

High-Temperature Crystal Chemistry of Ti_2O_3 : Structural Changes Accompanying the Semiconductor–Metal Transition

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The crystal structure of Ti_2O_3 at 23, 117, 177, 217, 292, 348, 440, and 595 °C has been determined from X-ray diffraction data collected on a single-crystal diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation and has been refined by least-squares techniques to weighted residuals of 0.020 to 0.040 (based on F_o) with about 125 reflections being used at each temperature. Ti_2O_3 was found at all temperatures to be iso-morphous with α -alumina (rhombohedral, space group $R\bar{3}c$). Changes in the structure with increasing temperature are non-linear. The uncorrected Ti–Ti vector parallel to the c axis across the shared octahedral face increases smoothly from 2.579 (2) Å at 23 °C to 2.725 (2) Å at 595 °C, a 5.7% increase, as the c axis increases from 13.611 (1) to 13.969 (2) Å. The metal–metal separation in the basal plane across the shared octahedral edge decreases over the same temperature interval from 2.994 (1) to 2.986 (1) Å, a 0.3% decrease, while the a decreases from 5.1580 (4) to 5.1263 (4) Å. Changes in metal–oxygen and oxygen–oxygen distances can be described as arising from the reorganization of the packing which accompanies the metal–metal distance changes. The changes in atomic positions with temperature are consistent with the model proposed by Goodenough to account for the semiconductor–metal transition experienced by Ti_2O_3 over the temperature range 100–350 °C. An anomalous reduction of the Ti site occupancy from 1.0 has been observed and attributed to an artifact of the refinement resulting from the approximations in the extinction correction.

Introduction

Titanium sesquioxide undergoes a gradual semiconductor–metal transition when warmed through the temperature range 400–600 K (Morin, 1959; Yahia & Frederikse, 1961; Honig & Reed, 1968). Accompanying the resistivity change are rapid, non-linear changes in the unit-cell parameters (Pearson, 1958; Eckert & Bradt, 1973*a*), though Ti_2O_3 remains isostructural with corundum (α - Al_2O_3) at all temperatures. Studies relating to the Ti_2O_3 transition over the last two decades have been recently reviewed (Honig & Van Zandt, 1975; Mott, 1974).

The most widely accepted model for the Ti_2O_3 semiconductor–metal transition involves a band-crossing mechanism. According to this model, first advanced by Goodenough (1960), a small gap between filled and empty d bands in the low-temperature band structure is gradually narrowed and closes as the transition takes place. Since the bands which cross are involved in metal–metal bonding, the Goodenough model predicts that specific changes in Ti–Ti separations should accompany the electrical transition. Namely, metal–metal vectors parallel to the hexagonal c axis should increase, while the metal–metal vectors in the basal plane should decrease as Ti_2O_3 is heated. These predicted bond-distance changes are parallel to the changes in

cell axes which are observed to accompany the transition.

Zeiger, Kaplan & Raccach (1971) and Zeiger (1975) have used cell-constant behavior to estimate bond-distance changes in both Ti_2O_3 and V_2O_3 . These distance changes were used in calculations of changes in physical properties accompanying the electrical transitions in these materials. However, a study of the high-temperature crystal structure of V_2O_3 has shown that the temperature-induced decrease in the c axis length is actually accompanied by an increase in the V–V distance along this axis (Robinson, 1975). Thus the atomic displacements accompanying the Ti_2O_3 electrical transition may not necessarily be reliably assessed from cell-constant data.

A preliminary report of the structure of Ti_2O_3 at 300 and 700 K, from powder X-ray intensity data, indicated that the fractional coordinates of the atoms change very little on heating (Simonyi & Raccach, 1973). However, these results may not be reliable since the results at 300 K do not agree closely with previous single-crystal X-ray studies of Ti_2O_3 (Newnham & De Haan, 1962; Robinson, 1974). Since no single-crystal study of the Ti_2O_3 structure at high temperature has yet been attempted, we have determined the crystal structure of Ti_2O_3 at eight temperatures between 23 and 600 °C, from Czochralski-grown single crystals.

Experimental

A single-crystal boule of Czochralski-grown Ti_2O_3 was provided by Professor J. M. Honig of this department (Reed, Fahey & Honig, 1967). Spheres with radii 0.0125 cm (crystal 1) and 0.0152 cm (crystal 2) were ground from fragments of the boule. The crystals were mounted in a random orientation on quartz fibers with Cotronics cement No. 944, a high-strength silica-based ceramic cement. The mounted crystals were placed in 0.5 mm quartz capillaries, which were continuously evacuated and baked out at 500°C overnight before being sealed under vacuum. Film data from other crystals from the same boule (Robinson, 1974), and diffractometer measurements on the present crystals confirmed the previously determined space group $R\bar{3}c$ (No. 167).

