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DETERMINATION OF LATTICE CONSTANTS, AND THERMAL EXPANSION COEFFICIENTS OF Ti_2O_3 AND OF ITS SOLID SOLUTIONS WITH Ti

BY

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A

THESIS

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Research Professor of Metallurgy

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CHAPTER I

INTRODUCTION

For the determination of the precise lattice constants of Ti_2O_3, it is very important to use a Ti_2O_3 as pure as possible.

Due to the formation of solid solution with titanium or oxygen, ranging from 32.5 to 34.5% O_2 by weight in the Ti-O binary system, it is very difficult to get a pure Ti_2O_3 (33.38% O_2 by weight) in the laboratory.

To determine the precise lattice constants of pure Ti_2O_3, therefore, the extrapolation method was used.

This method computes the respective constants for pure Ti_2O_3 from the values obtained with Ti_2O_3-Ti solid solutions by extrapolation. To carry out such an investigation on Ti_2O_3 the determinations as the following had to be made:

1) Determination of the exact lattice parameters of a substance having a composition close to Ti_2O_3.
2) Determination of the coefficients of thermal expansion (linear and volume expansion coefficients of the hexagonal and the rhombohedral unit cell, expansion coefficient of the axial ratio of the hexagonal unit cell, and interaxial angle expansion coefficient of the rhombohedral unit cell.)
3) Establishment of the change of the same parameters with small change in composition of the Ti_2O_3-Ti solid solution.
4) Determination of the experimental densities and the molecular weights of Ti_2O_3-Ti solid solutions.

These determinations would allow one :

5) To make conclusions concerning the perfection of Ti_2O_3-Ti solid solution and

6) To determine the parameters of pure Ti_2O_3.

For the evaluation of soundness of the crystal lattice of Ti_2O_3, experimental macroscopic densities of the samples used had to be determined.

CHAPTER II

REVIEW OF LITERATURE

The titanium-oxygen diagram developed by Ehrlich (1) in 1939 indicates the oxides TiO, Ti_2O_3 and TiO_2 as intermediate phases with increasing oxygen content. The crystal systems of these intermediate phases are cubic, hexagonal-rhombohedral and orthorhombic. Any one oxide can be easily transformed into another by heating with oxygen or titanium.

Ti_2O_3 is of particular interest, as the oxygen dissolved in titanium is probably present in the metal in this form.

Determination of lattice constants and x-ray density of Ti_2O_3 was done previously by Ehrlich (1), Lunde (2) and Zachariasen (3). The values obtained by them are as follows (in Å):

	a_{hex}	c_{hex}	a_{rh}	α (deg)	D(g/cm^3)
P. Ehrlich	5.141	13.61	--	--	4.486
G. Lunde	--	--	5.42	56° 32'	4.605
W. H. Zachariasen	5.15	13.56	5.42	56° 50'	4.601

Ehrlich (1) and Bumps (4) have also reported on the intermediate phase Ti_2O_3 containing from 32.5 to 34.5 per cent of oxygen by weight. In this range Ti_2O_3 forms solid solutions with titanium.

For the determination of the exact values of the lattice constants, it is very important to use a Ti_2O_3 as pure as possible.

In the previous reports, nothing was stated about the purity of Ti_2O_3, and the coefficients of thermal expansion were not determined at all. For the determination of the precise lattice parameter and the expansion coefficients, the asymmetric method developed by Straumanis and associates (14) in 1935-40, was used. The method is very suitable, precise, fast, and convenient also for other kinds of chemical work where x-ray examinations are useful.

The densities of the samples used were determined in the manner described by Aka(8).

CHAPTER III

EXPERIMENTAL PROCEDURE

I. The material used and the preparation of Ti_2O_3-Ti solid solutions.

1) Preparation of the samples.

The samples were prepared by heating titanium powder (+ 65 mesh, 98.27 per cent purity, supplied by the Belmont Smelting and Refining Works, Inc.), with the calculated amount of titanium dioxide (99.9 per cent purity, Fisher Scientific Company).

The dried materials were weighed, mixed, ground as well as possible, and heated in an alundum or zirconia crucible in a vacuum resistance furnace at 1400°C for four hours or more. To prevent a further oxidation of the samples by the oxygen remaining in the reaction tube after the evacuation, another crucible containing titanium powder, serving as a getter, was put in the reaction tube above the crucible.

The charges, usually sintered to one solid piece, were crushed, ground and stored in a dessicator.

2) Determination of free titanium and oxygen content in the samples.

For the determination of free titanium and oxygen content in the titanium oxygen alloys prepared, the hydrogen evolution method, as developed by Straumanis, Cheng and Schlechten(7), was used.

The respective Ti_2O_3-Ti alloy was dissolved in 60 ml of 6N HF. The hydrogen evolved was accumulated in a gas burette, and the volume readings were reduced to standard conditions. The oxygen content of the Ti_2O_3-Ti alloy was then calculated in per cent by weight by the following equation

$$O_2\ \% = 33.4 - 0.0475\ V \qquad (1)$$

V being the volume of H_2 developed per 1 gr. of alloy.

The apparatus for dissolving the samples and collecting the hydrogen was the same which was already available in the laboratory (7)

II. Apparatus for lattice parameter determination.

The description of the experimental method and apparatus was given by E. Z. Aka (8) in his thesis for a Doctor's degree. Reference should be made to his work or to the **later** publications (9, 10)

III. The sample mount.

The specimen used in this study consisted of a glass rod (0.08 mm in diameter, and 4-6 mm in length) coated with a thin layer of oil to which the powder to be examined was pasted.

Lithium-boron glass was used for the glass rod in order to decrease the absorption of x-rays.

After mounting, the powder specimen was carefully centered to prevent broadening of the diffraction lines. The exact centration and adjusting of the mount was made displacing the specimen holder by means of two adjusting screws.

After taking all necessary x-ray photographs with one specimen, the powder was removed from the glass rod by means of a thin aluminum strip moistened with acetone. Thus, the glass rod, once mounted to the sample holder could be used further for making other powder mounts.

All of these operations were performed under a microscope.

IV. Film measurement.

The distances between the peak intensities of corresponding rings (on the straight line, crossing the vertexes of the arcs) which are located symmetrically on either side of the point of entry or exit of the x-ray beam were measured in millimeters.

The difference in the average constant (the sum of readings of corresponding lines) for the back reflection lines and of the front reflection lines represents the circumference of the film cylinder at the time of measurement of the film. The most important lines for the present investigation are the back reflection lines, from which the precise back refraction angle φ can be calculated.

The distance in reading of the corresponding back reflection lines gives then the 4φ angle (in millimeters).

The correct reflection angles (Bragg) in degrees are obtained by multiplying them by a factor F (see in Table II).

The detail of the technique of film measurement is described by Straumanis(14).

V. Selection of proper radiation.

The proper radiation for Ti_2O_3 is that one which gives sharp lines in high back reflection region. The radiation was determined by comparing films taken with Cu, Fe, Cr, and Co targets under the same conditions.

Cobalt radiation was selected for the present investigation, because high back reflection angles of 77° and 82° were obtained on the films.

VI. Determination of lattice parameters and coefficients of thermal expansion.

X-ray photographs for determination of the exact lattice parameters and of the thermal expansion coefficients of Ti_2O_3-Ti solid solutions in form of powder were taken at constant temperatures between 10° and 60°C. The experiments were carried out in the x-ray thermostat which was capable of maintaining constant temperatures within ±0.02°C. To assure the temperature constancy of the powder mount, the loaded camera was held at a certain constant temperature for several hours before exposure.

Two or more photographs were taken at each constant temperature; some of the first lines and the two last lines were measured (see Table II), and the parameters a and c were calculated.

VII. Density determination.

A convenient and accurate method for determination of the density of fine powder was required to evaluate the soundness of the crystal lattice of Ti_2O_3. The accuracy of density determinations of powders can be improved by:

1) grinding the sample so that it does not contain any larger voids isolated from the surrounding medium. In other words, the material under examination should possess a hydraulic permeability as perfect as possible in all of its portions;

2) desorption of gases which adhere to the large surface of the finely divided powder and also are entrapped mechanically among the particles. The gases must be removed as completely as possible, because otherwise, the total volume of the powdered sample will appear larger than it actually is, and will lower the density.

These gases are commonly removed by outgasing, while applying mechanical agitation. However, this operation never goes smoothly (15)

The method reported here is essentially an improved modification of the method described by Barker and Martin (18) and is based on Archimedes' Principle. The following operations were performed in the density determination of Ti_2O_3-Ti solid solutions:

(1) Purest benzene in which the powder sample was insoluble was used, and the powder-liquid mixture was outgased as well as possible by the application of a suitable vacuum while stirring the mixture.

(2) The first weighing was done while the powdered material, to-

gether with its container, was completely immersed in the benzene at a temperature measured.

(3) The benzene in the container of the powdered material was evaporated completely after the first weighing.

(4) The second weighing of the dry powdered material was made in air.

CHAPTER IV

EXPERIMENTAL RESULTS

I. Composition of the samples.

The compositions of samples used for the present investigation are shown in Table I.

Table I

Composition of Ti_2O_3-Ti solid solutions.

	Sample I	Sample II
Weight of sample (in gr)	1.000	0.1706
Volume of H_2 developed (in ml/g)	5.6	25.79
Free Ti (in %)	0.8	3.67
O_2 content (in %)	33.1	32.17
Total Ti (in %)	67.2	67.87

II. The proper radiation.

Cobalt radiation, as already mentioned, was selected for the present investigation, because high back reflection angles of 77°and 82° were obtained on the films. Rotating and scanning the powder mounts during one and a half to two hours of exposure developed these lines (α_1 , as well as α_2) to a sufficient intensity for accurate measurements.

To reduce the effect of fluorescence of the specimen (background fogging) two pieces of thin aluminum foil were used to cover the back and front reflection regions of the film.

III. Indexing.

In order to index the film in accordance to the hexagonal unit cells, the following equation was used (12, 13):

$$\sin^2 \theta = \frac{\lambda^2}{4\ a^2} \left[4/3\ (h^2 + k^2 + hk) + \frac{a^2\ l^2}{c^2} \right] \qquad (2)$$

The **indices** of each line of the diffraction pattern were determined in sequence by means of comparison of the values of $\sin^2 \theta$, as calculated directly from the measurement of θ angles, and as computed from Ehrlich's constants for Ti_2O_3

$$\begin{aligned} \underline{a} &= 5.141\ \text{Å} = 5.1306\ \text{kX} \\ \underline{c} &= 13.61\ \text{Å} = 13.5825\ \text{kX} \end{aligned} \qquad (3)$$

using equation (2).

For the value of λ, the average wave length of Co radiation was used.

$$\begin{aligned} \alpha_1 &= 1.78529\ \text{kX} \\ \alpha_2 &= 1.78917\ \text{kX} \end{aligned} \qquad \text{ave.} = 1.787\ \text{kX} \qquad (4)$$

The hexagonal indices are tabulated in Table II.

The indices of the lines for the rhombohedral cell were then calculated from the hexagonal ones using equation (5)[10].

$$\begin{array}{lllll} H = & h & & +l \\ K = & & k & +l \\ U = & -h & -k & +l \end{array} \qquad (5)$$

where H, K, U are new rhombohedral indices, and h, k, l are the hexagonal indices.

IV. Calculation of the precise lattice constants and coefficients of thermal expansion of the hexagonal cell.

1) Determination of the lattice parameters of the hexagonal cell.

Using formulas (6) and (7) derived from equation (2), the hexagonal $\underline{a}$ and $\underline{c}$ constants were calculated from the values of Bragg angles of the two last lines.

$$\underline{a}^2 = \frac{\lambda^2 \left\{ l_2^2 \,(h_1^2 + k_1^2 + h_1k_1) - l_1^2 \,(h_2^2 + k_2^2 + h_2k_2) \right\}}{3 \left\{ l_2^2 \sin^2 \theta_1 - l_1^2 \sin^2 O_2 \right\}} \qquad (6)$$

Table II

Indices of the lines of Ti_2O_3 patterns, obtained with Cobalt radiation (Exposure 2 hrs.)

Intensity	v.s.	m.	s.	s.	m.	v.s.	m.	v.s.	m.	v.s.	m.
Reading (in mm)	61.160 37.895	65.094 33.959	71.095 27.861	72.250 26.701	75.765 23.165	84.768 14.096	190.279 108.369	163.156 135.458	162.495 136.132	157.933 140.767	156.897 141.756
Sum (in mm)	99.055	99.053	98.956	98.951	98.930	98.864	298.648	298.614	298.627	298.700	298.653
Difference (in mm)	23.265	31.135	43.234	45.549	52.600	70.672	81.910	27.698	26.363	17.166	15.141
Average of the ~~difference~~ **sum.** (in mm)				98.979					298.648		
Circumference (in mm)		298.648 - 98.979 = 199.669									
Factor		F = 360 / (4 X 199.669) = 0.450745									
θ (in deg.)	10.487	14.034	19.488	20.531	23.709	31.855	53.079	12.485 77.515	11.883 78.117	7.737 82.263	6.825 83.175
2θ	20.974	28.068	38.976	41.062	47.418	63.710	106.158	155.030	156.234	164.526	166.350
Sin θ	0.182	0.243	0.334	0.350	0.402	0.528	0.800	0.976	0.979	0.991	0.993
sin θ^2	0.03312	0.05905	0.11155	0.12250	0.16160	0.27878	0.64000	0.95257	0.95844	0.9821	0.98605
Indices	(0 0 3)	(0 1 2)	(1 0 4)	(1 1 0)	(1 1 3)	(1 1 6)	(0 0 12)	(1 3 10)	(1 3 10)	(3 0 12)	(3 0 12)

$$\underline{a}^2 = \frac{\lambda^2 \left\{ l_2^2 (h_1^2 + k_1^2 + h_1 k_1) - l_1^2 (h_2^2 + k_2^2 + h_2 k_2) \right\}}{3 \left\{ l_2^2 \sin^2\theta_1 - l_1^2 \sin^2\theta_2 \right\}} \qquad \underline{c}^2 = \frac{\lambda^2 \left\{ l_1^2 (h_2^2 + k_2^2 + h_2 k_2) - l_2^2 (h_1^2 + k_1^2 + h_1 k_1) \right\}}{4 \left\{ (h_2^2 + k_2^2 + k_2 h_2) \sin^2\theta_1 - (h_1^2 + k_1^2 + h_1 k_1) \sin^2\theta_2 \right\}}$$

$$\underline{a}^2 = \frac{(1.7853)^2 \left\{ (12^2 \times 13) - (10^2 \times 9) \right\}}{3 \times \left\{ (144 \times 0.95257) - (100 \times 0.98210) \right\}} = 26.50590975 \qquad \underline{c}^2 = \frac{(1.7853)^2 \left\{ (10^2 \times 9) - (12^2 \times 13) \right\}}{4 \left\{ (9 \times 0.95257) - (13 \times 0.98210) \right\}} = 184.6621079$$

Lattice constant (in kX) $\underline{a} = 5.14839$ $\underline{c} = 13.58907$

$$\underline{c}^2 = \frac{\lambda^2 \left\{ l_1^2 (h_2^2 + k_2^2 + h_2k_2) - l_2^2 (h_1^2 + k_1^2 + h_1k_1) \right\}}{4 \left\{ (h_2^2 + k_2^2 + h_2k_2) \sin^2\theta_1 - (h_1^2 + k_1^2 + h_1k_1) \sin^2\theta_2 \right\}} \qquad (7)$$

For the calculation, the indices of the two last doublets (1, 3, 10) for h_1, k_1, l_1 and (3, 0, 12) for h_2, k_2, l_2 were substituted. Of these lines only the α_1 lines were used, corresponding to the λ, (wave length of cobalt α_1 radiation = 1.78529 kX).

