Acta Cryst. (1959). **12**, 575

Crystal Structure Studies on Trititanium Pentoxide, Ti_3O_5

By Stig Åsbrink and Arne Magnéli

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

(*Received* 8 *December* 1958)

Trititanium pentoxide (Ti_3O_5) is dimorphic—a rapid, reversible phase transformation occurring at about 120 °C. The high-temperature modification is of the anosovite type (slightly deformed pseudobrookite structure). It can be stabilized at room temperature by small contents of iron.

The crystal structure of the low-temperature form has been determined. It is monoclinic, space group $C2/m$, with a cell content of 4 Ti_3O_5 and the unit-cell dimensions

$$a = 9{\cdot}752,\quad b = 3{\cdot}802,\quad c = 9{\cdot}442 \text{ Å};\quad \beta = 91{\cdot}55^\circ.$$

It may be described in terms of TiO_6 octahedra which are joined by sharing edges and corners to form an infinite three-dimensional framework. The structure is discussed and compared with the anosovite structure.

1. Introduction

In the course of an X-ray study of the phase relations in the titanium–oxygen system recently performed at this Institute (Andersson *et al.*, 1957*b*), a phase of the composition $TiO_{1{\cdot}67}$ was observed. Since the powder pattern of this substance differed completely from that of anosovite (trititanium pentoxide obtained from slag) reported by Zhdanov & Rusakov (1954), it was considered of interest to determine the structure of this phase and to study its relation to the anosovite structure.

2. Experimental

Details about the preparation and some other data concerning the $TiO_{1{\cdot}67}$ sample have been given in previous communications (Andersson *et al.*, 1957*b*; Åsbrink & Magnéli, 1957). At this point, it is only necessary to state that the substance was probably of a high purity (the titanium metal and titanium dioxide used in the synthesis were both better than 99·97% pure) and that no deviation was found from the stoichiometric composition Ti_3O_5. By heating the sample in a sealed evacuated silica tube at 1150 °C. for 10 days, it was possible to grow crystals suitable for single-crystal work.

Powder patterns were obtained by means of a G.M.-diffractometer using Cu $K\alpha$ radiation. The diffractometer was provided with an electric vacuum furnace which permitted studies of the sample at temperatures up to 1000 °C. Accurate unit-cell dimensions at room temperature were obtained from photographs taken in a Guinier focusing camera using strictly monochromatized Cu $K\alpha_1$ radiation. Potassium chloride was added to the specimen as an internal standard and an aluminium foil (35μ) covering the film was used to depress the background fogging.

A crystal resembling a rectangular prism with the dimensions $0{\cdot}06 \times 0{\cdot}025 \times 0{\cdot}01$ mm.^{3} was used for the single-crystal investigations which, so far, have been restricted to room temperature. Weissenberg photographs with Cu K radiation and using multiple-film techniques were taken with rotation around the direction of the longest edge of the crystal ($h0l$, $h1l$ and $h2l$). The intensities of the reflexions were estimated visually and the intensity scales of the various layer lines were correlated by means of a $0kl$ Weissenberg photograph and also, in a way described previously (Magnéli, 1948), by exposing parts of each of the diagrams $h0l$, $h1l$ and $h2l$ side by side on a pack of films and using identical exposure times and radiation conditions. It was not possible to register single-crystal data with Mo K radiation within a reasonable period of time.

3. Evidence of a phase transformation

The powder and single-crystal diagrams registered at room temperature were all the same, irrespective of the previous heat-treatment of the specimens which included quenching from the molten state or from temperatures between 1150 °C. and 400 °C. However, upon increasing the temperature of the powder sample above about 120 °C., the X-ray diagram changed into a quite different pattern. The change was easily reversed by lowering the temperature of the specimen. These observations evidently indicate the existence of two modifications of trititanium pentoxide stable below and above a transformation temperature of about 120 °C. The two forms will in the following be designated low-Ti_3O_5 and high-Ti_3O_5.

The existence of a phase transformation in this oxide has previously been concluded by Naylor (1946) from heat content measurements. There is, however, a considerable difference between the transformation temperature reported by him (about 175 °C.) and the (approximate) one observed in the present study.

The transformation seems to be a fairly rapid one at temperatures ranging from room temperature upwards. Thus, in a wide region around 120 °C., the powder reflexions of the unstable phase disappear while the general characteristics of the pattern of the stable one are formed within a period of time considerably less than one hour. The complete development of some reflexions of the latter to their normal intensities, however, takes a considerably longer time (several hours). Some reflexions in the pattern of the stable phase also occur with anomalous intensities at temperatures approaching the transformation point, 'forewarning' the change of structure.

The fact that single crystals grown at high temperatures after quenching were found to be single crystals of low-Ti_3O_5 shows that the phase transformation occurs 'within' the crystal which is thus not destroyed by this process.

