

## The Structure of $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> at 297 K

BY S.-H. HONG AND S. ÅSBRINK

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm,  
S-106 91 Stockholm, Sweden

(Received 31 July 1981; accepted 5 May 1982)

### Abstract

$\gamma$ -Ti<sub>3</sub>O<sub>5</sub> is monoclinic, *I2/c* (No. 15). Unit-cell dimensions at 297 K are:  $a = 9.9701$  (5),  $b = 5.0747$  (3),  $c = 7.1810$  (4) Å,  $\beta = 109.865$  (4)°, with  $V = 341.70$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.348$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.71073 \text{ \AA}) = 6.673 \text{ mm}^{-1}$ . The crystal structure has been determined from X-ray single-crystal data collected with a diffractometer. The number of symmetry-independent reflexions with observable intensity was 1595, and the number of observations/variables was ~40. The least-squares refinement ended in  $R = 0.0185$ ,  $R_w = 0.0219$ . The accuracy of the structure determination is:  $\sigma_{\text{Ti-Ti}} = 0.0001\text{--}0.0003$  Å,  $\sigma_{\text{Ti-O}} = 0.0003\text{--}0.0005$  Å and  $\sigma_{\text{O-O}} = 0.0005\text{--}0.0009$  Å.  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> has a structure derived from the rutile structure (*r*) by crystallographic shear ( $1\bar{2}1$ )<sub>r</sub>. The unit cell contains two Ti positions, one *at* and one *between* the shear planes, each with octahedral O coordination. The two types of octahedra form two different types of infinite chains, one by sharing edges and faces, and one by sharing corners. The chains and their connexions are analogous to those found in the two modifications of V<sub>3</sub>O<sub>5</sub>. There is a partial segregation of Ti<sup>III</sup> and Ti<sup>IV</sup>, and Ti<sup>IV</sup> concentrates at the shear-plane position.

### Introduction

The polymorphism and the phase transitions of Ti<sub>3</sub>O<sub>5</sub> have been extensively studied. In a phase analysis of the Ti–O system it was found that the room-temperature modification of a Ti<sub>3</sub>O<sub>5</sub> sample prepared at ~1420 K has a monoclinic structure (Andersson, Collén, Kuylenstierna & Magnéli, 1957); the crystal structure (Åsbrink & Magnéli, 1959), which was later called  $\beta$ -Ti<sub>3</sub>O<sub>5</sub>, is quite different from the orthorhombic pseudobrookite-type of structure (anosovite) assigned to Ti<sub>3</sub>O<sub>5</sub> some years earlier by Zhdanov & Rusakov (1954).

The pseudobrookite structure was, however, found to exist as a high-temperature modification in the binary Ti–O system ( $\alpha$ -Ti<sub>3</sub>O<sub>5</sub>). The detailed crystal structure of  $\alpha$ -Ti<sub>3</sub>O<sub>5</sub> was obtained from a single-crystal

investigation performed at about 450 K (G. Åsbrink & S. Åsbrink in Magnéli, Andersson, Westman, Kihlberg, Holmberg, Åsbrink & Nordmark, 1959). The rapid reversible reaction  $\alpha$ -Ti<sub>3</sub>O<sub>5</sub>  $\leftrightarrow$   $\beta$ -Ti<sub>3</sub>O<sub>5</sub> occurring at 423–433 K in the strictly binary system could, however, be depressed below room temperature in the presence of impurities, e.g. Fe.

The existence of a new monoclinic room-temperature modification,  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>, which transformed magnetically at ~250 K, was reported by Åsbrink, Åsbrink, Magnéli, Okinaka, Kosuge & Kachi (1971). Investigation of the crystal structure and of physical properties, such as the electrical conductivity, of the new Ti<sub>3</sub>O<sub>5</sub> phase was delayed owing to the difficulty of single-crystal growth. The present work was undertaken as part of studies of reversible structural transitions in Ti<sub>3</sub>O<sub>5</sub> and V<sub>3</sub>O<sub>5</sub>.

### Experimental

Single crystals of the  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> phase were obtained by chemical-transport reactions. Single-phase transport of  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> was performed in closed silica ampoules using TeCl<sub>4</sub> (99.99%, Mitsuwa Chemicals, Japan) as the transport medium. In this way, single crystals of the  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> phase were obtained for the first time by Hong (1982). In the course of the preparative work on  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>,  $\beta$ -Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>4</sub>O<sub>7</sub> and Ti<sub>2</sub>O<sub>3</sub> the previously unexplained sources of extra O and oxidation introduced into the transport system of titanium oxides (Mercier & Lakkis, 1973; Since, Ahmed & Mercier, 1977) were discovered in an analysis of these systematic and extensive experiments. A prediction method was proposed by Hong (1982) for the oxidation state of transported titanium oxides. This method takes account of the input amounts of TeCl<sub>4</sub>, of H<sub>2</sub>O liberated from the wall of the silica ampoule and of the starting material with varied chemical compositions (a mixture of  $\beta$ -Ti<sub>3</sub>O<sub>5</sub> and Ti<sub>2</sub>O<sub>3</sub> powders). The method invariably allowed high-quality single-phase transport of the  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> crystals, when the temperature of the crystallization zone was  $\leq 1200$  K.