The simple average of two (or more) values of the corresponding lattice constants was taken as the correct value at a certain constant temperature.

Tables III and IV show (1) the values of the lattice parameters of Ti_2O_3-Ti solid solutions obtained at different constant temperatures, and (2) the variation in the values at one constant temperature.

Figures (1) and (2) show that the values of the lattice parameter are related to temperature by a straight line equation. The constants (the slope and the intercept on the y-axis) of the straight line equation were calculated by the least square method (19) and are summarized in Table V.

2) The linear expansion coefficients of the hexagonal cell.

The thermal linear expansion coefficients of the hexagonal axes of the Ti_2O_3-Ti solid solution could also be computed from equation (8) as follows:

$$\alpha = \frac{a_{t_2} - a_{t_1}}{a_{t_1} (t_2 - t_1)} = \frac{\underline{a}}{\underline{a}\ t} = \frac{1}{\underline{a}} \frac{da}{dt} \qquad (8)$$

where α = thermal linear expansion coefficient, a_{t_1}, a_{t_2} = lattice constants (kX) at temperatures t_1 and t_2 (°C).

Assuming that the straight line relationship is still valid at that temperature interval. The linear expansion coefficients of the

Table III

Variation of the hexagonal lattice parameters of Sample I with temperature.

	Lattice Parameter a		Lattice Parameter c	
Temp. °C.	Parameter a in kx	Parameter a average in kx	Parameter c in kx	Parameter c average in kx
10.0	5.13702 5.13839	5.1377	13.60463 13.60150	13.6031
20.0	5.13881 5.13521 5.13845	5.1375	13.60489 13.61603 13.60284	13.6078
30.0	5.13548 5.13971 5.14014	5.1382	13.61494 13.60680 13.60486	13.6101
40.0	5.13516 5.13667 5.13796 5.13848 5.13869 5.13560 5.13816	5.1373	13.61865 13.61600 13.60924 13.60736 13.60785 13.61570 13.61559	13.6129
50.0	5.13792 5.13648 5.13829	5.1376	13.61726 13.61924 13.61667	13.6177
60.0	5.13762 5.13693	5.1380	13.61982 13.62136	13.6189

Table IV

Variation of the hexagonal lattice parameters of Sample II with temperature.

	Lattice parameter a		Lattice parameter c	
Temp. °C.	Parameter a in kx	Parameter a average in kx	Parameter c in kx	Parameter c average in kx
10.0	5.13052 5.13175	5.1311	13.62581 13.62623	13.6260
20.0	5.12958 5.12971	5.1296	13.62918 13.62887	13.6290
30.0	5.12813 5.13004 5.12956	5.1292	13.63598 13.63559 13.63333	13.6350
40.0	5.12680 5.12815	5.1275	13.64069 13.63619	13.6384
50.0	5.12986 5.12913	5.1295	13.63938 13.63997	13.6397
60.0	5.12852 5.12804	5.1283	13.64455 13.64542	13.6450

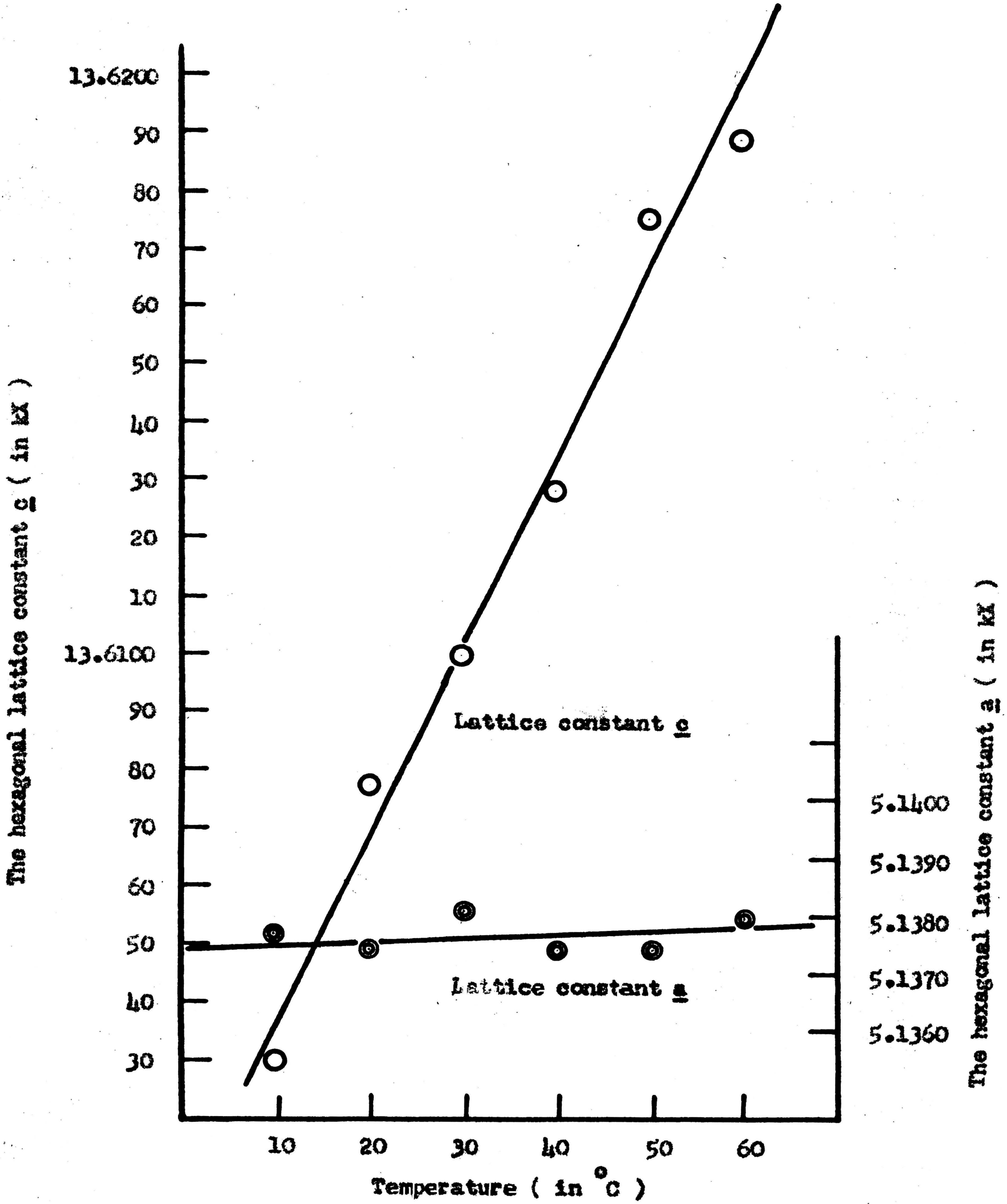

Fig. 1 The hexagonal lattice constants a and c of sample I versus temperature.

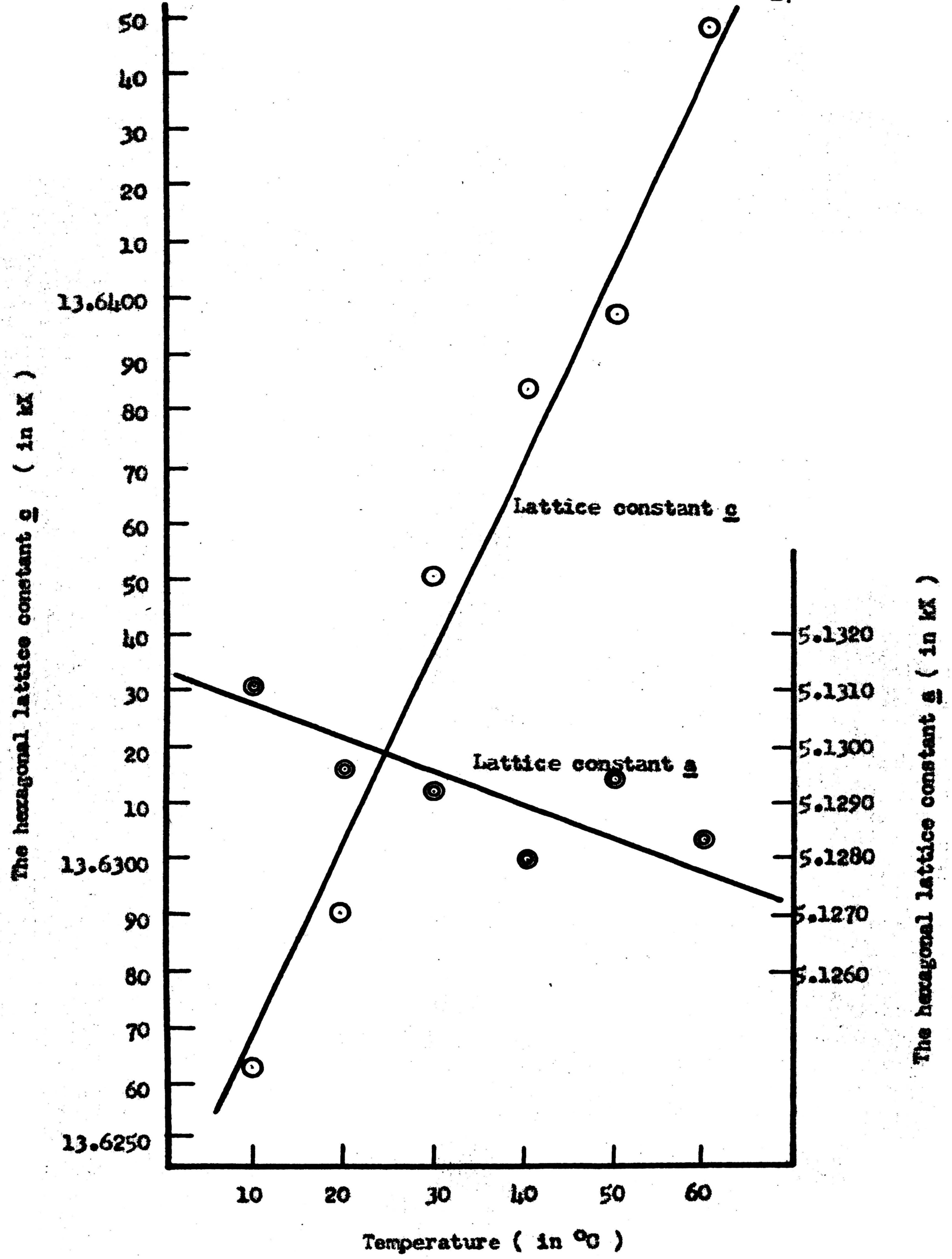

Fig. 2 The hexagonal lattice constants a and c of sample II versus temperature.

Table V

Straight line equation expressing the relation between temperature and lattice parameter.

Sample I	for the a constant	$a = 5.13767 + 0.000000857\ (t - 25.0)$
	for the c constant	$c = 13.60855 + 0.000318\ (t - 25.0)$
Sample II	for the a constant	$a = 5.13202 - 0.0000466\ (t - 25.0)$
	for the c constant	$c = 13.63179 + 0.000373\ (t - 25.0)$

(continued from p.13)

two axes between 10° and 60°C are expressed by equation (9).

$$\alpha_a = \frac{b_{(a)}}{a_{25°C}} \qquad \text{(For } \underline{a} \text{ constant)} \qquad (9)$$

$$\alpha_c = \frac{b_{(c)}}{c_{25°C}} \qquad \text{(For } \underline{c} \text{ constant)}$$

where, $a_{25.0°C}$ is the lattice a constant of the hexagonal cell at 25.0°C

$b_{(a)}$ is the slope da/dt for the lattice a constant

$c_{25.0°C}$ is the lattice c constant of the hexagonal cell at 25.0°C

$b_{(c)}$ is the slope dc/dt for the lattice a constant.

The calculated linear expansion coefficients of the axes of the hexagonal cell of the two samples, temperature region between 10° and 60°C, are summarized in Table VI.

Table VI

The linear expansion coefficients of the hexagonal unit cell of the two samples, temperature region between 10° and 60°C.

