On the Possibility of Forming 'Pseudosilicides'

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The concept of 'pseudosilicon' is very successful for the prediction of occurrence and structure of certain groups of non-metallic compounds. Experiments to extend this concept to metallic compounds show that the concept has to be modified. Two factors have been found to be of importance for determining if a 'pseudosilicide' will occur. One is the composition of the compound and the second is a geometrical factor which depends on the crystal structure type. It is known that compounds of the 'pseudosilicon' type, and also non-metallic 'pseudosilicon' oxide, have extremely narrow homogeneity ranges, but transition metal 'pseudosilicides' exhibit wide ranges which may spread far from the ideal composition of the 'pseudosilicide'. Alloys close to the composition of the 'pseudosilicide' show a chemical stabilization like increased oxidation resistance and also a volume contraction.

Two new true 'pseudosilicides' have been synthesized: $Hf_5(In_{0.5}Sb_{0.5})_3$ with $D8_8$ structure: $a = 8.46$ Å, $c = 5.79$ Å and $c/a = 0.684$; and $Mo(Al, P)_2$ with $C40$ structure: $a = 4.76$ Å, $c = 6.64$ Å and $c/a = 1.40$. Results are further reported on the following ternary sections: $Nb_3Al–Nb_3Sb$, $Nb_3Ga–Nb_3Sb$, $Nb_3In–Nb_3Sb$, $(Zr_5Al_3)–Zr_5Sb_3$, $Zr_5Ga_3–Zr_5Sb_3$, $(Zr_5In_3)–Zr_5Sb_3$ and $Ti_5Ga_3–(Ti_5Sb_3)$.

Introduction

It is well-known that the $A4$ (diamond) structure type observed in diamond, silicon, germanium and gray tin will occur only if the number of valence electrons per atom equals four. With two s and two p electrons per atom an sp^3 hybridization of the orbitals will occur which will result in four bonding orbitals directed toward the vertices of a tetrahedron. Each atom will thus try to have a tetrahedral surrounding of other atoms. When mixtures of elements are present, different structure types can be contrived, where each atom has four nearest neighbors in the described way. These are the tetrahedron-structures.

Table 1. *List of Grimm–Sommerfeld compounds for different valence-electron combinations*

1+7		2+6			
CuF		BeO	ZnO		
CuCl		BeS	ZnS	CdS	HgS
CuBr		BeSe	ZnSe	CdSe	HgSe
CuI	AgI	BeTe	MgTe ZnTe	CdTe	HgTe

3+5				4+4			
(BN)	AlN	GaN	InN	(CC)	SiC		
BP	AlP	GaP	InP		SiSi	Si–Ge	
BAs	AlAs	GaAs	InAs			GeGe	
	AlSb	GaSb	InSb				SnSn

(BN) and (CC) with tetrahedron structure are thermodynamically stable only under pressure.
Complete solid solution between Si and Ge.

If one has two B elements (those with filled d shells) one can obtain an average valence electron concentration of four by combining equal atomic numbers of elements with smaller and larger numbers of valence electrons according to

$$\frac{ne_{B^*} + me_{B'} + \cdots}{n + m + \cdots} = 4 \quad \text{for} \quad B_n^* B_m' \cdots \tag{1}$$

where e_{B^*} is the number of valence electrons of element B^* and n, m are composition parameters. There are 35 intermetallic binary compounds which are composed according to this rule. They have been called Grimm–Sommerfeld compounds and are listed in Table 1. The atoms occupy the sites of the diamond structure or a homeotect variation of it (Parthé, 1961) but are distributed in orderly fashion. The structure types are thus zincblende ($B3$), wurtzite ($B4$) or one of the other stacking variations (SiC structure types).

The principle and equation (1) can be extended to compounds with three or even more different elements. Examples are $CuAlS_2$, and $ZnGeP_2$ in the chalcopyrite structure or Al_2CO (Jeffrey & Lynton, 1958) and $BeSiN_2$ in a stacking variation of it or Cu_2FeSnS_4 with stannite structure.

Counting the valence electrons only, all the Grimm–Sommerfeld compounds and the multicomponent phases are isoelectronic with silicon or the other elements in the 4B group. They have also structures similar or related to that of silicon. One may call these compounds 'pseudosilicon'.