Crystals of  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> are black, and have the crystal faces (100) and (001) best developed. Their inter-section forms a very sharp edge parallel to the unique monoclinic *b* axis. The angle between the faces was easily confirmed under the microscope to be  $\beta^* \approx 70.1^\circ$ .

Accurate unit-cell parameters (*cf. Abstract*) were obtained from an optimally exposed powder film taken with a Guinier–Hägg focusing camera using Cu K $\alpha_1$  radiation [ $\lambda = 1.540598 \text{ \AA}$  (Deslattes & Henins, 1973); quartz monochromator]. A thin Al foil was used to reduce the severe fluorescent background blackening of the powder film, which was measured on a Mk II SAAB automatic film scanner (Abrahamsson, 1966) linked to an IBM 1800 computer. The measured powder diffraction pattern of  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> was parabolically corrected (Malmros & Werner, 1973) by five Si internal-standard lines [ $a = 5.431065 \text{ \AA}$  (Deslattes & Henins, 1973)]. Details of the refined powder diffraction pattern have been published elsewhere (Hong, 1982). Data concerning the intensity collection and reduction are given in Table 1.

A possible deviation from the ideal stoichiometry of the single-phase-transported  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> crystals was carefully checked by refining the unit-cell parameters. No changes of the unit-cell parameters larger than the measurement errors ( $\lesssim 2\sigma$ ) were observed even for the  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> crystals which were transported simultaneously with crystals of Ti<sub>4</sub>O<sub>7</sub> or Ti<sub>2</sub>O<sub>3</sub>. Furthermore, no differences were observed between the unit-cell parameters of vapour-transported and non-vapour-transported preparations.

A small crystal, volume  $\sim 3.6 \times 10^{-3} \text{ mm}^3$ , was cut from a large single crystal with well developed faces. The size was considered to be fairly optimal, taking into consideration the positive as well as the negative consequences of increasing crystal size, *i.e.* weighing improved observability and counting accuracy of the weak reflexions against increased absorption and extinction.

The crystal was mounted on a silica capillary with a low-temperature glue (Araldite AY103, hardener HY953F, Ciba–Geigy). Crystal quality and the space group were determined from Weissenberg photographs

Table 1. *Details of the intensity collection and the reduction and least-squares refinement*

Scan mode: $\omega$ scan
$\omega$ -scan speed: $1^\circ \text{ min}^{-1}$
$2\theta$ interval ( $^\circ$ ): 5–100
Number of measured unique reflexions: 3801
Number of possible unique reflexions: 1718
Number of observable unique reflexions [ $I_o > 2\sigma(I_o)$ ]: 1595
Range of transmission factor: 0.377–0.517
Number of refined parameters: 40
<i>g</i> (secondary extinction): $1.18(3) \times 10^4$
$R = \sum  A  / \sum  F_o  = 0.0185$
$R_w = (\sum wA^2 / \sum wF_o^2)^{1/2} = 0.0219$

along the [010] and [001] axes. The crystal was finally set up on a PAILRED diffractometer (inclination geometry) equipped with a device for non-ambient-temperature generation: 83–1120 K (Hong & Åsbrink, 1978, 1981).

A preliminary investigation of the structural transition  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>  $\leftrightarrow$   $\delta$ -Ti<sub>3</sub>O<sub>5</sub> was performed. The instantaneous and reversible transition was observed at  $T_t \approx 240 \text{ K}$ . A critical phenomenon consisting of sharp net intensity increases was observed at the transition point. This phenomenon was expected from previous studies of the V<sub>3</sub>O<sub>5</sub> phase transition (Åsbrink & Hong, 1979).

The diffraction intensities were collected at  $297 \pm 1 \text{ K}$  by using the diffractometer in the equi-inclination setting. The [010] crystal axis was parallel to the diffractometer  $\omega$  axis. Monochromatic Mo K $\alpha$  radiation was obtained from the (002) plane of a graphite monochromator (take-off angle  $\approx 6^\circ$ ). The diameter of the primary-beam tunnel was 1.0 mm. A scintillation detector was used together with a pulse-height analyzer. The NaI(Tl) scintillation crystal surface was carefully examined by counting a strong reflexion with the detector position offset in angles  $\nu$  and  $Y$ ; in this manner the whole surface of a  $5^\circ$  window was examined. The net intensity variation was  $\lesssim 1\%$ . In the actual measurements a detector window of  $3^\circ$  was found optimal, because it did not cut off any high-angle reflexions with the  $\omega$ -scan method used. Reflexion profiles, gross intensities and background counts were recorded in the intensity-collection procedure.

The intensities of all reflexions within the two quadrants of each reciprocal-lattice layer investigated ( $5^\circ \leq 2\theta \leq 100^\circ$ ) were measured. However, the intensities of the zero layer were collected over the whole circle in order to test the absorption correction. The number of layers was 10, corresponding to  $0 \leq k \leq 9$ . The maximum attainable equi-inclination angle,  $\sim 42^\circ$ , precluded  $k \geq 10$ . Three test reflexions (800, 208, 0,0,12) were measured at least at the beginning and the end of the recording of each layer. The maximum intensity fluctuation of the test reflexions was  $\lesssim 1\%$ .