Sample	α_a (in $\frac{kX}{°C}$)	α_c (in $\frac{kX}{°C}$)
I	1.668×10^{-7}	2.337×10^{-5}
II	-9.080×10^{-6}	2.736×10^{-5}

3) <u>The precise lattice parameters at 25.0°C.</u>

To check the accuracy of the lattice parameter determination, the values of the lattice constants obtained at different constant temperatures were reduced to one single temperature 25.0°C, using the linear expansion coefficients. (see Tables VI and VII).

The probable error and the standard deviation of the lattice constants were calculated by the equations (10) and (11).

$$S = \sqrt{\frac{\sum\{dx\}^2}{n - 1}} \qquad (10)$$

where, S = standard deviation

$\sum\{dx\}^2$ = sum of the squares of the deviations in the constants

n = the total number of values

Then, the most probable error S',

$$S' = 0.6745\ S \qquad (11)$$

The result of error calculation is given in Tables VII and VIII which shows that the reproducibility of the measurements is about 1: 10000 for the a constant, and about 1: 20000 for the c constant. No absorption correction is necessary for lattice constants using the described technique. (see Chap. III).

The application of the refraction correction is necessary to obtain the true lattice constant and in order to balance the lattice constants of the same substance obtained with different x-radiations(21, 22, 23, 24) The correction for refraction was introduced by the use of the equation derived by Ewald(24).

The author used the equation given by Jette(29), who transformed a respective Siegbahn's equation(13), $a = a_n\left(1 + \frac{\delta}{\sin^2\theta}\right)$, by introduction of a minor correction of 0.9 for anomalous dispersion, as suggested by Weigle, which resulted in the following relation:

$$\Delta \sin^2\theta = -\frac{11.58 \times \rho \times Z}{M} \times \frac{\lambda^2}{4} \times 10^{-6} \qquad (12)$$

where ρ = density

Z = number of electrons in the sample

M = molecular weight

λ = wave-length

Table VII

Lattice constants of Sample I reduced from the temperature of the measurement to 25.0°C.

The a constant

Temp.	Lattice Const. (in kX)	Reduced to 25.0°C	da	$\{da\}^2$
10.0	5.1377	5.13771	+0.00004	16×10^{-10}
20.0	5.1375	5.13750	-0.00017	289×10^{-10}
30.0	5.1382	5.13819	+0.00053	2809×10^{-10}
40.0	5.1373	5.13729	-0.00038	1444×10^{-10}
50.0	5.1374	5.13738	-0.00029	841×10^{-10}
60.0	5.1380	5.13797	+0.00030	900×10^{-10}
Total		30.82605		
Average	$a_{25.0°C}$ =	5.13768		6299×10^{-10}

Standard deviation S 35.4×10^{-5} kX

Most probable error S' ±0.00024 kX

Reproducibility 1:21400

The c constant

Temp.	Lattice Const. (in kX)	Reduced to 25.0°C	dc	$\{dc\}^2$
10.0	13.6031	13.60787	-0.00068	4624×10^{-10}
20.0	13.6078	13.60939	+0.00084	7056×10^{-10}
30.0	13.6101	13.60851	-0.00004	16×10^{-10}
40.0	13.6129	13.60813	-0.00042	1764×10^{-10}
50.0	13.6176	13.60965	+0.00110	12100×10^{-10}
60.0	13.6189	13.60777	-0.00078	6084×10^{-10}
Total		81.65132		31644×10^{-10}
Average	$c_{25.0°C}$ =	13.60855		

Standard deviation 79.55×10^{-5} kX

Most probable error ±0.0005 kX

Reproducibility 1:25000

Table VIII

Lattice constants of Sample II reduced from the temperature of the measurement to 25.0°C.

The a constant

Temp.	Lattice Const.	Reduced to 25.0°C.	da	$\{da\}^2$
	(in kX)			
10.0	5.1311	5.13040	+0.00072	5148 x 10^{-10}
20.0	5.1297	5.12947	-0.00021	441 x 10^{-10}
30.0	5.1292	5.12943	-0.00025	625 x 10^{-10}
40.0	5.1275	5.12820	-0.00148	21904 x 10^{-10}
50.0	5.1295	5.13067	+0.00099	9801 x 10^{-10}
60.0	5.1283	5.12993	+0.00025	625 x 10^{-10}
Total		30.77810		38580 x 10^{-10}
Average	$a_{25.0°C}$ =	5.12968		

Standard deviation 87.84 x 10^{-5} kX

Most probable error 0.0006 (in kX)

Reproducibility 1:8000

The c constant

Temp.	Lattice Const.	Reduced to 25.0°C.	dc	$\{dc\}^2$
	(in kX)			
10.0	13.6260	13.63160	-0.00019	361 x 10^{-10}
20.0	13.6290	13.63087	-0.00092	8464 x 10^{-10}
30.0	13.6350	13.63313	+0.00134	17956 x 10^{-10}
40.0	13.6384	13.63280	+0.00101	10201 x 10^{-10}
50.0	13.6397	13.63037	-0.00142	20164 x 10^{-10}
60.0	13.6450	13.63194	+0.00015	225 x 10^{-10}
Total		81.79071		57371 x 10^{-10}
Average	$c_{25.0°C}$ =	13.63179		

Standard deviation 107.12 x 10^{-5} (in kX)

Most probable error 0.00073 (in kX)

Reproducibility 1:19000

Using the following values:

$\rho = 4.59$ ...(W. A. Zachariasen)(3)

$M = 143.80$

$Z = 68$

$\lambda = 1.78529$ kX

it was obtained from equation (12)

$$\Delta \sin^2\theta = - 0.00003379 \qquad (13)$$

To calculate the value of $\Delta \sin\theta$ or $d \sin\theta$, equation (13) has to be differentiated

$$d \sin^2\theta = 2 \sin\theta \cdot \cos\theta \, d\theta \qquad (14)$$

From equation (13) and (14), it follows then:

$$2 \sin\theta \cdot \cos\theta \, d\theta = - 0.00003379 \qquad (15)$$

Thus, the correction for Bragg's angle was calculated by equation (15), using for θ the Bragg angles measured. The results are shown in Table IX.

The refraction corrections for the lattice constants themselves were calculated by comparing the values of lattice constants obtained with those calculated with the corrected Bragg angles, as shown in Table X.

Then the final and corrected lattice constants for the two samples at 20°C and 25°C were calculated using the refraction corrections of Table X, and are summarized in Table XI.

The kX unit can be easily converted to Angstrom unit by multiplying by 1.00202.

4) Thermal volume expansion coefficient of the hexagonal cell.

The volume of a hexagonal unit cell at temperature t is as follows:(13)

$$V_t = a_t^2 \, c_t \sin 120° = a_t^2 \, c_t \times \sqrt{3/2} \qquad (16)$$

Table IX

Refraction correction for the Bragg angles of the two last α_1 lines (Co radiation).

Sample	Film No.	θ_1 in ang. deg.	θ_2 in ang. deg.	$d\theta_1$	$d\theta_2$	Corrected θ_1 in ang. deg.	Corrected θ_2 in ang. deg.
I	940	77.467	82.077	-0.0046	-0.0071	77.462	82.070
II	983	77.494	81.840	-0.0046	-0.0069	77.489	81.833

Table X

Refraction correction for the constants a and c (Cobalt radiation).

Sample		Lattice const. calculated with θ in kX	Lattice const. calculated with θ corrected in kX	Refraction correction in kX
I	a	5.13792	5.13805	+0.00013
	c	13.61726	13.61743	+0.00017
II	a	5.12852	5.12865	+0.00013
	c	13.64455	13.64474	+0.00019

Table XI

The corrected lattice a and c constants at temperatures of 20.0°C and 25.0°C.

20.0°C

Sample		Corrected lattice constant (in kX)	Corrected lattice constant (in Å)
I	a	5.1378 ± 0.0002	5.1482
	c	13.6072 ± 0.0005	13.6347
II	a	5.13005 ± 0.0006	5.1404
	c	13.63011 ± 0.0007	13.6576

25.0°C

Sample		Corrected lattice constant (in kX)	Corrected lattice constant (in Å)
I	a	5.1378 ± 0.0002	5.1482
	c	13.6087 ± 0.0005	13.6362
II	a	5.1298 ± 0.0006	5.1402
	c	13.6320 ± 0.0007	13.6595

Thus, the volume of a cell at a certain temperature can also be calculated using equation (16), and the two linear expansion coefficients αa and αc, from a and c obtained other temperatures.

$$V_t = \frac{3}{2} \left\{ \underline{a} (1 + \alpha at)^2 \, \underline{c} (1 + \alpha_c t) \right\}$$

$$V_t = \frac{3}{2} \underline{a}^2 \underline{c} \left\{ 1 + (2\alpha_a + \alpha_c) t + (\alpha_a^2 + 2\alpha_a \alpha_c) t^2 + \alpha_a^2 \alpha_c t^3 \right\} \quad (17)$$

The equation (17), in which the values of $(\alpha_a^2 + 2\alpha_a \alpha_c)t^2$ and $(\alpha a^2 \alpha c)t^3$ are very small and can be neglected, results in

$$V_t = \frac{3}{2} \underline{a}^2 \underline{c} \left\{ 1 + (2\alpha_a + \alpha_c)t \right\} = V\left\{ (1 + \beta t) \right\} \quad (18)$$

or $$\beta = 2\alpha_a + \alpha_c \quad (19)$$

where β is the thermal volume expansion coefficient of the hexagonal cell.

Using the linear expansion coefficients of Table VI, the volume expansion coefficients, β, of the two samples were calculated. (see Table XII).

Table XII

Volume at 20.0° and 25.0°C and the volume expansion coefficients of the hexagonal unit cell temperature region between 10 and 60°C

	Volume expansion coeff. (between 10 and 60°C)	$V_{25.0°C}$ (in A°^{3})	$V_{20.0°C}$ (in A°^{3})
Sample I	2.370×10^{-5}	312.993	312.956
Sample II	9.200×10^{-6}	312.537	312.523

5) Change of the axial ratio, c/a, of the hexagonal cell with temperature.

The axial ratio of the hexagonal cell obtained at several temperatures are summarized in Table XIII.

Table XIII

The axial ratio, c/a, of the hexagonal unit cell at several temperatures.

Temp. (in °C)	c/a (Sample I)	c/a (Sample II)
10.0	2.6478	2.6560
20.0	2.6484	2.6569
25.0	2.6487	2.6574
40.0	2.6497	2.6589
60.0	2.6509	2.6609

Figure 3 shows that the axial ratio of the hexagonal cell is related to the temperature by a straight line equation. The constants of the straight line equations were calculated by the least squares method. Then the thermal expansion coefficients, δ of the axial ratio were computed from these equations. (see Table XIV).

Table XIV

Thermal expansion coefficients of the axial ratio of the hexagonal unit cell, δ, temperature region between 10° and 60°C.

Sample	Straight line equation	Expansion coefficient δ between 10 and 60°C.
I	$\{c/a\}_t = 2.64873 + 0.0000624\ (t-25.0)$	2.356×10^{-5}
II	$\{c/a\}_t = 2.65744 + 0.0000983\ (t-25.0)$	3.699×10^{-5}

V. Determination of the lattice parameter and of the thermal expansion coefficients of the rhombohedral cell.

1) The a_{rh} constant and the linear expansion coefficient.

The rhombohedral a_{rh} constant can be computed from the hexagonal $\underline{a}$ and $\underline{c}$ constants as follows (13).

$$a_{rh} = \frac{1}{3} \sqrt{3\,\underline{a}^2 + \underline{c}^2} \tag{20}$$

Using the values of the lattice constants in Å as given in Table VII, the rhombohedral a_{rh} lattice constants were calculated from equation (20). (see Table XV).

Table XV

Rhombohedral a_{rh} constants at several temperatures.

Temp. (in °C)	Sample I, a_{rh} (in Å)	Sample II, a_{rh} (in Å)
10.0	5.42961	5.43359
20.0	5.43054	5.43448
25.0	5.43096	5.43493
40.0	5.43230	5.43628
60.0	5.43409	5.43808

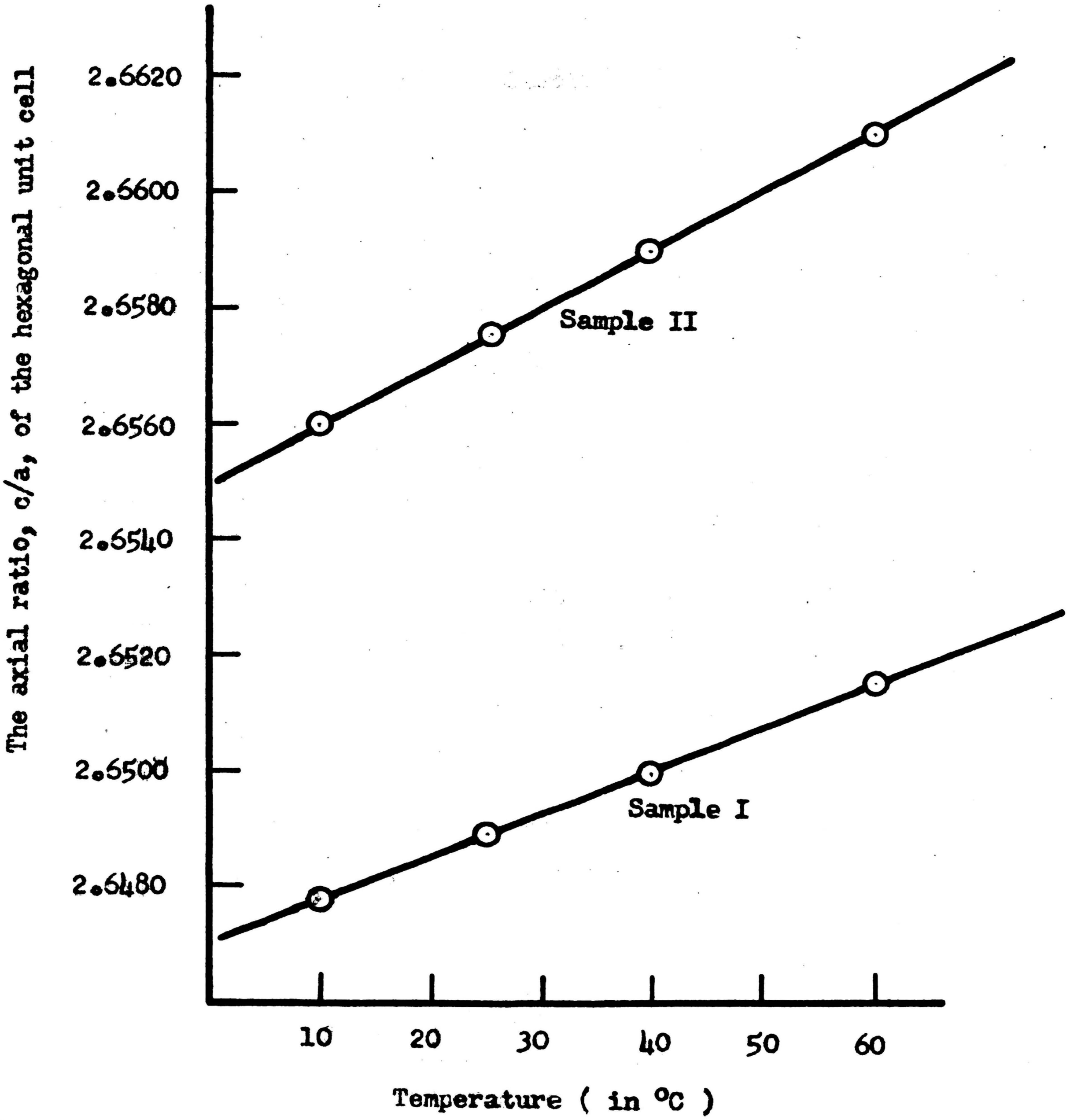

Fig. 3 The axial ratio, c/a, of the hexagonal unit cell versus temperature.

