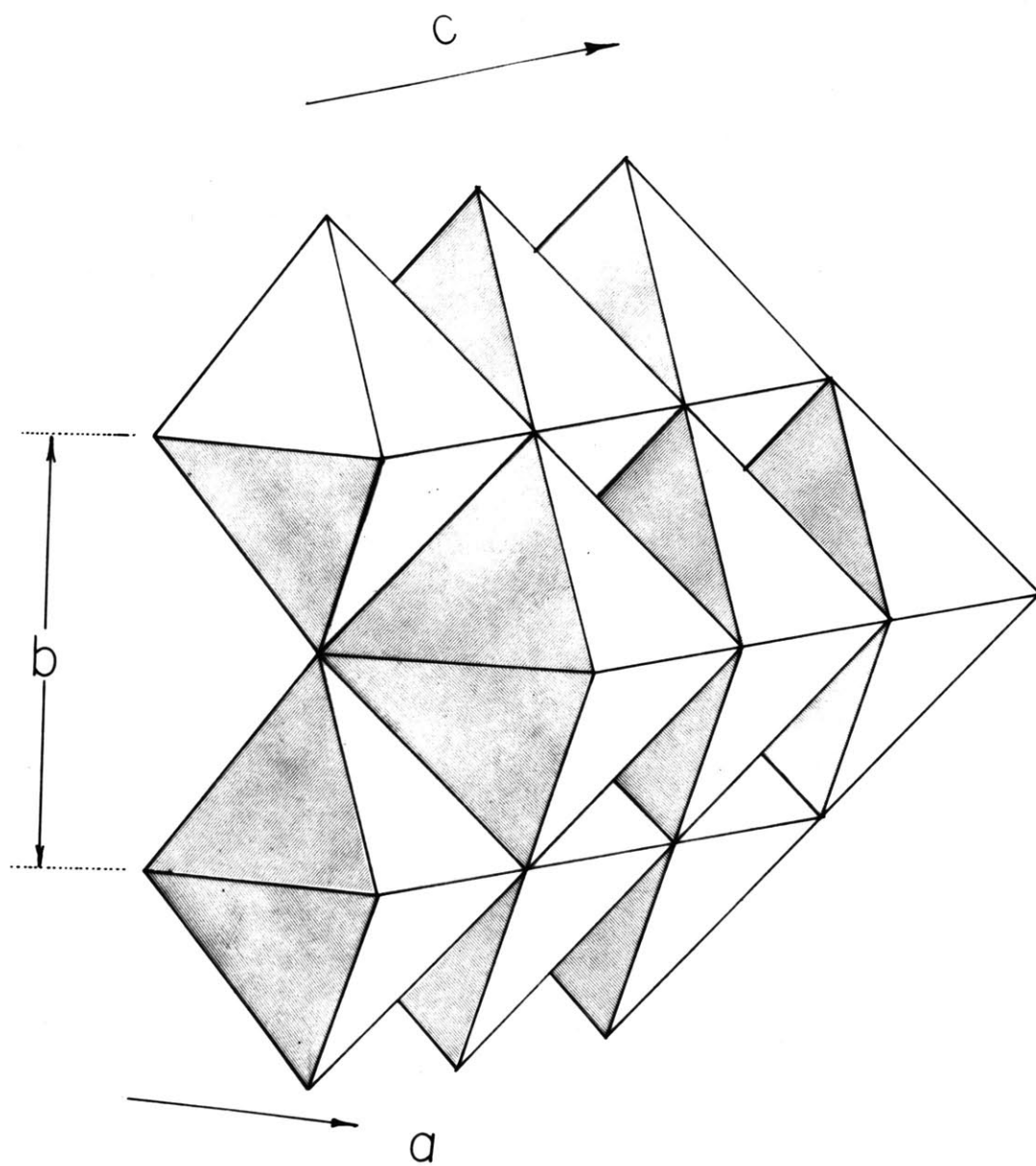


Fig. 7.

Clinographic projection of the structural unit
of $K_2Ti_6O_{13}$.

$4.24 - 2.8 = 1.44 \text{ \AA}$ diameter. The diameter of K^+ is 2.66 \AA , so that the only place where a K ion could fit in was one of the three cubic voids where the Ti octahedron chains were further apart, Fig. 7. Since a symmetry center occurs in the central empty position, placing a potassium at this position would provide only two potassium atoms per unit cell instead of the necessary four. The final positions of the K ions are therefore those labeled 1 and 3 in Fig. 6.

At this stage another minimum function $\underline{M}_2(\underline{x0z})$, based on the K-K peak, was made, and the result reproduced the proposed model structure (Fig. 8) which proved that the model was correct.

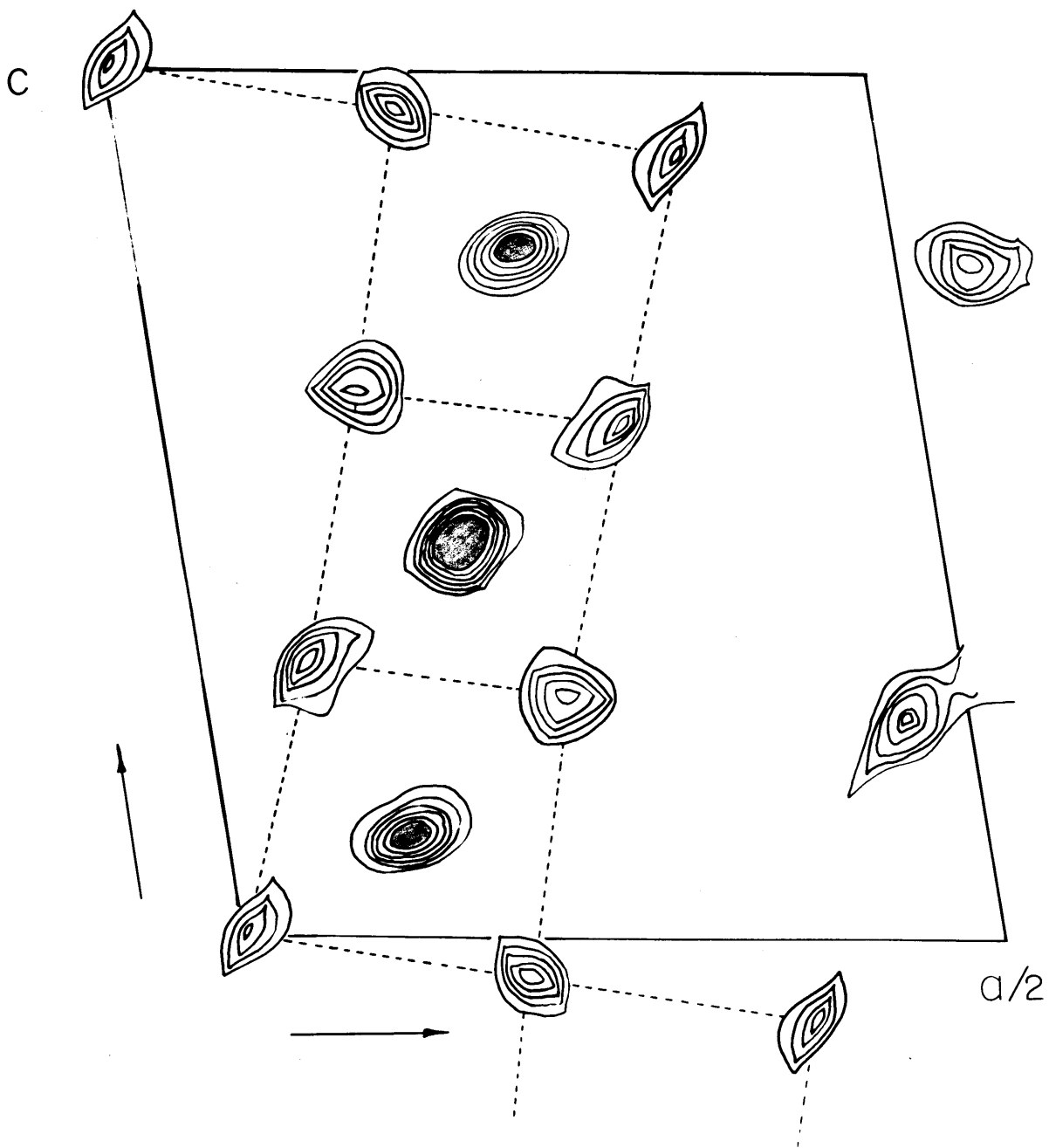


Fig. 8.
Minimum function $M_2(x, 0, z)$ based on the
K-K peak.