The 59 reflexions with the highest peak intensities were remeasured with the lower X-ray-tube power given by 30 kV and 10 mA (in the ordinary data collection 44 kV and 18 mA were used), to avoid counting losses; 28 of these significantly increased their intensities ( $>1\%$ ) after proper scaling. We found significant counting losses for peak intensities  $\gtrsim 10^4$  counts  $\text{s}^{-1}$ . The raw data were transformed to Lp-corrected net intensities with e.s.d.'s by the programs PAIL and DATRED (Brandt, 1971). The total number of recorded reflexions was 3801 and the number of non-extinct symmetry-independent reflexions was 1718. 1595 unique reflexions were considered observable, as they satisfied the relation  $I_o > 2\sigma(I_o)$ .

In the polarization correction the monochromator crystal was assumed to behave as an ideal mosaic crystal, an approximation which should be sufficiently accurate considering the very low Bragg angle of the monochromator reflexion  $\theta_M = 6.08^\circ$ . The intensities were corrected for absorption by the program *DATAP2* (Coppens, Leiserowitz & Rabinovich, 1965; local version). The linear-absorption coefficient,  $\mu = 6.673 \text{ mm}^{-1}$  for Mo  $K\alpha$ , was calculated from the mass-absorption coefficients given in *International Tables for X-ray Crystallography* (1974) and from the calculated density,  $D_x = 4.348 \text{ Mg m}^{-3}$ . The crystal could be described by 16 boundary planes, and the number of numerical-integration elements employed was 1728 ( $12 \times 12 \times 12$ ). After the absorption correction the maximum intensity difference between equivalent reflexions had decreased from  $\sim 6\%$  to  $\sim 2\%$ . Symmetry-equivalent reflexions, however, were not averaged because of an expected difference in extinction-correction values. The transmission factors varied from 0.377 to 0.517 for the reflexions 181 and 20 $\bar{2}$ , respectively. In connexion with the absorption correction preparatory calculations were also performed, by means of *DATAP2*, for the secondary-extinction correction according to Zachariasen (1967), modified for equi-inclination geometry by Åsbrink (1973).

### Structure determination

The reflexions  $hkl$  with observable intensity in  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> all have  $h + k + l = 2n$ . However,  $h0l$  are only observed with  $l = 2n$  ( $h = 2n$ ). The possible space groups are  $I2/c$  (No. 15) and  $Ic$  (No. 9). The centrosymmetric space group  $I2/c$  was tried initially because the  $\gamma$ -phase is one of the high-temperature modifications of Ti<sub>3</sub>O<sub>5</sub> ( $T_i \approx 240 \text{ K}$ ,  $\gamma\text{-Ti}_3\text{O}_5 \leftrightarrow \delta\text{-Ti}_3\text{O}_5$ ), and the high-temperature modification of V<sub>3</sub>O<sub>5</sub> (high-V<sub>3</sub>O<sub>5</sub>), which had an analogous powder pattern with the same systematic absences, had been found to have space group  $I2/c$  (Hong & Åsbrink, 1977, 1982). This choice proved to be correct.

As starting values the positional parameters of high-V<sub>3</sub>O<sub>5</sub> were used in the full-matrix least-squares calculations with the program *FALFA* (Koenig, 1971). Atomic scattering factors for O<sup>-</sup> and Ti<sup>1.67+</sup> including anomalous-dispersion corrections ( $f'$  and  $f''$ ) were obtained from *International Tables for X-ray Crystallography* (1974);  $f_o(\text{Ti}^{1.67+})$  was derived as:  $\frac{1}{2}\{f_o(\text{Ti}) + \frac{1}{3}[2f_o(\text{Ti}^{3+}) + f_o(\text{Ti}^{4+})]\}$ .

Initially only positional parameters, isotropic thermal-vibration coefficients and a scale factor were refined. This gave an  $R$  value of 0.053;  $R = \sum |\Delta| / \sum |F_o|$ , where  $\Delta = |F_o| - |F_c|$ . A secondary-extinction-correction variable was refined in the final round of calculations, in which all 10 positional and 28 anisotropic thermal-vibration parameters and a scale

factor were refined simultaneously. This resulted in a final  $R$  of 0.0185 and  $R_w = 0.0219$ , where  $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$  with a weighting function  $w^{-1} = \sigma^2(F_o) + 4 \times 10^{-5} F_o^2 + 2 \times 10^{-7} |F_o|^3$ . A weight analysis according to Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) gave a satisfactory result. The number of unique reflexions used in these calculations was 1595, and the degree of overdetermination (the number of observations/refined parameters) was  $\sim 40$ . The final atomic coordinates and equivalent isotropic thermal-vibration parameters (Hamilton, 1959) are presented in Table 2.\*

In the final stage of the least-squares calculations the convergence was very rapid and complete: all shifts in the atomic parameters were  $\leq 5 \times 10^{-7}$ , and the largest shifts, which occurred for the scale factor and extinction-correction variable, were less than  $10^{-4} \sigma$ . The final value of the isotropic secondary-extinction correction variable  $g$  was  $1.18(3) \times 10^4$  and 52 reflexions had  $y < 0.90$  ( $y = I_o/I_c$ ; Zachariasen, 1967). After the secondary-extinction correction the maximum difference of the structure amplitude between equivalent reflexions was much less than 1%; therefore, no averaging was made. A least-squares calculation with all unique reflexions including unobservable reflexions was not performed because the degree of overdetermination was already very high, and the number of accidentally unobserved reflexions was also very small (123 out of 1718 reflexions). However, the  $|F_c|$  values of the latter were all reasonably small.

