INTERMEDIATE PHASES IN THE SYSTEMS NIOBIUM–SELENIUM, NIOBIUM–TELLURIUM, TANTALUM–SELENIUM, AND TANTALUM–TELLURIUM

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SUMMARY

The phase relationships in the systems Nb–Se, Nb–Te, Ta–Se, and Ta–Te have been studied by X-ray diffraction and density measurements. The intermediate phases found in these systems are Nb_5Se_4, Nb_3Se_4, $Nb_{1+x}Se_2$ ($0.00 \leq x \leq 0.29$; three polytype modifications $2H$, $3R$, and $4H$), $\sim NbSe_4$ (three modifications α, β and γ), Nb_5Te_4, Nb_3Te_4, $NbTe_2$, $NbTe_4$, $Ta_{1+x}Se_2$ ($0.00 \leq x < 0.64$; five modifications $1T$, $2H$, $3R$, $4H$ ($4H_{(a)}$ or $4H_{(b)}$), and $6R$), $TaSe_3$, $TaTe_2$, and $TaTe_4$. The intermediate phases found by us are compared with those reported by previous investigators of these systems. Most of the apparent inconsistencies are explained and resolved.

INTRODUCTION

The binary systems of niobium or tantalum in combination with one of the pnigogen or chalcogen elements have, in recent years, received considerable attention. The interest of workers in this field may be exemplified by the frequency of papers dealing with the systems Nb–Se, Nb–Te, Ta–Se, and Ta–Te. Whereas little information regarding these systems was available five years ago, twenty-eight out of thirty-three papers dealing with these systems (see Refs. 1–33) have appeared since that time, of which twenty-five have been published in the last two years*. The various groups of researchers have worked and published their results independently, and it is therefore not very surprising to find that some of their results are conflicting. On the other hand, it is disappointing to note that the utilization of results in the literature is so slow that obvious discrepancies remain without comment.

The present authors have previously reported on the structural properties of intermediate phases[6,9,10,17,21,28–30,33] in the the systems Nb–Se, Nb–Te, Ta–Se, and Ta–Te. The purpose of this paper is to provide a comprehensive description of the results obtained in our phase-analytical surveys of these systems, and by comment and comparison with the information from the available literature, we hope to clarify which are intermediate phases and which are not. This discussion is prompted by the publication of two recent papers in this Journal[12,13].

The phase-analytical work with a given phase can, in outline, be divided into

* See also "note added in proof" on page 30.

four activities, each of which requires a satisfactory answer before the phase analyst can regard the work as completed. These activities consist of:

(1) Establishing the existence of the phase.

(2) Determining possible thermal conditions for its existence.

(3) Characterizing it for identification purposes by measurement of its chemical or physical properties.

(4) Stating its correct chemical composition.

A phase-analytical survey consists of providing unambiguous solutions to these four problems for all the phases of a system. In consideration of these factors, satisfactory surveys of the systems Nb–Se, Nb–Te, Ta–Se, and Ta–Te have not yet been reported. We find that the correct compositions of the intermediate phases in these systems have been frequently mis-stated. Bearing in mind that little value can be attached to the interpretation of measured chemical and physical properties on mixtures of two or more phases, the reliability of the characterization of some of the previously reported phases might be somewhat doubtful.

EXPERIMENTAL

The samples were prepared from 99.98% Nb, 99.92% Ta, 99.999 + % Te (Johnson, Matthey & Co., Ltd.), and 99.998% Se (Bolidens Gruvaktiebolag). A series of samples was prepared by heating weighed quantities of metal and chalcogen in different ratios in evacuated and sealed silica tubes. The samples were heated to various temperatures between 400 and 1350°C, and quenching in ice water as well as slow cooling was applied.

X-ray diffraction (oscillation, Weissenberg, precession, and Guinier photographs) and density measurements were carried out as previously described[6,9,10,21,28-30,33].

The existence of intermediate phases was established by the presence of their characteristic diffraction patterns in the X-ray powder (Guinier) photographs, and these patterns were used for a first, coarse characterization of the phases. The compositions of the intermediate phases were determined using the disappearing-phase principle on the X-ray powder photograph data and in some cases were also estimated from specific volume vs. composition (in wt. %) plots. For a more detailed description of these methods and their accuracy reference is made to JENSEN et al.[34]. Most of the intermediate phases considered in this paper have also been assigned a further characterization by the determination of their crystal structures (reported elsewhere[6,9,10,21,29,30,33]) which provides accurate confirmation of the compositions stated. The derived compositions have furthermore been tested by comparison of the pycnometrically observed densities with those calculated on the basis of the structural data.

A particular difficulty encountered in investigating the metal-rich parts of the Nb–Se, Nb–Te, Ta–Se, and Ta–Te systems is due to the presence of apparently unavoidable interfering reactions between Nb and SiO_2, and Ta and SiO_2, respectively. These reactions are easily demonstrated by comparatively short heat treatments (five days at 1000°C) of the pure metals in evacuated and sealed silica tubes. The silica tubes are found to be heavily attacked after these heat treatments and their contents give X-ray powder photographs which are quite different from those of the pure metals. The products of the reaction between Nb and SiO_2 can, from the X-ray powder

photograph data, be identified as NbO and Nb_5Si_3 in accordance with the previous findings of SCHÄFER AND DOHMANN[35]. Although the products of the reaction between Ta and SiO_2 are unidentified, they are thought to be analogous, *i.e.* tantalum oxide(s) and tantalum silicide(s).

The effects of the interfering reactions can be reduced (but not eliminated) by placing the samples in alumina crucibles inside the silica tubes. The reactions accordingly also take place *via* the gaseous phase. The latter observation is consistent with the findings of SCHÄFER AND DOHMANN[35] for the reaction between Nb and SiO_2. Contamination due to these reactions has been noticed in samples containing less than $\sim$65 at.% Se, $\sim$58 at.% Te, $\sim$66.7 at.% Se, and $\sim$66.7 at.% Te in the Nb–Se, Nb–Te, Ta–Se, and Ta–Te systems, respectively. The contamination is quite variable, even for samples with the same initial composition. The results obtained on highly contaminated samples are not included in this paper.