Chapter V.

Refinement of the structure

The coordinates of the idealized model of Fig. 6, adjusted for the true values of the cell constants, were used as input for two cycles of least-squares refinement. The Busing and Levy⁶ crystallographic least-squares program was used, and the individual isotropic temperature factors and the three scale factors were allowed to vary, together with the coordinates. For the first cycle, all three scale factors were set at 1.0, and the temperature factor was assumed to be 0.7 for all atoms. Atomic scattering curves^{7, 10, 5} for T^{+3} adjusted at low $\sin \theta$ for T^{+4} , for O^{-2} and K^{+} were used. After two cycles which adjusted the scale factors, the discrepancy factor \underline{R} was 39.1% and the refinement stopped.

The \underline{R} factor is defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

and the weighted \underline{R} factor is defined as

$$R' = \frac{\sum w ||F_o| - |F_c||^2}{\sum w |F_o|^2},$$

all summations taken over all \underline{hkl} . Busing and Levy's program minimizes $\underline{R'}$.

A Fourier refinement was next attempted¹². A three-dimensional Fourier synthesis was calculated assigning to F_{obs} the signs of F_{cal} as obtained from the last least-squares cycle. The Fourier synthesis was calculated using the program MIFRI written by Sly and Shoemaker¹¹ for the IBM 704 computer. After the first Fourier synthesis and structure factor calculation, the R factor dropped to 32.6% and after three more Fourier syntheses followed by structure factor calculations, an R factor of 24.2% was obtained.

At this point the displacement of all the atoms in the Fourier synthesis was very small, and a new least-squares refinement, again using Busing and Levy's program, was tried. After four cycles, the R factor was reduced to 16.0% and the refinement stopped. In each cycle of refinement some negative temperature factors had been obtained, which was attributed to the anomalous scatterer character of Ti. The Ti atoms were corrected for anomalous scattering³ and values were assigned for Ti atomic scattering values after Dauben and Templeton².

It was then decided that a new FORTRAN least-squares crystallographic program, SFLSQ2, written recently by C. T. Prewitt¹⁷ of this laboratory, should be used for further refinement. It is very easy to make changes in this program, such as in the weighting scheme, in the space group, or in the number of atoms affected by anomalous scattering, and it is also much faster than that of Busing and Levy.

The correction for anomalous scattering improved the

temperature factors, but did not appreciably improve the \underline{R} factor.

(An easy way to correct for anomalous scattering for the space groups $C2/m$, Cm and $C2$ is given in the Appendix.)

Since Prewitt's program also minimizes \underline{R}^{\dagger} , it was decided that a new weighting scheme should be tried. Up to this stage in the refinement, the weighting scheme proposed by Burnham^{15c} had been used; this implied that small standard deviations in the F_{obs} will give higher weights to these reflections. But this meant that in practice the refinement was based on the highest F_{obs} , since these were the ones with the lowest standard deviation; and at this stage only the light atoms were changing their positions appreciably. Therefore a weighting scheme was tried as follows:

$$\sqrt{w} = 1/\sigma$$

as before, but now

$$\text{if } F_{\text{obs}} > 4 F_{\text{obs min}},$$

$$\sigma = 1/F_{\text{obs}};$$

$$\text{if } F_{\text{obs}} < 4 F_{\text{obs min}},$$

$$\sigma = 4 F_{\text{obs min}}.$$

This had the advantage of basing the refinement on the medium-strength F 's, the higher and the lower F 's being assigned a smaller weight.

Three more cycles of refinement resulted in a final \underline{R} factor

of 12.4% for all reflections. Table 2 shows the values of the coordinates obtained from the first Fourier synthesis, and Table 3 shows the final coordinates of the structure.

At this stage an attempt was made to determine the true space group of potassium hexatitanate. The final atomic positions were submitted for refinement in the space groups C2 and Cm. After two cycles in space group C2 an \underline{R} factor of 12.4% was obtained (the same as that for C 2/m) and the deviation of all \underline{y} coordinates, but one, from the zero value, were smaller than the standard deviations. Space group Cm also permitted refinement up to 13.0%, but the standard deviations were very high and some of the temperature factors had very high values. Table 4 shows the coordinates of the atoms which were obtained for the space group C2. The space group problem is discussed further in the next chapter.

Finally, the coordinates given by Anderson¹⁶ for sodium hexatitanate were refined using $\text{K}_2\text{Ti}_6\text{O}_{13}$ data. After two cycles, the discrepancy factor was 20.6% and the coordinates were beginning to converge to $\text{K}_2\text{Ti}_6\text{O}_{13}$ coordinates, as is shown in Table 5.

Table 6 lists the observed and calculated structure factors for potassium hexatitanate after the last cycle of refinement. Reflections 200, 110, 220, 130 and 240 have been omitted on the basis of their high extinction, and the value of reflection 131 was found to be incorrect.

Table 2.

Potassium hexatitanate

Atomic coordinates in space group $C2/m$, as
obtained from Fourier synthesis.

Atom	x	y	z
Ti(1)	0.1181	0.0	0.1011
Ti(2)	0.1708	0.0	0.4259
Ti(3)	0.2350	0.0	-0.2250
K	0.4533	0.0	0.2417
O(1)	0	0	0
O(2)	0.2017	0.0	0.2083
O(3)	0.0875	0.0	0.3433
O(4)	0.290	0.0	-0.4267
O(5)	0.1450	0.0	-0.4233
O(6)	0.3583	0.0	-0.1000
O(7)	0.1817	0.0	-0.0900

Table 3.

Potassium hexatitanate: Final atomic coordinates in space
group $C2/m$.

Atom	x	$\sigma(x)$	y	z	$\sigma(z)$	B
Ti(1)	0.1142	0.0001	0.0	0.0980	0.0002	0.47 ± 0.09
Ti(2)	0.1716	0.0001	0.0	0.4386	0.0002	0.60 ± 0.09
Ti(3)	0.2325	0.0001	0.0	-0.2238	0.0002	0.50 ± 0.09
K	0.4540	0.0002	0.0	0.2474	0.0003	1.11 ± 0.09
O(1)	0.		0.	0.		0.6 ± 0.2
O(2)	0.2370	0.0006	0.0	0.237	0.001	0.6 ± 0.2
O(3)	0.0764	0.0006	0.0	0.291	0.001	0.6 ± 0.2
O(4)	0.2964	0.0006	0.0	-0.428	0.001	0.2 ± 0.2
O(5)	0.1330	0.0006	0.0	-0.384	0.001	0.4 ± 0.2
O(6)	0.3591	0.0006	0.0	-0.109	0.001	0.4 ± 0.2
O(7)	0.1677	0.0006	0.0	-0.083	0.001	0.6 ± 0.2

Table 4.