Interatomic distances calculated with the program *DISTAN* (A. Zalkin, Berkeley, California; local version by A. G. Nord and B. G. Brandt) are in Tables 3 and 5. Figs. 1–4 were obtained by the use of the program *ORTEP* (Johnson, 1965; local version by I. Carlborn and A. G. Nord).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36931 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ( $\times 10^6$  for Ti;  $\times 10^5$  for O atoms) and isotropic temperature factors  $B_{\text{eq}}$  ( $\times 10^3$ ; Hamilton, 1959) equivalent to the final anisotropic ones

Numbers in parentheses are e.s.d.'s in the last significant digits, as elsewhere in this paper. Space group  $I2/c$  (No. 15 in an alternative orientation): coordinates of equivalent positions 8( $f$ ), 4( $e$ ) and 4( $b$ ) are (0,0,0);  $\pm(x,y,z)$ ;  $x, \bar{y}, \frac{1}{2} + z$ ;  $\pm(0,y,\frac{1}{2})$  and  $\pm(0,\frac{1}{2},0)$ ;  $0, \frac{1}{2}, \frac{1}{2}$ , respectively.

	$I2/c$	$x$	$y$	$z$	$B_{\text{eq}}$ ( $\text{Å}^2$ )
Ti(1)	8( $f$ )	370992 (10)	488050 (17)	89804 (14)	368 (2)
Ti(2)	4( $b$ )	0	$\frac{1}{2}$	0	360 (2)
O(1)	8( $f$ )	68944 (5)	83681 (8)	53592 (7)	493 (7)
O(2)	8( $f$ )	58096 (5)	34457 (7)	63893 (7)	426 (7)
O(3)	4( $e$ )	0	30804 (11)	$\frac{1}{2}$	444 (9)

Table 3. *Interatomic distances (Å)*

*e* or *f* next to an O—O distance means that the distance is a shared edge or part of a shared face, respectively. *e*, *f* or *c* next to a Ti—Ti distance means that the distance is *across* a shared edge, face or corner, respectively. Averages in parentheses are corrected for irregularity of the octahedron (see text).

Ti(1)—O(1)	1.8813 (4)	Ti(2)—O(1) × 2	1.9971 (4)
—O(1)	1.9851 (4)	—O(2) × 2	2.0389 (4)
—O(2)	1.9981 (5)	—O(3) × 2	2.0425 (3)
—O(2)	2.0276 (5)	Average	2.0262 (2)
—O(3)	2.0567 (4)		(2.0255)
—O(2)	2.1740 (5)	O(2)—O(1) <i>e</i> × 2	2.7186 (6)
Average	2.0205 (2)	—O(3) <i>e</i> × 2	2.7422 (5)
	(2.0081)	O(1)—O(3) × 2	2.8152 (5)
O(2)—O(2) <i>e</i>	2.6242 (8)	—O(3) × 2	2.8975 (6)
—O(2) <i>f</i>	2.6269 (9)	—O(2) × 2	2.9834 (6)
—O(3) <i>f</i> × 2	2.6939 (6)	O(2)—O(3) × 2	3.0230 (6)
—O(1) <i>e</i>	2.7186 (6)	Average	2.8633
—O(3) <i>e</i>	2.7422 (5)	Ti(1)—Ti(1) <i>f</i>	2.8087 (3)
—O(1)	2.8370 (6)	Ti(2)—Ti(1) <i>e</i> × 2	2.9611 (1)
—O(1)	2.9156 (6)	—Ti(1) <i>e</i> × 2	3.0633 (1)
—O(1)	2.9617 (6)	Ti(1)—Ti(1) <i>e</i>	3.2481 (2)
—O(1)	2.9834 (6)	—Ti(1) <i>c</i> × 2	3.4362 (2)
O(1)—O(3)	3.0424 (5)	Ti(2)—Ti(1) <i>c</i> × 2	3.5327 (2)
—O(2)	3.1103 (6)	—Ti(2) <i>c</i> × 2	3.5905 (2)
Average	2.8292	Ti(1)—Ti(1) <i>c</i> × 2	3.5926 (2)

### Discussion

The crystal structure of  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> can be described as hexagonal-close-packed O atoms with the octahedral interstices partly filled with Ti atoms. The Ti-containing octahedra form chains of two types, which run parallel to [001] (*cf.* Fig. 1). One type of chain is composed of double octahedra, each of which is formed from two Ti(1)—O octahedra sharing a common face. The double octahedra are coupled together in the chain by having edges in common. The chains of the double octahedra are mutually connected in the (1 $\bar{1}$ 0) and (110) planes by sharing corners. The other type of chain is composed of single Ti(2)—O octahedra which are coupled together by sharing corners. The chains of the two types are connected to each other by sharing octahedral corners and edges in the directions [100] and [010], respectively. A similar framework of the crystal structure was found in high- as well as in low-V<sub>3</sub>O<sub>5</sub> (Åsbrink, 1977, 1980).

