

On the Phase Relationships in the Titanium-Antimony System. The Crystal Structures of Ti_3Sb

ARNE KJEKSHUS, FREDRIK GRØNVOLD and
JENS THORBJØRNSEN*

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway

By using different melting methods four new titanium antimonides have been identified:

The cubic Ti_3Sb phase, prepared in an arc furnace, is found to have the lattice constant $a = 5.2186 \text{ \AA}$. The pycnometric density is 6.137 g cm^{-3} at 25°C . The crystal structure of the cubic Ti_3Sb phase is of the β -W type.

The tetragonal Ti_3Sb phase, prepared in alumina crucibles in a carbon resistance furnace, is found to have a body-centered unit cell with dimensions: $a = 10.465 \text{ \AA}$, $c = 5.2639 \text{ \AA}$. The pycnometric density is 6.070 g cm^{-3} at 25°C . The space group is $I4/mcm (D_{4h}^{18})$ and the unit cell contains 24 Ti and 8 Sb in the positions: $(0,0,0; 1/2,1/2,1/2) + 4 \text{ Ti in } (a) \pm 0,0,1/4$; $4 \text{ Ti in } (b) 0,1/2,1/4; 1/2,0,1/4$; $16 \text{ Ti in } (k) \pm (x,y,0; \bar{y},x,0; x,\bar{y},1/2; y,x,1/2)$ with $x_1 = 0.0766$, $y_1 = 0.2228$ and $8 \text{ Sb in } (h) \pm (x,1/2 + x,0; 1/2 + x,\bar{x},0)$ with $x_2 = 0.1635$.

The structure of the tetragonal Ti_3Sb phase is closely related to the β -W type structure of the cubic Ti_3Sb phase.

Cubic crystals are transformed into tetragonal crystals on melting in alumina crucibles, while tetragonal crystals remain tetragonal after melting in the arc furnace. Possible reasons for the apparently irreversible transformation of the two phases are discussed.

The orthorhombic $Ti_{1.7}Sb$ phase, prepared in the carbon resistance furnace, is found to have lattice constants $a = 10.172 \text{ \AA}$, $b = 8.348 \text{ \AA}$ and $c = 7.135 \text{ \AA}$. The probable space groups are $Pmma (D_{2h}^5)$, $Pmc2_1 (C_{2v}^2)$ and $Pma2 (C_{2v}^4)$.

The orthorhombic $Ti_{1.2}Sb$ phase, prepared in the carbon resistance furnace, is found to have lattice constants $a = 14.55 \text{ \AA}$, $b = 16.34 \text{ \AA}$, and $c = 5.31 \text{ \AA}$. The probable space groups are $Pbam (D_{2h}^8)$ and $Pba2 (C_{2v}^8)$.

The redetermined lattice constants of the hexagonal $TiSb$ phase, prepared in the carbon resistance furnace, are $a = 4.115 \text{ \AA}$ and $c = 6.264 \text{ \AA}$.

* Present address: Reynolds Metals Company, Portland, Oregon, U.S.A.

As result of X-ray studies of titanium antimony alloys Nowotny and coworkers¹⁻³ reported the existence of four intermediate phases: Ti_4Sb , $Ti_{2.5}Sb$, $TiSb$ and $TiSb_2$. The Ti_4Sb phase^{1,2} was prepared by heating weighed amounts of pure antimony and Degussa titanium in porcelain (Pythagoras) tubes in a carbon resistance (Nernst-Tammann) furnace at 1600°C. The alloys were afterwards annealed at 600°C and quenched, or in some cases slowly cooled, to room temperature. The crystallographic properties of this phase were determined from X-ray powder photographs. By comparing visually estimated intensities with those obtained by calculations, Nowotny *et al.*² concluded that the Ti_4Sb phase had a structure of the Ni_3Sn -($D0_{19}$)-like type. The deviating composition was accounted for by assuming 0.2 titanium atoms, corresponding to the formula $Ti_3(Ti_{0.2}Sb_{0.8})$, to be distributed at random over the antimony positions.

The $Ti_{2.5}Sb$ phase³ was synthesized by melting appropriate amounts of the elements in crucibles of carbon using either a Tammann high pressure furnace or a high frequency induction furnace. The crystal structure of $Ti_{2.5}Sb$ was determined by Auer-Welsbach *et al.*³ by means of single crystal and powder photographs to be of the Cu_2Sb -($C38$)-like type but with doubled c -axis. The parameter values $z_{Ti} = 0.133$ and $z_{Sb} = 0.353$ were determined from the intensities of the $00l$ reflections. Substitution of 0.15 antimony atoms for titanium atoms, corresponding to the formula $Ti_2(Ti_{0.15}Sb_{0.85})$ was thought to explain the excess of titanium and the observed density.

The $TiSb$ phase with $NiAs$ -($B8$)-type structure and the $TiSb_2$ phase with $CuAl_2$ -($C16$)-type structure were prepared and examined^{1,2} as described for the Ti_4Sb phase. These two phases were also obtained by melting titanium and antimony in the right proportions in open crucibles under halide flux.

Using different methods of preparation, the existence of four different, intermediate phases has been established in this institute^{4,5}. The present paper gives an account of the crystal structure determinations for two different phases with composition Ti_3Sb . In addition, some preliminary phase-analytical observations of two more titanium antimonides are reported.

After being informed about the present work, Matthias *et al.*⁶ have duplicated the preparation of the cubic Ti_3Sb phase and shown that it is a superconductor with a transition temperature of 5.8°K.

EXPERIMENTAL

The titanium metal used in this study was "iodide" titanium in rods supplied through A. D. MacKay, Inc., New York. A spectrographic analysis showed the presence of about 30 ppm of Fe and Mn and less than 10 ppm Cu. No analysis of non-metallic impurities was carried out.