Potassium hexatitanate: Atomic coordinates in space group C2.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
Ti(1)	0.1143	0.0001	-0.004	0.008	0.0979	0.0002	0.49 \pm 0.09
Ti(2)	0.1716	0.0001	0.006	0.007	0.4386	0.0002	0.59 \pm 0.09
Ti(3)	0.2324	0.0001	0.006	0.007	-0.2238	0.0002	0.51 \pm 0.09
K	0.4541	0.0001	0.007	0.008	0.2472	0.0003	1.17 \pm 0.09
O(1)	0.		0.		0.		0.6 \pm 0.2
O(2)	0.2366	0.0006	0.01	0.01	0.238	0.001	0.6 \pm 0.2
O(3)	0.0766	0.0006	0.011	0.008	0.291	0.001	0.5 \pm 0.2
O(4)	0.2963	0.0006	-0.003	0.008	-0.428	0.001	0.3 \pm 0.2
O(5)	0.1328	0.0006	0.006	0.009	-0.384	0.001	0.5 \pm 0.2
O(6)	0.3589	0.0006	0.021	0.008	-0.1092	0.0009	0.4 \pm 0.2
O(7)	0.1681	0.0006	-0.007	0.009	-0.084	0.001	0.7 \pm 0.2

Table 5.

Results of refining potassium hexatitanate starting with Anderson's sodium hexatitanate as trial coordinates.

Atom	Sodium hexatitanate				Potassium hexatitanate after 2 cycles of refinement			
	x	$\sigma(x)$	z	$\sigma(z)$	x	$\sigma(x)$	z	$\sigma(z)$
Ti(1)	0.1137	0.0005	0.0895	0.0009	0.0048	0.0002	0.1002	0.0003
Ti(2)	0.1705	0.0004	0.4332	0.0010	0.1718	0.0002	0.4401	0.0003
Ti(3)	0.2287	0.0006	-0.2274	0.0010	0.2332	0.0002	0.2236	0.0004
Na or K	0.4540	0.0008	0.2508	0.0014	0.4545	0.0002	0.2477	0.0004
O(1)	0		0		0		0	
O(2)	0.228	0.002	0.247	0.004	0.242	0.002	0.238	0.003
O(3)	0.071	0.001	0.291	0.002	0.0794	0.0008	0.292	0.001
O(4)	0.282	0.002	-0.426	0.004	0.301	0.001	-0.425	0.002
O(5)	0.124	0.001	-0.383	0.002	0.136	0.001	-0.384	0.001
O(6)	0.358	0.002	-0.116	0.004	0.3586	0.0008	-0.103	0.001
O(7)	0.167	0.001	-0.073	0.002	0.169	0.001	-0.081	0.002

Table 6.

Potassium hexatitanate: Observed and calculated structure factors.

h	k	l	F _{obs}	F _{cal}
0	0	1	49.49	52.46
0	0	2	147.90	131.66
0	0	3	172.93	174.56
0	0	4	109.90	116.81
0	0	5	18.76	5.70
0	0	6	383.43	430.20
0	0	7	64.19	36.55
0	0	8	54.27	56.03
0	0	9	268.84	313.45
0	0	10	40.58	19.69
0	0	11	45.90	40.28
2	0	-10	27.16	44.39
2	0	-9	28.75	15.99
2	0	-8	165.93	183.47
2	0	-7	72.50	70.26
2	0	-6	333.19	334.03
2	0	-5	231.42	252.07
2	0	-4	17.20	19.91
2	0	-3	151.28	134.95
2	0	-2	103.77	117.39
2	0	-1	58.92	47.36
2	0	1	232.60	212.25
2	0	2	99.33	70.58
2	0	3	431.54	397.63
2	0	4	17.45	23.47
2	0	5	120.26	114.83
2	0	6	168.60	176.64
2	0	7	90.44	81.38
2	0	8	25.73	43.44
2	0	9	285.88	318.28
2	0	10	114.50	83.17
2	0	11	88.22	98.69
4	0	-10	19.20	37.44
4	0	-9	69.65	91.36
4	0	-8	114.45	118.84
4	0	-7	61.05	66.72

4	0	-6	47.33	42.20
4	0	-5	360.51	394.02
4	0	-4	169.49	193.77
4	0	-3	68.97	62.32
4	0	-2	353.99	388.57
4	0	-1	19.19	16.92
4	0	0	88.32	99.88
4	0	1	150.01	145.20
4	0	2	204.96	168.53
4	0	3	103.28	99.08
4	0	4	532.63	512.15
4	0	5	134.20	121.90
4	0	6	196.62	181.31
4	0	7	121.54	94.81
4	0	8	26.89	16.73
4	0	9	339.79	45.68
4	0	10	239.39	221.99
4	0	11	32.05	28.31
6	0	-9	21.81	30.22
6	0	-8	241.24	326.57
6	0	-7	20.34	26.16
6	0	-6	333.05	14.27
6	0	-5	118.59	126.30
6	0	-4	50.96	42.74
6	0	-3	102.21	108.15
6	0	-1	108.85	123.50
6	0	0	29.25	18.16
6	0	1	294.20	337.85
6	0	2	77.75	67.04
6	0	3	187.32	148.12
6	0	4	338.12	324.73
6	0	5	120.69	91.45
6	0	6	35.23	33.62
6	0	7	388.20	426.17
6	0	8	81.24	74.65
6	0	9	27.62	22.08
6	0	10	144.08	115.77
6	0	11	70.64	83.89
8	0	-9	67.10	67.83
8	0	-8	178.37	166.29
8	0	-7	219.79	294.42
8	0	-6	44.39	42.20
8	0	-5	63.58	60.91
8	0	-4	99.12	97.46

8	0	-3	22.45	26.91
8	0	-2	23.59	13.94
8	0	-1	345.07	349.69
8	0	0	115.39	97.22
8	0	1	194.56	222.31
8	0	2	89.34	120.31
8	0	3	22.32	36.84
8	0	4	337.27	347.86
8	0	5	31.08	18.46
8	0	6	29.48	29.87
8	0	7	107.00	82.37
8	0	8	154.81	120.05
8	0	9	87.11	74.77
8	0	10	262.56	299.10
10	0	-8	37.30	35.87
10	0	-7	162.77	137.77
10	0	-6	138.47	135.99
10	0	-5	75.73	68.79
10	0	-4	364.60	394.92
10	0	-3	110.93	97.65
10	0	-2	47.81	37.85
10	0	-1	235.85	184.83
10	0	0	181.55	154.48
10	0	1	117.38	102.84
10	0	2	352.41	402.38
10	0	3	181.75	208.32
10	0	4	89.75	99.97
10	0	5	228.84	261.65
10	0	6	48.01	50.05
10	0	7	21.93	24.09
10	0	8	125.31	143.24
10	0	9	56.00	69.80
10	0	10	14.60	17.76
12	0	-7	188.82	149.35
12	0	-6	27.32	12.80
12	0	-5	57.52	45.52
12	0	-4	196.88	154.19
12	0	-3	31.70	30.20
12	0	-2	71.45	37.80
12	0	-1	299.58	275.03
12	0	0	20.28	11.91
12	0	1	105.86	83.03
12	0	2	117.50	119.30
12	0	3	18.57	23.38