NAMING OF THE INTERMEDIATE PHASES

The previous authors have used somewhat different notations for naming the intermediate phases in the Nb–Se, Nb–Te, Ta–Se, and Ta–Te systems. Without a careful inspection of the notations adopted in the various papers, the reader might be considerably confused. Thus we find it appropriate to present a brief description of the nomenclature used in this paper:

(1) The chemical formula has only been used as the symbol to designate an intermediate phase if this designation is unambiguous, *i.e.* in the cases where only one phase exists at each composition.

Some of the previous authors, *e.g.* NOVOSELOVA *et al.*[18], use notations of the type γ-phase, $NbTe_{2.33-4.00}$, which has been simplified to γ-$NbTe_3$ by REVOLINSKY *et al.*[13]. Double notations of this type are unnecessary and in the form used by REVOLINSKY *et al.* they might even be misleading due to the danger of confusing with the common use of Greek characters to distinguish different modifications of one and the same phase. (See (3) below.)

(2) In order to distinguish and designate the various polytypes of layer structures a prefix is added to the formula. The first part of this prefix is an integer which corresponds to half the number of X layers (X = metalloid) within the unit repeat distance along the c axis. (All the layer structures considered in this paper have an even number of X layers. Half the number of X layers is furthermore equal to the number of complete XMX triple-layers (M = metal) per unit length of the c axis.) The second part of the prefix is a letter which gives the symmetry of the unit cell, *e.g.* T, H, or R depending upon whether the symmetry is trigonal, hexagonal, or rhombohedral. To differentiate between different polytypes with equal numbers of X layers and equal crystal symmetry, a letter subscript in parentheses is included as a third part of the prefix. The symbol $4H_{(b)}$-$Ta_{1+x}Se_2$ may be given as an example of the complete designation of an intermediate phase of this type.

This scheme of notation follows that introduced by RAMSDELL[36] for naming polytypes of SiC (and later used by MITCHELL[37] for naming polytypes of CdI_2), except for a factor of one half in the numerical part of the prefix.

The present notation agrees with that previously used by BROWN AND BEERNTSEN[14] (see also REVOLINSKY *et al.*[13]) for naming the polytypes of $NbSe_2$ and $TaSe_2$.

If the second (and a possible third) part of the prefix is substituted by the letter *s* the notations used by KADIJK *et al.*[11] (see also JELLINEK[38,39]) for naming the NbSe$_2$ and TaSe$_2$ polytypes are obtained. The letter *s* is an abbreviation for slabs, and the total prefix *ns* indicates according to KADIJK *et al.* that the repeat unit in the *c* direction has a thickness of *n XMX* slabs (also called triple-layers or sandwiches). It must be mentioned that the letter *s* in the notations of KADIJK *et al.*[11], is almost superfluous as the information is given by the number *n*.

(3) Greek characters have been used to denote different modifications of intermediate phases for which the structural relationships are less marked (or unknown) and where the above rational nomenclature is difficult to apply.

PHASE ANALYTICAL RESULTS

A survey of the intermediate phases reported by the previous investigators[1-33] of the systems Nb–Se, Nb–Te, Ta–Se, and Ta–Te is given in Tables I–IV. The only intermediate phases found in the present phase-analytical study of these systems are Nb$_5$Se$_4$, Nb$_3$Se$_4$, Nb$_{1+x}$Se$_2$ ($0.00 \leqq x \leqq 0.29$; three modifications $2H$, $3R$, and $4H$), $\sim$NbSe$_4$ (three modifications α, β, and γ), Nb$_5$Te$_4$, Nb$_3$Te$_4$, NbTe$_2$, NbTe$_4$, Ta$_{1+x}$Se$_2$ ($0.00 \leqq x < 0.64$; five modifications $1T$, $2H$, $3R$, $4H$ ($4H_{(a)}$ or $4H_{(b)}$), and $6R$), TaSe$_3$, TaTe$_2$, and TaTe$_4$. The formulae of these phases constitute the first horizontal row in Tables I–IV. Application of the data stated in the literature for identification purposes makes it possible (in most cases with absolute certainty) to divide the intermediate phases described by the previous investigators into the same categories. Phases which are apparently identical, according to the available data, have been listed in the same column in Tables I–IV. The original designations of the phases used by the various authors have been retained in the construction of Tables I–IV. Abbreviated symbols indicating the kind of identification (characterizing properties) given by these authors have also been included.

Brief considerations and comments on the phase relationships in the four systems are presented below.

THE Nb–Se SYSTEM

In a coarse classification (Table I) of the Nb–Se system it is reasonable to consider essentially four intermediate phases, *i.e.* Nb$_5$Se$_4$, Nb$_3$Se$_4$, Nb$_{1+x}$Se$_2$, and NbSe$_4$.

The Nb$_5$Se$_4$ phase
Nb$_5$Se$_4$ has a tetragonal Ti$_5$Te$_4$ type structure[6]. The structure provides good characterization and determines the composition of this phase. No composition range of the Nb$_5$Se$_4$ phase is indicated. This phase has previously only been found by SELTE AND KJEKSHUS[6], who state that it is difficult to obtain because of the reaction between Nb and SiO$_2$. The latter observation may explain why the Nb$_5$Se$_4$ phase has not been detected by the other investigators of the Nb–Se system.

The Nb$_3$Se$_4$ phase
The crystal structure of Nb$_3$Se$_4$ has been determined by SELTE AND KJEKSHUS[9].

