Classification of Structures Built up of Centred Trigonal Prisms and Ordering Principles in Ternary Rare-Earth–Transition-Metal Silicide, Germanide and Gallide Structures

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Abstract

The great majority of the known crystal structures built up only of centred trigonal prisms can be classified according to (*a*) the number of different prism-axis directions, (*b*) the dimensionality of the AlB_2-type fragments, (*c*) the value of the prism-linkage coefficient, (*d*) the ratio of the number of centred prisms to the number of W-type segments and (*e*) the numbers of prism-centre sites with different waist-contact type. Many ternary rare-earth–transition-metal silicide, germanide and gallide structures are characterized by transition-metal and Si-, Ge- or Ga-centred trigonal rare-earth prisms. Atom ordering on the prism-centre sites is to be expected whenever the transition element and the main-group element tend to induce different rare-earth prism shapes. The atom ordering is characterized by the absence of transition-metal–rare-earth and transition-metal–transition-metal waist contacts. This ordering principle not only explains the structures and compositions of the known ordered compounds, but also allows a prediction of the compositions for full order of compounds where a random distribution of prism sites has been reported previously. The application of this ordering principle is demonstrated on earlier-reported $Ce_{14}Ni_8Si_9$, for which at the predicted, slightly different, composition $Ce_{14}Ni_6Si_{11}$ a fully ordered structure is verified.

Introduction

A great number of binary compounds R_xT_y, R_xM_z and of ternary compounds $R_xT_yM_z$ (R = rare-earth element, Y, Sc; T = transition element; M = main-group element of the third and fourth group) have structures which are characterized by centred trigonal rare-earth prisms. These structures can be grouped in strictly geometrical terms by denoting the different prism-axis directions or by describing the kind of AlB_2-type fragments found in the structure. However, two principal efforts have been made previously to classify these structures in correlating structural

features with the composition of these compounds. In one case use of the prism-linkage coefficient was made (Parthé & Moreau, 1977; Parthé, 1981). In the second case the structures were interpreted as an intergrowth of two construction elements: centred trigonal prisms and segments built up as the W structure (Grin', Yarmolyuk & Gladyshevskii, 1979, 1982; Gladyshevskii & Grin', 1981). In both methods the particular nature of the elements occupying the prism-centre sites was of no special importance and consequently no statements were made for ternary compounds $R_xT_yM_z$ concerning the ordering of the T and M atoms on the prism-centre sites. Some of the ternary compounds are partially disordered and have ranges of composition with the same content of rare earth but the T/M ratio varying. However, there seems to exist in many cases one composition where full ordering is possible. For some of the previously published crystal structures the arrangement of the T and M atoms on the prism-centre sites was not investigated or the phases studied were either off-composition for full ordering or not in thermal equilibrium and consequently T and M atoms were reported to be randomly distributed over the available sites. Recently a few well ordered $R_xNi_ySi_z$ phases have been structurally analysed. With this information at hand it now appears interesting to search for general ordering principles, which correlate structural features with the compositions of the *ordered ternary* compounds. These principles should not only explain the seemingly complicated compositions of some of the ordered compounds but should also lead to hypothetical formulae for full order of all those phases where a random arrangement of T and M atoms has been reported.

The different approaches to the classification of ternary structures with trigonal prisms

In the following discussion we shall restrict ourselves only to those structures where all R atoms participate in the formation of trigonal prisms and where all T

and/or M atoms are at the centres of those prisms. As demonstration examples we shall use the four ordered structures shown in Fig. 1: Gd_3NiSi_2 (Klepp & Parthé, 1981), $Ce_7Ni_2Si_5$ (Mis'kiv, 1974), $Pr_{14}Ni_6Si_{11}$ (Hovestreydt, Klepp & Parthé, 1983) and LaPtSi (Klepp & Parthé, 1982). These structures are characterized by one short unit-cell axis ($\sim$4 Å) which corresponds to an edge of a rectangular prism face. All four structures are projected in Fig. 1 along this short axis.

(a) Classification according to the number of directions of the trigonal-prism axes

With this simple geometrical classification scheme which does not relate to the compositions of the compounds, all structures under consideration can be grouped into three principal categories, one being further subdivided into two subsections. The earlier proposed classification based only on parallel or 'coplanar' prism-axis directions (Kripyakevich, 1977) is too coarse for a subdivision of the many structures which have become known in the meantime.

(I) All prism axes are parallel to each other. A structural example for this category is found with the CrB structure.*

(II) There are two different prism-axis directions.

