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Complex Structures of Intermetallic Compounds Interpreted as Intergrowth of Segments of Simple Structures

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By the end of 1982 more than 2000 structure types [1a] were known for intermetallic compounds (elements, binary and multicomponent alloys) according to «Pearson's Handbook of Crystallographic Data for Intermetallic Phases» [1b]. Restricting ourselves to the ternary lanthanoid-transition metal-silicides, germanides, stannides, borides, aluminides, and gallides, we are still confronted with about 150 types, of which at least two thirds form new atom arrangements which cannot be considered ternary ordered derivatives of binary structure types. – There is always arbitrariness in attempting to describe any crystal structure for the reason that one should take into account the chemistry of the compound, its physical properties, and its geometrical relationships to other structures. This challenge is particularly difficult to overcome with intermetallic compounds because in this case the lack of information on the nature of the chemical bonding does not allow an easy understanding of their physical properties and leaves also a (too) large degree of freedom in their crystal-chemical interpretation. If, with particularly well-chosen compounds, we can improve our vision by wearing, for example, «von Schnering's spectacles» [2] which allow to discover clusters in any structure..., belonging to the category of cluster compounds, these do not provide a satisfactory view of the structures of pure intermetallics. For this class of compounds we need another kind of spectacles! – One of the most successful approaches to the problem consists in interpreting complex structures of intermetallic compounds as being built up from «building units», such as slabs, columns, or blocks, characteristic of simple structure types. As an example we shall show that some 30 of the structure types found with ternary lanthanoid alloys can be described as linear combinations of slabs derived from 6 simple structure types. On the whole, more than one third of all 150 structure types can be interpreted as an intergrowth of various simple structure segments. Structure series, which group structures containing segments derived from the same parent structures, can then be considered, and new structure types can be predicted, by imagining different combinations of segments. This provides a useful guideline for material scientists who are searching for new compounds with interesting physical properties such as superconductivity or magnetism.

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1. Introduction

Intermetallic compounds have quite often not only compositions which are difficult to memorize, but also complicated crystal structures which defy an easy interpretation. Complicated crystal structures and compositions are also found with organic and nonmetallic inorganic compounds. In this case, however, there are known crystal-chemical rules – charge compensation in ionic compounds, ligand arrangement due to a particular hybridization of the central atom, stability of filled electron shells, etc. ... – which make the composition and, in many cases also, the atom arrangement understandable. For the intermetallics only few such rules exist and they are not generally applicable for a wide range of compounds. Structure-energy calculations from first principles have so far not made it possible to predict crystal structures of intermetallics. On the

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contrary, for band structure calculations the knowledge of the crystal structure is a prerequisit. For a given combination of metallic elements we can at present neither predict the number of intermetallic phases, their compositions, nor their crystal structures.

Intermetallic crystal structures are usually described by concentrating on the coordination polyhedra of the individual atoms. It will be shown that it is advantageous in certain cases to consider larger entities, that means groups of atoms. In particular, we want to demonstrate that a number of complex structures can be conveniently interpreted as an intergrowth of segments of simple structures. This method of describing complex structures makes it not only easier to comprehend and to memorize them, but enables us in certain cases also to predict the atom arrangement and the elemental composition of yet unknown structure types.

The idea to describe selected structures as stacking variants of common structural slabs originated in the twenties and the thirties (close-packed element structures, SiC polytypes, CdI_2 polytypes, Friauf-Laves phases), and notations for these stacking variants were developed in the fourties and fifties (*Wyckoff-Jagodzinski, Zhdanov;* see for example a discussion on the subject by *Trigunayat* and *Chadha* [3]). In the fifties and sixties a number of complex intermetallic crystal structures could be described by considering the stacking of (more or less planar) monoatomic layers with triangular, hexagonal, quadratic etc. meshes, a method derived from considerations on the densest packing of spheres (*Frank* and *Kasper* [4, 5], *Shoemaker* and *Shoemaker* [6]). A generalized layer description and standard representation of inorganic structure types was proposed several years later by *Lima-de-Faria* and *Figueiredo* [7–9]. The idea that complex structures could be considered as combinations of simple structure segments was extended in the seventies to include also columns, blocks, or interpenetrating frameworks. *Andersson* et al. [10, 11] showed that a large number of inorganic structures (including alloys, oxides, and some minerals) are built up from units of simpler structures, put together in different ways which can be described by the application of different symmetry operations (translations, rotations, or reflections) or by an interpenetration. At about the same time, in the seventies, the late Prof. *Kripyakevich* and his coworkers at the Lemberg (L'vov) University intensified their work on homologous structure series, grouping structures containing common structure segments characteristic of simple parent structures. They further undertook a systematic study of structures to be expected by stacking different slabs and the derivation of the corresponding space groups [12–14]. We shall use here essentially the definitions as they have been formulated in the Russian publications.

2. The Different Kinds of Structure Series: Definitions and Examples

2.1. Definitions

Structure series: A structure series groups structures which can be considered as being constructed from structure segments of two (or more) parent structures, combined in different proportions and/or in a different way of stacking. The parent structures are not necessarily both known in nature. In special cases the parent structures may themselves be stacking variants of a common structural element or may be members of another structure series.

Linear, two-dimensional, or three-dimensional structure series: In a linear structure series the structure segments of the parent structures are infinite layers (slabs) which are stacked in one direction. In a two-dimensional structure series the structure segments of the parent structures are infinite columns (triangular, hexagonal, rhombic, rectangular, square) which are stacked in two dimensions. In a three-dimensional structure series the structure segments of the parent structures are blocks which are stacked in three dimensions.

Homogeneous or inhomogeneous structure series: In the case of homogeneous structure series the parent structures are geometrically related. They can be considered themselves as stacking variants or site occupation variants or deformation variants where corresponding atoms have similar coordinations. If the parent structures are stacking variants with same composition, naturally all members of the structure series must have the same composition. If the parent structures are site occupation variants, the members of the structure series may have different compositions. In the case of an inhomogeneous structure series, the parent structures are different in construction [*]. When the parent structures exceptionally have the same overall composition, the members of a series will have the same composition too, however, in the general case the members of an inhomogeneous structure series have different compositions. It is then possible to derive a chemical formula which is a function of the numbers of the different types of structure segments.

2.2. Examples [**]

Examples for linear homogeneous structure series:

a) Without change of composition: Close-packed element structures. The four structure types: Mg, Cu, Nd, and Sm represent the most simple example for a linear homogeneous structure series. The common infinite slab is a hexagonal monoatomic close-packed layer. There are two simple stacking modes for which the neighbouring layers, above and below a given layer, are either sideways displaced in the same direction for the same amount (hexagonal stacking, Mg-structure) or displaced in opposite directions (cubic stacking, Cu-structure). All members of the structure series can be characterized by the percentage of these two stacking modes. In Fig. 1 are represented the stacking sequences of the four structure types in a plane perpendicular to the hexagonal layers. Interestingly enough, elemental Yttrium crystallizes with the Mg-type at normal pressure, but changes its structure with increasing pressure and adopts successively all four close-packed structure types [17] in the order as given in Fig. 1.

b) With change of composition: Structure series formed from slabs with $CaCu_5$- and $CeCo_3B_2$-types [18]. The $CeCo_3B_2$-type is a ternary site occupation variant of the binary $CaCu_5$-type. Five members of a linear homogeneous structure series are found in the system Ce-Co-B. If m slabs $CeCo_5$ of type $CaCu_5$ are intergrown with n slabs $CeCo_3B_2$, the resulting formulae is $Ce_{m+n}Co_{5m+3n}B_{2n}$. In Fig. 2 are shown projections of the two parent structures, $CeCo_5$ and $CeCo_3B_2$, together with structures of the series where m = 1 and n = 1,

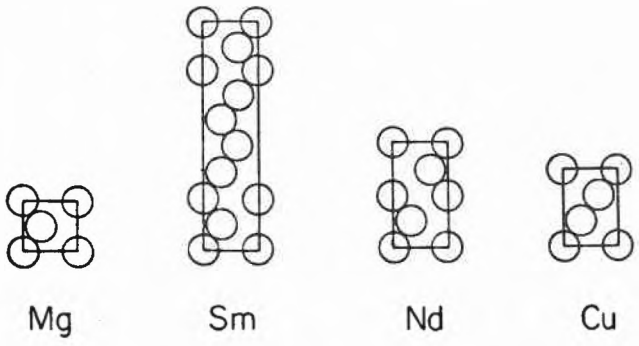


Fig. 1. Arrangement of the atoms in the (11$\bar{2}$0) plane for the four types of close-packed element structures.

[*] Intentionally we avoid to use here the general term «homologous structure series» found in the literature to designate inhomogeneous structure series and also homogeneous structure series when the parent structures have different compositions.

[**] Literature references for structure types, when not given in the text, can be found in *Structure Reports* and [15, 16].