TABLE I

THE INTERMEDIATE PHASES OF THE Nb–Se SYSTEM*

Authors	Nb_5Se_4	Nb_3Se_4	$2H\text{-}Nb_{1+x}Se_2$	$3R\text{-}Nb_{1+x}Se_2$	$4H\text{-}Nb_{1+x}Se_2$	$\alpha\text{-}NbSe_4$	$\beta\text{-}NbSe_4$	$\gamma\text{-}NbSe_4$
BRIXNER[3]			$x\text{-}NbSe_2$ u, sg, e $NbSe$ u, sg		$\beta\text{-}NbSe_2$ u, sg, d, e			
KOERTS[4]			$NbSe_2$ u					
REVOLINSKY et al.[5]			$NbSe_2$ $(NbSe_{1.90-2.25})$ e					
SELTE AND KJEKSHUS[6]	Nb_5Se_4 u, s, d	Nb_3Se_4						
BEERNTSEN et al.[7]			$l.t.\text{-}NbSe_2$ e, u, s		$h.t.\text{-}NbSe_2$ u, s			
BOES[8]			$NbSe_3$ u, e, l					
SELTE AND KJEKSHUS[9]	Nb_5Se_4	Nb_3Se_4 u, s, d	$Nb_{1+x}Se_2$					
SELTE AND KJEKSHUS[10]		Nb_3Se_4	$Nb_{1+x}Se_2$ $(0.00 \leqq x \leqq 0.05,$ $0.17 \leqq x \leqq 0.29)$ u, s, d			"$NbSe_4$"		
KADIJK et al.[11]			$2s\text{-}NbSe_2$ u, s $2s\text{-}Nb_{1+x}Se_2$	$3s\text{-}NbSe_2$ u, s $3s\text{-}Nb_{1+x}Se_2$	$4s\text{-}NbSe_2$ u, s $4s\text{-}Nb_{1+x}Se_2$	$NbSe_3$?		

Investigator							
SCHÄFER AND FUHR[12]		$NbSe_{1.1}$ u					
REVOLINSKY et al.[13]		β-NbSe? t	γ-$Nb_{1.3-1.5}Se_2$** t; ε-$NbSe_2$ ($Nb_{1.05}Se_2$–$NbSe_2$) u, s, t; α-NbSe? t	δ-$Nb_{1.14}Se_2$ u, s, t	ζ-$NbSe_2$ ($Nb_{1.05}Se_2$–$NbSe_2$) u, s, t	η-$NbSe_2$? u, sg, t	η-$NbSe_3$? u, sg, t	
BROWN AND BEERNTSEN[14]			2H-$NbSe_2$ u, s	3R-$NbSe_2$ u, s	4H-$NbSe_2$ u, s			
REVOLINSKY et al.[15]			ε-$NbSe_2$ ($Nb_{1.05}Se_2$–$NbSe_2$) e; α-NbSe?	δ-$Nb_{1.14}Se_2$ e	ζ-$NbSe_2$ ($Nb_{1.05}Se_2$–$NbSe_2$) e	η-$NbSe_2$? e	η-$NbSc_3$? e	
SELTE AND KJEKSHUS[16]	Nb_3Se_4 m		$Nb_{1+x}Se_2$ m			"$NbSe_4$" m		
SELTE AND KJEKSHUS[17]	Nb_3Se_4 m					α-$NbSe_4$ u	β-$NbSe_3$ u, sg	~$NbSc_4$
Present	Nb_3Se_4		2H-$Nb_{1+x}Se_2$ (0.00 ≦ x ≦ 0.29) u	3R-$Nb_{1+x}Se_2$ (x = 0.11) u	4H-$Nb_{1+x}Se_2$ (x = 0.05) u	α-$NbSc_4$	β-$NbSe_4$	γ-$NbSe_4$ X-ray

* The phases reported by the previous investigators are included in the table with their original designations and the attached letters indicate the kind of characterization provided.

The following abbreviations have been used: u = unit cell dimensions, s = crystal structure, sg = space group, d = pycnometric density, m = magnetic susceptibility, e = electrical properties (electrical conductivity, thermoelectric power, Seebeck coefficient, superconduction transition temperature), l = lubricating properties, t = thermal stability.

Identical phases are listed in the same column. When the identification is uncertain, either due to lack of data or inconsistencies, a question mark is attached to the formula.

** Probably a mixture of several phases.

The formula Nb_3Se_4 is ascertained by the structure determination and by the comparison of the pycnometrically observed density with that calculated on the basis of the structural data. No indication of range of homogeneity is obtained.

The hexagonal $NbSe_{1.1}$ phase reported by SCHÄFER AND FUHR[12] is obviously identical with the Nb_3Se_4 phase, although their analytically determined composition must accordingly be incorrect. (Comparison of unit-cell dimensions have been used to confirm the identity. SCHÄFER AND FUHR prepared single crystals of this phase by chemical-transport reactions using iodine as a transport agent. Single crystals of Nb_3Se_4 have been obtained by the same technique in the present study.)

The $Nb_{1+x}Se_2$ phase

The $Nb_{1+x}Se_2$ phase crystallizes in at least three polytype modifications. The crystal structures of these polytypes, named $2H$-$Nb_{1+x}Se_2$, $3R$-$Nb_{1+x}Se_2$, and $4H$-$Nb_{1+x}Se_2$, have been determined by SELTE AND KJEKSHUS[10], KADIJK et al.[11], and BROWN AND BEERNTSEN[14]. $2H$-$Nb_{1+x}Se_2$, $3R$-$Nb_{1+x}Se_2$, and $4H$-$Nb_{1+x}Se_2$ have characteristic and closely-related layer structures.

The $Nb_{1+x}Se_2$ phase has a homogeneity range within the limits 60.8 and 66.67 at.% Se ($0.00 \leq x \leq 0.29$) for slowly-cooled samples. The limits of the homogeneity range have been estimated from the dimensional variations in the unit cell(s) of $2H$-$Nb_{1+x}Se_2$ ($3R$-$Nb_{1+x}Se_2$ and $4H$-$Nb_{1+x}Se_2$) as a function of composition and by application of the disappearing-phase principle in the interpretation of the X-ray powder photograph data. As indicated by the formula $Nb_{1+x}Se_2$, density measurements have shown that the solid solution takes place by addition of Nb atoms as the composition of the phase varies from $Nb_{1.00}Se_2$ to $Nb_{1.29}Se_2$.