Horiuchi, Tokonami, Morimoto, Nagasawa, Bando & Takada (1971) have pointed out that V<sub>3</sub>O<sub>5</sub> (monoclinic) can be considered as a member of the homologous series V<sub>n</sub>O<sub>2n-1</sub> (4 ≤ n ≤ 8, triclinic; Andersson, 1954) derived from the rutile structure (*r*) by crystallographic shear (1 $\bar{2}$ 1)<sub>r</sub>. Analogously,  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> can be considered as a member of the homologous series Ti<sub>n</sub>O<sub>2n-1</sub> (4 ≤ n ≤ 10, triclinic; Andersson, Collén, Kuylenstierna & Magnéli, 1957). With this view, the eightfold Ti position Ti(1) in the double-octahedral chains is situated *at* the shear planes, while the fourfold

position Ti(2) in the single-octahedral chains is situated midway *between* the shear planes (*cf.* Fig. 2).

The average distances  $\overline{\text{Ti}(1)\text{—O}}$  and  $\overline{\text{Ti}(2)\text{—O}}$  [2.0205 (2) and 2.0262 (2) Å, respectively] seem to indicate that the valencies of the two independent Ti atoms are rather similar. However, the centrosymmetric Ti(2)—O octahedron is far more regular than the Ti(1)—O octahedron (*cf.* Figs. 3 and 4), and a consequence of the logarithm relation between bond

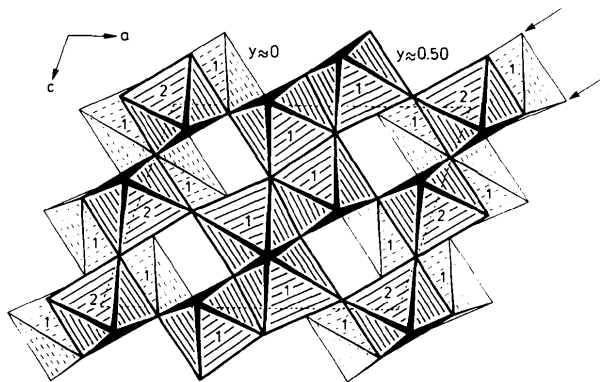


Fig. 1. The coupling of octahedra in  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>: [010] projection of two layers of octahedra ( $y \approx 0$  and  $y \approx 0.50$ ). Numbers 1 and 2 denote Ti(1)—O and Ti(2)—O octahedra, respectively. The two arrows limit a section which is presented in Fig. 2.

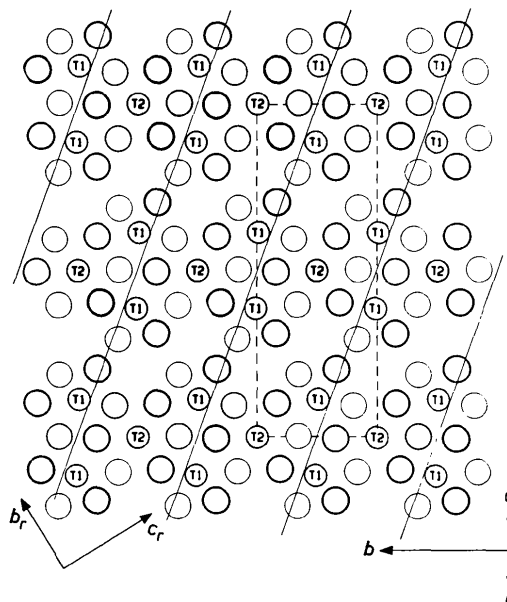


Fig. 2. A projection on (101) of the section between the arrows in Fig. 1, showing the hexagonal close packing of O atoms in  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>. The axes of the rutile subcell are denoted *b*, and *c<sub>r</sub>*. Circles marked T1 and T2 indicate Ti positions Ti(1) and Ti(2), respectively, and empty circles indicate O atoms. The thickness of the circles indicates the height difference of atom positions. The oblique full lines indicate the intersections of the slanting shear planes with (101) at  $x + z = 1$ . The dashed lines indicate the unit cell of  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub>.

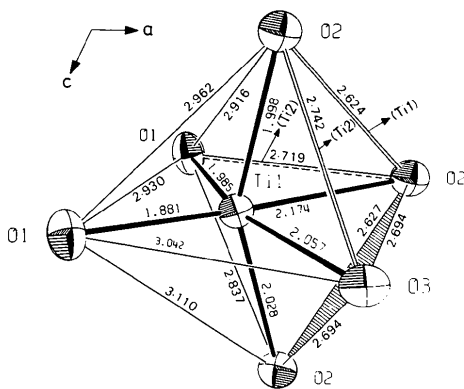


Fig. 3. Atom Ti(1) with the O coordination octahedron. The common face shared with another Ti(1)—O octahedra is shaded. Common edges shared with adjacent octahedra are indicated by double lines, and the edges shared with Ti(1)—O and Ti(2)—O octahedra are marked with  $\rightarrow$ (Ti1) and  $\rightarrow$ (Ti2), respectively. All thermal ellipsoids in this paper are scaled to enclose 95% probability.

