

On the Arsenides and Antimonides of Niobium

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The phase relationships in the systems niobium-arsenic and niobium-antimony have been studied by X-ray methods. Density determinations and magnetic susceptibility measurements have been carried out. Three new, intermediate phases have been identified:

1. NbAs_2 , with monoclinic structure, $a = 9.357 \text{ \AA}$, $b = 3.3823 \text{ \AA}$, $c = 7.792 \text{ \AA}$, $\beta = 119.46^\circ$. The pycnometric density is 7.41 g cm^{-3} at 25°C . The unit cell contains four formula units and the possible space groups are $C2$, Cm , and $C2/m$.

2. Nb_3Sb_4 , with tetragonal Ti_3Te_4 type structure, $a = 10.314 \text{ \AA}$, $c = 3.5566 \text{ \AA}$. The pycnometric density is 8.17 g cm^{-3} at 25°C .

3. NbSb_2 , with monoclinic structure, $a = 10.239 \text{ \AA}$, $b = 3.6319 \text{ \AA}$, $c = 8.333 \text{ \AA}$, $\beta = 120.07^\circ$. The pycnometric density is 8.22 g cm^{-3} at 25°C . The unit cell contains four formula units and the possible space groups are $C2$, Cm , and $C2/m$.

The lattice dimensions and observed densities of the NbAs and Nb_3Sb phases are:

NbAs , $a = 3.4517 \text{ \AA}$, $c = 11.680 \text{ \AA}$, $d_{\text{pycn}} = 7.93 \text{ g cm}^{-3}$

Nb_3Sb , $a = 5.2643 \text{ \AA}$, $d_{\text{pycn}} = 8.83 \text{ g cm}^{-3}$

The NbAs , NbAs_2 , and NbSb_2 phases have diamagnetic susceptibilities, whereas the Nb_3Sb and Nb_3Sb_4 phases show weak temperature-independent paramagnetism.

When this investigation was started the existence of only one niobium arsenide (with composition $\text{NbAs}_{1.80}$) had been described in the literature.¹ Studies of this system have, however, since then been independently carried out by Boller and Parthé² and the present authors.³ As a result of these studies the crystal structure of NbAs is now known.

The existence of a niobium antimonide phase, *i. e.* the Nb_3Sb phase, has been reported by Matthias *et al.*⁴, Wood *et al.*⁵, and Nevitt.⁶

EXPERIMENTAL

Materials. The niobium metal used in this study was "Spectrographically standardized niobium" from Johnson, Matthey & Co., Ltd. Two batches of this niobium (here called I and II) were used. According to the supplied analysis niobium I contained 250 ppm of Ni and traces of Cu, Ag, Ti, Fe, and Si, whereas niobium II contained (in ppm): Fe (500), Si (100), Pb (80), Mg (2), Mn (1), and Ta (100). Niobium II, which originally con-

tained $\text{NbH}_{0.69}$, had been dehydrogenated⁷ in vacuum, but contained nevertheless traces of hydrogen.

The metallic arsenic was delivered by American Smelting and Refining Co. and reported to contain 99.999 % arsenic. The only reported impurities were a very faint trace of Cu and Pb. The high purity antimony from Bradley Mining Co., San Francisco, contained (in ppm): As (10), Cu (3), Fe (3), and Pb (2).

Preparation. The samples were prepared by heating accurately weighed quantities of niobium and arsenic or antimony, respectively, in evacuated and sealed silica tubes. In some cases crucibles of pure alumina were placed inside the silica tubes.

Samples with composition 20.00, 25.00, 33.33, 40.00, 50.00, 60.00, 66.67, and 75.00 atomic % As were made from niobium I and samples with 20.00, 25.00, 28.57, 33.33, 40.00, 44.44, 50.00, 55.56, 60.00, 66.67, and 75.00 atomic % As were made from niobium II. All samples were first heated at 1000°C for 2 days, then at 720°C for 14 days and finally quenched in ice water.

Samples with composition 20.00, 25.00, 33.33, 40.00, 50.00, 60.00, 66.67, and 75.00 atomic % Sb were made from niobium I and samples with 20.00, 25.00, 28.57, 33.33, 40.00, 44.44, 50.00, 55.56, 60.00, 66.67, and 75.00 atomic % Sb were made from niobium II. These samples were first heated at 1000°C for 2 days then at 800°C for 14 days and finally quenched in ice water. A similar series of niobium (II) antimonide samples was slowly cooled from 800°C to room temperature over a period of 30 days. Niobium (II) antimonides containing 16.67, 20.00, 25.00, 33.33, 38.46, and 40.00 atomic % Sb were melted in a carbon resistance (Nernst-Tammann) furnace at approximately 1350°C. (The temperature was measured with an optical pyrometer.) When the furnace reached the desired temperature, the sample was removed and quenched in water.

X-Ray diffraction. All samples were crushed and X-ray photographs were taken in a Guinier focusing camera of 80 mm diameter using strictly monochromatized $\text{CuK}\alpha_1$ radiation. X-Ray photographs were also taken in a Weissenberg camera with 57.3 mm diameter and in a Debye-Scherrer camera with 114.6 mm effective diameter and asymmetric film mounting.

For the calculation of lattice constants by the Guinier method, potassium chloride (Analar, The British Drug Houses Ltd., $a = 6.2919 \text{ \AA}$) was added to the specimen as an internal standard. Lattice constants are expressed in Ångström units on the basis of $\lambda (\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$.

Density measurements. The density of the samples was determined by the pycnometric method 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.

Magnetic measurements. The magnetic susceptibilities were measured by the Gouy method at three different maximum field strengths ($H_{\text{Max}} = 4015, 4700, \text{ and } 5110 \text{ O}$). The samples were filled in evacuated and sealed Pyrex tubes of 3 mm internal diameter and to a height of about 85 mm.

RESULTS

A. Niobium arsenides

In the niobium-arsenic system two intermediate phases, *i.e.* the NbAs phase and the NbAs₂ phase, were identified. The specific volume *versus* weight % As, *cf.* Fig. 1, had breaks in the linearity at these compositions.

