X-Ray Study of Titanium Selenides

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Three intermediate phases have been characterized in titanium-selenium samples heat-treated at 800 and 600°C: the $TiSe_{0.95}$-phase, the $TiSe_{1.05}$-phase and the $TiSe_{1.20-2.00}$-phase. The $TiSe_{0.95}$-phase has an orthorhombic, NiAs-like structure, $a = 3.494$ Å, $c = 6.462$ Å, space group $Pcmn$ (D_{2h}^{16}) with $\sim 4Ti$ and ~ 4 Se atoms in positions $\pm (x,1/4,z; 1/2+x,3/4,1/2-z)$, $x_{Ti} = 0.19$, $z_{Ti} = 0.01$, $x_{Se} = 0.58$ and $z_{Se} = 0.22$. The $TiSe_{1.05}$-phase is hexagonal of NiAs-like type, $a = 3.571$ Å $c = 6.297$ Å, for a sample heat-treated at 600°C, with 5 % vacant titanium positions probably distributed at random. The phase is presumably identical with a phase earlier designated as Ti_3Se_2. The $TiSe_{1.20-2.00}$-phase is hexagonal at the titanium-rich limit, undergoes a monoclinic deformation with increasing selenium content, and is hexagonal again in the range from about $TiSe_{1.4}$ to $TiSe_{2.00}$. From $TiSe_{1.20}$ to $TiSe_{1.30}$ the changes in structure are so large that some discontinuity in the form of a two-phase region might be expected at lower temperatures. A low-symmetric structure is observed for $TiSe_{1.60}$ when heat-treated at 800°C. Observed densities are only between one and two per cent lower than those calculated from the X-ray data assuming a subtractive solid solution, $Ti_{2-x}Se_2$ with $0.17 < x < 1$, in the range $TiSe_{1.20-2.00}$.

In the titanium selenium system Ehrlich[1] described the existence of a solid solution in the range TiSe to $TiSe_2$ with hexagonal structure and continuously changing lattice constants. The structure was found to be of NiAs-like type at the composition TiSe, and of $Cd(OH)_2$-like type at the composition $TiSe_2$. The structure of $TiSe_2$ had earlier been determined by Oftedal[2]. In two respects Ehrlich's results differed from those obtained for the related selenides of vanadium[3], chromium[4], iron[5], cobalt[6] and nickel[7]; *viz.* that no deformation of the hexagonal structure was observed in the range around $MeSe_{1.3}$, and that the discrepancy between observed densities and those calculated on the basis of the X-ray data in the TiSe-region was considerably larger than for any of the other systems. It therefore became one of the objects of this investigation, which was started in 1947 as part of a series of investigations on transition metal chalcogenides, to study these points in more detail by means of X-ray methods and density measurements.

The presence of a deformed structure in the composition range $TiSe_{1.2}$ to $TiSe_{1.4}$ was soon established [8], but the density determinations were inconsistent, indicating the presence of a varying amount of impurities, either picked up during preparation, or due to the instability of the samples under atmospheric conditions. A reinvestigation of the titanium selenium system in the range TiSe to $TiSe_2$ was therefore carried out using titanium of higher purity, and improved experimental technique. In the meantime, new results were reported by Hahn * and Ness, first in a short note [9], and afterwards in more detail [10]. They found that the composition of the TiSe-phase extended on the titanium-rich side of TiSe to about $TiSe_{0.75}$. The structure was reported as hexagonal with lattice constants twice as large as found by Ehrlich [1] both in the a- and c-directions, but without any change with composition from TiSe to $TiSe_{0.75}$. A second modification of TiSe was obtained in the form of crystals grown from the vapor phase. The symmetry was reported as trigonal, and the dimensions of the hexagonal cell about the same as of the first modification in the a-direction, but somewhat more than twice as large in the c-direction. In the composition range $TiSe_{0.70}$ to $TiSe_{0.50}$ a new phase was observed with simple NiAs-like structure. The phase was formally designated as Ti_3Se_2 ($TiSe_{0.67}$) and structurally, with support from density determinations, as $Ti_2(Ti_{0.4}Se_{1.6})$, *i.e.*, as a NiAs-type structure with the excess Ti atoms occupying vacant Se-positions. Investigations of samples with composition TiSe, Ti_2Se_3 and $TiSe_2$ have also been carried out by McTaggart and Wadsley [11], who reported good agreement between their results and those of Hahn and Ness on the superstructure of TiSe, and the results of Ehrlich for the two other samples.

There is a rather striking discrepancy between the cell dimensions given by Hahn and Ness for the subcell of TiSe and those given by Ehrlich [1], indicating that the TiSe of the former is equivalent to $TiSe_{1.2}$ of the latter. Thus, if Ehrlich's samples represent the correct compositions more closely than those by Hahn and Ness, the unexpected occurrence of a NiAs-type structure way over on the metal-rich side among the chalcogenides might be explained on the basis of impure samples. In order to get an answer to this question, additional samples had to be prepared in the titanium-rich region.

[EXPERIMENTAL

High purity titanium prepared by the iodide (van Arkel) process, and containing more than 99.9 % Ti was obtained from the Imperial Chemical Industries, Ltd. By spectrographic analysis the following amounts of impurities were found: about 0.01 % Fe, Mg, Si and Sn, and about 0.001 % Al and Cu. The titanium came in form of a bar, from which small turnings were made. Highly refined selenium was kindly placed at our disposal by Bolidens Gruvaktiebolag. According to their analysis it contained 0.0002 % Cu, 0.0007 % Fe, 0.01 % S, 0.003 % Te and 0.003 % non volatile matter.