It has been difficult to obtain consistent, reproducible results within the homogeneity range due to the close structural relationship between $2H$-$Nb_{1+x}Se_2$, $3R$-$Nb_{1+x}Se_2$, and $4H$-$Nb_{1+x}Se_2$. A large number of the samples in this concentration range contained a mixture of two or three of the polytypes. The most consistent results are obtained after relatively short heat treatment. Re-annealing has generally not improved the samples, but has occasionally worsened the homogeneity. Usually, we have been able to prepare samples containing pure $2H$-$Nb_{1+x}Se_2$ for $0.00 \leq x \leq 0.05$ and $0.17 \leq x \leq 0.29$. (Many samples with $0.17 \leq x \leq 0.29$ contained a mixture of two or three of the polytypes.) $3R$-$Nb_{1+x}Se_2$ and $4H$-$Nb_{1+x}Se_2$ have been obtained only in samples with bulk compositions corresponding to $x \geq 0.05$, most frequently in the range $0.05 \leq x < 0.17$, and have almost invariably been obtained in admixture with one or two of the other polytypes. $3R$-$Nb_{1+x}Se_2$ has only been observed as a single phase at the composition $\sim Nb_{1.11}Se_2$. Approximately constant lattice dimensions* of $3R$-$Nb_{1+x}Se_2$ are obtained, regardless of whether the samples consist of a mixture of polytypes or not. The unit cell dimensions** of $4H$-$Nb_{1+x}Se_2$ are also found to be approximately constant in all our samples. The purest samples of $4H$-

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* The values $a = 3.459$ Å, $c = 18.79$ Å have been found for $3R$-$Nb_{1.11}Se_2$. These values agree reasonably well with those given by KADIJK et al.[11] ($x > 0$?), BROWN AND BEERNTSEN[14] ($x > 0$), and REVOLINSKY et al.[13] ($x = 0.14$).
** The values $a = 3.449$ Å, $c = 25.19$ Å have been obtained for $4H$-$Nb_{1+x}Se_2$ in a sample with bulk composition corresponding to $x = 0.05$. These values are in reasonably good agreement with those stated by KADIJK et al.[11] ($x = 0.00$), BROWN AND BEERNTSEN[14] ($x = 0.00$), and REVOLINSKY et al.[13] ($0.00 \leq x \leq 0.05$).

$Nb_{1+x}Se_2$ have been observed for a composition corresponding to $x=0.05$, which approaches an apparently single phase of $4H$-$Nb_{1+x}Se_2$. (The possible simultaneous presence of $2H$-$Nb_{1+x}Se_2$ and $4H$-$Nb_{1+x}Se_2$ is difficult to exclude on the basis of the present X-ray powder photograph data.)

The present results agree with those of SELTE AND KJEKSHUS[10], KADIJK et al.[11], REVOLINSKY et al.[13,15], and BROWN AND BEERNTSEN[14] regarding the structural characterization of the three polytypes of the $Nb_{1+x}Se_2$ phase. Bearing in mind the difficulties in obtaining reproducible results throughout the homogeneity range, the present results may be essentially consistent with those of the previous studies in respect of the occurrence of the various polytypes as a function of composition and temperature of preparation. A detailed consideration of the apparent discrepancies of Table I is in any case not justified at present. (See also the $Ta_{1+x}Se_2$ phase.)

The NbSe₄ phase

The existence of three intermediate phases with compositions in the range 66.7–100 at.% Se has been established in the Nb–Se system. The exact compositions of these phases have not been determined, but two of them have been designated the composition $NbSe_4$ (named α-$NbSe_4$ and β-$NbSe_4$) on the basis of relationships in lattice dimensions and crystal symmetry with $NbTe_4$. The composition of the third phase is even less certain, but it is named γ-$NbSe_4$ for the lack of a better notation. α-$NbSe_4$ and β-$NbSe_4$ are characterized by the dimensions of their tetragonal unit cells[17], and X-ray powder data for characterization of γ-$NbSe_4$ is given in Table V (see APPENDIX). Attempts are now being made to determine the crystal structure of β-$NbSe_4$ in order to establish its correct composition.

The rather limited data presented by REVOLINSKY et al.[13,15] for their η-$NbSe_3$ phase (the composition has been corrected to $NbSe_4$ in the note added in proof), suggests that their phase may be identical with the α-$NbSe_4$ or β-$NbSe_4$ found by us.

THE Nb–Te SYSTEM

Four intermediate phases Nb_5Te_4, Nb_3Te_4, $NbTe_2$, and $NbTe_4$ have been observed in the Nb–Te system (cf. Table II).

The Nb₅Te₄ phase

Nb_5Te_4 is isostructural with Nb_5Se_4[6]. Comments already presented for the Nb_5Se_4 phase are indeed relevant also for the Nb_5Te_4 phase.

The X-ray powder photograph data, unit cell and observed density published by NOVOSELOVA et al.[18] and GRIGORJAN et al.[19] for their α-phase, $NbTe_{0.18-0.82}$, are inconsistent with the corresponding data for the Nb_5Te_4 phase. As an alternative interpretation, essentially consistent with the results, it may be suggested that their samples have been strongly contaminated with NbO and Nb_5Si_3. NbO and Nb_5Si_3 are the products of the reaction between Nb and SiO_2 and our suggestion appears accordingly to be quite plausible (see EXPERIMENTAL and also Refs. 6, 10, and 40).

The Nb₃Te₄ phase

Nb_3Te_4 is isostructural with Nb_3Se_4; it is well characterized and its stoichiometric composition is accurately determined[9].

TABLE II

THE INTERMEDIATE PHASES OF THE Nb–Te SYSTEM*

Authors	Nb_5Te_4	Nb_3Te_4	$NbTe_2$	$NbTe_4$
NOVOSELOVA et al.[18]		β-phase ($NbTe_{1.00-1.70}$) e		γ-phase ($NbTe_{2.33-4.00}$) e
GRIGORJAN et al.[19]		β-phase ($NbTe_{1.00-1.70}$) u		γ-phase ($NbTe_{2.33-4.00}$) u
BRIXNER[3]			$NbTe_2$ u, sg, d, e $NbTe$ u, sg	
CHAIGNEAU AND SANTARROMANA[20]			$NbTe_2$ u, d	
SELTE AND KJEKSHUS[6]	Nb_5Te_4 u, s, d	Nb_3Te_4		
BOES[8]			$NbTe_2$ u, e, l	
SELTE AND KJEKSHUS[9]	Nb_5Te_4	Nb_3Te_4 u, s, d	$NbTe_2$?	
SELTE AND KJEKSHUS[21]			$NbTe_2$?	$NbTe_4$ u, s, d
SCHÄFER AND FUHR[12]		$NbTe_{1.0}$ u	$NbTe_2$	
REVOLINSKY et al.[13]		α-NbTe?	β-$NbTe_2$ ($1M$-$NbTe_2$, $Nb_{1.06}Te_2$–$NbTe_2$) u, sg	γ-$NbTe_3$ u, sg
SELTE AND KJEKSHUS[16]	Nb_5Te_4 m	Nb_3Te_4 m	$NbTe_2$? m	$NbTe_4$ m
BROWN[22]			$NbTe_2$ u, s, d	
Present	Nb_5Te_4	Nb_3Te_4	$NbTe_2$? X-ray, d	$NbTe_4$

* See the footnote to Table I.