The antimony was "High purity antimony" from Bradley Mining Co., San Francisco. According to the supplied analysis it contained the following impurities (in ppm): As (10), Cu (3), Fe (3) and Pb (2).

Several different techniques were tried for preparing the titanium-antimony alloys. In some preliminary experiments alloys were prepared by heating titanium and antimony in evacuated, sealed silica tubes. However, contamination of the alloys due to reaction with silica then always took place. According to Auer-Welsbach *et al.*³ the compound Ti_5Si_3 is formed by this reaction.

One series of alloys with composition ranging from Ti_3Sb to $TiSb$ was prepared in an electric arc furnace (Degussa Volio) by melting weighed amounts of titanium and antimony, previously mixed and compacted. A protective atmosphere of argon gas was present in the furnace during the melting process. Using a pressure of about 4 atm no preferential loss of antimony from the samples was seen, while melting *in vacuo* gave visible loss of antimony.

In the same composition range a second series of alloys was made by melting weighed quantities of the elements in crucibles of pure alumina, placed inside silica tubes which were evacuated and sealed. The samples were melted in a carbon resistance (Nernst-Tammann) furnace at temperatures ranging from 1400 to 1600°C. Temperatures were measured with an optical pyrometer. When the furnace reached the desired temperature, the sample was immediately removed and quenched in ice water. If the temperature had exceeded 1550°C, the silica tubes often broke during quenching.

The alloys could not be heated in contact with alumina at these temperatures for a longer time, as reactions then were seen to take place. Furthermore it was noticed that pure titanium is able to reduce alumina. This reaction was unsuspected in view of the thermochemical discussion by Kubaschewski and Dench⁷ related to the production of Ti-Al alloys from TiO_2 and excess Al at 1000°C. Nevertheless, a reduction of alumina might apparently well take place at higher temperatures.

The melted alloys were bright shiny and metallic looking, while the sintered alloys were in form of a gray to black powder. The alloys were crushed and finely ground and X-ray powder photographs were taken in cameras with 114.6 mm effective diameter and asymmetric film mounting. In most cases filtered copper radiation was used, while chromium radiation was used to obtain greater dispersion in the photographs of the tetragonal Ti_3Sb samples. The lattice constants are expressed in Å units, taking $\lambda_{CuK\alpha_1} = 1.54050$ Å and $\lambda_{CrK\alpha_1} = 2.28962$ Å. Results from Nowotny and coworkers¹⁻³, expressed in kX, have been transformed to Å by multiplication by the factor 1.00202. The lattice constant of the cubic phase was found by extrapolation according to the method of Nelson and Riley⁸.

Oscillation and Weissenberg photographs were taken with CuK -radiation using a Weissenberg camera of 57.3 mm diameter.

The density of the samples was determined pycnometrically at 25°C with kerosene as displacement liquid. To remove gases adsorbed by the sample, the pycnometer was filled with kerosene under vacuum. The samples weighed from 2 to 3 g.

RESULTS

In the titanium-antimony system the existence of four new, intermediate phases was established, *i.e.* the cubic and tetragonal Ti_3Sb phases, the $Ti_{1.7}Sb$ phase and the $Ti_{1.2}Sb$ phase. Furthermore, the existence of the $TiSb$ phase reported by Nowotny and Pesl¹ was confirmed. The $TiSb_2$ phase found by Nowotny and Pesl¹ was not studied here. By the experimental technique used in this study no samples containing the Ti_4Sb and $Ti_{2.5}Sb$ phases reported by Nowotny and coworkers¹⁻³ were obtained.

A. The cubic Ti_3Sb phase

Powder photographs of samples prepared in the arc furnace showed the presence of a phase which could be indexed on the basis of a cubic unit cell, *cf.* Table 1. Inferred from the powder photographs, the amount of the other phases seems to disappear close to the stoichiometric ratio 3:1. A series of density measurements, *cf.* Table 2, was then carried out for an accurate determination of the composition of this phase. The specific volume *versus* weight % Sb plot shown in Fig. 1 had a break in the linearity at 45.9 weight % Sb (25.0 atomic % Sb), ascertaining the composition to be Ti_3Sb .

Table 1. Powder photograph data of cubic Ti_3Sb taken with CuK -radiation, α_2 and β lines omitted.

$\sin^2\Theta \times 10^4$	hkl	I_{obs}	I_{calc}	$\sin^2\Theta \times 10^4$	hkl	I_{obs}	I_{calc}
—	100	0	0	5670	510	2.4	0.8
437	110	12.3	14.3	—	431	—	1.5
—	111	0	0	—	511	0	0
873	200	13.9	15.5	—	333	0	0
1092	210	14.6	13.8	6330	520	2.5	0.9
1312	211	30.2	34.1	—	432	—	1.8
1746	220	2.7	2.2	6538	521	6.9	6.6
—	300	0	0	6978	440	3.6	3.9
—	221	0	0	—	522	0	0
2181	310	3.8	3.1	—	441	0	0
—	311	0	0	7412	530	1.8	0.8
—	222	0	0.02	—	433	—	0.8
2837	320	3.4	2.6	—	531	0	0
3056	321	17.7	15.8	7849.6	600	5.5	0.9
3491	400	4.2	3.8	—	442	—	3.8
—	410	0	0	8065	610	1.3	1.1
—	322	0	0	—	611	—	4.0
3929	411	2.3	1.2	8284.5	532	12.8	8.2
—	330	0	0.6	8722	620	1.7	1.1
—	331	0	0	—	621	—	0
4361	420	4.4	4.5	—	540	0	0
4582	421	2.8	2.4	—	443	—	0
4800	332	4.7	4.0	9154.0	541	3.4	2.7
5236	422	0.9	0.8	—	533	0	0
—	500	0	0	—	622	0	0.00
—	430	0	0	9804.5	630	5.6	3.0
					542		6.0

The lattice constant of the sample with the composition Ti_3Sb is found in Table 2 together with the lattice constants of the Ti_3Sb -phase in the samples Ti_4Sb , $\text{Ti}_{3.5}\text{Sb}$, $\text{Ti}_{2.5}\text{Sb}$ and Ti_2Sb . As the lattice constant is almost invariant for specimens with different initial proportions of the components, no composition range of the cubic Ti_3Sb -phase is noticeable.