Unit-cell parameters and intensities were measured on an Enraf-Nonius CAD-4 fully automated diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation. The diffractometer was equipped with a single-crystal heater constructed for use with κ geometry (Rice & Robinson, 1977). An incident-beam collimator of 0.8 mm diameter at a takeoff angle of 4.0° was used with a receiving aperture located 173 mm from the crystal. The pulse-height analyzer used with the scintillation counter was set to admit approximately 95% of the diffracted $\text{Mo } K\alpha$ intensity. Following centering of the crystal at room temperature, a set of 15 reflections widely separated in reciprocal space was centered and used to determine an orientation matrix for use in intensity-data collection. Alignment at higher temperatures was achieved by adjusting the centering of the crystal, then centering the orientation reflections and calculating a new orientation matrix. Precise unit-cell parameters were determined by centering the $K\alpha_1$ ($\lambda = 0.70926 \text{ \AA}$) peak for 28 reflections, $80^\circ < 2\theta < 100^\circ$, at both positive and negative 2θ and taking the average as the diffraction angle. Hexagonal cell parameters and their e.s.d.'s (Tables 1 and 3) were calculated by least-squares refinement of the observed 2θ values with the program *LCR-2* (Williams, 1964).

The intensities of a unique set of reflections with $6^\circ < 2\theta < 65^\circ$ (~125 reflections) were collected at each temperature. This set was chosen so that each reflection had the lowest Eulerian χ angle of its equivalent reflections. This procedure was used because the single-crystal heater was found to have the greatest temperature stability when kept upright. The heater was stable to $\pm 3^\circ$ at temperatures below 350°C, and $\pm 10^\circ$ at 650°C. For crystal 1 it was possible to choose an entire data set with $-5^\circ < \chi < +20^\circ$. Since the orientation of crystal 2 made some measurements at high χ unavoidable, care was taken to manually adjust the temperature for each reflection with $\chi > +40^\circ$.

The θ - 2θ scanning technique with a variable scanning speed was used with a 2θ range of $1.0^\circ +$

$0.2^\circ \tan \theta$ centered on the average peak position. The aperture was set at $3.0 + 2.11 \tan \theta$ mm wide by 6 mm high. Reflections were scanned twice at a rate necessary to accumulate a minimum net count of 1000 counts above background. The maximum rate for this slower scan was set at $20.1^\circ \text{ min}^{-1}$. If the results of the two slow scans were statistically different, the scan was repeated until agreement was reached. Those reflections which were too weak to give the desired net count were scanned twice at a rate of $1.3^\circ \text{ min}^{-1}$. The intensities of 90% of the reflections were well above the minimum count required. Background counts were made for one-quarter of the scan time at each end of both scans.

Intensity and cell-parameter data were collected for crystal 1 at 348°, then at 292, 217, 177, 117, 23, 595, and 440°C. Room-temperature cell-parameter data were collected thrice during the experiment: before heating the crystal [$a = 5.1565$ (3), $c = 13.611$ (1) Å], after the first two runs [$a = 5.1564$ (6), $c = 13.617$ (2) Å], and after the first six runs [$a = 5.1570$ (4), $c = 13.610$ (1) Å]. Since no significant change in cell constants was observed, it was concluded that crystal 1 was not oxidized during the collection of these data sets. Intensity and cell-parameter data were collected for crystal 2 at 23, 355, and 597°C in that order. Whereas crystal 1 was kept at high temperatures for long periods of time during data collection, the data for crystal 2 were collected as quickly as possible to minimize changes caused by oxidation.

Integrated intensities, I , were obtained from the expression $I = C - 2B$, where C is the sum of the counts collected during the two slower scans, and B is the sum of the background counts during these scans. A standard deviation was assigned to each measured intensity with the expression $\sigma(I) = [C + 4B]^{1/2}$. The data were corrected for Lorentz-polarization effects assuming an ideal monochromator polarization correction. The crystals were measured on a microscope with a micrometer eyepiece and a spherical absorption correction was applied (crystal 1 $\mu R = 0.95$; crystal 2 $\mu R = 1.12$). The reflections were reindexed so as to belong to the same one-twelfth of reciprocal space. All reflections with $I < \sigma$ were set equal to $\sigma/2$ and included in the refinement; there were five reflections in this category in each data set.

