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Scandium Binary and Ternary Alloy Systems and Intermetallic Compounds*

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Scandium is the first d-element and a member of the rare earths family. The available data, published until the beginning of 1997, on scandium binary and ternary alloy systems and intermetallic compounds with other elements (with the exception of halogens, hydrogen, oxygen, sulphur and nitrogen) have been reviewed. Data about 65 binary and about 200 ternary systems have been generalized. The crystal chemical analysis of 462 investigated intermetallic compounds (out of 554 known to date) belonging to 155 structure types has been carried out. Some regularities and peculiarities of scandium alloy systems and the crystal chemistry of its intermetallics have been found. It has been shown that scandium is the linking element between the rare earths and the *d*-elements. From the crystal chemical point of view, scandium appears to be closer to 4a elements, especially to Zr and Hf, rather than to the other rare earths. Functional relations between the compositions and structures of compounds and the factors governing these changes have been analysed. It has been shown that the found regularities are useful for investigation of new systems, synthesis of new intermetallic compounds and investigation of their crystal structures.

INTRODUCTION

Scandium is the first d-element. It is also a member of the family of rare earths (RE) (along with Y, La and the lanthanides). It is produced in small

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quantities in the world (a few hundreds of kilograms per year) and has had limited application in practice. Lack of concentrated deposits of scandium minerals resulted in high prices and low utilization of scandium containing products. Most of the scandium produced is a by-product from uranium processing in the countries that have this technology. Ukraine is among this limited group of countries. Scandium is a perspective metal owing to its specific properties, *e.g.* high melting temperature, 1814 K, which is close to the melting temperature of iron metal, small density, 2.989 g cm^{-3}, which is compatible with the density of Al, *etc*. These properties determine the prospects of scandium application in the production of material for spacecraft, in electronics and some other areas.[1] New uses and applications will be developed only from new fundamental and applied studies of scandium and its compounds. This will cause an increase in scandium production and a decrease of its price.

First data on the investigation of scandium systems and on the synthesis of scandium compounds with other metal or semimetallic elements (with the exception of 7b group elements, hydrogen, oxygen, sulphur and nitrogen) were published in the early sixties.[2,3] They were prepared by electric arc melting pieces of pure elements under an inert gas atmosphere (usually argon). In 1979, the number of synthesized compounds rose to more than two hundred.[4] Up to the beginning of 1997, 134 binary and 420 ternary scandium intermetallic compounds were known. Previous comprehensive treatment of scandium as an element and its alloys and compounds had been done more than 20 years ago.[5] Since that time, numerous new investigations on scandium alloy systems and intermetallic compounds have been published. Since the author has been working in the field of chemical and structural investigations of scandium based systems and compounds for more than twenty years, it seems that now is the time to overview all the known data to date.

A systematic analysis and generalization of the available experimental data on phase diagrams and compounds can contribute to improving the existing semiempirical and theoretical concepts. Some regularities can also be used to predict the type and properties of not yet investigated systems. Below some regularities and pecularities of scandium alloy systems and intermetallics found as a result of experimental data analysis are summarised below. Such data are regarded as the basic data for the synthesis and development of new materials.

BINARY SCANDIUM ALLOY SYSTEMS

Binary Sc-E (E=element) phase diagrams were investigated in the whole or partial concentration region for the majority of elements. These data are presented in a summarised form in Figure 1. The data were obtained primarily from the original papers supplied by relevant handbooks.[4,6,7] There are no data about 24 binary systems out of the 89 possible ones.

All the investigated 65 Sc-E binary phase diagrams can be divided into four types.

1. Systems with complete mutual solubility of components in liquid and solid (at least one region occurs). Binary compounds do not occur. (E=3a- (except Eu, Yb, U), 4a-element).

2. Systems with immiscibility gaps in liquid (system of monotectic type). Binary compounds do not occur (E=2a-, 3a-element (Eu, Yb, U).

3. Systems with low or practically absent mutual solubility of components in solid (systems of eutectic type). Binary compounds do not occur (E=5a-, 6a-element).

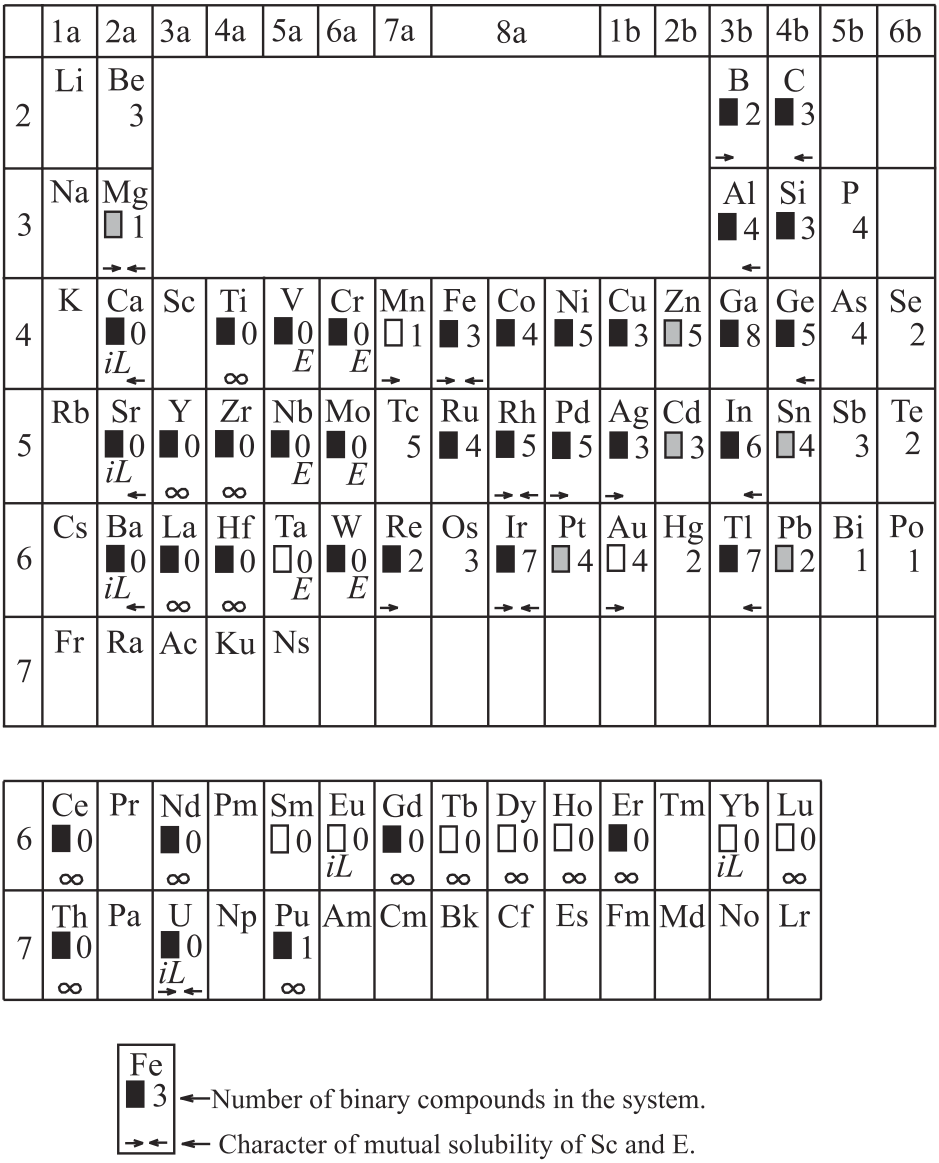
4. Systems with one or more binary compounds. Limited mutual solubility of components in solid. (E=2a-, 7a-8a, 1b-6b-element).

There are only two exceptions – the systems with U and Pu. Pu forms one binary compound with Sc and in the Sc-U system appreciable limited mutual solubility of components in solid occurs. All rare earths (with the exception of Eu and Yb) and the 4a elements Ti, Zr and Hf are completely miscible with Sc in liquid and solid. It is necessary to stress that Sc is the only element among rare earths that forms continuous solid solutions with other rare earths and with 4a elements. Zr and Hf having nearly the same atomic radius as Sc (0.1602, 0.1580 and 0.1641 nm, respectively) usually form binary systems of eutectic type with other rare earths, for *e.g.* Zr-Y, Zr-Gd, Zr-Dy, Zr-Er, Hf-Y, Hf-Er.[6]

Only Eu and Yb among all rare earths form immiscibility gaps with Sc in liquid and solid. Difference in valences of these two rare earths and Sc is, perhaps, the main reason for this difference in interaction. Divalent state is more typical of Eu and Yb whereas the other rare earths are usually trivalent. The same divalent state is characteristic of alkaline earths, which are also immiscible with Sc in liquid and solid. Therefore, it is possible to predict the same type of binary phase diagrams of Sc with alkaline metals. These elements differ even more from Sc in the valence state and other properties (melting temperature, electronegativity, *etc.*) than alkaline earths.

All 5a–6a elements form with Sc binary systems of eutectic type with very low mutual solubility in solid. With an increase transition element of the melting temperature, the eutectic point shifts towards the melting point of scandium.