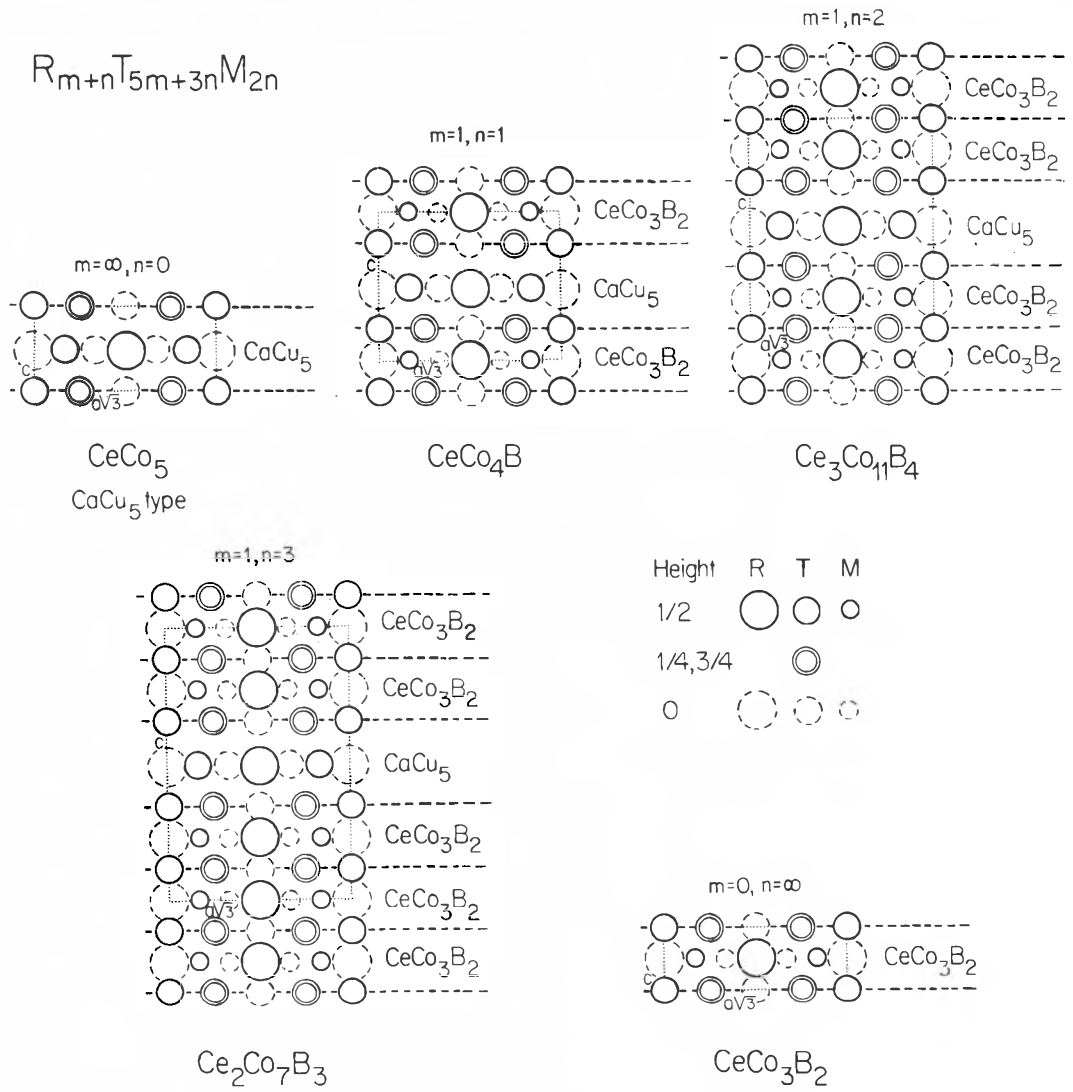


Fig. 2. Members of the $R_{m+n}T_{5m+3n}M_{2n}$ structure series of intergrown binary and ternary $CaCu_5$-type slabs observed in the system Ce-Co-B.

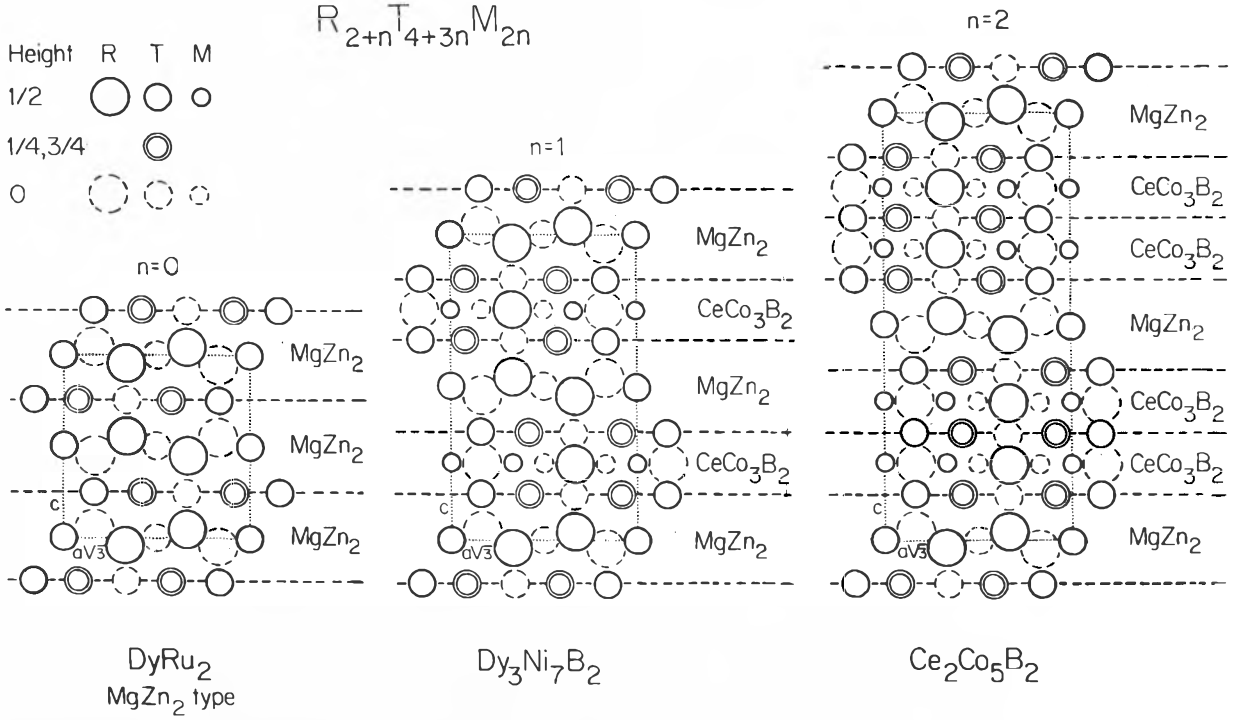


Fig. 3. The $R_{2+n}T_{4+3n}M_{2n}$ structure series of a binary Laves-(for example $MgZn_2$-)type slab intergrown with n $CeCo_3B_2$-type slabs.

2, or 3 respectively. Another member of this structure series with m = 2 and n = 1 is found in the system Nd-Ni-B; as can be easily verified from the formula the composition of the compound is $Nd_3Ni_{13}B_2$.

Examples for linear inhomogeneous structure series:

a) With change of composition: Structure series formed with Laves-type slabs and $CeCo_3B_2$-type slabs[19]. This structure series occurs with ternary rare-earth metal(R)-transition metal(T)-borides and has the formula $R_{2+n}T_{4+3n}B_{2n}$ where n indicates the number of $CeCo_3B_2$-type slabs (RT_3M_2) which are stacked on top of one Laves-type slab (R_2T_4). In Fig. 3 are shown projections for the structures with n = 0, 1, and 2. The structure for n infinite can be found in Fig. 2. For a plot in a ternary R-T-B phase diagram of the compositions of the members of this structure series and of the series discussed above see Fig. 13.

b) Without change of composition: Structure series formed with $ZrFe_4Si_2$-type slabs and $CeRe_4Si_2$-type slabs[20]. As shown in Fig. 4 the $NdRe_4Si_2$ structure consists of a mixture of both kinds of slabs in equal proportions.