The alloys were prepared by heating accurately weighed quantities of the elements in small crucibles of alumina placed inside silica tubes, 15 mm i.d. and 50 mm high, which

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* According to an agreement between Professor Hahn and Professor Haraldsen to avoid unnecessary duplication of work we have concentrated our investigation on titanium selenides in the range TiSe to $TiSe_2$. The diverging results obtained for samples with composition around TiSe made further studies in this range necessary.

were then evacuated and sealed. In the course of the present investigation samples with the following compositions were prepared: $TiSe_{0.60}$, $TiSe_{0.95}$, $TiSe_{1.00}$, $TiSe_{1.05}$, $TiSe_{1.10}$, $TiSe_{1.20}$, $TiSe_{1.30}$, $TiSe_{1.40}$, $TiSe_{1.50}$, $TiSe_{1.60}$, $TiSe_{1.70}$, $TiSe_{1.80}$, $TiSe_{1.90}$, $TiSe_{2.00}$ and $TiSe_{2.50}$.

Preparations in the composition range $TiSe_{1.10}$ to $TiSe_{2.50}$ were heated slowly to 1000°C, kept at this temperature for 24 h, and afterwards at 800°C for 48 h. The sample tubes were then cooled to room temperature with the furnace. To prevent reactions with the atmosphere, the opening of the silica tubes and crushing and other handling of the alloys was done under pure nitrogen in a dry-box. About two-thirds, or 2 g, of each sample was transferred to a pycnometer for density measurements, and the rest to small silica tubes for annealing at 600°C for one month. In some cases the silica tubes were opened after the initial treatment at 1 000°C and the content transferred to a new tube for annealing at 800°C. The annealed alloys were cooled with the furnace and then examined by X-rays.

Alloys richer in titanium than $TiSe_{1.10}$ were difficult to equilibrate by this method, and different techniques were tried. The reaction mixture was first heated at 400 to 500°C until selenium could no longer be observed and then transferred to a carbon resistance (Tammann) furnace. Heating for one hour at about 1 250°C was tried without success, and finally a heating for 3 to 5 min at about 1 500°C was adopted. To prevent the silica tubes from collapsing at this temperature, argon gas at a pressure of 10 to 12 cm Hg was let into the tubes before sealing them off. The samples were cooled to about 1 100°C with the furnace and then quenched in ice-water to avoid cracking of the silica tubes. The further treatment was as described above.

The titanium-rich samples were sintered products with greyish, metallic luster. With increasing selenium content the color changed to violet. The only titanium-rich alloy that was partly melted after heating to 1 500°C was $TiSe_{0.60}$. Single crystals were present in some of the alloys.

X-ray powder photographs were taken of all samples at about 20°C in 11.48 cm diameter cameras with asymmetric film mounting using iron radiation. The lattice constants are expressed in Å units on the basis of $\lambda FeK\alpha_1 = 1.93597$ Å. The probable error in the lattice constants is estimated to be 0.02 % for the hexagonal structures, and 0.04 % for the monoclinic structure. Lattice constants taken from earlier investigations have been transformed from kX to Å by multiplication by the factor 1.00202.

Density determinations were carried out at 25°C in a pycnometer that could be filled with kerosene under vacuum. Approximately 2 g of substance were used in each experiment. The standard error in the density measurements is estimated to be of the order of 0.3 %.

RESULTS AND DISCUSSION

Samples in the range $TiSe_{0.60}$ to TiSe gave X-ray powder photographs showing the presence of a phase with structure different from what had been earlier reported by Ehrlich[1] and by Hahn and Ness[8] as major constituent. Although the structure was of NiAs-like type, it showed considerable line splitting, indicating lower symmetry than hexagonal. No other phases were observed in the $TiSe_{0.95}$ samples, whether they had been heat-treated at 800 or 600°C, while both $TiSe_{0.60}$ and TiSe were two-phase preparations. The photographs of $TiSe_{0.60}$ contained many weak lines that were not from metallic titanium, and thus perhaps from a sub-selenide of titanium. The origin of these lines has not been pursued further, the attention being primarily focused on the range $TiSe_{0.95}$ to $TiSe_2$. Only small differences between the X-ray photographs of samples heated at 800 and 600°C were observed in most cases; only for $TiSe_{1.05}$, $TiSe_{1.40}$ and $TiSe_{1.60}$ marked influences of temperature were noted (see below).

TiSe was found to contain some lines from a structure of the NiAs-type, in addition to those from the lower symmetric structure, and the composition of the lower symmetric phase should thus be close to $TiSe_{0.95}$. Its range of homo-

geneity is probably rather narrow, since there are only slight shifts in the positions of the X-ray reflections. A reservation with regard to its composition must be made, however, as the titanium selenides in this composition range are rather reactive and easily oxidizable. A slight reaction with the sintered alumina crucibles, which contain about 0.5 % of silica, would lower the titanium content of the titanium selenides, due to the formation of compounds between titanium, silicon, aluminum and oxygen. The composition of the titanium selenide phase in $TiSe_{0.95}$ might thus be closer to TiSe. With this reservation, the phase is provisionally designated as *the* $TiSe_{0.95}$-*phase*.