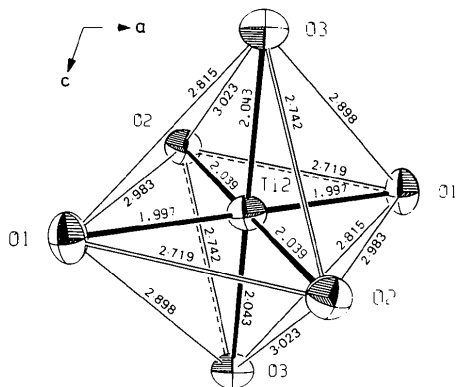


Fig. 4. Atom Ti(2) with the O coordination octahedron having a symmetry centre. Double lines indicate edge sharing with other octahedra, all containing Ti(1).

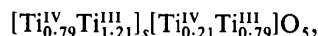
length and bond strength (Pauling, 1947) is that an increased distortion of a coordination polyhedron with a central atom of a given valency leads to an increased average bond length.

A comparison between the two types of Ti octahedra is therefore possible only after a 'normalization' of each; *i.e.* one must derive the quite regular equivalent of each. This may be done by making use of the logarithmic relation, from which a correction term, to be added to the observed average value, may be derived (*cf.* Allmann, 1975). If the logarithmic relation is written  $d_i = d(1)(1 - q \ln S_i)$ , the correction term is  $-d(1)q \ln[\bar{S}/(S_1 S_2 \dots S_n)^{1/n}]$ , where  $d_i$  is the observed length of the  $i$ th bond (Å),  $S_i$  is the corresponding bond strength,  $d(1)$  is defined as the length of a bond of unit strength  $q$  is a constant,  $n$  is the coordination number, and  $\bar{S} = \sum_{i=1}^n S_i/n$ . In the present case,  $n = 6$ , and  $d(1)$  and  $q$  were given the values 1.836 Å and 0.1648,

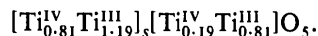
respectively (*cf.* below). The normalized average Ti—O distances are given in parentheses, below the observed, in Table 3. There is obviously a valency difference between Ti(1) and Ti(2).

The actual valencies, obtained as the bond-strength sums for the Ti(1) and Ti(2) octahedra, are 3.40 and 3.21, respectively. The bond-strength sums for the whole unit cell add up to 40.01 (ideal value 40.00). The general reliability of the values used for the constants  $d(1)$  and  $q$  was tested by the successful application to several other titanium oxides with octahedrally coordinated Ti, the crystal structures of which are all known with a high or very high accuracy in the Ti—O bond lengths. The results are summarized in Table 4.

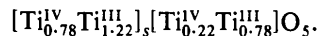
The derived distribution of tri- and tetravalent Ti in  $\gamma$ -Ti<sub>3</sub>O<sub>5</sub> corresponds to the formula



where [ ]<sub>s</sub> and [ ] correspond to metal-atom positions *at* shear planes and *between* shear planes, respectively. In order to investigate the accuracy of the distribution numbers, calculations were made using considerably changed values for  $d(1)$  and  $q$ . Thus,  $d(1) = 1.85$  Å and  $q = 0.15$  resulted in bond-strength sums of 3.41 and 3.19, respectively (total sum 40.02), corresponding to the formula



Another pair of parameters [ $d(1) = 1.82$  Å and  $q = 0.1818$ ] gave the sums 3.39 and 3.22, respectively (total sum 40.00), corresponding to



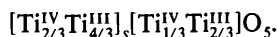
The deviations from the previously obtained distribution are thus very small. However, both these new

Table 4. Mean Ti valencies in oxides containing octahedrally coordinated Ti, obtained in bond-strength calculations using the expression  $\ln S_i = [1 - d_i/d(1)]/q$ , where  $d(1) = 1.836$  and 1.833 Å for the room-temperature and low-temperature phases, respectively, and  $q = 0.1648$

Compound	Derived mean valency	Ideal mean valency	Crystal structure reference
Ti <sub>2</sub> O <sub>3</sub>	2.996	3.000	Robinson (1974); Rice & Robinson (1976)
$\gamma$ -Ti <sub>3</sub> O <sub>5</sub>	3.334	3.333	This work
Ti <sub>4</sub> O <sub>7</sub>	3.508	3.500	Marezio, McWhan, Dernier & Remeika (1973)
Ti <sub>4</sub> O <sub>7</sub> (120 K)	3.514	3.500	Marezio, McWhan, Dernier & Remeika (1973)
Ti <sub>5</sub> O <sub>9</sub>	3.627	3.600	Marezio, Tranqui, Lakkis & Schlenker (1977)
Ti <sub>5</sub> O <sub>9</sub> (115 K)	3.585	3.600	Marezio, Tranqui, Lakkis & Schlenker (1977)
TiO <sub>2</sub> (rutile)	4.001	4.000	Abrahams & Bernstein (1971)

pairs of values for  $d(1)$  and  $q$  gave considerably worse results for  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$ , viz the mean valencies 2.96 and 4.06, and 3.03 and 3.95, respectively (cf. Table 4). We conclude that the pair of values for  $d(1)$  and  $q$  (1.836 Å and 0.1648, respectively) originally presented is the preferable pair and that the distribution derived from it is fairly accurate.