(IIa) The two directions are perpendicular to each other. The MoB structure* serves as an example as well

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* For a drawing of the CrB, FeB and MoB structures see Hohnke & Parthé (1966).
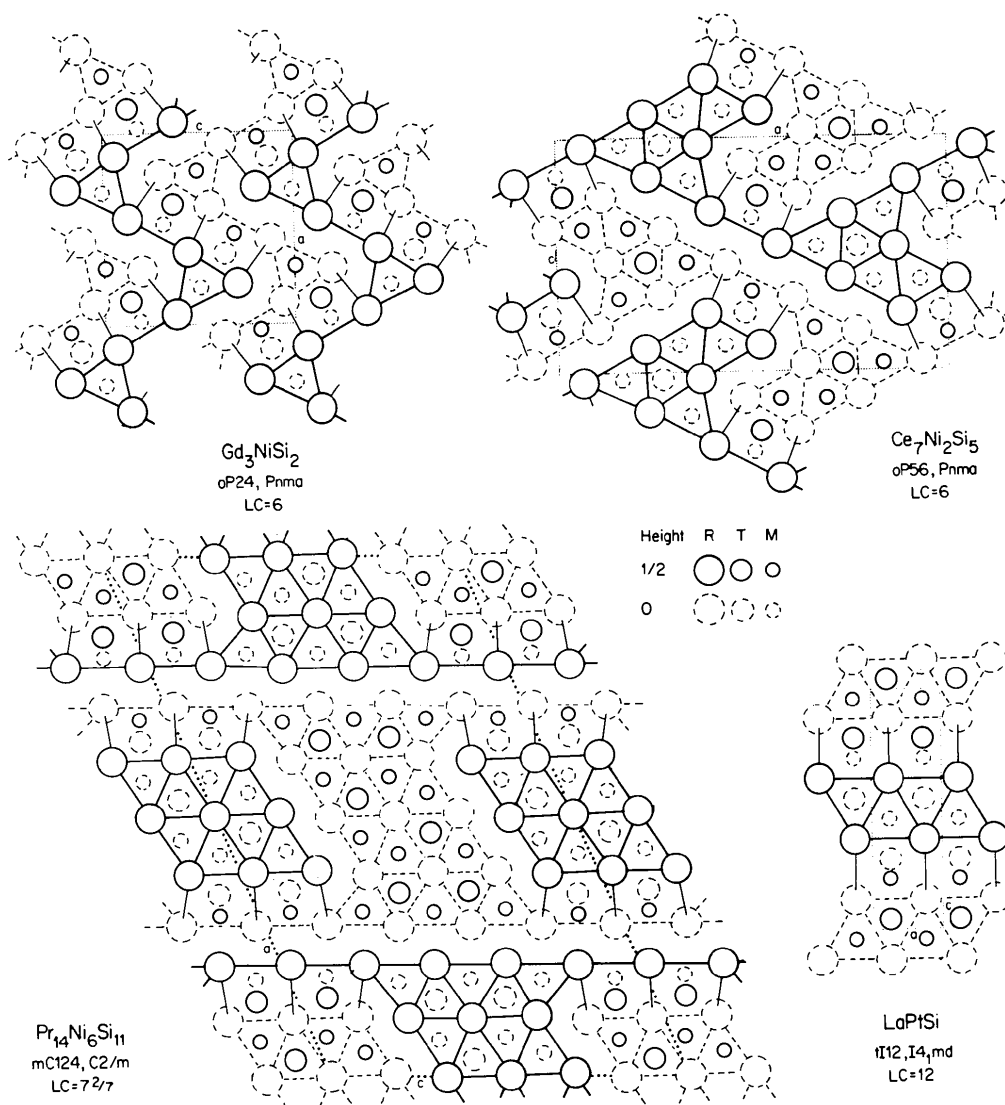

Fig. 1. Four ordered rare-earth–transition-metal silicide structures built up of T- or M-centred trigonal rare-earth prisms.

as the structures of $Pr_{14}Ni_6Si_{11}$ and LaPtSi, shown in Fig. 1.

(II*b*) The two directions are not perpendicular. The FeB structure* is an example.

(III) More than two different prism-axis directions occur. Three different prism-axis directions are found in Gd_3NiSi_2 and $Ce_7Ni_2Si_5$. Note that pairs of prisms with a common rectangular face must have their axis directions either parallel or perpendicular.

(*b*) Classification according to the kinds of AlB_2-type fragments found in the structure

Gladyshevskii & Grin' (1981) divide the structures with trigonal-prismatic atom coordination into three categories depending on the dimensionality of the AlB_2-type fragments which can be recognized in the structure: two-dimensionally infinite segments (sheets of various kinds), one-dimensionally infinite segments (columns or column assemblies of various kinds) or, finally, finite-volume fragments. Also this classification does not relate to the composition of the compounds.