The elements of all other groups form binary compounds with scandium. The number of binary compounds in each system is indicated in Figure 1. Within each large period, Sc forms the highest number of binary compounds with 8a and 3b elements. In the rows of p-elements, number of binary compounds decreases with the increase of the group number of element. The



	1a	2a	3a	4a	5a	6a	7a	8a			1b	2b	3b	4b	5b	6b
2	Li	Be 3											B ■2 →	C ■3 ←		
3	Na	Mg ▨1 →←											Al ■4 ←	Si ■3	P 4	
4	K	Ca ■0 iL ←	Sc	Ti ■0 ∞	V ■0 E	Cr ■0 E	Mn □1 →	Fe ■3 →←	Co ■4	Ni ■5	Cu ■3	Zn ▨5	Ga ■8	Ge ■5 ←	As 4	Se 2
5	Rb	Sr ■0 iL ←	Y ■0 ∞	Zr ■0 ∞	Nb ■0 E	Mo ■0 E	Tc 5	Ru ■4	Rh ■5 →←	Pd ■5 →	Ag ■3 →	Cd ▨3	In ■6 ←	Sn ▨4	Sb 3	Te 2
6	Cs	Ba ■0 iL ←	La ■0 ∞	Hf ■0 ∞	Ta □0 E	W ■0 E	Re ■2 →	Os 3	Ir ■7 →←	Pt ▨4	Au □4 →	Hg 2	Tl ■7 ←	Pb ▨2	Bi 1	Po 1
7	Fr	Ra	Ac	Ku	Ns											

6	Ce ■0 ∞	Pr	Nd ■0 ∞	Pm	Sm □0	Eu □0 iL	Gd ■0 ∞	Tb □0 ∞	Dy □0 ∞	Ho □0 ∞	Er ■0 ∞	Tm	Yb □0 iL	Lu □0 ∞
7	Th ■0 ∞	Pa	U ■0 iL →←	Np	Pu ■1 ∞	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fe
■ 3 ←Number of binary compounds in the system.
→← ← Character of mutual solubility of Sc and E.

Figure 1. Summarised data about binary Sc-E phase diagrams. Phase diagram is investigated in 75–100% of the concentration range (black symbol), or in 25–57% (grey symbol), or in less than 25% (empty symbol). Lack of symbol means the phase diagram has not yet been investigated. Characters of mutual solubility of Sc and E: miscibility gap in the liquid state occurs (*iL*), mutual solubility in the solid state is <1 at.%, simple eutectic, no binary compound occurs (*E*), solubility of Sc in solid E is > 1 at.% (→), solubility of E in solid Sc is > 1 at.% (←), at least one continuous solid solution of Sc and E occurs (∞).

number of binary compounds changes negligibly with the increase of the period number.

114 binary intermetallic scandium compounds of defined crystal structure crystallize in 29 different compositions and belong to 56 structure types (Table I). Most of them occur in constant compositions. In the cases of compounds with variable composition, their homogeneity ranges usually do not exceed 1 to 5 at.%. The only two exceptions are compounds ScMg(β′) and ScC_{1-x}. Scandium intermetallics very often occur at stoichiometries ScE (30 compounds), ScE_2 (20 compounds), ScE_3 (9 compounds), Sc_2E (8 compounds) and Sc_5E_3 (8 compounds). Thus, more than 55% of binary scandium intermetallics (75 compounds of the 134 known) occur only at five simple stoichiometries out of the 29 known to date. At these stoichiometries, compounds crystallize in different structure types depending on the position of

TABLE I

Stoichiometries and structure types of binary scandium intermetallics

Formula	Number of compounds	Structure type	Formula	Number of compounds	Structure type
ScE_{13}	1	$NaZn_{13}$	ScE	30	CsCl, AuCu, NaCl, CrB, NiAs
ScE_{12}	2	$ThMn_{12}$, UB_{12}			
ScE_7	2	Mn, $ScCd_7$	$Sc_{11}E_{10}$	1	$Ho_{11}Ge_{10}$
Sc_3E_{17}	1	Ru_3Be_{17}	Sc_6E_5	2	Ti_6Ge_5
ScE_5	2	$CaCu_5$	Sc_5E_4	4	CsCl, Ti_5Ga_4, Sm_5Ge_4, $Ho_{11}Ge_{10}$
Sc_5E_{24}	1	Mn			
$Sc_{13}E_{58}$	1	$Gd_{13}Cd_{58}$	Sc_4E_3	1	Th_3P_4
ScE_4	2	$MoNi_4$	Sc_3E_2	6	Cr_3C_2 S_3Sb_2, Gd_3Ga_2, V_3As_2
Sc_2E_7	1	Ce_2Ni_7			
ScE_3	9	$AuCu_3$, $SnNi_3$	Sc_5E_3	8	Mn_5Si_3, Yb_5Sb_3
ScE_2	20	$MgZn_2$, $MgCu_2$, $MgNi_2$, $MoSi_2$, AlB_2, KHg_2, $ZrGa_2$, $ZrSi_2$, $ScSn_2$	Sc_2E	8	Ti_2Ni, Al_2Cu, Co_2Si, Ni_2In, Cu_2Sb
			Sc_7E_3	2	Th_7Fe_3, Sc_7As_3
$ScE_{1.74}$	1	$MgCu_2$	$Sc_{11}E_4$	3	$Sc_{11}Ir_4$
Sc_3E_5	2	Tm_3Ga_5, Pu_3Pd_5	Sc_3E	3	Ni_3Sn, Fe_3C, Sc_3Co
Sc_2E_3	3	AlB_2, Ti_7S_{12}, Sc_2S_3	$Sc_{57}E_{13}$	4	$Sc_{57}Rh_{13}$
Sc_3E_4	1	Sc_3C_4	$Sc_{29}E_6$	1	$Sc_{29}Fe_6$
			$Sc_{44}E_7$	2	$Mg_{44}Rh_7$

the element in the periodic table. Some binary compounds occur in two ($ScFe_2$, $ScNi_5$, Sc_4C_3, $ScSi_{1.5}$, Sc_3P_2) or in three (Sc_3As_2) polymorphic modifications. The crystal structures of polymorphic forms are structurally related.

TERNARY SCANDIUM ALLOY SYSTEMS

It is assumed that the data of a given ternary system are complete if at least one isothermal section of the system has been investigated in 3/4 of the concentration region. There are about 70 such Sc-M-X ternary systems, preferably with M=d-, f-element and X=B, Al, Ga, C, Si, Ge (Figure 2). About 40 ternary systems, preferably with Si and Ge, were investigated by the author. The relevant data for these systems are summarised in Figures 3 and 4. However, additional ternary compounds that are stable in the limited temperature range may exist in such ternary systems. They, of course, will not be observed by investigating the system at one temperature only or if only a part of the system has been studied. A total of 420 ternary scandium intermetallic compounds have been synthesized. The crystal structure has been determined for 348 compounds (more than 80%). These compounds belong to 111 structure types.

The crystal structure has been investigated most completely for ternary compounds of the Sc-M-X systems with M=3d, 4d, 5d, 4f-element and with X=B, Al, Ga (102 compounds) as well as with X=C, Si, Ge (178 compounds). Their compositions are given in Figure 5. Similarly as in the case of binary systems, also within the sequence of these ternary systems Sc-M-B, Sc-M-Al and Sc-M-Ga *etc.*, within each period of the periodic table the number of ternary compounds usually increases with increasing the atomic number of component M (Figures 3 and 4). The group 8a elements form the largest number of ternary compounds. Among the systems containing 3b and 4b elements, the ternary systems with B differ considerably from those with Al and Ga. Also, the C systems behave in a different way when compared with the Si and Ge ones. These systems differ in the number of the occurring ternary compounds and in their compositions (Figures 3–5). Ternary compounds $ScMB_2$ (No 30 in the Figure 5(a)) and $ScMC_2$ (No 31 in the Figure 5(b)) are exceptions in this sense. However, even in these cases the crystal structures of $ScMB_2$ and $ScMC_2$ are different from the structures of $ScMAl_2$, $ScMSi_2$ or $ScMGe_2$. In all other cases, the stoichiometries of ternary borides and carbides are different from the stoichiometries of ternary compounds of their neighbours among 3b and 4b elements. It is known in the inorganic chemistry that, within a given group of the periodic table, the elements of the second period differ considerably in their properties from those belonging to other periods. This difference exists also among their intermetallic compounds.