The pycnometric density of Ti_3Sb at 25°C , *cf.* Table 2, is found to be in agreement with the density calculated from the X-ray data, 6.201 g cm^{-3} , assuming two ($Z_c = 1.98$) Ti_3Sb -groups per unit cell.

Table 2. Lattice constants and pycnometric densities of samples containing the cubic Ti_3Sb phase.

Sample	a (Å)	Density (g cm^{-3})
Ti_4Sb	5.2187	5.801
$\text{Ti}_{3.5}\text{Sb}$	5.2188	5.956
Ti_3Sb	5.2186	6.137
$\text{Ti}_{2.5}\text{Sb}$	5.2184	6.251
Ti_2Sb	5.2184	6.381

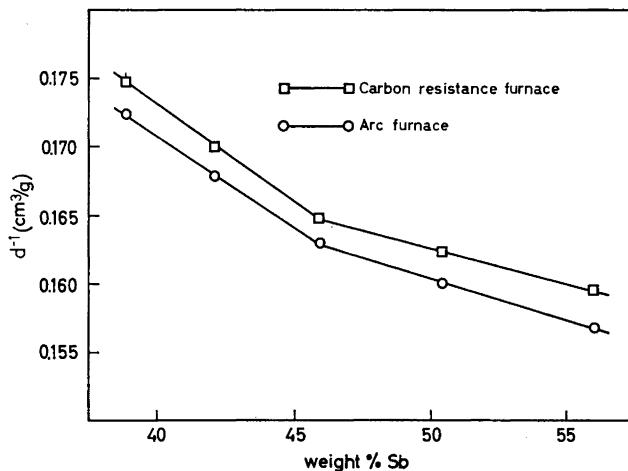


Fig. 1. Reciprocal densities as function of composition for samples synthesized in carbon resistance and arc furnace.

Many related Me_3X compounds of the transition metals have a structure of the $\beta\text{-W}$ (W_3O) type. The $\beta\text{-W}$ structure, cf. Fig. 2, is described in space group $Pm\bar{3}n$ (O_h^3) with

- 6 Me in (d) $1/4, 1/2, 0$; $0, 1/4, 1/2$; $1/2, 0, 1/4$;
 $3/4, 1/2, 0$; $0, 3/4, 1/2$; $1/2, 0, 3/4$.
 2 X in (a) $0, 0, 0$; $1/2, 1/2, 1/2$.

As the missing reflections in the powder photographs were in agreement with the extinctions for this space group, a comparison of observed and calculated

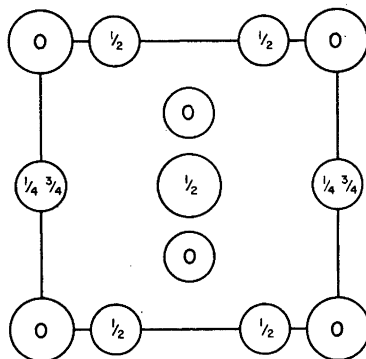


Fig. 2. Projection of one unit cell of the $\beta\text{-W}$ type structure. Large circles represent antimony atoms and small circles titanium atoms. Figures give the z -parameters.

Table 3. Powder photograph data of tetragonal Ti_3Sb taken with CrK -radiation, α_2 and β lines omitted.

$\sin^2\theta \times 10^4$	hkl	I_{obs}	I_{calc}	$\sin^2\theta \times 10^4$	hkl	I_{obs}	I_{calc}
240	110	8.5	9.4	—	640	0	2.4
481	200	6.5	8.6	6298	413	46	39.2
—	220	0	3.2	—	602	0	0.2
1074	211	40.5	38.1	6690	622	12	10.7
1200	310	14	16.4	6820	721	19.5	18.2
1898	002	35	33.7	6948	730	11.5	8.3
—	400	0	0.0	—	433	0	0.1
2034	321	31.5	26.1	7571	004	18	17.6
—	112	0	1.3	—	800	0	0.3
2159	330	33.5	31.1	7731	523	35	28.3
2378	202	50	48.7	—	114	0	0.4
2398	420	46.5	43.9	—	651	0	2.3
2514	411	113	124.8	7880	712	19	15.9
2853	222	14.5	12.4	—	552	5.7	5.7
3094	312	10.5	8.5	—	204	0	1.0
—	510	0	0.0	8119	642	54.5	46.2
—	431	0	0.0	—	820	12.4	12.4
3814	402	18.5	14.4	8252	811	40.5	28.2
—	440	2.9	2.9	—	741	8.4	8.4
3949	521	43.5	38.5	8328	543	4.5	5.3
4057	332	30.5	23.6	—	224	0	0.7
—	530	7.3	7.3	8613	660	32	30.5
4299	422	17	12.9	—	613	0	0.1
—	600	6.7	6.7	8765	314	3.5	6.0
—	620	0	0.3	8835	732	31.5	25.4
4865	213	11.5	9.3	—	750	0	1.7
—	611	0.1	0.1	9212	831	13.5	14.2
—	512	0	0.0	—	404	0	0.1
5392	541	6.5	4.3	9550	802	33.5	31.7
—	442	0	0.9	9574	840	6	4.2
5821	323	4	5.7	9643	633	11.5	12.1
5868	631	3	4.5	9722	334	35.5	52.5
—	532	10.0	10.0	9813	910	26.5	38.9
5973	710	26	7.0				
—	550	2.5	2.5				

intensities for the reflections was carried out. The intensities of the reflections were calculated using the formula

$$I_{calc} = 10^{-5} \times |F|^2 \times Lp \times v$$

For the calculation of the structure amplitudes, Thomas-Fermi model values of f , taken from *Internationale Tabellen*, were used throughout this paper. No corrections for absorption and temperature factors were applied. The observed intensities were obtained from photometer recordings and referred to a relative, absolute scale by making the sums of I_{obs} and I_{calc} equal. As can be seen from Table 1 the agreement between the two sets of values is very good, and leaves no doubt about the correctness of the proposed structure.