(*c*) Classification according to the value of the prism-linkage coefficient

The prism-linkage coefficient LC denotes the average number of prisms in which one R atom participates (Parthé & Moreau, 1977; Parthé, 1981). LC corresponds to six times the ratio of number of trigonal prisms to number of R atoms in one unit cell. The composition of a compound $R_xT_yM_z$ is directly related to LC. With

$$\frac{x}{y+z} = \frac{6}{LC} \qquad (1)$$

the composition can be written as $R_6(T,M)_{LC}$. The value of LC can vary from LC = 1, where only isolated trigonal prisms occur [for example, the Pd_6P structure determined by Andersson, Kaechansilp, Casteleiro Soto & Rundqvist (1974)], to LC = 12, where the whole space is completely filled up with trigonal prisms (examples are the AlB_2 and $ThSi_2$ structure types). In Fig. 1 the LC values of the four structures are indicated.

(*d*) Classification according to the number of centred trigonal prisms and the number of W-type segments per unit cell

In this classification the structures are considered as an intergrowth of two construction elements. The space of one unit cell consists of a certain number of T- or M-centred rare-earth prisms, say n, which are intergrown with a number, say m, of (deformed) W-type segments. The W-type segments fill the gaps between the centred trigonal prisms. A W-type segment unit

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* See previous footnote.

corresponds to half the volume of the unit cell of the well known cubic body-centred W-type structure (see Fig. 2) and is formed by R atoms only (Grin', Yarmolyuk & Gladyshevskii, 1979, 1982; Gladyshevskii & Grin', 1981).*

In the structures shown in Fig. 1 the two construction elements are represented in different ways. The T- and M- centred trigonal R prisms appear with both types of representation as given in Fig. 2. The W-type segments, when they are present in the structures, appear only as types (*a*) and (*c*) according to Fig. 2. All atoms are at two heights only, displaced by half a translation unit (full and dashed circles). In other structures, particularly those with non-parallel and non-perpendicular prism-axis directions the recognition of the W-type segments is not always easy. One notes that the W-type segments are often deformed. The n and m values of the four structures shown in Fig. 1 are tabulated in Table 1 together with other structures characterized by centred trigonal prisms.

The composition of a compound $R_xT_yM_z$ is directly related to the number of W-type segments, m, and the number of centred rare-earth prisms, n, in the unit cell. With

$$\frac{x}{y+z} = \frac{m}{n} + \frac{1}{2} \qquad (2)$$

the composition can be rewritten as $R_{m+\frac{1}{2}n}(T,M)_n$ or $R_{(m/n)+\frac{1}{2}}(T,M)$ with $m + \frac{1}{2}n$ atoms per unit cell. It should be noted that it is not always possible to interpret a structure with *two* construction elements only. For example, to interpret the Pd_6P structure with LC = 1 one needs three different intergrown construction elements (centred prisms, non-centred prisms, and W-type segments). Gladyshevskii & Grin' (1981) give an extended formula $R_{m+\frac{1}{2}n}(T,M)_{n-k}$ where k is the number of empty prisms per unit cell which allows classification of a greater number of structures including many outside the field of immediate interest here.

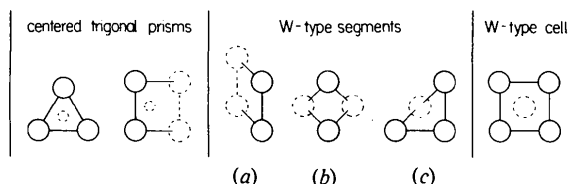* In the Russian papers the W-type segment is called the α-Fe-type segment.

Fig. 2. The two construction elements: centred trigonal prisms and W-type segments in the different forms (*a,b,c*) as they may appear in the drawings of the structures presented in Figs. 1, 5 and 7. A projection of one complete W-type unit cell is also given on the right-hand side of the figure. Large circles: rare-earth atoms; small circles: T or M atoms. Fully drawn circles and dashed circles differ by half a translation unit in height.

Table 1. *List of selected structure types built up of centred prisms with one short unit-cell dimension corresponding to an edge of a rectangular prism face*

For definitions of m, Δ, n and W_i see text. For references on binary structure types see Parthé & Moreau (1977) and for ternary structure types, Parthé & Chabot (1983).