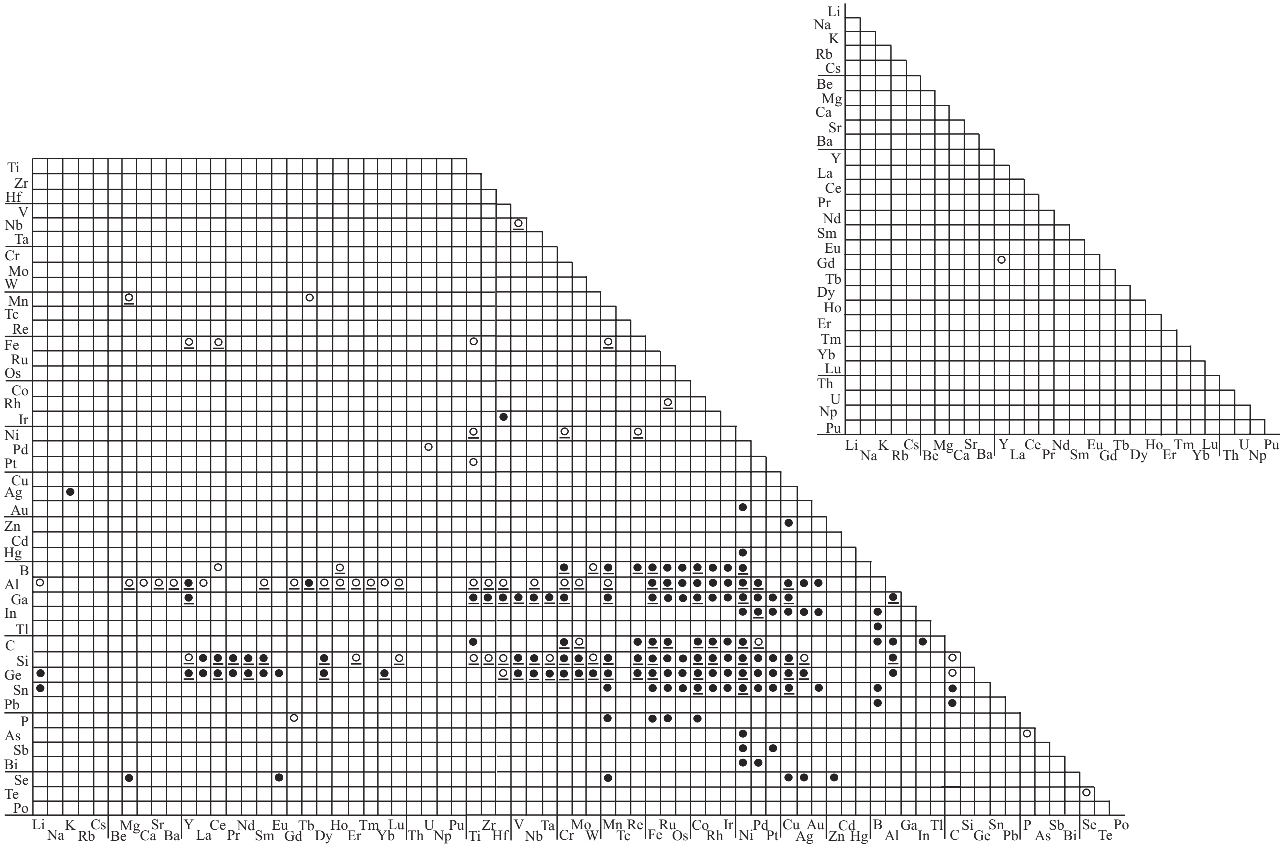
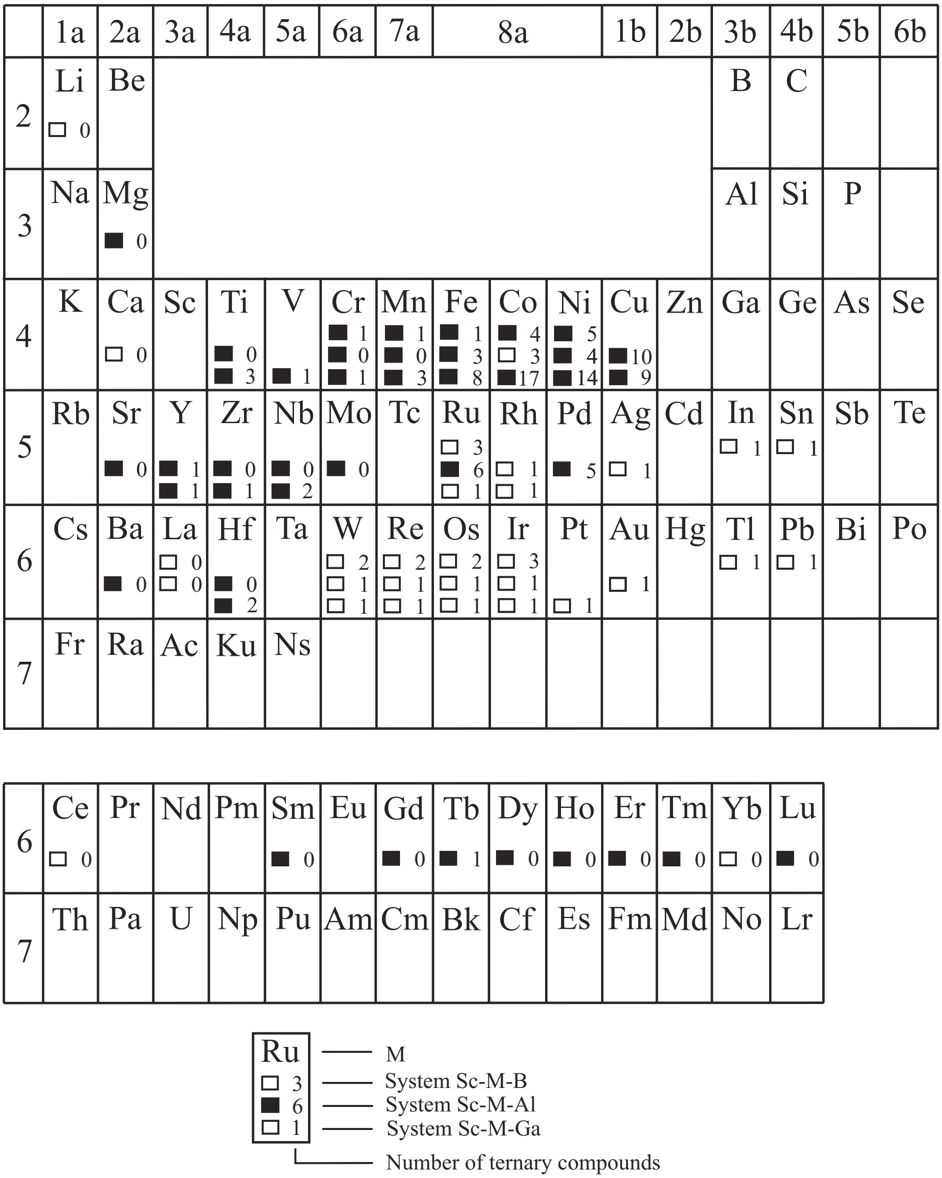


Figure 2. Summarised data about the investigation of phase diagrams of Sc-M-X, Sc-M-M' and Sc-X-X' ternary systems. Phase equilibria are established in the whole concentration region or in part of it (dash), ternary compounds do not occur (empty circle), ternary compounds occur (filled circle). Lack of any symbol means the system has not yet been investigated.



	1a	2a	3a	4a	5a	6a	7a	8a			1b	2b	3b	4b	5b	6b
2	Li □ 0	Be											B	C		
3	Na	Mg ■ 0											Al	Si	P	
4	K	Ca □ 0	Sc	Ti ■ 0 ■ 3	V ■ 1	Cr ■ 1 ■ 0 ■ 1	Mn ■ 1 ■ 0 ■ 3	Fe ■ 1 ■ 3 ■ 8	Co ■ 4 □ 3 ■ 17	Ni ■ 5 ■ 4 ■ 14	Cu ■ 10 ■ 9	Zn	Ga	Ge	As	Se
5	Rb	Sr ■ 0	Y ■ 1 ■ 1	Zr ■ 0 ■ 1	Nb ■ 0 ■ 2	Mo ■ 0	Tc	Ru □ 3 ■ 6 □ 1	Rh □ 1 □ 1	Pd ■ 5	Ag □ 1	Cd	In □ 1	Sn □ 1	Sb	Te
6	Cs	Ba ■ 0	La □ 0 □ 0	Hf ■ 0 ■ 2	Ta	W □ 2 □ 1 □ 1	Re □ 2 □ 1 □ 1	Os □ 2 □ 1 □ 1	Ir □ 3 □ 1 □ 1	Pt □ 1	Au □ 1	Hg	Tl □ 1	Pb □ 1	Bi	Po
7	Fr	Ra	Ac	Ku	Ns											

6	Ce □ 0	Pr	Nd	Pm	Sm ■ 0	Eu	Gd ■ 0	Tb ■ 1	Dy ■ 0	Ho ■ 0	Er ■ 0	Tm ■ 0	Yb □ 0	Lu ■ 0
7	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 3. Summarised data about Sc-M-B(Al, Ga) and Sc-X-B(Al, Ga) ternary systems. Phase equilibria are established in the whole concentration region or in a part of it (■), only separate alloys have been investigated (□). Lack of a symbol means the system has not yet been investigated.

Intermetallic compounds of scandium with the 6b-elements Se, Te and Po are different from all the above treated mentioned scandium compounds.

