

Fig. 5. The potassium ion-oxygen atom interaction, viewed along the c axis. Broken lines represent hydrogen bonds. For Roman numerals associated with atoms, see Table 6.

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The Ordered Structure of Ti_3O

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The ordered Ti_3O structure has been redetermined with the use of transmission electron diffraction in an electron microscope. This structure consists essentially of a close-packed hexagonal arrangement of titanium atoms with every second layer of octahedral interstices normal to the c axis vacant. One third of the oxygen sites in the occupied layers are empty and these vacancies have an ordered arrangement in the direction of the c axis. The space group is $P312$ (no. 149) and the unit-cell dimensions are: $a = 5.1418$, $c = 14.308$ Å.

Oxygen dissolves in the octahedral interstices of the titanium lattice up to 34 at. % (Ehrlich, 1941; Bumps, Kessler & Hansen, 1953). As there is one octahedral site for each titanium atom in the close-packed hexagonal structure, only half of the available interstitial

sites are occupied at the limiting composition, Ti_2O . X-ray diffraction studies of Ti_2O (Andersson, Collen, Kuylenstierna & Magnéli, 1957) have indicated the existence of an ordered structure of the anti- CdI_2 type in which the oxygen atoms occupy alternate layers of octahedral sites normal to the c axis and, as a result of ordering, the titanium atoms surrounding the oxygen atoms are forced slightly apart in the c direction.

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This structure is stable at oxygen contents lower than the composition Ti₂O, indicating the existence of random vacancies in the oxygen layers. At the composition Ti₃O one-third of the oxygen sites in the occupied layers are empty. Holmberg (1962) observed one weak reflexion in addition to those expected from the Ti₂O structure in specimens containing 25 at.% O annealed for one month at 400°C and consequently described the structure of Ti₃O as a superstructure of the Ti₂O unit cell. The parameters of this superstructure are:

$$a' = \sqrt{3}a \quad \text{and} \quad c' = 2c$$

where a and c refer to a unit cell of the same size as Ti₂O.

In the present investigation thin foils of the ordered structure of Ti₃O were examined by electron diffraction in an electron microscope. This technique was selected because of the ease of recording photographically the weak reflexions expected from the ordering of oxygen atoms. The existence of multiple scattering processes prevents the use of diffracted electron intensity measurements in a structure analysis, but from the observations a reciprocal lattice showing the allowed reflexions may be constructed and hence the possible space group(s) deduced.

Thin foils suitable for transmission electron microscopy and powdered samples for X-ray diffraction studies were prepared from heat treated bulk specimens of 25.0 at.% O which had been made by arc melting iodide-refined titanium with titanium dioxide. More detailed descriptions of specimen preparation are reported elsewhere (Jostsons & McDougall, 1967; Watanabe, Castles, Jostsons & Malin, 1967). X-ray diffraction examination showed that a small change occurred in the c parameter of arc melted specimens after annealing for 5 weeks at 400°C. The lattice parameters at 20°C, based on a unit cell of the same size as Ti₂O, were found to be:

$$a = 2.9687 \pm 0.0003, \quad c = 4.7760 \pm 0.0004 \text{ \AA}$$

for arc melted specimens,

and

$$a = 2.9687 \pm 0.0003, \quad c = 4.7694 \pm 0.0004 \text{ \AA}$$

for specimens annealed at 400°C.

The diffraction patterns were obtained with a 19 cm Bradley camera with Cu $K\alpha$ radiation. Lattice parameters were calculated by a least-squares method (Hess, 1951) in which individual measurements were weighted according to the Nelson-Riley (Nelson & Riley, 1945) function.

Electron diffraction patterns from foils of the arc melted material were similar to those expected from the Ti₂O structure; e.g. reflexions were observed for

$$000l: l \text{ odd}$$

and

$$hkil: h-k=3n \text{ and } l \text{ odd}$$

which would be absent from the patterns of titanium with a random arrangement of oxygen atoms.

The ordered Ti₂O structure was also observed in chill cast specimens. Reflexions additional to those expected from the Ti₂O structure were observed from foils of specimens annealed at 400°C. Examination of a large number of foils of different orientations revealed that the extra reflexions were situated on the electron diffraction patterns at distances from the origin of $\frac{1}{3}$ and $\frac{2}{3}$ that of $(h, h, \bar{2}h, l)_{\text{Ti}_2\text{O}}$ *. This observation is incompatible with the structure previously reported by Holmberg (1962) since $(h, h, \bar{2}h, l)_{\text{Ti}_2\text{O}}$ becomes $(3h, 0, \bar{3}h, 2l)_{\text{Ti}_3\text{O}}$, giving irrational indices for many superlattice reflexions. The possibility that the superlattice reflexions were due to dynamical double diffraction was eliminated by the tilting experiments suggested by Fujime, Watanabe & Ogawa (1964).

The cell proposed by Holmberg was deduced from only one superlattice reflexion, $10\bar{1}1$, in addition to that expected from the Ti₂O structure. This reflexion was not detected in the present investigation even though the electron diffraction method is more sensitive for the observation of such weak reflexions. This discrepancy is not understood because the compositions of the alloys in the two studies are identical, as shown by the excellent agreement in the lattice parameters for alloys heat treated under the same conditions.