LC	Structure type	Pearson's classification symbol	Space group	*	m	Δ	n	m/n	W_0†	W_1†	W_2†	W_3†	Composition for ordered $R_xT_yM_z$ No T–R waist contact	Neither T–R nor T–T waist contact	Remarks
2	Re₃B	oC16	Cmcm	I	10	4	4	5/2	0	0	0	4	—	—	Order verified
4	Y₃Co₂	oP20	Pnnn	I	8	2	8	1	0	4	4	0	—	—	With Co and Ga no order expected
4	Dy₃Ni₂	mC20	C2/m	I	8	2	8	1	0	4	4	0	—	—	Order verified
6	CrB	oC8	Cmcm	III	2	0	4	1/2	4	4	0	0	R_3TM_2	R_3TM_2	Order verified
6	Gd₃NiSi₂	oP24	Pnma	III	6	0	12	1/2	4	4	4	0	R_3TM_2	R_5TM_4	Order verified
6	Y₁₀Co₇Ga₃	oP40	Pnma	III	10	0	20	1/2	8	4	8	0	$R_5T_2M_3$	$R_7T_2M_5$	Order needs to be verified, should lead to larger unit cell
6	Ce₇Ni₅Si₅	oP56	Pnma	IIa	14	0	28	1/2	8	12	8	0	$R_7T_2M_5$	$R_{14}T_6M_{11}$	Order verified
7¼	Pr₁₄Ni₆Si₁₁	mC124	C2/m	I	22	0	68	11/34	32	28	8	0	$R_{14}T_8M_9$	R_3TM_3	Order verified
8	Y₃NiSi₃	oI14	Immm	I	2	0	8	1/4	4	4	0	0	$R_3T_2M_2$		
12	LaPtSi	tI12	I4₁md	IIa	0	0	8	0	8	0	0	0	RT_2	RTM	Order verified
12	AlB₂	hP3	P6/mmm	I	0	0	2	0	2	0	0	0	RT_2	RTM	Order not yet found, could lead to lower space-group symmetry and same unit cell (Klepp & Parthé, 1982)

* Subdivision according to the number of prism-axis directions (see text).
† In general terms, the various kinds of waist contact depend on the number of prism-forming atoms which are in waist contact with a given central atom.

The prism-linkage coefficient LC can be related with the m/n ratio according to

$$\frac{m}{n} = \frac{6}{LC} - \frac{1}{2} \quad \text{or} \quad LC = \frac{6}{\dfrac{m}{n} + \frac{1}{2}}. \quad (3)$$

The variation of LC with the ratio m/n is shown in Fig. 3.

(e) *Subdivision according to the different kinds of waist contacts of the atoms centring the trigonal prisms*

In the structures of interest here all atoms at the prism centres have nine neighbours. In addition to the six R atoms of the surrounding trigonal prism, there are three more neighbours in the central plane perpendicular to the prism axis. These three atoms are said to be in waist contact with the central atom. Depending on the number of rare-earth atoms in waist contact with one given prism-centre atom one can distinguish between four different types of waist contact, shown in Fig. 4. For waist contact of type 0, 1, 2 or 3 there are 0, 1, 2, or 3 rare-earth atoms in waist contact. The dotted lines in Fig. 4 are the waist-contact lines, imaginary lines which connect a prism-centre atom with its three waist contacts.

We shall denote by W_i the number of atoms at the prism centres/unit cell with waist contact of type i. It is obvious that

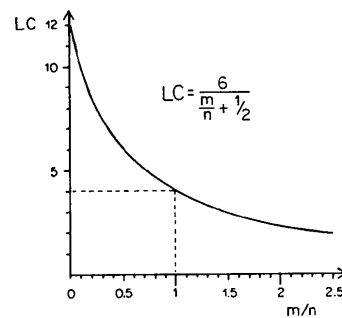$$n = \sum_{i=0}^{3} W_i \quad \text{for} \quad R_{m+\frac{1}{3}n}(T,M)_n. \quad (4)$$

Fig. 3. The variation of LC with the ratio m/n. These parameters apply to compounds which are built up of centred rare-earth prisms and have the compositions $R_6(T,M)_{LC}$ or $R_{(m/n)+\frac{1}{2}}(T,M)$.

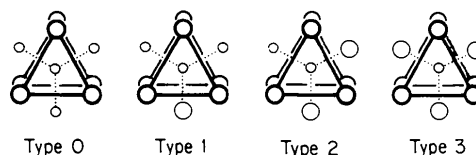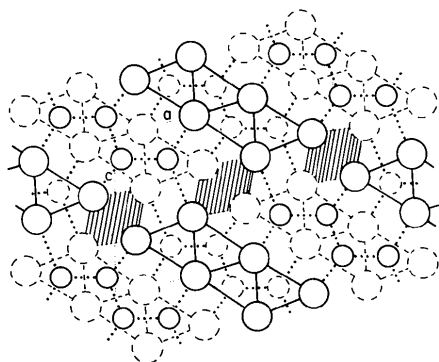Type 0   Type 1   Type 2   Type 3

Fig. 4. The four types of waist contact which a prism centre can have with 0, 1, 2 or 3 rare-earth atoms in waist contact. Large circles: rare-earth atoms; small circles: T or M atoms; the waist-contact lines are dotted.

Dy$_3$Ni$_2$

mC20, C2/m

LC=4

Fig. 5. The structure of Dy$_3$Ni$_2$ with LC = 4, $m = n = 8$, $W_0 = W_3 = 0$, $W_1 = W_2 = 4$ and $\Delta = 2$. Dy: large circles, Ni: small circles. The atoms are at two heights, only differing by $\frac{1}{2}b$, and indicated by full or dashed circles. The waist-contact lines of all Ni atoms are shown with dotted lines. The W-type segments which are not crossed by waist-contact lines are hatched.