Least-squares refinements with both isotropic and anisotropic temperature factors were carried out for each set of intensity data with the *RFINE2* program written by Finger (1972). The initial atomic parameters in the space group $R\bar{3}c$ were those of Robinson (1974), transformed from rhombohedral to hexagonal coordinates. The program minimized $\sum w(F_o - F_c)^2$ with the scattering factor curves for Ti^{3+} and O^0 (Cromer & Waber, 1965) corrected for real and imaginary anomalous dispersion (Cromer, 1965). (Use of Ti^{3+} vs Ti^0 scattering curves had no noticeable effect on the

Table 1. Crystallographic data for Ti₂O₃, crystal 1, with standard deviations in parentheses

Parameter	23°C	117°C	177°C	217°C	292°C	348°C	440°C	595°C
a_{hex} (Å)	5.1570 (4)	5.1571 (4)	5.1417 (3)	5.1348 (5)	5.1286 (3)	5.1260 (4)	5.1257 (4)	5.1251 (4)
c_{hex} (Å)	13.610 (1)	13.631 (1)	13.731 (1)	13.783 (2)	13.839 (2)	13.878 (2)	13.914 (2)	13.957 (2)
V (Å ³)	313.46	313.95	314.38	314.71	315.24	315.81	316.59	317.48
c/a	2.639	2.643	2.670	2.684	2.698	2.707	2.715	2.723
Ti								
z	0.34485 (5)	0.34499 (6)	0.34549 (6)	0.34595 (6)	0.34648 (5)	0.34674 (5)	0.34699 (5)	0.34754 (6)
Occupancy	0.950 (13)	0.952 (14)	0.925 (14)*	0.930 (16)	0.943 (14)	0.952 (13)	0.939 (12)	0.935 (13)
β_{11}^{\ddagger}	65 (6)	75 (5)	86 (6)	91 (6)	104 (6)	107 (5)	120 (5)	143 (6)
β_{33}^{\ddagger}	5.4 (6)	6.4 (7)	6.4 (7)	7.3 (8)	8.1 (7)	8.3 (7)	10.1 (6)	12.2 (7)
O								
x	0.3133 (4)	0.3133 (5)	0.3127 (5)	0.3118 (6)	0.311 (5)	0.3107 (5)	0.3111 (5)	0.3101 (5)
β_{11}^{\ddagger}	76 (10)	90 (10)	107 (12)	117 (13)	118 (11)	118 (11)	132 (11)	163 (11)
β_{22}^{\ddagger}	87 (12)	99 (14)	122 (15)	133 (17)	140 (15)	140 (14)	150 (14)	190 (15)
β_{33}^{\ddagger}	6.6 (12)	8.4 (13)	12.1 (14)	11.7 (14)	12.1 (12)	12.1 (11)	14.2 (11)	17.8 (12)
β_{13}^{\ddagger}	1.9 (13)	2.4 (14)	2.0 (17)	3.5 (18)	4.1 (15)	4.4 (15)	3.6 (16)	4.2 (16)
R	0.027	0.029	0.032	0.034	0.031	0.033	0.033	0.031
R_{wt}	0.030	0.033	0.036	0.040	0.034	0.028	0.033	0.034
n	125	125	125	125	123	125	125	125
s^{\ddagger}	4.3 (3)	4.3 (4)	3.7 (4)	4.0 (4)	4.5 (4)	4.3 (4)	2.8 (3)	4.2 (4)
B_{Ti}	0.48	0.56	0.62	0.67	0.76	0.77	0.89	1.07
B_{O}	0.59	0.70	0.90	0.94	0.97	0.97	1.09	1.37
S	1.25	1.34	1.51	1.64	1.34	1.27	1.35	1.29

* Significant at 5% level.

† Times 10⁴. For Ti, $\beta_{11} = \beta_{22}$, $\beta_{12} = \frac{1}{2}\beta_{11}$, and $\beta_{23} = \beta_{13} = 0$; for O, $\beta_{12} = \frac{1}{2}\beta_{22}$ and $\beta_{23} = 2\beta_{13}$. The form of the anisotropic temperature factor T is $T = \exp(-\sum_i \sum_j h_i h_j \beta_{ij})$.‡ Times 10⁵.

Table 2. Uncorrected and corrected interatomic distances (Å) and bond angles (°) for crystal 1

For a given distance the top entry is the uncorrected distance which is equal to the lower limit or riding distance within experimental error. The bottom entry is the upper limit of the distance. The non-correlated distance is the average of the two entries.