Attainment of equilibrium in the TiSe-range was rather difficult to achieve. This was apparent from the fact that the slight differences between powder photographs obtained of samples heated at 1000 and 800°C persisted after the 600°C heat-treatment. The results obtained for the 600°C series were thus in some cases dependent upon the previous history of the sample and corresponded to those obtained by the original heat-treatment at 1000°C for the titanium-rich samples. In this series $TiSe_{1.05}$ was found to be a one-phase preparation with a hexagonal structure of the NiAs-type. At the composition $TiSe_{1.10}$ a two-phase region was again observed, and the composition of the phase with NiAs-type structure thus lies around $TiSe_{1.05}$. This phase will be called *the* $TiSe_{1.05}$-*phase* until its unit cell content can be more precisely determined. In the 800°C series this phase was not present except as one constituent of the $TiSe_{1.10}$ sample. This indicates that the $TiSe_{1.05}$-phase is only stable at higher temperatures. At the composition $TiSe_{1.20}$ a single phase is again observed, with cell dimensions gradually changing with composition. Its upper limit is close to the composition $TiSe_{2.00}$, in agreement with the results by Ehrlich. This phase will be called *the* $TiSe_{1.20-2.00}$-*phase*. At higher selenium contents elemental selenium was observed. Each of the three intermediate phases will now be discussed in more detail.

The $TiSe_{0.95}$-*phase*. Small crystals of the $TiSe_{0.95}$-phase were found in a sample that had been heated at about 1500°C for 5 min. By means of oscillation and Weissenberg photographs the symmetry was found to be orthorhombic. The unit cell dimensions were more accurately determined from powder photographs, and found to be:

$$a = 6.222 \text{ Å}, \quad b = 3.494 \text{ Å}, \quad c = 6.462 \text{ Å}.$$

This refers to a sample of $TiSe_{0.95}$ that had been annealed at 800°C for one week. Powder photograph data for this compound are listed in Table 1.

Small variations in lattice constants due to the heat treatment were noted, as can be seen from the values listed in Tables 2 and 3 for the 800°C and 600°C series, respectively. The differences between the values for $TiSe_{0.60}$ and $TiSe_{0.95}$ are within the limits of error, indicating that the titaniumrich limit of the phase is above $TiSe_{0.95}$. The TiSe-samples show lattice constants that differ somewhat from those of $TiSe_{0.95}$, and also the presence of small amounts of another phase. Thus it can be concluded that the phase has a narrow range of homogeneity between the composition $TiSe_{0.95}$ and $TiSe_{1.00}$.

The unit cell was assumed to contain four TiSe formula units, which require a density of 5.997 g cm^{-3}. The observed density of TiSe, 5.80 g cm^{-3}, was considered to agree well with the calculated value in view of the reactivity of

Table 1. Powder photograph data of TiSe$_{0.95}$ taken with iron radiation, a_2 and β-lines omitted.

$\sin^2\Theta \times 10^4$	I_{obs}	hkl	I_{calc}	$\sin^2\Theta \times 10^4$	I_{obs}	hkl	I_{calc}
—	—	101	1.2	6285	vw	501	3.4
911	vw	002	5.5	6552	st —	314	13
—	—	200	0.4	—	—	205	2.6
—	—	110	0.8	—	—	115	2.7
—	—	102	0.9	6676	st	{413	15
1201	st	201	55			024	11
1244	vst	111	100	6816	vw	510	4.1
1680	w	012	8.5	6921	vw	124	3.0
1874	st	202	32	—	—	420	1.0
1918	vst	112	72	—	—	502	0.4
1970	m	211	22	7053	w +	511	10
2272	w	103	17	—	—	130	0.0
2420	w(+ β)	301	7.9	7178	w +	421	10
—	—	212	0.8	7282	vw	323	3.4
2955	st	310	27	7358	w +	131	10
3003	vw	203	6.7	7386	st	215	17
3042	m	113	18	—	—	404	0.1
3081	m	{020	20	—	—	224	0.0
		302	1.7	7723	vw	512	2.0
—	—	311	0.3	—	—	032	1.5
—	—	121	0.1	7847	vw	{305	2.4
3610	w	004	8.6			422	2.9
—	—	213	0.1	8058	m	132	16
3858	m	{104	2.4	—	—	503	0.1
		312	10	—	—	006	0.1
—	—	400	0.8	—	—	414	1.6
—	—	022	1.2	—	—	106	0.5
—	—	220	1.0	—	—	315	0.8
4113	w +	401	8.8	—	—	600	1.9
4204	vw	{303	2.4			{513	7.0
		122	0.2	8869	st	224	0.0
4279	m	221	14			016	13
4376	w —	014	2.6	8926	vw	{033	0.0
—	—	204	0.0			125	5.3
—	—	114	0.6	8963	st	{601	2.6
4773	vw	402	1.5			423	17
4867	vw	411	2.8	9080	st	{206	4.6
4955	st —	{222	13			330	18
		313	0.0	9121	m	116	12
5347	m —	{123	6.8	9165	m	133	15
		214	1.0	9345	m	{331	0.0
5504	w +	321	4.2			521	14
—	—	412	0.4	—	—	405	2.0
5779	w	304	2.6	9611	st	602	3.1
—	—	105	1.7	9645	st(+ a_2)	{504	2.5
5908	w +	403	5.2			225	16
6071	m	223	5.4	9705	w	611	9.7
6153	vw	322	2.2	—	—	216	6.4

Table 2. Lattice constants of the titanium selenides after annealing for one week at 800°C.