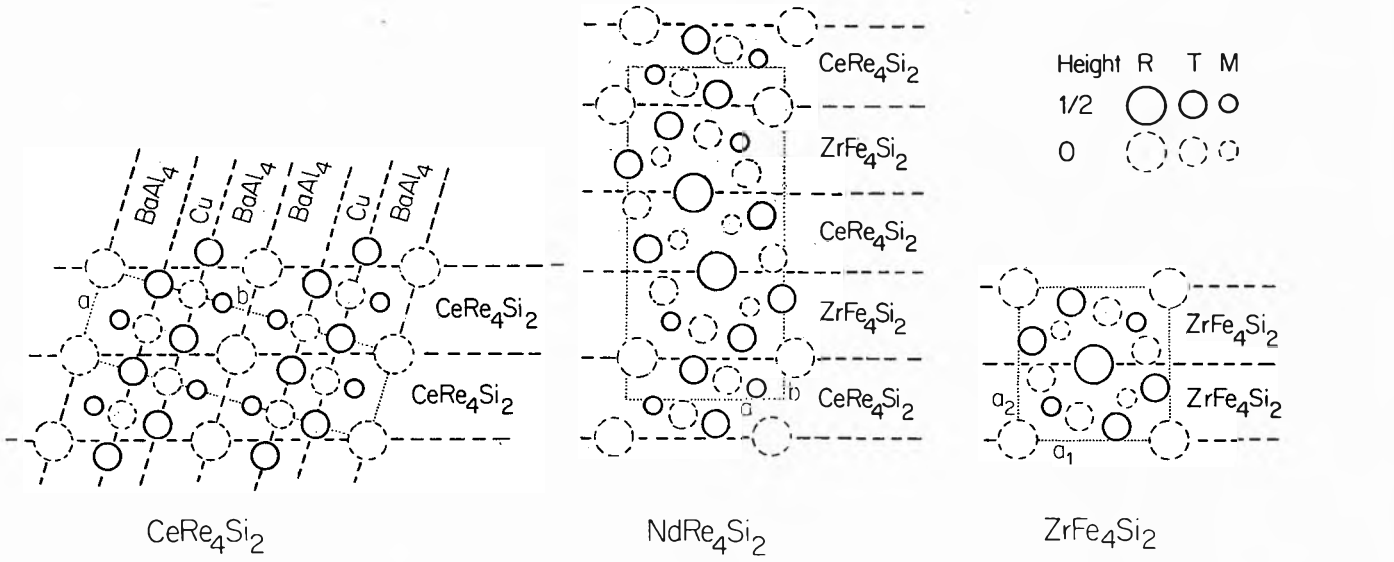


Fig. 4. Three structure types of an inhomogeneous linear structure series with same composition.

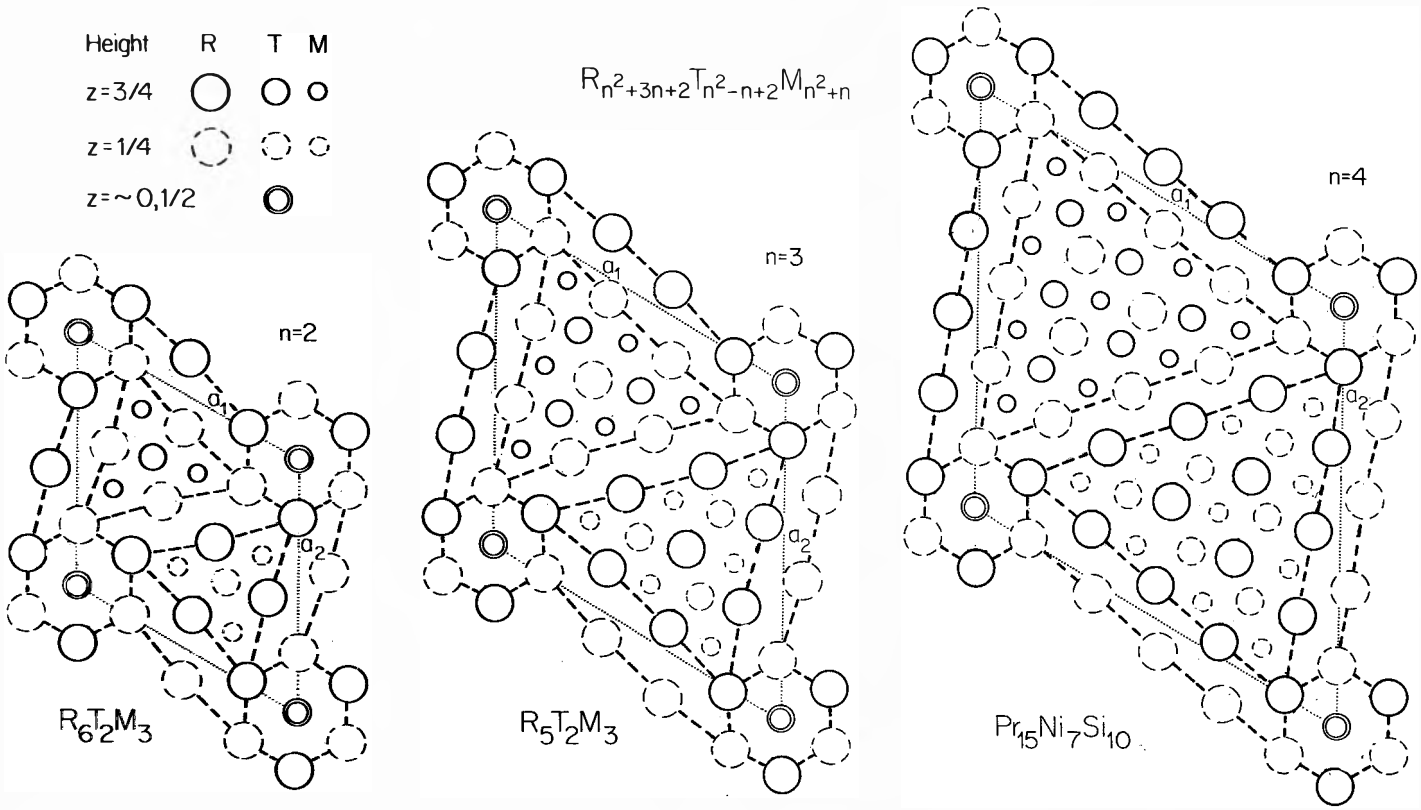


Fig. 5. Three members of the $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ structure series characterized by infinite triangular columns of different diameter with ternary AlB_2-type, infinite hexagonal columns of same diameter with NiAs-type, and infinite rhombic two-atom layer thick columns of different width with W-type. Concerning the structure with n = 2 and 3, two Ce-Ni-silicides have been reported, however the atom ordering on the prism center sites in the triangular columns still needs to be verified experimentally.

Example for a two-dimensional inhomogeneous structure series:

Structure series formed of infinite triangular columns with (ternary ordered) AlB_2-type, infinite hexagonal columns with NiAs-type, and infinite rhombic columns with W-type[21]. This structure series is found with Ce(Pr)-Ni-silicides and has the formula $R_{n^2+3n+2}T_{n^2-n+2}M_{n^2+n}$ where n indicates the number of joined trigonal prisms along one of the basal edges of the triangular columns. One notes that the formula for this two-dimensional structure series is characterized by a quadratic expression in n. In this case the composition points will be found on a parabola-like curve in a ternary phase diagram. The structures with n = 2, 3, and 4 are shown in Fig. 5. The infinite rhombic columns with W-type, two atom layers thick, are located between the triangular columns. These segments increase in width with an increase of the base of the triangular columns. The hexagonal columns with NiAs-type, centered around the *c*-axis of the hexagonal unit cells have the same diameter (and composition) for all members of the structure series.

Example for a three-dimensional structure series:

The structure of $Sc_6Ni_{16}Si_7$ ($Mg_6Cu_{16}Si_7$-type, a ternary variant of the Th_6Mn_{23}-type), containing 116 atoms in the cubic unit cell, can be described as built up from two kinds of finite structure blocks, arranged in the way shown in Fig. 6. Inside the blocks the atoms occupy the vertices of concentric polyhedra. The sequence of these nested polyhedra in unit A (octahedron, cube, cube-octahedron) is identical to that found in the Ca_3Ag_8 type (left part of Fig. 6), of which a ternary ordering variant, $Ce_3Ni_6Si_2$, is known, whereas the polyhedron sequence in unit B (central atom, cube, octahedron, cube-octahedron) is characteristic of the W-type derivatives (right part of Fig. 6). The outermost polyhedron of both units is a cube-octahedron whose atoms are shared, forming the interface framework shown in the central part of Fig. 6. The composition of units A and B are $Sc_3Ni_8Si_3$ and $Sc_3Ni_8Si_4$ respectively, taking into account that also the atoms at the vertices of the octahedra are in common. The resulting composition is $Sc_6Ni_{16}Si_7$ for the arrangement shown in the middle part of Fig. 6 which is the only arrangement known at present for structures belonging to the series with Ca_3Ag_8- and W-type blocks.