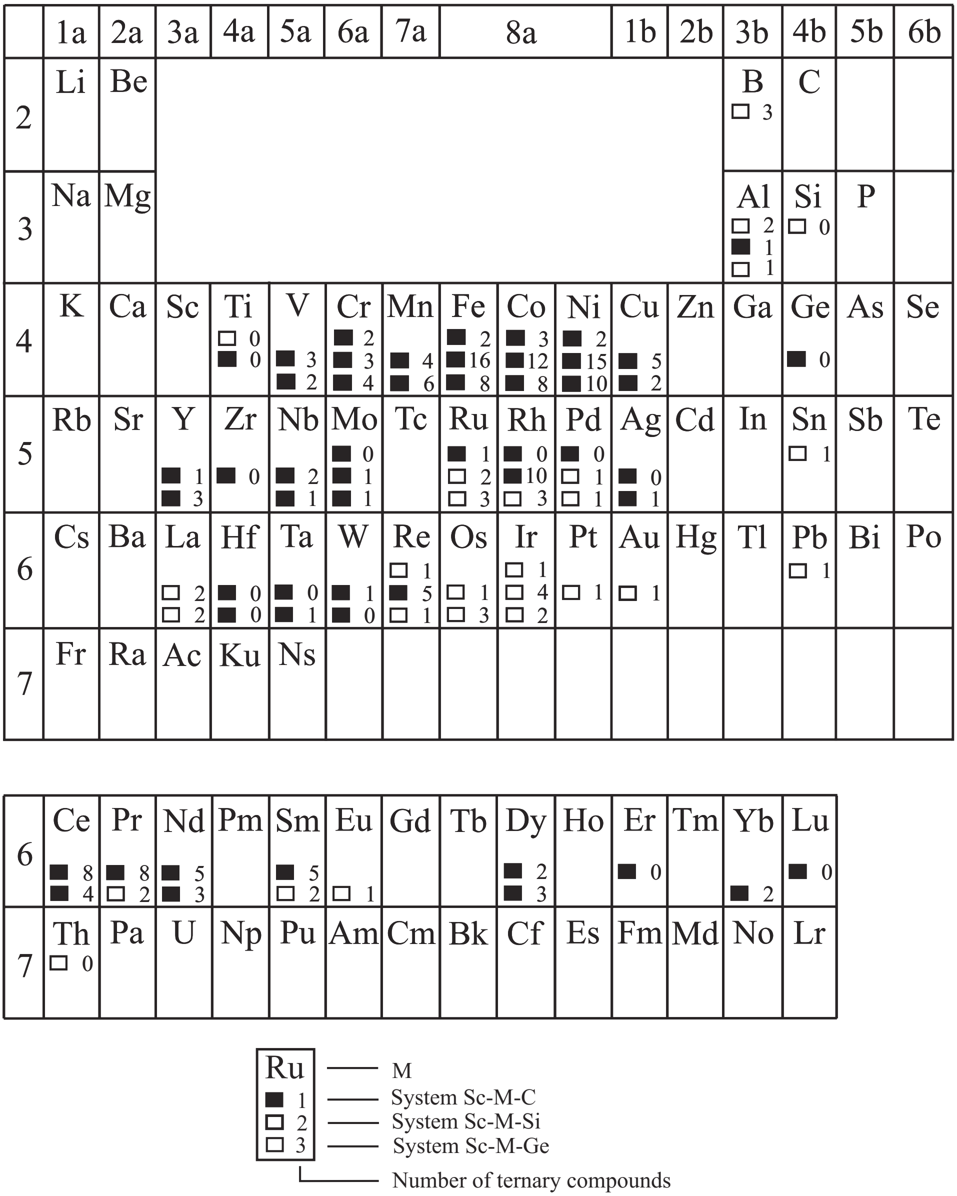


Figure 4. Summarised data about Sc-M-C(Si, Ge) and Sc-X-C(Si, Ge) ternary systems. Meanings of symbols – see Figure 3.

They crystallize in structures typical of halogenides, oxides, sulphides and other ionic compounds (NaCl, Al_2MgO_4, Fe_2CaO_4, $ErCuS_2$, ErAgAs structure types).[7] In these structure types, each atom is coordinated by the atoms of

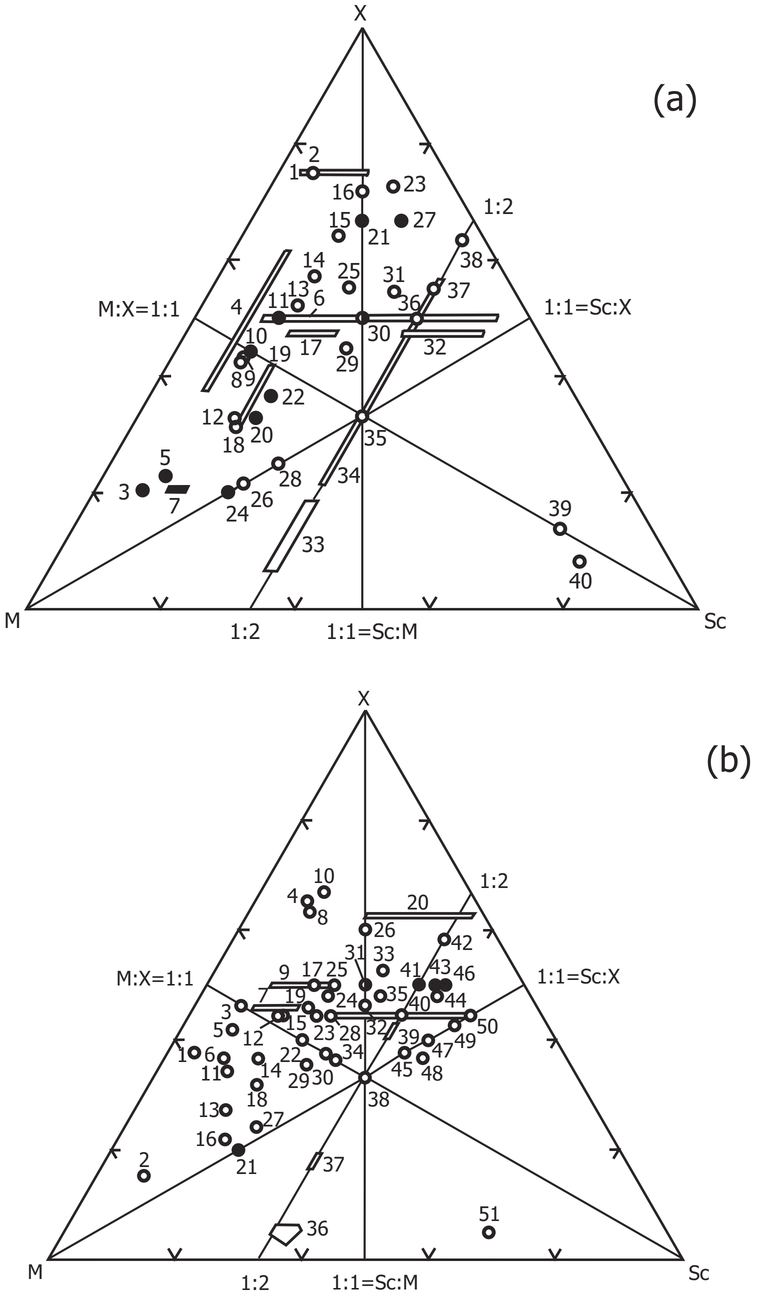


Figure 5. Compositions (plotted in at.% and indicated by numbers) of ternary compounds with established crystal structure in the systems: Sc-M-X (M=3d, 4d, 5d, 4f-element; X=B (filled circles), Al, Ga (empty circles) – (a); X=C (filled circles), Si, Ge (empty circles) – (b). Some characteristic cross sections are marked.

other elements. Sc atoms are surrounded by 6b atoms and *vice versa*. The coordination of the surrounding atoms is preferably octahedral and/or tetrahedral. At the same time, these compounds show a metallic shine and a semimetal type of electrical conductivity.[8–10] These compounds represent borderline cases between metallic and semimetal behaviour. Contrary to these compounds, the atoms in the structures of typical intermetallic compounds are surrounded by different atoms and also by the same atoms. The coordination number of atoms in intermetallics is rather high, from 6 up to 20. Most of the scandium containing phosphides and arsenides belong to the structure types typical of intermetallics, *e.g.* TiNiSi, $ZrFe_4Si_2$, $Zr_2Fe_{12}P_7$ *etc.*[7]

A large number of ternary Sc-M-X compounds occur at stoichiometries that lie on three cross sections of a ternary phase diagram *i.e.* at the atomic ratios Sc:X=1:1, Sc-M=1:1, M:X=1:1 and on the section with a Sc content of 33.3 at.%, (Figure 5). More than half of the ternary compounds of 3b and 4b elements with known crystal structures (55 ternary compounds with X=B, Al, Ga and 111 compounds with X=C, Si, Ge) occur on these four characteristic cross sections. In general, about 2/3 of all scandium ternary intermetallics known to date appear only on four appointed sections of phase diagrams and have considerably simple stoichiometries. This regularity was discovered earlier on a limited series of Sc-M-X (M=3d element; X=Si, Ge) systems.[11–12] However, this seems to be characteristic of all the ternary systems of scandium. As mentioned by Villars,[13] simple stoichiometric ratios are generally preferred by intermetallic compounds.

The largest number of ternary compounds are those with the simplest composition ScMX (61 compounds in all; No 35 and No 38 in Figures 5(a) and 5(b), respectively); $ScMX_2$ (19 compounds; No 30 and No 31, respectively), ScM_2X (18 compounds; No 28 in Figure 5(a)), ScM_2X_2 (10 compounds; No 22 in Figure 5(b)). A similar regularity has been found for binary scandium intermetallics.

As one can see from Figure 5, more than 90% of all scandium intermetallic compounds appear in the ternary system region where the scandium content is not higher than about 50 at.% and which is limited by sections Sc:M=1:1 with X content from 0 to 33.3 at.% and Sc:X=1:1 with M content from 0 to 33.3 at.%.

A comparison of the investigated ternary systems of scandium of the related ternary systems with other rare earths elements[14] reveals that, especially for the light rare earths, the ternary compounds often occur in cases of a larger RE content (> 50 at.%). In this feature, scandium systems are closer to the systems of d-elements, especially those of the 4a group Ti, Zr and Hf.