Composition	$a\ (b\sqrt{3})$ in Å	b in Å	c in Å	β
TiSe$_{0.60}$	6.222	3.494	6.462	(90°)
TiSe$_{0.95}$	6.222	3.494	6.462	(90°)
TiSe$_{1.00}$	{ 6.223	3.488	6.469	(90°)
	{ (6.18)	3.57	6.21	(90°)
TiSe$_{1.05}$	(6.185)	3.571	6.189	(90°)
TiSe$_{1.10}$	{ (6.185)	3.571	6.30	(90°)
	{ (6.185)	3.571	6.21	(90°)
TiSe$_{1.20}$	(6.187)	3.572	6.195	(90°)
TiSe$_{1.30}$	6.378	3.564	2 × 6.012	90.92°
TiSe$_{1.40}$	6.353	3.572	2 × 6.006	90.61°
TiSe$_{1.50}$	(6.226)	3.598	5.989	(90°)
TiSe$_{1.60}$	—	—	—	(90°)
TiSe$_{1.70}$	(6.185)	3.571	5.992	(90°)
TiSe$_{1.80}$	(6.163)	3.558	5.992	(90°)
TiSe$_{1.90}$	(6.144)	3.547	5.997	(90°)
TiSe$_{2.00}$	(6.126)	3.537	6.005	(90°)

Table 3. Lattice constants of the titanium selenides after annealing for one month at 600°C.

Composition	$a\ (b\sqrt{3})$ in Å	b in Å	c in Å	β
TiSe$_{0.60}$	6.223	3.485	6.469	(90°)
TiSe$_{0.95}$	6.222	3.494	6.467	(90°)
TiSe$_{1.00}$	{ 6.223	3.488	6.469	(90°)
	{ (6.18)	3.57	6.30	(90°)
TiSe$_{1.05}$	(6.185)	3.571	6.301	(90°)
TiSe$_{1.10}$	{ (6.185)	3.571	6.30	(90°)
	{ (6.185)	3.571	6.21	(90°)
TiSe$_{1.20}$	(6.185)	3.571	6.188	(90°)
TiSe$_{1.30}$	6.389	3.561	2 × 5.995	90.83°
TiSe$_{1.40}$	(6.235)	3.600	5.987	(90°)
TiSe$_{1.50}$	(6.228)	3.596	5.979	(90°)
TiSe$_{1.60}$	(6.185)	3.571	5.983	(90°)
TiSe$_{1.70}$	(6.171)	3.563	5.985	(90°)
TiSe$_{1.80}$	(6.154)	3.553	5.990	(90°)
TiSe$_{1.90}$	(6.135)	3.542	5.994	(90°)
TiSe$_{2.00}$	(6.126)	3.537	6.002	(90°)
TiSe$_{2.50}$	(6.130)	3.539	5.999	(90°)

the sample. It was not felt that the observed densities could give more reliable informations about the stoichiometry and unit cell content of the TiSe$_{0.95}$-phase.

The structure of TiSe$_{0.95}$ was obviously NiAs-like and closely related to that of FeAs[12] and MnP[13]. When choosing the axial orientation as above, so that the relationship with the NiAs-type structure is clearly brought out, the missing reflections are $hk0$ when $h + k = 2n + 1$, and $0kl$ when $l = 2n + 1$. The highest symmetric space group is thus *Pcmn* (D_{2h}^{16}). In this space group

Table 4. Interatomic distances in the structure of $TiSe_{0.95}$ (in Å).

Ti — Se = 2.52	Ti — 2 Ti = 3.21	Se — 2 Se = 3.48
Ti — 2 Se = 2.56	Ti — 2 Ti = 3.49	Se — 2 Se = 3.49
Ti — 2 Se = 2.70	Ti — 2 Ti = 4.00	Se — 4 Se = 3.59
Ti — Se = 2.78	Ti — 2 Ti = 4.43	Se — 2 Se = 3.89
		Se — 2 Se = 4.14

the NiAs-type structure is realized by placing all atoms in the fourfold positions $x,1/4,z$; $\bar{x},3/4,\bar{z}$; $1/2+x, 3/4, 1/2-z$; $1/2-x,1/4,1/2+z$; with $x_1 = 1/4$ and $z_1 = 0$ for the metal atoms and $x_2 = 7/12$ and $z_2 = 1/4$ for the non-metal atoms. For complete superposition the origin has to be translated to $1/4,1/4,0$.

Intensities of the reflections were calculated using the formula

$$I = \text{const} \times F^2 \times Lp \times \nu$$

The best agreement between calculated and observed intensities was obtained with $x_{Ti} = 0.19$, $z_{Ti} = 0.01$, $x_{Se} = 0.58$ and $z_{Se} = 0.22$. The results of the calculations are listed in Table 1, with the intensity of the strongest reflection adjusted to 100.

The interatomic distances calculated for this structure are listed in Table 4, and a projection of the structure on (010) is shown in Fig. 1. As can be seen, the regular octahedral arrangement of metal atoms around the non-metal atoms, characteristic of the NiAs-type structure is distorted with half of the selenium atoms being definitely closer to the titanium atom than the rest. No strong titanium-titanium bonds are present in this structure, as evidenced by the shortest distance being 3.21 Å.