B. The tetragonal Ti_3Sb phase

Powder photographs of samples prepared in the Nernst-Tammann furnace show the presence of a phase with tetragonal structure, *cf.* Table 3. Powder photographs of various samples of Ti_6Sb , Ti_5Sb and Ti_4Sb contain some of the strongest reflections from $\alpha\text{-Ti}$, while powder photographs of Ti_2Sb contain reflections from a phase richer in antimony with probable composition $\text{Ti}_{1.7}\text{Sb}$. The additional reflections are weak on photographs of samples with composition $\text{Ti}_{3.5}\text{Sb}$ and $\text{Ti}_{2.5}\text{Sb}$ and are absent on photographs of samples with composition Ti_3Sb . A more accurate determination of the composition of the phase was obtained from a plot of the specific volume *versus* weight % Sb, *cf.* Fig. 1, and by means of metallographic methods. Thus the composition of the phase is ascertained to be Ti_3Sb .

The lattice constants of the tetragonal Ti_3Sb phase in the samples Ti_4Sb , $\text{Ti}_{3.5}\text{Sb}$, Ti_3Sb , $\text{Ti}_{2.5}\text{Sb}$ and Ti_2Sb are listed in Table 4. The slight expansion of the unit cell, which takes place in the range Ti_3Sb to $\text{Ti}_{2.5}\text{Sb}$ indicates that the tetragonal Ti_3Sb phase has a narrow range of homogeneity on the antimony-rich side of Ti_3Sb .

The observed density, *cf.* Table 4, indicates that the unit cell contains 8 ($Z_c = 7.94$) Ti_3Sb -groups. The calculated density for Ti_3Sb from the X-ray measurements is 6.116 g cm^{-3} .

Single crystals of Ti_3Sb were found in samples quenched from 1450°C . The single crystals were needle-shaped and oscillation and Weissenberg photographs showed tetragonal symmetry, Laue symmetry $4/mmm$, with the *c*-axis along the needle axis. Missing reflections on the photographs were:

$$\begin{aligned} hkl & \text{ when } h + k + l = 2n + 1 \\ hk0 & \text{ when } (h + k = 2n + 1) \\ 0kl & \text{ when } k = 2n + 1 \text{ and } l = 2n + 1 \end{aligned}$$

Characteristic space groups are accordingly $I4/mcm (D_{4h}^{18})$, $I4cm (C_{4v}^{10})$ and $I\bar{4}c2 (D_{2d}^{10})$. All possible space groups have symmetry $p4m$ in the 001-projection with $a' = b' = \frac{1}{2} \sqrt{2} a$.

Determination of the structure. The intensities of the $hk0$ and hkl -reflections were estimated visually from "multiple film" Weissenberg photographs taken with CuK -radiation and were corrected for Lorentz and polarization factors. No corrections for absorption, extinction and temperature factors were applied.

Table 4. Lattice constants and pycnometric densities of samples containing the tetragonal Ti_3Sb phase.

Sample	a (Å)	c (Å)	Density (g cm^{-3})
Ti_4Sb	10.468	5.2640	5.721
$\text{Ti}_{3.5}\text{Sb}$	10.464	5.2637	5.876
Ti_3Sb	10.465	5.2639	6.070
$\text{Ti}_{2.5}\text{Sb}$	10.476	5.2688	6.161
Ti_2Sb	10.475	5.2692	6.270

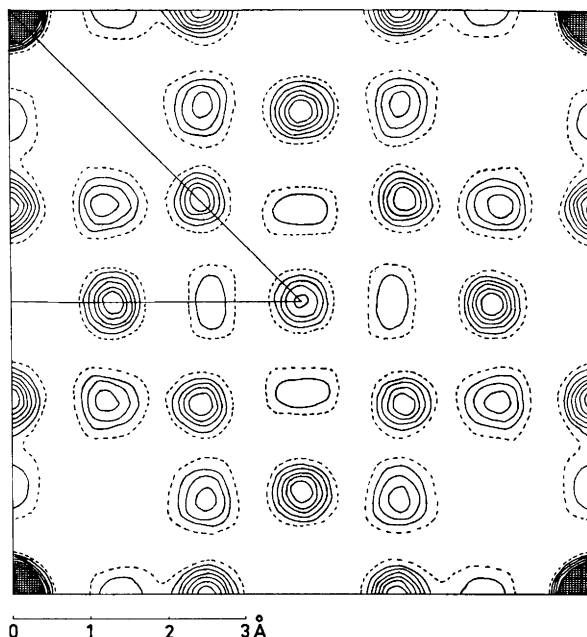


Fig. 3. Patterson projection on 001 of the tetragonal Ti_3Sb . Only the primitive unit cell is drawn. The contours are at equal but arbitrary intervals. Zero contours are broken and negative contours are omitted.

On the basis of the corrected $F(hk0)^2$ -values a Patterson map was computed, cf. Fig. 3. As the cubic and tetragonal Ti_3Sb phase have related lattice dimensions $a_{\text{tet}} \approx 2a_{\text{cub}}$, $c_{\text{tet}} \approx c_{\text{cub}}$, relationships with the β -W structure was looked for in the Patterson map. It was indeed possible to rearrange the atoms in the β -W structure in agreement with the Patterson map. Based on these approximate atomic parameters structure factors were calculated, and after adjusting F_o and F_c to the same scale $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.29$ was found, indicating the main features of the proposed structure to be correct.