Constant compositions of ternary compounds and the absence of solid solutions on the basis of binary compounds are other characteristic features of scandium systems (with the exception of the systems Sc-M-Ga with

M=RE or 4a element). However, do solid solutions of phases with narrow homogeneity regions exist in some systems. Sometimes a substitution of Sc and M atoms occurs and sometimes the M and the X atoms are mutually substituted. There is no doubt that the atomic size factor has a dominant influence on the formation of solid solutions and their nature (solid solutions of substitution, of inclusion or of subtraction of atoms). Examples of solid solutions of substitution are presented in Table II. It is interesting to note that all ternary compounds which form such solid solutions crystallize in the structures characteristic of binary compounds.

However, the influence of other factors (besides the atomic size factor) on the interaction of the elements is obvious when comparing ternary systems R-Sc-Si and R-Zr(Hf)-Si, (Table III). Although the atomic size of Sc, Zr and Hf are nearly the same, the interaction of 4a elements with the rare earths in binary and ternary systems is different from that in the corresponding systems of Sc with the rare earths. This does not depend on whether RE is a light or heavy rare earth. In binary systems Sc is completely miscible with Ce and Y while Y-Zr and Y-Hf systems are of the eutectic type with low mutual solubility of the components in the solid. The immiscibility gaps in liquid and solid occur in Ce-Hf system.[6] The same character may be predicted for the Ce-Zr binary system.

Thus, the position of scandium in the family of rare earths is to some extent unique. It sometimes behaves like a typical RE element (*e.g.* showing

TABLE II

Mutually substituted atoms in the structures of ternary compounds of the Sc-M-X systems

Mutually substituted atoms				Atomic radii ratio		Structure type
Sc	M	X	M	r_{Sc}/r_M	r_X/r_M	
Sc-	Y, Nd, Sm, Dy			0.91–0.93		$\alpha ThSi_2$, AlB_2
	Y, Tb			0.91; 0.92		$TiNi_3$
	V			1.22		Ti_6Ge_5
	Nb, Mo			1.13; 1.18		Mn_5Si_3; $Ho_{11}Ge_{10}$
	Y, Ta, Mo, W			0.91–1.18		Sm_5Ge_4
	Ti, Zr			1.12; 1.03		$Ho_{11}Ge_{10}$
		Al-	Ni, Fe, Ru, Pd		1.12–1.04	$MgZn_2$
		Ga-	Fe, Cu		1.10; 1.09	$ThMn_{12}$
			Fe, Co, Ni		1.10–1.12	$MgZn_2$, $MgCu_2$
			Ni, Cu		1.12; 1.09	$CaIn_2$
		Si-	Mn, Fe, Co, Ni		1.03–1.08	$MgZn_2$
		Ge-	Cr, Mn		1.03; 1.06	$Ho_{11}Ge_{10}$

TABLE III

Comparison of the characteristics of the R-M-Si (R=Y, Ce; M=Sc, Zr, Hf) ternary systems

Characteristic	Systems					
	Y–M-Si			Ce-M-Si		
	Sc	Zr	Hf	Sc	Zr	Hf
Total number of ternary compounds	1	1	0	8	3	0
Occurrence of continuous solid solutions	+	–	–	–	–	–
Averaged mutual solubility of R and M in solid solutions at 600 °C (at. %)	30	10	<5	<5	<2	<2
Maximum mutual solubility of R and M in solid in binary R-M systems[6]	100	3	1	100	5	1
References	15	14	14	14	14	14

complete miscibility, except with Eu and Yb), however, in other cases it exhibits behaviour more similar to the d-elements (*e.g.* displaying complete miscibility with them too, namely with Zr and Hf). This peculiarity of scandium is also observed in ternary systems. Therefore, it is a linking element between the rare earth and the d transition elements. Zr, Hf and heavy rare earths are elements with which scandium forms statistical mixtures of atoms, up to a complete mutual substitution in the structures. With other elements, scandium occupies regular atomic positions in the structures and forms, as usual, ternary compounds of constant composition.

CRYSTAL CHEMISTRY OF SCANDIUM INTERMETALLIC COMPOUNDS

462 investigated (114 binary, 348 ternary) intermetallic compounds of scandium belong to 155 structure types. The 27 most frequently occurring scandium intermetallic structure types are presented in Table IV. They are arranged according to the decrease of the number of existing compounds. Structure types with the same number of representatives are arranged following the increase of the number of atoms per unit cell, which is indicated by Pearson's symbol.

Most of the structure types that scandium intermetallics crystallize can also be found among intermetallic compounds of other rare earths, as well as among intermetallics of 4a elements. However, taking into consideration all the 155 structure types of scandium intermetallics, from a crystal chemical point of view, scandium appears to be closer to 4a elements, especially to Zr and Hf, rather than to the other rare earths.

TABLE IV

Structure types of intermetallic compounds of scandium

Structure type	Pearson's symbol	Space group	Number of compounds	Including	
				binary	ternary
$MgZn_2$	hP12	$P6_3/mmc$	20	6	14
TiNiSi	oP12	$Pnma$	19	0	19
$MnCu_2Al$	cF16	$Fm3m$	18	0	18
CsCl	cP2	$Pm3m$	16	16	0
$Mg_6Cu_{16}Si_7$	cF116	$Fm3m$	15	0	15
$CaTiO_3$	cP5	$Pm3m$	14	0	14
ZrNiAl	hP9	$P\bar{6}2m$	14	0	14
$Ce_2Sc_3Si_4$	oP36	$Pnma$	12	0	12
ScCeSi	tI12	$I4/mmm$	11	0	11
Sm_5Ge_4	oP36	$Pnma$	10	1	9
$ZrCrSi_2$	oP48	$Pbam$	10	0	10
$MgCu_2$	cF24	$Fd3m$	9	5	4
AlB_2	hP3	$P6/mmm$	8	3	5
Mn_5Si_3	hP16	$P6_3/mcm$	8	6	2
$AuCu_3$	cP4	$Pm3m$	7	7	0
$CaIn_2$	hP6	$P6_3/mmc$	7	0	7
Mo_2FeB_2	tP10	$P4/mbm$	7	0	7
MgAgAs	cF12	$F\bar{4}3m$	7	0	7
$ThMn_{12}$	tI26	$I4/mmm$	7	1	6
$HfFe_6Ge_6$	hP13	$P6/mmm$	6	0	6
$U_4Re_7Si_6$	cI34	$Im3m$	6	0	6
$Ho_{11}Ge_{10}$	tI84	$I4/mmm$	6	2	4
CrB	oS8	$Cmcm$	5	4	1
$ZrSi_2$	oS12	$Cmcm$	5	1	4
$YCrB_4$	oP24	$Pbam$	5	0	5
$Zr_4Co_4Ge_7$	tI34	$I4/mmm$	5	0	5
Ti_2Ni	cF96	$Fd3m$	5	3	2

From more than half of the ternary compounds studied so far – 207 (about 60%) belong to only 25 structure types with up to 19 representatives. (Table IV) 10 structure types out of these 25 types occur also in binary compounds or are superstructures to the corresponding binary prototypes. In the group of 27 most frequently occurring structure types of scandium intermetallics, there are 9 structure types, *viz.* $MgZn_2$, CsCl, AlB_2, $MgCu_2$, Mn_5Si_3, $AuCu_3$, CrB, $ZrSi_2$, Ti_2Ni, observed for 51 binary scandium intermetallics (46%) of 5 stoichiometric compositions. As it is seen from Pearson's symbol, compounds with simple structures and small number of atoms in the unit cell (from 2 up to 20) and with high symmetry (not lower than orthorhombic) occur most frequently. Only 5 structure types among 155 types are monoclinic. 28 and 77 structure types, respectively, have only two or one representative among scandium intermetallics. Their compositions and crystal structures are not usually simple. $Mg_{44}Rh_7$ type has the highest number of atoms – 408 in the unit cell.

Formation of comparatively simple, highly symmetrical crystal structures is characteristic not only of scandium intermetallics but it is typical of intermetallics in general.[13] This is due to the metallic bonding prevailing in intermetallics. Structures of higher complexity appear frequently in compounds with covalent bonding.

There are different relations within various structure types, which is also the case of scandium intermetallics. These relations are summarised in Table V. They are illustrated using the examples of structure types of scandium intermetallics. The relations between structure types of intermetallic compounds are treated in more detail by Kripyakevich.[16] The proposed systematization of structure types of intermetallic and other related compounds is based on the analysis of the coordination surrounding (coordination number, CN and shape of coordination polyhedra, CP) of the smallest atoms in the structure.

The atomic size factor has a dominant influence on the distribution of atoms in ternary phases. The largest atoms in the structure normally occupy atomic sites with the largest CN and the smallest atoms occupy positions with the smallest CN. Scandium atoms are very often the largest ones in the structures, with the exceptions however if other RE elements are their partners. In those cases, scandium atoms occupy atomic sites with a medium CN value. Ternary aluminides, gallides, silicides and germanides sometimes form isotypic compounds which belong to the same structure types, e.g. ZrNiAl, $Mg_6Cu_{16}Si_{7.}$[7] The Al and Ga atoms in these structures are usually larger than the transition element atoms. Therefore, they occupy opposite sites in comparison with the isotypic ternary scandium transition element silicides and germanides, in which Si and Ge atoms are usually the smallest. Sometimes, this causes a change of the stoichiometry of compounds: $Sc_6Co_{16}Si_7$ $Sc_6Co_7Ga_{16}$, $Ce_2Sc_3Ge_4$ $V_3Sc_2Ge_4$, $ScCo_3C$ $SnSc_3B$.