	23°C	117°C	177°C	217°C	292°C	348°C	440°C	595°C
Ti(1)—Ti(2)	2.582 (2) 2.592	2.590 (2) 2.601	2.622 (2) 2.636	2.645 (1) 2.659	2.670 (2) 2.686	2.685 (1) 2.701	2.699 (1) 2.717	2.722 (2) 2.743
Ti(1)—Ti(3)	2.994 (1) 3.002	2.994 (1) 3.003	2.987 (1) 2.997	2.984 (1) 2.996	2.983 (1) 2.995	2.983 (1) 2.995	2.984 (1) 2.998	2.985 (1) 3.003
Ti(1)—O(1)	2.068 (2) 2.081	2.070 (2) 2.086	2.074 (2) 2.093	2.077 (2) 2.096	2.081 (2) 2.102	2.083 (2) 2.104	2.088 (2) 2.113	2.093 (2) 2.123
Ti(1)—O(5)	2.024 (1) 2.037	2.024 (1) 2.040	2.021 (1) 2.040	2.020 (1) 2.040	2.018 (1) 2.040	2.018 (1) 2.040	2.017 (1) 2.042	2.017 (2) 2.048
O(1)—O(2)	2.798 (4) 2.808	2.798 (4) 2.811	2.784 (4) 2.801	2.773 (4) 2.790	2.764 (4) 2.781	2.759 (4) 2.777	2.762 (4) 2.782	2.753 (5) 2.778
O(1)—O(4)	2.791 (1) 2.802	2.793 (1) 2.807	2.803 (1) 2.819	2.807 (1) 2.825	2.812 (1) 2.830	2.816 (1) 2.834	2.821 (1) 2.842	2.824 (1) 2.850
O(1)—O(5)	2.879 (1) 2.889	2.882 (1) 2.894	2.893 (1) 2.908	2.900 (1) 2.916	2.907 (1) 2.923	2.912 (1) 2.928	2.916 (1) 2.934	2.923 (1) 2.946
O(4)—O(5)	3.071 (2) 3.080	3.071 (2) 3.082	3.065 (2) 3.079	3.065 (2) 3.080	3.064 (2) 3.080	3.065 (2) 3.080	3.063 (2) 3.080	3.067 (2) 3.090
O(1)—Ti(1)—O(2)	85.16 (7)	85.03 (7)	84.30 (7)	83.77 (6)	83.23 (7)	82.93 (7)	82.80 (8)	82.34 (8)
O(1)—Ti(1)—O(4)	85.98 (2)	86.02 (2)	86.35 (2)	86.46 (2)	86.60 (3)	86.69 (2)	86.81 (3)	86.85 (3)
O(1)—Ti(1)—O(5)	89.41 (5)	89.45 (5)	89.86 (5)	90.12 (5)	90.33 (6)	90.47 (6)	90.48 (6)	90.64 (6)
O(1)—Ti(1)—O(6)	169.96 (8)	169.42 (8)	169.42 (8)	168.98 (7)	168.54 (8)	168.32 (8)	168.24 (9)	167.78 (9)
O(4)—Ti(1)—O(5)	98.64 (3)	98.66 (3)	98.59 (3)	98.68 (3)	98.78 (4)	98.80 (3)	98.80 (4)	98.98 (4)
Ti(1)—O(1)—Ti(2)	77.24 (9)	77.42 (9)	78.41 (9)	79.13 (9)	79.85 (10)	80.25 (10)	80.44 (10)	81.06 (11)
Ti(1)—O(2)—Ti(3)	94.02 (2)	93.98 (2)	93.65 (2)	93.54 (2)	93.40 (3)	93.30 (3)	93.19 (3)	93.15 (3)
Ti(2)—O(2)—Ti(3)	132.29 (5)	132.30 (5)	132.45 (5)	132.56 (4)	132.61 (5)	132.65 (5)	132.59 (5)	132.76 (5)

refinement.) Weights were taken as $w = 1/\sigma(F) = 4F^2/\sigma^2(F^2)$. Correction for extinction (Zachariasen, 1967) reduced F_c by as much as 50%. No reflections were rejected from the refinement.

Since sample oxidation at high temperatures might be expected to pose a problem in this system, and since some oxygen temperature factors were negative during the initial stages of refinement, the Ti site occupancy was refined for all data sets. An apparent metal deficiency was observed in all cases, in the range 5–8% Ti vacancies (see Tables 1 and 3). This occupancy refinement had significant effects on the extinction parameter, s , but no noticeable effects on the refinement of the atomic positions (shifts < 0.5 e.s.d.) and little effect on the temperature factors (shifts < 2 e.s.d.). Introduction of variable occupancy resulted in improvement of the model at the 0.5 to 5% level (Hamilton, 1965) in several of the refinements. These cases are noted in Tables 1 and 3. In the other cases the change in occupancy was not significant.