A completely statistical distribution of  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$  on the available metal-atom positions would be represented by the formula



There is, thus, a concentration of  $\text{Ti}^{\text{IV}}$  in the metal-atom sites at the shear planes. This is in accordance with observations made previously on other trimetal pentoxides with the  $\text{V}_3\text{O}_5$ -type crystal structure (cf. Åsbrink, 1980; Table 3).

It is not yet known if and how the valency distribution is changed in the phase transformation to  $\delta\text{-Ti}_3\text{O}_5$  at ~240 K. A single-crystal structure investigation of the latter phase is in progress. Judging from the results of the measurements of magnetic susceptibility, the structural change from  $\gamma$  to  $\delta\text{-Ti}_3\text{O}_5$  is entirely different from the one leading from high- to low- $\text{V}_3\text{O}_5$ . This is also evident from the fact that the space group of  $\delta\text{-Ti}_3\text{O}_5$  is either  $P2/a$  or  $Pa$  whereas it is  $P2/c$  for low- $\text{V}_3\text{O}_5$ .

Concerning the individual Ti—O bonds in  $\gamma\text{-Ti}_3\text{O}_5$ , one finds that in the noncentrosymmetric octahedron the shortest Ti(1)—O bond of 1.8813 Å involves the only O atom which belongs neither to a shared face nor to a shared edge. The longest Ti(1)—O bond of 2.1740 Å, on the other hand, connects Ti to the O atom that is involved in the largest number of face and edge sharings (cf. Fig. 3). Analogous observations were made for low- and high- $\text{V}_3\text{O}_5$ , and they may be explained as effects of repulsions between central metal atoms.

Concerning the average Ti—O bond lengths of 2.0205 and 2.0262 Å (cf. Table 3) for the two octahedra in  $\gamma\text{-Ti}_3\text{O}_5$  at 297 K, one finds comparable average Ti—O bond lengths of 2.006, 2.006, 2.004 and 2.018 Å for the four octahedra in  $\text{Ti}_4\text{O}_7$  at 298 K (Marezio, McWhan, Dernier & Remeika, 1973). The overall average Ti—O bond length of 2.023 Å for  $\gamma\text{-Ti}_3\text{O}_5$  is slightly longer than the corresponding value of 2.009 Å for  $\text{Ti}_4\text{O}_7$ . This difference is quite natural when one considers the average valencies of 3.33 and 3.50 for the Ti cations in  $\gamma\text{-Ti}_3\text{O}_5$  and  $\text{Ti}_4\text{O}_7$ , respectively. By interpolating the Ti—O bond lengths of 1.965 and 2.05 Å, obtained from Shannon & Prewitt's (1969) ionic radii, for  $\text{TiO}_2$  (rutile) and  $\text{Ti}_2\text{O}_3$ , respectively, one obtains 2.022 and 2.008 Å for  $\gamma\text{-Ti}_3\text{O}_5$  and  $\text{Ti}_4\text{O}_7$ , respectively, which are in excellent accordance with the observed overall averages of 2.023 and 2.009 Å.

Table 5. Oxygen coordination and O—Ti distances (Å)

O(1)—Ti(1)	1.8813 (4)	O(3)—Ti(2) × 2	2.0425 (3)
—Ti(1)	1.9851 (4)	—Ti(1) × 2	2.0567 (4)
—Ti(2)	1.9971 (4)	Average	2.0496
Average	1.9545		
O(2)—Ti(1)	1.9981 (5)		
—Ti(1)	2.0276 (5)		
—Ti(2)	2.0389 (4)		
—Ti(1)	2.1740 (5)		
Average	2.0597		

Concerning the Ti—Ti distances in  $\gamma\text{-Ti}_3\text{O}_5$  (cf. Table 3), the shortest distance, 2.8087 Å, is found across a shared octahedral face ( $f$ ), and the corresponding value is 2.811 Å in  $\text{Ti}_4\text{O}_7$  at 298 K. The second-shortest distances in the range 2.9611–3.2481 Å are found across a shared octahedral edge ( $e$ ), and the corresponding values are 2.895–3.280 Å in  $\text{Ti}_4\text{O}_7$ . The interatomic distances across an octahedral corner ( $c$ ) in  $\gamma\text{-Ti}_3\text{O}_5$  are in the range 3.4362–3.5926 Å; the corresponding values are 3.417–3.806 Å in  $\text{Ti}_4\text{O}_7$ .

In  $\beta\text{-Ti}_3\text{O}_5$  the shortest Ti—Ti distance is 2.61 (1) Å, across a shared octahedral edge, implying a strong intermetallic bond between ordered trivalent Ti atoms (Åsbrink & Magnéli, 1959). This bond is considerably weakened in the phase transition to  $\alpha\text{-Ti}_3\text{O}_5$ , the new distance being 2.83 Å (Åsbrink & Åsbrink in Magnéli *et al.*, 1959). As only a partial ordering of  $\text{Ti}^{\text{III}}$  exists in  $\gamma\text{-Ti}_3\text{O}_5$ , no intermetallic bonding can be expected, nor is it observed. The crystal structure determination of  $\delta\text{-Ti}_3\text{O}_5$  will answer the question whether there are Ti—Ti bonds formed in the phase transformation at ~240 K. The magnetic data indicate such a possibility (cf. Åsbrink *et al.*, 1971; Sävborg, 1980).