4. Preliminary structural data concerning high-Ti_3O_5

The powder pattern of high-Ti_3O_5 was found to be similar to that of the orthorhombic anosovite (pseudobrookite type) reported by Zhdanov & Rusakov (1954) except that certain lines of the former were split into doublets. This could be accounted for by assuming high-Ti_3O_5 to have a slightly deformed monoclinic anosovite structure with the following unit-cell dimensions at temperatures somewhat above the transition point:

$$a = 9{\cdot}82,\quad b = 3{\cdot}78,\quad c = 9{\cdot}97\ \text{Å},\quad \beta = 91{\cdot}0^\circ.$$

At higher temperatures, the monoclinic angle gradually approaches 90°.

The unit-cell data given by Zhdanov & Rusakov (1954) for anosovite (containing considerable amounts of other elements) are:

$$a = 9{\cdot}474,\quad b = 3{\cdot}754,\quad c = 9{\cdot}734\ \text{Å},\quad \beta = 90^\circ.$$

The similarity between the unit-cell dimensions and the intensities of the powder reflexions of the two specimens suggests that their atomic arrangements are approximately the same.

Studies by one of the present authors (S.Å.) have revealed that quite small contents of iron (*e.g.* in the preparation $(Ti_{0{\cdot}97}Fe_{0{\cdot}03})_3O_5$) stabilize the high-$Ti_3O_5$ structure at room temperature. With higher contents of iron, the monoclinic deformation decreases and, for the preparation $(Ti_{0{\cdot}92}Fe_{0{\cdot}08})_3O_5$, the angle β is very close to 90°. These results evidently are in conformity with the suggestion by Zhdanov & Rusakov (1954) that anosovite should represent a high-temperature modification of trititanium pentoxide stabilized at room temperature by the magnesium content of their specimen.

5. Derivation of the low-Ti_3O_5 structure

The Weissenberg photographs of low-Ti_3O_5 showed the structure to be monoclinic. The systematic extinctions were those characteristic of the space-groups $C2/m$, Cm and $C2$, *i.e.* reflexions hkl with $h+k$ odd absent.

The Guinier powder photograph gave the following unit-cell dimensions, referred to the lattice parameter of potassium chloride $a = 6{\cdot}2919$ Å at 20 °C. (Hambling, 1953):

$$a=9{\cdot}752\pm0{\cdot}001,\ b=3{\cdot}8020\pm0{\cdot}0005,\ c=9{\cdot}442\pm0{\cdot}001\ \text{Å},$$
$$\beta = 91{\cdot}55^\circ\pm0{\cdot}01^\circ\,.$$

With a cell content of 12 formula units of $TiO_{1{\cdot}67}(4\ Ti_3O_5)$, this gives a calculated density of 4·245 in good agreement with the observed value of 4·20. The powder pattern has been published in a previous report (Andersson *et al.*, 1957*a*).

The fact that $|F(h0l)|^2$ was found throughout to be equal to $|F(h2l)|^2$ (within the limits of experimental error and assuming a reasonable temperature factor) indicated that all the atoms of the structure are situated in two planes (m) normal to the b axis and that the symmetry consequently is not $C2$. This was confirmed by the intensity distribution in the $0kl$ photograph. The section $P(u0w)$ in the Patterson function was thus calculated, the coefficients

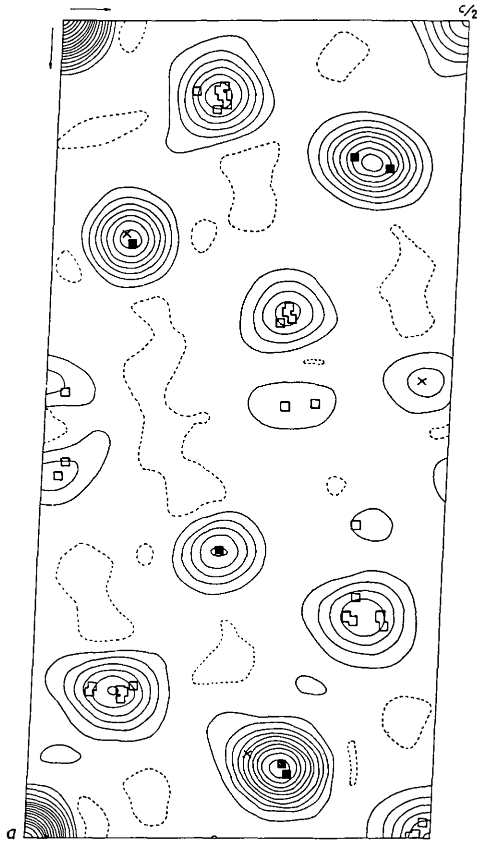


Fig. 1. Patterson function. Section at $v = 0$. ■ and × represent Ti–Ti vectors of multiplicity 4 and 2 respectively, □ Ti–O vectors of multiplicity 4.

$$\sum_{k=-\infty}^{\infty} |F(hkl)|^2$$

being replaced by the expressions

$$\tfrac{1}{2}\{|F(h0l)|^2+|F(h2l)|^2\}+|F(h1l)|^2.$$

(The calculations were performed by means of the digital computer BESK using a programme designed by Westman, Blomqvist and Åsbrink (1959).) The two terms were assumed to be proportional to the sums obtained for all reflexions with k even and k odd respectively. The asymmetric unit of $P(u0w)$ is shown in Fig. 1. The C centering of the structure gives the section $P(u\frac{1}{2}w)$ an identical appearance except for a translation by $a/2$.