The $TiSe_{1.05}$-phase. As far as it can be judged from the X-ray powder photographs of samples heat-treated at 600°C, this phase has a hexagonal structure of the NiAs-type with lattice constants:
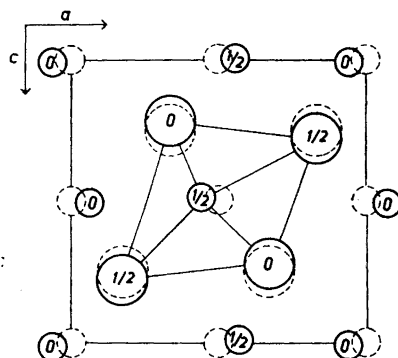
$a = 3.571$ Å, $c = 6.301$ Å.

Fig. 1. Projection of the orthorhombic TiSe-structure on (010). Fully drawn large circles indicate selenium atoms and small circles titanium atoms. Broken circles show ideal positions for a NiAs-type structure.

The powder photograph data are listed in Table 5. The density of this phase, as estimated from the observed values for TiSe and $TiSe_{1.10}$ given in Table 8, is 5.77 g cm^{-3}. The corresponding cell content is 1.88 Ti atoms and 1.97 Se atoms and indicates that the selenium positions are virtually completely occupied, while about 5 % of the titanium positions are empty.

The absence of superstructure reflections makes it reasonable to assume a certain randomness in the distribution of the vacancies, in accordance with observations made in other chalcogenide systems at about the same composition. Thus, Grønvold and Haraldsen [14] found no superstructure lines for iron sulfides with composition around $FeS_{1.10}$. The only extra reflections observed by Jellinek [15] for $CrS_{1.12}$ ("Cr_7S_8") were 001 and 111. Their presence were interpreted to mean that the vacancies on the metal lattice were confined to every other layer perpendicular to the c-axis. This conclusion presupposes that the chromium positions are 0,0,0 and 0,0,1/2 and the sulfur positions $\pm$ (1/3,2/3,1/4) exactly. This assumption, although probable, has not yet been verified.

The quality of the intensity data obtained for $TiSe_{1.05}$ precludes a decision between ordered and random distribution of the vacancies. Intensities have been calculated for two possibilities, one assuming random distribution of vacancies over the 0,0,0 and 0,0,1/2 positions, the other assuming all vacancies in one of these positions. The former alternative can be described in terms of the space group $C6/mmc$ (D_{6h}^4) with 1.9 Ti atoms in (a) 0,0,0; 0,0,1/2, and 2 Se atoms in (d) 1/3,2/3,3/4; 2/3,1/3,1/4, the latter in terms of the space group $C\bar{3}m1$ (D_{3d}^3) with 1 Ti atom in (a) 0,0,0, 0.9 Ti atoms in (b) 0,0,1/2 and 2 Se atoms in (d) 1/3,2/3,z; 2/3,1/3,$\bar{z}$, with $z = 1/4$. The intensities calculated for these two alternatives differ practically only in that reflections hhl for $l = 2n + 1$ are not completely extinct for the latter. They are found under the same heading I' in Table 5, and both are equally well in accord with the observed data since no such reflections were observed.

Table 5. Powder photograph data for $TiSe_{1.05}$, taken with iron radiation, and results of intensity calculations.

$\sin^2\Theta \times 10^4$	hkl	I_{obs}	I'	I''	$\sin^2\Theta \times 10^4$	hkl	I_{obs}	I'	I''
—	001	—	0.01	0	4878	202	6	5.9	5.8
945	002	3	1.9	1.1	—	113	—	0.00	0
—	100	—	0.2	0.8	—	005	—	0.00	0
1221	101	35	35	30	6048	203	4	3.3	2.7
1925	102	30	26	26	6718	114	12	11	10
—	003	—	0.00	0	—	210	—	0.02	0.08
2942	110	12	14	13	6881	105	3	3.4	2.8
3107	103	8	7.7	6.4	7089	211	10	6.8	5.7
—	111	—	0.01	0	—	204	—	0.02	0.08
3782	004	3	3.0	2.8	7803	212	10	11	11
3871	112	1	1.3	0.7	—	006	—	0.2	0.1
—	200	—	0.02	0.07	8816	300	5	8.2	7.7
4149	201	6	4.8	4.1	—	115	—	0.01	0
—	104	—	0.02	0.1	8980	213	10	11	9.2

The good overall agreement indicates, however, that the main features of the proposed structure are correct. In this structure each titanium atom is octahedrally surrounded by six selenium atoms at distances of 2.59 Å. Each titanium atom is further surrounded by two titanium atoms at a slightly shorter distance (3.15 Å) than in the orthorhombic $TiSe_{0.95}$-structure (3.21 Å).

The X-ray data obtained for the $TiSe_{1.05}$-phase showed striking similarities with the data for the Ti_3Se_2-phase reported by Hahn and Ness [10]. This phase had a hexagonal NiAs-like structure with unit cell dimensions $a = 3.574 \pm 0.005$ Å, $c = 6.322 \pm 0.005$ Å. On the basis of the observed density, 5.54 g cm^{-3}, Hahn and Ness concluded that the cell content was 2.4 Ti atoms and 1.6 Se atoms and stated that the calculated intensities of the X-ray reflections assuming 2 Ti atoms in 0,0,0 and 0,0,1/2, and 0.4 Ti + 1.6 Se atoms in $\pm$(1/3, 2/3,1/4) agreed so well with the observed data that the correctness of the proposed structure seemed ascertained. In our opinion this conclusion is unwarranted and the intensities calculated for this assumption — see column labelled I in Table 5 — are in no better agreement with the observed intensities than those for the two other alternatives, which both refer to a much higher selenium to titanium atom ratio.

