

## The crystal structure of potassium hexatitanate $\text{K}_2\text{Ti}_6\text{O}_{13}$

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With 11 figures

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### Auszug

Die Struktur von Kaliumhexatitanat wurde neu bestimmt. Die Raumgruppe ist  $C2/m$ . Die Elementarzelle mit  $a = 15,582 \pm 0,006 \text{ \AA}$ ,  $b = 3,82 \pm 0,01 \text{ \AA}$ ,  $c = 9,112 \pm 0,001 \text{ \AA}$ ,  $\beta = 99,764^\circ \pm 0,008^\circ$  enthält  $2(\text{K}_2\text{Ti}_6\text{O}_{13})$ . Dreidimensionale Interferenzdaten wurden mit einem Zählrohr-Diffraktometer gewonnen und für Absorption und mit dem Lorentz-Polarisations-Faktor korrigiert. Im späteren Stadium der Untersuchung wurde auch eine Korrektur für anomale Streuung der Ti-Atome angebracht.

Eine dreidimensionale Patterson-Synthese deutet eine Struktur an, die sich aus Ti-Oktaedern aufbaut, deren eine Hauptachse der 2-zähligen Achse parallel ist. Ein Strukturmodell, das die richtige Zahl der O-Atome ergab, wurde mittels der Minimumfunktion bestätigt.

In dieser Struktur sind die Ti-Oktaeder durch Kanten und Ecken zu Ketten verknüpft, mit Zwischenräumen für die K-Ionen. Sie wurde zuerst durch dreidimensionale Fourier-Synthesen und schließlich nach der Ausgleichsmethode verfeinert, bis zum Endwert  $R = 12,4\%$  für alle Interferenzen. Individuelle Temperaturfaktoren und Atomabstände stimmen mit Literaturdaten überein.

### Abstract

The crystal structure of potassium hexatitanate has been determined. The space group is  $C2/m$  and the cell dimensions are  $a = 15.582 \pm 0.006 \text{ \AA}$ ,  $b = 3.82 \pm 0.01 \text{ \AA}$ ,  $c = 9.112 \pm 0.001 \text{ \AA}$ ,  $\beta = 99.764 \pm 0.008^\circ$ . This unit cell contains  $2(\text{K}_2\text{Ti}_6\text{O}_{13})$ .

Three-dimensional intensity data were collected by means of a single-crystal Geiger-counter diffractometer and the intensities were corrected for Lorentz-polarization factors 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. A model structure which gave the correct number of oxygens in this symmetry was confirmed by means

of the minimum function. This structure, consisting of chains of Ti octahedra sharing edges and corners, with some tunnels where the K ions can fit, 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.

### Introduction

Even though the octahedral coordination seems to be the most common one in the Ti—O compounds, ANDERSSON and WADSLEY<sup>1</sup> had found, not long ago, a five-coordinated Ti in  $K_2Ti_2O_5$ . It appeared, then, of interest to determine the structure of  $K_2Ti_6O_{13}$ , a compound of the same family whose unit cell and space group had been reported in 1959 by BERRY *et al.*<sup>2</sup>

Recently ANDERSSON and WADSLEY<sup>3</sup> published the structures of sodium and rubidium titanates which are obviously isotypic with our potassium titanate. A comparison between their results and ours is also given here.

### Unit cell and space group

Crystals of potassium titanate synthesized by melting  $TiO_2$  and  $K_2CO_3$  were kindly furnished for our work by Dr. H. S. YOUNG of E. I. Du Pont de Nemours and Co. 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 good extinction under the polarizing microscope was chosen, and three Weissenberg photographs corresponding to the levels 0, 1, and 2, with the 2-fold axis as the rotation axis, were taken from it. The intensity distribution was found to correspond to the monoclinic symmetry  $C2/m$ ,  $Cm$ , or  $C2$ . For the first stages of the structure determination it was assumed to be  $C2/m$ . This ambiguity is discussed further in the section of refinement. Every reflection was indexed on the basis of a monoclinic cell of approximate dimensions  $a = 15.5 \text{ \AA}$ ,  $b = 3.82 \text{ \AA}$ ,  $c = 9.1 \text{ \AA}$  and  $\beta = 99.5^\circ$ . More exact values for the  $a$  and  $c$  axes and the  $\beta$  angle were

<sup>1</sup> STEN ANDERSSON and E. D. WADSLEY, The crystal structure of  $K_2Ti_2O_5$ . *Acta Chem. Scand.* **15** (1961) 663–669.

<sup>2</sup> K. L. BERRY, V. D. AFTANDILIAN, W. W. GILBERT, E. P. H. MEIBOHM and H. S. YOUNG, Potassium tetra- and hexatitanates. *J. Inorg. Nucl. Chem.* **14** (1960) 231–239.

<sup>3</sup> STEN ANDERSSON and A. D. WADSLEY, The structure of  $Na_2Ti_6O_{13}$  and  $Rb_2Ti_6O_{13}$  and the alkali metal titanates. *Acta Crystallogr.* **15** (1962) 194–201.

obtained from a precision back-reflection Weissenberg photograph<sup>4</sup>. These results were adjusted by means of a least-squares calculation using a program written by BURNHAM<sup>5</sup> for the IBM 709 computer. The value of the  $b$  axis was obtained as an average of one rotation photograph and two precession photographs with the  $a$  and  $c$  axes as precessing axes respectively.

Table 1. *Unit cell dimensions of potassium hexatitanate*

	BERRY <i>et al.</i> <sup>2</sup>	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
$\beta$	99.6°	99.764° ± 0.008°

The final values for the cell constants are in good agreement with the ones previously reported as shown on Table 1. Using these values and assuming  $2(\text{K}_2\text{Ti}_6\text{O}_{13})$  per cell, the calculated density is 3.581 g/cm<sup>3</sup>, very close to the observed value<sup>2</sup> of 3.58.

### Intensity measurement

A prismatic crystal of dimensions  $0.0923 \times 0.0213 \times 0.2272$  mm was chosen. 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 was easily oriented optically. The orientation was corrected by means of precession photographs.

The collection of the intensities was made with a single-crystal diffractometer<sup>6</sup> using an argon-filled Geiger counter as the detector.  $\text{CuK}\alpha$  radiation was used, and the generator was run uniformly at 35kV and 15mA. 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

<sup>4</sup> M. J. BUERGER, X-ray crystallography (John Wiley, New York, 1942), 435–465.

<sup>5</sup> CHARLES WILSON BURNHAM, The structures and crystal chemistry of the aluminum-silicate minerals. Ph. D. Thesis, M.I.T., August, 1961.

<sup>6</sup> MARTIN J. BUERGER, Crystal-structure analysis. (John Wiley and Sons, New York, 1960) 590.

instead, three different scale factors were used: one for all reflections measured without aluminum foil, and the other two for each set of reflections measured with the two different aluminum foils. The uniformity of the x-ray beam was checked according to the technique described by BURNHAM<sup>5</sup>, and the white radiation effect<sup>7</sup> was found to be negligible.