     Identity between Nb_3Te_4 and the phase $NbTe_{1.0}$ reported by SCHÄFER AND FUHR[12] seems evident, despite the incorrect composition stated by the latter authors.

     The β-phase, $NbTe_{1.00-1.70}$, described by NOVOSELOVA et al.[18] and GRIGORJAN et al.[19], is, according to the available data, probably also identical with Nb_3Te_4. The X-ray patterns published by NOVOSELOVA et al. suggest to us a narrow, rather than an extended range of homogeneity for their phase. The apparent disagreement in respect of the range of homogeneity of this phase may thus be overcome.

The NbTe₂ phase

NbTe₂ is, according to the present study, characterized by the X-ray powder photograph data listed in Table VI (see APPENDIX). Inferred from the X-ray powder photographs, the disappearing-phase principle gave a composition close to the stoichiometric ratio 1:2. No significant shifts were obtained in the positions of the reflections on the X-ray powder photographs for samples with different initial proportions of the components, and the homogeneity range of this phase is accordingly rather narrow. Further support for the formula NbTe₂ was obtained from a specific volume *vs.* wt.% Te plot which showed a sharp break in the linearity at a composition corresponding to NbTe₂.

The present study concurs with the previous studies by BRIXNER[3], BOES[8], CHAIGNEAU AND SANTARROMANA[20], SCHÄFER AND FUHR[12], REVOLINSKY *et al.*[13], and BROWN[22] regarding the existence of a phase with composition NbTe₂. (REVOLINSKY *et al.* and BROWN propose a narrow range of homogeneity extending from NbTe₂ to Nb₁.₀₆Te₂.) We have, however, been unable to match our diffraction data (Table VI) with their structural data, despite numerous attempts*. The most comprehensive of these structural data is due to BROWN[22], who has derived a complete, and chemically very plausible, crystal structure from single-crystal X-ray data. BROWN claims furthermore that his NbTe₂ phase (and accordingly also that of REVOLINSKY *et al.*) is identical with the NbTe₂ phase of BRIXNER[3] and CHAIGNEAU AND SANTARROMANA[20]. The structural data of BRIXNER have been confirmed by BOES[8] and SCHÄFER AND FUHR[12]. Further work is, however, needed to reveal the discrepancies between BROWN's and the present study.

Comparison of BRIXNER's structural data for his phases NbTe₂ and NbTe, suggests very strongly that the composition of the latter phase is incorrect and that the two phases in reality are identical, *i.e.* NbTe₂.

The NbTe₄ phase

The crystal structure of NbTe₄ has been determined by SELTE AND KJEKSHUS[21]. (Only the structure of the subcell is known, but since the additional reflections on oscillation and Weissenberg photographs were faint, the complete structure might be regarded as a slightly perturbed superstructure of that of the subcell.) The stoichiometric formula NbTe₄ is ascertained by the structure determination and by the comparison of the pycnometrically observed density with that calculated on the basis of the structural data.

The γ-phase, NbTe₂.₃₃₋₄.₀₀, reported by NOVOSELOVA *et al.*[18] and GRIGORJAN *et al.*[19] is, according to their X-ray data, no doubt identical with NbTe₄. The disagreement in respect of the range of homogeneity seems to reflect the weakness of the disappearing-phase principle in phase-analytical work by X-ray powder methods. (This statement applies also to the corresponding discussion of the Nb₃Te₄ phase above.) Our interpretation of the X-ray patterns published by NOVOSELOVA *et al.*[18] suggests furthermore a narrow composition range for their phase.

The γ-NbTe₃ phase reported by REVOLINSKY *et al.*[13] is also identical with NbTe₄. The disagreement in respect of composition is removed by the note added in

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* Some features of the data listed in Table VI are consistent with the unit cells of various sizes and symmetries proposed by the previous authors[3,8,12,13,20,22], but a far from perfect fit is attained with any.

proof, where REVOLINSKY *et al.* confirm that they accept the formula $NbTe_4$ found by SELTE AND KJEKSHUS[21].

THE Ta–Se SYSTEM

According to the present study, the Ta–Se system (Table III) can be described roughly as having only two intermediate phases, *i.e.* $Ta_{1+x}Se_2$ and $TaSe_3$. Our results for the metal-rich part of the Ta–Se system are, however, less satisfactory than those obtained in the corresponding part of the Nb–Se system. Most of the samples in this concentration region have invariably been contaminated with impurities (in some cases in rather large amounts) resulting from the apparently unavoidable reaction between Ta and SiO_2. The present result concerning the suggested non-occurrence of intermediate phases with compositions between Ta and $Ta_{1+x}Se_2$ should thus be regarded as somewhat tentative.

The $Ta_{1+x}Se_2$ phase

Six polytype modifications of the $Ta_{1+x}Se_2$ phase have been reported, namely $1T$-$Ta_{1+x}Se_2$, $2H$-$Ta_{1+x}Se_2$, $3R$-$Ta_{1+x}Se_2$, $4H_{(a)}$-$Ta_{1+x}Se_2$, $4H_{(b)}$-$Ta_{1+x}Se_2$, and $6R$-$Ta_{1+x}Se_2$. The six polytypes have characteristic and closely-related layer structures according to structure determinations by KADIJK *et al.*[11], BROWN AND BEERNTSEN[14], and BJERKELUND AND KJEKSHUS[30].