It is of interest to find to what degree the concept of 'pseudosilicon' can be extended to predict the formation and the structure of compounds in multicomponent systems. In the case of compounds of silicon with non-metallic elements, the same exchange of 'pseudosilicon' for silicon does occur. If one considers, for example, silicon oxide SiO_2 the formula

for a 'pseudosilicon' oxide is $(B_{0.5}^{III}B_{0.5}^{V})O_2$. A good example is $AlPO_4$ for which all three different quartz (SiO_2) structures have been reported. Other 'pseudosilicon' oxides $(B_{0.5}^{III}B_{0.5}^{V})O_2$ occur as $BAsO_4$, $AlAsO_4$, $GaPO_4$ and many more (Dachille & Roy, 1959). Another example is $AlPS_4$, a 'pseudosilicon' sulfide which crystallizes with a structure similar to the SiS_2 structure (Weiss & Schäfer, 1960). All these compounds have an extremely small homogeneity range. In distinction to the cases discussed below all these compounds have equal numbers of 3B and 5B atoms.

We undertook to investigate the formation of transition metal 'pseudosilicides'. We were interested in studying the possibility of synthesizing compounds like $T_n(B_{0.5}^{III}B_{0.5}^{V})_m$ corresponding to a known true silicide T_nSi_m where T means any transition metal.

We wanted to know if the crystal structure of 'pseudosilicides' would be related to those of true silicides and we also were interested to see if the ratio of $B^{III}:B^V$ was of importance in controlling the stability of these compounds. Accordingly, we investigated a few sections of ternary phase diagrams, one component being a transition metal and the other two components being proper B elements, as, for example, 3B and 5B elements. This study did enable us to state whether or not a ternary compound with silicide structure existed and if the homogeneity range of these 'pseudosilicides' was as narrow as in the case of non-metallic 'pseudosilicon' compounds.

Sample preparation

The well mixed metal powders were pressed into pellets and induction-melted in boron nitride crucibles

Table 2. *Experimental results of $T_3B^{III}-T_3B^V$ sections*

$T_3B^{III}-T_3B^V$	Structure type	Lattice parameter	Remarks
Nb_3Al-Nb_3Sb	$D(A15)$ (Cr_3O) structure over complete range from Nb_3Al to Nb_3Sb	Nearly linear increase of lattice constants from 5·183 Å for Nb_3Al to 5·263 Å for Nb_3Sb	See also Rothwarf, Dickson, Thiel, Parthé & Boller (1962)
Nb_3Ga-Nb_3Sb	$D(A15)$ structure at $Nb_3(Ga_{0.5}Sb_{0.5})$	For $Nb_3(Ga_{0.5}Sb_{0.5})$ $a=5·22_8$ Å	Most probably complete solid solution Nb_3Ga-Nb_3Sb
Nb_3In-Nb_3Sb	No single phase $D(A15)$ structure for sample composed as $Nb_{0.75}In_{0.125}Sb_{0.125}$. Free indium always present		Nb_3In can be made only under pressure (Banus, Reed, Gates, Lavine & Kafalas, 1962). No stabilization occurs by partial replacement of In with Sb