Figure 4 shows that the a_{rh} constant is related to temperature by a straight line equation. The constants of the straight line equations were calculated as mentioned previously. The linear expansion coefficients, α_{rh} are summarized in Table XVI.

Table XVI

Thermal linear expansion coefficient of the rhombohedral a_{rh} constant, α_{rh} between 10° and 60°C.

Sample	Straight line equation	Expansion coefficient α_{rh} between 10° and 60°C.
I	$a_{rh\,t} = 5.43096 + 8.934 \times 10^{-5}\,(t-25.0)$	1.6450×10^{-5}
II	$a_{rh\,t} = 5.43493 + 9.967 \times 10^{-5}\,(t-25.0)$	1.6499×10^{-5}

2) The interaxial α angle.

The rhombohedral interaxial angle α is derived from the followingrelation:

$$\sin \frac{\alpha}{2} = \frac{\underline{a}/2}{a_{rh}} \qquad (21)$$

Substituting for a_{rh} equation (20), equation (22) is obtained

$$\sin \frac{\alpha}{2} = \frac{3\,\underline{a}}{2\sqrt{3\,\underline{a}^2 + \underline{c}^2}} \qquad (22)$$

with which the interaxial α angle, was calculated. (see Table XVII).

Figure 5 shows that the change in the rhombohedral interaxial α angle is related to the temperature by a straight line equation.

The thermal interaxial angle expansion coefficient, γ , of the rhombohedral cell of the two samples was calculated from the straight line equation and is listed in Table XVIII.

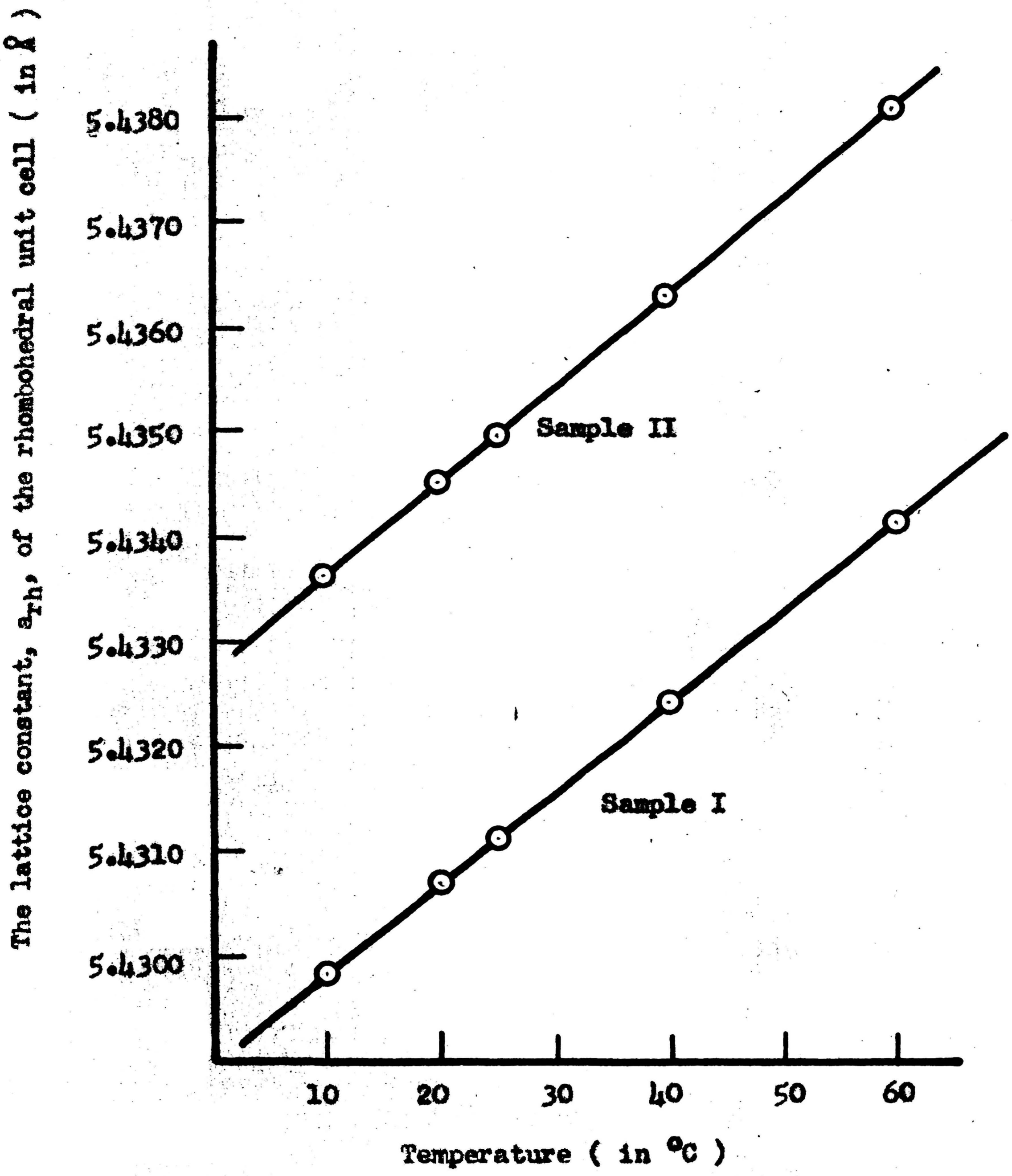

Fig. 4 The lattice constant, a_{rh}, of the rhombohedral unit cell versus temperature

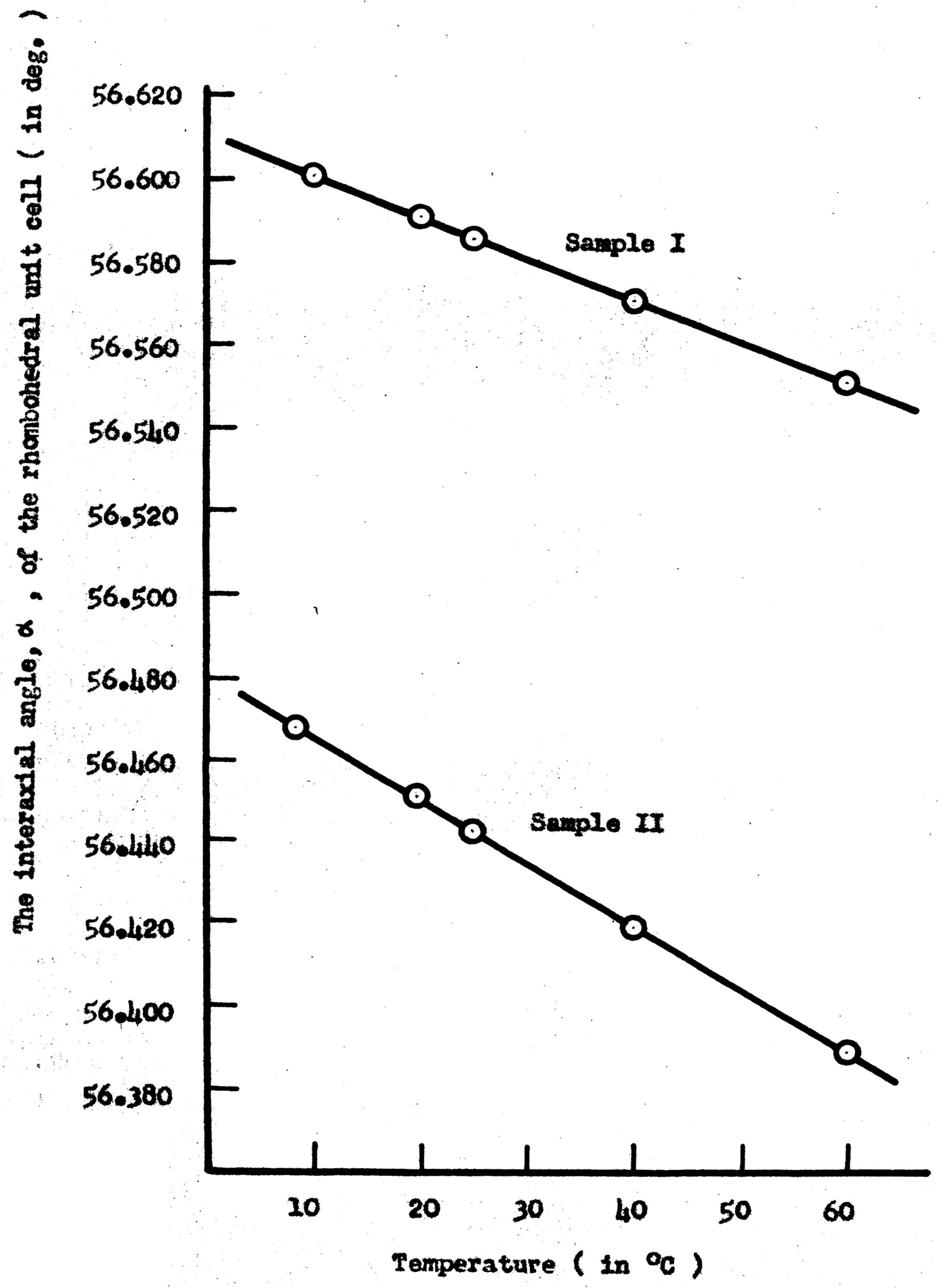

Fig. 5 The interaxial angle, α , of the rhombohedral unit cell versus temperature.

Table XVII

The interaxial α angle of the rhombohedral unit cell at several temperatures.

Temp. in °C	Sample I α (in ang. deg.)	Sample II α (in ang. deg.)
10.0	56.600	56.466
20.0	56.590	56.450
25.0	56.586	56.442
40.0	56.570	56.418
60.0	56.550	56.388

Table XVIII

Thermal interaxial angle expansion coefficient of the rhombohedral unit cell between 10° and 60°C.

Sample	Straight line equation (in ang. deg.)	Expansion coefficient (in $\frac{\text{ang. deg.}}{^\circ C}$) between 10° and 60°C.
I	$\alpha_t = 56.575 - 0.000996\ (t - 25.0)$	-1.761×10^{-5}
II	$\alpha_t = 56.442 - 0.00156\ (t - 25.0)$	-2.763×10^{-5}

3) Volume expansion coefficient of the rhombohedral cell.

The volume of the rhombohedral cell is expressed as follows:

$$V_{rh} = a_{rh}^3 \sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha} \qquad (23)$$

The calculated volumes of the rhombohedral cell of the two samples are summarized in Table XIX.

Figure 6 shows that the volume of the rhombohedral cell is related to the temperature by a straight line equation.

The constants of the straight line equations were calculated and are summarized in Table XX.

Thermal volume expansion coefficients were calculated from the obtained straight line equations and are summarized in Table XIX.