12	0	4	18.64	15.57
12	0	5	165.57	206.38
12	0	6	103.66	124.19
12	0	7	21.37	8.74
12	0	8	239.19	296.61
12	0	9	17.54	12.34
14	0	-6	232.37	192.67
14	0	-5	27.28	24.75
14	0	-4	46.72	33.04
14	0	-3	113.30	111.86
14	0	-2	168.92	132.46
14	0	-1	39.83	35.14
14	0	0	180.17	162.67
14	0	1	45.56	47.24
14	0	2	193.03	202.21
14	0	3	58.18	62.89
14	0	4	63.95	48.22
14	0	5	83.23	77.73
14	0	6	107.76	109.66
14	0	7	66.23	69.88
14	0	8	160.22	175.09
14	0	9	32.49	29.65
16	0	-4	55.25	48.97
16	0	-3	276.19	266.21
16	0	-2	17.50	6.68
16	0	-1	74.25	74.92
16	0	0	54.03	46.15
16	0	1	132.86	134.95
16	0	2	85.92	79.38
16	0	3	263.30	254.45
16	0	4	40.93	39.87
16	0	5	19.20	33.69
16	0	6	115.87	109.41
16	0	7	51.75	46.35
18	0	-2	66.75	47.38
18	0	-1	20.21	25.61
18	0	0	194.34	186.74
18	0	1	77.80	67.36
18	0	2	33.18	29.91
18	0	3	47.50	49.17
18	0	4	61.61	65.73
18	0	5	44.87	30.48
1	1	-10	147.07	159.47
1	1	-9	95.84	82.28

1	1	-8	143.87	131.56
1	1	-7	21.99	11.45
1	1	-6	196.46	203.82
1	1	-5	165.73	156.73
1	1	-4	200.49	203.02
1	1	-3	79.27	83.34
1	1	-2	267.18	235.26
1	1	-1	71.76	74.88
1	1	1	11.84	3.58
1	1	2	160.86	170.68
1	1	3	150.66	148.77
1	1	4	137.61	143.26
1	1	5	12.86	10.17
1	1	6	276.17	273.95
1	1	7	49.64	56.37
1	1	8	70.83	62.91
1	1	9	51.95	49.05
1	1	10	86.68	89.23
3	1	-10	28.77	15.34
3	1	-9	60.26	72.34
3	1	-8	186.48	179.03
3	1	-7	174.55	190.65
3	1	-6	253.10	264.08
3	1	-5	182.97	196.64
3	1	-4	50.94	51.86
3	1	-3	202.80	238.31
3	1	-2	112.37	125.74
3	1	-1	207.13	281.53
3	1	0	320.07	369.98
3	1	1	444.26	372.62
3	1	2	209.20	202.72
3	1	3	36.10	32.84
3	1	4	16.03	5.72
3	1	5	195.57	193.46
3	1	6	276.25	276.62
3	1	7	106.55	107.15
3	1	8	123.10	121.22
3	1	9	196.01	159.49
3	1	10	147.19	137.56
5	1	-9	21.21	28.73
5	1	-8	133.83	138.17
5	1	-7	105.70	112.57
5	1	-6	21.93	26.79
5	1	-5	222.49	245.97

5	1	-4	13.81	116.21
5	1	-3	38.35	42.98
5	1	-2	85.32	85.89
5	1	-1	118.36	153.28
5	1	0	38.70	12.39
5	1	1	83.07	81.98
5	1	2	17.32	12.29
5	1	3	251.51	216.81
5	1	4	380.41	335.49
5	1	5	169.78	147.77
5	1	6	52.44	57.57
5	1	7	134.28	128.98
5	1	8	89.62	63.43
5	1	9	217.67	183.31
5	1	10	252.45	238.32
7	1	-9	120.30	128.00
7	1	-8	59.81	51.60
7	1	-7	17.36	25.79
7	1	-6	108.34	111.35
7	1	-5	148.57	170.75
7	1	-4	160.75	191.81
7	1	-3	204.79	249.49
7	1	-1	206.47	219.39
7	1	0	84.42	59.25
7	1	1	48.98	49.83
7	1	2	20.41	19.07
7	1	3	182.75	167.80
7	1	5	274.64	236.49
7	1	6	24.32	21.29
7	1	7	190.08	147.34
7	1	8	29.16	15.59
7	1	9	99.01	96.68
7	1	10	113.51	100.38
9	1	-8	241.41	203.85
9	1	-7	186.15	184.83
9	1	-6	77.94	89.95
9	1	-5	59.11	49.16
9	1	-4	69.79	77.76
9	1	-3	24.63	15.79
9	1	-2	309.12	296.33
9	1	-1	374.44	341.29
9	1	1	213.42	218.74
9	1	2	234.63	274.76
9	1	3	61.82	64.56

9	1	4	125.86	133.52
9	1	5	41.73	31.35
9	1	6	139.08	132.38
9	1	7	266.03	250.83
9	1	8	267.12	281.83
9	1	9	104.47	117.70
9	1	10	56.08	78.04
11	1	-7	342.37	276.00
11	1	-6	108.76	84.94
11	1	-5	66.92	36.63
11	1	-4	202.82	155.61
11	1	-3	45.59	28.44
11	1	-2	198.20	143.74
11	1	-1	92.55	76.35
11	1	0	116.35	195.33
11	1	1	15.63	15.94
11	1	2	324.48	415.64
11	1	3	62.90	66.32
11	1	4	151.69	176.28
11	1	5	156.21	191.54
11	1	6	42.55	223.99
11	1	7	45.35	144.64
11	1	8	173.67	214.85
11	1	9	25.66	26.93
13	1	-6	42.95	34.98
13	1	-5	154.59	138.33
13	1	-4	407.36	376.23
13	1	-3	200.68	189.95
13	1	-2	122.86	103.81
13	1	-1	157.41	121.18
13	1	0	188.21	162.83
13	1	1	72.77	163.35
13	1	2	323.33	350.68
13	1	3	194.97	206.06
13	1	4	156.82	162.73
13	1	5	224.20	245.53
13	1	6	141.83	149.93
13	1	7	21.04	17.72
13	1	8	48.64	149.83
13	1	9	10.40	18.98
15	1	-5	60.67	61.39
15	1	-4	38.48	37.56
15	1	-3	222.17	213.84
15	1	-2	77.63	75.21

15	1	-1	203.25	170.77
15	1	0	226.88	228.11
15	1	1	138.00	132.66
15	1	2	104.14	96.51
15	1	3	64.90	57.64
15	1	4	14.86	20.68
15	1	5	163.91	161.68
15	1	6	194.80	233.34
15	1	7	164.51	179.79
15	1	8	186.84	209.34
17	1	-2	11.86	8.48
17	1	-1	105.89	94.38
17	1	0	297.35	313.13
17	1	1	40.41	34.67
17	1	2	64.60	57.50
17	1	3	168.20	180.62
17	1	4	46.58	37.28
17	1	5	52.42	43.34
17	1	6	151.09	156.65
0	2	1	30.71	28.59
0	2	2	115.64	108.40
0	2	3	142.45	147.09
0	2	4	89.27	86.90
0	2	5	23.80	6.12
0	2	6	372.49	441.19
0	2	7	34.83	32.59
0	2	8	37.46	46.07
0	2	9	275.17	277.73
2	2	-9	36.09	14.64
2	2	-8	150.20	159.46
2	2	-7	58.94	60.15
2	2	-6	304.75	344.87
2	2	-5	204.73	200.71
2	2	-4	28.74	19.34
2	2	-3	150.17	158.22
2	2	-2	68.16	70.15
2	2	-1	33.09	28.48
2	2	1	209.49	186.56
2	2	2	62.56	61.81
2	2	3	409.82	366.51
2	2	4	17.89	27.89
2	2	5	95.25	89.91
2	2	6	137.13	141.42
2	2	7	68.78	63.59