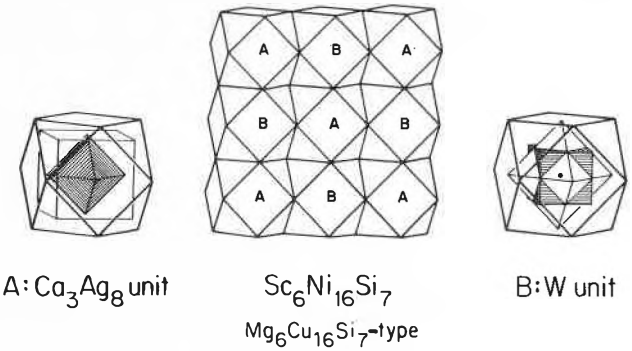


Fig. 6. Two kinds of nested polyhedra units: Ca_3Ag_8-unit (A) and W-unit (B), and their arrangement in cubic $Sc_6Ni_{16}Si_7$ with $Mg_6Cu_{16}Si_7$-type. For $Sc_6Ni_{16}Si_7$ only the outer cube-octahedra of the polyhedra units in the front half of the unit cell are shown.

The description in terms of units of concentric polyhedra was first applied to γ-brasses (*Bradley* and *Jones*[22]) and has been further extended by us[23] for the interpretation of other cubic structures with large unit cells.

3. Characterization of Structural Slabs

A great number of the structures of ternary intermetallic compounds can be considered as being members of linear inhomogeneous structure series. Scarce are however the cases where a parent structure is known with the same elements. In certain cases the parent structures are found in systems where one or some of the elements have been replaced by their homologues in the Periodic Table, or correspond to the structures found under different temperature and pressure conditions. As an example, one can mention the rare-earth elements which under normal pressure and temperature conditions are close-packed but have, from La to Ho, a high temperature modification with the body-centered W-type structure. Whenever slabs of rare-earth elements occur in an intergrowth structure, the rare-earth atoms are never close-packed, but have an arrangement which corresponds to the W-type.

The recognition of the parent structures of the intergrown slabs is not without problems. It may be difficult to identify a particular parent structure because of its unusual orientation within the slab. In this respect is it useful to have at hand a catalogue of drawings of possible parent structures in different orientations and properly classified according to the two-dimensional mesh of the atoms at the interface. Intergrowth between two slabs is possible only if the two interfaces have the same atom arrangement. In Fig. 7 are shown, for the different kinds of intergrowth structures in which we are interested here, the four different types of meshes corresponding to the arrangements of the atom sites in four types of interfaces: the square mesh which may be considered as primitive or centered, a centered rectangular mesh, and the triangular and Kagomé meshes which both have an orthohexagonal cell with axial ratio $3^{1/2}$.

4. Intergrowth of Slabs with Square Mesh Interfaces

For interfaces with square-primitive or square-centered meshes a catalogue of drawings of slabs, derived from different parent structures, has been prepared by *Grin'* et al.[14]. It is reproduced in a redrawn version with minor modifications in Fig. 8. The traces of the interfaces are indicated with dashed lines. The slabs are labeled by the name of the parent structure type, and

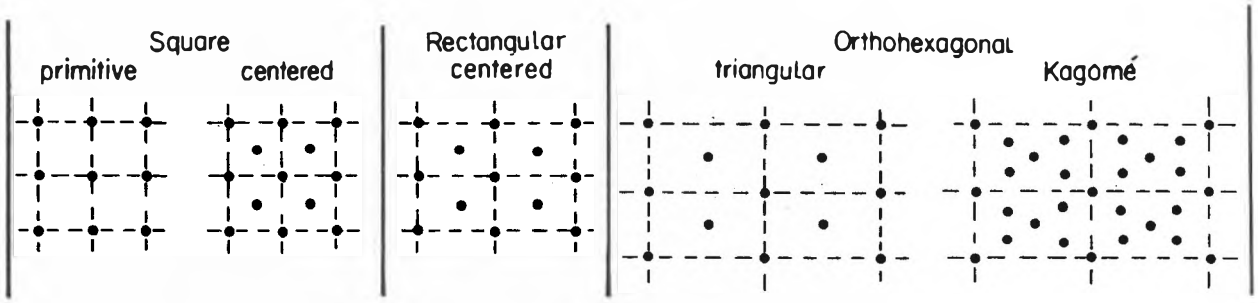


Fig. 7. The different mesh types of the slab interfaces.

they have been further characterized by the direction of the normal to the interface [hkl] and the Miller-indices of the plane of projection (hkl), both referred to the unit cell vectors of the parent structure type. The slabs correspond either to simple segments of a parent structure, to an intergrowth of two such identical segments (upper part of Fig. 8), or to a hybrid slab

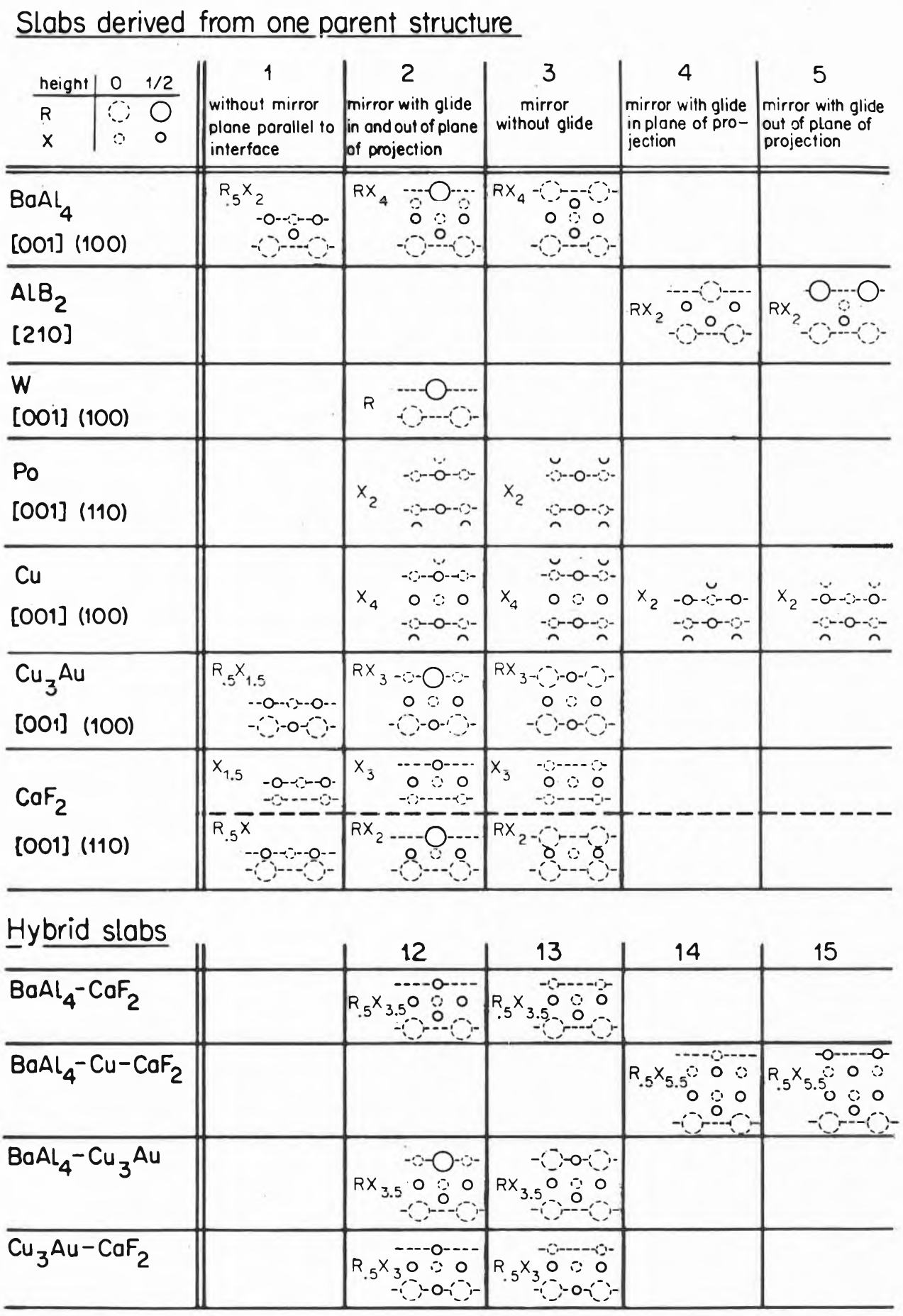


Fig. 8. Catalogue of drawings of slabs with square-primitive or square-centered mesh interfaces.

formed from segments of two or three different structures (lower part). The different slabs in the upper part of Fig. 8 are classified according to the kind of symmetry plane present in the middle of the slab and parallel to the interface. The numbers in the heading of the columns are codes for the five different kinds of mirror planes: 1 no mirror plane parallel to the interface, 2 mirror plane with glide in and out of the plane of projection, 3 mirror plane without glide, 4 mirror plane with glide in the plane of projection, and 5 mirror plane with glide out of the plane of projection. In the case of the α-Po- and Cu-type slabs, with centered meshes at both interfaces, the determination of the type of symmetry plane and the corresponding proper assignment of the number code is possible only if the mutual disposition of the atoms in neighbouring slabs is known. This has been indicated in Fig. 8 by showing half-circles outside the slab. The hybrid slabs, characterized by a two-digit number code (lower part of Fig. 8), have no symmetry plane parallel to the interface.