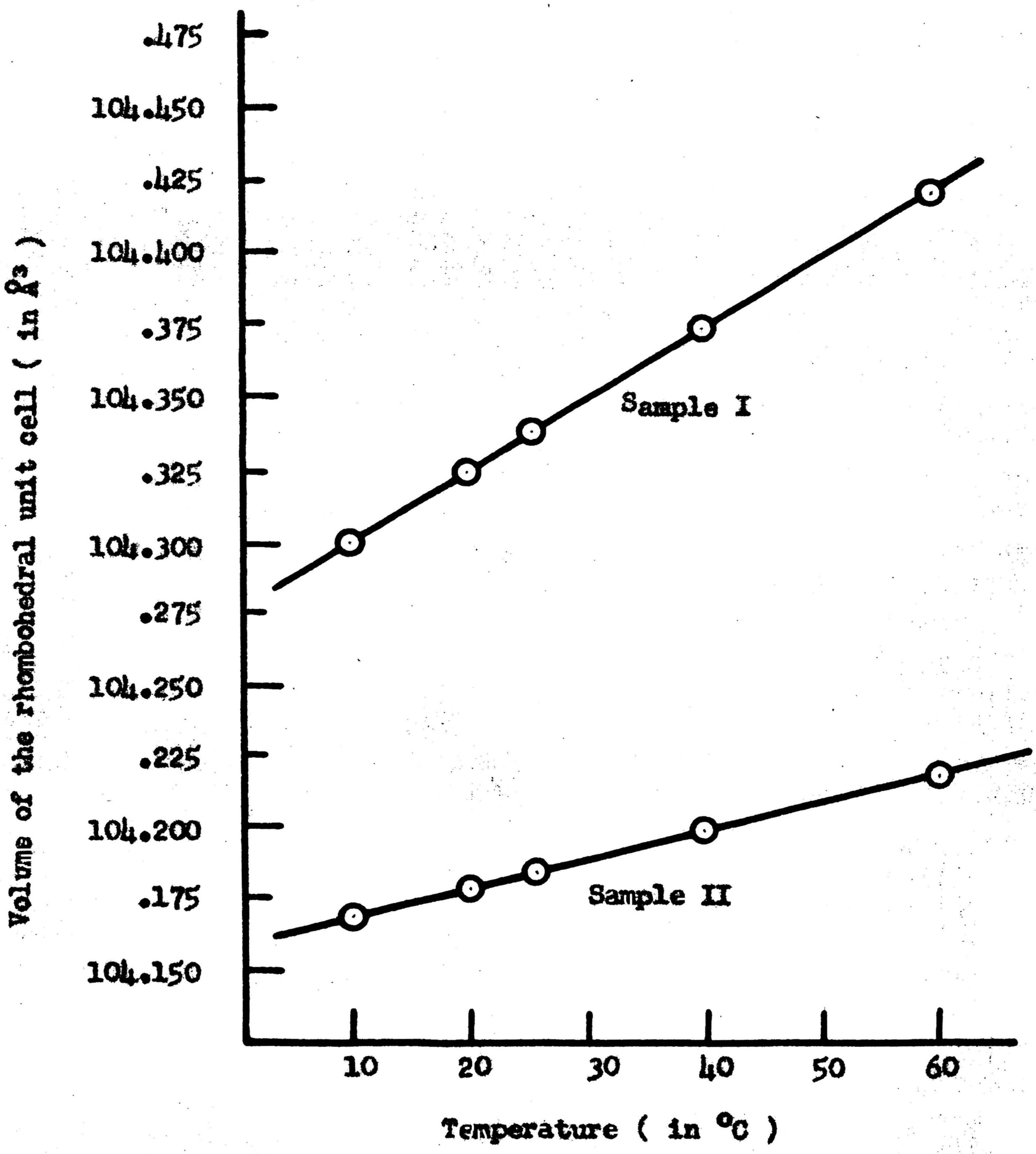

Fig. 6 Volume of the rhombohedral unit cell versus temperature.

Table XIX

The volumes of the rhombohedral unit cell of the two samples at several temperatures.

Temp. in °C	V_{rh} of sample I (in $Å^3$)	V_{rh} of sample II (in $Å^3$)
10.0	104.295	104.166
20.0	104.322	104.175
25.0	104.336	104.179
40.0	104.360	104.194
60.0	104.420	104.216

Table XX

Thermal volume expansion coefficients of the rhombohedral unit cell between 10° and 60°C, and the straight line equation.

Sample	Straight line equation	Volume expansion coefficient, β_{rh} between 10° and 60°C
I	$104.33208 + 0.00242\,(t-25.0)$	2.320×10^{-5}
II	$104.16023 + 0.00096\,(t - 25.0)$	9.216×10^{-6}

VI. Density of Samples I and II.

The density was computed by equation (24) derived from that of Baker and Martin:

$$d_s^t = (d_e - d_g)\,\frac{(b - c)}{(b - c) - (a - z)} + d_g \qquad (24)$$

where, d_s^t = density of the sample at temperature t°C

d_l = density of the liquid medium at temperature t°C

d_g = density of air at temperature t°C and pressure of the balance room

b = weight of the cup, the platinum wire and the sample in air

c = weight of the cup and platinum wire in air

z = weight of the cup and platinum wire immersed in the benzene at temperature t°C.

a = weight of the cup, platinum wire and the sample in the benzene at temperature t° C.

The density of the sample at any other temperature was calculated by the following equation:

$$d_s^{t_1} = d_s^{t_2} \left\{ 1 + \beta (t_2 - t_1) \right\} \qquad (25)$$

The method reported here is theoretically sound. It seems to be an accurate and convenient method for determination of the density of solids. Further refinements for closer control of experimental conditions are possible, such as the provision of a means for maintaining a constant level of the liquid medium evaporating in the cabinet of the analytical balance. The densities obtained with samples I and II are listed in Tables XXI and XXII.

Table XXI

Determination of the density of the sample I.

Run No.	I	II	III	IV
Experimental (mm Hg.)	730.9	733.2	731.7	740.1
conditions (°C)	25.0	25.0	24.7	23.0
Density of benzene at experimental conditions (g/cm^3)	0.873402	0.873402	0.87383	0.87544
Density of air at experimental conditions (g/cm^3)	0.001138	0.001138	0.001139	0.001161
Weight of the cup in air (with Pt wire)(g)	6.6324	6.6325	6.0302	6.6326
Weight of the cup in benzene (with Pt wire) (g)	4.1536	4.1521	3.7822	4.1499
Weight of the cup with sample in benzene (with Pt wire) (g)	4.3059	4.2910	3.9348	4.3387
Weight of the cup with sample in air (with Pt wire) (g)	6.8204	6.8039	6.2186	6.8658
Density reduced to 25°C (g/cm^3)(eq.25)	4.5945	4.6013	4.5996	4.5998
Average density at 25°C for I to IV (g/cm^3)		4.5988		
Deviation dd_s	-0.0043	+0.0025	+0.0008	+0.0010
$\{dd_s\}^2$	1849×10^{-8}	625×10^{-8}	64×10^{-8}	100×10^{-8}
Most probable error		± 0.002		
Density of the sample I at 25°C (calculated with equation (25). (in g/cm^3)		4.5988 ± 0.0020		
Density of the sample I at 20°C (calculated with equation (25). (in g/cm^3)		4.5993 ± 0.002		

Table XXII

Determination of the density of the sample II.

Run No.	I	II	III	IV
Experimental (mm Hg) conditions (°C)	731.2 24.3	730.9 26.0	731.9 23.5	740.0 22.8
Density of benzene at experimental conditions (g/cm^3)	0.87415	0.872332	0.875006	0.87575
Density of air at experimental conditions (g/cm3)	0.001142	0.001134	0.001143	0.001161
Weight of the cup in air (with Pt wire) (g)	6.6328	6.0298	6.6323	6.0286
Weight of the cup in benzene (with Pt wire) (g)	4.1511	3.7836	4.1486	3.7818
Weight of the cup with sample in benzene (with Pt wire) (g)	4.5373	4.0689	4.5890	4.3083
Weight of the cup with sample in air (with Pt wire) (g)	7.1092	6.3815	7.1759	6.6785
Density reduced to 25°C. (eq. 25)(g/cm3)	4.16139	4.6155	4.6102_5	4.6138
Average density at 25°C for I to IV (g/cm3)		4.61336		
Deviation dd_s	+0.00054	+0.00214	-0.00311	+0.00044
$\{dd_s\}^2$	2916×10^{-10}	45796×10^{-10}	96721×10^{-10}	1936×10^{-10}
Most probable error		+0.0015		
Density of the sample II at 25.0°C (calculated with equation (25) (in g/cm^3)		4.6134 ± 0.0015		
Density of the sample II at 20.0°C (calculated with equation (25) (in g/cm^3)		4.6136 ± 0.0015		

CHAPTER V

DISCUSSION

I. Remarks on error elimination.

The powder method is connected with various sources of error. All conditions which cause a deviation of diffraction lines from the positions determined by Bragg's law are referred to as the sources of error. Therefore, if the work is not proper, errors may be introduced into parameter determinations through numerous possibilities. These possibilities may conveniently be classified according to the stage of their occurrence in the process.

1) Errors may be caused during the production of the diffraction by:

- a) Absorption of x-rays by the specimen
- b) Eccentricity of the specimen with respect to the axis of the film cylinder.
- c) Form of the specimen
- d) Deviation of cross-section of camera from a perfect circle
- e) Direction of primary beam not being perpendicular to the specimen
- f) Inexact knowledge of the temperature of the substance
- g) Use of improper x-radiation

2) Errors may be involved before and while measuring and evaluating the diffraction pattern by:

- a) Film shrinkage and non-uniform shrinkage of films after development
- b) Change of the length of film during the time of measurement
- c) Inexact determination of the equatorial line of the powder pattern.

- d) Inexact determination of the peak-intensity position of diffraction spectra
- e) Inaccurate measurements

3) Finally errors may be caused by crystaloptical factors:

- a) Refractive index of the crystal for x-rays
- b) Divergence of x-rays after diffraction
- c) Condition of diffraction spectra

The errors mentioned are eliminated by the present technique as follows:

1.a. Absorption displaces diffraction lines in the direction of larger θ; making the parameter appear smaller. This effect can be largely eliminated making the powder mount thin and transparent to x-rays.

Even heavy metals like tungsten cause only a very slight line displacement if the sample is thin.

1.b. The modus of construction of the camera used does not allow any appreciable eccentricity of the specimen with respect to the camera axis.

1.c. The effect of the form of specimen is least if its cross section is circular. Round specimens were therefore employed.

1.d. Cameras with perfect cylindrical internal surfaces can easily be secured by the present technique of metal machining. The films are pressed tightly against the camera wall so that a noticeable error is excluded.

1.e. If the primary x-ray beam makes an angle γ with the specimen, the diffraction spectra do not disperse symmetrically with respect to the equatorial line of the pattern. However, this error is negligible, and is avoided by the contraction of the camera.

1.f. Temperature fluctuations affect the magnitude of the lattice parameter. To exclude this source of error the experiments were performed at constent temperatures.

1.g. It is necessary to have diffraction lines with θ angles in the range of 78° to 87° in order to carry out precise lattice parameter determinations.

Interplanar spacings of crystals as calculated from x-ray diffraction lines vary with the position of the lines on the film. These spacings are determined by Bragg's equation:

$$1/d = (\quad 2/\lambda n) \sin \theta$$

It is evident that if measurements of reflections are made whose θ angles fall in the vicinity of 90°, the d's of the planes corresponding to these reflections, because of the sin function, can be determined with much greater reproducibility than those whose θ's occur at lower angles. For this reason, lattice constants based upon measurements of reflections in the region θ approaching 90° are very precise. Under equal conditions, they are more precise, then are the other θ's at lower angles.

2.a. and b. Although localized changes of length of films are possible, this condition exercises a very small effect on the results, if the films are treated carefully.

2.c. If worked as follows, no appreciable errors in the determination of the equatorial line of the powder pattern can occur. The film is first placed on the carriage of the comparator so that the cross-hair of the microscope runs through the center of the film, and then gradually adjusted until the cross-hair of the objective coincides with the vertexes of all Debye-rings on the film. Thus, finally the cross-hair of the objective is in perfect alignment with the equatorial line of the powder pattern.

2.d. The comparator used allows determination of peak intensities of sharp lines with an accuracy as high as 0.005 mm. Here the accuracy depends on the sharpness, intensity, and uniformity of lines: and these, in turn, on x-ray optical factors and properties of the powder, such as particle size, mosaic structure, etc. Differences in peak intensity and gravity center of the lines were disregarded.

2.e. During measurements, the carriage of the comparator must be moved in one direction only. Since it was necessary to take a number of readings of the same line, the carriage was moved a little back and then advanced again to the peak intensity of the line to make the reading.

3.a. From a measured glancing angle θ, not the actual lattice constant but a slightly smaller value is obtained, due to the deviation from Bragg's law. These deviations are greater, the lower the order of diffraction. The corrected Bragg's equation, as derived by Ewald, is as follows:

$$n\lambda = 2d\left(1 - 5.40\,\rho\,\frac{d^2}{n^2}\,10^{-6}\right)\sin\theta \qquad (26)$$

n = order of diffraction

d = the lattice spacing

ρ = density of the crystal

This formula is valid only for the symmetrical reflection. In spite of the well established formula and theories, the magnitude of the symmetrical reflection correction is still uncertain in their application to various crystals, especially in powder patterns (24, 29).

3.b. The divergence of the x-ray beam does not actually lead to errors but causes complications in the errors arising from other sources.

The divergence of the x-ray beam gives rise to a distortion of the size of the x-ray reflection which reaches the film. The arrangement of the collimeter system minimizes the effect of divergence of x-rays, if the aperture of the pinhole is of the order of 0.8 mm (8).

3.c. Favorable conditions of breadth, intensity, and uniformity of the last lines facilitate the achievement of greater accuracy.

II. Determination of the molecular weight and x-ray density of Ti_2O_3-Ti solid solutions.

Information concerning the soundness of the crystal lattice can be obtained computing either the x-ray density, d_x, or the molecular weight, M_x, and comparing them with the macroscopic values. The formula for computation, if Siegbahn's wavelengths (in X. U. or in kX) are used, is:

$$M_x = k.N_s \cdot v \cdot d/n \qquad \text{(g/mole)} \qquad (27)$$

N_s being Siegbahn's Avogadro number (6.0594×10^{23}).

v = volume of the unit cell in $kX^3 \times 10^{-24}$

d = density in gram per cubic centimeter

n = number of molecules per unit cell

k = correction factor which eliminates the errors that were made determinating N_s and wavelengths.

The necessity of such a factor (1.00020 ± 0.00003) for exact molecular weight calculations was emphasized by Straumanis in 1944. However, if the wavelengths are expressed in Å units, the equations for M_x and d_x are:

$$M_x = N_o\, v'\ \ d/n \qquad (28)$$

$$d_x = n\, M/\, N_o\, v' \qquad (29)$$

where, v' is the volume of the unit cell in $(\text{Å})^3 \times 10^{-24}$, and N_o is the absolute Avogadro's number = 6.02403×10^{23} mole^{-1} (chemical scale). **The values**

for v and d should **be obtained at the same temperature.**

Concerning n, the number of molecules in the unit cell of Ti_2O_3, which belongs to the corumdum type, and has, according to Bragg (52), twelve molecules in the hexagonal unit cell, or two molecules in the rhombohedral unit cell, evidently corresponding to the crystallographic ratio a:c = 1:1.365. When the ratio is 1:2.73, as it also was found in this investigation, there are six molecules in the hexagonal unit cell and two molecules in the rhombohedral unit cell, according to Shearer's rule.