Table 3. *Experimental results of $T_5B_3^{III}-T_5B_3^V$ sections*

$T_5B_3^{III}-T_5B_3^V$	Structure type	Lattice parameter				Remarks
$(Zr_5Al_3)-Zr_5Sb_3$	$D8_8$ structure from Zr_5Sb_3 up to $Zr_5(Al_{0.87}Sb_{0.13})_3$	Zr	Al	Sb	a (Å) c (Å)	Minimum c/a ratio at approximate composition of pseudosilicide. Zr_5Sb_3 chemically unstable, but it becomes stable by partial replacement of Sb by Al starting from $Zr_5(Al_{0.18}Sb_{0.82})_3$
		64·0	04·0	32·0	8·446 5·798	
		62·5	07·5	30·0	8·442 5·783	
		62·5	12·5	25·0	8·378 5·730	
		62·5	18·7	18·8	8·326 5·708	
		62·5	25·0	12·5	8·294 5·702	
		62·5	27·5	10·0	8·276 5·694	
				atomic%		
$Zr_5Ga_3-Zr_5Sb_3$	$D8_8$ structure over complete range	$Zr_5(Ga_{0.5}Sb_{0.5})_3$ $a=8·248$, $c=5·696$ Å, $c/a=0·691$				Pseudosilicide chemically very stable; increased oxidation resistance
$(Zr_5In_3)-Zr_5Sb_3$	$D8_8$ structure from Zr_5Sb_3 up to $\simeq Zr_5(In_{0.8}Sb_{0.2})_3$. Slight Zr excess (64 atomic% instead of 62·5) necessary in all cases to obtain single phase pattern	Zr	In	Sb	a (Å) c (Å)	Zr_5In_3 does not form. The pseudosilicide composition is reached from Zr_5Sb_3 side. Chemical stabilization of pseudosilicide; there also minimum of c/a ratio
		64	07	29	8·449 5·796	
		64	16	20	8·446 5·767	
		64	18	18	8·446 5·767	
		64	24	12	8·446 5·775	
		64	29	07	8·440 5·781	
				atomic%		
$Ti_5Ga_3-(Ti_5Sb_3)$	$D8_8$ structure from Ti_5Ga_3 up to $Ti_5(Ga_{0.5}Sb_{0.5})_3$. With more Sb no $D8_8$ phase any more	Increase from Ti_5Ga_3 $a=7·609$, $c=5·288$ Å, $c/a=0·695$ to $Ti_5(Ga_{0.5}Sb_{0.5})_3$ with $a=7·783$, $c=5·345$ Å, $c/a=0·687$				Ti_5Sb_3 is unknown. The pseudosilicide composition is reached from the Ti_5Ga_3 side
$(Hf_5In_3)-(Hf_5Sb_3)$	$Hf_5(In_{0.5}Sb_{0.5})_3$ with $D8_8$ structure. Probably also extensive homogeneity range	$Hf_5(In_{0.5}Sb_{0.5})_3$ $a=8·46$, $c=5·79$ Å, $c/a=0·684$				True pseudosilicide: No $D8_8$ structures in the binary systems

under an inert atmosphere of argon. The alloys thus formed were homogenized in sealed off evacuated silica tubes at 1000 °C for 24 hours.

Experimental results

Only sections of T–B^{III}–B^V ternary systems have been studied in this laboratory, namely T_3B^{III}–T_3B^V, $T_5B_3^{III}$–$T_5B_3^V$ and TB_2^{III}–TB_2^V (T=transition metal, B=B metal). For brevity the results are presented in the form of tables.

Table 2 shows the results of T_3B^{III}–T_3B^V sections. There is no indication of any ternary compounds at the correct composition for the 'pseudosilicide' $T_3(B_{0.5}^{III}B_{0.5}^V)$. In the first two ternary mixtures, complete solid solutions exist and the lattice parameters change regularly. Also a compound of the composition

Table 4. *d-Spacings and observed intensities*

(Cu $K\alpha$)

Hf$_5$(In$_{0.5}$Sb$_{0.5}$)$_3$ with $D8_8$ structure			Mo(Al, P)$_2$ with $C40$ structure		
$hkil$	d (Å)	I_0	$hkil$	d (Å)	I_0
$10\bar{1}0$	(7·31)	—	$10\bar{1}0$	4·126	mw
$11\bar{2}0$	(4·22)	—	$10\bar{1}1$	3·504	vs
$20\bar{2}0$	3·659	w	$10\bar{1}2$	2·584	ms
$11\bar{2}1$	3·411	vw	$11\bar{2}0$	2·372	vs, coinc.
0002	2·887	mw	$11\bar{2}1$	2·240	vvs
$21\bar{3}0$	2·760	m	0003	2·213	ms
$10\bar{1}2$	2·688	mw	$20\bar{2}0$	2·062	m
$21\bar{3}1$	2·495	vvs	$11\bar{2}2$	1·833	s
$30\bar{3}0$	2·436	s, coinc.	$11\bar{2}3$	1·620	mw
$11\bar{2}2$	2·385	vs	$21\bar{3}0$	1·556	w
$20\bar{2}2$	2·273	w	$10\bar{1}4$	1·532	m
$22\bar{4}0$	(2·11)	—	$21\bar{3}1$	1·516	m
$31\bar{4}0$	2·027	vw	$20\bar{2}3$	1·509	m
$21\bar{3}2$	(2·00)	—			
$22\bar{4}1$	1·977	vw			
$31\bar{4}1$	1·914	mw			

$Nb_{0.75}In_{0.125}Sb_{0.125}$ which would be isoelectronic with the well known Nb_3Sn does not form. With our method of pressure-free heating the end product always contained free indium.