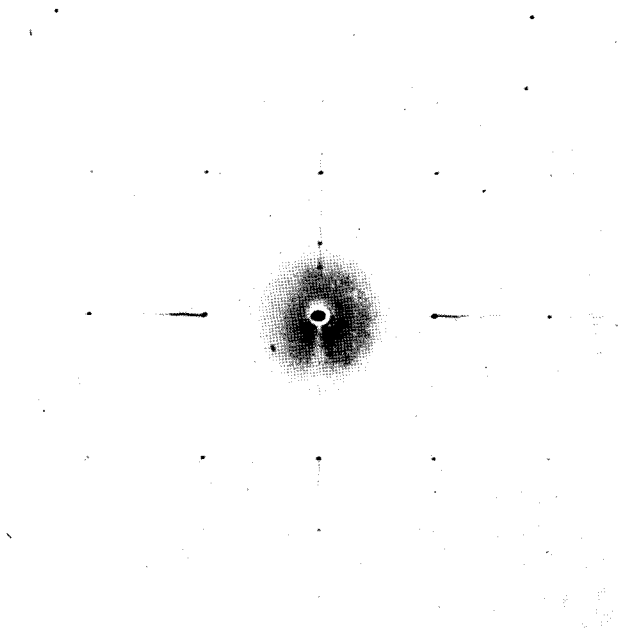


Fig. 1. Zero-level *a*-axis precession photograph, (*c*\* is vertical)

To determine the integrated intensity, each peak was scanned and from the total number of counts, which represented the intensity of the peak plus the background, the background was subtracted. This background was determined for each peak as an average from the number of counts/sec counted at a fixed point on both sides of the peak, multiplied by the number of seconds during which the peak was scanned. When a zero or "negative" value was found it was set equal to 1/3 the lowest positive value observed<sup>5</sup>.

<sup>7</sup> KARL FISCHER and THEO HAHN, Untergrundskorrektur für Einkristall-Zählrohr-Diffraktometer. *Z. Kristallogr.* **116** (1961) 27–35.

The integrated intensities were corrected for Lorentz-polarization factors using the method described by PREWITT<sup>8</sup> and for absorption. The program written for the 709 IBM computer by BURNHAM<sup>5</sup> corrects absorption effects for a prismatic crystal with an approximate error of 3.8% as used in this case.

### Structure determination

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

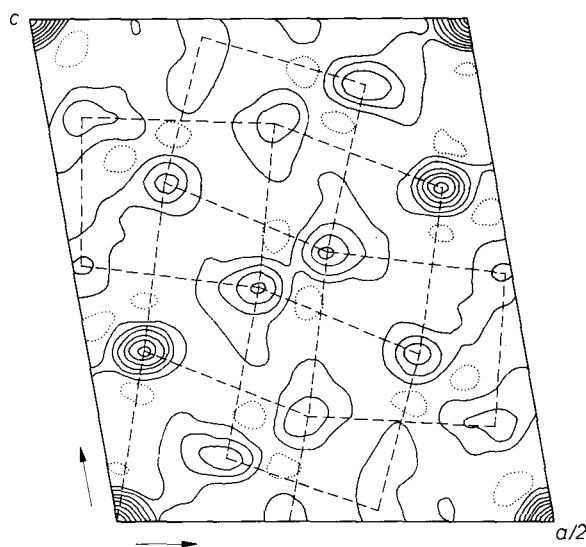


Fig. 2. Patterson projection  $P(xz)$

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. 1).

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, definitely fixes the position of the potassium atoms.

A two-dimensional Patterson synthesis (Fig. 2) projected along the  $b$  axis of the crystal showed a square arrangement of peaks which

<sup>8</sup> CHARLES T. PREWITT, The parameters  $\gamma$  and  $\varphi$  for equi-inclination, with application to the single-crystal counter diffractometer. *Z. Kristallogr.* **114** (1960) 355–360.

confirmed that the structure was based on Ti octahedra with their axes parallel to the  $b$  axis. In the symmetry  $C2/m$ , this implies that the basic structure would be a sort of layer structure, with atoms only

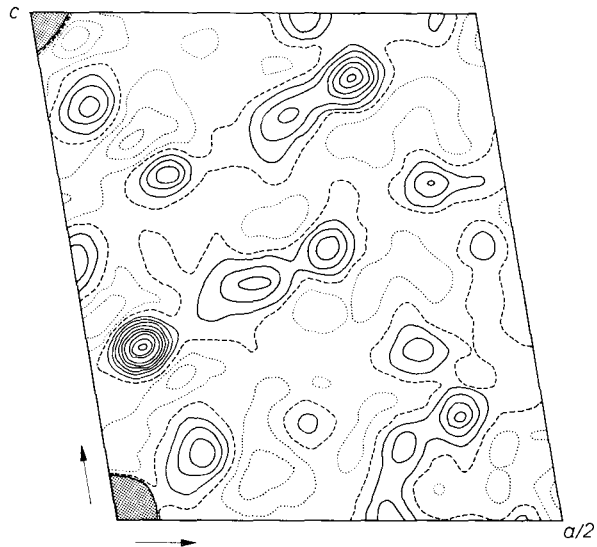


Fig. 3. Three-dimensional Patterson, section  $P(x0z)$

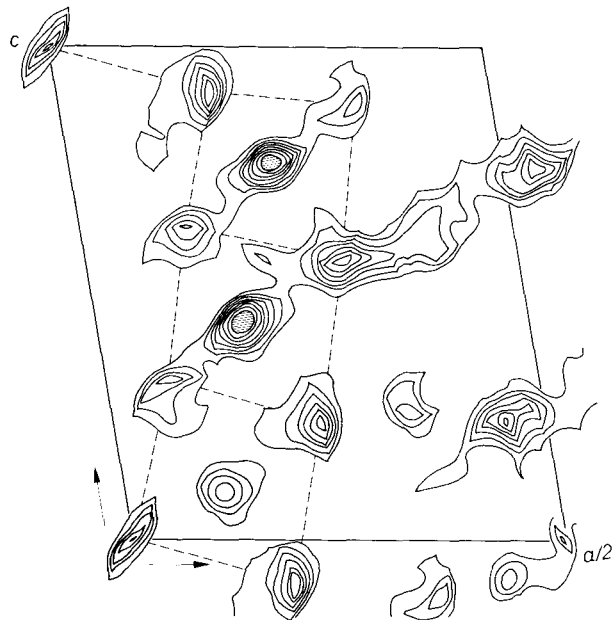


Fig. 4. Minimum function  $M(x0z)$ , based on an O—O peak

at the values zero and  $\frac{1}{2}$  for the  $y$  coordinate due to the short length of the  $b$  axis. Effectively, a three-dimensional Patterson synthesis showed no peaks except at the sections  $y = 0$  and  $y = \frac{1}{2}$ ; both sections