2	2	8	31.14	34.84
2	2	9	281.56	280.55
2	2	10	97.36	74.46
4	2	-9	59.27	78.62
4	2	-8	111.76	104.13
4	2	-7	47.19	56.07
4	2	-6	34.19	36.50
4	2	-5	338.78	404.03
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4	2	-3	55.38	53.09
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4	2	-1	19.85	12.12
4	2	0	67.68	65.47
4	2	1	114.73	102.91
4	2	2	155.54	120.71
4	2	3	89.37	77.57
4	2	4	510.38	453.88
4	2	5	105.52	94.41
4	2	6	174.48	149.21
4	2	7	108.57	83.59
4	2	8	21.00	12.74
4	2	9	40.53	39.43
4	2	10	205.67	196.92
6	2	-8	256.40	290.10
6	2	-7	22.13	22.13
6	2	-6	22.15	14.23
6	2	-5	99.57	104.81
6	2	-4	31.54	30.49
6	2	-3	78.22	78.14
6	2	-1	88.42	82.48
6	2	0	23.00	21.38
6	2	1	307.45	358.13
6	2	2	48.25	44.14
6	2	3	134.15	105.62
6	2	4	277.33	234.25
6	2	5	87.01	74.29
6	2	6	40.36	26.19
6	2	7	403.64	363.06
6	2	8	80.59	64.37
6	2	9	22.07	19.62
8	2	-8	190.65	149.45
8	2	-7	255.80	259.75
8	2	-6	38.51	40.21
8	2	-5	56.75	59.45
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8	2	-3	41.01	20.23
8	2	-2	30.65	13.10
8	2	-1	299.40	258.41
8	2	0	90.16	76.05
8	2	1	167.91	187.74
8	2	2	91.66	105.71
8	2	3	34.59	35.05
8	2	4	258.14	277.40
8	2	5	24.47	15.35
8	2	6	29.91	24.34
8	2	7	89.83	72.08
8	2	8	109.10	103.15
8	2	9	59.79	67.48
10	2	-7	145.20	122.59
10	2	-6	167.66	118.85
10	2	-5	77.98	59.14
10	2	-4	388.31	338.20
10	2	-3	112.66	82.73
10	2	-2	32.23	30.56
10	2	-1	214.56	154.27
10	2	0	137.97	118.35
10	2	1	89.20	78.82
10	2	2	343.32	406.06
10	2	3	157.30	166.16
10	2	4	78.81	82.73
10	2	5	191.79	225.45
10	2	6	25.91	38.27
10	2	7	24.52	23.05
10	2	8	95.96	124.10
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12	2	-5	34.00	39.57
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12	2	0	19.42	11.97
12	2	1	69.42	68.33
12	2	2	117.47	103.74
12	2	3	21.03	17.13
12	2	4	22.07	13.64
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14	2	3	55.97	57.74
14	2	4	16.09	39.98
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14	2	7	58.66	63.74
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16	2	0	36.48	40.76
16	2	1	137.55	118.67
16	2	2	83.71	69.31
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16	2	4	39.85	38.10
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3	3	2	138.36	122.99
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5	3	-1	72.25	81.11
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5	3	2	25.64	17.27
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5	3	4	306.71	278.86
5	3	5	119.42	96.25
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7	3	-5	126.99	136.22
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7	3	-1	177.90	142.21
7	3	0	41.49	34.20
7	3	1	56.19	44.07
7	3	2	28.97	22.02
7	3	3	100.66	114.61
7	3	4	314.74	296.27
7	3	5	189.95	159.59
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7	3	7	117.10	115.91
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9	3	-4	57.26	51.46
9	3	-3	18.25	17.00
9	3	-2	260.76	205.11
9	3	-1	269.28	237.66
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9	3	2	176.54	183.55
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9	3	4	87.82	93.98
9	3	5	19.32	26.87
9	3	6	84.60	104.33
9	3	7	163.24	195.54
11	3	-4	143.92	124.11
11	3	-3	31.17	19.64
11	3	-2	123.47	103.99
11	3	-1	87.57	66.80
11	3	0	76.00	63.25
11	3	1	13.78	4.14
11	3	2	268.88	298.30
11	3	3	38.55	45.78
11	3	4	127.54	126.94
11	3	5	123.48	140.33
11	3	6	15.13	17.45
13	3	-2	97.53	80.59
13	3	-1	113.29	94.93
13	3	0	138.18	117.33
13	3	1	57.12	50.27
13	3	2	253.36	262.48
13	3	3	146.24	154.54
13	3	4	123.33	124.67
0	4	-1	7.65	14.53
0	4	2	76.24	57.32
0	4	3	110.85	94.00
0	4	4	63.77	50.00
0	4	5	12.49	4.56
2	4	-4	11.81	20.59
2	4	-3	120.66	106.95
2	4	-2	38.10	37.85
2	4	-1	9.08	14.45
2	4	1	120.40	104.05
2	4	2	33.20	42.57
2	4	3	306.02	282.80
2	4	4	24.41	24.87
2	4	5	67.79	58.30
4	4	-4	85.99	94.40
4	4	-3	37.94	38.24
4	4	-2	235.59	274.17
4	4	-1	11.65	10.93
4	4	0	46.37	36.64
4	4	1	59.38	59.40

4	4	2	93.54	69.83
4	4	3	48.92	50.88
4	4	4	366.97	349.76
4	4	5	65.75	63.79
6	4	-3	53.08	45.63
6	4	-2	377.26	355.34
6	4	-1	73.95	45.56
6	4	0	25.45	17.40
6	4	1	234.75	229.04
6	4	2	33.59	21.36
6	4	3	63.12	61.86
6	4	4	125.48	141.48
8	4	-1	183.55	157.91
8	4	0	53.73	51.81
8	4	1	133.65	130.18
8	4	2	75.54	74.89

Chapter VI.

Description and discussion of the structure.

A projection on (010) of the final structure of $K_2Ti_6O_{13}$ is shown in Fig. 9. It consists basically of a unit of three Ti octahedra sharing edges in the square section, and this unit repeats itself in a zigzag way along the b axis. In this open frame there are no unshared corners, and the potassium ions are located in the tunnels between the structural units.

Table 7 shows the interatomic distances in the structural unit. Each Ti atom is surrounded by six oxygens in a distorted octahedron, and all are displaced from the center of the octahedron in the direction of the open sites where the K ions occur.

The potassium atoms are located at the center of a distorted cube defined by eight oxygen atoms. The potassium atoms are displaced from the center of the cube in the direction of the central void. Fig. 10 shows the environment of the different atoms in the structure. Assuming bond strength of $4/6$ for Ti and $1/8$ for K, it turns out that Pauling's electrostatic valence rule is not in general satisfied:

(a) The nearest neighbors of O(1) and O(7) are two Ti and four K atoms, so they have a net charge of $-2 + 2 \times \frac{4}{6} + 4 \times \frac{1}{8} = -\frac{1}{6}$.