The x-ray densities of Ti_2O_3-Ti solid solutions at 20° and 25°C were calculated by equation (29), using the following data:

number of molecules in the hexagonal unit cell	$n = 6.0000$
molecular weight of Ti_2O_3	$M = 143.80$
Avogadro number	$N_o = 6.02403 \times 10^{23}$
Volume of the hexagonal unit cell, **v', of the** samples at 20°C and 25°C	v' = see Table XII

The results are summarized in Table XXIII and correspond with the macroscopic densities at 20° and 25°C.

Also, the x-ray molecular weights of Ti_2O_3 solid solutions were calculated by the equation (28).

The relative error by which the density and the molecular weights were affected, was estimated as follows:

The x-ray molecular weight M_x of a hexagonal unit cell, using equation (27) reduces to:

$$M_x = \frac{k\ N_s\ v\ d}{n} = \frac{N_s}{n}\left[k \cdot v \cdot d\right] = \frac{N_s}{n}\left[\frac{3}{2}\,a^2\,c \cdot d \cdot k\right] =$$

$$\text{const}\ (a^2\ c\ d\ k) \qquad (30)$$

$$\ln M_x = \ln \text{const} + 2 \ln \underline{a} + \ln \underline{c} + \ln d + \ln k \qquad (31)$$

$$d \ln M_x = d \ln \text{const.} + d(2 \ln \underline{a}) + d \ln \underline{c} + \ln k \qquad (32)$$

$$\frac{d\ M_x}{M_x} = \frac{2d\underline{a}}{\underline{a}} + \frac{d\underline{c}}{\underline{c}} + \frac{dd_s}{ds} + \frac{dk}{k} \qquad (33)$$

The final error, due to the propagation of errors, is:

$$\frac{\Delta M_x}{M_x} = \pm\left[\left(\frac{2d\underline{a}}{\underline{a}} \times f_1\right)^2 + \left(\frac{d\underline{c}}{\underline{c}} \times f_2\right)^2 + \left(\frac{dd_s}{ds} \times f_3\right)^2 + \left(\frac{dK}{K} \times f_4\right)^2\right]^{1/2} \qquad (34)$$

where $d\underline{a}$, $d\underline{c}$, dds, dK, are the standard deviations of the separate measurements, $\frac{d\underline{a}}{\underline{a}}$, $\frac{d\underline{c}}{\underline{c}}$, the relative errors, and f_1, f_2, the safety factors, each of them $\gg 1$.

The necessity of these factors follows from a consideration that relative errors are accidental or random errors: they reflect the quality of the measurements, but they do not contain the systematic error, which is undoubtedly in any measurement, and which may be even several times as large as the accidental error.

It is the task of the investigator to estimate the value of the factor, f, for each kind of measurement, so that the systematic error becomes included in the deviation.

It was assumed in the case of molecular weight determinations that

$$f_1 = f_2 = f_3 = f_4 = 2 \qquad (35)$$

would take care of systematic errors.

Assuming that

	For Sample I	For Sample II
$\frac{d\underline{a}}{\underline{a}} =$	4.67×10^{-5}	11.7×10^{-5}
$\frac{d\underline{c}}{\underline{c}} =$	3.99×10^{-5}	5.30×10^{-5}
$\frac{dd_s}{ds} =$	43.5×10^{-5}	32.6×10^{-5}
$\frac{dK}{K} =$	3.00×10^{-5}	3.00×10^{-5}

equations as follows were obtained from equation (34) for the total error (ΔM_x) of the molecular weight for both samples:

for sample I $\quad \Delta M_x = 8.95 \times 10^{-4} \times M \quad$ (36)

for sample II $\quad \Delta M_x = 8.11 \times 10^{-4} \times M \quad$ (37)

The deviation, ΔM_x, may be called "Standard Absolute Deviation", for which with the data of x-ray molecular weights of Table XXIV, it was obtained

	ΔM_x	M_x
for sample I	± 0.129	144.52 ± 0.13
for sample II	± 0.117	144.77 ± 0.12

For the x-ray density and for the number of molecules in the unit cell the same calculations were done and it was obtained for the Standard Absolute Deviation, Δdx, and $\Delta n'$.

	Δd_x	d_x
for sample I	± 0.07	4.5760 ± 0.07
for sample II	± 0.11	4.5825 ± 0.11

	$\Delta n'$	n'
for sample I	± 0.0055	6.126 ± 0.0055
for sample II	± 0.0053	6.484 ± 0.0053

The chemical molecular weights of Ti_2O_3-Ti solid solutions, **calculated** from the results of the chemical analysis, are as follows:

for sample I	141.54
for sample II	133.95

Figure 7 shows the variation of the x-ray and the chemical (macroscopic) molecular weight with free Ti content in the solid solution.

The extrapolated chemical molecular weight for pure Ti_2O_3 was calculated from the straight line equation, and it was found to be 143.65 which agrees with the value from atomic weights 143.80 within 0.1%. It follows from the Tables XXIII and XXIV that the macroscopic densities

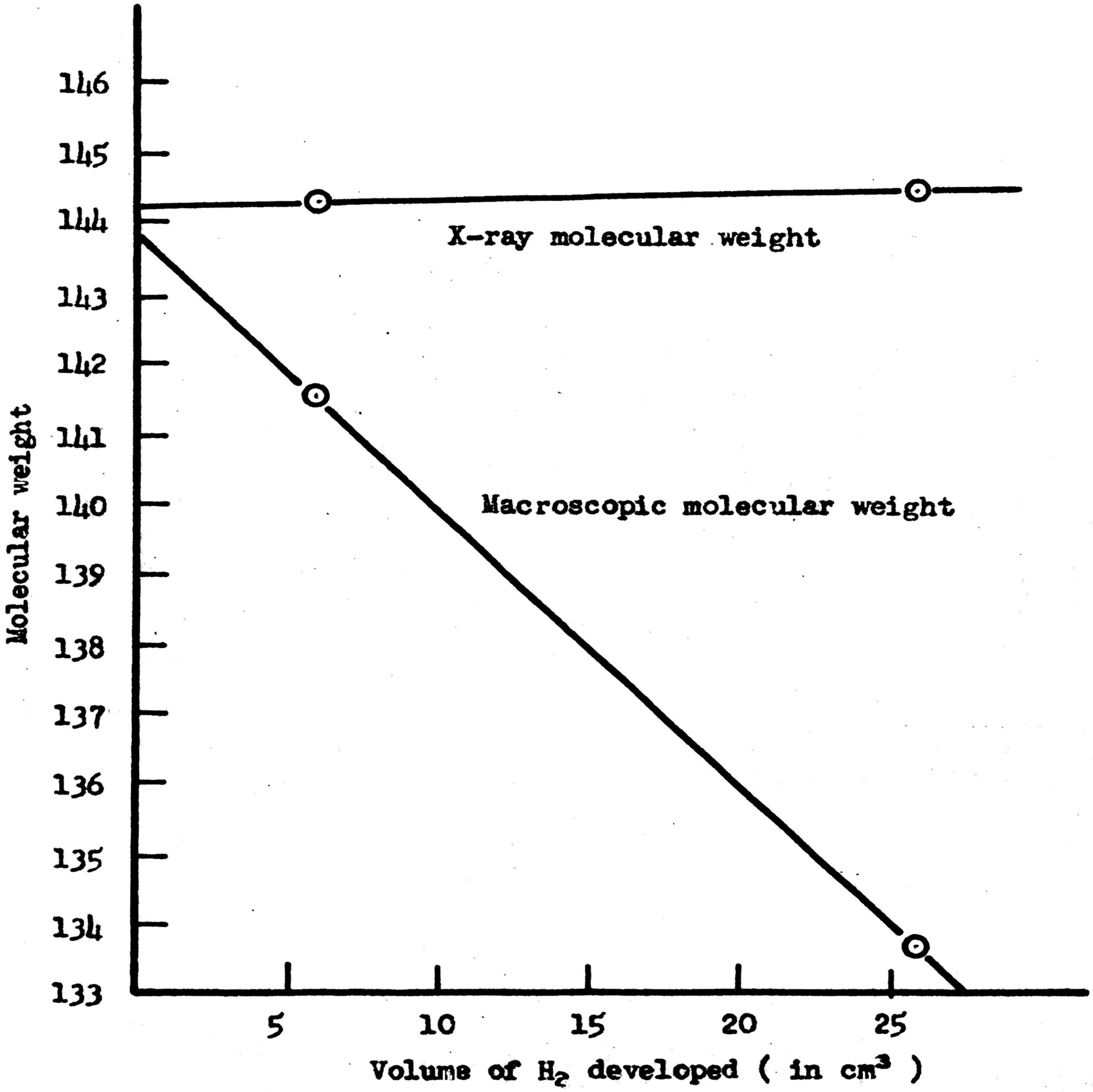

Fig. 7 The relation between molecular weight (x-ray and macroscopic) and free titanium content in Ti_2O_3-Ti solid solution

Table XXIII

X-ray densities and macroscopic densities of Ti_2O_3-Ti solid solutions at temperature 20.0° and 25.0°C.

	X-ray density		Macroscopic density	
Temperature	20.0°C	25.0°C	20.0°C	25.0°C
Sample I	4.5766	4.5760	4.5993	4.5988
Sample II	4.5827	4.5825	4.6136	4.6134
	extrapolated values			
Pure Ti_2O_3	4.5749	4.5742	4.5953	4.5948
References:	W. H. Zachariasen$^{(3)}$	4.58	W. H. Zachariasen	4.6014 (25°C)
	G. Lunde$^{(2)}$	4.605	P. Ehrlich$^{(1)}$	4.486
			C. H. Shomate$^{(53)}$	4.56
			C. Friedel$^{(54)}$	4.601 (10°C)

Table XXIV

Molecular weight of Ti_2O_3 and of solid solutions.

Sample	Volume of developed H_2 in ml	Free Ti content in %	X-ray molecular wgt. (M_x)	Chemical (macroscopic) molecular weight (M)	Difference (M_x-M)
I	5.6	0.8	144.52 + 0.13	141.54	+ 2.98
II	25.8	3.67	144.76 ∓ 0.12	133.95	+ 10.82
Pure Ti_2O_3	0.00	0.00	144.45 ±	143.65	0.80

	Difference	Difference in %
Difference between the chemical macroscopic molecular weight of Pure Ti_2O_3 and the extrapolated chemical (macroscopic) molecular weight.	0.15	0.103%

Table XXV

Variation of the number of molecules in the hexagonal unit cell of Ti_2O_3 and of solid solutions with free Ti content.

				References	
Sample	I	II	Pure Ti_2O_3	Zachariasen	Ehrlich
Volume of developed H_2 in ml.	5.6	25.8	0.00		
Free Ti content in %	0.8	3.67	0.00		
Volume of hexagonal unit cell (in Å^3) at 25°C	312.99314	312.53701	Extrapolated value 313.11959	313.30	313.35
Macroscopic density at 25°C	4.5988	4.6134	Extrapolated value 4.5948	4.6014	4.486
Chemical (macroscopic) molecular (at 25°C) weight	141.54	133.95	143.80	143.80	143.80
Number of molecules in the unit cell	n' 6.12615	n' 6.48436	6.02684 theoretical value 6.00000	n' 6.03909	n' 5.88871
Number of interstitials for one hexagonal unit cell	0.126	0.484	0.027	0.039	-0.111

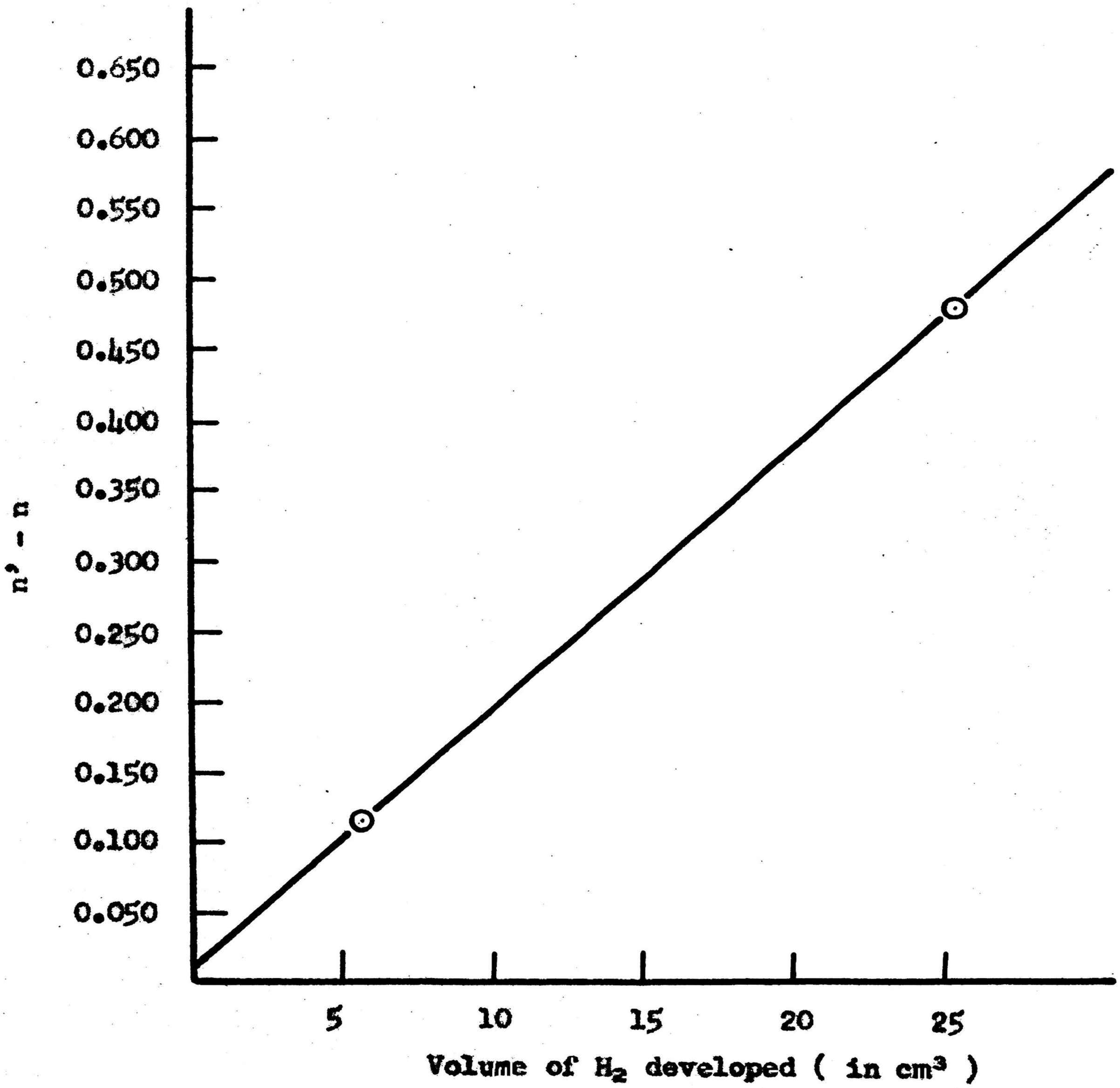

Fig. 8 Variation of the number of interstitials in the hexagonal unit cell with increasing free titanium content in the Ti_2C_3-Ti solid solution