One can further obtain the relation

$$m = \tfrac{1}{2}W_1 + W_2 + \tfrac{1}{2}W_3 + \Delta, \qquad (5)$$

where Δ indicates the number of tungsten-type segments/unit cell which are not crossed by a waist-contact line. A structure with $W_0 = W_3 = 0$, $W_1 = W_2 = 4$ and $\Delta = 2$ is shown in Fig. 5. In the drawings shown in Fig. 1 all W-type segments are crossed by waist-contact lines, thus $\Delta = 0$.

In Table 1 are listed crystal structures built up from centred trigonal prisms ordered with increasing value of LC. There is given the classification according to the number of directions of trigonal axes, the m, Δ and n values together with W_0, W_1, W_2 and W_3 values. With decreasing rare-earth content (that means increasing LC value) we note that the relative Δ values decrease to zero and the relative W_0 values increase. Relative is to be meant here in relation either to the corresponding m values or to the W_1, W_2 and W_3 values of the structures.

The shape of the trigonal prism

It is known from the studies of binary structures with trigonal rare-earth prisms (for example, structures with FeB and CrB type) that the relative dimensions of the R_6T prisms are different from those of the R_6M prisms. The relative prism dimensions can be expressed by their w/s and their w/u ratio as defined in Fig. 6(a).* The

* For the case of the CrB- and FeB-type structures the equations to obtain w/s and w/u from the lattice constants have been given by Klepp & Parthé (1980) and Parthé (1981).

data for binary rare-earth compounds with CrB and/or FeB type, plotted in Fig. 6(b), indicate that R_6M prisms are stretched and R_6T prisms are compressed (Hohnke & Parthé, 1966; Parthé, 1981). The same trend is true for the other binary structures containing trigonal prisms [see, for example, the discussion for U$_3$Si$_2$-type compounds (Le Roy, Moreau, Paccard & Parthé, 1977)].

The degree of elongation or compression of the trigonal prisms depends on the group number and the period number of the element at the prism centre. We note in Fig. 6(b) that gallides have much less elongated prisms than those in silicides and Rh compounds have much less compressed prisms compared to Pd compounds. For the further discussions it would be of interest to know more of the shape of Co-centred prisms. There are no RCo compounds with CrB or FeB structure; however, Y$_3$Co$_2$ is built up of segments cut from the CrB structure (Moreau, Parthé & Paccard, 1975). According to Grover, Coles, Sarkissian & Stone (1982), Y$_3$Co$_2$ is metastable; however, this has no influence on this discussion. The w/s values of the Y$_6$Co prisms are $3\cdot975/3\cdot914 = 1\cdot02$; they are thus slightly elongated.* For a comparison, the prisms in Dy$_3$Ni$_2$ with the same prism linkage but oriented in a different way (Moreau, Paccard & Parthé, 1974) have w/s values of $3\cdot662/4\cdot333 = 0\cdot85$,* which are in agreement with the values for the compressed prisms in

* It should be noted that the s value has to be measured parallel to the direction of the zigzag chains of the prism-centre atoms.
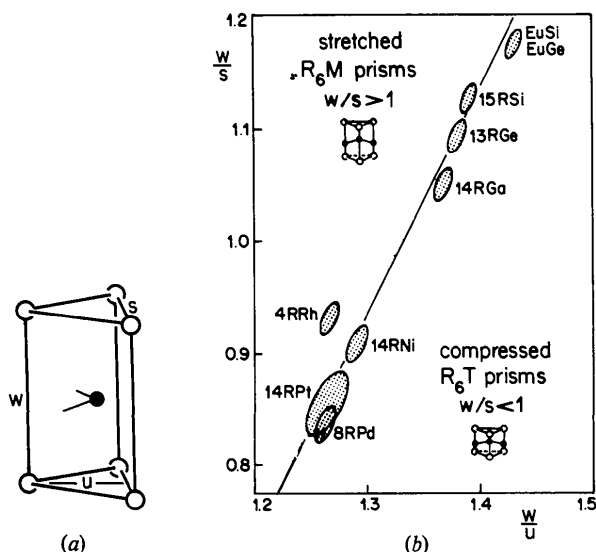

Fig. 6. (a) Parameters used to characterize the shape of the trigonal prisms in FeB- and CrB-type structures. The two bond lines which extend from the central prism atom connect to the next B atoms in the zigzag chain. (b) The w/s and w/u ratios for the trigonal prisms in RT and RM compounds with FeB and /or CrB structure type.

RNi compounds with CrB and/or FeB structure type. We note that the decrease of the prism compression on replacing the element at the prism centre with one further to the left in the periodic system is observed not only with Pd- and Rh- but also Ni- and Co-containing compounds.

As will be seen later, the tendency for the different prism-centre elements to have different rare-earth prism shapes is one of the reasons for the atom ordering in the ternary compounds. From Fig. 6(b) and the discussion above on R_6Co prisms we can conclude that Co and Ga atoms require, in their binary rare-earth compounds, rare-earth prism shapes which are not too different from each other.