The experimental results from investigations on $T_5B_3^{III}$–$T_5B_3^V$ sections are given in Table 3. Only one ternary 'pseudosilicide' was found. $Hf_5(In_{0.5}Sb_{0.3})_3$ crystallizes with $D8_8$ (Mn_5Si_3) structure with probably statistical distribution of In and Sb atoms on the Si atom sites of the Mn_5Si_3 structure. The space group is $P6_3/mcm$ ($D6_h^3$) and there are 4 Hf in $4d$ and 6 Hf in $6g$ with $x_{Hf} \simeq 0.24$ and 6 In or Sb in $6g$ with $x \simeq 0.615$; d-spacings and observed intensities are given in Table 4. The intensities check well with those calculated for isoelectronic Hf_5Sn_3 (Boller, Nowotny & Wittmann, 1960).

In the other T_5B_3 sections a $D8_8$ phase is known as a binary phase at least in one binary system and it extends into the ternary region up to or even further than the 'pseudosilicide' composition $T_5(B_{0.5}^{III}B_{0.5}^V)_3$. While the binary $D8_8$ phases with 3 B or 5 B metals are chemically often unstable (Boller & Parthé, 1963) — for example, Zr_5Sb_3 decomposes in air in half an hour — the ternary $D8_8$ phases do not oxidize at room temperature and are generally better crystallized than the binary ones. These facts indicate that the partial molar free energy of zirconium in the ternary alloy is significantly reduced unless kinetic effects play a role, which one would not expect. One concludes that a thermodynamic stabilization occurs close to the composition of a 'pseudosilicide' $T_5(B_{0.5}^{III}B_{0.5}^V)_3$. Another indication of this is the observed minimum of the c/a ratio at the approximate 'pseudosilicide' composition. Fig. 1 shows the results for binary systems with Zr_5Sb_3 as
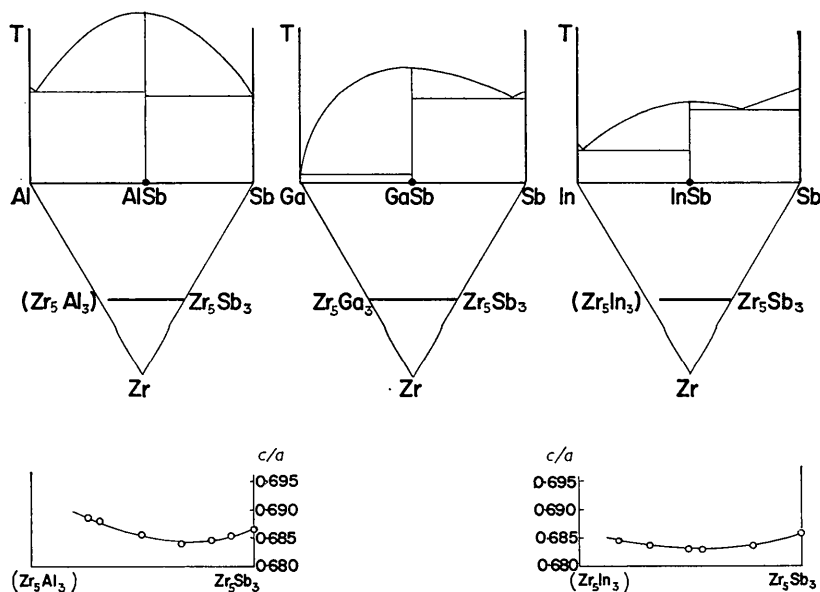

Fig. 1. Axial ratios and homogeneity limits of ternary $D8_8$ phases

one component and Zr_5Al_3, Zr_5Ga_3 and Zr_5In_3 as second component. While the compounds corresponding to 'pseudosilicon' (AlSb, GaSb and InSb) show very small homogeneity ranges, the 'pseudosilicides' may spread about the ideal composition to a great extent.

Experiments to synthesize 'pseudodisilicides' $T(B_{0.5}^{III}B_{0.5}^{V})_2$ were undertaken by melting together a transition metal and $B^{III}B^{V}$ Grimm–Sommerfeld compounds. The chemical reactions between Zr or Nb and InSb or GaAs gave monoarsenides or monoantimonides according to $Zr + InSb \rightarrow ZrSb + In$ or $Nb + GaAs \rightarrow NbAs + Ga$ and $Zr + GaAs \rightarrow ZrAs + Ga$. Later AlP was used which in size compares better to silicon (AlP: $B3$ type, $a = 5\cdot42$ Å; Si: $A4$ type, $a = 5\cdot4199$ Å). A true 'pseudosilicide' $Mo(Al,P)_2$ with the $C40$ ($CrSi_2$) structure type was successfully synthesized. There are no $C40$ structures in the binary systems. The hexagonal unit cell has the following dimensions: $a = 4\cdot76$ Å and $c = 6\cdot64$ Å with $c/a = 1\cdot40$. Space group is $P6_222$ (D_6^4). 3Mo are in $3c$ and 6Al or P in $6i$ with $x \simeq \frac{1}{6}$. The d-spacings and observed intensities of this 'pseudosilicide' are given in Table 4. The intensities check with those calculated for the $C40$ structure type. It was not possible to obtain this phase without the presence of other phases. Experiments are under way to determine the exact homogeneity limits.