The atomic parameters were refined further by means of four Fourier and one difference synthesis. R decreased to 0.19 after the last Fourier synthesis and to 0.132 after the difference synthesis. The observed and calculated $F(hk0)$ -values are listed in Table 5 and the final Fourier map is shown in Fig. 4. The corresponding parameters, referred to the body-centered axes, are:

- 4 Ti I in 0,0 etc.
- 4 Ti II in $0, \frac{1}{2}$ etc.
- 16 Ti III in $x_1 = 0.0766, y_1 = 0.2228$ etc.
- 8 Sb in $x_2 = 0.1635, y_2 = \frac{1}{2} + x_2 = 0.6635$ etc.

In terms of the highest symmetric space group, $I4/mcm (D_{4h}^{18})$, all atoms are in special positions with fixed z -coordinates. For symmetry reasons only

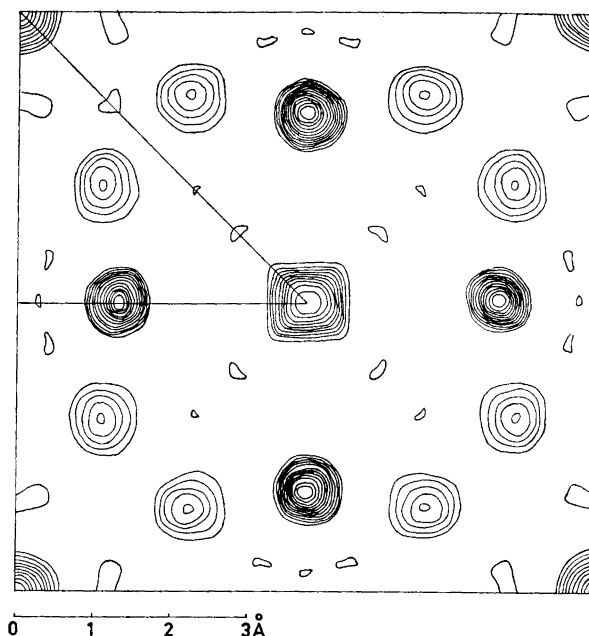


Fig. 4. Fourier projection of the primitive unit cell of tetragonal Ti_3Sb on 001. Contours are drawn at every $10 \text{ e } \text{Å}^{-2}$. Zero and negative contours omitted.

On the basis of the relationships found between cubic and tetragonal Ti_3Sb it seemed reasonable to assume that the z -coordinates in tetragonal Ti_3Sb were the same as for the corresponding atoms in cubic Ti_3Sb . It turned out, however, that z -values of 0 and $\frac{1}{2}$ for Ti I were unreasonable considering the interatomic distances Ti I—Ti III. Therefore, z -parameter values of $\frac{1}{4}$ and $\frac{3}{4}$ were chosen for both Ti I and Ti II. In order to verify these z -parameters, intensities were calculated in the same way as for cubic Ti_3Sb and compared with those obtained from photometer recordings of powder photographs. As can be seen from Table 3 the agreement between the two sets of values is good and leaves no doubt about the correctness of the proposed structure.

The deduced atomic arrangement, *cf.* Fig. 5, is thus: $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$

- 4 Ti I in (a) $0,0,\frac{1}{4}; 0,0,\frac{3}{4}$.
- 4 Ti II in (b) $0,\frac{1}{2},\frac{1}{4}; \frac{1}{2},0,\frac{1}{4}$.
- 16 Ti III in (k) $x,y,0; \bar{x},\bar{y},0; \bar{y},x,0; y,\bar{x},0;$
 $x,\bar{y},\frac{1}{2}; \bar{x},y,\frac{1}{2}; y,x,\frac{1}{2}; \bar{y},\bar{x},\frac{1}{2},$
 with $x_1 = 0.0766, y_1 = 0.2228$.
- 8 Sb in (h) $x,\frac{1}{2} + x,0; \bar{x},\frac{1}{2} - x,0; \frac{1}{2} + x,\bar{x},0, \frac{1}{2} - x,x,0$
 with $x_2 = 0.1635$.

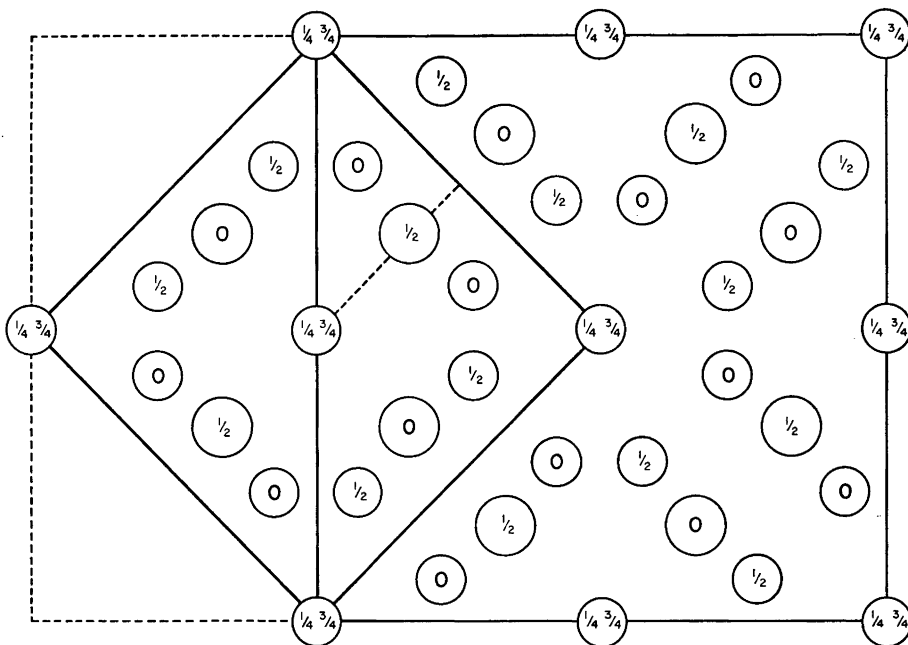


Fig. 5. Projection of the unit cell of tetragonal Ti_3Sb on 001. Large circles represent antimony atoms and small circles titanium atoms. Figures give the z -parameters. Both the primitive and the body-centered unit cell are indicated.