Grin' et al[14] have published tables which allow to derive the space group for any real or hypothetical intergrowth structure built up of the slabs shown in Fig. 8. As input they need the one- or two-digit codes of the slabs used and the symmetrical or unsymmetrical disposition of the different slabs in the slab stacking sequence.

The slab stacking sequence of an intergrowth structure is obtained by writing down the characteristics of the slabs in the order they occur in the structure. A heavy vertical line marks the interface between two slabs. In the simple notation the slabs are characterized by the name of the parent structure(s) with the number code of Fig. 8 added as superscript. The slabs can be further characterized by denoting within square brackets the actual chemical composition of the slab in the ternary structure. Reference to Fig. 8 should then allow to derive all atom sites in the complete intergrowth structure. However in the case of ternary structures, the atom occupation (either T or M) of the sites denoted by X is not always unambigously defined, although the space group derived from the tables given by *Grin'* et al.[14] is correct[*].

As an example for the generation of a linear structure from slabs given in Fig. 8, we formulate the slab sequence for $CeRe_4Si_2$, shown in Fig. 4, which is here considered as an intergrowth structure of two $BaAl_4$-type slabs and one Cu-type slab.

$CeRe_4Si_2$: $(2\ BaAl_4^1 \mid Cu^4)_2$
where $BaAl_4 = [Ce_{1/2}ReSi]$ and $Cu = [Re_2]$

As seen in Fig. 4 in one translation unit along *b* there are six intergrown slabs. For this reason a parenthesis and a subscript 2 have been added in the complete formula for the stacking sequence.

In Table 1 is given a list of 28 ternary structure types found with lanthanoide, Sc, Y, Zr, Hf, or U alloys and which all can be interpreted as a linear intergrowth of the slabs given in Fig. 8. For the construction of these different intermetallic structures only two or at most three different kinds of slabs are necessary, and all slabs are derived from only six simple parent structures: $BaAl_4$, AlB_2, W, Po, CaF_2, and Cu or Cu_3Au.

In Fig. 9 are plotted the compositions of ternary intergrowth structures where one kind of slab has the $BaAl_4$-type and composition RT_2M_2. The other slabs are taken either from the element structures (W-type for rare earth elements, Cu-type for transition elements, and Po-type for main group elements) or from the binary AlB_2-type which has been reported for certain binary lanthanoid silicides, germanides, or gallides. As can be seen in Fig. 9, structures built up of two segments are on the tie line between the two parent structure types, as for example $ScNi_2Si_3$ and $CeNiSi_2$, shown in Fig. 10. The structure of $ScNiSi_3$, a low symmetry variant of the $SmNiGe_3$-type, is

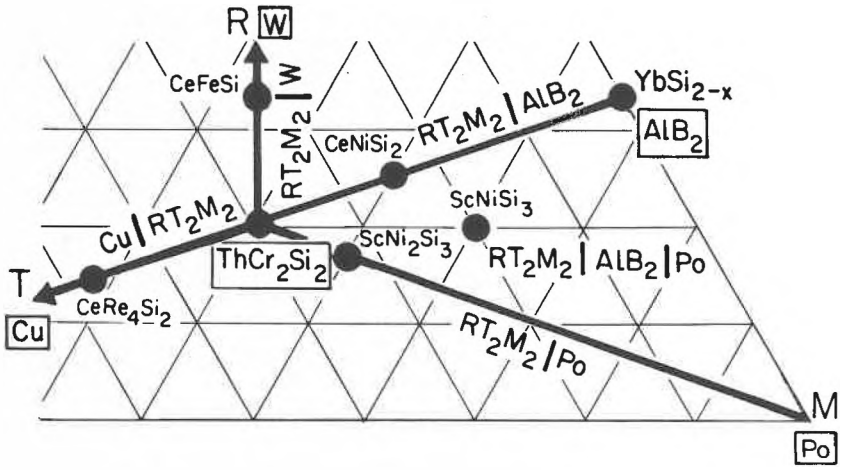


Fig. 9. Compositions of intergrowth structures containing $BaAl_4$-type slabs of composition RT_2M_2 in a general phase diagram R-T-M. Solid lines join parent structures. The framed formulae indicate their structure types. The ordered $BaAl_4$-type is known as $ThCr_2Si_2$-type.

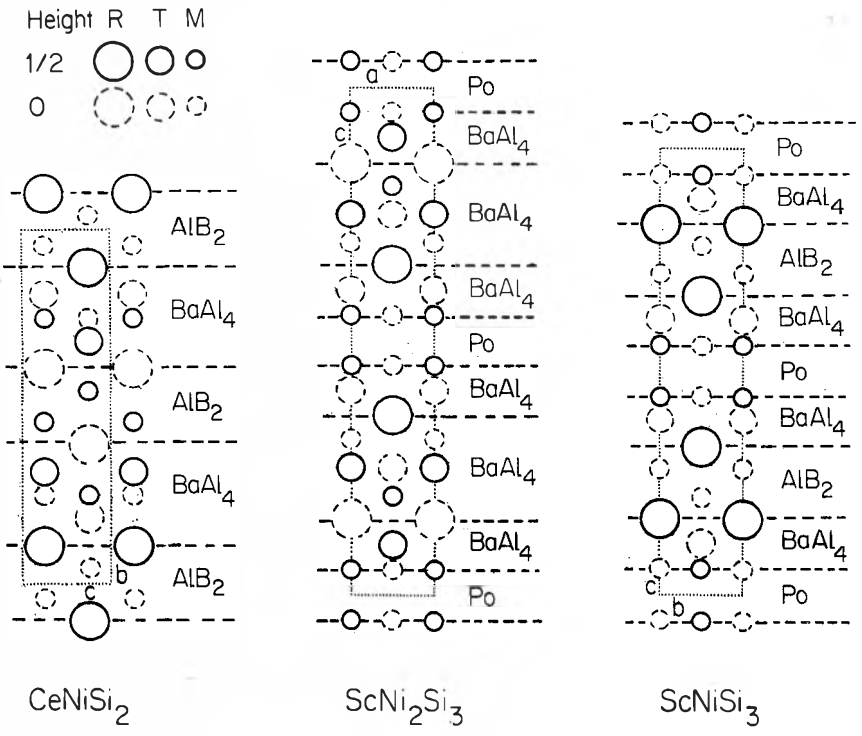


Fig. 10. $CeNiSi_2$, $ScNi_2Si_3$, and $ScNiSi_3$ (non-centrosymmetrical deformation variant of the $SmNiGe_3$-type), three structures containing $ThCr_2Si_2$-type slabs which are intergrown with AlB_2-type or Po-type slabs or both kinds of slabs respectively.

[*] It should also be mentioned that the symmetry code applies to the arrangement of R and X atom sites. In the case of T and M atom ordering on the X sites an original mirror plane might not exist anymore.

Table 1. List of structure types found with ternary lanthanoide, Sc, Y, Zr, Hf, and U alloys and which can be interpreted as linear intergrowth of different slabs with square-mesh interfaces. In the second column is listed the classification symbol after *Pearson*[1b,39] and in the third column the space group. For the notation of slab sequences see text.