(b) O(2) and O(4) have as nearest neighbors four Ti, so that their valence is oversaturated and they have a net charge of

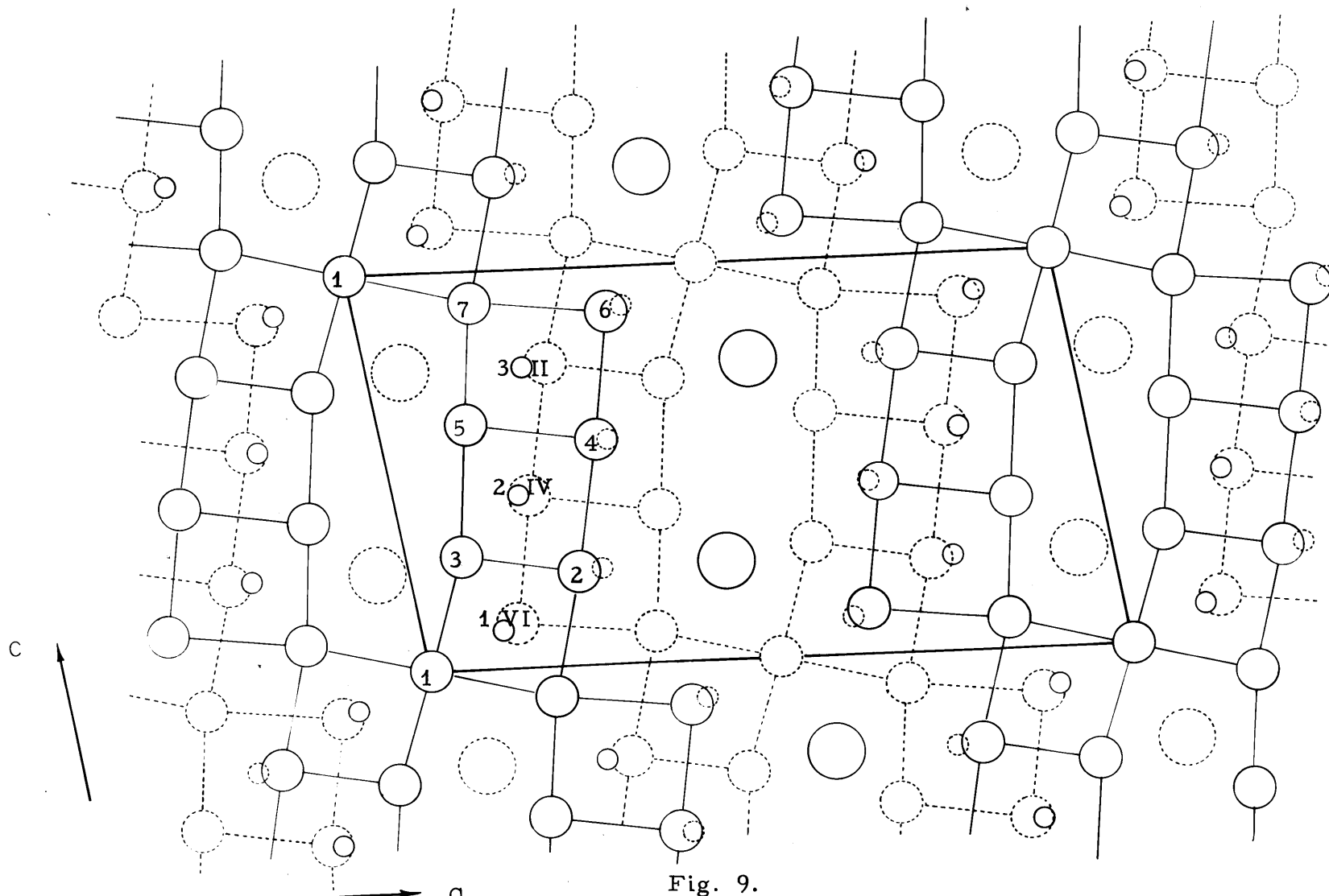


Fig. 9.

Final structure of Potassium hexatitanate projected along the b axis.
 (Large circles represent K ions, medium size circles represent O atoms, little circles represent Ti atoms).

Table 7. Interatomic distances in $K_2Ti_6O_{13}$.

	No.	Distance		No.	Distance
Ti(1) - O(1)	1	1.86 Å	O(2) - O(IV)	2	2.71 Å
Ti(2) - O(2)	1	2.11	O(3) - O(IV)	2	2.88
Ti(1) - O(3)	1	1.96	O(4) - O(IV)	2	2.62
Ti(1) - O(7)	1	1.98	O(5) - O(IV)	2	2.91
Ti(1) - O(VI)	2	1.95			
O(1) - O(7)	1	2.85	Ti(3) - O(4)	1	2.28
O(2) - O(7)	1	2.98	Ti(3) - O(5)	1	1.95
O(2) - O(3)	1	2.62	Ti(3) - O(6)	1	2.07
O(1) - O(3)	1	2.48	Ti(3) - O(7)	1	1.78
O(1) - O(VI)	2	2.96	Ti(3) - O(II)	2	4.93
O(7) - O(VI)	2	2.70	O(4) - O(5)	1	2.65
O(2) - O(VI)	2	2.58	O(4) - O(6)	1	2.98
O(3) - O(VI)	2	2.80	O(5) - O(7)	1	2.72
			O(6) - O(7)	1	3.04
Ti(2) - O(2)	1	2.28	O(4) - O(II)	2	2.71
Ti(2) - O(3)	1	1.84	O(5) - O(II)	2	2.95
Ti(2) - O(4)	1	2.11	O(6) - O(II)	2	2.59
Ti(2) - O(IV)	2	2.22	O(7) - O(II)	2	2.93
Ti(2) - O(5)	1	1.83			
O(2) - O(3)	1	2.62	K - O(1)	2	3.14
O(2) - O(4)	1	3.07	K - O(3)	2	2.36
O(3) - O(5)	1	2.98	K - O(5)	2	2.77
O(4) - O(5)	1	2.65	K - O(7)	2	2.91