By inspection of the curve, the presence of a third phase with an approximate composition Nb₃As might be suggested. This interpretation is impeded, however, by an interfering reaction between niobium and silica for metal content higher than ~50 atomic % Nb. (The disturbing reaction with silica could be avoided by use of the hydrogen-free niobium I. In this case, however, the samples did not reach equilibrium, probably because of too large particle size of niobium I. Experiments showing the importance of the particle size

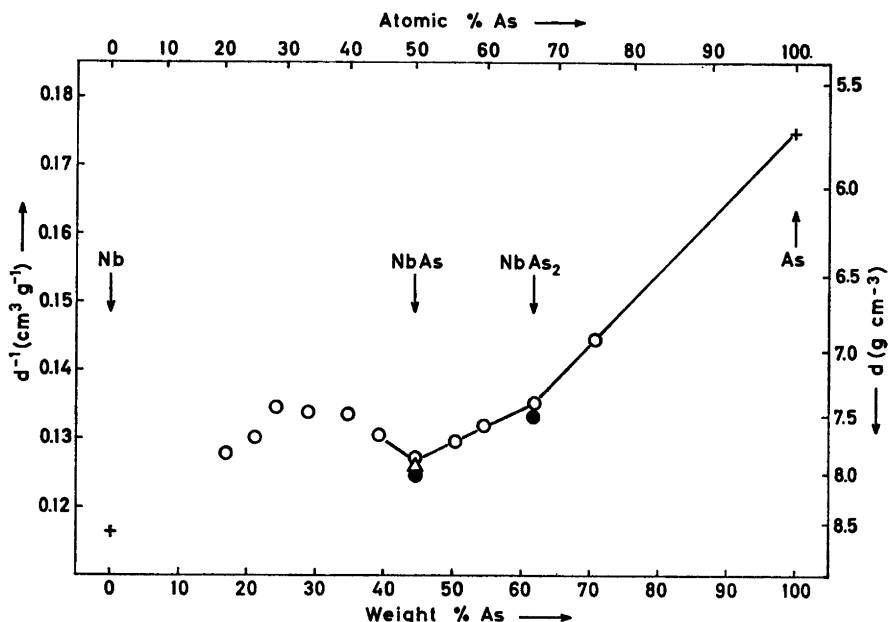


Fig. 1. Reciprocal densities as function of composition for niobium-arsenic samples quenched from 720°C (O). The density of NbAs (Δ) prepared by thermal decomposition of NbAs₂ at 1100°C and the densities of NbAs and NbAs₂ (●) calculated from the X-ray data are included.

of the niobium metal in the reaction have been carried out and will be published in a forthcoming paper.) Most samples in this concentration range contained a mixture of three phases, *i.e.* the NbAs phase, the NbO phase and the Nb₅Si₃ phase.⁹ (The NbO and Nb₅Si₃ phases have lower densities than the Nb and NbAs phases and may thus provide a qualitative explanation of the first decrease in density below 44.64 weight % As (50 atomic % As) in Fig. 1.) Guinier photographs of some samples contain reflections from a yet unidentified phase (different from SiO₂ (see section B), Nb, NbO, Nb₅Si₃, NbAs, and NbAs₂). It was unfortunately rather difficult to obtain consistent, reproducible results. Before any conclusive statements can be given a new investigation with pure hydrogen-free niobium has to be undertaken for arsenic content < 50 atomic % As.

The NbAs phase. Guinier photographs of the NbAs phase were indexed on the basis of a tetragonal unit cell, *cf.* Table 1. The lattice constants of the sample with composition NbAs are found in Table 2, together with the lattice constants of the NbAs phase from samples where NbAs is in equilibrium with other phases. The lattice dimensions being approximately constant show that the homogeneity range must be rather narrow. The unit cell dimensions given by Boller and Parthé,² included in Table 2, are in perfect agreement with the values found in this study.

Table 1. Guinier photograph data of NbAs taken with strictly monochromatized $\text{CuK}\alpha_1$ -radiation.

I_{obs}	$\sin^2\Theta \times 10^5$		hkl	I_{obs}	$\sin^2\Theta \times 10^5$		hkl
	obs	calc			obs	calc	
st	5 414	5 414	101	m	28 798	28 812	213
st	6 958	6 962	004	m	35 778	35 772	215
vst	8 893	8 894	103	m	39 838	39 836	220
vst	11 701	11 698	112	w	40 250	40 209	109
vst	15 859	15 854	105	vw	45 208	45 249	301
st	19 923	19 918	200	m	46 208	46 212	217
w	25 329	25 331	211	w	46 808	46 795	224
m	26 303	26 296	107	w	47 758	47 758	208
m	26 874	26 880	204	w	48 726	48 733	303
w	27 854	27 840	008				

Table 2. Lattice constants of the NbAs phase.

Sample	a (Å)	c (Å)	c/a
NbAs ^a	3.4517	11.680	3.3838
NbAs ^b	3.4523	11.677	3.3824
Nb ₂ As ^c	3.4521	11.676	3.3822
NbAs _{1.25} ^c	3.4518	11.676	3.3826
NbAs ^d	3.45 ₂	11.67 ₉	3.38 ₄

^a Thermal decomposition of NbAs₂ at 1100°C. ^b Thermal decomposition of NbAs₂ in a carbon resistance furnace at 1300°C. ^c Quenched from 720°C. ^d Quoted from Boller and Parthé.²

As the reaction between niobium and silica was noticed already at a concentration of ~ 54.5 atomic % As, we could not at this stage distinguish between a sharp stoichiometric or slightly non-stoichiometric composition. Some samples of the NbAs phase were therefore made by thermal decomposition of NbAs₂. The residual crystalline phase was found to contain only NbAs after complete degradation at 1100°C.