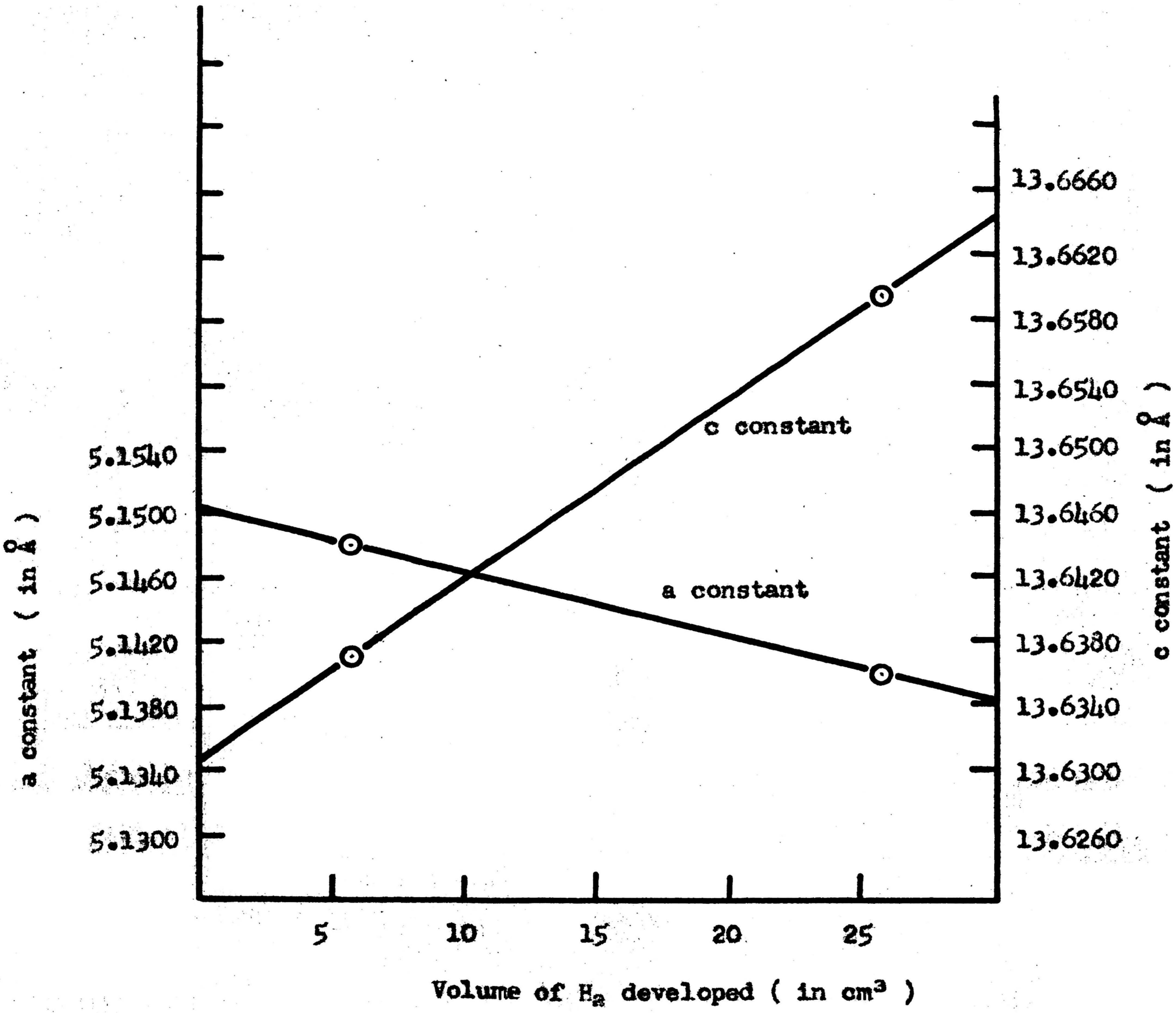

Fig. 9 The hexagonal a and c constants versus free titanium content in Ti_2O_3-Ti solid solution at 25°C.

Table XXVI

Lattice constants (extrapolated) of the hexagonal unit cell of pure Ti_2O_3 at temperatures 20.0°C and 25.0°C.

Sample	Volume of developed H_2 in ml	Free Ti content in %	The hexagonal *a* lattice constant (in Å)	The hexagonal *c* lattice constant (in Å)
Temperature 20.0°C				
I	5.6	0.8	5.1482	13.6347
II	25.8	3.67	5.1404	13.6576
			(Extrapolated value)	(Extrapolated value)
Pure Ti_2O_3	0.00	0.00	5.1504	13.6284
Temperature 25.0°C				
I	5.6	0.8	5.1482	13.6362
II	25.8	3.67	5.1402	13.6595
			(Extrapolated value)	(Extrapolated value)
Pure Ti_2O_3	0.00	0.00	5.1505	13.6297
References:	P. Ehrlich		5.141 (Å)	13.61 (Å)
	W. H. Zachariasen		5.15 (Å)	13.56 (Å)

Table XXVII

Lattice constant (extrapolated) of the rhombohedral unit cell of pure Ti_2O_3 at temperature 20.0°C and 25.0°C.

Temperature 20.0°C

Sample	Volume of H_2 developed in ml	Free Ti content in %	The rhombohedral lattice constant, a_{rho} (in Å)	Calculated by eq. (20) using the hexagonal extra-polated lattice constants (a_{hex} and c_{hex}) (in Å)
I	5.6	0.8	5.43054	
II	25.8	3.67	5.43448	
			(Extrapolated value)	
Pure Ti_2O_3	0.00	0.00	5.42945	5.42948
Temperature 25.0°C				
I	5.6	0.8	5.43096	
II	25.8	3.67	5.43493	
			(Extrapolated value)	
Pure Ti_2O_3	0.00	0.00	5.42991	5.42984

References:		
	G. Lunde	(5.42 Å)
	W. H. Zachariasen	(5.42 Å)
	P. Ehrlich	(5.421 Å)

Table XXVIII

Interaxial α angle (extrapolated) of the rhombohedral unit cell of pure Ti_2O_3 at temperature 20.0°C and 25.0°C.

Temperature 20.0°C

Sample	Volume of H_2 developed in ml	Free Ti content in %	Interaxial angle of the rhombohedral cell in ang. deg.	Calculated by equation (22) using the hexagonal extrapolated lattice constants (a_{hex} and c_{hex}) in ang. deg.
I	5.6	0.8	56.590	
II	25.8	3.67	56.450	
			(Extrapolated value)	
Pure Ti_2O_3	0.00	0.00	56.629	56.628

Temperature 25.0°C

Sample	Volume of H_2 developed in ml	Free Ti content in %	Interaxial angle of the rhombohedral cell in ang. deg.	Calculated by equation (22) using the hexagonal extrapolated lattice constants (a_{hex} and c_{hex}) in ang. deg.
I	5.6	0.8	56.586	
II	25.8	3.67	56.442	
			(Extrapolated value)	
Pure Ti_2O_3	0.00	0.00	56.626	56.624
References:	G. Lunde		56.533	
	W. H. Zachariasen		56.833	

CHAPTER VI

SUMMARY

The conclusions derived from the results of the present investigation are summarized as follows:

1) The lattice parameters of the hexagonal cell at 25°C (in Å) are:

For sample I	$\underline{a} = 5.1482$	$\underline{c} = 13.6362$
for sample II	$\underline{a} = 5.1402$	$\underline{c} = 13.6595$

2) The axial ratio, c/a, at 25°C is

for sample I	2.6487
for sample II	2.6574

3) The lattice parameter of the rhombohedral cell at 25°C, a_{rh} (in Å) is

for sample I	5.4305
for sample II	5.4349

4) The interaxial α angle of the rhombohedral cell at 25°C (in deg.) is

for sample I	56.584
for sample II	56.442

The various thermal linear expansion coefficients of samples I and II were determined as follows:

1) The linear expansion coefficient, α_a, for the hexagonal constant in (Å/°C) is

for sample I	1.668×10^{-7}
for sample II	-9.080×10^{-6}

2) The linear expansion coefficient, α_c, for the hexagonal constant in (Å/°C) is

for sample I	2.337×10^{-5}
for sample II	2.736×10^{-5}

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for sample II	5.4349

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for sample I	1.668×10^{-7}
for sample II	-9.080×10^{-6}

2) The linear expansion coefficient, α_c, for the hexagonal constant in (Å/°C) is

for sample I	2.337×10^{-5}
for sample II	2.736×10^{-5}

3) The change in the axial ratio, δ in (1/°C) is:

for sample I 2.356×10^{-5}

for sample II 3.699×10^{-5}

4) The linear expansion coefficient, α_{rh}, for the rhombohedral cell in (Å/°C) is

for sample I 1.6450×10^{-5}

for sample II 1.6499×10^{-5}

5) The volume expansion coefficient β for the hexagonal cell in (Å^3/°C) is

for sample I 2.370×10^{-5}

for sample II 9.200×10^{-5}

6) The volume expansion coefficient, β_{rh}, for the rhombohedral cell in (Å^3/°C) is

for sample I 2.320×10^{-5}

for sample II 9.216×10^{-6}

7) The angle expansion coefficient Γ, for the rhombohedral interaxial angle in $(\frac{\text{deg}}{°\text{C}})$ is

for sample I -1.820×10^{-5}

for sample II -2.763×10^{-5}

Although there are no data available in the literature concerning the thermal expansion coefficients of Ti_2O_3, the values reported here are reliable, as shown by the error calculations.

The thermal linear expansion coefficient, α_a, of the hexagonal a constant of Ti_2O_3-Ti solid solution was very small and changed very little in the temperature range from 10° to 60°C.

However, the hexagonal c constant increased remarkably with temperature, exhibiting a much larger thermal expansion coefficient.

Concerning the thermal linear expansion coefficient and the composition of the oxide: that of the hexagonal a constant decreases with increasing free Ti content (contraction of a with increasing free titanium content), while the coefficient of the hexagonal c constant increased with increasing free titanium content (increase of the hexagonal c constant).

The volume of the hexagonal unit cell of Ti_2O_3-Ti solid solution increased with increasing free titanium content, and also the volume expansion coefficient increased.

The axial ratio, c/a, being around 2.65, increased with temperature and also increased with increasing free titanium content in the solid solution.

The a_{rh} constant increased with increasing free titanium content in the solid solution. The thermal linear expansion coefficient of a_{rh} constant increased also slightly.

The interaxial angle of the rhombohedral unit cell of Ti_2O_3-Ti solid solution, as well as its angle expansion coefficient, decreased with increasing free titanium content.

The x-ray density of pure Ti_2O_3 calculated from equation (29) using the extrapolated volume of the hexagonal unit cell of pure Ti_2O_3 at 25°C was 4.574. This compared favorably with 4.58 obtained by Zachariasen.

The experimental (macroscopic) density of pure Ti_2O_3 was 4.594. The value obtained was always higher than the x-ray density, indicating the presence of interstitials in the solid solutions.

From the diagram of n'-n (the number of interstitial molecules in the solid solution) versus free titanium content (by chemical analysis), the degree of imperfection of pure Ti_2O_3 could be calculated. The pure oxide also contains some interstitial (probably Ti) atoms.

The hexagonal and the rhombohedral lattice constants for pure Ti_2O_3 were obtained by linear extrapolation of the constants of the solid solutions at 25°C to the free titanium content = zero.

$\underline{a} = 5.1505 \pm 0.0006$ (Å)

$\underline{c} = 13.6297 \pm 0.00071$ (Å)

$a_{rh} = 5.4295 \pm 0.0006$ (Å)

$\alpha = 56.626$ (in deg.) $\pm$ 0.001

The obtained constants for the hexagonal and the rhombohedral unit cell of pure Ti_2O_3 are more reliable than those in the literature, because it is not certain whether the previous investigators had a compound of a composition corresponding exactly to the formula Ti_2O_3.

APPENDIX

A. Accuracy of the thermometers used in the experiments.

Accuracy of the thermometers used in the X-ray thermostat, and in the analytical balance were within 0.1°C. The thermometers were calibrated by comparison with the normal thermometer.

B. Wave length of X-ray used in the experiments.

Target	Radiation	Wave length
Co	β	1.61744
	α_1	1.78529
	α_2	1.78919

C. Film measurements.

The individual line readings and lattice constant calculations from all films measured during experiments are recorded below.

1. Sample I (Ti 66.1%, O_2 33.9%, H_2 developed 5.6 cm^3).

Co-radiation is selected and used for production of powder pattern at all temperatures. Only three sets of lines in the front reflection region, namely (104), (110) and (116), and (1 3 10) and (3 0 12) in the back reflection region are measured, and the lattice constants are calculated from the last two lines, (1 3 10) and (3 0 12).