On the basis of the present observations a new unit cell, such that $(0, 0, 0, l)_{\text{Ti}_2\text{O}}$ becomes $(0, 0, 0, 3l)_{\text{Ti}_3\text{O}}$, is proposed. The new cell is a superstructure of Ti₂O containing nine Ti₂O unit cells and has the following lattice parameters:

$$a' = \sqrt{3}a \quad \text{and} \quad c' = 3c.$$

The following systematic absences were observed in the electron diffraction patterns:

$$(0, 0, 0, l)_{\text{Ti}_3\text{O}}: \text{extinction for } l \neq 3n$$

$$(h, h, \bar{2}h, l)_{\text{Ti}_3\text{O}}: \text{extinction for } l \neq 3n.$$

From these observations the structure of Ti₃O was obtained by trial and error procedures and is formally described as:

Space group: $P312$ (no. 149)

Unit-cell dimensions: $a = 5.1418, c = 14.308 \text{ \AA}$.

Unit-cell content: 6 Ti₃O

1 O in $1(b)$: $0, 0, \frac{6}{12}$;

1 O in $(1d)$: $\frac{1}{3}, \frac{2}{3}, \frac{6}{12}$;

2 O in $2(i)$: $\frac{2}{3}, \frac{1}{3}, \frac{2}{12}; \frac{2}{3}, \frac{1}{3}, \frac{10}{12}$;

2 O in $2(h)$: $\frac{1}{3}, \frac{2}{3}, \frac{2}{12}; \frac{1}{3}, \frac{2}{3}, \frac{10}{12}$;

18 Ti in $6(l)$: $x, y, z; \bar{y}, x-y, z; y-x, \bar{x}, z;$

$\bar{y}, \bar{x}, \bar{z}; x, x-y, \bar{z}; y-x, y, \bar{z};$

with

$$x=0, y=\frac{2}{3}, z=0.079;$$

$$x=\frac{1}{3}, y=0, z=0.254;$$

$$x=0, y=\frac{2}{3}, z=0.412.$$

In a unit cell with $a' = \sqrt{3}a$ there are three octahedral sites in each layer normal to the c axis, and thus there

* $(h, k, i, l)_{\text{Ti}_2\text{O}}$ and $(h, k, i, l)_{\text{Ti}_3\text{O}}$ refer to reflexions from the Ti₂O and Ti₃O structures respectively.

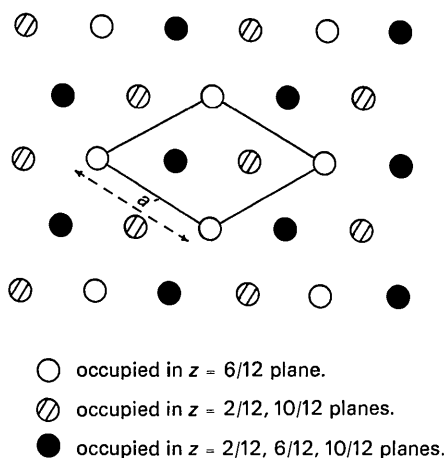


Fig. 1. Projection of oxygen atoms onto the (0001) plane. The full lines indicate the Ti_3O unit cell.

are three ways in which the two oxygen atoms can be arranged in each occupied layer. The other methods of arranging the oxygen-vacancy combinations did not, however, adequately account for all of the observed reflexions.

Table 1. *A comparison of the calculated structure factors and the observed structure factors of Holmberg (1962)*

The calculated structure factors are scaled to give a value of $|F|_{\text{calc.}} = 150$ for the $(0006)_{\text{Ti}_3\text{O}}$ reflexion.

$(h, k, l)_{\text{Ti}_3\text{O}}$	$(h, k, l)_{\text{Ti}_2\text{O}}$	$ F _{\text{obs}}$	$ F _{\text{calc}}$
0003	0001	*	10
0006	0002	150	150
0009	0003	52	48
00012	0004	141	128
00015	0005	41	33
00018	0006	71	73
30 $\bar{3}$ 0	11 $\bar{2}$ 0	139	133
30 $\bar{3}$ 3	11 $\bar{2}$ 1	*	3
30 $\bar{3}$ 6	11 $\bar{2}$ 2	121	114
30 $\bar{3}$ 9	11 $\bar{2}$ 3	39	36
30 $\bar{3}$ 12	11 $\bar{2}$ 4	95	105
30 $\bar{3}$ 15	11 $\bar{2}$ 5	19	29
10 $\bar{1}$ 0	$\frac{1}{3}$ (11 $\bar{2}$ 0)	*	3
20 $\bar{2}$ 0	$\frac{2}{3}$ (11 $\bar{2}$ 0)	*	7
10 $\bar{1}$ 1	$\frac{1}{3}$ (11 $\bar{2}$ 1)	*	2

* Not observed with X-rays by Holmberg (1962).

The z parameters were calculated on the assumption that the distortion in the titanium layers is similar to that observed by Holmberg (1962) in Ti_2O . A comparison between the calculated structure factors and the observed values of Holmberg (1962) is given in Table 1. Titanium and oxygen atoms were considered to be neutral and self consistent field scattering factors were used for oxygen and Thomas-Fermi values for titanium as given in *International Tables for X-ray Crystallography* (1962).

The structure of Ti_3O consists essentially of a close-packed hexagonal arrangement of titanium atoms with every second layer of octahedral interstices normal to the c axis vacant. One-third of the oxygen sites in the occupied layers are empty and these vacancies have an ordered arrangement in the direction of the c axis. The packing of oxygen atoms is shown as a projection on the basal plane in Fig. 1. The packing sequence of planes of atoms normal to the c axis can be described as

$$A\gamma B A\Delta B A\gamma B: A\gamma B A\Delta B A\gamma B:$$

where the Roman letters represent planes of titanium atoms, Greek letters planes of oxygen/vacancy combinations and the colon represents the end of each unit cell.

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