The composition NbAs was ascertained by density measurements. The pycnometric densities of NbAs prepared by direct synthesis and thermal decomposition of NbAs₂ were 7.83 and 7.93 g cm⁻³, respectively, in close agreement with the density 8.01 g cm⁻³ calculated for NbAs_{1.00} from the X-ray data (assuming four ($Z_c = 3.96$) NbAs-groups per unit cell). Further evidence of the composition NbAs_{1.00} is obtained through the structure determination.^{2,3}

Missing reflections on the photographs were:

- hkl when $h + k + l = 2n + 1$
 hkl when $2k + l = 2n$ or $4n + 1$
 $0kl$ when $(k + l = 2n + 1)$
 hhl when $(2h + l = 2n$ or $4n + 1)$

The space group is $I4_1$ or $I4_1md$. The crystal structure of NbAs has been discussed previously.^{2,3} (A projection of the NbAs structure is shown in Fig. 4 for comparison with the Ti_5Te_4 type structure of Nb_5Sb_4 . In either of the two space groups 4Nb are in (a) with $z = 0$, and 4As are in (a) with $z = 0.416 \pm 0.001 \approx 5/12$.)

The NbAs₂ phase. Guinier photographs of the NbAs₂ phase were indexed as monoclinic, cf. Table 3. The lattice constants of NbAs₂ are listed in Table 4 together with the lattice constants of the NbAs₂ phase for the samples NbAs_{1.25} and NbAs₃ with NbAs₂ in equilibrium with NbAs and As, respectively. The homogeneity range of the NbAs₂ phase is rather narrow, according to the almost invariable unit cell dimensions.

Table 3. Guinier photograph data of NbAs₂ taken with strictly monochromatized $CuK\alpha_1$ -radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
w	1 291	1 289	001	w	21 161	21 183	31 $\bar{4}$
m	2 754	2 753	20 $\bar{1}$	m	21 471	21 508	203
w	3 572	3 576	200	m	22 127	22 129	51 $\bar{2}$
w	4 502	4 508	20 $\bar{2}$	w	22 454	22 477	11 $\bar{4}$
vw	5 151	5 155	002	w	23 497	23 491	22 $\bar{1}$
w	6 076	6 078	110	vw	24 323	24 317	220
vw	6 309	6 312	11 $\bar{1}$	w	24 687	24 665	60 $\bar{2}$
vst	8 419	8 423	111	w	25 223	{ 25 240	20 $\bar{5}$
m	8 836	8 841	20 $\bar{3}$			{ 25 249	22 $\bar{2}$
st	9 128	9 123	11 $\bar{2}$	vw	25 402	25 408	40 $\bar{5}$
st	11 014	11 011	40 $\bar{2}$	vw	27 040	27 039	51 $\bar{4}$
st	11 361	{ 11 351	31 $\bar{1}$	w	27 141	27 132	60 $\bar{1}$
st	11 600	{ 11 367	40 $\bar{1}$	w	27 464	27 463	604
st	11 600	11 599	003	w	27 546	27 530	510
m	12 053	12 051	31 $\bar{2}$	w	27 889	27 901	402
st	13 228	{ 13 229	310	m	29 591	{ 29 582	22 $\bar{3}$
m	13 337	{ 13 233	40 $\bar{3}$			{ 29 616	31 $\bar{5}$
m	13 337	13 345	11 $\bar{2}$	m	31 768	31 752	42 $\bar{2}$
m	14 292	14 300	400	w	32 171	32 176	600
m	14 500	14 511	11 $\bar{3}$	m	32 343	32 340	023
st	15 330	15 328	31 $\bar{3}$	w	32 719	32 728	60 $\bar{5}$
w	15 731	15 751	204	m	33 982	33 974	423
w	19 791	19 812	401	m	34 093	34 097	511
st	20 745	20 741	020				

Table 4. Lattice constants of the NbAs₂ phase (in samples quenched from 720°C).

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
NbAs _{1.25}	9.356	3.3824	7.792	119.44
NbAs ₂	9.357	3.3823	7.792	119.46
NbAs ₃	9.357	3.3827	7.792	119.45

The observed density of NbAs₂, 7.41 g cm⁻³, indicates that the unit cell contains four ($Z_c = 3.96$) NbAs₂-groups. The calculated density of NbAs₂ from the X-ray measurements is 7.50 g cm⁻³.

The systematic extinctions were of the type:

hkl absent when $h + k = 2n + 1$

$h0l$ absent when $l = 2n + 1$

$0k0$ absent when $k = 2n + 1$

Characteristic space groups are accordingly $C2$, Cm , and $C2/m$.*

* Note added in proof. While this article has been in press an independent confirmation of the existence of the NbAs and NbAs₂ phases has been published by Saini *et al.*²³ Their lattice dimensions and observed densities are:

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°) or <i>c/a</i>	d_{obs} (g cm ⁻³)
NbAs	3.453 ± 0.002		11.672 ± 0.005	3.380	8.11
NbAs ₂	9.354 ± 0.002	3.381 ± 0.002	7.799 ± 0.002	119.43 ± 0.08	7.01

B. Niobium antimonides

In the niobium-antimony system the existence of two new, intermediate phases was established, *i.e.* the Nb₅Sb₄ phase and the NbSb₂ phase. Furthermore, the existence of the previously described⁴⁻⁶ Nb₃Sb phase was confirmed.

The results of density measurements of two series of alloys for phase analysis are shown in Fig. 2. The specific volume *versus* weight % Sb plot had breaks in the linearity at compositions corresponding to NbSb₂ and \sim Nb₃Sb. The results from the two series did not differ much, *cf.* Fig. 2.

An inspection of the Guinier photographs of these alloys showed that the samples contained phases which did not belong to the niobium-antimony system. For samples with composition ≤ 60 atomic % Sb crystallization of the silica tubes was noticed. Samples with antimony content ≤ 50 atomic % Sb contained furthermore two more phases, *i.e.* the NbO phase and the Nb₅Si₃ phase. The disturbing reactions with silica leading to these phases could best be reduced by placing the alloys in alumina crucibles inside the silica tubes, or by use of niobium I. (Samples containing niobium I did not reach equilib-