C. Some phase-analytical data

In addition to the two Ti_3Sb phases just reported, two other previously unknown phases, the $Ti_{1.7}Sb$ phase and the $Ti_{1.2}Sb$ phase, were identified in the titanium-rich (> 50 at. % Ti) part of the system. The exact composition ranges of the phases have not been determined, and the formulae only indicate their approximate composition. Phase-analytical work using metallographic and X-ray powder methods and density measurements is still in progress and only a few observations will be mentioned here.

The $Ti_{1.7}Sb$ phase. X-Ray powder photographs of different samples in the range around Ti_2Sb contained reflections from a new phase with composition somewhere in this concentration range. This phase was obtained by either of the melting methods outlined in the experimental part. By means of metallographic methods the approximate composition of this phase is found to be $Ti_{1.7}Sb$, which is in agreement with the composition estimated using the disappearing phase method on the powder photographs.

Single crystals of the $Ti_{1.7}Sb$ phase were obtained with bipyramidal shape in different melts. Oscillation and Weissenberg photographs showed that the crystals had orthorhombic symmetry. With the approximate unit cell dimen-

Table 6. Powder photograph data of $Ti_{1.7}Sb$ taken with CrK-radiation, a_2 and β lines omitted.

I_{obs}	$\sin^2\Theta \times 10^4$		hkl	I_{obs}	$\sin^2\Theta \times 10^4$		hkl
	obs	calc			obs	calc	
vw	954	953	211	w	4164	4166	142
w	1032	1030	002	vw	4212	4209	323
m	1140	1137	121	vw	4309	4307	014
m	1262	1259	220	w	4396	4384	512
vw	1348	1345	112	vw	4513	4516	233
m	1399	1398	301	w	5299	{5293	441
m	1909	1909	122			{5311	620
vw	1955	1950	031			{5448	314
w	2027	2026	400	vw	5460	{5453	143
vw	2076	2077	131			{5466	251
m	2152	2150	321	w	5565	5569	621
st	2287	{2284	401	vw	5814	5811	034
		{2289	222	m	6237	6235	523
w	2338	2632	113	vw	6572	6563	105
vw	2476	2472	411	vw	6876	6276	603
w	2508	2505	013	m	7180	7175	533
w	2781	2778	420	m	7326	7315	125
vw	2842	2849	132	m	7479	7473	514
vw	2920	2922	322	m	7988	7987	722
m	3018	{3009	040	w	8106	8105	800
		{3012	213	vw	8272	8268	344
w	3578	3576	223	w	8551	8551	811
vw	3724	3718	430	w	8572	8568	633
vw	3808	3808	422	m	8796	8796	460
vw	3862	3862	332	w	8900	8897	552
vw	4025	{4009	033				
		{4093	042				

sions from the single crystal data the lattice constants of the $Ti_{1.7}Sb$ phase were determined from the powder photographs, *cf.* Table 6, to be:

$$a = 10.172 \text{ \AA}, \quad b = 8.346 \text{ \AA}, \quad c = 7.135 \text{ \AA}.$$

The only systematic missing reflections were of the type $hk0$ absent when $h = 2n + 1$. The probable space groups are thus $Pmma$ (D_{2h}^5), $Pmc2_1$ (C_{2v}^2) and $Pma2$ (C_{2v}^4).

The $Ti_{1.2}Sb$ phase. Samples with composition in the range about $Ti_{1.2}Sb$ give very complicated powder photographs and the phases are not easily identified by X-ray methods. By metallographic technique, however, two phases with approximate composition $Ti_{1.2}Sb$ and $TiSb$ could be identified. In the same way as the $Ti_{1.7}Sb$ phase, the $Ti_{1.2}Sb$ phase was obtained by either of the melting methods.

Table 7. Powder photograph data of low angle reflections of $Ti_{1.2}Sb$ taken with CuK -radiation, α_2 and β lines omitted.

I_{obs}	$\sin^2\theta \times 10^4$		hkl	I_{obs}	$\sin^2\theta \times 10^4$		hkl
	obs	calc			obs	calc	
vw	329	327	121	st	1039	1031 1038 1043	610
w	386	384	140				161
w	448	{448 452	400	222			
			330				
w	489	484	311	w	1078	1070	132
vw	536	537	420	w	1128	1122	261
w	589	584	150	vw	1208	{1201 1209	270
w	611	608	340				630
vw	666	668	250	vw	1310	{1308 1310 1312	621
w	678	678	241				242
w	725	723	510	vw	1421	{1419 1422 1426	412
w	826	{818 828	341				631
			160	080			
w	882	878	251	vw	1514	1510	252
w	895	892	112	vw	1607	1605	711
m	1006	{1000 1004 1009 1010	521	vw	1678	{1670 1672	162
			450	m	1780	{1775 1783	721
			600				651
			061	731			
m	1017	{1014 1018	441	w	1854	{1790 1846 1851	570
			351	452	602		

In most of the samples melted in the Nernst-Tammann furnace long needle-shaped crystals were obtained. Oscillation and Weissenberg photographs showed the crystals to be orthorhombic with unit cell dimensions:

$$a = 14.55 \text{ \AA}, \quad b = 16.34 \text{ \AA}, \quad c = 5.31 \text{ \AA}.$$

Missing reflections were: $0kl$ when $k = 2n + 1$ and $h0l$ when $h = 2n + 1$. This is characteristic of the space groups $Pbam$ (D_{2h}^9) and $Pba2$ (C_{2v}^8). In Table 7 are listed the lines found in the low angle region on a powder photograph of the $Ti_{1.2}Sb$ sample.