The structures of many binary and ternary scandium borides and carbides may be deducted from other structure types by multiple substitution of larger atoms by B-B or C-C pairs or by inclusion of B or C atoms into the

TABLE V

Types of relations between the structure types of scandium intermetallics

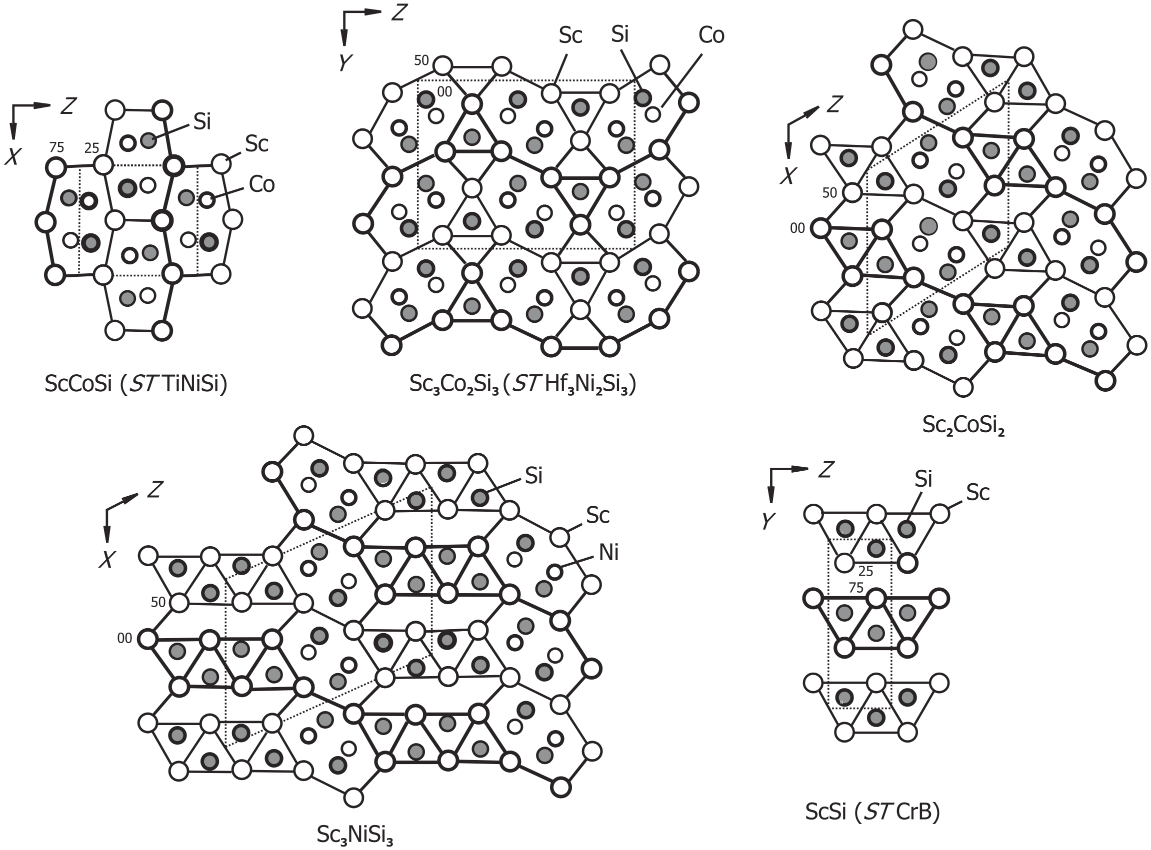
Type of relation	Operation of transition from the parent to the resulting type	Examples of structure types	
		Parent type(s)	Resulting type
I. Positions of all atoms are the same.	I. Ordered substitution of atomic positions by different atoms (superstructure)	Sm_5Ge_4	$Ce_2Sc_3Si_4$
		La_2Sb	Mo_2FeB_2
		$CaIn_2$	ScAuSi
II. Positions of all atoms are roughly the same.	II. Distortion (internal and/or external).	$CaIn_2$	KHg_2
		$CeCo_3B_2$	$ErIr_3B_2$
III. Positions of part of atoms are the same.	IIIa. Multiple substitution of atoms ($1 \rightarrow 2$).	FClPb	$ScCoC_2$
		$CaCu_5$	$ThMn_{12}$
	IIIb. Addition (subtraction) of atoms.	$AuCu_3$	$CaTiO_3$
		NaCl	Sc_2S_3
	IIIc. Redistribution of part of atoms and cavities.	MgAgAs	MgLiAl
	IIId. Redistribution of atoms.	Th_2Zn_{17}	Th_2Ni_{17}
IV. Fragments of both structures are the same.	IV. Different stacking types of fragments (homeotypic rows or structures).	$MgZn_2$	$MgCu_2$
		AlB_2	$ThSi_2$
		TiNiSi	ZrNiAl
V. Roughly the same fragments, but different ratios.	Va. One-dimentional stacking of fragments.	($CaCu_5$, Zr_4Al_3)	$HfFe_6Ge_6$
		($CeGa_2Al_2$, Po)	$ScNi_2Si_3$
	Vb. Two-dimentional stacking of fragments.	(CrB, TiNiSi)	Sc_2CoSi_2, Sc_3NiSi_3
	Vc. Three-dimentional stacking of fragments.	(Fe, AlB_2, FeB)	$Ce_2Sc_3Si_4$
		(Fe, AlB_2)	Th_7Fe_3

holes of the parent structure types. The same applies to the structures of scandium intermetallics with 6b elements. The Ti_7S_{12}, NiAs, $ErAgSe_2$, Al_2MgO_4 structure types can be obtained by inclusion of cations of metals into the octahedral and tetrahedral holes of different packings (usually close-packed ones) of 6b anions. Very frequently, inclusion of atoms causes a distortion of the parent close-packed structure.

A large group of scandium intermetallics contain fragments of simpler structure types connected in different manners. Some of these hybrid structures contain fragments of two, three or even more structure types. The initial fragments usually are distorted during their bonding into the hybrid structure. Such distortions are minimal in linear hybrid structures. Dimensions of the initial fragments, their number and the kind of mutual bonding determine the dimensions and the symmetry of the resulting hybrid structure. Fragments of the following structure types: Po (empty cube), Fe (body-centered cube), AlB_2 (body-centered trigonal prism) and $BaAl_4$ (body-centered tetragonal antiprism) are often observed as the initial fragments for hybrid structures. Besides, atomic groups (clusters) octahedron and icosahedron shaped are also found as structure fragments. The initial fragments can be eliminated from the parent structures along the axes of the unit cells or eliminated randomly in comparison to these axes. Substitutions of atomic positions of the same structure fragments by different atoms with different sizes cause distortions of the same fragments in different structures. In the following discussion, possible distortions of structure fragments will not be taken into consideration and the name of ideal clusters, will be used.

While analysing the compositions of scandium intermetallic compounds, we have pointed to the regularity of the occurrence of a large number of compounds on some characteristic cross sections of phase diagrams (see Figure 5). The crystal structures of these compounds, which are in two-phase equilibria with each other, are related and contain one or more mutual fragments, but in different ratios. For example, on cross-section Sc:X=1:1 of the ternary systems Sc-M-X (M=Fe, Co, Ni; X=Si, Ge), the following ternary compounds occur: ScMX (*ST* TiNiSi), $Sc_3M_2X_3$ (*ST* $Hf_3Ni_2Si_3$), Sc_2MX_2 (*ST* Sc_2CoSi_2), Sc_3MX_3 (*ST* Sc_3NiSi_3) and ScX (*ST* CrB) (Figure 6). Compositions of these ternary compounds are indicated by the numbers 38, 45, 47 and 49 in Figure 5(b). These compounds form an interesting series of structures $ScMX \rightarrow Sc_3M_2X_3 \rightarrow Sc_2MX_2 \rightarrow Sc_3MX_3 \rightarrow ScX$.[17,18] As seen from Figure 6, three intermediate members of this row contain fragments of the outer two, ScMX and ScX. In this row the Sc:X ratio remains the same, 1:1, however the decrease of the number of M atoms causes the decrease and, finally, disappearance of the TiNiSi-type fragments. The number of CrB-type fragments increases from the $Sc_3M_2X_3$ structure towards ScX. Thus, TiNiSi and CrB are the parent structure types of the homological series of structures with three known members. It is possible to predict the existence of other members in this series and construct their hypothetical structures. In particular, if one unit cell of ScSi is added along the c direction in the Sc_3NiSi_3 (I) structure, a structure of the same symmetry (SG $C2/m$) represented by the formula Sc_4NiSi_4 (II) is obtained. The monoclinic unit cell of this hypothetical structure will have the following dimensions: $a(II) \approx a(I) \approx 1.0$ nm, $b(II) \approx b(I) \approx 0.4$ nm, $c(II) \approx c(I) + c(ScSi) \approx 1.65$ nm, $\beta = 95–98^{o}$.[18] Taking into account that the CrB type structure is the linear hybrid structure of AlB_2 and Fe types, the structures of the above discussed homological series are thus two-dimensional hybrids of three structure types, *viz.* Fe, AlB_2 and TiNiSi.