Ordering of T and M elements on prism-centred sites

The tendency for the T elements to have compressed and for the M elements to have stretched trigonal rare-earth prisms in their binary structures cannot easily be reconciled in the ternary structures, when the R_6T and R_6M prisms are interconnected. In Table 2 are listed the average w/s ratios for all crystallographically different rare-earth prisms found in the four structures shown in Fig. 1. In the ternary structures the M elements retain essentially their elongated rare-earth prisms and the linked R_6T prisms are not as compressed as in the binary structures; they are even stretched. In this case restrictions on the possible waist contacts of the T atoms occur. The evidence gained from the structures shown in Fig. 1 indicates that the T

Table 2. *List of $\bar{w}/\bar{s}$ values characterizing the shapes of the centred trigonal rare-earth prisms found in the four structures shown in Fig.* 1

Only data for crystallographically nonequivalent prisms are given. $\bar{w}$ is the mean value of the height and $\bar{s}$ is the mean value of the six edges of the two triangular faces of each prism. The orientations of the prism axes are indicated by $\perp$ or $\parallel$ which means they are either perpendicular or parallel to the plane of projection of Fig. 1.

	$\bar{w}/\bar{s}$ for R_6Si prism		$\bar{w}/\bar{s}$ for R_6Ni or R_6Pt prism	
	$\perp$	$\parallel$	$\perp$	$\parallel$
Gd$_3$NiSi$_2$	1·10	0·99	–	0·94
Ce$_7$Ni$_2$Si$_5$	1·10	1·05	1·17	0·98
	1·09			
	1·08			
	1·06			
Pr$_{14}$Ni$_6$Si$_{11}$	1·10	1·03	1·12	1·04
	1·08	1·03	1·10	0·99
	1·08		1·08	
	1·08		1·08	
	1·08			
	1·08			
	1·07			
	1·07			
	1·06			
LaPtSi	1·01 $\equiv$	1·01	1·01 $\equiv$	1·01

element can occupy the centre of a stretched or nearly uncompressed rare-earth prism only if the two following conditions are satisfied:

(1) The transition element can no longer have rare-earth waist contacts. Thus all transition elements are found only on the sites with waist contact of type 0.

(2) The transition element can no longer have other transition metals in waist contact, only M atoms being allowed for the waist contact. Thus, depending on the prism arrangement, it may happen that only a fraction of the trigonal-prismatic sites of type 0 can be occupied by T atoms. A similar ordering rule excluding $T–T$ contacts was recently announced for ternary BaAl$_4$-type derivative structures (Parthé, Chabot, Braun & Engel, 1983).

The hypothetical compositions of structures with trigonal prisms allowing only sites with waist contact of type 0 to be occupied by T elements are given in the third-last column of Table 1. The second-last column gives the expected composition if $T–T$ waist contacts are also forbidden.

These ordering principles explain not only the atom arrangement in the ordered structures, but also the composition of the ordered rare-earth–nickel(platinum) silicides and germanides.

Ternary ordered structures are to be expected with compounds having 60 or less at.% rare earth.[*] A number of binary types built up of trigonal prisms with 50 or more at.% rare earth are listed in the upper part of Table 1. Here, all prism-centre sites have rare-earth atoms in waist contact. This implies that in these structure types $W_0 = 0$ and thus ternary ordered structures should not form. A recent review of ternary rare-earth–transition-metal silicides, germanides and gallides (Parthé & Chabot, 1983) indicates the absence of ordered ternary compounds rich in rare-earth elements and built up as these binary structures. The lower limit of the rare-earth content is 33 at.%. In this case ThSi$_2$ (or AlB$_2$)-type derivative structures are formed where $W_1 = W_2 = W_3 = 0$.

These rules for atom ordering at the prism-centre sites do not apply necessarily to ternary rare-earth–cobalt gallides since there is little or no difference in the shape of the R_6Co and R_6Ga prisms. In Y$_{10}$Co$_7$Ga$_3$