A serious discrepancy apparently exists with regard to the composition of the titanium-rich selenides, and we assume that this must be sought in the methods of preparation. Certainly, the utmost care needs to be taken in order to avoid oxide and silicide formation of the samples. In the present research, turnings of "iodide" titanium were used in the reaction and the greatest care taken to keep the samples out of contact with air and moisture. Hahn and Ness [10] used titanium in the form of decomposed hydride (for which no analytical data was given). It seems to us that in the work by Hahn and Ness side reactions might have seriously reduced the amount of titanium available for selenide formation and increased the selenium content of the titanium selenides accordingly.

The $TiSe_{1.20-2.00}$-*phase.* At the composition $TiSe_{1.20}$ another phase with hexagonal structure is observed in pure state. The a-axis is equal to that for the $TiSe_{1.05}$-phase within the limits of experimental error, while the c-axis is about 2 % shorter. For $TiSe_{1.20}$ the c-axis is slightly below the value found in the two-phase region, indicating that $TiSe_{1.20}$ is within the homogeneity range of the phase. No superstructure reflections were seen on the powder photographs, but that does not prove their non-existence. Especially in the 600°C sample some ordering might be expected.

A pronounced change in the appearance of tbe X-ray photographs is seen from $TiSe_{1.20}$ to $TiSe_{1.30}$. The basic structure is no longer hexagonal but monoclinic, and the cell dimensions determined are listed in Tables 2 and 3 for samples annealed at 800 and 600°C, respectively. Powder photograph data for the 600°C series sample are given in Table 6. They indicate clearly a doubling of the c-axis. The dimensional changes for the a- and c-axes are so large from $TiSe_{1.20}$ to $TiSe_{1.30}$, see Fig. 2, that a two-phase region might be expected at lower temperatures.

From the composition $TiSe_{1.30}$ on, the unit cell dimensions change more regularly, but in a somewhat different way depending upon the heat treatment. For the 600°C series, the monoclinic deformation has disappeared already

Table 6. Powder photograph data of $TiSe_{1.30}$, 600°C series, taken with iron radiation, a_2- and β-lines omitted.

I_{obs}	$\sin^2\Theta \times 10^4$ obs	$\sin^2\Theta \times 10^4$ calc	hkl	I_{obs}	$\sin^2\Theta \times 10^4$ obs	$\sin^2\Theta \times 10^4$ calc	hkl
vw	819	803	011	w $-$	4120	4120	$\bar{2}22$
w	1054	1029	$\bar{1}11$	st	4140	4148	222
		1040	004	vw	4660	4656	$\bar{4}04$
		1037	111	w	4773	4768	404
w	1178	1164	$\bar{2}02$	m	4878	4886	$\bar{2}24$
w $+$	1204	1192	202	w	4948	4942	224
st	1238	1221	$\bar{1}12$	w $-$	5937	5932	$\bar{4}06$
w $-$	1249	1235	112	w $+$	6108	6100	406
w $-$	1340	1325	013	w	6197	6176	$\bar{2}26$
w $-$	1743	1729	211	w	6277	6260	226
w $-$	1887	1903	$\bar{2}12$	vw	6392	—	?
w $+$	1938	1930	$\bar{2}04$	w $-$	6710	6702	$\bar{5}12$
m	2005	1986	204	w $-$	6792	6772	512
		1994	$\bar{1}14$	st	6886	6890	$\bar{3}18$
m	2036	2022	114	m	7062	7058	318
vw	2100	2120	$\bar{3}01$	st	7133	7133	$\bar{1}32$
w $-$	2153	2140	301			7147	132
w $-$	2233	2222	$\bar{2}13$	m	7443	7453	$\bar{1},1,10$
vw	2629	2630	$\bar{3}03$	m	7497	7508	2,0,10
st	2808	2803	310	w	7612	7612	$\bar{4}24$
m	2970	2956	020	m	7728	7724	424
w	3216	3216	022	st	7932	7934	134
		3220	$\bar{2}06$	w	8264	8264	600
w $+$	3290	3291	$\bar{1}16$	vw	8612	—	?
		3304	206	st	8714	8716	$\bar{5}16$
w	3336	3333	116			8716	330
vw	3380	3394	$\bar{1}07$	m	8897	8888	$\bar{4}26$
w	3804	3802	$\bar{3}14$	w $+$	9045	9056	426
w	3884	3886	314	m	9188	9203	$\bar{1}36$
		3902	$\bar{4}02$	st	9245	9245	136
vw	3940	3958	402				
vw	3995	3996	024				