The choice of point positions was restricted (1) by the absence of a maximum at $u = 0$, $w = \frac{1}{2}$ in $P(u0w)$ (which excluded the possibility of titanium atoms occupying positions $2(a)+2(c)$ or $2(b)+2(d)$ in the space group $C2/m$), (2) by the length of the b axis being only 3·8 Å (which indicated that four titanium atoms or four oxygen atoms could not occupy the positions $2(a)+2(b)$ or $2(c)+2(d)$) and (3) by the requirement that all the atoms should be situated in mirror planes. Thus, only the positions $4(i)$ of $C2/m$ or $2(a)$ of Cm were possible.

Assuming the symmetry to be the higher one ($C2/m$), it was possible to find an atomic arrangement compatible with the appearance of the Patterson function and giving calculated F values in acceptable conformity with the observed ones. While the electron-density projection $\varrho(xz)$ (Fig. 2) showed an overlapping of titanium and oxygen atoms, the section $\varrho(x0z)$ was well resolved as is apparent in Fig. 3. When calculating this section, the summation over k was obtained by making use of the reflexions $h0l$, $h1l$ and $h2l$ in a manner analogous to that employed when calculating $P(u0w)$.

The structure factors calculated from the atomic coordinates given by $\varrho(x0z)$ and an isotropic temperature factor were found to correspond to a R index of 0·13. (All structure factors were computed by means of BESK using a programme designed by Åsbrink, Blomquist and Westman (1959) and applying the analytical expressions for the scattering factors of unionized atoms given by Vand, Eiland & Pepinsky, 1957.)

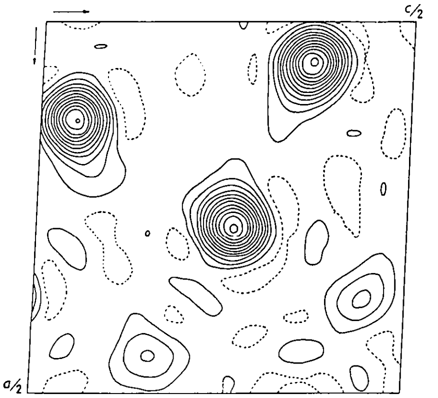


Fig. 2. Electron-density function. Projection along [010]. Contours at arbitrary intervals.

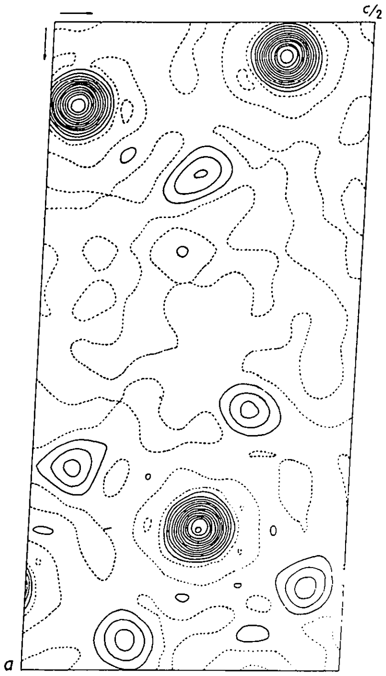


Fig. 3. Electron-density function. Section at $y = 0$. Arbitrary scale.

The refinement included the reiterated use of back-shift and difference syntheses (Lipson & Cochran, 1953) and the introduction of individual, isotropic temperature factors (Leung, Marsh & Schomaker, 1957), *viz.* 1·03, 1·28, 1·66 and 1·93 Å^2 for B_{Ti}, $B_{\text{O}_{1\text{-}3}}$, B_{O_4} and B_{O_5} respectively. In this way, the R index (calculated, according to Hamilton, 1955, by summation over all reflexions and by giving non-observed ones values of F_o equal to $1/\sqrt{3}$ of the minimum observable value in the corresponding region of reflexion) was brought down to 0·088. Table 2 gives a comparison of the observed and calculated F values. The titanium–titanium and titanium–oxygen vectors required by the structure are indicated in Fig. 1.