In order to investigate the cause for the apparent Ti deficiency in crystals 1 and 2, cell-parameter and intensity data were collected at room temperature for three more Ti_2O_3 crystals from the same boule, crystals 3, 4, and 5. None of these latter crystals were mounted under vacuum. Crystals 3 and 4 were chosen to be rather large (diameter = 0.029 cm) and fairly small (diameter = 0.0095 cm) spherical crystals respectively; these were ground at the same time as crystals 1 and 2 (over three years before the present experiment). Crystal 5 was prepared in the following way. The density of a massive boule fragment (~ 2.3 g) was determined by the Archimedes method to be $4.590(1)$ g cm $^{-3}$, corresponding to slightly metal-rich Ti_2O_3 ($\rho_{calc} = 4.57$ for $TiO_{1.500}$). This fragment was cleaved and a chip from its interior was ground under nitrogen to a sphere. This was immediately mounted and completely immersed in epoxy cement. Thus crystal 5 had no opportunity to oxidize and was almost certainly stoichiometric. Data from a quadrant of reciprocal space were collected, equivalent reflections were averaged and refinement was carried out as before. These crystals also refined as if 5 to 7% deficient in Ti. In each case the deficiency was significant at the 0.5% level. When the 12 reflections most strongly affected by extinction were omitted from the refinement of crystals 3, 4, and 5, the deficiency decreased to about 3% and was no longer significant. Changes in the other parameters were less than two standard deviations. The possible reasons for this apparent non-stoichiometry, which we believe to be an artifact of refinement, will be discussed below.

Final R values varied from 0.020 to 0.040. Fourier difference maps calculated from the final F_o 's and F_c 's of representative data sets showed residual electron densities of less than 0.2 e \AA^{-3} . Values of the standard deviation of an observation of unit weight are listed in Tables 1 and 3 as S . The final atom parameters listed in

these tables with the variance-covariance matrix were used to calculate the distances and angles and their e.s.d.'s reported in Tables 2 and 4. Tables 3 and 4 contain the results of the refinements and distance-angle calculations for crystals 2–5. Since these results essentially duplicate the results found with crystal 1, they have been deposited.*

Results

Ti_2O_3 is isomorphous with $\alpha-Al_2O_3$ at all temperatures. This structure consists of an approximate hexagonally closest packed array of oxide ions with metal ions in two-thirds of the octahedral holes. Each metal ion has four near metal neighbors, one sharing an octahedral face of the coordination polyhedron [Ti(1)–Ti(2) in Fig. 1] and three sharing edges of the octahedron [Ti(1)–Ti(3) in Fig. 1].

The thermal expansion of Ti_2O_3 is markedly different from that of α -alumina and other corundum structure compounds. Al_2O_3 , Cr_2O_3 , $\alpha-Fe_2O_3$, and Rh_2O_3 expand by 0.4–0.5% in an approximately linear fashion over the temperature range 23–600°C (Krikorian, 1960; Eckert & Bradt, 1973*b*). The expansion of Ti_2O_3 is sigmoidal with an inflection point in the temperature curves of both axes at about 175°C. The a axis decreases from 5.1580(4) Å at 23°C to 5.1263(4) Å at 595°C, a drop of 0.6%, while the c axis increases by 2.6% from 13.611(1) to 13.969(2) Å over the same temperature interval. (The cell constants, atomic parameters, and bond distances discussed

* These data and lists of observed and calculated structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32220 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

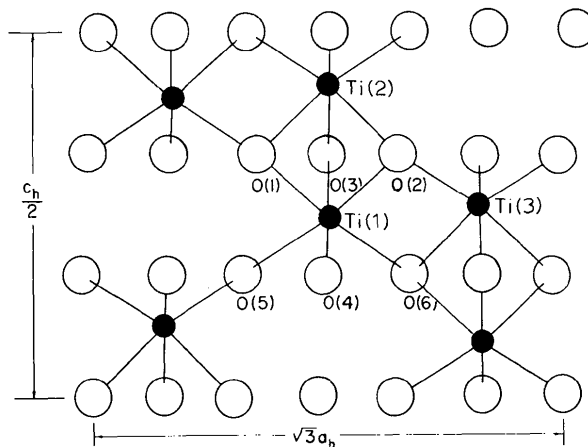


Fig. 1. A projection of the Ti_2O_3 structure on a plane perpendicular to the $[110]$ axis.

in this section are averages of the values for crystals 1–5 at room temperature, and for crystals 1 and 2 at 595 °C.) The a axis undergoes its greatest change between 100 and 300 °C, then levels off at higher temperatures. By contrast, the c axis is seen to be still increasing rather steeply at the highest temperature.