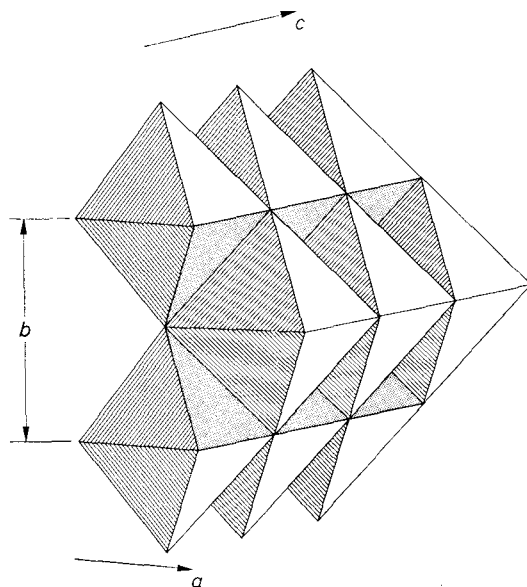


Fig. 5. Clinographic projection of the structural unit of  $K_2Ti_6O_{13}$

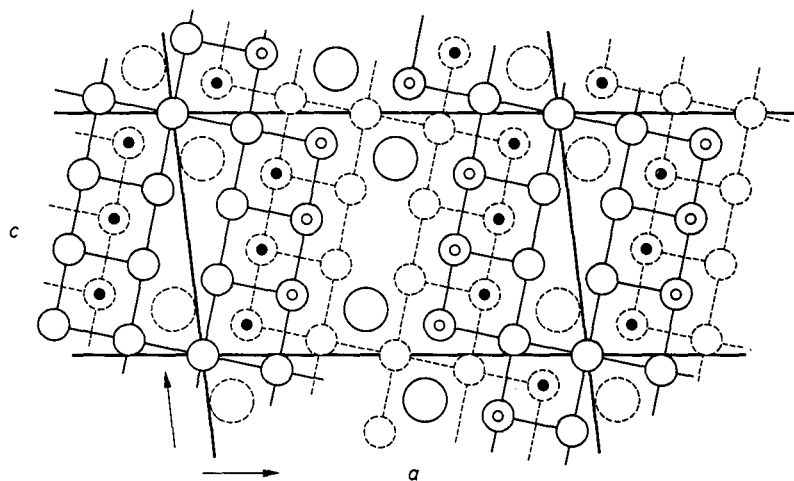


Fig. 6. Projection of the model structure of  $K_2Ti_6O_{13}$  along the  $b$  axis

are related by an inversion center at the point  $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$  for this space group. Therefore the three-dimensional work required in the use of image-seeking functions was reduced to the study of the section  $P(x0z)$  of Fig. 3.

Minimum functions<sup>9</sup> based on different peaks of  $P(x0z)$  were formed, and although these did not give an unambiguous result (because the peaks used were not single peaks); they all agreed in outlining a configuration of three squares, each with a peak in the

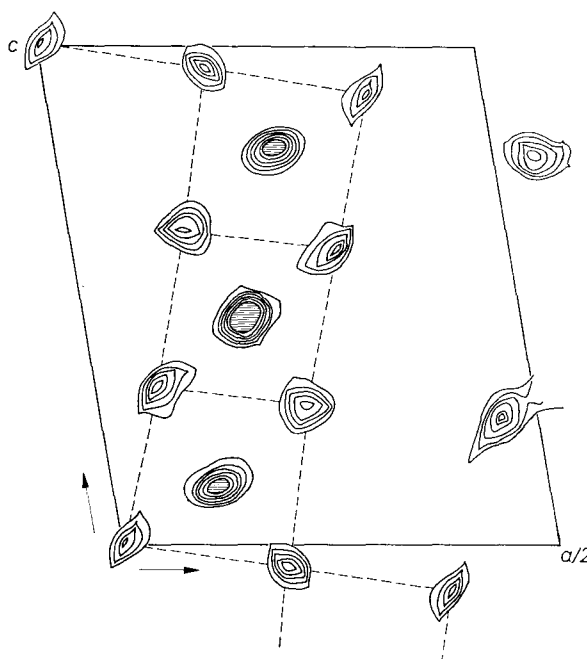


Fig. 7. Minimum function  $M(x0z)$ , based on a K-K peak

center, sharing edges so that they formed a row making a small angle with the direction of the  $c$  axis (Fig. 4). Recalling that the substructure reflections previously mentioned indicated a motif repeated three times along the  $c$  axis, there was enough evidence to prove that the basic unit was three Ti octahedra sharing edges, even though the relative weights of the peaks identified with the Ti atoms were not equal.

<sup>9</sup> MARTIN J. BUEGER, *Vector Space*. (John Wiley and Sons, New York, 1959.)



The number of oxygens, 26 in the complete cell, required that at least one should be placed at an inversion center, and this was placed at the origin, in agreement also with the minimum function of Fig. 4. This fixed the position of the basic motif, and the symmetry elements produced the other three octahedra to complete a set having composition  $\text{Ti}_6\text{O}_{13}$ . A clinographic projection of the structural unit is shown in Fig. 5, and a projection of the model structure along the  $b$  axis is shown in Fig. 6.

The position of the four potassium atoms shown in Fig. 6 was unambiguously determined. The three cubic voids, where the chains

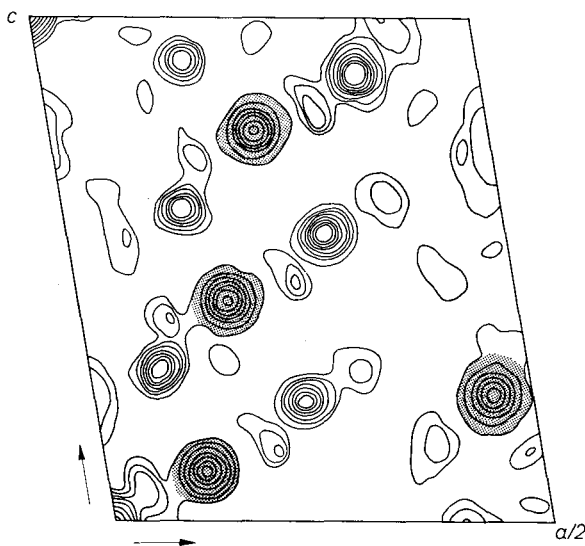


Fig. 8. Final electron-density section  $\rho(x0z)$

of octahedra are furthest apart, were the only places where an atom of diameter  $2.66 \text{ \AA}$  could fit. Both external voids are equivalent and have a multiplicity of four, the central one has a multiplicity of two. Since there are four potassium atoms per unit cell, this last possibility was discarded.

Another minimum function  $M(x0z)$ , based on the K—K peak, was now made (Fig. 7). Its similarity with the proposed model structure was a proof of the correctness of the model.