The $Ta_{1+x}Se_2$ phase has a homogeneity range within the limits 55.0 and 66.67 at.% Se ($0.00 \leq x < 0.64$) for slowly-cooled samples. The extension of the composition range has been estimated from the changes in the dimensions of the unit cells of the various polytypes as a function of composition and using the disappearing-phase principle in the interpretation of the X-ray powder photograph data. The comparison of the pycnometrically observed densities with those calculated from the structural data confirms that the solid solution takes place according to the formula $Ta_{1+x}Se_2$.

Our previous statements concerning the difficulties in obtaining reproducible results within the homogeneity range of the $Nb_{1+x}Se_2$ phase are equally valid also for the $Ta_{1+x}Se_2$ phase. Although most of our samples within the composition range of the $Ta_{1+x}Se_2$ phase have turned out to contain a mixture of two or three of the polytypes, some general trends have been noticed for the occurrence of the different polytypes of $Ta_{1+x}Se_2$. $1T$-$Ta_{1+x}Se_2$ and $4H$-$Ta_{1+x}Se_2$ have been obtained only for $x = 0.00$, *i.e.* at the stoichiometric composition $TaSe_2$. (It should be noted that we have been unable to distinguish between $4H_{(a)}$-$Ta_{1+x}Se_2$ and $4H_{(b)}$-$Ta_{1+x}Se_2$ on the basis of our present data.) Samples containing pure $2H$-$Ta_{1+x}Se_2$ have been obtained for $0.00 \leq x < 0.03$ and $0.25 < x < 0.64$. $3R$-$Ta_{1+x}Se_2$ and $6R$-$Ta_{1+x}Se_2$ have been noted for $0.03 < x < 0.25$, however, invariably in mixture with one or two of the other polytypes. (For details regarding the structural data, reference is made to BJERKELUND AND KJEKSHUS[30].)

Except for the uncertainty regarding $4H_{(a)}$-$Ta_{1+x}Se_2$ and $4H_{(b)}$-$Ta_{1+x}Se_2$, our structural characterization of the various polytypes of the $Ta_{1+x}Se_2$ phase appears to be in agreement with that of KADIJK *et al.*[11], BROWN AND BEERNTSEN[14], and REVOLINSKY *et al.*[13]. As was the case for the $Nb_{1+x}Se_2$ phase, a detailed consideration of the apparent discrepancies of Table III with regard to the occurrence of the polytypes as a function of composition is not considered to be justified.

TABLE III

THE INTERMEDIATE PHASES OF THE Ta–Se SYSTEM*

Authors	$Ta_{1+x}Se_2$						$TaSe_3$
	$1T$-$Ta_{1-x}Se_2$	$2H$-$Ta_{1+x}Se_2$	$3R$-$Ta_{1+x}Se_2$	$4H_{(a)}$-$Ta_{1+x}Se_2$	$4H_{(b)}$-$Ta_{1-x}Se_2$	$6R$-$Ta_{1-x}Se_2$	
Ariya et al.[23]		x-phase?					higher selenide?
Brixner[3]		α-TaSe₂ u, sg, d, e TaSe u, sg	β-TaSe₂ u, sg, e				
Brixner[24]			TaSe₂ u, sg, e				
Aslanov et al.[36]	α-TaSe₂ u	β-TaSe₁.₉₈ u, d, e				δ-TaSe₁.₉₈ u	TaSe₃ e
Aslanov et al.[27]							TaSe₃ u
Boes[8]		TaSe₂ u, e, l					
Bjerkelund and Kjekshus[28]							TaSe₃ u, d, m
Kadijk et al.[11]		2s-TaSe₂ u, s 2H-TaSe₂ u, s	3s-TaSe₂ u, s	4s-TaSe₂ u, s		6s-TaSe₂ u, s	TaSe₃?
Brown and Beerntsen[14]					4H-TaSe₂ u, s		
Revolinsky et al.[18]		ε-TaSe₂ (2H-TaSe₂) u, s α-TaSe? β-TaSe? γ-Ta₁.₃Se₂?		ζ-TaSe₂?	4H-TaSe₂ u, s	δ-Ta₁.₆₅₋₁.₀₂Se₂?	η-TaSe₃? t
Bjerkelund and Kjekshus[29]	1T-Ta₁₋ₓSe₂ (x = 0.00) u, s, t						TaSe₃ u, s, d
Bjerkelund and Kjekshus[30]		2H-Ta₁₋ₓSe₂ (0.00 ≦ x < 0.03; 0.25 < x < 0.64) u, s	3R-Ta₁₊ₓSe₂? (0.03 < x < 0.25) u	4H-Ta₁₊ₓSe₂? (x = 0.00) u	4H-Ta₁₊ₓSe₂? (x = 0.00) u	6R-Ta₁₋ₓSe₂? (0.03 < x < 0.25) u	
Present	1T-Ta₁₋ₓSe₂ (x = 0.00)	2H-Ta₁₋ₓSe₂ (0.00 ≦ x < 0.03; 0.25 < x < 0.64)	3R-Ta₁₊ₓSe₂? (0.03 < x < 0.25)	4H-Ta₁₊ₓSe₂? (x = 0.00)	4H-Ta₁₋ₓSe₂? (x = 0.00)	6R-Ta₁₋ₓSe₂? (0.03 < x < 0.25)	TaSe₃

* See the footnote to Table I.

The available information on the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases suggests, as previously pointed out by KADIJK et al.[11] (see also JELLINEK[38,39]), that the relationships between the different polytypes are governed not only by thermodynamics, but that the kinetics of crystal growth are of importance. The current theory for the formation of polytype phases (cf. MITCHELL[37] where further references also are given) assumes that polytypism results from the spiral growth of crystals, initiated by screw dislocations. The exposed steps from which the various polytypes grow must be of different heights and contain at least one departure from the "ideal" (basic) structure of the phase. This theory of polytypism would, according to MITCHELL[37], be proved reasonably well if the crystals of a given polytypic substance show each of the following features:

(1) Growth spirals.

(2) Spiral step heights of various magnitudes.

(3) Structures which could be interpreted as having resulted from dislocations of various magnitudes in an "ideal" (basic) crystal structure.

To test the theory MITCHELL[37] has used CdI_2, for which he reports the existence of at least 32 different polytypes. The three characteristic features have been satisfactorily confirmed by the experimental data for CdI_2, indicating that the theory is essentially correct.