The cell parameters measured in this work agree rather well from crystal to crystal, with the exception of the parameters at 595 °C for crystal 1 and 597 °C for crystal 2. These c parameters differ by about 10 e.s.d.'s and the a parameters by about 5 e.s.d.'s with the parameters of crystal 2 being larger. Since the room-temperature cell parameters of neither crystal were checked after the runs at these temperatures, it is possible that some oxidation may have occurred in one or both cases.

The room-temperature cell constants of this study are in agreement with those of Prewitt, Shannon, Rogers & Sleight (1969), and Robinson (1974), as well as with measurements on powdered Ti_2O_3 at 23, 300 and 650 °C made in this department (Rice & Robinson, 1975). However, our cell constants differ slightly from those of Straumanis & Ejima (1962), Newnham & De Haan (1962), and Abrahams (1963). As far as can be seen (only figures are presented), the temperature behavior of our lattice constants agrees roughly with Pearson (1958) but much less well with Rao, Loehman & Honig (1968) and Eckert & Bradt (1973*a*). However, the lattice constants in the latter two reports were calculated from very limited data sets, often with only two data points at $\theta < 30^\circ$ for each temperature studied. Eckert & Bradt (1973*a*) also admitted to having problems with sample oxidation. The discrepancies between different sets of unit-cell constants may also reflect stoichiometry and purity differences. At the high temperatures necessary for preparation or growth of crystals, Ti_2O_3 is highly reactive towards the atmosphere and crucible materials used, so that pure, stoichiometric Ti_2O_3 is quite difficult to prepare.

The c/a ratio of room temperature Ti_2O_3 is 2.64, a value which is considerably smaller than those found for most corundum structure oxides (Prewitt *et al.*, 1969). The c/a ratios of Al_2O_3 , Cr_2O_3 , Ga_2O_3 , Fe_2O_3 and Rh_2O_3 all fall in the range 2.70–2.74 (V_2O_3 , on the other hand, shows the anomalously high c/a ratio of 2.83). With heating, the Ti_2O_3 c/a ratio increases to the more normal value of 2.73 at 597 °C.

The major change in the Ti_2O_3 atomic coordinates with heating is in the metal z parameter. This increases in a sigmoidal fashion, changing by 25 e.s.d.'s from room temperature to 595 °C. The oxygen x parameter decreases upon heating by only four e.s.d.'s. Simonyi & Racciah (1973) reported a significantly smaller increase in metal z than we observe, and reported an oxygen x which increases with increasing temperature.

The anisotropic temperature parameters do not appear particularly accurate and vary significantly from

crystals 1 and 2 to crystals 3, 4, and 5. This may be due in part to the behavior of the Ti occupancy, which will be discussed below, and in part to the differing data sets for the two classes of crystals. However, the equivalent isotropic B 's of the Ti and O atoms do show an approximately linear increase with temperature for crystals 1 and 2.

The room-temperature atomic coordinates reported in this work agree well with those of Newnham & De Haan (1962) and Robinson (1974). Since the details of this structure have been fully discussed by these authors, we shall concentrate on the changes induced by temperature.

The effect of the changes in atomic positions and cell dimensions on the metal–metal distances is shown in Tables 2 and 4. The distance between the mean positions of the Ti atoms which share octahedral faces of their coordination polyhedra, Ti(1)–Ti(2), increases from 2.579 (2) Å at 23 °C to 2.725 (2) Å at 595 °C. This amounts to an increase of 5.7%, compared with the 2.6% increase in the c axis over this temperature interval. The greatest change in each case occurs in the region 100–300 °C; no levelling off at higher temperatures is seen in either case. A plot of Ti(1)–Ti(2) vs c is approximately linear.