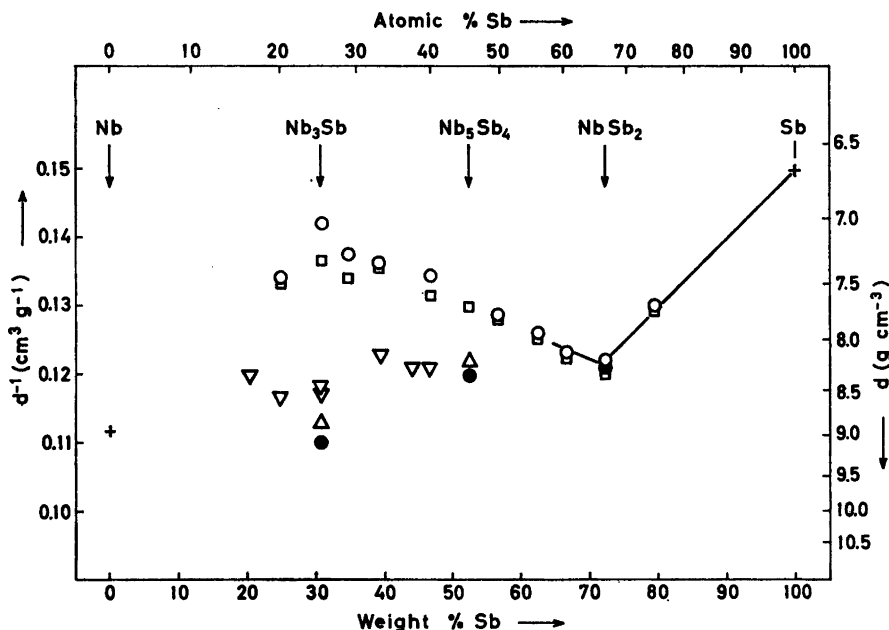


Fig. 2. Reciprocal densities as function of composition for two series of niobium-antimony samples quenched (O) and slowly cooled (□) from 800°C and one series synthesized in carbon resistance furnace (▽) at 1350°C. The densities of Nb₃Sb and Nb₅Sb₄ (Δ) prepared by thermal decomposition of NbSb₂ at 850 and 1000°C, respectively, and the densities of Nb₃Sb, Nb₅Sb₄, and NbSb₂ (●) calculated from the X-ray data are included.

rium.) To make the period of heating short the carbon resistance furnace was used when preparing the third series of alloys. As seen from Fig. 2 the densities of samples made according to this method differ considerably from the two previous series. However, the results are not entirely reproducible and the formation of foreign phases is not eliminated. The phase analytical work by density measurements has therefore failed to bring out the existence of other phases than the NbSb₂ phase.

The observed densities of the two first series of alloys are rather different from those calculated from the X-ray data. Our tentative explanation of these discrepancies is simple and instructive and will be briefly outlined here. The presence of small quantities of crystallized SiO₂, the NbO phase, and the Nb₅Si₃ phase with lower densities accounts for a density depression of the samples. The largest effect is due to the presence of silica which has a considerably lower density than the niobium antimonides.

A regular variation in the specific volume *versus* weight % Sb plot was noticed in Fig. 2. By inspection a correlation between the weight of niobium metal in the alloys and the density depression was observed. As seen from Fig. 3, ($d_{\text{calc}} - d_{\text{obs}}$) increases with increasing weight of niobium. As the largest

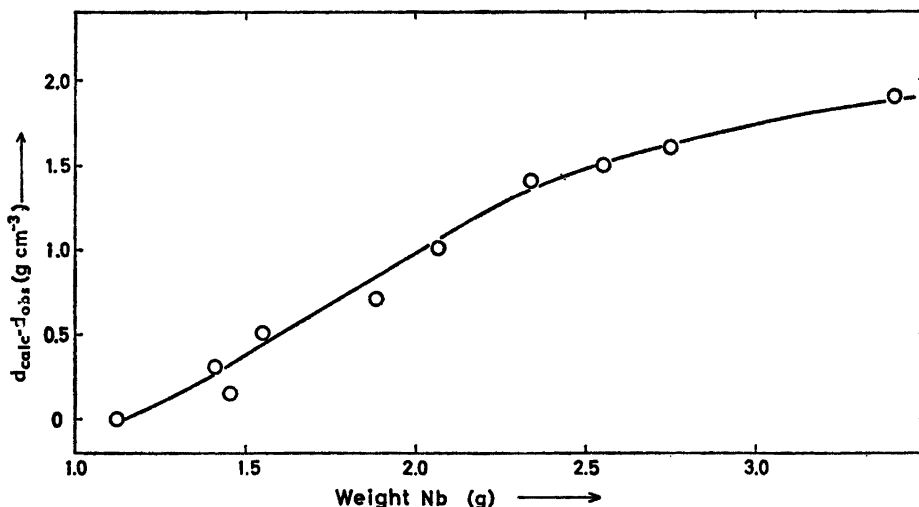


Fig. 3. The density depression ($d_{\text{calc}} - d_{\text{obs}}$) as a function of the total weight of niobium in the niobium-antimony samples prepared at 800°C.

contribution to the density depression is undoubtedly due to the presence of silica, it is suggested that the crystallization of silica is proportional to the amount of niobium. The simple proportionality is masked by the presence of the NbO and Nb₅Si₃ phases.

A corresponding observation was not made in the niobium-arsenic system (see p. 1182). The presence of crystallized SiO₂ could not be observed in the Guinier photographs of the niobium arsenides. This is consistent with observations¹⁰ from many other similar systems where it is found that the amount of crystallized SiO₂ also depends on the metalloïd component. The visible attack in silica tubes increases according to this observation from arsenic to antimony. Furthermore, the amount of niobium used to prepare the arsenides was almost constant (1.0–1.3 g) and also smaller than for the antimonides.

The Nb₃Sb phase. Guinier photographs of samples with antimony content less than 44 atomic % Sb showed the presence of a phase which could be indexed on the basis of a cubic unit cell. The lattice constants for two samples Nb₄Sb and Nb₂Sb are listed in Table 5. The indexed reflections are no doubt due to the Nb₃Sb phase. It was impossible to produce the samples free from the interfering SiO₂, NbO, and Nb₅Si₃ phases by heating the elements in the stoichiometric 3:1 ratio in silica tubes. This finding is in agreement with the previous reports⁴⁻⁶ on the Nb₃Sb phase.

Improved results were obtained when using alumina crucibles placed inside the silica tubes and short heat treatment in the carbon resistance furnace. However, the purest samples of the Nb₃Sb phase were obtained by thermal decomposition of the NbSb₂ phase. The residual dark grey powder prepared by complete degradation at 1000°C contained the Nb₃Sb phase and only

Table 5. Lattice constant of the Nb₃Sb phase.