The polytypes of the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases are closely-related structurally to those of CdI_2. $Ta_{1+x}Se_2$ and CdI_2 have even one polytype in common, i.e. that corresponding to $1T$-$Ta_{1+x}Se_2$ with $x=0.00$ (normally denoted the $Cd(OH)_2$-type). It seems natural therefore to attempt an explanation of the observed polytypism of the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases in terms of the same theory.

(1) Growth spirals on the (001) faces of the hexagonal plate-shaped crystals of the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases have been observed by microscopic examination.

(2) Indication of spiral step heights of various magnitudes has been obtained, but no quantitative measurements have been carried out to confirm this point.

(3) The screw dislocation theory of crystal growth supplies a satisfactory mechanism for generating the structures of the known polytypes of the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases. The basic crystal structure of these phases is considered to be that of $2H$-$Nb_{1+x}Se_2$ ($2H$-$Ta_{1+x}Se_2$), which is consistent with the observation that this polytype is noticed far more frequently than the others. The structures of the polytypes $3R$-$Nb_{1+x}Se_2$ ($3R$-$Ta_{1+x}Se_2$), $4H_{(a)}$-$Ta_{1+x}Se_2$ ($4H$-$Nb_{1+x}Se_2$), and $4H_{(b)}$-$Ta_{1+x}Se_2$ can be generated from one or two co-operating screw dislocations acting along [001] with Burgers vector(s) equal to half the c axis of $2H$-$Nb_{1+x}Se_2$ and $2H$-$Ta_{1+x}Se_2$ respectively. The structure of the polytype $1T$-$Ta_{1+x}Se_2$ can be accounted for by assuming an alternate arrangement of the initial Ta and Se atoms as they take their places at the bottom of a growing step. In order to explain the occurrence of the polytype $6R$-$Ta_{1+x}Se_2$ the effects of both screw dislocations and alternate arrangement of the Ta and Se atoms at the bottom of the growing step must be considered. (For a more detailed discussion reference is made to MITCHELL[37] and JELLINEK[38].)

It is well known that chemical impurities and interstitial atoms can produce dislocations and, accordingly, also give rise to polytypes. Chemical impurities (resulting from the reactions between Nb and SiO_2 and Ta and SiO_2 respectively) and interstitial atoms (as indicated by the formulae $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$) are indeed present in these phases. The observed polytypism of the $Nb_{1+x}Se_2$ and $Ta_{1+x}Se_2$ phases

is therefore consistent with expectation. It may finally be predicted that further polytypes of these phases will occur.

The TaSe₃ phase

The crystal structure of $TaSe_3$ has been solved by BJERKELUND AND KJEKS-HUS[29]. The comparison of observed and calculated densities[28,29] and the characteristic crystal structure determine the stoichiometric formula $TaSe_3$.

The X-ray data for the $TaSe_3$ phase of ASLANOV et al.[26,27] gives unambiguous confirmation of identity with the present $TaSe_3$ phase.

The situation with respect to the η-$TaSe_3$ phase reported by REVOLINSKY et al.[13] is rather unclear. REVOLINSKY et al. state that η-$TaSe_3$ is isostructural with η-$NbSe_3$. (Compare the comments regarding the $NbSe_4$ phase. It must furthermore be emphasized that we have invariably obtained the same $TaSe_3$ phase in our samples despite numerous attempts in which different preparation temperatures and varying initial compositions of the samples have been used.) REVOLINSKY et al.[13] have apparently changed their minds with respect to the composition of their phase and state in the note added in proof that their corrected formula should be η-$TaSe_4$.

THE Ta–Te SYSTEM

The existence of two intermediate phases, i.e. $TaTe_2$ and $TaTe_4$, has been established by our study of the Ta–Te system (cf. Table IV). In view of the contamination of our Ta-rich samples, resulting from reaction between Ta and SiO_2, considerations concerning the possible existence of the two modifications of the $TaTe_{0.85-1.2}$ phase reported by UKRAINSKII et al.[31,32] and the β-$TaTe$ phase reported by REVOLINSKY et al.[13] seem hardly to be justified.

The TaTe₂ phase

Characterization and determination of composition for the $TaTe_2$ phase has been carried out as previously described for $NbTe_2$ (cf. Table VI).

BROWN[22] has shown that $TaTe_2$ is isostructural with $NbTe_2$, and states that his $TaTe_2$ phase (and accordingly that of REVOLINSKY et al.[13]) is identical with the $TaTe_2$ phase of BRIXNER[3] and the $TaTe_{1.5-2.0}$ phase of UKRAINSKII et al.[31,32]. (The $TaTe_2$ phase of BOES[8] is obviously identical with that of BRIXNER.)

REVOLINSKY et al.[13] and BROWN[22] state that their $TaTe_2$ phase exhibits a range of homogeneity extending from $TaTe_2$ to $TaTe$ (for samples prepared below 800°C), but they have not published any data supporting this statement, cf. BRIXNER[3]. Although this investigation has been concluded without giving a satisfactory answer to whether the present $TaTe_2$ phase is identical with that of BROWN[22] it has definitely shown that our $TaTe_2$ phase has a rather narrow range of homogeneity.

The TaTe₄ phase

$TaTe_4$ is isostructural with $NbTe_4$; the crystal structure of the subcell has been determined by BJERKELUND AND KJEKSHUS[33]. (Regarding characterization and composition, see our comments on the $NbTe_4$ phase.)

The $TaTe_3$ phase found by UKRAINSKII et al.[31] and the γ-$TaTe_3$ phase (the composition has been corrected to $TaTe_4$ in the note added in proof) found by REVO-

TABLE IV

THE INTERMEDIATE PHASES OF THE Ta–Te SYSTEM*

Authors	$TaTe_2$	$TaTe_4$
UKRAINSKII et al.[31]	β-phase ($TaTe_{1.5-2.0}$)	$TaTe_3$ u, e
UKRAINSKII et al.[32]	β-phase ($TaTe_{1.5-2.0}$) u, e	
BRIXNER[3]	$TaTe_2$ u, sg, d, e TaTe u, sg	
BOES[8]	$TaTe_2$ u, e, l	
BJERKELUND AND KJEKSHUS[28]		$TaTe_4$ u, d, m
BJERKELUND AND KJEKSHUS[33]		$TaTe_4$ u, s, d
REVOLINSKY et al.[13]	$1M$-$TaTe_2$ u, sg, t (α-$Ta_{2.0-1.0}Te_2$, < 800°C) (β-$Ta_{1.16-1.0}Te_2$, > 800°C)	γ-$TaTe_3$ u, sg
BROWN[22]	$TaTe_2$ u, s, d	
Present	$TaTe_2$? X-ray, d	$TaTe_4$

* See the footnote to Table I.