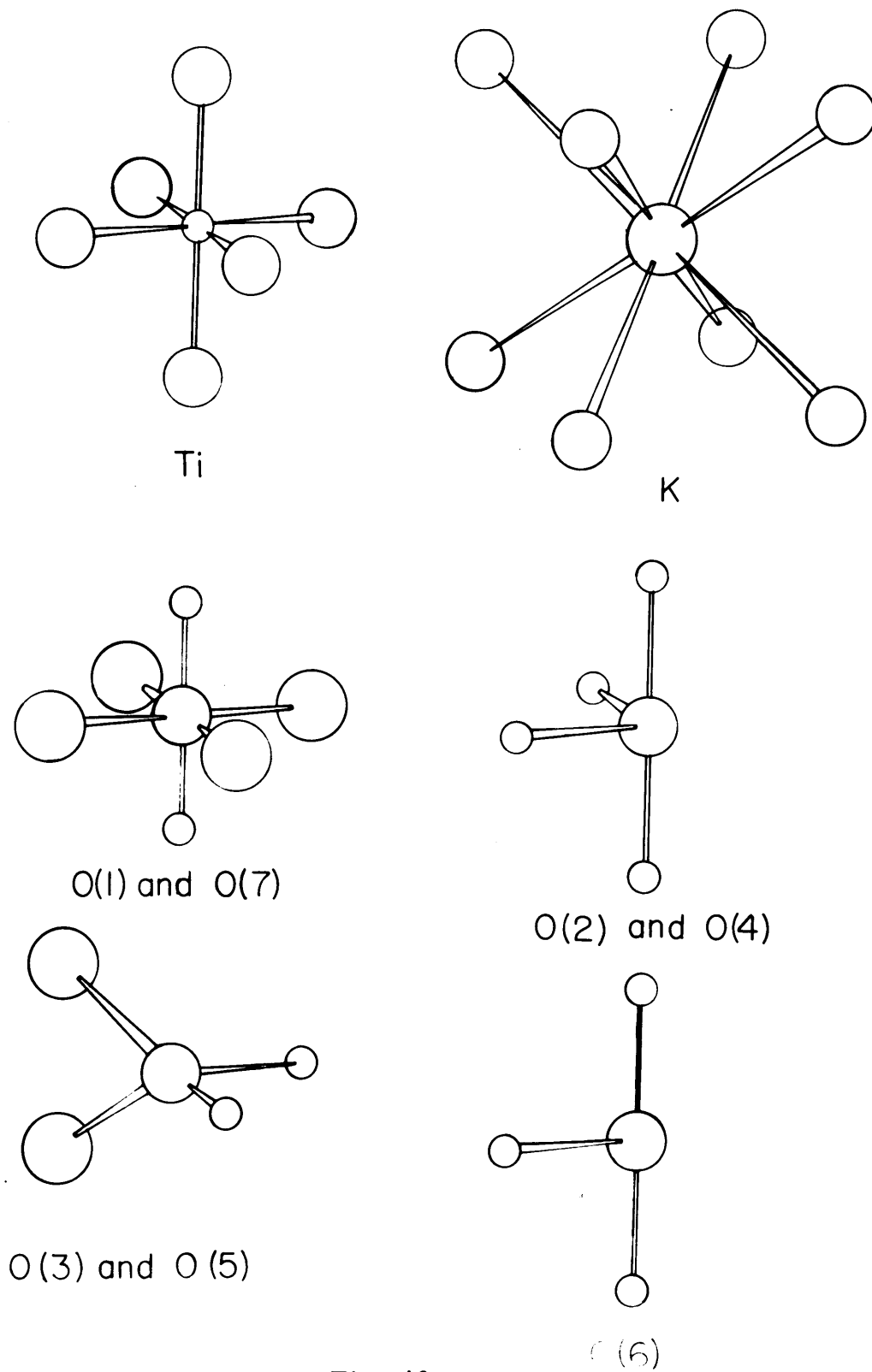


Fig. 10.
 Environment of atoms in $K_2Ti_6O_{12}$
 (Ideal positions)

$$- 2 + 4 \times \frac{4}{6} = + \frac{4}{6}.$$

(c) O(3) and O(5) have as neighbors two Ti and two K, so they have a net charge of $-2 + 2 \times \frac{4}{6} + 2 \times \frac{1}{8} = -\frac{5}{12}$.

(d) O(6) has as only nearest neighbors three Ti, and has a zero net charge, so is the one that satisfies Pauling's rules exactly.

Now, if it is assumed that the bond strength is inversely proportional to the bond distance, the acentric position of the Ti within the octahedra can be explained as being necessary to achieve the electrical neutrality. The effect, as shown in Table 7, is that the distances from Ti(1) are as follows:

$$\text{Ti(1) - O(1)} = 1.86 \text{ \AA}$$

$$\text{Ti(1) - O(2)} = 2.11$$

$$\text{Ti(1) - O(3)} = 1.96 ,$$

therefore Ti(1) contributes more than $\frac{4}{6}$ to compensate the unsaturated oxygens (1) and (3), but less to the oversaturated O(2). The same is true with respect to Ti(2):

$$\text{Ti(2) - O(3)} = 1.84 \text{ \AA}$$

$$\text{Ti(2) - O(2)} = 2.28$$

$$\text{Ti(2) - O(5)} = 1.83$$

$$\text{Ti(2) - O(4)} = 2.11 .$$

Again Ti(2) is closer to the unsaturated atoms O(3) and O(5) than to the oversaturated atoms O(2) and O(4).

Similarly, the acentric position of the potassium ion within the cube can be explained as an effort to compensate the less saturated atoms of the structure, namely O(5) and O(3):

$$K - O(5) = 2.77 \text{ \AA}$$

$$K - O(7) = 2.91 .$$

Again the ion is closer to the less saturated of the oxygens.

There is one problem left: why was it impossible to determine the true space group of the structure? This must be the subject of another investigation. Nevertheless, it is necessary to point out that this may be explained as the result of a certain amount of disorder in the crystal. In this particular case, since the structure is a layer structure, the problem could be merely one of stacking faults. This supposition is supported by the appearance of the final electron density map (Fig. 11) and the difference synthesis (Fig. 12).

In the electron-density map it is possible to observe some small additional peaks close to those belonging to the structure. The same peaks appear in the difference synthesis, Fig. 12. It is also possible to see that these additional peaks outline the same structural model as that for $K_2Ti_6O_{13}$, but are displaced along a vector approximately equal to half the Ti(1) - O(1) vector. If it is true that there are stacking fault problems, this would also explain why the R factor of the refinement could not be reduced below 12.4% even though the intensity data were good.

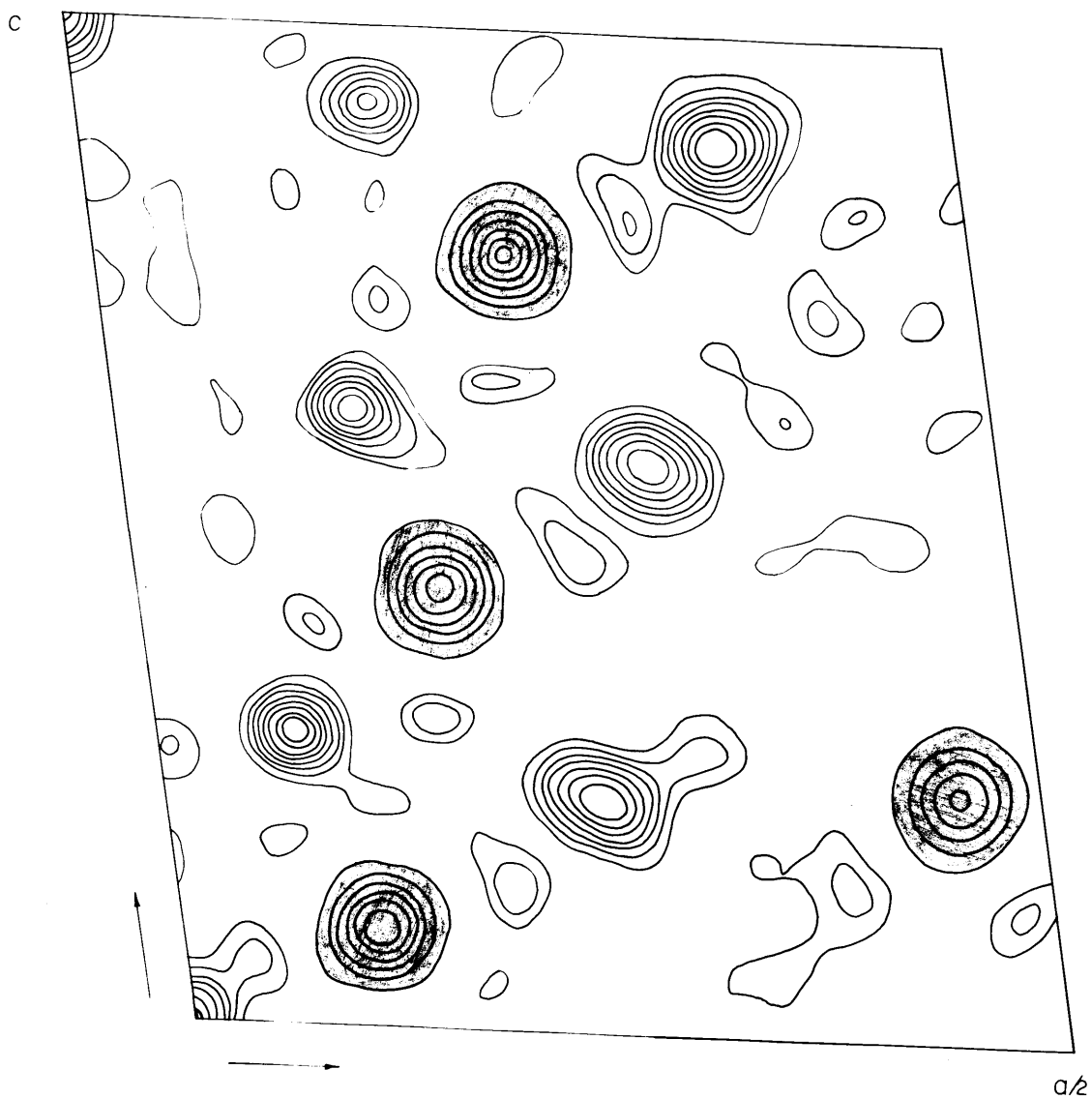


Fig. 11.