$BaAl_4 \mid AlB_2$				
$CeNiSi_2$	oS16	Cmcm	$(BaAl_4^2 \mid AlB_2^4)_2$	$BaAl_4 = [CeNi_2Si_2]$, $AlB_2 = [CeSi_2]$
$NdNiGa_2$	oS16	Cmmm	$(BaAl_4^3 \mid AlB_2^4)_2$	$BaAl_4 = [NdNi_2Ga_2]$, $AlB_2 = [NdGa_2]$
$Ce_3Ni_2Si_8$	oS26	Cmmm	$(2\,BaAl_4^2 \mid AlB_2^4)_2$	$BaAl_4 = [CeNiSi_3]$, $AlB_2 = [CeSi_2]$
$U_3Ni_4Si_4$	oI22	Immm	$(BaAl_4^2 \mid 2\,AlB_2^4)_2$	$BaAl_4 = [UNi_2Si_2]$, $AlB_2 = [UNiSi]$
$BaAl_4 \mid CaF_2$				
$HfCuSi_2$	tP8	P4/nmm	$BaAl_4^2 \mid CaF_2^2$	$BaAl_4 = [HfCu_2Si_2]$, $CaF_2 = [HfSi_2]$
$SrZnBi_2$	tI16	I4/mmm	$(BaAl_4^2 \mid CaF_2^3)_2$	$BaAl_4 = [SrZn_2Bi_2]$, $CaF_2 = [SrBi_2]$
$Zr_3Cu_4Si_6$	tI26	I4/mmm	$(2\,BaAl_4^2 \mid CaF_2^2)_2$	$BaAl_4 = [ZrCu_2Si_2]$, $CaF_2 = [ZrSi_2]$
$LaNiGa_6$ [a]	tP16	P4/mmm	$(2\,BaAl_4\text{-}CaF_2^{13})_2$	$BaAl_4\text{-}CaF_2 = [La_{1/2}Ni_{1/2}Ga_3]$
Ce_2NiGa_{10}	tI26	I4/mmm	$(BaAl_4^2 \mid 2\,BaAl_4\text{-}CaF_2^{13})_2$	$BaAl_4 = [CeGa_4]$, $BaAl_4\text{-}CaF_2 = [Ce_{1/2}Ni_{1/2}Ga_3]$
Ce_4NiGa_{18} [b]	tI46	I4/mmm	$(3\,BaAl_4^2 \mid 2\,BaAl_4\text{-}CaF_2^{13})_2$	$BaAl_4 = [CeGa_4]$, $BaAl_4\text{-}CaF_2 = [Ce_{1/2}Ni_{1/2}Ga_3]$
$BaAl_4 \mid W$				
CeFeSi	tP6 PbFCl-type	P4/nmm	$BaAl_4^2 \mid W^2$	$BaAl_4 = [CeFe_2Si_2]$, W = [Ce]
CeScSi	tI12	I4/mmm	$(BaAl_4^3 \mid W^2)_2$	$BaAl_4 = [CeSc_2Si_2]$, W = [Ce]
$BaAl_4 \mid Po$				
$ScNi_2Si_3$	tI24	I4/mmm	$(BaAl_4^1 \mid BaAl_4^2 \mid BaAl_4^1 \mid Po^3)_2$	$BaAl_4^1 = [Sc_{1/2}NiSi]$, $BaAl_4^2 = [ScNi_2Si_2]$, Po = [Si_2]
$BaAl_4 \mid Cu$				
$CeRe_4Si_2$	oS14	Cmmm	$(2\,BaAl_4^1 \mid Cu^4)_2$	$BaAl_4 = [Ce_{1/2}ReSi]$, Cu = [Re_2]
$AlB_2 \mid W$				
$Er_4(Ni_3Si)$	oS8 CrB-type	Cmcm	$(AlB_2^4 \mid W^2)_2$	$AlB_2 = [ErNi_{1\,1/2}Si_{1/2}]$, W = [Er]
Y_3NiSi_3	oI14	Immm	$(2\,AlB_2^4 \mid W^2)_2$	$AlB_2 = [YNi_{1/2}Si_{1\,1/2}]$, W = [Y]
$AlB_2 \mid CaF_2$				
Sc_4CoSi_7	oS12 $ZrSi_2$-type derivative	Cmcm	$(AlB_2^4 \mid CaF_2^2)_2$	$AlB_2 = [ScCo_{1/2}Si_{1\,1/2}]$, $CaF_2 = [ScSi_2]$
$Cu_3Au \mid CaF_2$				
$HoCoGa_5$	tP7	P4/mmm	$2\,Cu_3Au\text{-}CaF_2^{13}$	$Cu_3Au\text{-}CaF_2 = [Ho_{1/2}Co_{1/2}Ga_{2\,1/2}]$
Ho_2CoGa_8	tP11	P4/mmm	$2\,Cu_3Au\text{-}CaF_2^{13} \mid Cu_3Au^3$	$Cu_3Au\text{-}CaF_2 = [Ho_{1/2}Co_{1/2}Ga_{2\,1/2}]$, $Cu_3Au = [HoGa_3]$
$BaAl_4 \mid AlB_2 \mid CaF_2$				
$U_2Ni_2Si_7$	oS22	Cmmm	$(2\,BaAl_4\text{-}CaF_2^{13} \mid AlB_2^4)_2$	$BaAl_4\text{-}CaF_2 = [U_{1/2}NiSi_{2\,1/2}]$, $AlB_2 = [USi_2]$
Pr_3NiGa_{10}	oP14	Pmmm	$2\,BaAl_4\text{-}CaF_2^{13} \mid 2\,AlB_2^4$	$BaAl_4\text{-}CaF_2 = [Pr_{1/2}Ni_{1/2}Ga_3]$, $AlB_2 = [PrGa_2]$
$EuMg_3Ge_3$	oS28	Cmcm	$(BaAl_4\text{-}CaF_2^{13} \mid CaF_2^2 \mid BaAl_4\text{-}CaF_2^{13} \mid AlB_2^4)_2$	$BaAl_4\text{-}CaF_2 = [Eu_{1/2}Mg_2Ge_{1\,1/2}]$, $CaF_2 = [Mg_2Ge]$, $AlB_2 = [EuGe_2]$
Hf_2CuSi_4	oS28	Cmcm	$(BaAl_4^2 \mid CaF_2^2 \mid AlB_2^4 \mid CaF_2^2)_2$	$BaAl_4 = [HfCu_2Si_2]$, $CaF_2 = [HfSi_2]$, $AlB_2 = [HfSi_2]$
$Ho_3Co_2Si_7$	oS24	Amm2	$(BaAl_4^2 \mid CaF_2^1 \mid BaAl_4^1 \mid AlB_2^4)_2$	$BaAl_4^2 = [HoCoSi_3]$, $CaF_2 = [Ho_{1/2}Si]$, $BaAl_4^1 = [Ho_{1/2}CoSi]$, $AlB_2 = [HoSi_2]$
$BaAl_4 \mid AlB_2 \mid Cu_3Au$				
$La_3Co_2Sn_7$	oS24	Cmmm	$(2\,BaAl_4\text{-}Cu_3Au^{13} \mid AlB_2^4)_2$	$BaAl_4\text{-}Cu_3Au = [LaCoSn_{2\,1/2}]$, $AlB_2 = [LaSn_2]$
$BaAl_4 \mid AlB_2 \mid Cu$				
$LaRe_2Si_2$	oI20	Imma	$(BaAl_4^1 \mid AlB_2^4 \mid BaAl_4^1 \mid Cu^5)_2$	$BaAl_4 = [La_{1/2}ReSi]$, $AlB_2 = [LaSi_2]$, Cu = [Re_2]
$BaAl_4 \mid AlB_2 \mid Po$				
$SmNiGe_3$	oS20	Cmmm	$(BaAl_4^1 \mid AlB_2^4 \mid BaAl_4^1 \mid Po^3)_2$	$BaAl_4 = [Sm_{1/2}NiGe]$, $AlB_2 = [SmGe_2]$, Po = [Ge_2]
$BaAl_4 \mid CaF_2 \mid Cu$				
$Ce_3Ni_2Ga_{15}$	tP40	P4/nmm	$2\,BaAl_4^2 \mid BaAl_4^{2*} \mid 2\,BaAl_4^2 \mid BaAl_4\text{-}CaF_2^{13} \mid CaF_2^1 \mid Cu^2 \mid CaF_2^1 \mid BaAl_4\text{-}CaF_2^{13}$	$BaAl_4^2 = [CeGa_4]$, $BaAl_4^{2*} = [CeNi_2Ga_2]$, $BaAl_4\text{-}CaF_2 = [Ce_{1/2}Ni_{1/2}Ga_3]$, $CaF_2 = [Ni_{1/2}Ga]$, Cu = [Ga_4]

[a] Arrangement of Ni-defects causes a doubling of unit cell.
[b] Due to partial occupation of a Ga-site by Ni-atoms the composition in the original publication is given as $Ce_4Ni_2Ga_{17}$.
Literature references in *Structure Reports*, further[14,16], except for $Zr_3Cu_4Si_6$[24], Pr_3NiGa_{10}[25], Ce_4NiGa_{18}[26], $Ce_3Ni_2Ga_{15}$[27], and $SmNiGe_3$[28].

composed of three kinds of slabs and is found in the triangle defined by the compositions of the three parent structure types.