Film No. 937 Temp. 60°C Exp. 1.5 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	62.702 31.781	68.672 25.810	69.835 24.643	160.584 132.583	155.504 137.910
Sum (in mm)	94.483	94.482	94.478	293.437	293.414
Average (in mm)		94.481		293.426	
Circumference (in mm)	198.945				
Factor	0.452386				
θ (in deg).				77.4549	82.0407

Lattice constant a = 5.13762 kX c = 13.61982 kX

Film No. 938 Temp. 60°C Exp. 1.5 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	70.364 39.425	76.330 33.458	77.505 32.281	168.313 140.570	163.266 145.630
Sum (in mm)	109.789	109.788	109.786	308.883	308.896
Average (in mm)		109.788		308.889	
Circumference (in mm)	199.101				
Factor	0.452031				
θ (in deg.)				77.4593	82.0280

Lattice constant a = 5.13693kX c = 13.62136 kX

Film No. 939 Temp. 50°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	68.893 37.955	74.865 31.983	76.037 30.800	166.896 139.198	161.809 144.277
Sum (in mm)	106.848	106.848	106.837	306.094	306.086
Average (in mm)		106.844		s06.090	
Circumference (in mm)	199.246				
Factor	0.451702				
θ (in deg.)				77.4888	82.0808

Lattice constant a = 5.13648kX c = 13.61924 kX

Film No. 940 Temp. 50°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	62.712	68.681	69.856	160.645	155.541
	31.765	25.795	24.612	132.910	138.018
Sum (in mm)	94.477	94.476	94.468	293.555	293.559
Average (in mm)		94.474		293.557	
Circumference (in mm)	199.083				
Factor	0.452072				
θ (in deg.)				77.4618	82.0783
Lattice constant	a = 5.13829kX		c = 13.61667 kX		

Film No. 941 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.686	71.659	72.832	163.595	158.503
	34.718	28.721	27.554	135.996	141.089
Sum (in mm)	100.399	100.380	100.386	299.591	299.592
Average (in mm)		100.388		299.592	
Circumference (in mm)	199.204				
Factor	0.451798				
θ (in deg.)				77.5308	82.1325
Lattice constant	a = 5.13516kX		c = 13.61865kX		

Film No. 942 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	64.323	70.341	72.479	162.373	157.245
	33.310	27.296	25.139	134.700	139.823
Sum (in mm)	97.633	97.637	97.618	297.073	297.068
Average (in mm)		97.629		297.071	
Circumference (in mm)	199.442				
Factor	0.451259				
θ (in deg.)				77.5123	82.1382
Lattice constant	a = 5.13667 kX		c = 13.616001 kX		

Film No. 950 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	71.821	77.839	79.022	170.016	164.795
	40.689	34.667	33.486	142.341	147.546
Sum (in mm)	112.510	112.506	112.508	312.357	312.341
Average (in mm)		112.508		312.349	
Circumference (in mm)	199.481				
Factor	0.450358				
			θ (in deg.)	77.536	82.232
Lattice constant	a = 5.13796 kX		c = 13.60924 kX		

Film No. 951 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	68.942	70.103		160.888	155.665
	25.829	24.664		133.274	138.498
Sum (in mm)	94.771	94.767		294.162	294.163
Average (in mm)	94.769			294.163	
Circumference (in mm)	199.394				
Factor	0.451367				
			θ (in deg.)	77.536	82.251
Lattice constant	a = 5.13848kX		c = 13.60736 kX		

Film No. 953 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	68.942	70.103		160.875	155.662
	25.829	24.664		133.245	138.463
Sum (in mm)	94.771	94.767		294.120	294.125
Average (in mm)	94.769			294.123	
Circumference (in mm)	199.354				
Factor	0.451458				
			θ (in deg.)	77.526	82.235
Lattice constant	a = 5.13869kX		c = 13.60785 kX		

Film No. 954 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	67.502	73.521	74.665	165.517	160.385
	36.375	30.353	29.212	137.899	143.033
Sum (in mm)	103.877	103.874	103.877	303.416	303.418
Average (in mm)		103.876		303.417	
Circumference (in mm)	199.541				
Factor	0.451035				
θ (in deg.)				77.583	82.174

Lattice constant a = 5.13560 kX c = 13.6157 kX

Film No. 955 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	64.634	70.621	71.777	162.522	157.357
	33.685	27.678	26.516	134.876	140.033
Sum (in mm)	98.319	98.299	98.293	297.398	297.390
	75.336				
	22.956				
Sum (in mm)	98.292				
Average (in mm)		98.301		297.394	
Circumference (in mm)	199.093				
Factor	0.452050				
θ (in deg.)				77.503	82.169

Lattice constant a = 5.13816 kX c = 13.61559 kX

Film No. 943 Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	70.697	76.711	77.873	168.654	163.521
	39.673	33.653	32.495	141.083	146.228
Sum (in mm)	110.370	110.364	110.368	309.737	309.749
Average (in mm)		110.367		309.743	
Circumference (in mm)	199.376				
Factor	0.451408				
θ (in deg.)				77.554	82.194

Lattice constant a = 5.13548 kX c = 13.61494 kX

Film No. 944 Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	68.279	74.275	75.442	166.121	160.928
	37.278	31.304	30.128	138.460	143.656
Sum (in mm)	105.557	105.579	105.570	304.581	304.583
Average (in mm)		105.569		304,583	
Circumference (in mm)	199.014				
Factor	0.452229				
θ (in deg.)				77.4909	82.189

Lattice constant a = 5.13971 kX c = 13.6068 kX

Film No. 944 (Repetition) Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.637	72.640	73.792	164.513	159.280
	35.674	29.667	28.515	136.859	142.059
Sum (in mm)	102.311	102.307	102.307	301.372	301.339
Average (in mm)		102.308		301.355	
Circumference (in mm)	199.048				
Factor	0.452152				
θ (in deg.)				77.496	82.214

Lattice constant a = 5.14014 kX c = 13.60486 kX

Film No. 945 Temp. 20°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.940	72.941	74.101	164.990	159.736
	36.865	29.864	28.703	137.378	142.637
Sum (in mm)	102.805	102.805	102.804	302.368	302.373
Average (in mm)		102.805		302.371	
Circumference (in mm)	199.560				
Factor	0.450978				
θ (in deg.)				77.548	82.289

Lattice constant a = 5.13881kX c = 13.60489 kX

Film No. 946 Temp. 20°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	63.025	69.976	70.147	160.491	155.382
	32.125	26.171	25.007	133.104	138.206
Sum (in mm)	95.150	95.147	95.154	293.595	293.588
Average (in mm)		95.150		293.592	

Circumference (in mm) 198.442

Factor 0.453533

θ (in deg.) 77.579 82.210

Lattice constant a = 5.13521 kX c = 13.61603 kX

Film No. 947 Temp. 20°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	71.748	77.785	78.918	169.876	164.589
	40.799	34.761	33.631	142.277	147.553
Sum (in mm)	112.547	112.546	112.549	312.153	312.142
Average (in mm)		112.547		312.148	

Circumference (in mm) 199.601

Factor 0.450899

θ (in deg.) 77.556 82.318

Lattice constant a = 5.13845 kX c = 13.60284 kX

Film No. 948 Temp. 10°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.117	71.115	72.239	163.178	157.909
	34.019	28.021	26.899	135.664	140.932
Sum (in mm)	99.136	99.136	99.138	298.842	298.841
Average (in mm)		99.137		298.842	

Circumference (in mm) 199.705

Factor 0.450664

θ (in deg.) 77.600 82.349

Lattice constant a = 5.13702 kX c = 13.60463 kX

Film No. 949 Temp. 10°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.876 34.823	71.894 28.820	73.031 27.627	164.010 136.463	158.704 141.766
Sum (in mm)	100.699	100.714	100.698	300.473	300.470
Average (in mm)		100.704		300.472	

Circumference (in mm) 199.768
Factor 0.450522

θ (in deg.) 77.589 82.369

Lattice constant a = 5.13839 kX c = 13.60150 kX

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2. Sample II (Ti 67.8%, O_2 32.2%, H_2 developed cm^3).

The oxygen content in Ti_2O_3 was determined by the hydrogen evolution method dissolving the sample in HF (6N), and it was 32.2%. Only three sets of lines in the front reflection region, namely (104), (110) and (116), and (1 3 10), (3 0 12) in the back reflection region are measured, and the lattice constants are calculated from the last two lines (1 3 10) and (3 0 12).

Film No. 987 Temp. 10°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	69.215 38.153	75.194 32.166	76.410 30.962	167.570 139.993	162.533 145.044
Sum (in mm)	107.368	107.370	107.372	307.563	307.577
Average (in mm)		107.370		307.570	

Circumference (in mm) 200.200
Factor 0.449550

θ (in deg.) 77.603 82.138

Lattice constant a = 5.13052 kX c = 13.62581 kX

Film No. 988 Temp. 10°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.201	72.212	73.420	164.493	159.460
	35.176	29.167	27.956	136.941	141.980
Sum (in mm)	101.377	101.379	101.376	301.434	301.440
Average (in mm)		101.377		301.437	
Circumference (in mm)	200.060				
Factor	0.449865				
			θ (in deg.)	77.605	82.136

Lattice constant a = 5.13175 kX c = 13.62623 kX

Film No. 985 Temp. 20°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	70.253	76.254	77.472	168.453	163.455
	39.253	33.256	32.041	140.909	145.906
Sum (in mm)	109.506	109.510	109.513	309.362	309.361
Average (in mm)		109.510		309.362	
Circumference (in mm)	199.852				
Factor	0.450333				
			θ (in deg.)	77.596	82.097

Lattice constant a = 5.12958 kX c = 13.62918 kX

Film No. 986 Temp. 20°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	69.110	75.142	76.331	167.405	162.401
	38.155	32.123	30.935	139.841	144.844
Sum (in mm)	107.265	107.265	107.266	307.246	307.245
Average (in mm)		107.265		307.246	
Circumference (in mm)	199.981				
Factor	0.450042				
			θ (in deg.)	77.595	82.099

Lattice constant a = 5.12971 kX c = 13.62887 kX

Film No. 975 Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.472	72.465	73.679	164.849	159.922
	35.532	29.538	28.322	137.139	142.065
Sum (in mm)	102.004	102.003	102.001	301.988	301.987
Average (in mm)		102.003		301.988	
Circumference (in mm)	199.985				
Factor	0.450044				
θ (in deg.)				77.529	81.964

Lattice constant a = 5.13004 kX c = 13.63559 kX

Film No. 976 Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	67.995	74.027	75.236	166.323	161.395
	37.047	31.010	29.802	138.718	143.641
Sum (in mm)	105.042	105.037	105.038	305.041	305.036
Average (in mm)		105.039		305.039	
Circumference (in mm)	200.000				
Factor	0.450000				
θ (in deg.)				77.578	82.011

Lattice constant a = 5.128134 kX c = 13.63598 kX

Film No. 977 Temp. 30°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.774	71.795	73.009	164.085	159.127
	34.867	28.854	27.639	136.458	141.402
Sum (in mm)	100.641	100.649	100.648	300.543	300.529
Average (in mm)		100.646		300.536	
Circumference (in mm)	199.890				
Factor	0.450247				
θ (in deg.)				77.561	82.019

Lattice constant a = 5.129562 kX c = 13.633330 kX

Film No. 978 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	67.914	73.914	75.140	166.209	161.329
	36.882	30.886	29.653	138.597	143.466
Sum (in mm)	104.796	104.800	104.793	304.806	304.795
Average (in mm)		104.796		304.801	

Circumference (in mm) 200.005
Factor 0.449988

θ (in deg.) 77.575 81.962

Lattice constant a = 5.126802 kX c = 13.640693 kX

Film No. 979 Temp. 40°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.892	72.865	74.076	165.144	160.217
	35.872	29.896	28.689	137.540	142.460
Sum (in mm)	102.764	102.761	102.765	302.684	302.677
Average (in mm)		102.763		302.681	

Circumference (in mm) 199.918
Factor 0.450184

θ (in deg.) 77.578 82.009

Lattice constant a = 5.12815 kX c = 13.63619 kX

Film No. 980 Temp. 50°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	71.731	77.705	78.938	170.093	165.207
	40.746	34.774	33.543	142.356	147.225
Sum (in mm)	112.477	112.479	112.481	312.459	312.432
Average (in mm)		112.479		312.446	

Circumference (in mm) 199.967
Factor 0.450074

θ (in deg.) 77.516 81.907

Lattice constant a = 5.12913 kX c = 13.63997 kX

Film No. 981 Temp. 50°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.486	72.471	73.686	164.859	159.872
	35.489	29.504	28.286	137.087	141.868
Sum (in mm)	101.975	101.975	101.972	301.945	301.940
Average (in mm)		101.974		301.943	
Circumference (in mm)	199.969				
Factor	0.450069				
θ (in deg.)				77.501	81.897

Lattice constant a = 5.12986 kX c = 13.63938 kX

Film No. 982 Temp. 60°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	65.507	71.503	72.712	163.894	159.079
	34.520	28.525	27.317	136.118	140.942
Sum (in mm)	100.027	100.028	100.029	300.012	300.021
Average (in mm)		100.028		300.017	
Circumference (in mm)	199.989				
Factor	0.450024				
θ (in deg.)				77.500	81.838

Lattice constant a = 5.12804 kX c = 13.64542 kX

Film No. 983 Temp. 60°C Exp. 2 hrs.

	Front Reflection			Back Reflection	
Reading (in mm)	66.992	72.955	74.201	165.303	160.479
	35.920	29.958	28.715	137.523	142.354
Sum (in mm)	102.912	102.913	102.916	302.523	302.833
Average (in mm)		102.914		302.829	
Circumference (in mm)	199.915				
Factor	0.450191				
θ (in deg.)				77.494	81.840

Lattice constant a = 5.12852 kX c = 13.64455 kX

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