at the composition $TiSe_{1.40}$. The a-axis decreases steadily towards the composition $TiSe_{2.00}$, while the c-axis goes through a minimum in the range $TiSe_{1.50}$ to $TiSe_{1.60}$ with a very slight increase towards the limiting value for $TiSe_{2.00}$. For the 800°C series, the monoclinic deformation still exists at the composition $TiSe_{1.40}$, but $TiSe_{1.50}$ gives photographs showing a hexagonal structure only. At the composition $TiSe_{1.60}$ the structure is no longer of the simple hexagonal type. The powder photographs show considerable line splitting, indicating the presence of a phase with low-symmetric structure and perhaps more than one phase. Powder photograph data for the new structure are found in Table 7. By heating a sample showing this line splitting to 960°C and quenching it in ice-water the hexagonal structure is obtained, and it persists after heat-treatment for one month at 600°C. Similarly, a sample showing the low-
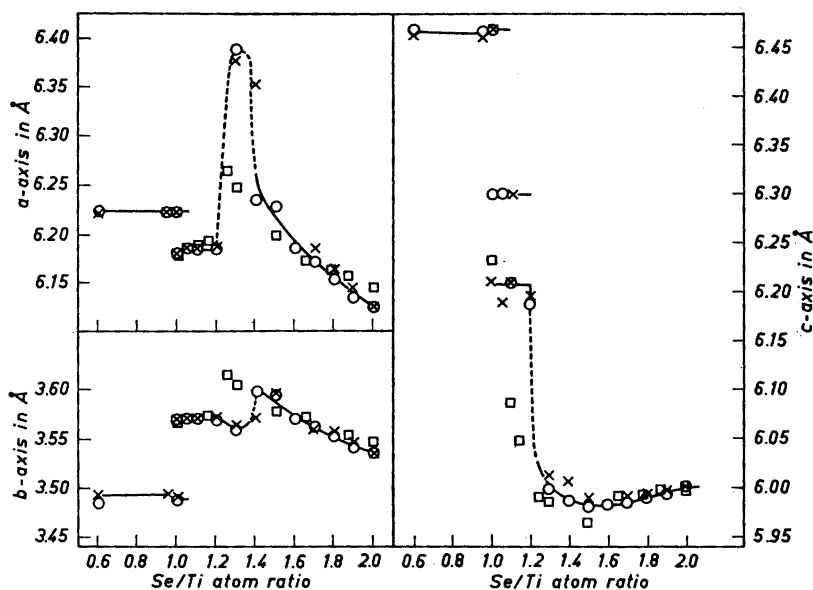
Fig. 2. Variations in lattice constants of titanium selenides as function of composition in the range $TiSe_{0.60}$ to $TiSe_{2.00}$. Results both for the 800°C series (×) and 600°C series (O) are shown, and likewise earlier results by Ehrlich (□). The slight monoclinic distortions for $TiSe_{1.30}$ and $TiSe_{1.40}$, and the doubling of the *c*-axis in that range are not shown. Added in proof: The circle coinciding with the cross for the *b*-axis at the composition $TiSe_{0.95}$ was inadvertently omitted.

symmetric structure before the 600°C annealing also shows it afterwards. This is another indication that true equilibrium is not attained at 600°C. In the composition range $TiSe_{1.70}$ to $TiSe_{2.00}$ only slight differences between the lattice constants determined for the two series of samples occur, and they are supposedly mainly due to variable success in preventing the samples from decomposing during heat-treatment and cooling. The results from the 600°C series are considered to be the most reliable.

A comparison of the present results with those obtained by Ehrlich[1] shows reasonable agreement in the range above $TiSe_{1.4}$, see Fig. 2. For samples richer in titanium the divergences with regard to the length of the *c*-axis are rather large and indicate close relationships between Ehrlich's $TiSe_{1.00}$ sample and the present $TiSe_{1.20}$ sample. The cell dimensions reported by McTaggart and Wadsley [11] for $TiSe_{1.5}$ ($a = 3.595$, $c = 5.994$ Å) and for $TiSe_2$ ($a = 3.535$, $c = 6.004$ Å) and those by Oftedal [2] for $TiSe_2$ ($a = 3.533$, $c = 5.995$ Å) agree well with those reported here. The powder photograph data presented by Hahn and Ness [10] for the TiSe-phase "1. Modifikation" indicate close relationships with our samples in the range $TiSe_{1.20}$ to $TiSe_{1.30}$. The length of the *c*-axis changes enormously with composition from $TiSe_{0.95}$ to $TiSe_{1.3}$ and lets us conclude that neither the $TiSe_{1.0}$ nor the $TiSe_{0.75}$ preparation by Hahn and Ness were richer in titanium than our $TiSe_{1.20}$. With regard to the "2. Modifikation" of

Table 7. Powder photograph data of $TiSe_{1.60}$, taken with iron radiation, a_2 and β-lines omitted.

I_{obs}	$\sin^2\Theta \times 10^4$	I_{obs}	$\sin^2\Theta \times 10^4$	I_{obs}	$\sin^2\Theta \times 10^4$
w	269	w	3364	st	7097
vw	320	w	3389	m	7181
vw	805	w	3951	w +	7485
m	1066	vw	4021	m	7557
v st	1248	w +	4146	st −	7796
vw	1777	m	4223	w	7911
vw	1918	w	4918	m	8692
m	2023	w	4953	st	9081
w	2051	w +	6190	m	9131
w	2065	w	6277	w	9217
st	2927	st	7034	m	9254
m	3328				

the TiSe-phase, the listed X-ray powder data show more resemblance to our data for $TiSe_{1.30}$ than for $TiSe_{1.00}$, the only two compositions for which a quadrupling of one of the axes ($4c = 25.8$ Å for $TiSe_{1.00}$, $4a = 25.6$ Å for $TiSe_{1.30}$) would give some agreement with the data by Hahn and Ness ($c = 27.4$ Å), but no conclusions can be reached at present.