5. Intergrowth of Slabs with Other Mesh Types at the Interfaces

Intergrowth of slabs with rectangular centered mesh interfaces:

Only two kinds of slabs are shown in Fig. 11: CsCl with interface normal [110] and axial ratio $2^{1/2}$ and $CaCu_5$ with interface normal [210] and axial ratio $(3/2)^{1/2}$. An intergrowth structure built up of these slabs is $PrCo_2Ga$[29], with the following slab stacking sequence:

$PrCo_2Ga$, oP8, Pmma : $CsCl \mid CaCu_5$

where $CsCl = [PrCo]$ and $CaCu_5 = [PrCo_3Ga_2]$

An intergrowth between these slabs is possible because the atoms at the interface form a mesh with an axial ratio inter-

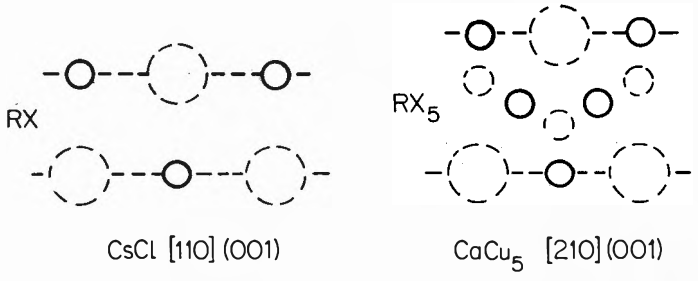


Fig. 11. Two kinds of slabs with rectangular centered mesh interfaces. The difference in height between the atoms drawn with solid respectively dashed lines is ½. Large circles correspond to rare earth atoms, small circles to X-atoms (T- or M-atoms).

mediate between the two theoretical values.

Intergrowth of slabs with orthohexagonal triangular or Kagomé mesh[*] interfaces:

In the upper part of Fig. 12 are shown three slabs which have as interface an orthohexagonal triangular mesh. An intergrowth structure based on two of these slabs is YFe_2Si_5 (in consideration of Si defects the composition is actually $YFe_2Si_{4½}$) which has the following slab stacking sequence:

YFe_2Si_5, hP16, $P6_3/mmc$: $(WC \mid 2\ W)_2$
where $WC = [Y_2Si_2]$ and $W = [Fe_2Si_4]$

Three kinds of slabs with a Kagomé mesh at the interfaces are shown in the lower part of Fig. 12. Intergrowth structures containing these slabs are listed in Table 2. Members of an inhomogeneous structure series of intergrown Laves- and $CaCu_5$-type slabs are shown in Fig. 3, while Fig. 2 presents members of a homogeneous structure series of intergrown binary and ternary $CaCu_5$-type slabs. The different binary and ternary compounds formed of binary and/or ternary Laves- and/or $CaCu_5$-type slabs with Kagomé mesh interfaces can be grouped in five linear structure series. As shown in Fig. 13 the compositions of the members of these five series are found on five straight lines in a R-T-M phase diagram. The members of the $R_{n+2}T_{3n+3}M_{2n+1}$ structure series with n = 1 and 2, where n indicates the number of $CeCo_3B_2$-type slabs for every Mg_2Cu_3Si-type slab, have been found only very recently by *Paccard* et al.[30]. It would be worthwhile to check if related compounds with other stackings exist.

There are known structures constructed of slabs with both kinds of orthohexagonal mesh interfaces. The structure type $CeNi_5Sn$ is built up of three kinds of slabs with the following slab stacking sequence:

$CeNi_5Sn$, hP28, $P6_3/mmc$:
$(CaCu_5 \mid ¼\ Zr_4Al_3 \mid BiF_3 \mid ¼\ Zr_4Al_3)_2$
where $CaCu_5 = [Ce_2Ni_{10}]$,
$¼\ Zr_4Al_3 = [Ni_3Sn]$, $BiF_3 = [Ce_2Ni_4Sn_2]$

As shown in Fig. 14, the $CaCu_5$-type slab is separated from the ternary W-type slab (BiF_3-type slab) by a two-atom layer thin Zr_4Al_3-type slab. This slab shares a Kagomé mesh interface with the $CaCu_5$-type slab and a triangular mesh interface with the BiF_3-type slab.

A new series with the general formula $R_{n+1}T_{3n+2}M_{2n+2}$[**], where n slabs derived from the $CaCu_5$-type (RT_3M_2) are intergrown with one slab of the $CaRh_2B_2$-type

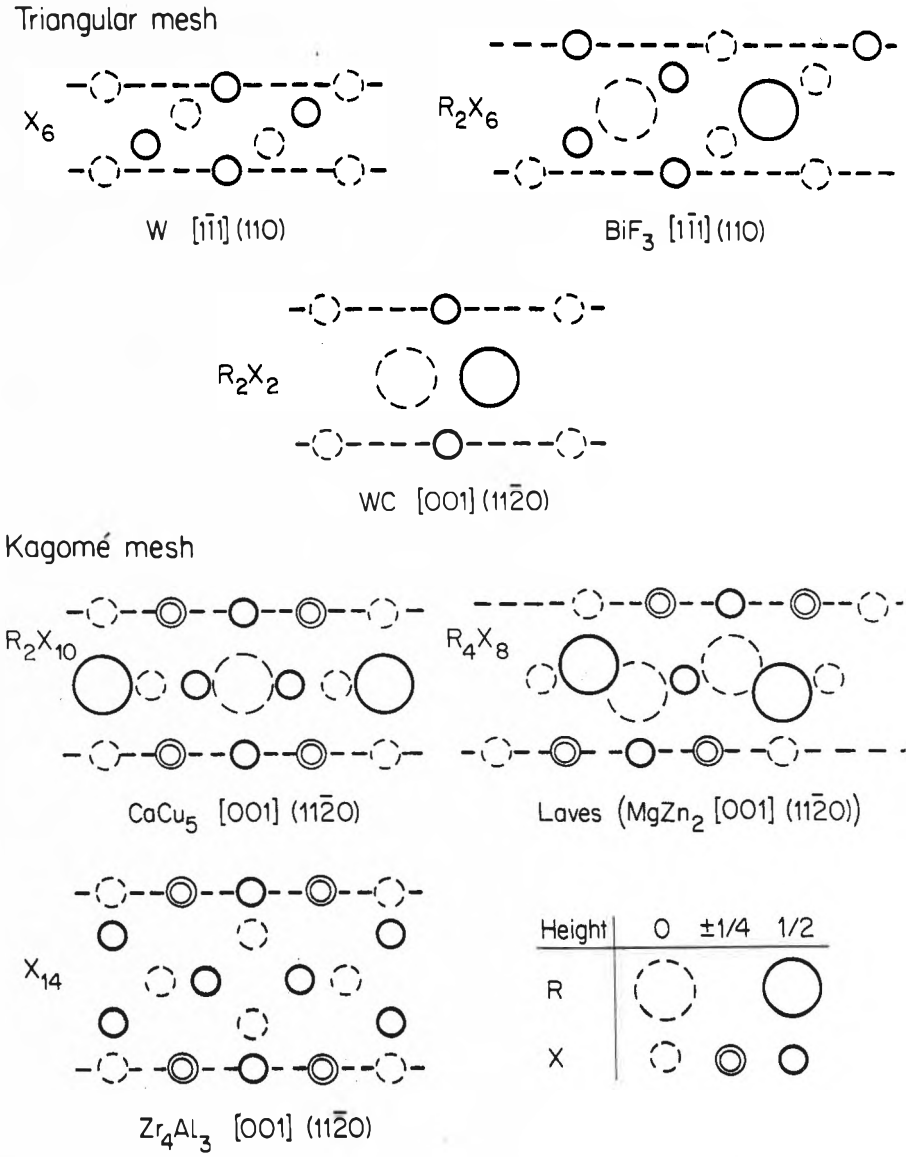


Fig. 12. Slabs with orthohexagonal triangular and orthohexagonal Kagomé mesh interfaces. The Laves-type slab has been taken from the structure of $MgZn_2$, it is however also found in all other Laves-phases such as $MgCu_2$, $MgNi_2$, etc.

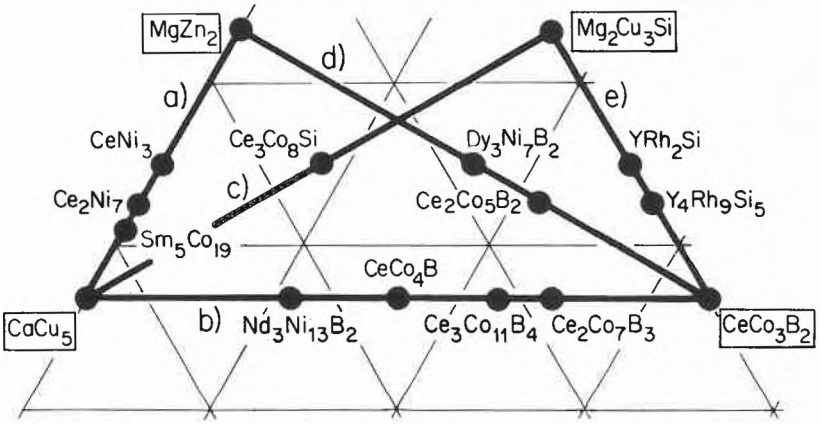
Table 2: List of structure types found with ternary lanthanoide alloys and which can be interpreted as linear intergrowth of slabs with orthohexagonal Kagomé mesh interfaces. The small letters in front of the chemical formulae refer to the structure series for which the composition lines and general formulae are given in Fig. 13.