Figure 8 is the electron density  $\rho(x0z)$  of potassium hexatitanate after the refinement was completed. The close correspondence with the minimum functions of Fig. 4 and 7 is evident.

### Refinement of the structure

The coordinates of the model structure shown in Fig. 6, adjusted for the true values of the cell constants, were submitted for two cycles of least-squares refinement in the IBM 709 computer. BUSING and LEVY's<sup>10</sup> 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 to 1.0 and a temperature factor of 0.7 was assumed for all atoms. Atomic scattering curves<sup>11,12,13</sup> for  $\text{Ti}^{+3}$  (adjusted at small  $\sin\theta$  values for  $\text{Ti}^{+4}$ ), for  $\text{O}^{-2}$  and  $\text{K}^+$  were used. After two cycles, which adjusted the scale factors, the discrepancy factor  $R$  was 39.1% and the refinement stopped.

A Fourier refinement<sup>6</sup> was next attempted. A three-dimensional Fourier synthesis was calculated in the IBM 709 computer, using the program MIFRI<sup>14</sup>, assigning to the  $F_{\text{ob}}$ 's the signs of the  $F_{\text{cal}}$ 's, as obtained from the second least-squares cycle. After the first Fourier synthesis followed by a structure-factor calculation the  $R$  factor dropped to 32.6% and, after three more cycles of the Fourier refinement, converged to an  $R$  factor of 24.2%.

The coordinates, as obtained from the last Fourier synthesis, were submitted again to least-squares refinement, and after four cycles the  $R$  factor was reduced to 16%. In each cycle of refinement some negative temperature factors had been obtained and this was attributed in part to the anomalous scattering character of Ti. A new FORTRAN least-squares crystallographic program SFLSQ2, written recently by C. T. PREWITT<sup>15</sup> of our laboratory, which allows corrections for anomalous scattering<sup>16</sup>, was used from this point on. DAUBEN and

<sup>10</sup> WILLIAM R. BUSING and HENRY A. LEVY, A crystallographic least-squares refinement program for IBM 704. Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1959.

<sup>11</sup> R. E. WATSON and A. J. FREEMAN, Hartree-Fock atomic scattering factors for the iron transition series. *Acta Crystallogr.* **14** (1961) 27–37.

<sup>12</sup> T. SUZUKI, Atomic scattering factor for  $\text{O}^{-2}$ . *Acta Crystallogr.* **13** (1960) 279.

<sup>13</sup> A. J. FREEMAN, Atomic scattering factors for spherical and aspherical charge distributions. *Acta Crystallogr.* **12** (1959) 261–271.

<sup>14</sup> WILLIAM G. SLY and DAVID P. SHOEMAKER, MIFRI: Two and three dimensional crystallographic Fourier summation program for IBM 704 computer (program description and manual of operation). Technical report, Office of Ordnance Research contract DA-19-020-RD-4696 (1960).

<sup>15</sup> CHARLES T. PREWITT (1962), Personal communication.

<sup>16</sup> DAVID H. TEMPLETON, X-ray dispersion effects in crystal-structure determinations. *Acta Crystallogr.* **8** (1955) 842.

TEMPLETON'S<sup>17</sup> atomic scattering values were assigned to the three Ti atoms and this correction improved the temperature factors but not the  $R$ . Up to this point, BURNHAM'S<sup>5</sup> weighting scheme had been used and it was decided that HUGHES'<sup>18</sup> weighting scheme should be tried. BURNHAM'S weighting scheme bases the refinement on the

Table 2. *Potassium hexatitanate. Atomic coordinates before Fourier refinement*

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 $\pm$ 0.09
Ti(2)	0.1716	0.0001	0.0	0.4386	0.0002	0.60 $\pm$ 0.09
Ti(3)	0.2325	0.0001	0.0	-0.2238	0.0002	0.50 $\pm$ 0.09
K	0.4540	0.0002	0.0	0.2474	0.0003	1.11 $\pm$ 0.09
O(1)	0	0	0	0		0.6 $\pm$ 0.2
O(2)	0.2370	0.0006	0.0	0.237	0.001	0.6 $\pm$ 0.2
O(3)	0.0764	0.0006	0.0	0.291	0.001	0.6 $\pm$ 0.2
O(4)	0.2964	0.0006	0.0	-0.428	0.001	0.2 $\pm$ 0.2
O(5)	0.1330	0.0006	0.0	-0.384	0.001	0.4 $\pm$ 0.2
O(6)	0.3591	0.0006	0.0	-0.109	0.001	0.4 $\pm$ 0.2
O(7)	0.1677	0.0006	0.0	-0.083	0.001	0.6 $\pm$ 0.2

higher  $F_{ob}$ 's, which is very convenient for the first stages since it uses the structure factors with the more reliable phases; HUGHES' weighting scheme gives a higher weight to the medium-strong  $F$ 's.

<sup>17</sup> CAROL H. DAUBEN and DAVID H. TEMPLETON, A table of dispersion corrections for x-ray scattering of atoms. *Acta Crystallogr.* 8 (1955) 841-842.

<sup>18</sup> E. W. HUGHES, The crystal structure of melamine. *J. Amer. Chem. Soc.* 63 (1941) 1737-1752.

Table 4. *Potassium hexatitanate. Final 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	0.008	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	$0.7 \pm 0.2$

After three more cycles the refinement converged to an  $R$  factor of 12.4% for all reflections. Table 2 shows the values of the initial atomic coordinates ( $R = 39.1\%$ ) and in Table 3 the final coordinates, corresponding to an  $R$  of 12.4%, are listed.

The coordinates given by ANDERSON and WADSLEY<sup>3</sup> for sodium hexatitanate were also submitted for refining, but using  $K_2Ti_6O_{13}$  intensity data. After two cycles, which adjusted the scale factors, the discrepancy factor was 20.6% and the coordinates were beginning to converge to the  $K_2Ti_6O_{13}$  values, as shown on Table 4.

Table 5 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 reflection 131 because its value was found to be incorrect.

#### Space group

At this stage the result of varying the space group of potassium hexatitanate was investigated. The final atomic coordinates were submitted for refinement in the space groups  $Cm$  and  $C2$ .

Space group  $Cm$  permitted refinement down to  $R = 13\%$ . But the resulting high standard deviations and the very high values for the temperature factors allowed us to discard this space group as a possibility.