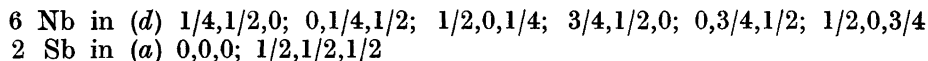
Sample	<i>a</i> (Å)	Method of preparation
Nb ₃ Sb	5.2643	Thermal decomposition of NbSb ₂ at 1000°C Al ₂ O ₃ crucibles and carbon resistance furnace Quenched from 800°C Quenched from 800°C
Nb ₃ Sb	5.2648	
Nb ₃ Sb	5.2649	
Nb ₃ Sb	5.2649	
Nb ₃ Sb	5.26	Quoted from Matthias <i>et al.</i> ⁴
Nb ₃ Sb	5.262 ± 0.002	Quoted from Wood <i>et al.</i> ⁵
Nb ₃ Sb	5.2621 ± 0.0003	Quoted from Nevitt ⁶

traces of Nb₅Sb₄, NbO, and Nb₅Si₃. The lattice constant of this sample is found in Table 5 together with the lattice constant of the sample Nb₃Sb prepared in the carbon resistance furnace and those of previous determinations.⁴⁻⁶ As the lattice constant is almost invariable as regards specimens with different initial proportions of the components and different method of preparation, no composition range of the Nb₃Sb phase is noticeable. The accordance with the previous values is reasonable although the present values fall beyond the limits of error given by Wood *et al.*⁵ and Nevitt.⁶

The pycnometric density of the sample prepared by thermal decomposition of NbSb₂ is 8.83 g cm⁻³. With a unit cell content of two (*Z*_c = 1.94) Nb₃Sb-groups the calculated density from the X-ray measurements is 9.11 g cm⁻³. Considering the small contamination of this sample the discrepancy of 3 % gives no reason to reject the stoichiometric formula Nb₃Sb.

The crystal structure of Nb₃Sb. Attempts to obtain single crystals of the Nb₃Sb phase were unsuccessful and the present examination like the previous ones⁴⁻⁶ was accordingly based on powder photograph data.

According to Matthias *et al.*⁴, Wood *et al.*⁵, and Nevitt⁶ Nb₃Sb should be listed among substances having β-W type structure. The β-W structure is described in space group *Pm3n* with:



Both Wood *et al.*⁵ and Nevitt⁶ have compared observed and calculated intensities and obtained comparatively good agreement. However, for some reflections the two of them found considerable disagreement and therefore concluded there to be a possibility of Nb₃Sb having another structure.

For this reason a new comparison of observed and calculated intensities of the reflections was carried out. The relative intensities of the reflections on the Debye-Scherrer photographs were determined from photometer recordings of the films. Multiple-film photographs were used to avoid errors in the estimation of the highest and weakest intensities on the photographs. Corrections for the resolution of *Kα*₁₋₂ doublets were carried out according to the method of Rae and Barker.¹¹

Table 6. Powder photograph data of Nb₃Sb taken with CuK-radiation, α_2 and β lines omitted.

$h^2+k^2+l^2$	I_{obs}	I_{calc}	$h^2+k^2+l^2$	I_{obs}	I_{calc}
2	1.6	1.8	24	0.0	0.1
4	25.8	27.1	26	0.5	0.4
5	54.1	60.1	29	15.0	13.0
6	51.5	59.2	30	13.0	11.7
8	0.3	0.3	32	11.4	10.2
10	0.4	0.4	34	0.5	0.2
12	4.4	3.5	36	9.1	8.1
13	13.9	12.6	37	5.5	5.0
14	30.6	29.6	38	20.8	21.3
16	12.5	10.2	40	0.4	0.2
18	0.4	0.3	42	0.7	0.4
20	9.0	8.4	44	7.2	6.2
21	12.7	11.8	45	37.2	34.9
22	8.6	7.4	46	48.6	50.7

The calculated values taken from Wood *et al.*⁵ are listed in Table 6 together with the present observed values. As can be seen from Table 6 the agreement between the two sets of values is very good, $R = \Sigma|I_{\text{calc}} - I_{\text{obs}}| / \Sigma I_{\text{obs}} = 0.095$, and leaves no doubt about the correctness of the proposed structure.

Even better agreement could have been obtained by applying absorption correction as seen from the systematic variation in $I_{\text{calc}} - I_{\text{obs}}$, *cf.* Table 6, from positive to negative with increasing Θ . Thus the absorption and temperature factors do not cancel in this case. An absorption correction should normally have been attempted, because the dimensions of the sample were not particularly small and its absorption large ($\mu_{\text{Nb}_3\text{Sb}} = 1720 \text{ cm}^{-1}$). Nevertheless this correction was not carried out as even the uncorrected set of I_{obs} removed the doubts of Wood *et al.*⁵ and Nevitt.⁶

One of the reasons for the better results obtained in the present study is probably the increased purity of the sample.

The interatomic distances are only slightly altered by the new data. Each niobium atom is coordinated to two niobium atoms in linear chains at a distance of 2.632 Å, to eight more niobium atoms at a distance of 3.224 Å, and to four antimony atoms in a tetrahedral arrangement (2.943 Å). Each antimony atom is coordinated to twelve niobium atoms at the corners of an icosahedron.

The shortest Nb-Nb distance is definitely shorter than in metallic niobium (2.858 Å according to Neuberger¹² and Edwards *et al.*¹³). For a detailed discussion of the interatomic distances in Nb₃Sb and other phases with β -W type structure reference is made to Wood *et al.*⁵, Nevitt,⁶ Geller,¹⁴ and Pauling.¹⁵

The Nb₅Sb₄ phase. Guinier photographs of different samples in the concentration range ~30 to ~60 atomic % Sb contained reflections from a phase of tetragonal symmetry *cf.* Table 7. The additional reflections from other phases are weak on photographs of samples with composition near 44 atomic % Sb.

Table 7. Guinier photograph data of Nb_5Sb_4 taken with strictly monochromatized $\text{CuK}\alpha_1$ -radiation.