Laves | $CaCu_5$				
– Ternary Laves- (Mg_2Cu_3Si-) and binary $CaCu_5$-type slabs				
c)	Ce_3Co_8Si	hP24	$P6_3/mmc$	$(Mg_2Cu_3Si \mid CaCu_5)_2$
– Binary Laves- (Mg_2Zn_4-) and ternary $CaCu_5$- ($CeCo_3B_2$-)type slabs				
d)	$Dy_3Ni_7B_2$	hP24	$P6_3/mmc$	$(Mg_2Zn_4 \mid CeCo_3B_2)_2$
d)	$Ce_2Co_5B_2$	hP36	$P6_3/mmc$	$(Mg_2Zn_4 \mid 2\,CeCo_3B_2)_2$
– Ternary Laves- (Mg_2Cu_3Si-) and ternary $CaCu_5$- ($CeCo_3B_2$-)type slabs				
e)	YRh_2Si	hP24	$P6_3/mmc$	$(Mg_2Cu_3Si \mid CeCo_3B_2)_2$
e)	$Y_4Rh_9Si_5$ [a]	hR54	$R\bar{3}m$	$(Mg_2Cu_3Si \mid 2\,CeCo_3B_2)_3$
$CaCu_5 \mid CaCu_5$				
– Ternary $CaCu_5$- ($CeCo_3B_2$-) and binary $CaCu_5$-type slabs				
b)	$Nd_3Ni_{13}B_2$	hP18	P6/mmm	$CeCo_3B_2 \mid 2\,CaCu_5$
b)	$CeCo_4B$	hP12	P6/mmm	$CeCo_3B_2 \mid CaCu_5$
b)	$Ce_3Co_{11}B_4$	hP18	P6/mmm	$2\,CeCo_3B_2 \mid CaCu_5$
b)	$Ce_2Co_7B_3$	hP24	P6/mmm	$3\,CeCo_3B_2 \mid CaCu_5$
$Zr_4Al_3 \mid CaCu_5$				
– Binary Zr_4Al_3- and ternary $CaCu_5$- ($CeCo_3B_2$-)type slabs				
	$HfFe_6Ge_6$	hP13	P6/mmm	$Zr_4Al_3 \mid CeCo_3B_2$
				$Zr_4Al_3 = [Fe_3Ge_4]$, $CeCo_3B_2 = [HfFe_3Ge_2]$

[a] Ternary variant of the rhombohedral Gd_2Co_7-type.

[*] This net of triangles and hexagons corresponds to «kagomé», a three-way bamboo weave used for the production of baskets (kago = basket in Japanese; mé = eye in Japanese).

[**] The formula given in the original paper[31] is expressed in a different manner.



a) $R_{2+n}T_{4+5n}$ structure series: $Mg_2Zn_4 \mid n\ CaCu_5$
b) $R_{m+n}T_{5m+3n}M_{2n}$ structure series: $m\ CaCu_5 \mid n\ CeCo_3B_2$
c) $R_{2+n}T_{3+5n}M$ structure series: $Mg_2Cu_3Si \mid n\ CaCu_5$
d) $R_{2+n}T_{4+3n}M_{2n}$ structure series: $Mg_2Zn_4 \mid n\ CeCo_3B_2$
e) $R_{2+n}T_{3+3n}M_{1+2n}$ structure series: $Mg_2Cu_3Si \mid n\ CeCo_3B_2$

Fig. 13. The five structure series of intergrown binary or ternary Laves- and/or $CaCu_5$-type slabs. The framed formulae indicate the parent structure types.

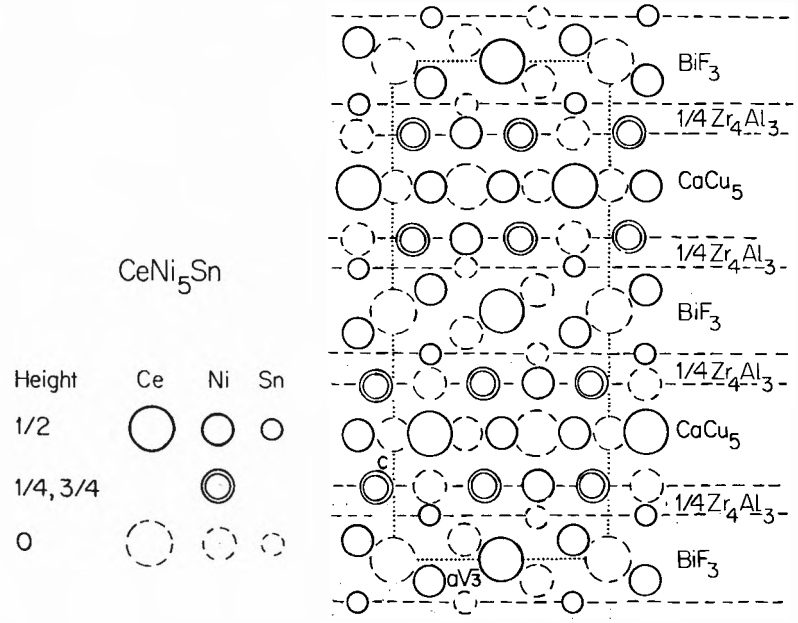


Fig. 14. The $CeNi_5Sn$ structure (projection along [11$\bar{2}$0]), interpreted as an intergrowth of three kinds of slabs, derived from the $CaCu_5$-, BiF_3-(W ordering variant), and Zr_4Al_3-types respectively.

(RT_2M_2), was recently reported by *Jung* [31]. Structures of this series with n = 0, 1, 2, 4, 6, and ∞ have been observed with R = Ca or Sr, T = Rh, and M = B. The $CaRh_2B_2$-type is geometrically related to the $CaCu_5$-type, but some atoms are missing in the Kagomé mesh layers resulting in a rectangular mesh.

6. Concluding Remarks and Outlook

We have shown a few examples of how complicated ternary crystal structures can be interpreted as an intergrowth of slabs or other segments of simple structures. The atom arrangements of the parent structures used in this survey are relatively simple, but there are known in the literature other crystal structures which can be described with segments taken from more complicated parent structures and which have also different types of interfaces. For example, $Pr_6Ni_7Si_4$ can be described as a linear intergrowth of $ThSi_2$- and $Y_3Rh_2Si_2$-type slabs according to *Hovestreydt* and *Parthé* [32]. Furthermore, some structures can be considered as linear homogeneous combinations of slabs which themselves are formed by an inhomogeneous combination of simpler structure segments. This occurs, for example, with the $W_6(W,Fe,Si)_7$, $Nb_6(Ni,Al)_7$, W_5Fe_7 structure series in which the common slab itself is a combination of Laves- and Zr_4Al_3-type columns as shown by *Kripyakevich* and *Yarmolyuk* [33].

The fact that, of the about 150 known structure types of ternary lanthanoid-transition metal-silicides and homologues, more than one third can be interpreted as an intergrowth of segments of simple parent structures, proves the usefulness of this approach. A similar description, based on the combination of segments of simple structures, has also been successfully applied to «sulfosalts»[*] and related compounds (*Makovicky* [35]). The success of this interpretation considering structural segments should stimulate similar studies on complicated crystal structures found with other element combinations.

The «segment intergrowth» concept is not only a useful tool for strictly geometrical description of crystal structures, but it could have also a physical sens if one refers to the observations made with lattice imaging techniques, using a high resolution electron microscope. Most of the investigations, until now, have been realized on oxides [36], but interesting results have also been obtained on intermetallic phases such as, for example, Mo_3CoSi [37]. The structure of this compound can be described, according to *Andersson* [38], as built up from structural columns derived from the Cr_3Si (A15)-type by applying appropriate crystallographic shear operations. The results of the electron microscope study revealed the presence of planar defects, limiting different structural domains in the sample. It could be shown that these microdomains were also built up from Cr_3Si-type units, blocks, or columns, arranged in similar, but different, ways with respect to the Mo_3CoSi structure.

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[*] Sulfosalts in a strict definition [34] are metallic compounds of general composition $M_xB_yA_z$ where M = Au, Ag, Hg, Tl, Pb, Fe, Co, Ni; B = As, Sb, Bi; A = S, Se, Te and where the valence electrons of the atoms M and B complete the octets of the atoms A. If As, Sb, or Bi contribute all their five valence electrons we have normal valence compounds, however there exist also sulfosalts where two electrons remain with the As-, Sb-, or Bi-atoms.

[1] a) According to the commonly accepted definition, to be considered as isotypic (same structure type) two structures must have the same composition, the same space group, similar relative unit cell dimensions (axial ratios, angles), same sets of point positions, with same or similar adjustable parameters, occupied by corresponding atoms, having the same or similar coordinations. – b) P. Villars, L.D. Calvert: *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, to be published by the American Metals Society, Metals Park OH, 1985.
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