The Ti–Ti distance across the shared octahedral edge, Ti(1)–Ti(3), decreases from 2.994 (1) Å at 23 °C to 2.983 (1) Å at 292 °C. A gradual increase to 2.986 (1) Å at 595 °C is then seen. Thus Ti(1)–Ti(3) decreases by 0.3% from 23 to 595 °C, while a decreases 0.6% over the same interval. The reason that Ti(1)–Ti(3) starts to increase at high temperatures, while a continues to decrease slightly, is that the Ti(1)–Ti(3) distance is a function of both a and c . Thus the larger increase in c and z_{Ti} offsets the small decrease in a , causing the Ti–Ti distance to increase. A plot of Ti(1)–Ti(3) vs a is non-linear, with a minimum at a values corresponding to $\sim 300^\circ\text{C}$.

Changes in metal–oxygen and oxygen–oxygen distances with temperature are shown in Tables 2 and 4. The distance from Ti(1) to the O in the shared octahedral face of the coordination polyhedron, Ti(1)–O(1), increases from 2.067 (2) Å at 23 °C to 2.096 (2) Å at 595 °C, a change of 14 e.s.d.'s. At the same time, the distance between face-shared O atoms, O(1)–O(2), decreases from 2.797 (4) to 2.755 (5) Å. Thus as Ti(1) and Ti(2) move apart, their face-shared O atoms move together. The distance from Ti(1) to the O opposite to the shared face, Ti(1)–O(5), decreases slightly from 2.026 (1) Å at 23 °C to 2.017 (2) Å at 595 °C. The O atoms in this unshared face of the octahedron may move together very slightly; O(4)–O(5) changes from 3.073 (2) to 3.067 (3) Å. The distances between O atoms in different closest-packed layers, O(1)–O(4) and O(1)–O(5), increase substantially from 23 to 595 °C since the separation of these layers increases by one-half the change in M(1)–M(2).

The changes in bond distances considered above reflect changes in distances between the mean positions of the atoms rather than the mean interatomic distances. The correlations between the thermal displacements of the atoms must be known to calculate the mean distances. These correlations are not known; only the upper and lower bounds of the thermally corrected interatomic distances can be determined. These are reported in Tables 2 and 4. The lower bounds are equal to the uncorrected bond lengths and to interatomic distances calculated with the riding approximation (Busing & Levy, 1962).

The variation in thermal corrections as the sample changes temperature are difficult to judge. A decreasing thermal correction to the Ti(1)–Ti(3) distance would slightly augment the decrease in this separation over the 23–595°C range. On the other hand, an increasing correction could imply that there is no change or even an increase in the mean Ti(1)–Ti(3) distance. Likewise, the changes in the Ti(1)–O(5) and O(4)–O(5) distances are small in comparison with thermal corrections, so that these changes may not be significant. However, it is clear that the Ti(1)–Ti(2), Ti(1)–O(1), O(1)–O(2), O(1)–O(4) and O(1)–O(5) distance changes are real since they are significantly greater than any possible thermal correction.

It should be noted that the effect of the Ti occupancy refinement was to increase slightly the magnitude of the temperature parameters. Thus the thermal corrections reported represent an upper bound to the true corrections to bonds.

Discussion

It appears that the apparent Ti deficiency in crystals 1–5 was not a real effect, but rather an artifact of refinement resulting from the approximations in the extinction correction. For instance, when the reflections affected most strongly by extinction were removed from the refinement of crystals 3, 4, and 5, the apparent Ti deficiency was reduced from 5 to 3% and was no longer significant. The physical (electrical conductivity; density) and crystallographic characteristics of the crystals are those of stoichiometric Ti_2O_3 . Crystal 5 was shown to be stoichiometric by density measurement; both the density and the cell constants of Ti_2O_3 are sensitive functions of stoichiometry (Straumanis & Ejima, 1962). Since the room-temperature cell parameters and atomic positions of crystals 1–4 agree with those of crystal 5, all crystals must be close to stoichiometric. Further, the room-temperature cell constants of crystal 1 were the same before and after the runs at 117, 177, 217, 292, and 348°C, showing that no oxidation took place during these experiments. Moreover, the apparent deficiencies correspond to stoichiometries far outside the stability range for Ti_2O_3 : $\text{Ti}_2\text{O}_{2.84}$ to $\text{Ti}_2\text{O}_{3.15}$ (Ehrlich, 1939; Straumanis &

Ejima, 1962). Since the introduction of each metal vacancy in Ti_2O_3 requires the creation of three Ti^{4+} ions to balance the charge, and Ti^{4+} lacks the *d* electron used in Ti–Ti bonding in this system (see below), one would expect the metal–metal bond distances to be highly dependent on stoichiometry. However, though crystals 1–5 show varying degrees of metal deficiency at room temperature, the atomic positions in these crystals are identical within experimental error.