The crystal chemical analysis shows that there are relations between the structures of compounds occurring on other cross-sections, *e.g.* R:M=1:1



ScCoSi (*ST* TiNiSi)

$Sc_3Co_2Si_3$ (*ST* $Hf_3Ni_2Si_3$)

Sc_2CoSi_2

Sc_3NiSi_3

ScSi (*ST* CrB)

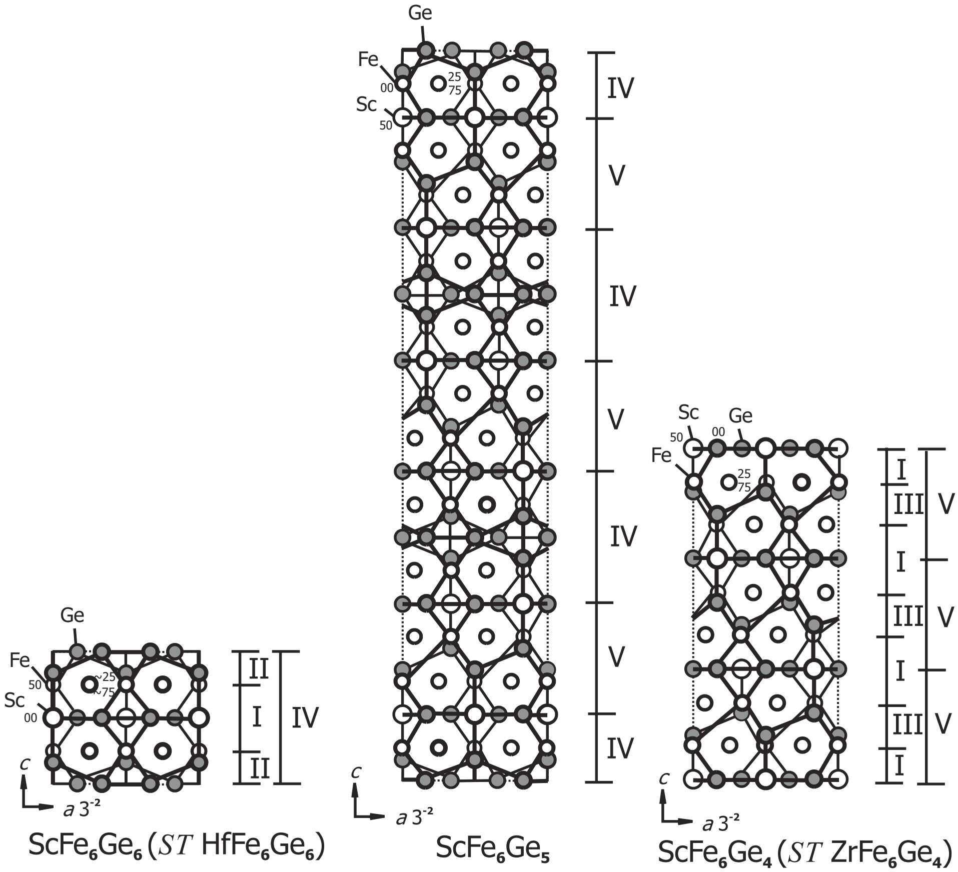
Figure 6. Relations between the structures (presented in projections along 010 or 100) of compounds occurring on the Sc:Si=1:1 cross section of the Sc-M-Si ternary systems. Unit cells and structure fragments are indicated by dotted and solid lines, respectively.

Sc:M=1:2, which are in equilibria with each other in the systems. These compounds contain at least one mutual fragment or atomic cluster. Sometimes, they form homologous series of structures. This fact can be used to investigate of compounds of unknown crystal structure. However, there are now a number of powerful program packages for the determination of crystal structures by direct methods. However, the application of direct methods to structure determination using powder X-ray data is sometimes unsuccessful, especially for complex structures. In such cases, the knowledge of structure relations between compounds which are in equilibria becomes very useful if the structures of some of them are known.

Such an approach was applied to determination of the crystal structure of $ScFe_6Ge_5$.[19] In the ternary systems Sc-Mn-Ge and Sc-Fe-Ge on the cross-sections Sc:M=1:6 (M=Mn, Fe), the following compounds exist: ScM_6Ge_6 (M=Mn, Fe), $ScFe_6Ge_5$ and ScM_6Ge_4 (M=Mn, Fe). Their compositions are marked as No 3, 5 and 6 in Figure 5(b), respectively. Germanides ScM_6Ge_6 and ScM_6Ge_4 belong to the structure types $HfFe_6Ge_6$ [20] and $ZrFe_6Ge_4$, [21] respectively. The $HfFe_6Ge_6$ structure type can be deducted from the $CaCu_5$-type by a multiple substitution of the pair of X-X atoms for M atoms in every second layer (Figure 7). The structure of $HfFe_6Ge_6$ (IV) is also a linear hybrid of the $CaCu_5$ (I) and the Zr_4Al_3 (II) types, whereas the structure of the $ZrFe_6Ge_4$ type (V) is a linear hybrid of the $CaCu_5$ (I) and Fe_3Sn_2 (III) types (Figure 7). It can be also considered as the structure resulting from an inclusion of R(Sc) atoms into the Fe_3Sn_2 structure.

Expecting genetic relations between the structures of $ScFe_6Ge_5$ and $ScFe_6Ge_6$ (IV) and $ScFe_6Ge_4$ (V), with which the first one is in equilibrium, a theoretical model was deducted for the crystal structure of $ScFe_6Ge_5$ as a linear hybrid of fragments IV and V. This model, containing 72 atoms in the unit cell, is presented in Figure 7. The dimensions of fragments IV and V, their quantities, 3+3 and symmetry allowed to determine roughly the unit cell dimensions and the symmetry: SG $R\bar{3}m$, $a \approx 0.5$ nm, $c \approx 4.4$ nm. This theoretically predicted structure has been experimentally confirmed by X-ray powder diffraction data, the refined lattice parameters are: a=0.5063(1) nm, c=4.411(1) nm.[19]

The change of compound compositions is related to the changes of atom coordination. The structure types of scandium intermetallics have been classified on the basis of CN and the CP shape of the smallest atoms in the structure. In some cases, X atoms are the smallest in the structures but sometimes M atoms are the smallest ones, especially if M is a *d* element. It was found that the compounds with a high M content (> 50 at.%) and a low X content (< 30 at.%) frequently have CN 12 and the CP of icosahedra and cubooctahedra for the smallest atoms. The compounds of the central part of ternary systems with the Sc content 15 up to 30 at.% and the X content between 30 and 50 at.% have CN 8 (+1 or 2) and a CP of tetragonal antiprism



$ScFe_6Ge_6$ (*ST* $HfFe_6Ge_6$) $ScFe_6Ge_5$ $ScFe_6Ge_4$ (*ST* $ZrFe_6Ge_4$)

Figure 7. Relations between the structures (presented in the projections on the plane of the large diagonal of the hexagonal basis) $ScFe_6Ge_6$, $ScFe_6Ge_5$ and $ScFe_6Ge_4$. Fragments of the structures: I – $CaCu_5$, II – Zr_4Al_3, III – Fe_3Sn_2, IV – $ScFe_6Ge_6$, V – $ScFe_6Ge_4$. Unit cells are indicated by dotted lines.

for the smallest atoms. For the high X (> 50 at.%) and Sc (> 30 at.%) content, the compounds are characterised by a trigonal prismatic coordination of the smallest atoms, CN 6 (+1, 2 or 3). At a high Sc content, binary compounds have icosahedral coordination of the smallest atoms. These regularities are invalid in the systems of X elements with a pronounced nonmetal character, *e.g.* B, C, As. Scandium intermetallics with these elements have, as usual, trigonal prismatic, octahedral (CN 6) and tetrahedral (CN 4) coordination of X atoms.

Figure 8 presents the transformations of the CP of atoms observed in the structures: cubooctahedron (CN 12) → icosahedron with two tetrangular planes (CN 12) → normal icosahedron (CN 12) → trigonal prism with additional atoms (CN 6 (+3)) → tetragonal antiprism with additional atom (CN 8(+1)) → octahedron (CN 6) and also transformation of trigonal prism with additional atom (CN 6 (+1)) → octahedron (CN 6). Numerous examples of these CP can be found in original papers dealing with the structures of intermetallic compounds. Namely, CP (a) from Figure 8 is observed for the atoms of $AuCu_3$ *ST*, $[AuCu_{12}]$ and $[CuAu_4Cu_8]$.[16] Slightly distorted cubooctahedra $[ScRh_6Ge_6]$ exist in the $Sc_4Rh_7Ge_6$ structure (*ST* $U_4Re_7Si_6$ [22]). CP (b) and (c) have Cu atoms in the $CaCu_5$ type structure.[16] With formation of the $CeCo_3B_2$ type superstructure with ordered distribution of Co and B atoms in the two Cu sites of the binary propotype $CaCu_5$ the *c*/*a* (=0.600) ratio re-