I_{obs}	$\sin^2\Theta \times 10^5$		hkl	I_{obs}	$\sin^2\Theta \times 10^5$		hkl
	obs	calc			obs	calc	
m	1 116	1 115	110	m	27 561	27 541	541
w	2 234	2 230	200	m	27 882	27 870	550
m	4 459	4 459	220	m	28 790	28 785	332
w	5 245	5 245	101	vw	28 980	28 985	640
w	5 567	5 574	310	w	33 240	33 244	512
st	7 464	7 475	211	st	34 234	34 230	721
vst	9 701	9 705	301	w	37 697	37 704	532
st	10 031	10 033	330	m	38 676	38 688	651
st	11 148	11 148	420	vw	40 901	40 916	{741
st	14 167	14 164	411				{811
w	14 491	14 492	510	w	41 047	41 048	622
m	18 629	18 623	501	w	41 236	41 248	750
m	18 755	18 752	002	w	44 978	44 979	213
m	18 946	18 952	530	vw	45 347	45 372	831
w	20 848	20 853	521	m	46 625	46 625	552
w	22 287	22 296	620	m	47 213	47 209	303
vw	23 201	23 211	222	vw	47 745	47 737	642

Thermal decomposition of NbSb_2 , which was first noticed at $\sim 830^\circ\text{C}$, gave a residuum of composition $\text{Nb}_{1.21}\text{Sb}$, *i.e.* approximately Nb_5Sb_4 . (Further decomposition of Nb_5Sb_4 to Nb_3Sb takes place above $\sim 950^\circ\text{C}$.) The Guinier photograph of this sample showed the presence of faint amounts of NbSb_2 , NbO , and Nb_5Si_3 .

The lattice constants of the Nb_5Sb_4 phase in the latter sample and those in the samples Nb_3Sb and $\text{NbSb}_{1.5}$ are listed in Table 8. The slight variations in unit cell dimensions indicate that the homogeneity range of the phase is rather narrow.

The hkl reflections are absent when $h + k + l = 2n + 1$ in the Guinier photographs. Characteristic space groups are accordingly $I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$, $I4m2$, $I\bar{4}2m$, and $I4/mmm$.

Table 8. Lattice constants of the Nb_5Sb_4 phase.

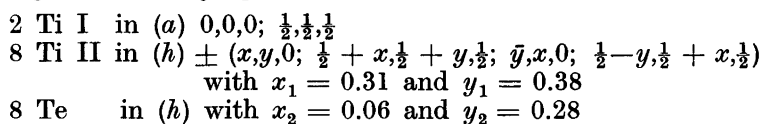
Sample	a (Å)	c (Å)	c/a
Nb_5Sb_4^a	10.314	3.5566	0.3448
Nb_5Sb^b	10.317	3.5574	0.3448
$\text{NbSb}_{1.5}^b$	10.318	3.5569	0.3447

^a Thermal decomposition of NbSb_2 at 850°C . ^b Quenched from 800°C .

The observed density, 8.17 g cm^{-3} , indicates that the unit cell contains two ($Z_c = 1.94$) Nb_5Sb_4 -groups. The calculated density from the X-ray data is 8.35 g cm^{-3} . Considering the experimental conditions the agreement between the two values is satisfactory.

The crystal structure of Nb_5Sb_4 . Attempts to obtain single crystals were in vain and the structure determination was accordingly based on powder data.

A tetragonal structure of a phase Ti_5Te_4 has been described by Grønvold *et al.*¹⁶ As there were obvious relationships between the intensities of the reflections from Nb_5Sb_4 and Ti_5Te_4 the possibility of the compounds being isostructural was investigated. In terms of the space group $I4/m$ the atomic arrangement in Ti_5Te_4 is as follows:



(The values of the variable parameters have been rounded off.) These parameters were used in the calculation of intensities on the Guinier photographs. A reasonable agreement between observed and calculated intensities was obtained indicating that the proposed structure is correct. Further refinement of the parameters was not attempted.

The shortest interatomic distances calculated on the basis of the above parameters are listed in Table 9. The coordination in the Ti_5Te_4 type structure of Nb_5Sb_4 is seen from left the part of Fig. 4. The niobium coordination around the Nb I atoms (which is the same as in niobium metal) corresponds to the eight short Nb I-Nb II distances in Table 9. This length is only about 3 % larger than that of pure niobium. (The shortest interatomic niobium-niobium distances in Nb_3Sb are about 8 % shorter than in pure niobium.) For a detailed description of the Ti_5Te_4 structure reference is made to Grønvold *et al.*¹⁶

Table 9. Interatomic distances in Nb_5Sb_4 (Å).

Nb I	-2 Nb I : 3.557	Sb	-1 Nb I : 2.95
	-8 Nb II: 2.92		-2 Nb II: 2.74
	-4 Sb : 2.95		-2 Nb II: 2.76
			-1 Nb II: 2.79
Nb II	-2 Nb I : 2.92		-2 Sb : 3.557
	-2 Nb II: 3.28		-4 Sb : 3.77
	-2 Nb II: 3.45		-2 Sb : 4.27
	-2 Nb II: 3.557		-2 Sb : 4.35
	-2 Sb : 2.74		
	-2 Sb : 2.76		
	-1 Sb : 2.79		

Six phases are known with the Ti_5Te_4 structure, *i.e.* Ti_5Te_4 ,¹⁶ V_5S_4 ,¹⁷ V_5Se_4 ,¹⁸ Nb_5Se_4 ,¹⁹ Nb_5Te_4 ,¹⁹ and Nb_5Sb_4 , while V_5Te_4 ²⁰ has a monoclinic structure of similar dimensions. The existence of a niobium antimonide with the Ti_5Te_4 structure indicates that the occurrence of this structure is not governed by

normal valence rules. This result is probably consistent with the close relationship between the Ti_5Te_4 type atomic arrangement and the metallic state. Further comments will have to await more experimental data.