The atomic parameters thus obtained are given in

Table 1. *Final positional parameters and their standard errors*

All the atoms occupy point positions $4(i)$ of space group $C2/m$, $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0)+x, 0, z;\ \bar{x}, 0, \bar{z}$

	x	z	σx	σz
Ti_1	0·1280	0·0440	±0·0004	±0·0004
Ti_2	0·7786	0·2669	±0·0004	±0·0004
Ti_3	0·0538	0·3659	±0·0004	±0·0004
O_1	0·676	0·060	±0·003	±0·002
O_2	0·241	0·245	±0·003	±0·003
O_3	0·588	0·345	±0·002	±0·002
O_4	0·953	0·158	±0·002	±0·002
O_5	0·866	0·441	±0·002	±0·002

Table 2. *Observed and calculated structure factors for low-temperature* Ti_3O_5

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
0,0,$\overline{12}$	21	−23	401	106	−109	91$\bar{6}$	< 8	−10	117	43	−41
0,0,$\overline{11}$	20	21	601	61	58	11$\bar{5}$	17	17	317	21	−16
2,0,$\overline{11}$	<10	7	801	<14	7	31$\bar{5}$	43	44	517	53	51
4,0,$\overline{11}$	43	40	10,0,1	38	40	51$\bar{5}$	69	−67	717	17	18
0,0,$\overline{10}$	89	−79	12,0,1	14	−14	71$\bar{5}$	35	−33	917	14	14
2,0,$\overline{10}$	<11	7	202	55	59	91$\bar{5}$	<10	−5	118	31	28
4,0,$\overline{10}$	16	−17	402	12	−14	11,1,$\bar{5}$	< 5	8	318	17	−15
6,0,$\overline{10}$	< 8	8	602	109	124	11$\bar{4}$	17	−14	518	80	80
00$\bar{9}$	63	−58	802	34	35	31$\bar{4}$	< 8	−7	718	26	−26
20$\bar{9}$	50	51	10,0,2	29	−32	51$\bar{4}$	12	−11	119	43	−42
40$\bar{9}$	37	34	12,0,2	14	−18	71$\bar{4}$	<10	−8	319	28	−26
60$\bar{9}$	<12	−6	203	67	−75	91$\bar{4}$	103	104	519	< 9	0
80$\bar{9}$	14	12	403	12	−13	11,1,$\bar{4}$	< 7	2	719	< 6	7
00$\bar{8}$	29	26	603	55	−55	11$\bar{3}$	64	67	1,1,10	62	−58
20$\bar{8}$	<14	0	803	<14	13	31$\bar{3}$	< 7	7	3,1,10	46	47
40$\bar{8}$	47	44	10,0,3	38	−41	51$\bar{3}$	25	25	5,1,10	12	15
60$\bar{8}$	102	−94	204	225	−226	71$\bar{3}$	12	−15	1,1,11	< 7	−6
80$\bar{8}$	<11	−7	404	<11	−4	91$\bar{3}$	<10	13	3,1,11	< 6	4
00$\bar{7}$	35	−28	604	43	43	11,1,$\bar{3}$	21	−20			
20$\bar{7}$	<13	−6	804	29	32	11$\bar{2}$	41	41	0,2,$\overline{11}$	16	18
40$\bar{7}$	<14	−11	10,0,4	10	16	31$\bar{2}$	30	−34	0,2,$\overline{10}$	65	−66
60$\bar{7}$	20	−18	205	47	42	51$\bar{2}$	132	−147	2,2,$\overline{10}$	< 8	6
80$\bar{7}$	<13	−2	405	<12	9	71$\bar{2}$	<10	8	4,2,$\overline{10}$	13	−15
10,0,$\bar{7}$	40	47	605	64	68	91$\bar{2}$	<10	1	02$\bar{9}$	49	−49
00$\bar{6}$	35	−29	805	33	−34	11,1,$\bar{2}$	26	30	22$\bar{9}$	44	43
20$\bar{6}$	169	180	10,0,5	24	−24	11$\bar{1}$	37	−43	42$\bar{9}$	28	29
40$\bar{6}$	<11	−8	206	30	−25	31$\bar{1}$	25	24	62$\bar{9}$	< 7	−5
60$\bar{6}$	<14	12	406	41	−36	51$\bar{1}$	37	−38	02$\bar{8}$	24	23
80$\bar{6}$	27	−23	606	<14	−12	71$\bar{1}$	47	47	22$\bar{8}$	<11	1
10,0,$\bar{6}$	20	22	806	29	−26	91$\bar{1}$	50	56	42$\bar{8}$	37	37