The TiSb phase. X-Ray powder photographs of the $TiSb$ phase were indexed on the basis of a hexagonal unit cell. The redetermination of the lattice constants gave the result:

$$a = 4.115 \text{ \AA}, \quad c = 6.264 \text{ \AA}, \quad c/a = 1.560$$

Whether the difference between the values given here and the results by Nowotny and Pesl¹ ($a = 4.07_0 \text{ \AA}$; $c = 6.30_6 \text{ \AA}$) reflects the difference in thermal history of the alloys, or indicates an extended homogeneity range, or is due to impurities is not clear at the moment.

DISCUSSION

In the β -W structure of the cubic Ti_3Sb phase, *cf.* Fig. 2, each titanium atom is coordinated to two titanium atoms in linear chains at a distance $a/2$, to eight more titanium atoms at a 22.5 % larger distance, and to four antimony atoms in a tetrahedral arrangement. Each antimony atom is coordinated to twelve titanium atoms at the corners of an icosahedron. The interatomic distances between nearest neighbours in cubic Ti_3Sb are listed in Table 8.

Table 8. Interatomic distances in cubic Ti_3Sb (Å).

Ti	— 2 Ti	: 2.609
	— 8 Ti	: 3.195
	— 4 Sb	: 2.917
Sb	— 12 Ti	: 2.917

The shortest Ti—Ti distance is definitely shorter than in metallic titanium. The shortest interatomic distances are 2.896 Å for α -Ti according to Clark⁹ and 2.843 Å for β -Ti according to Levinger¹⁰. In many of the titanium compounds with β -W structure, listed by Geller¹¹, even shorter Ti—Ti distances than the one found here are observed.

The observed interatomic distances can also be compared with the values predicted from the metallic radii¹². If antimony retains one of its usual valences, 1.56 or 3, the twelve Ti—Sb bonds should have bond numbers 0.13 or 0.25. Using the single bond radius value of 1.324 Å for Ti and 1.391 Å for Sb, with an electronegativity correction of 0.008 Å, the expected Ti—Sb bond distances for the two different valence states are 3.239 Å and 3.068 Å, respectively. The observed value 2.917 Å agrees better with that calculated for a valence 3 for Sb than for the usual metallic valence 1.56, but even this value is considerably larger than the observed one. To account for the discrepancy one can either accept a set of special β -W radii (*cf.* Geller^{11,13} and Pauling¹⁴), or assume a higher bond number for the Ti—Sb bonds¹⁴. Higher bond numbers would obtain, according to Pauling¹², if one electron were transferred from the hyperelectronic Sb atom to the hypoelectronic Ti atom, thus increasing the valences by one. The calculated Ti—Sb bond distance for this valence, 2.993 Å is still appreciably larger than the observed value. Using the effective metallic radius for Ti given by Pauling¹⁴ for the β -W structure, a shorter Ti—Sb bond distance value of 2.940 Å for the same bond number 0.33 is calculated. For the ten Ti—Ti bonds with a bond number of 0.20, and using the β -W radius value for singlebonded Ti of 1.271 Å, the calculated bond distance is 3.058 Å, or rather close to the weighed mean (3.078 Å) of the observed values.

In order to derive the structure of tetragonal Ti_3Sb from the β -W type structure of cubic Ti_3Sb , displacements of some of the atoms must be performed. The main difference between the two structures consists in a movement of the Ti I atoms as indicated by the arrows in Fig. 6 and a translation of these atoms of magnitude $c/4$ along the c -axis. Moreover, a characteristic difference is produced by the change from cubic to tetragonal symmetry, *cf.* Figs. 5 and 6.

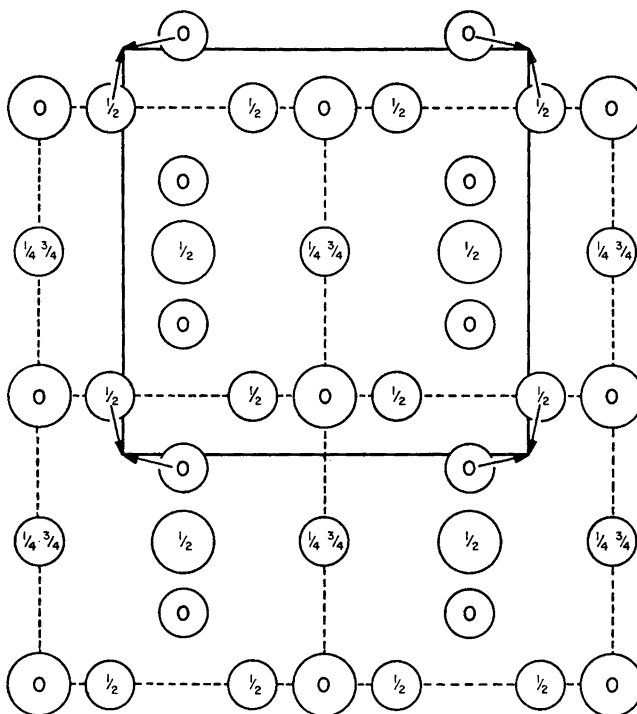


Fig. 6. Projection of four unit cells of cubic Ti_3Sb in relation to the 001 projection of the primitive unit cell of tetragonal Ti_3Sb .

Chains of Ti atoms, characteristic of the cubic Ti_3Sb structure are also present in the tetragonal structure. In the tetragonal structure Ti I and Ti II form chains only along the c -axis, while perpendicular to it the chains are broken due to the relative displacement of the Ti I atoms and by the change to tetragonal symmetry. The configuration of the eight Ti III atoms around each Ti I is found to be that of a slightly distorted square antiprism. The Ti II atoms are coordinated to eight Ti III atoms at the corners of an even more distorted rectangular antiprism and to four antimony atoms at the corners of a tetrahedron. Each Ti III atom is surrounded by eleven titanium atoms and four antimony atoms, *cf.* Fig. 5. Each antimony atom is coordinated to ten titanium atoms and two antimony atoms at the corners of an irregular icosahedron.