Two cycles of refining in space group  $C2$  lead to  $R = 12.4\%$ , the same as that for  $C2/m$ , and the deviation of all but one  $y$  coordinate from the zero value required by  $C2/m$  were smaller than the standard deviations (Table 6). Two facts, then, pointed to the space group  $C2/m$  and not  $C2$  as the true space group of potassium hexatitanate:

Table 5. Potassium hexatitanate, observed and calculated structure factors

h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>
0 0 1	49.5	52.5	6 0 3	187.3	148.1	14 0 0	232.4	192.7	3 1 1	207.1	281.5
0 0 2	147.9	131.7	6 0 4	338.1	324.7	14 0 1	27.3	24.8	3 1 0	320.1	370.0
0 0 3	172.9	174.6	6 0 5	120.7	91.5	14 0 2	46.7	33.0	3 1 1	444.3	372.6
0 0 4	109.9	116.8	6 0 6	35.2	33.6	14 0 3	113.3	111.9	3 1 2	209.2	202.7
0 0 5	18.8	5.7	6 0 7	388.2	426.2	14 0 4	168.9	132.5	3 1 3	36.1	32.8
0 0 6	383.4	430.2	6 0 8	81.2	74.7	14 0 5	39.8	35.1	3 1 4	16.0	5.7
0 0 7	64.2	36.6	6 0 9	27.6	22.1	14 0 6	180.2	162.7	3 1 5	195.6	193.5
0 0 8	54.3	56.0	6 0 10	144.1	115.8	14 0 7	45.6	47.2	3 1 6	276.3	276.6
0 0 9	268.8	313.5	6 0 11	70.6	83.9	14 0 8	193.0	202.2	3 1 7	106.6	107.2
0 0 10	40.6	19.7	8 0 0	67.1	67.8	14 0 9	58.2	62.9	3 1 8	123.1	121.2
0 0 11	45.9	40.3	8 0 1	178.4	166.3	14 0 10	64.0	48.2	3 1 9	196.0	159.5
2 0 0	27.2	44.4	8 0 2	219.8	294.4	14 0 11	83.2	77.7	3 1 10	147.2	137.6
2 0 1	28.8	16.0	8 0 3	44.4	42.2	14 0 12	107.8	109.7	5 1 0	21.2	28.7
2 0 2	165.9	183.5	8 0 4	65.6	60.9	14 0 13	66.2	69.9	5 1 1	133.8	138.2
2 0 3	72.5	70.3	8 0 5	99.1	97.5	14 0 14	160.2	175.1	5 1 2	105.7	112.6
2 0 4	333.2	334.0	8 0 6	22.5	26.9	14 0 15	32.5	29.7	5 1 3	21.9	26.8
2 0 5	231.4	252.1	8 0 7	23.6	13.9	16 0 0	55.3	49.0	5 1 4	222.5	246.0
2 0 6	17.2	19.9	8 0 8	345.1	349.7	16 0 1	276.2	266.2	5 1 5	13.8	16.2
2 0 7	151.3	135.0	8 0 9	115.4	97.2	16 0 2	17.5	6.7	5 1 6	38.4	43.0
2 0 8	103.8	117.4	8 0 10	194.6	222.3	16 0 3	74.3	74.9	5 1 7	85.3	85.9
2 0 9	58.9	47.4	8 0 11	89.3	120.3	16 0 4	54.0	46.2	5 1 8	118.4	153.3
2 0 10	232.6	212.3	8 0 12	22.3	36.8	16 0 5	132.9	135.0	5 1 9	38.7	12.4
2 0 11	99.3	70.6	8 0 13	337.3	347.9	16 0 6	85.9	79.4	5 1 10	83.1	82.0
2 0 12	431.5	397.6	8 0 14	31.1	18.5	16 0 7	263.3	254.5	5 1 11	17.3	12.3
2 0 13	17.5	23.5	8 0 15	29.5	29.9	16 0 8	40.9	39.9	5 1 12	251.5	216.8
2 0 14	120.3	114.8	8 0 16	107.0	82.4	16 0 9	19.2	33.7	5 1 13	380.4	335.5
2 0 15	168.6	176.6	8 0 17	154.8	120.1	16 0 10	115.9	109.4	5 1 14	169.8	147.8
2 0 16	90.4	81.4	8 0 18	87.1	74.8	16 0 11	51.8	46.4	5 1 15	52.4	57.6
2 0 17	25.7	43.4	8 0 19	262.6	299.1	18 0 0	66.8	47.4	5 1 16	134.3	129.0
2 0 18	285.9	318.3	10 0 0	37.3	35.9	18 0 1	20.2	25.6	5 1 17	89.6	63.4
2 0 19	114.5	83.2	10 0 1	162.8	137.8	18 0 2	194.3	186.7	5 1 18	217.7	183.3
2 0 20	88.2	98.7	10 0 2	138.5	136.0	18 0 3	77.8	67.4	5 1 19	252.5	238.3
4 0 0	19.2	37.4	10 0 3	75.7	68.8	18 0 4	33.2	29.9	7 1 0	120.3	128.0
4 0 1	69.7	91.4	10 0 4	364.6	394.9	18 0 5	47.5	49.2	7 1 1	59.8	51.6
4 0 2	114.5	118.8	10 0 5	110.9	97.7	18 0 6	61.6	65.7	7 1 2	17.4	25.8
4 0 3	61.1	66.7	10 0 6	47.8	37.9	18 0 7	44.9	30.5	7 1 3	108.3	111.4
4 0 4	47.3	42.2	10 0 7	235.9	184.8	1 1 0	147.1	159.5	7 1 4	148.6	170.8
4 0 5	360.5	394.0	10 0 8	181.6	154.5	1 1 1	95.8	82.3	7 1 5	160.8	191.8
4 0 6	169.5	193.8	10 0 9	117.4	102.8	1 1 2	143.9	131.6	7 1 6	204.8	249.5
4 0 7	69.0	62.3	10 0 10	352.4	402.4	1 1 3	22.0	11.5	7 1 7	206.5	219.4
4 0 8	394.0	388.6	10 0 11	181.8	208.3	1 1 4	196.5	203.8	7 1 8	84.4	59.3
4 0 9	19.2	16.9	10 0 12	89.8	100.0	1 1 5	165.7	156.7	7 1 9	49.0	49.8
4 0 10	88.3	99.9	10 0 13	228.8	261.7	1 1 6	200.5	203.0	7 1 10	20.4	19.1
4 0 11	150.0	145.2	10 0 14	48.0	50.1	1 1 7	79.3	83.3	7 1 11	182.8	167.8
4 0 12	205.0	168.5	10 0 15	21.9	24.1	1 1 8	267.2	235.3	7 1 12	274.6	236.5
4 0 13	103.3	99.1	10 0 16	125.3	143.2	1 1 9	71.8	74.9	7 1 13	24.3	21.3
4 0 14	532.6	512.2	10 0 17	96.0	69.8	1 1 10	11.8	3.6	7 1 14	190.1	147.3
4 0 15	134.2	121.9	10 0 18	14.6	17.8	1 1 11	160.9	170.7	7 1 15	29.2	15.6
4 0 16	196.6	181.3	12 0 0	188.8	149.4	1 1 12	150.7	148.8	7 1 16	99.0	96.7
4 0 17	121.5	94.8	12 0 1	27.3	12.8	1 1 13	137.6	143.3	7 1 17	113.5	100.4
4 0 18	26.9	16.7	12 0 2	57.5	45.5	1 1 14	12.9	10.2	9 1 0	241.4	203.9
4 0 19	39.8	45.7	12 0 3	196.9	154.2	1 1 15	276.2	274.0	9 1 1	186.2	184.8
4 0 20	239.4	222.0	12 0 4	31.7	30.2	1 1 16	49.6	56.4	9 1 2	77.9	90.0
4 0 21	32.1	28.3	12 0 5	71.5	37.8	1 1 17	70.8	62.9	9 1 3	59.1	49.2
6 0 0	21.8	30.2	12 0 6	299.6	275.0	1 1 18	52.0	49.1	9 1 4	69.8	77.8
6 0 1	241.2	326.6	12 0 7	20.3	11.9	1 1 19	86.7	89.2	9 1 5	24.6	15.8
6 0 2	20.3	26.2	12 0 8	105.9	83.0	3 1 0	28.8	15.3	9 1 6	309.1	296.3
6 0 3	33.1	14.3	12 0 9	117.5	119.7	3 1 1	60.3	72.3	9 1 7	374.4	341.3
6 0 4	118.6	126.3	12 0 10	18.6	23.4	3 1 2	186.5	179.0	9 1 8	213.4	218.7
6 0 5	51.0	42.7	12 0 11	18.6	15.6	3 1 3	174.6	190.7	9 1 9	234.6	274.8
6 0 6	102.2	108.2	12 0 12	165.6	206.4	3 1 4	253.1	264.1	9 1 10	61.8	64.6
6 0 7	108.9	123.5	12 0 13	103.7	124.2	3 1 5	183.0	196.6	9 1 11	125.9	133.5
6 0 8	29.3	18.2	12 0 14	21.4	8.7	3 1 6	50.9	51.9	9 1 12	41.7	31.4
6 0 9	294.2	337.9	12 0 15	239.2	296.6	3 1 7	202.8	238.3	9 1 13	139.1	132.4
6 0 10	77.8	67.0	12 0 16	17.5	12.3	3 1 8	112.4	125.7	9 1 14	266.0	250.8