00$\bar{5}$	12	11	10,0,6	37	−35	11,1,$\bar{1}$	21	−22	62$\bar{8}$	82	−79
20$\bar{5}$	47	42	207	84	−78	110	110	138	02$\bar{7}$	29	−24
40$\bar{5}$	50	−44	407	62	59	310	26	−27	22$\bar{7}$	<11	−6
60$\bar{5}$	70	−70	607	26	25	510	< 8	3	42$\bar{7}$	<11	−9
80$\bar{5}$	23	22	807	41	41	710	26	−27	62$\bar{7}$	16	−15
10,0,$\bar{5}$	16	−12	10,0,7	< 6	−11	910	21	22	82$\bar{7}$	< 8	−2
00$\bar{4}$	19	17	208	<14	2	11,1,0	79	−84	02$\bar{6}$	29	−23
20$\bar{4}$	23	−23	408	76	68	111	39	44	22$\bar{6}$	134	139
40$\bar{4}$	43	39	608	27	22	311	57	−58	42$\bar{6}$	<11	−6
60$\bar{4}$	41	−40	808	46	−44	511	36	−42	62$\bar{6}$	10	11
80$\bar{4}$	93	87	209	20	−16	711	24	23	82$\bar{6}$	20	−19
10,0,$\bar{4}$	35	31	409	42	−39	911	17	18	02$\bar{5}$	<10	8
00$\bar{3}$	116	119	609	12	11	11,1,1	13	14	22$\bar{5}$	40	34
20$\bar{3}$	92	94	2,0,10	<13	2	112	< 4	0	42$\bar{5}$	40	−35
40$\bar{3}$	38	−41	4,0,10	43	41	312	12	14	62$\bar{5}$	59	−62
60$\bar{3}$	9	10	6,0,10	16	17	512	12	−15	82$\bar{5}$	20	18
80$\bar{3}$	26	−23	2,0,11	<10	−3	712	116	134	10,2,$\bar{5}$	8	−10
10,0,$\bar{3}$	19	16	4,0,11	35	36	912	17	−14	02$\bar{4}$	19	13
12,0,$\bar{3}$	33	−41				11,1,2	17	−16	22$\bar{4}$	27	−21
00$\bar{2}$	27	−27	1,1,$\overline{11}$	28	27	113	15	−13	42$\bar{4}$	32	28
20$\bar{2}$	43	50	3,1,$\overline{11}$	23	23	313	21	−21	62$\bar{4}$	36	−33
40$\bar{2}$	220	−237	1,1,$\overline{10}$	< 9	−9	513	34	−31	82$\bar{4}$	71	72
60$\bar{2}$	9	−10	3,1,$\overline{10}$	21	−21	713	<10	4	10,2,$\bar{4}$	25	26
80$\bar{2}$	<14	13	5,1,$\overline{10}$	< 7	−6	913	<10	−10	02$\bar{3}$	83	81
10,0,$\bar{2}$	26	25	11$\bar{9}$	21	−20	11,1,3	61	−51	22$\bar{3}$	72	69
12,0,$\bar{2}$	< 8	3	31$\bar{9}$	49	50	114	34	−29	42$\bar{3}$	34	−29
00$\bar{1}$	17	17	51$\bar{9}$	< 9	7	314	129	−135	62$\bar{3}$	<11	8
20$\bar{1}$	< 5	−4	71$\bar{9}$	24	23	514	46	42	82$\bar{3}$	20	−19
40$\bar{1}$	19	23	11$\bar{8}$	<10	7	714	<10	12	10,2,$\bar{3}$	13	14
60$\bar{1}$	9	11	31$\bar{8}$	49	46	914	32	33	02$\bar{2}$	22	−17
80$\bar{1}$	76	73	51$\bar{8}$	21	−18	11,1,4	13	−13	22$\bar{2}$	33	33
10,0,$\bar{1}$	19	−20	71$\bar{8}$	74	−71	115	49	49	42$\bar{2}$	150	−165
12,0,$\bar{1}$	< 8	−3	11$\bar{7}$	12	11	315	28	−22	62$\bar{2}$	<11	−10
000	—	424	31$\bar{7}$	46	−43	515	26	24	82$\bar{2}$	<11	10
200	26	−28	51$\bar{7}$	<10	−3	715	52	50	10,2,$\bar{2}$	22	21
400	12	−12	71$\bar{7}$	38	−35	915	43	−44	02$\bar{1}$	14	10
600	47	−49	91$\bar{7}$	41	40	116	64	−62	22$\bar{1}$	< 5	−2
800	<14	7	11$\bar{6}$	77	70	316	<10	−7	42$\bar{1}$	15	15
10,0,0	40	−36	31$\bar{6}$	75	72	516	32	−31	62$\bar{1}$	<11	7
12,0,0	45	−42	51$\bar{6}$	<10	12	716	25	23	82$\bar{1}$	59	66
201	69	−81	71$\bar{6}$	<10	7	916	72	−69	10,2,$\bar{1}$	18	−17