LINSKY et al.[13] are undoubtedly identical with the present $TaTe_4$ phase. (The unit cell dimensions have been used to confirm identity.) The composition stated by the former authors is, however, somewhat erroneous.

THE Nb–S AND Ta–S SYSTEMS

Although the Nb–S and Ta–S systems have not been included in the present study, it has been considered to be of some interest to quote the intermediate phases of these systems for a brief comparison with those of the Nb–Se, Nb–Te, Ta–Se, and Ta–Te systems. The existence of the following intermediate phases is reported in the Nb–S and Ta–S systems: NbS_{1-x} ($x \approx 0.1$–?, at > 850°C), l.t.-NbS_{1-x} ($x \approx 0.0$–0.15, at < 800°C), $2H$-$Nb_{1+x}S_2$ ($x \approx 0.30$–0.43, at > 1100°C), $3R$-$Nb_{1+x}S_2$ ($x \approx 0.12$–0.5, at 800°C; $x \approx 0.12$–0.25, at 1100°C), $2H$-NbS_2 (at > 850°C), $3R$-NbS_2 (at < 800°C), NbS_3, $2H$-$Ta_{1+x}S_2$ ($x \approx 0.2$–0.35), $6R$-$Ta_{1+x}S_2$ ($x \approx 0.2$), $3R$-$Ta_{1+x}S_2$ ($x \approx 0.15$), random-TaS_2, $6R$-TaS_2, $3R$-TaS_2, $2H$-TaS_2, $1T$-TaS_2, and TaS_3. (The results of JELLINEK et al.[41], JELLINEK[38,39] and BJERKELUND AND KJEKSHUS[28] have been quoted.)

Two similarities are seen on comparing the intermediate phases of the $M-X$ systems (M = Nb or Ta, X = S, Se, or Te):

(1) The existence of a polychalcogenide phase has been established in all the $M-X$ systems (NbS$_3$, ~NbSe$_4$, NbTe$_4$, TaS$_3$, TaSe$_3$, and TaTe$_4$).

(2) The sulfur and selenium systems of niobium and tantalum have, in common, phases with a general formula $M_{1+x}X_2$. Ranges of homogeneity have been observed for these phases, which furthermore, form several structurally closely-related polytypes.

APPENDIX

TABLE V

X-RAY POWDER PHOTOGRAPH DATA (CuKα$_1$-RADIATION) FOR CHARACTERIZATION OF γ-NbSe$_4$

$sin^2\theta \times 10^5$ and I_{obs}.

871 m	4600 vw	6134 m	9015 w
877 m	4624 vw	6549 w	9093 st
1476 vst	4685 vw	6751 w	9186 w
1636 st	4792 vw	7074 vw	9292 w
1688 st	4906 m	7320 vw	9414 m
1865 vw	4939 m	7455 w	9518 m
1886 vw	4984 vw	7535 m	9621 m
2342 w	5143 vw	7711 m	10407 m
2414 w	5460 w	7814 w	10659 m
3577 m	5529 w	7917 m	10987 w
4241 vw	5918 w	8100 w	11283 w

TABLE VI

X-RAY POWDER PHOTOGRAPH DATA (CuKα$_1$-RADIATION) FOR CHARACTERIZATION OF NbTe$_2$ AND TaTe$_2$

$sin^2\theta \times 10^5$ and I_{obs}		$sin^2\theta \times 10^5$ and I_{obs}		$sin^2\theta \times 10^5$ and I_{obs}	
NbTe$_2$	TaTe$_2$	NbTe$_2$	TaTe$_2$	NbTe$_2$	TaTe$_2$
769 vw	*781 w*		8629 vw	*15827 vw*	*15836 vw*
	1246 vw	*9077 w*	*9113 m*		*16211 vw*
1344 m	*1315 st*		9862 vw	*17296 st*	*17448 st*
	2724 vw	10226 vw	10094 vw	*17924 m*	*17684 m*
	3130 vw	10298 vw	10359 m	18173 vw	
3912 vw	*3932 vw*	10740 vw	10740 w	18415 vw	18497 w
4412 vw		10929 vw	10891 w	18844 vw	18653 vw
4482 vw		*11239 m*	*11123 st*	19255 vw	19255 w
	5226 vw		11195 w		19635 vw
5396 w	*5286 vw*	*11369 w*	*11289 m*		19916 vw
	5929 vw	*12133 vw*	*11872 w*		20477 vw
6168 vw	*6147 vw*		12265 vw	*21608 vw*	*21121 w*
6958 st	*7005 st*	12408 vw	12451 w	22405 vw	22341 vw
7115 vw			12506 w	22713 vw	22505 vw
7184 vw		12779 vw	12860 w	22937 vw	22962 w
7282 vst	*7277 vst*	14063 vw	14088 w	23312 vw	
7908 vw	7767 vw		14805 vw	23749 vw	24218 w
8282 vw			15264 vw	24323 vw	24522 m
8347 vw		15642 vw	15516 vw	24909 w	24943 m

Reflections which appear to be corresponding reflections for NbTe$_2$ and TaTe$_2$ are printed in italics.
Pycnometric densities at 25.00°C: NbTe$_2$ 7.33 g cm^{-3}; TaTe$_2$ 9.16 g cm^{-3}.

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Note added in proof, April 12th, 1966

Since this article was accepted for publication two further articles[42,43] have appeared which deal with the properties of $2H\text{-}Nb_{1+x}Se_2$ and $2H\text{-}Ta_{1+x}Se_2$, respectively. The conclusions of the present are, however, unaffected.