Table 5. (Continued)

h k l	$ F_{obs.} $	$ F_{calc.} $	h k l	$ F_{obs.} $	$ F_{calc.} $	h k l	$ F_{obs.} $	$ F_{calc.} $	h k l	$ F_{obs.} $	$ F_{calc.} $
9 1 8	267.1	281.8	0 2 7	34.8	32.6	8 2 $\bar{2}$	30.7	13.1	1 3 $\bar{6}$	111.7	143.2
9 1 9	104.5	117.7	0 2 8	37.5	46.1	8 2 $\bar{1}$	299.4	258.4	1 3 $\bar{5}$	97.1	103.9
9 1 10	56.1	78.0	0 2 9	275.2	277.7	8 2 0	90.2	76.1	1 3 $\bar{4}$	126.2	134.9
11 1 $\bar{7}$	342.4	276.0	2 2 $\bar{9}$	36.1	14.6	8 2 1	167.9	187.7	1 3 $\bar{3}$	114.7	120.1
11 1 $\bar{6}$	108.8	84.9	2 2 $\bar{8}$	150.2	159.5	8 2 2	91.7	105.7	1 3 $\bar{2}$	174.6	174.8
11 1 $\bar{5}$	66.9	36.6	2 2 $\bar{7}$	58.9	60.2	8 2 3	34.6	35.1	1 3 $\bar{1}$	41.6	46.7
11 1 $\bar{4}$	202.8	155.6	2 2 $\bar{6}$	304.8	344.9	8 2 4	258.1	277.4	1 3 2	104.1	98.8
11 1 $\bar{3}$	45.6	28.4	2 2 $\bar{5}$	204.7	200.7	8 2 5	24.5	15.4	1 3 3	136.1	127.0
11 1 $\bar{2}$	198.2	143.7	2 2 $\bar{4}$	28.7	19.3	8 2 6	29.9	24.3	1 3 4	100.7	90.9
11 1 $\bar{1}$	92.6	76.4	2 2 $\bar{3}$	150.2	158.2	8 2 7	89.8	72.1	1 3 5	25.8	7.5
11 1 0	116.4	95.3	2 2 $\bar{2}$	68.2	70.2	8 2 8	109.1	103.2	1 3 6	220.5	203.4
11 1 1	15.6	5.9	2 2 $\bar{1}$	33.1	28.5	8 2 9	59.8	67.5	1 3 7	20.0	38.1
11 1 2	324.5	415.6	2 2 1	209.5	186.6	10 2 $\bar{7}$	145.2	122.6	1 3 8	50.3	46.6
11 1 3	62.9	66.3	2 2 2	62.6	61.8	10 2 $\bar{6}$	167.7	118.9	1 3 $\bar{7}$	101.8	144.1
11 1 4	151.7	176.3	2 2 3	409.8	366.5	10 2 $\bar{5}$	78.0	59.1	1 3 $\bar{6}$	156.9	183.8
11 1 5	156.2	191.5	2 2 4	17.9	27.9	10 2 $\bar{4}$	388.3	338.2	1 3 $\bar{5}$	122.0	133.9
11 1 6	42.6	24.0	2 2 5	95.3	89.9	10 2 $\bar{3}$	112.7	82.7	1 3 $\bar{4}$	19.1	31.9
11 1 7	45.4	44.6	2 2 6	137.1	141.4	10 2 $\bar{2}$	32.2	30.6	1 3 $\bar{3}$	137.2	148.9
11 1 8	173.7	214.9	2 2 7	68.8	63.6	10 2 $\bar{1}$	214.6	154.3	1 3 $\bar{2}$	93.8	106.6
11 1 9	25.7	26.9	2 2 8	31.1	34.8	10 2 0	138.0	118.4	1 3 $\bar{1}$	142.6	174.8
13 1 $\bar{6}$	43.0	35.0	2 2 9	281.6	280.6	10 2 1	89.2	78.8	1 3 0	247.6	285.8
13 1 $\bar{5}$	154.6	138.3	2 2 10	97.4	74.5	10 2 2	343.3	406.1	1 3 1	339.1	287.9
13 1 $\bar{4}$	407.4	376.2	4 2 $\bar{9}$	59.3	78.6	10 2 3	157.3	166.2	1 3 2	138.4	123.0
13 1 $\bar{3}$	200.7	190.0	4 2 $\bar{8}$	111.8	104.1	10 2 4	78.8	82.7	1 3 3	16.7	14.8
13 1 $\bar{2}$	122.9	103.8	4 2 $\bar{7}$	47.2	56.1	10 2 5	191.8	225.5	1 3 4	17.7	8.3
13 1 $\bar{1}$	157.4	121.2	4 2 $\bar{6}$	34.2	36.5	10 2 6	25.9	38.3	1 3 5	143.6	128.3
13 1 0	188.2	162.8	4 2 $\bar{5}$	338.8	404.0	10 2 7	24.5	23.1	1 3 6	224.2	197.5
13 1 1	72.8	63.4	4 2 $\bar{4}$	143.6	148.0	10 2 8	96.0	124.1	1 3 7	102.5	88.8
13 1 2	323.3	350.7	4 2 $\bar{3}$	55.4	53.1	10 2 9	55.4	62.2	1 3 8	100.6	97.3
13 1 3	195.0	206.1	4 2 $\bar{2}$	335.9	355.0	12 2 $\bar{7}$	34.0	39.6	1 3 $\bar{7}$	64.5	81.7
13 1 4	156.8	162.7	4 2 $\bar{1}$	19.9	12.1	12 2 $\bar{6}$	154.5	134.5	1 3 $\bar{6}$	19.9	20.8