Table 2 (*cont.*)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
020	—	238	422	14	−12	824	27	26	427	50	49
220	19	−17	622	83	95	10,2,4	14	14	627	21	21
420	< 8	−7	822	30	31	225	37	32	827	33	34
620	38	−38	10,2,2	27	−27	425	<11	6	228	<11	1
820	<11	6	223	47	−53	625	58	61	428	57	55
10,2,0	29	−30	423	<10	−9	825	28	−29	628	20	19
221	51	−50	623	43	−44	10,2,5	15	−21	229	13	−13
421	80	−86	823	<11	12	226	23	−22	429	33	−33
621	47	45	10,2,3	30	−35	426	34	−30	629	8	9
821	<11	6	224	153	−158	626	10	−9	2,2,10	< 8	2
10,2,1	33	34	424	<10	−5	826	23	−21	4,2,10	30	35
222	37	39	624	37	36	227	67	−67			

Table 1 together with the standard deviations estimated essentially according to Cruickshank, (1949).

6. Description and discussion of the low-Ti_3O_5 structure

The structure thus derived is shown in Fig. 4 (bottom). It may be described in terms of distorted TiO_6 octahedra which are joined by sharing edges and corners to form an infinite three-dimensional framework. The extension of the *b* axis is given by octahedra sharing corners. Normally to this direction, octahedra joined by edges form characteristic endless 'flights of steps' extending in the *c* direction. Adjacent 'flights' (with Ti atoms at $y = 0$ and $y = \frac{1}{2}$ respectively) are mutually

Table 3. *Interatomic distances*

Atom	Number and kind of neighbouring atoms	Distance (Å)
Ti_1	$2 \times Ti_1$	3·174±0·010
	Ti_1	2·610±0·010
	$2 \times Ti_2$	3·168±0·007
	Ti_2	3·097±0·007
	Ti_3	3·143±0·007
	$2 \times O_1$	1·96 ±0·04
	O_1	2·17 ±0·04
	O_2	2·17 ±0·03
	O_4	2·04 ±0·03
	O_4	2·04 ±0·03
Ti_2	$2 \times Ti_3$	3·067±0·007
	Ti_3	2·818±0·007
	O_1	2·18 ±0·04
	$2 \times O_2$	1·95 ±0·03
	O_3	2·01 ±0·03
	O_4	2·01 ±0·03
	O_5	1·83 ±0·02
Ti_3	Ti_3	2·767±0·010
	O_2	2·18 ±0·03
	$2 \times O_3$	1·94 ±0·03
	O_4	2·17 ±0·03
	O_5	1·99 ±0·02
	O_5	1·97 ±0·02
O_1	$2 \times O_1$	2·66 ±0·07
	$2 \times O_2$	2·65 ±0·05
	O_2	3·01 ±0·05
	O_3	2·84 ±0·04
	O_4	2·83 ±0·04
	$2 \times O_4$	3·05 ±0·04
	$2 \times O_4$	3·04 ±0·04
O_2	$2 \times O_3$	2·61 ±0·04
	$2 \times O_4$	2·94 ±0·04
	O_4	2·91 ±0·04
	$2 \times O_5$	2·90 ±0·04
	O_5	3·17 ±0·04
O_3	$2 \times O_4$	2·89 ±0·04
	O_5	2·83 ±0·04
	$2 \times O_5$	3·04 ±0·04
	$2 \times O_5$	2·81 ±0·04
O_4	O_4	3·14 ±0·05
	O_5	2·83 ±0·03
O_5	$2 \times O_5$	3·17 ±0·04
	O_5	2·82 ±0·04

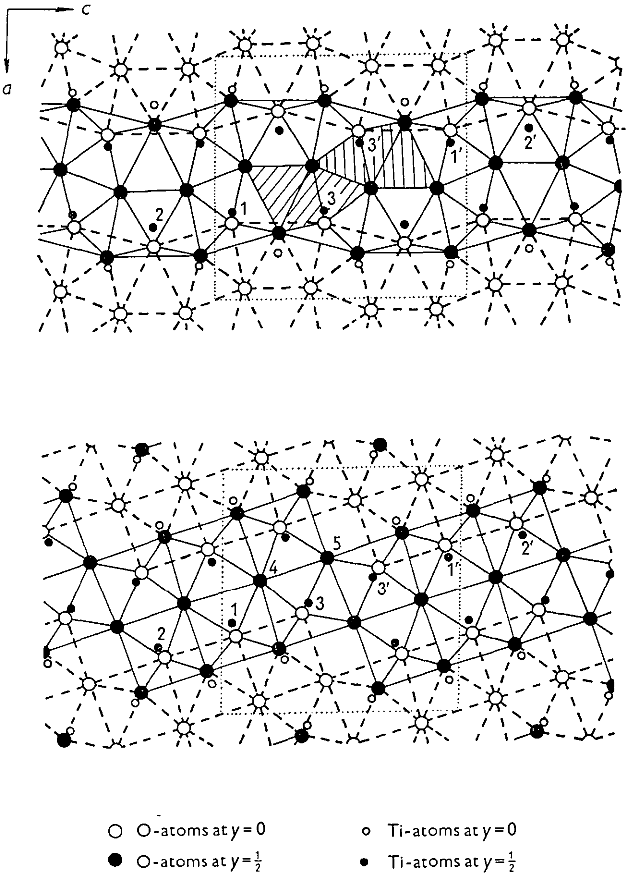


Fig. 4. Crystal structures of high-temperature Ti_3O_5 (monoclinic anosovite type) (top) and of low-temperature Ti_3O_5 (bottom). Unit cells indicated by dotted lines.

connected by sharing edges situated obliquely to the *ac* plane.