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[*] Starting with a T-centred trigonal prism the smallest possible prism grouping, allowing the T atom to have only M atoms in waist contact, consists of four prisms joined by their rectangular faces. In the case that all prism axes are parallel and that triangular faces of the prisms are shared with other prisms such that infinite quadruple prism columns with triangular cross section are formed, the structure has a prism-linkage coefficient of 4 and should have a composition R_6TM_3 (60 at.% R). The hexagonal structure of Ce$_6$Ni$_2$Si$_3$ (Bodak, Gladyshevskii & Kharchenko, 1974) has this prism grouping; however, no atom ordering on the prism-centre sites has been reported. Further, there are extra Ni atoms in the space between the prism columns leading to composition $R_6T_2M_3$. Experiments are under way to restudy the atom ordering in this structure.
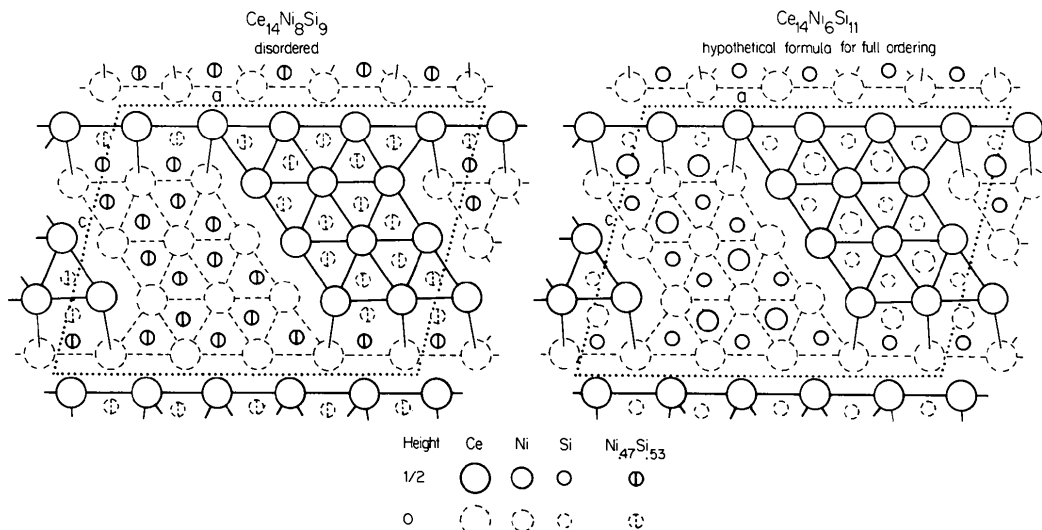
Fig. 7. The disordered $Ce_{14}Ni_8Si_9$ structure after Mis'kiv (1973) and a hypothetical structure with full atom ordering and composition
$Ce_{14}Ni_6Si_{11}$.

(Grin', Yarmolyuk & Gladyshevskii, 1979) some of the Co atoms have not only Co but also Y atoms in waist contact. However, since Co and Ga differ only by four electrons the determination of the atom ordering on the prism-centre sites by X-ray diffraction methods is not without problems.

Application of ordering principle to $Ce_{14}Ni_8Si_9$

The ordering principles can be used to predict the composition for full atom ordering in the case of rare-earth–nickel(platinum) silicide and germanide structures where a random occupation of prism-centre sites by T and M atoms has been reported. We shall discuss here as an example the case of $Ce_{14}Ni_8Si_9$ which, according to Mis'kiv (1973), crystallizes with a primitive monoclinic structure as shown on the left of Fig. 7. The Ni and Si atoms are supposed to occupy the prism-centre sites at random. Application of the ordering principle suggests that the T and M atoms can be arranged in an ordered structure as shown on the right-hand side of Fig. 7 and the composition of this ordered structure would then be $Ce_{14}Ni_6Si_{11}$. It was of interest to verify this hypothesis. We have thus performed a crystal structure analysis on a compound with composition $Ce_{14}Ni_6Si_{11}$ and found an ordered structure with an atom ordering as predicted – with a larger unit cell, however (Hovestreydt & Parthé, 1983). The new ordered centred monoclinic structure is isotypic to $Pr_{14}Ni_6Si_{11}$, shown in Fig. 1. The hypothetical primitive $Ce_{14}Ni_6Si_{11}$ structure (Fig. 7) and the actual centred $Ce_{14}Ni_6Si_{11}$ structure (Fig. 1) are closely related. They are, following the discussion by

Hovestreydt, Klepp & Parthé (1983), simply structure-slabs stacking variants. The ordering principle does not permit a prediction as to which of the two ordered structures should be formed.

Further experimental studies are being undertaken to verify the ordering principle with other ternary compounds built up from centred trigonal rare-earth prisms.

References

ANDERSSON, Y., KAECHANSILP, V., CASTELEIRO SOTO, M. & RUNDQVIST, S. (1974). Acta Chem. Scand. Ser. A, 28, 797–802.
BODAK, O. I., GLADYSHEVSKII, E. I. & KHARCHENKO, O. I. (1974). Sov. Phys. Crystallogr. 19, 45–46.
GLADYSHEVSKII, E. I. & GRIN', YU. N. (1981). Sov. Phys. Crystallogr. 26, 683–689.
GRIN', YU. N., YARMOLYUK, YA. P. & GLADYSHEVSKII, E. I. (1979). Sov. Phys. Crystallogr. 24, 263–266.
GRIN', YU. N., YARMOLYUK, YA. P. & GLADYSHEVSKII, E. I. (1982). Sov. Phys. Crystallogr. 27, 413–417.
GROVER, A. K., COLES, B. R., SARKISSIAN, B. V. B. & STONE, H. E. N. (1982) J. Less-Common Met. 86, 29–36.
HOHNKE, D. & PARTHÉ, E. (1966). Acta Cryst. 20, 572–582.
HOVESTREYDT, E., KLEPP, K. & PARTHÉ, E. (1983). Acta Cryst. C39, 422–425.
HOVESTREYDT, E. & PARTHÉ, E. (1983). To be published.
KLEPP, K. & PARTHÉ, E. (1980). Acta Cryst. B36, 774–782.
KLEPP, K. & PARTHÉ, E. (1981). Acta Cryst. B37, 1500–1504.
KLEPP, K. & PARTHÉ, E. (1982). Acta Cryst. B38, 1105–1108.
KRIPYAKEVICH, P. I. (1977). Structure Types of Intermetallic Compounds (in Russian). Moscow: Nauka.