13 1 5	224.2	245.5	4 2 0	67.7	65.5	12 2 $\bar{5}$	22.5	26.6	1 3 $\bar{5}$	163.2	187.1
13 1 6	141.8	149.9	4 2 1	114.7	102.9	12 2 $\bar{4}$	46.0	29.7	1 3 $\bar{4}$	25.7	6.9
13 1 7	21.0	17.7	4 2 2	155.5	120.7	12 2 $\bar{3}$	275.0	239.9	1 3 $\bar{3}$	59.0	58.6
13 1 8	48.6	49.8	4 2 3	89.4	77.6	12 2 0	19.4	12.0	1 3 $\bar{2}$	18.6	26.6
13 1 9	10.4	9.0	4 2 4	510.4	453.9	12 2 1	69.4	68.3	1 3 $\bar{1}$	72.3	81.1
15 1 $\bar{5}$	60.7	61.4	4 2 5	105.5	94.4	12 2 2	117.5	103.7	1 3 0	17.3	5.4
15 1 $\bar{4}$	38.5	37.6	4 2 6	174.5	149.2	12 2 3	21.0	17.1	1 3 1	45.7	71.0
15 1 $\bar{3}$	222.2	213.8	4 2 7	108.6	83.6	12 2 4	22.1	13.6	1 3 2	25.6	17.3
15 1 $\bar{2}$	77.6	75.2	4 2 8	21.0	12.7	12 2 5	158.8	181.9	1 3 3	173.9	135.8
15 1 $\bar{1}$	203.3	170.1	4 2 9	40.5	39.4	12 2 6	96.2	106.8	1 3 4	306.7	278.9
15 1 0	226.9	228.1	4 2 10	205.7	196.9	12 2 7	24.2	8.8	1 3 5	119.4	96.3
15 1 1	138.0	132.7	6 2 $\bar{8}$	256.4	290.1	12 2 8	233.5	264.5	1 3 6	55.6	40.7
15 1 2	104.1	96.5	6 2 $\bar{7}$	22.1	22.1	14 2 $\bar{6}$	29.9	30.7	1 3 7	93.6	86.9
15 1 3	64.9	57.6	6 2 $\bar{6}$	22.2	14.2	14 2 $\bar{5}$	101.2	96.6	1 3 8	70.3	51.3
15 1 4	14.9	20.7	6 2 $\bar{5}$	99.6	104.8	14 2 $\bar{4}$	150.2	114.9	1 3 $\bar{6}$	92.1	86.1
15 1 5	163.9	161.7	6 2 $\bar{4}$	31.5	30.5	14 2 $\bar{3}$	27.5	33.9	1 3 $\bar{5}$	127.0	136.2
15 1 6	194.8	233.3	6 2 $\bar{3}$	78.2	78.1	14 2 0	162.2	143.2	1 3 $\bar{4}$	123.5	137.7
15 1 7	164.5	179.8	6 2 $\bar{2}$	88.4	82.5	14 2 1	41.6	44.9	1 3 $\bar{3}$	148.8	169.2
15 1 8	186.8	209.4	6 2 0	23.0	21.4	14 2 2	164.1	176.2	1 3 $\bar{2}$	266.8	301.9
17 1 $\bar{2}$	11.9	8.5	6 2 1	307.5	358.1	14 2 3	56.0	57.7	1 3 $\bar{1}$	177.9	142.2
17 1 $\bar{1}$	105.9	94.4	6 2 2	48.3	44.1	14 2 4	16.1	40.0	1 3 0	41.5	34.2
17 1 0	297.4	313.1	6 2 3	134.2	105.6	14 2 5	73.6	67.6	1 3 1	56.2	44.1
17 1 1	40.4	34.7	6 2 4	277.3	234.3	14 2 6	92.1	95.8	1 3 2	29.0	22.0
17 1 2	64.6	57.5	6 2 5	87.0	74.3	14 2 7	58.7	63.7	1 3 3	100.7	114.6
17 1 3	168.2	180.6	6 2 6	40.4	26.2	16 2 $\bar{2}$	14.8	5.3	1 3 4	314.7	296.3
17 1 4	46.6	37.3	6 2 7	403.6	363.1	16 2 $\bar{1}$	63.7	65.0	1 3 5	190.0	159.6
17 1 5	52.4	43.3	6 2 8	80.6	64.4	16 2 0	36.5	40.8	1 3 6	31.7	17.3
17 1 6	151.1	156.7	6 2 9	22.1	19.6	16 2 1	137.6	118.7	1 3 7	117.1	115.9
0 2 1	30.7	28.6	8 2 $\bar{8}$	190.7	149.5	16 2 2	83.7	69.3	1 3 $\bar{5}$	50.1	38.2
0 2 2	115.6	108.4	8 2 $\bar{7}$	255.8	259.8	16 2 3	235.2	227.3	1 3 $\bar{4}$	57.3	51.5
0 2 3	142.5	147.1	8 2 $\bar{6}$	38.5	40.2	16 2 4	39.9	38.1	1 3 $\bar{3}$	18.3	17.0
0 2 4	89.3	86.9	8 2 $\bar{5}$	56.8	59.5	16 2 5	24.0	29.5	1 3 $\bar{2}$	260.8	205.1
0 2 5	23.8	6.1	8 2 $\bar{4}$	88.3	82.7	1 3 $\bar{8}$	68.5	99.1	1 3 $\bar{1}$	269.3	237.7
0 2 6	372.5	441.2	8 2 $\bar{3}$	41.0	20.2	1 3 $\bar{7}$	25.8	8.9	1 3 0	169.1	151.6