One might envision that an apparent decrease in Ti population in the usual Ti site might arise if the metal ions were disordered into the other, normally empty octahedral interstices in the oxide lattice. A twinning operation corresponding to a 60° rotation about the *c* axis might also give an appearance of lessened Ti occupancy in the normal site. However, no evidence was found for either disorder or twinning.

These results show that crystals 1–5 were close to being chemically stoichiometric (at least at temperatures under 350°C), and were not disordered or twinned. The apparent deficiency was observed to be dependent on crystal size and on the presence or absence of strongly extinguished reflections. Thus this odd behavior probably arises from inadequate correction for absorption and extinction. However, atomic positions and cell constants do not seem to depend on the apparent Ti occupancy, so that arguments based on changes in bond distances and angles assume that the samples either were stoichiometric or behaved as if they were in all important respects.

The changes in interatomic distances observed in Ti_2O_3 when it is heated from 23 to 595°C are too great to be attributable to the anharmonicity of atomic vibrations. The sigmoidal temperature dependence of these changes also differs from the near-linear behavior normally associated with thermal expansion. Thus the structural changes which occur must be due to electronic effects associated with the semiconductor metal transition which Ti_2O_3 undergoes in this temperature range.

The most rapid changes in all the structural parameters of Ti_2O_3 occur over the temperature range 100–300°C, the greatest change between consecutive temperatures studied occurring from 117 to 177°C. It is in this same 100–300°C range that Ti_2O_3 shows a 50-fold drop in resistivity (Honig & Reed, 1968), a specific heat anomaly (Barros, Chandrashekar, Chi, Honig & Sladek, 1973), and significant changes in elastic constants (Chi & Sladek, 1973), magnetic susceptibility (Pearson, 1958), and Raman spectrum (Mooradian & Raccach, 1971).

Though several of the atomic separations in Ti_2O_3 change significantly on heating, the entire structural change can be satisfactorily described as the result of the lengthening of the Ti(1)–Ti(2) distance. The remaining positional changes would then occur as the packing reorganizes to minimize changes in Ti–O bon-

ded distances. As Ti(1) and Ti(2) move apart, O(1) and O(2) draw closer together to offset as much as possible the lengthening of the Ti(1)—O(1) bond. The closest-packed oxide layers move apart [as shown by the increases in the O(1)—O(4) and O(1)—O(5) distances] so that the Ti(1)—O(5) distance remains reasonably constant. Thus the lengthening of the *c* axis with heating is due to the increase in the Ti(1)—Ti(2) separation, while the *a* axis decrease occurs as O(1), O(2) and O(3) follow the metal motion and move in towards the *c* axis. The change in the Ti(1)—Ti(3) distance with heating is small, and is attributable to the movement of the shared O(2) toward the *c* axis, pulling Ti(3) along with it.

The observed structural changes are consistent with Goodenough's (1960) band-crossing model for the Ti₂O₃ semiconductor-metal transition. The model postulates a lower-lying valence band of *a*₁ symmetry derived from *d* orbitals of the metal atoms with large lobes extending primarily along the *c* axis and a higher-lying conduction band of *e*_π symmetry resulting from overlap of *d* orbitals of *π* symmetry directed primarily parallel to the *ab* plane. At low temperatures, the Fermi level falls in the narrow gap between the *a*₁ and *e*_π bands. As the temperature is raised, electrons are promoted across the gap into the conduction band. The consequent depopulation of the *a*₁ band, which is bonding between Ti(1) and Ti(2), causes the Ti(1)—Ti(2) distance to increase. As the metals move apart the *a*₁ band is destabilized, causing it to rise in energy. Eventually the *a*₁ and *e*_π bands cross, causing the observed metallic behavior.

The observed increase in the Ti(1)—Ti(2) distance is consistent with the postulated reduction of electron density in the *a*₁ band during the electrical transition. It is not clear why the Ti(1)—Ti(2) distance shows steep increases in the 348–595 °C temperature range; at these temperatures the semiconductor-metal transition is complete, and no significant changes in resistivity are seen. Perhaps the thermal expansion of the Ti(1)—Ti(2) distance induces further destabilization and depopulation of the *a*₁ band, thus weakening and lengthening this bond more than would be expected from thermal effects alone. While the reduction in electron density in the *a*₁ band results in significant changes in the Ti(1)—Ti(2) bond length, the accompanying increase in electron density in the *e*_π band does not cause any appreciable decrease in the Ti(1)—Ti(3) distance, even though the band is of correct symmetry to be bonding between these two atoms. From our experimental results it appears that the *e*_π band is essentially non-bonding in nature.

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