Several interatomic distances of the structure are listed in Table 3. The Ti–Ti distances of TiO_6 octahedra joined by corners are throughout of a normal length, *viz.* not below 3·8 Å. The Ti–Ti distances of octahedra sharing edges divide themselves into three markedly different groups, *viz.* (1) 3·17–3·07 Å, (2) 2·82 Å and 2·77 Å and (3) 2·61 Å. The lengths (2) and (3) are considerably less than those reported for the Ti–Ti distances in the metal (2·93 Å in α-Ti) and in the dioxide (2·96 Å in rutile).

Several instances are previously known of metal–metal distances in oxides and other compounds falling below those present in the metallic state. In these compounds the metal atoms occur in valency states lower than their maximum ones, *i.e.* they possess valency electrons that are not engaged in bonding metal to non-metal. The excess electrons may give rise to metal–metal bonds. It has been pointed out that there exists for several compounds of this type a relation between the short metal–metal distance and the number of excess valency electrons available per close metal–metal contact, the distance decreasing with increasing number of electrons (Magnéli & Andersson, 1955; Marinder & Magnéli, 1957).

In low-Ti_3O_5, formal valencies may be assigned to the various Ti atoms by considering how the adjacent O atoms are held in common by their metal atom neighbours. In this way, valencies of 3, $3\frac{1}{3}$ and $3\frac{2}{3}$ can be calculated for the Ti_1, Ti_2 and Ti_3 atoms respectively. The Ti_1 atom only takes part in one close metal–metal contact (2·61 Å), *viz.* across a centre of symmetry with another Ti_1 atom. Evidently there are two electrons available for this bond. For the non-linear row of atoms Ti_2–Ti_3–Ti_3–Ti_2 with metal–metal distances of 2·82, 2·77 and 2·82 Å, there is a total of two electrons which might be engaged in forming metal–metal bonds. The qualitative relation between metal–metal distance and number of valence electrons available per close metal–metal contact evidently seems to be valid also in this oxide. The shortest Ti–Ti distance (2·61 Å) may be compared with the short V–V distance of 2·65 Å in vanadium dioxide which also corresponds to two excess valency electrons (Andersson, 1956; Magnéli & Andersson, 1955).

Ti–O distances occur within the range 2·18–1·83 Å with an average of 2·03 Å. The O_1 and O_2 atoms are both surrounded by four Ti atoms in a distorted tetrahedral arrangement at a mean distance of 2·06 Å. This may be compared with the conditions in dititanium trioxide, where the oxygen atoms have four titanium neighbours, tetrahedrally arranged at distances of 2·02 and 2·08 Å (Westman *et al.*, unpublished results). The O_4 atom in low-Ti_3O_5 also has four adjacent metal atoms at around 2·07 Å. These latter metal atoms are, however, situated in a planar arrangement. For the O_3 and O_5 atoms, the distances are significantly shorter, *viz.* they co-ordinate three Ti atoms at average distances of 1·97 and 1·93 Å respectively. In rutile, there is a similar triangular arrangement of metal atoms at 1·944 (2 ×) and 1·988 Å from the central O atom (Baur, 1956).

The O–O distances are of reasonable lengths throughout, ranging from 3·17 to 2·61 Å. It is noticed that the octahedron edge corresponding to the shortest Ti–Ti contact (2·61 Å) is rather long (3·14 Å). In molybdenum dioxide (Magnéli, 1948) and vanadium dioxide (Andersson, 1956) a similar elongation of edges shared by metal–oxygen octahedra has been observed to be associated with the occurrence of close metal–metal contacts.

7. Comparison of the two modifications

Fig. 4 (top) shows an anosovite-type structure which is very nearly that of high-Ti_3O_5. (The unit-cell dimensions are those found in this investigation while the atomic positions correspond to those reported by Zhdanov & Rusakov (1954) for anosovite.) The structure might also be described as being a monoclinically deformed pseudobrookite type with all the metal atoms alike.

As opposed to low-Ti_3O_5, all the TiO_6 octahedra of the high-temperature form share 6 edges with their neighbours (5, 6 or 7 shared edges in the former), which gives all the metal atoms of high-Ti_3O_5 the same formal valency of $3\frac{1}{3}$. Assuming the interatomic distances to be similar to those found in anosovite, no bonds should exist between the Ti atoms of high-Ti_3O_5.

A comparison of the structures of the two modifications reveals certain structural analogies which are also reflected in the similarity in unit-cell dimensions (*cf.* 4 and 5). Thus high-Ti_3O_5 may be described as built up of endless, wave-like double-rows of TiO_6 octahedra extending in the *c* direction. These double-rows are evidently analogous to the 'flights of steps' in the structure of low-Ti_3O_5.