Conclusions

The concept of 'pseudosilicon' cannot be extended to metallic 'pseudosilicides' without restrictions. The experimental results indicate that two factors are of importance for determining if a 'pseudosilicide' will occur. These factors are the composition of the 'pseudosilicide' and, depending upon the structure type, also size-ratio between T-metal atoms and average of 'pseudosilicon' atoms.

The influence of the composition as a deciding factor may be understood if one assumes that the interactions between B^{III} and B^{V} atoms require that the atoms are positioned close together in the structure. In a compound with very high transition metal content the B atoms will most probably be far apart and interactions will not occur. This is certainly the case with the β-tungsten (Cr_3O) structure type. Samples with composition $T_3(B_{0.5}^{III}B_{0.5}^{V})$ exhibit no different properties from any other sample of the series of solid solutions between T_3B^{III} and T_3B^{V}.

The first indications of a special stabilization of a 'pseudosilicide' composition occur in T_5B_3 solid solutions, noticeable in increased oxidation resistance and volume contraction. $Hf_5(In, Sb)_3$ is a true ternary 'pseudosilicide'. In distinction to compounds denoted 'pseudosilicon' the B^{III} and B^{V} atoms are most possibly statistically distributed in the structure.

(Because of nearly equal scattering factors of In and Sb no statement can be made for $Hf_5(In, Sb)_3$ but also $Zr_5(Al_{0.5}Sb_{0.5})_3$ showed no trace of superstructure lines.) A second characteristic feature is the large width of the homogeneity range. The exact composition of the 'pseudosilicon' according to equation (1) is obviously not too important.

One would expect that 'pseudosilicides' $T(B_{0.5}^{III}B_{0.5}^{V})_2$ form more readily; owing to the abundance of B metals more interactions between these occur. $Mo(Al, P)_2$ is a true ternary 'pseudosilicide' with $C40$ ($CrSi_2$) structure. (Owing to nearly equal scattering factors of Al and P it is not possible to state if Al and P are ordered or not.) 'Pseudosilicides' between small transition metals and larger 'pseudosilicon elements' do not form. These observations are in agreement with the result of an earlier study on normal disilicides (Nowotny & Parthé, 1954), in which it was demonstrated that the disilicide structures occur only if the radius ratio transition metal atom: silicon atom is inside some narrow limits.

The wide homogeneity range observed by the 'pseudosilicides' with $D8_8$ structure was an indication that the 'pseudosilicon' did not need to correspond exactly to equation (1). Any deviation from equation (1) brings about a deviation of the avarage valence electron concentration of four. The experimental results on 'pseudosilicides' may now be used to make statements about the valence electron contribution of real silicon in real silicides. The ability of silicon to provide four electrons for bonding is not of key importance for the formation and stability of transition metal silicide structures.

References

BANUS, M. D., REED, T. B., GATOS, E. C., LAVINE, M. C. & KAFALAS, J. A. (1962). J. Phys. Chem. Solids, 23, 971.

BOLLER, H., NOWOTNY, H. & WITTMANN, A. (1960). Mh. Chem. 91, 1174.

BOLLER, H. & PARTHÉ, E. (1963). Mh. Chem. 94, 225.

DACHILLE, F. & ROY, R. (1959). Z. Kristallogr. 111, 451.

JEFFREY, G. A. & LYNTON, H. (1958). Bull. Amer. Phys. Soc. Ser. II, 3, 231.

NOWOTNY, H. & PARTHÉ, E. (1954). Planseeber. 2, 34.

PARTHÉ, E. (1961). Z. Kristallogr. 115, 52.

ROTHWARF, F., DICKSON, C., THIEL, R., PARTHÉ, E. & BOLLER, H. (1962). Bull. Amer. Phys. Soc. Ser. II. 7, 322.

WEISS, A. & SCHÄFER, H. (1960). Naturwissenschaften, 47, 495.