In rutile each O atom coordinates three Ti atoms; in  $\gamma\text{-Ti}_3\text{O}_5$  the O atoms are three- or four-coordinated (cf. Table 5). One observes that the three-coordinated O has a significantly larger thermal vibration than the four-coordinated O atoms (cf. Table 2), which is reasonable. An analogous observation was made in high- and low- $\text{V}_3\text{O}_5$ .

Reports on the crystal structure of  $\delta\text{-Ti}_3\text{O}_5$  and of the results of electrical-conductivity measurements of  $\gamma$ - and  $\delta\text{-Ti}_3\text{O}_5$  will appear elsewhere.

We wish to express our sincere gratitude to Professors Arne Magnéli and Peder Kierkegaard for their valuable comments and for the excellent facilities placed at our disposal, and to Dr Sven Westman for correcting the English of the paper. One of us (SHH) is also grateful for a grant from P. E. Lindahl's foundation. This work has been supported by the Swedish Natural Science Research Council.

#### References

- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1971). *J. Chem. Phys.* **55**, 3206–3211.

- ABRAHAMSSON, S. (1966). *J. Sci. Instrum.* **43**, 931–933.
- ALLMANN, R. (1975). *Monatsh. Chem.* **106**, 779–793.
- ANDERSSON, G. (1954). *Acta Chem. Scand.* **8**, 1599–1606.
- ANDERSSON, S., COLLÉN, B., KUYLENSTIERNA, U. & MAGNÉLI, A. (1957). *Acta Chem. Scand.* **11**, 1641–1652.
- ÅSBRINK, G., ÅSBRINK, S., MAGNÉLI, A., OKINAKA, H., KOSUGE, K. & KACHI, S. (1971). *Acta Chem. Scand.* **25**, 3889–3890.
- ÅSBRINK, S. (1973). Unpublished.
- ÅSBRINK, S. (1977). Fourth European Crystallographic Meeting, Oxford, PII. 86.
- ÅSBRINK, S. (1980). *Acta Cryst.* **B36**, 1332–1339.
- ÅSBRINK, S. & HONG, S.-H. (1979). *Nature (London)*, **279**, 624–625.
- ÅSBRINK, S. & MAGNÉLI, A. (1959). *Acta Cryst.* **12**, 575–581.
- BRANDT, B. G. (1971). *Chem. Commun. Univ. Stockholm*, No. II.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 45. Oxford: Pergamon Press.
- DESLATTES, R. D. & HENINS, A. (1973). *Phys. Rev. Lett.* **31**, 972–975.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HONG, S.-H. (1982). *Acta Chem. Scand. Ser. A*, **36**, 207–217.
- HONG, S.-H. & ÅSBRINK, S. (1977). Fourth European Crystallographic Meeting, Oxford, PII. 85.
- HONG, S.-H. & ÅSBRINK, S. (1978). *Acta Cryst.* **A34**, S344.
- HONG, S.-H. & ÅSBRINK, S. (1981). *J. Appl. Cryst.* **14**, 43–50.
- HONG, S.-H. & ÅSBRINK, S. (1982). *Acta Cryst.* **B38**, 713–719.
- HORIUCHI, H., TOKONAMI, M., MORIMOTO, N., NAGASAWA, K., BANDO, Y. & TAKADA, T. (1971). *Mater. Res. Bull.* **6**, 833–843.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOENIG, D. (1971). Unpublished.
- MAGNÉLI, A., ANDERSSON, S., WESTMAN, S., KIHLEBORG, L., HOLMBERG, B., ÅSBRINK, S. & NORDMARK, C. (1959). *Studies on the Crystal Chemistry of Titanium, Vanadium and Molybdenum Oxides at Elevated Temperatures. Final Technical Report 1*, DA-91-591-EUC-935, pp. 18–23.
- MALMROS, G. & WERNER, P. E. (1973). *Acta Chem. Scand.* **27**, 493–502.
- MAREZIO, M., MCWHAN, D. B., DERNIER, P. D. & REMEIKA, J. P. (1973). *J. Solid State Chem.* **6**, 213–221.
- MAREZIO, M., TRANQUI, D., LAKKIS, S. & SCHLENKER, C. (1977). *Phys. Rev. B*, **16**(6), 2811–2821.
- MERCIER, J. & LAKKIS, S. (1973). *J. Cryst. Growth*, **20**, 195–201.
- PAULING, L. (1947). *J. Am. Chem. Soc.* **69**, 543–553.
- RICE, C. E. & ROBINSON, W. R. (1976). *Mater. Res. Bull.* **11**, 1355–1360.
- ROBINSON, W. R. (1974). *J. Solid State Chem.* **9**, 255–260.
- SÄVBORG, Ö. (1980). *Mater. Res. Bull.* **15**, 171–176.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- SINCE, J., AHMED, S. & MERCIER, J. (1977). *J. Cryst. Growth*, **40**, 301–303.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
- ZHDANOV, G. S. & RUSAKOV, A. V. (1954). *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **9**, 165–210.