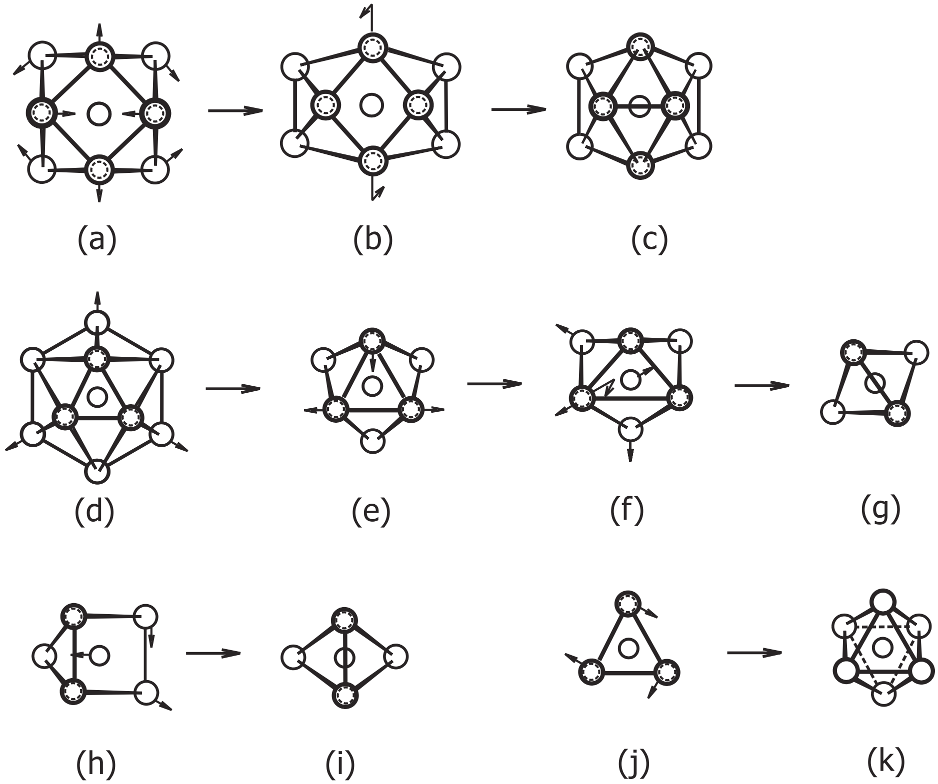


Figure 8. Coordination polyhedra (CP) of atoms: cubooctahedron (a), icosahedron with two tetrangular planes (b), normal icosahedron in two projections (c, d), trigonal prism with three additional atoms centering its side planes (e), tetragonal antiprism with one additional atom centering its basis (f), octahedron in different projections (g, i, k), trigonal prism with one additional atom centering its side plane (h), trigonal prism (j). Arrows next to atoms show approximate direction of their shifts, which cause a transformation of this CP into the neighbouring one, indicated by a long arrow (for additional explanation see text).

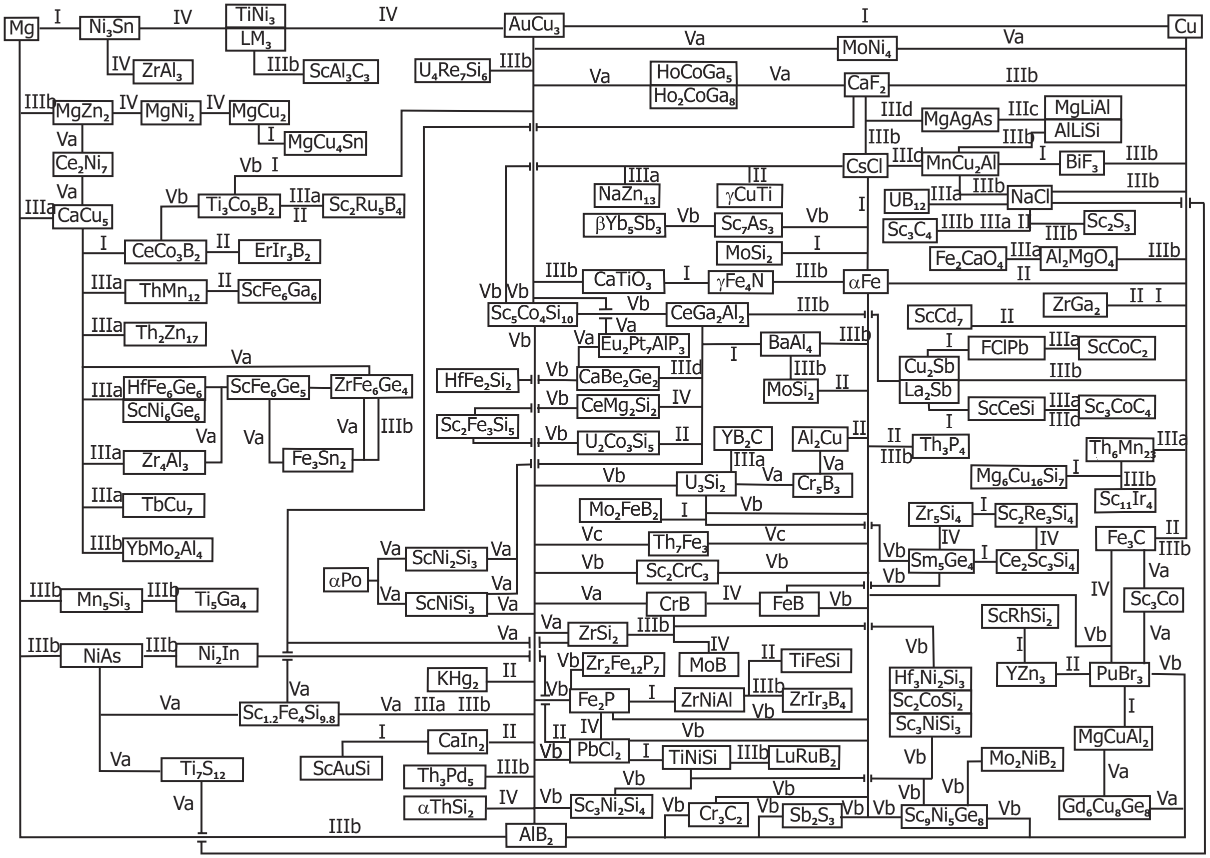


Figure 9. Relations between structure types of scandium intermetallic compounds as derived from the basic two close-packed structures, Mg (*hcp*) and Cu (*fcc*). Roman numerals I–V indicate the ways of transformations between the structures used in TABLE V.

markably decreases in comparison with the binary RM_5 structures (c/a=0.774–0.822). This is caused by substitution of two boron atoms for two cobalt atoms in the unit cell. The CP of boron atoms changes from icosahedron to a trigonal prism with three additional atoms.[23] This example shows the mechanism of the transformation of the (d)-type CP into (e)-type CP (see Figure 8). A classical representative of the (e)-type CP is the AlB_2-type structure.[16] A CP of the (f) type can be found in $BaAl_4$ or $CeGa_2Al_2$ *ST* [16] or $Sc_4Rh_7Ge_6$ (*ST* $U_4Re_7Si_6$ [22]). An intermediate position between the CP of (d) and (e) type Co atoms have in the structure of $Sc_5Co_4Si_{10}$.[24] This structure is a two-dimensional hybrid of the following four types: AlB_2 (trigonal prisms [$SiSc_6$]), CsCl (empty tetrahedra [Sc_2Si_2]), $AuCu_3$ (cubooctahedra [$ScSi_{12}$]) and $CeGa_2Al_2$ (tetragonal antiprisms [$CoSc_4Si_4$]). CP intermediate between (f) and (g) and between (h) and (i) (or (i), (k)) contains the structure of V_3As_2-type.[25] Transformation of CPs of atoms can also occur in the opposite direction, from CN 6 to CN 12. This is caused by the change of the dimensions of different atoms and their ratios in the structures. Other types of the coordination surrounding of the smallest atoms in the structures of intermetallic compounds are more rarely observed.

Figure 9 presents generalized relations between the majority of the structure types of scandium intermetallics. Some of these relations have been established earlier.[4] Relations between the structure types published after 1980 have been established by the author. Analysis of structure types of intermetallic compounds enables enrichment and broadening of the data on the relations between structure types. These investigations are the basic ones for determination of the nature of intermetallics and functional relations between the compositions and the structures of compounds as well as the factors governing these changes. They contribute to the understanding of functional relations between the structures and physical properties of solids.

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SAŽETAK

Sustav skandijevih binarnih i ternarnih slitina i intermetalni spojevi

Bogdan Ya. Kotur

Skandij je prvi od d-elemenata i pripada skupu rijetkih zemalja. Dan je pregled do početka 1997. objavljenih i raspoloživih podataka, o sustavima skandijevih binarnih i ternarnih slitina i intermetalnih spojeva s drugim elementima (izuzevši halogene, vodik, kisik, sumpor i dušik). Prikazani su podatci za približno 65 binarnih i 200 ternarnih sustava. Provedena je kristalokemijska analiza za 462 proučavana intermetalna spoja (od 554 danas poznatih) koji spadaju u 155 strukturnih tipova. Pokazano je da je skandij element koji povezuje rijetke zemlje i d-elemente. S kristalokemijskog gledišta čini se da je skandij sličniji elementima 4. skupine, osobito Zr i Hf, nego kovinama rijetkih zemalja. Analizirani su funkcijski odnosi između sastava i struktura spojeva i čimbenici koji upravljaju tim odnosima. Uočene pravilnosti pokazale su se korisnima za istaživanje novih sustava, za sintezu novih intermetalnih spojeva te za proučavanje njihovih kristalnih struktura.