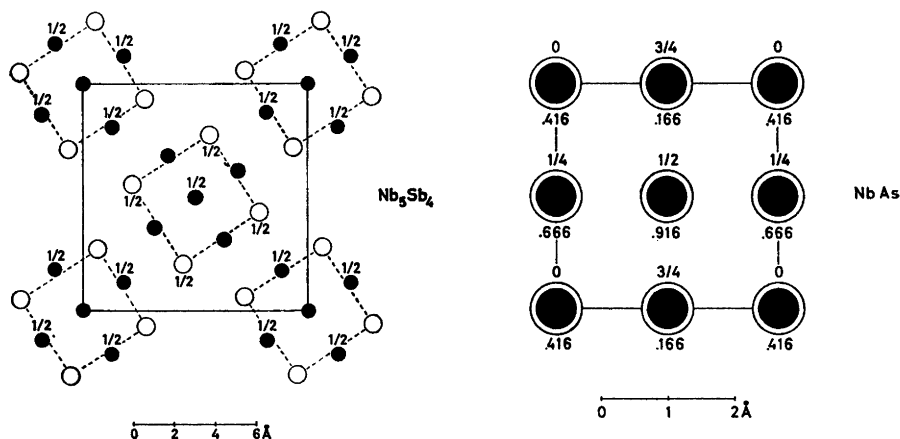


Fig. 4. A comparison of the NbAs and Nb_5Sb_4 structures. Both structures are projected along [001]. Filled circles represent metal atoms and open circles represent metalloid atoms. The numbers indicate fractions of the c -axis.

The relationship between the structures of NbAs and Nb_5Sb_4 is shown in Fig. 4. The dashed squares in the diagram to the left resemble the NbAs unit shown to the right. The notable difference is the stacking of the atomic layers perpendicular to [001].

The $NbSb_2$ phase. The existence of the $NbSb_2$ phase was clearly demonstrated in Fig. 2. $NbSb_2$ was easily obtained by heating mixtures of the elements, without the interfering, simultaneous formation of NbO and Nb_5Si_3 . During the heat treatment the samples were subject to sintering. Needle shaped, single crystals up to 2 mm long were obtained of this phase.

Guinier photographs of the $NbSb_2$ phase were indexed as monoclinic, cf. Table 10. The lattice constants of $NbSb_2$ are listed in Table 11 together with the lattice constants of the $NbSb_2$ phase for the samples NbSb and $NbSb_3$. The homogeneity range of the $NbSb_2$ is supposedly narrow.

The observed densities of a quenched and a slowly cooled sample are respectively 8.22 g cm^{-3} and 8.35 g cm^{-3} . Assuming an unit cell content of four ($Z_c = 3.98$ and 4.04) $NbSb_2$ -groups the corresponding calculated density from the X-ray measurements is 8.26 g cm^{-3} .

The systematic extinctions were of the type:

$$hkl \text{ absent when } h + k = 2n + 1$$

$$h0l \text{ absent when } (l = 2n + 1)$$

$$0k0 \text{ absent when } (k = 2n + 1)$$

Characteristic space groups are accordingly $C2$, Cm , and $C2/m$.

Table 10. Guinier photograph data of NbSb₂ taken with strictly monochromatized CuK α_1 -radiation.

I_{obs}	$\sin^2\theta \times 10^5$		hkl	I_{obs}	$\sin^2\theta \times 10^5$		hkl
	obs	calc			obs	calc	
m	2 295	2 302	20 $\bar{1}$	w	23 072	23 076	51 $\bar{4}$
w	3 012	3 022	200	w	23 120	23 124	60 $\bar{4}$
m	4 555	4 563	002	w	23 345	23 388	510
w	5 244	5 254	110	m	25 706	25 698	22 $\bar{3}$
w	5 460	5 464	11 $\bar{1}$	w	25 855	25 860	31 $\bar{5}$
vst	7 311	7 325	111	st	27 203	27 201	42 $\bar{2}$
m	7 702	7 706	20 $\bar{3}$	st	27 203	27 202	600
st	7 957	7 956	11 $\bar{2}$	vw	27 518	27 501	42 $\bar{1}$
st	9 216	9 209	40 $\bar{2}$	w	27 843	27 807	60 $\bar{5}$
w	9 508	9 509	40 $\bar{1}$	st	28 262	28 258	023
vst	9 653	9 648	31 $\bar{1}$	vw	28 522	28 518	005
vst	10 261	10 266	003	m	29 206	29 181	511
m	11 192	10 278	31 $\bar{2}$	m	29 206	29 183	42 $\bar{3}$
st	11 302	11 191	40 $\bar{3}$	m	30 131	30 084	420
st	11 675	11 299	310	vw	31 866	31 822	22 $\bar{4}$
st	12 090	11 306	202	st	32 318	32 259	71 $\bar{3}$
w	12 723	11 678	112	w	33 511	33 521	403
vst	13 200	12 092	400	w	33 940	33 926	601
w	13 825	12 730	11 $\bar{3}$	w	34 944	34 943	421
vw	16 944	13 191	31 $\bar{3}$	w	35 632	35 617	31 $\bar{6}$
m	17 984	13 830	20 $\bar{4}$	m	36 567	36 542	51 $\bar{6}$
vw	18 361	16 951	401	m	36 861	36 864	223
w	18 847	17 992	020	vw	37 223	37 254	512
vw	19 662	18 385	31 $\bar{4}$	w	38 052	38 034	80 $\bar{2}$
m	19 784	18 872	203	m	38 421	38 425	115
vw	19 854	19 698	51 $\bar{3}$	w	39 707	39 660	80 $\bar{5}$
vw	20 266	19 784	11 $\bar{4}$	w	40 006	39 991	42 $\bar{5}$
st	21 421	19 860	51 $\bar{1}$	w	40 237	40 228	22 $\bar{5}$
w	21 997	20 295	22 $\bar{1}$	st	40 725	40 715	314
w	22 225	21 444	312	w	41 146	40 734	11 $\bar{6}$
vw	22 538	21 999	40 $\bar{5}$	w	41 533	41 116	62 $\bar{4}$
w	22 735	22 236	20 $\bar{5}$	m	41 533	41 513	423
		22 550	022	w	42 096	41 523	710
		22 761	60 $\bar{1}$			42 088	422

Table 11. Lattice constants of the NbSb₂ phase.