LE ROY, J., MOREAU, J. M., PACCARD, D. & PARTHÉ, E. (1977). *Acta Cryst.* B33, 2414–2417.

MIS'KIV, M. G. (1973). Thesis, Ivano Franko Univ., Lvov, USSR.

MIS'KIV, M. G. (1974). *Visn. L'viv. Derzh. Univ. Ser. Khim.* 15, 17–21.

MOREAU, J.-M., PACCARD, D. & PARTHÉ, E. (1974). *Acta Cryst.* B30, 2583–2586.

MOREAU, J.-M., PARTHÉ, E. & PACCARD, D. (1975). *Acta Cryst.* B31, 747–749.

PARTHÉ, E. (1981). *Structure and Bonding in Crystals*, edited by M. O'KEEFFE & A. NAVROTSKY, Vol. II, ch. 25, pp. 256–296. New York: Academic Press.

PARTHÉ, E. & CHABOT, B. (1983). In *Handbook on Physics and Chemistry of Rare Earths*, Vol. 6, edited by K. A. GSCHNEIDNER JR & L. EYRING. Amsterdam: North-Holland. In the press.

PARTHÉ, E., CHABOT, B., BRAUN, H. F. & ENGEL, N. (1983). *Acta Cryst.* B39, 588–595.

PARTHÉ, E. & MOREAU, J. M. (1977). *J. Less-Common Met.* 5? 1–24.

Coordination Polyhedra and Structures of Alloys: Binary Alloys of Niobium (and Tantalum) with Group IIIb and IVb Elements

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Abstract

Nb and Ta are found to exhibit a range of coordination numbers (CN) from 10 to 17 in their alloys with Group IIIb and IVb elements. The IIIb and IVb elements in these binary alloys have a CN ranging from 6 to 14. The polyhedra around Nb, Ta, IIIb and IVb elements have been characterized and a description of the polyhedra in terms of certain symbols is suggested. The structures of the binary alloys considered have been described in terms of polyhedra packing. *Most of the structures examined so far could be built up with one or two polyhedra*, only in a few cases are more than two polyhedra required.

Introduction

A fruitful approach to understanding the crystal-chemical features of alloy structures is to consider the coordination spheres around particular atoms. Frank & Kasper (1958, 1959) considered the coordination geometries around an atom as made up of only triangular faces and examined the topological and geometrical properties of the triangulated shells with CN's 12, 14, 15 and 16. The coordination characteristics of structural types with high coordination numbers have been studied by Kripyakevich (1960). He has also deduced the characteristics of the polyhedra with CN's 12 to 17, 20, 22, 24.

A glance through the literature on the crystal structures of alloys shows that very few papers (Brown, 1957, 1959; Girgis, Petter & Pupp, 1975) deal with the coordination polyhedra as building blocks of the structure. Such a description of structures, even though not supported by any specific theory of the structures, arises from observations of their peculiarities and the most general inferences that can be drawn from them (Black, 1956). *An approach to characterize the polyhedra in various known binary alloys and use them to build up the structures* has been introduced by Bhandary & Girgis (1977b). Their aim was to present a simple description of the complex alloy structures and to classify the known structure types. The aim of this study is to verify the general applicability of this model for binary intermetallic compounds. We examined for this purpose the alloys of Nb (Ta) with Group IIIb and IVb elements.

Coordination polyhedra

In order to define a coordination polyhedron it is essential to limit the coordination sphere of an atom. Brunner (1977) proposed the '$1/d$ method'. The normalized $1/d_n$, where d_n is the interatomic distance between the central atom and the nth neighbour, *versus* the number of atoms, are represented in a histogram. The widest range in which no atoms are present is called the 'max. gap'. The number of neighbours before the 'max. gap' is taken to be the coordination number (CN). The atoms (neighbours) constitute the coordination polyhedron for the corresponding (central) atom.

Nb and Ta exhibit a range of CN's from 10 to 17 in these alloys; the CN of the b elements ranges from 6 to 14. The geometries of these coordinations (coordination polyhedra) have been characterized and are listed