Electron density section $\rho(x0z)$

(Contours at equal but arbitrary intervals; each contour of a shaded peak correspond to five of the unshaded ones).

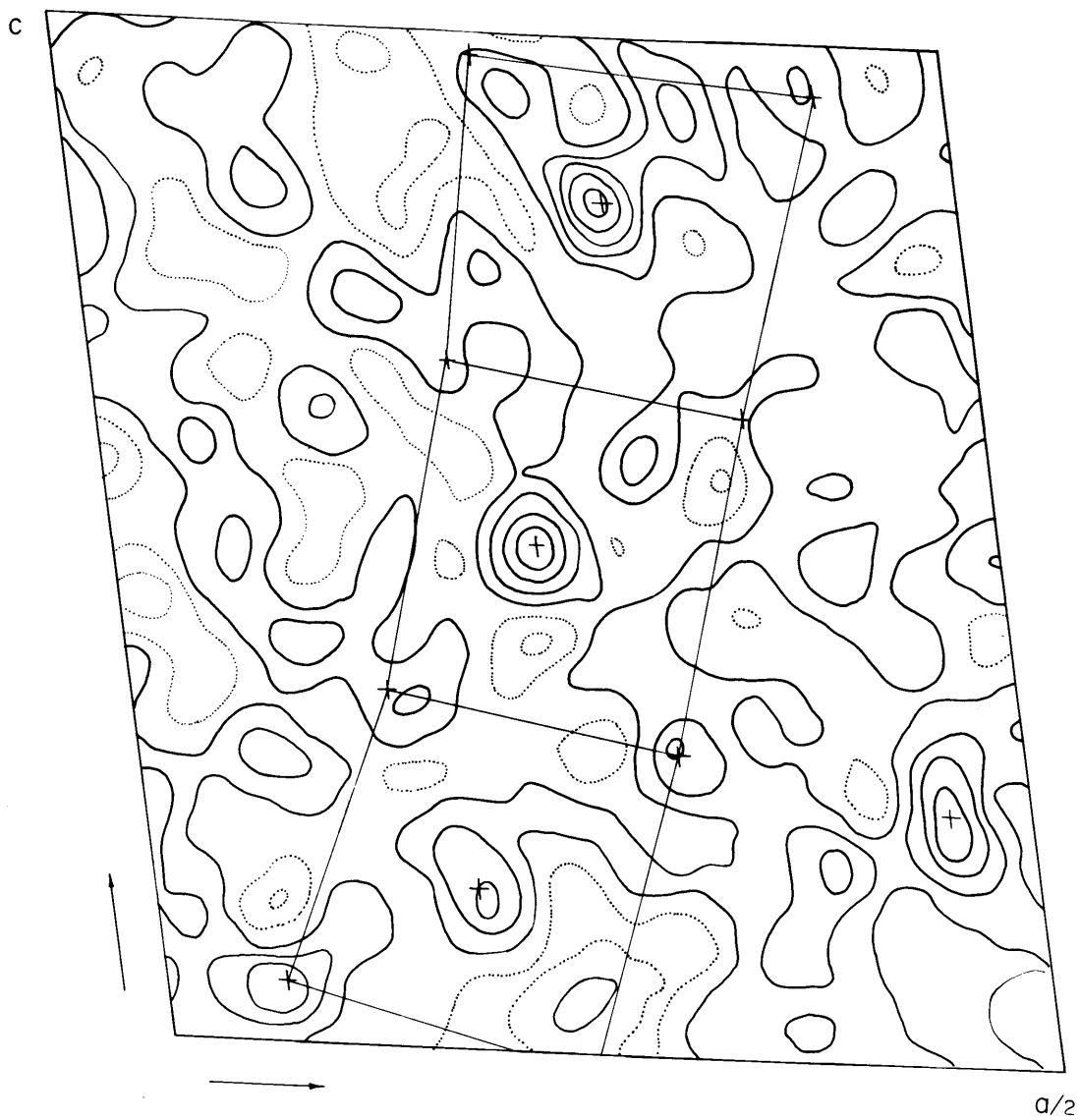


Fig. 12.

Difference synthesis section $\Delta\psi(x0z)$
(Contours at equal but arbitrary intervals)

Appendix.

Structure factors for the space groups C 2/m, Cm and C2 corrected for anomalous scattering.

The general structure factor $F(hkl)$ can be written in terms of its real and imaginary components as

$$F(hkl) = A^{\dagger} + iB^{\dagger}, \text{ where}$$

$$A^{\dagger} = \sum \sum f_r \cos 2\pi(hx_r + ky_r + lz_r) e^{-\beta_r \frac{\sin^2 \theta}{\lambda^2}}$$

$$B^{\dagger} = \sum \sum f_r \sin 2\pi(hx_r + ky_r + lz_r) e^{-\beta_r \frac{\sin^2 \theta}{\lambda^2}}$$

where the summations are taken over the different kinds of atoms in the unit cell and over all the different equivalent positions of those atoms.

$$f_r = \text{atomic scattering factor for atom } r$$

$$\beta_r = \text{temperature factor for atom } r$$

When the atom is an anomalous scatterer,

$$f_r = f_{or} + \Delta f_r^{\dagger} + i\Delta f_r^{\prime\prime}, \quad (1)$$

and both A^{\dagger} and B^{\dagger} become complex. Formula (1) cannot be used any longer in its original sense, and it is necessary to determine the new real and imaginary components of the structure factor. Call

$$A_1 = \sum f \cos 2\pi(hx + ky + lz) e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

$$B_1 = \sum f \sin 2\pi(hx + ky + lz) e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

the summation extending over all equivalent positions in a unit cell.

For the space group C 2/m

$$A_1 = 8f \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin 2\theta}{\lambda^2}}$$

$$B_1 = 0$$

$$A_1 = A_R + iA_I$$

$$A_R = 8(f_0 + \Delta f') \cos 2\pi(hx + lz) e^{-\beta \frac{\sin 2\theta}{\lambda^2}}$$

$$A_I = 8\Delta f'' \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin 2\theta}{\lambda^2}}$$

It is also possible to express the structure factor as

$$F(hkl) = A + iB$$

where $A = \sum_i A_R^i$

$$B = \sum_i A_I^i,$$

the summation being taken over all atoms in the cell. Note that the centric space group becomes acentric.

For the space group Cm

$$A_1 = 4f \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin 2\theta}{\lambda^2}}$$

$$B_1 = 4f \sin 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin 2\theta}{\lambda^2}}$$

$$A_1 = A_R + iA_I$$

$$B_1 = B_R + iB_I$$

$$F(hkl) = \Sigma(A_1 + iB_1) = \Sigma(A_R + A_I + iB_R - B_I).$$

Therefore the real and imaginary parts of the structure factor are

$$A = \Sigma(A_R - B_I)$$

$$B = \Sigma(A_I + B_R)$$

$$F(hkl) = A + iB,$$

where

$$A_R = 4(f_o + \Delta f'') \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

$$A_I = 4\Delta f'' \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

$$B_R = 4(f_o + \Delta f'') \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

$$B_I = 4\Delta f'' \sin 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

For the space group C2

$$A_1 = 4f \cos 2\pi(hx + lz) \cos 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

$$B_1 = 4f \cos 2\pi(hx + lz) \sin 2\pi ky e^{-\beta \frac{\sin^2 \theta}{\lambda^2}}$$

The same transformation formulae as for space group Cm are used:

$$A = \Sigma(A_R - B_I)$$

$$B = \Sigma(A_I + B_R)$$

$$F = A + iB,$$

with the summation taken over all atoms; but of course the form of

B_R and B_I are different, according to the expression for B_1 .

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