Table 5. (Continued)

h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>	h k l	F <sub>obs.</sub>	F <sub>calc.</sub>
9 5 1	170.4	155.2	11 5 5	125.5	140.3	2 4 $\bar{2}$	58.1	37.9	4 4 5	65.8	63.8
9 5 2	176.5	185.6	11 5 6	15.1	17.5	2 4 $\bar{1}$	9.1	14.5	6 4 $\bar{5}$	55.1	45.6
9 5 3	40.2	40.6	13 5 $\bar{2}$	97.5	80.6	2 4 1	120.4	104.1	6 4 $\bar{2}$	377.3	355.3
9 5 4	87.8	94.0	13 5 $\bar{1}$	115.3	94.9	2 4 2	33.2	42.6	6 4 $\bar{1}$	74.0	45.6
9 5 5	19.3	26.9	13 5 0	138.2	117.3	2 4 3	306.0	282.8	6 4 0	25.5	17.4
9 5 6	84.6	104.3	13 5 1	57.1	50.3	2 4 4	24.4	24.9	6 4 1	234.8	229.0
9 5 7	165.2	195.5	13 5 2	255.4	262.5	2 4 5	67.8	58.3	6 4 2	55.6	21.4
11 5 $\bar{4}$	145.9	124.1	13 5 3	146.2	154.5	4 4 $\bar{4}$	86.0	94.4	6 4 3	63.1	61.9
11 5 $\bar{5}$	51.2	19.6	13 5 4	125.3	124.7	4 4 $\bar{3}$	37.9	38.2	6 4 4	125.5	141.5
11 5 $\bar{2}$	125.5	104.0	0 4 $\bar{1}$	7.7	14.5	4 4 $\bar{2}$	235.6	274.2	8 4 $\bar{1}$	185.6	157.9
11 5 $\bar{1}$	87.6	66.3	0 4 2	76.2	57.3	4 4 $\bar{1}$	11.7	10.9	8 4 0	53.7	51.8
11 5 0	76.0	63.3	0 4 3	110.9	94.0	4 4 0	46.4	36.6	8 4 1	133.7	130.2
11 5 1	13.8	4.1	0 4 4	65.8	50.0	4 4 1	59.4	59.4	8 4 2	75.5	74.9
11 5 2	268.9	298.3	0 4 5	12.5	4.6	4 4 2	93.5	69.8			
11 5 3	38.6	45.8	2 4 $\bar{4}$	11.8	20.6	4 4 3	48.9	50.9			
11 5 4	127.5	126.9	2 4 $\bar{5}$	120.7	107.0	4 4 4	367.0	349.8			

1. The  $y$  coordinates, when allowed to vary, tend spontaneously to the value zero, characteristic of  $C2/m$ .

2. If equally correct, a lower least-squares minimum is to be expected for the space group of lower symmetry, on account of the extra degrees of freedom<sup>19</sup>. But the  $R$  values were found to be equal for both space groups.

### Description and discussion of the structure

A projection on (010) of the final structure of potassium hexatitanate is shown in Fig. 9. It consists basically of a unit of three Ti octahedra sharing edges in a plane, and this unit repeats itself in a zigzag way in the direction of 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.

Figure 10 shows the environment of the different atoms in the model structure. In the real structure each Ti atom is surrounded by six oxygens in a distorted octahedron, and all Ti are displaced from the center of the octahedron in the direction of the open sites, where the nearest potassium ions occur. The potassium atoms are displaced from the center of a distorted cube (defined by eight oxygen atoms) toward the empty cubic void. Now if we try to verify PAULING's electrostatic valence rule, we find a justification for the deviation of our structure from the ideal one in Fig. 6.

<sup>19</sup> D. W. J. CRUICKSHANK, H. LYNTON and (in part) G. A. BARCLAY, A reinvestigation of the crystal structure of thortveitite,  $Sc_2Si_2O_7$ . Acta Crystallogr. **15** (1962) 491–498.

Assuming bond strength of  $4/6$  for Ti and  $1/8$  for K, the oxygen atoms will have the following net charges:

(a) O(1) and O(7), whose nearest neighbors are two Ti and four K atoms, will have a net charge of  $-1/6$ .

(b) O(2) and O(4) have as neighbors four Ti, their valence will be oversaturated and will have a net charge of  $+4/6$ .

Table 7. *Interatomic distances in potassium hexatitanate*

	No.	Distance		No.	Distance
Ti(1)—O(1)	1	1.86 Å	O(2)—O(IV)	2	2.71 Å
Ti(1)—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	2.03
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

(c) O(3) and O(5) have as closest neighbors two Ti and two K, their net charge will be  $-5/12$ .

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

Now, if it is assumed that the bond strength is inversely proportional to the interatomic distance, it turns out that the acentric position of the Ti atoms and the K atoms within their coordination polyhedra are necessary to achieve electrical neutrality. The effect, as shown in the interatomic distances listed in Table 7, is that Ti(1) is closer to the unsaturated oxygens O(1) and O(3) than to the over-



saturated O(2), thus contributing more than 4/6 to compensate O(1) and O(3), but less than 4/6 to O(2). The same behavior can be observed of Ti(2), which is closer to the unsaturated atoms O(3) and O(5) relative to the oversaturated O(2) and O(4). This is also true for Ti(3), whose distances to O(5) and O(7) are smaller than the distance to O(6), the saturated atom, and much smaller than the distance to the oversaturated atom O(4).

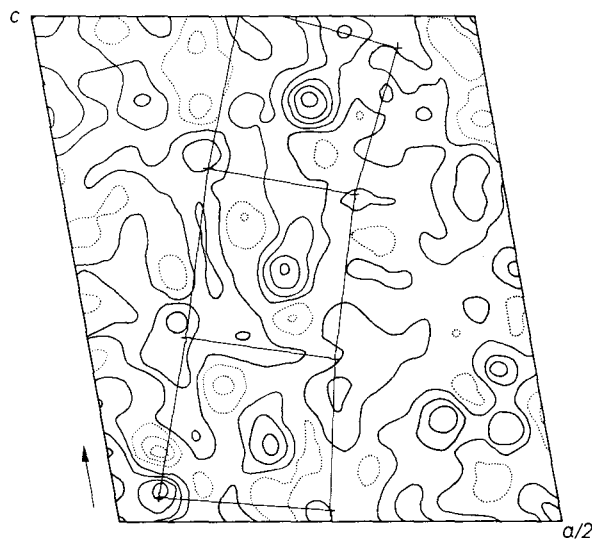


Fig. 11. Final difference synthesis  $\Delta\rho(x_0z)$

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

The only problem left is to explain why the refinement could not be continued below an  $R$  value of 12.4% even though the intensity data were reasonably good. A possible explanation is that there may be 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. 8) and the difference synthesis section  $\Delta\rho(x_0z)$  of Fig. 11. In the electron-density map it is possible to observe some small additional peaks between those belonging to the structure; in the initial stages of the analysis these were thought to be the series-termination ripples from the Ti peaks. The same peaks

appear in the difference Fourier synthesis (Fig. 11), outlining the row of squares characteristic of the section  $y = 1/2$  of potassium hexatitanate. It is possible then to say that the difference synthesis map  $\Delta\rho(x\theta z)$  reproduces the electron-density section  $\rho(x \frac{1}{2} z)$  of potassium hexatitanate with its origin displaced along a vector approximately equal to half the Ti(1)—O(1) vector.

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