The interatomic distances between nearest neighbours in tetragonal Ti_3Sb calculated for the final parameters are listed in Table 9. The errors indicated are standard deviations calculated according to Cruickshank¹⁵. No comparison between observed and calculated bond distances is carried out for tetragonal Ti_3Sb , since even in the case of cubic Ti_3Sb the basis for the calculation is uncertain.

Table 9. Interatomic distances in tetragonal Ti_3Sb (Å).

Ti	I	—	2 Ti	I	: 2.632
			12 Ti	III	: 2.794 ± 0.011
Ti	II	—	2 Ti	II	: 2.632
			8 Ti	III	: 3.285 ± 0.011
			4 Sb		: 2.755 ± 0.003
Ti	III	—	2 Ti	I	: 2.794 ± 0.011
			2 Ti	II	: 3.285 ± 0.011
			1 Ti	III	: 2.970 ± 0.021
			2 Ti	III	: 3.082 ± 0.021
			2 Ti	III	: 3.407 ± 0.021
			2 Ti	III	: 3.487 ± 0.021
			1 Sb		: 2.780 ± 0.012
			1 Sb		: 2.790 ± 0.012
			2 Sb		: 3.029 ± 0.012
Sb		—	2 Ti	II	: 2.755 ± 0.003
			2 Ti	III	: 2.780 ± 0.012
			2 Ti	III	: 2.790 ± 0.012
			4 Ti	III	: 3.029 ± 0.012
			2 Sb		: 3.671 ± 0.004

In order to study relative stabilities of the two crystalline phases, samples first melted in the arc furnace were remelted in the Nernst-Tammann furnace, and *vice versa*. By this treatment, the cubic crystals were changed into tetragonal crystals, while the tetragonal crystals remained unchanged after melting in the arc furnace. Thus, the transformation is apparently irreversible.

It is known in other instances that small amounts of impurities can stabilize more or less foreign structures, *e.g.* a pseudobrookite structure for Ti_3O_5 is found already at an iron concentration of 0.23 weight % Fe ($x = 0.03$ in $(Ti_{1-x}Fe_x)_3O_5$) according to Andersson *et al.*¹⁶ Spectrographic analysis of samples containing the tetragonal Ti_3Sb phase showed the presence of about 3/10 % Al and 3/10 % Si as impurities. Samples of the cubic Ti_3Sb phase were, however, only found to contain the same amounts of impurities as the titanium and antimony used. On melting samples with composition Ti_3Sb in the arc furnace together with different small amounts of Al, Si, Al_2O_3 and SiO_2 they all still gave X-ray photographs characteristic of the cubic Ti_3Sb phase. The presence of impurities like oxygen and nitrogen might perhaps explain the stability of the tetragonal structure. Thus, cubic Ti_3Sb is obtained by remelting tetragonal Ti_3Sb in an arc furnace with small amounts of pure titanium. The explanation of this as due to differences in composition of the two phases, seems unreasonable since, for example, the alloy $Ti_{3.5}Sb$ remains tetragonal after remelting in the arc furnace. Indeed, the pure titanium might act as an absorber of the oxygen and nitrogen present in the alloy.

Including the four phases reported here eight phases have been described in the titanium-antimony system. Their characteristic crystallographic properties are listed in Table 10. In view of the present discussion about the relative stability of cubic and tetragonal Ti_3Sb , and as the present study could not confirm the existence of the Ti_4Sb phase and the $Ti_{2.5}Sb$ phase reported by Nowotny and coworkers¹⁻³, the possibility that these phases also might be

Table 10. Pycnometric densities and crystallographic data for phases reported in the titanium-antimony system.

Phase	\bar{d} (g cm ⁻³)	a (Å)	b (Å)	c (Å)	c/a	Structure type	Reference
Ti ₄ Sb	—	5.958	—	4.807	0.807	Hex.-Ni ₃ Sn	Nowotny <i>et al.</i> ²
Ti ₃ Sb	6.137	5.2186	—	—	—	Cub.- β W	Present
Ti ₃ Sb	—	5.217	—	—	—	Cub.- β W	Matthias <i>et al.</i> ⁶
Ti ₃ Sb	6.070	10.465	—	5.2639	0.508	Tetr.	Present
Ti _{2.5} Sb	5.90	4.01	—	14.5	3.63	Tetr.-Cu ₂ Sb	Auer-Welsbach <i>et al.</i> ³
Ti _{1.7} Sb	—	10.172	8.348	7.135	—	Orthor.	Present
Ti _{1.2} Sb	—	14.55	16.34	5.31	—	Orthor.	Present
TiSb	—	4.07 ₀	—	6.30 ₈	1.55	Hex.-NiAs	Nowotny and Pesl ¹
TiSb	—	4.115	—	6.264	1.560	Hex.	Present
TiSb ₂	—	6.66 ₆	—	5.81 ₇	0.87 ₃	Tetr.-CuAl ₂	Nowotny and Pesl ¹

stabilized by impurities should not be overlooked. With attention focused on the Ti₄Sb phase it should be noted that a lattice constant variation of only 2 to 4 % between the isostructural phases Ti₄Sb, Ti₄Pb (Nowotny and Pesl¹⁷) and Ti₃Al* (Anderko *et al.*¹⁸) is much smaller than the 10 to 23 % difference expected due to the difference in metallic radii of Sb, Pb and Al. This point is perhaps worth a further study in view of the observed reaction between Ti and Al₂O₃.

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* The Ti₂Al phase reported by Ence and Margolin¹⁹ is probably belonging to the homogeneity range of the Ti₃Al phase.

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