Results of the density determinations are presented in Table 8 and in Fig. 3. Data were only obtained for samples heat-treated at 800°C. The observed values are in reasonable agreement with those calculated on the basis of subtraction of titanium atoms only with changing composition from Ti_2Se_2 to $TiSe_2$. It can be seen that the observed densities are considerably higher than those by Ehrlich, except for compositions close to $TiSe_2$, where the preparation of pure and well defined samples offers no special problems. The density value reported by McTaggart and Wadsley for $TiSe_2$ agrees with the theoretical value, while those for $TiSe_{1.5}$ and TiSe are low. Values reported by Hahn and Ness for two TiSe samples are also low. The discrepancies found by Ehrlich between observed

Table 8. Observed and calculated densities in g cm^{-3} for the titanium selenides. The atomic weight unit is taken to be 1.6602×10^{-23} g.

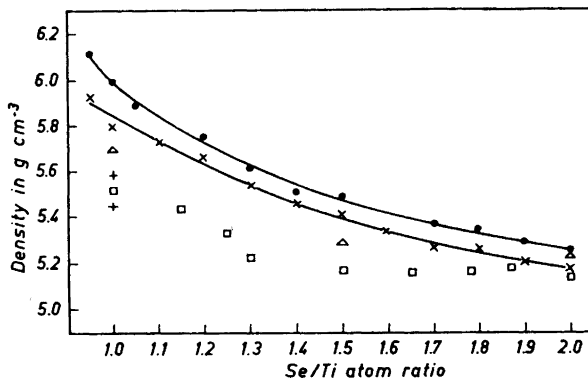| Sample	D_{obs}	D_{calc}	Sample	D_{obs}	D_{calc}
$TiSe_{0.95}$	5.93	6.116	$TiSe_{1.50}$	5.41	5.484
$TiSe_{1.00}$	5.80	5.997	$TiSe_{1.60}$	5.34	—
$TiSe_{1.05}$	—	5.848	$TiSe_{1.70}$	5.27	5.376
$TiSe_{1.10}$	5.73	—	$TiSe_{1.80}$	5.26	5.335
$TiSe_{1.20}$	5.66	5.758	$TiSe_{1.90}$	5.20	5.294
$TiSe_{1.30}$	5.54	5.622	$TiSe_{2.00}$	5.17	5.252
$TiSe_{1.40}$	5.45	5.514			

Fig. 3. Observed (×) and calculated (●) densities for titanium selenides heat-treated at 800°C. Earlier observed values by Ehrlich (□), McTaggart and Wadsley (△) and Hahn and Ness (+) are also shown.

and calculated densities for titanium selenides and tellurides $(D_{obs}/D_{calc} = 0.90$ for TiSe and 0.86 for TiTe) were interpreted by him [16] as caused by vacant lattice sites and due to the presence of strong "atomic bonds" between the metal atoms. In view of the data presented here this conclusion seems unwarranted, and the present authors ascribe the large differences between observed and calculated densities for the titanium selenides observed by earlier investigators as mainly due to experimental errors. It should also be remarked that for the iron selenides where the principle of both empty metal and non-metal positions was first thought to apply [5], the low density in the range around FeSe can be accounted for by the presence of the phase $FeSe_{0.96}$ with lower density.

The interatomic distances change comparatively little within the range of the $TiSe_{1.20-2.00}$-phase. In the range $TiSe_{1.30}$ to $TiSe_{1.40}$ some distortion of the octahedral arrangement around the titanium atoms apparently takes place, and further work is needed to clear up the details. It is expected, however, that the deformation of the structures are closely related to those for $NiSe_{1.25}$[17] and Cr_3S_4 [15]. For $TiSe_{1.20}$, $TiSe_{1.50}$ and $TiSe_{2.00}$ the following interatomic distances are found, see Table 9.

Table 9. Interatomic distances in the structures of $TiSe_{1.20}$, $TiSe_{1.50}$ and $TiSe_{2.00}$ (in Å).

$TiSe_{1.20}$	$TiSe_{1.50}$	$TiSe_{2.00}$
Ti — 6 Se = 2.58	Ti — 6 Se = 2.56	Ti — 6 Se = 2.54
Ti — 1.3 Ti = 3.09	Ti — 0.7 Ti = 2.99	—
Se — 5 Ti = 2.58	Se — 4 Ti = 2.56	Se — 3 Ti = 2.54
Se — 6 Se = 3.57	Se — 6 Se = 3.60	Se — 6 Se = 3.54
Se — 6 Se = 3.69	Se — 6 Se = 3.64	Se — 6 Se = 3.63

The titanium-selenium distances decrease with increasing selenium content as is expected due to the lowering of the number of coordinated titanium atoms around selenium. Using the metallic radii derived by Pauling [18], the following radius sums ($r_{Ti} + r_{Se}$) are obtained: $TiSe_{1.20}$, $1.377 + 1.286 = 2.663$ Å; $TiSe_{1.50}$, $1.377 + 1.257 = 2.634$ Å; $TiSe_{2.00}$, $1.377 + 1.219 = 2.596$ Å. For TiSe the expected distance for six-coordination would be $1.377 + 1.31 = 2.687$ Å, while the average distance in the $TiSe_{0.95}$-phase is 2.63 Å, and the distances in the $TiSe_{1.05}$-phase are 2.59 Å. The shorter distances observed in all cases might indicate a metallic valence higher than four for titanium.

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