Sample	a (Å)	b (Å)	c (Å)	β (°)
NbSb	10.239	3.6321	8.333	120.07
NbSb ₂	10.239	3.6319	8.333	120.07
NbSb ₃	10.237	3.6326	8.332	120.06

C. Magnetic properties

The magnetic susceptibilities of NbAs, NbAs₂, Nb₃Sb, Nb₅Sb₄, and NbSb₂ have been measured at temperatures between 90 and 725°K. The results, *cf.*

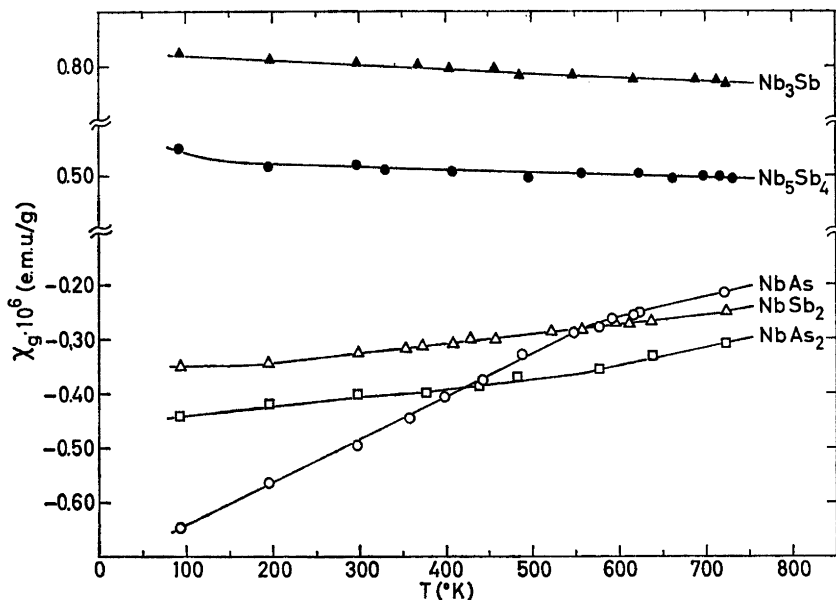


Fig. 5. The magnetic susceptibilities of NbAs, NbAs₂, Nb₃Sb, Nb₅Sb₄, and NbSb₂ as a function of temperature.

Fig. 5, show either diamagnetic or weak almost temperature-independent paramagnetic susceptibilities.

The expected diamagnetism resulting from the atomic cores in the three diamagnetic substances NbAs, NbAs₂, and NbSb₂ are of the same size as observed. The core contributions are -0.44×10^{-6} , -0.57×10^{-6} , and -0.59×10^{-6} e.m.u. per gram NbAs, NbAs₂, and NbSb₂, respectively. (These values were calculated from the diamagnetic corrections -9×10^{-6} e.m.u. per mole Nb⁵⁺ according to Klemm²¹ and -64.6×10^{-6} e.m. u. per mole As³⁻ and -94.4×10^{-6} e.m.u. per mole Sb³⁻ according to Angus.²²) By subtracting these values from the measured susceptibilities the total susceptibilities of localized, non-bonding electrons, valence electrons and conduction electrons are obtained. The measurements show that no unpaired *d*-electrons are present on the niobium atoms and suggest a covalent type of chemical bonding in NbAs, NbAs₂ and NbSb₂. Further details concerning the chemical bonding will be reported in a forthcoming paper.

The core contributions are -0.30×10^{-6} and -0.44×10^{-6} e.m.u. per gram Nb₃Sb and Nb₅Sb₄, respectively. The differences in magnetic properties of these substances compared with the previous discussed NbAs, NbAs₂,

and NbSb_2 reflects the difference in chemical bonding. Nb_3Sb and Nb_5Sb_4 are expected to have a metallic type of bonding and the observed paramagnetism should accordingly be associated with a paramagnetic contribution resulting from the spin of the electrons in the conduction band.

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REFERENCES

1. Heinerth, E. and Biltz, W. *Z. anorg. allgem. Chem.* **198** (1931) 175.
2. Boller, H. and Parthé, E. *Acta Cryst.* **16** (1963) 1095.
3. Furusest, S. and Kjekshus, A. *Acta Cryst.* *In press.*
4. Matthias, B. T., Wood, E. A., Corenzwit, E. and Bala, V. B. *J. Phys. Chem. Solids* **1** (1956) 188.
5. Wood, E. A., Compton, V. B., Matthias, B. T. and Corenzwit, E. *Acta Cryst.* **11** (1958) 604.
6. Nevitt, M. V. *Trans. Met. Soc. AIME* **212** (1958) 350.
7. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **18** (1964) 697.
8. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
9. Schäfer, H. and Dohmann, K.-D. *Z. anorg. allgem. Chem.* **299** (1959) 197.
10. Kjekshus, A. *Unpublished results.*
11. Rae, A. I. M. and Barker, W. W. *Acta Cryst.* **14** (1961) 1208.
12. Neuberger, M. C. *Z. Krist.* **A 93** (1936) 158.
13. Edwards, J. W., Speiser, R. and Johnston, H. L. *J. Appl. Phys.* **22** (1951) 424.
14. Geller, S. *Acta Cryst.* **9** (1956) 885; *Ibid.* **10** (1957) 380.
15. Pauling, L. *Acta Cryst.* **10** (1957) 374.
16. Grønvold, F., Kjekshus, A. and Raaum, F. *Acta Cryst.* **14** (1961) 930.
17. Grønvold, F., Haraldsen, H., Pedersen, B. and Tufto, T. *To be published.*
18. Røst, E. and Gjertsen, L. *Z. anorg. allgem. Chem.* **328** (1964) 299.
19. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **17** (1963) 2560.
20. Grønvold, F., Hagberg, O. and Haraldsen, H. *Acta Chem. Scand.* **12** (1958) 971.
21. Klemm, W. *Z. anorg. allgem. Chem.* **246** (1941) 347.
22. Angus, W. R. *Proc. Roy. Soc. (London)* **A 136** (1932) 573.
23. Saini, G. S., Calvert, L. D. and Taylor, J. B. *Can. J. Chem.* **42** (1964) 630.

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