In Fig. 4 the atoms have been numbered in a way which emphasizes this structural similarity. It is obvious that the Ti atoms 1 and 2 and the O atoms surrounding them have very nearly the same sites in both phases. A rearrangement of the $Ti_3(Ti_{3'})$ and $O_3(O_{3'})$ atoms and of the O atoms indicated by the areas shaded in Fig. 4 (top) to form two TiO_6 octahedra sharing an edge should constitute the only essential atomic displacements necessary to transform the high-Ti_3O_5 into the low-Ti_3O_5 structure.

It is planned to carry out further investigations on this phase transformation in trititanium pentoxide by means of X-ray methods and also by other techniques.

This research has been sponsored in part by the Office, Chief of Research and Development, U.S. Department of Army, through its European Office, under contract number DA-91-508-EUC-245, and in part by the Swedish Natural Science Research Council. Thanks are also due to the Swedish Board for Computing Machinery for making BESK available to us. The valuable assistance of Mrs Stina Nord and Mr Sten Andersson is gratefully acknowledged.

References

ANDERSSON, G. (1956). *Acta Chem. Scand.* **10**, 623.

ANDERSSON, S., COLLÉN, B., KRUUSE, G., KUYLENSTIERNA, U., MAGNÉLI, A., PESTMALIS, H. & ÅSBRINK, S. (1957*a*). *Acta Chem. Scand.* **11**, 1653.

ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957*b*). *Acta Chem. Scand.* **11**, 1641.

ÅSBRINK, S., BLOMQVIST, G. & WESTMAN, S. (1959). *Ark. Kemi, Min. Geol.* (In press.)

ÅSBRINK, S. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1606.

BAUR, W. H. (1956). *Acta Cryst.* **9**, 515.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

FILONENKO, N. E., KUDRYAVTSEV, V. I. & LAVROV, I. V. (1952). *Doklady Akad. Nauk. S.S.S.R.* **86**, 561.

HAMBLING, P. G. (1953). *Acta Cryst.* **6**, 98.

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.

LEUNG, Y. C., MARSH, R. E. & SCHOMAKER, V. (1957). *Acta Cryst.* **10**, 650.

LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, p. 277. London: Bell.

MAGNÉLI, A. (1948). *Acta Chem. Scand.* **2**, 501.

MAGNÉLI, A. & ANDERSSON, G. (1955). *Acta Chem. Scand.* **9**, 1378.

MARINDER, B.-O. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1635.

NAYLOR, B. F. (1946). *J. Amer. Chem. Soc.* **68**, 1077.

VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**. 303.

WESTMAN, S., BLOMQVIST, G. & ÅSBRINK, S. (1959). *Ark. Kemi, Min. Geol.* (In press.)

WESTMAN, S., NORDMARK, C. & SUNDHOLM, A. (To be published.)

ZHDANOV, G. S. & RUSAKOV, A. V. (1954). *Trudy Inst. Krist., Akad. Nauk S.S.S.R.* **9**, 165.

Acta Cryst. (1959). **12**, 581

The Crystal Structure of the Dipotassium Salt of Methylene-*bis*-Nitrosohydroxylamine, $CH_2(N_2O_2K)_2$

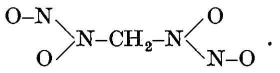
BY JOHN H. BRYDEN

Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.

(*Received* 31 *December* 1958)

Crystals of the dipotassium salt of methylene-*bis*-nitrosohydroxylamine are orthorhombic, having the unit-cell dimensions $a_0 = 26{\cdot}40$ Å, $b_0 = 12{\cdot}81$ Å, and $c_0 = 3{\cdot}95$ Å. The space group is *Fdd*2, and there are eight molecules per unit cell.

The structure was deduced and refined by Fourier and least-squares methods. The anion has the following configuration:



There is a two-fold axis through the methylene group. The N–CH_2–N bond angle is slightly less than tetrahedral. Resonance occurs among the N–N and N–O bonds, and accordingly the CN_2O_2 grouping is nearly planar. The CH_2–N bond is significantly longer than the usual carbon–nitrogen single bond length.

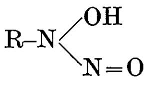
Introduction

Salts of methylene-*bis*-nitrosohydroxylamine were first prepared by Wilhelm Traube (1894) by the reaction of nitric oxide with acetone in the presence of alkali:

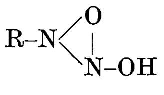
$$2\,NO+CH_3.CO.CH_3+3\,OH^- \rightarrow CH_2(N_2O_2)_2^{--}+CH_3COO^-+2\,H_2O.$$

During his extensive investigations Traube (1898) prepared many compounds containing the grouping $-N_2O_2H$, usually as salts since the free acids are quite unstable. Among the compounds he describes is the monopotassium salt of methylene-*bis*-nitrosohydroxylamine, but not the dipotassium salt. The disodium salt is ordinarily obtained as the monohydrate; the dipotassium salt, however, is anhydrous.

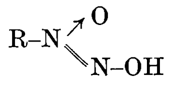
A number of possible structures were proposed by Traube (1895, 1898) for the $-N_2O_2H$ grouping:



I



II



III