Ternary BaAl$_4$-Type Derivative Structures

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Abstract

Ternary BaAl$_4$-type derivative structures are frequently found with rare-earth–transition-metal silicides and germanides with the rare-earth atoms occupying the Ba sites and the two other kinds of atoms distributed in ordered fashion on the Al sites. The possible ternary BaAl$_4$-type derivative structures with the same unit cell as BaAl$_4$ are investigated. If it is assumed that transition-metal–transition-metal contacts are to be excluded only seven hypothetical BaAl$_4$-type derivative structures are possible. Three of these are already known as ThCr$_2$Si$_2$, CaBe$_2$Ge$_2$ and BaNiSn$_3$ types. Segments of these three structures and of other BaAl$_4$-type derivative structures are found in various intergrowth structures. The BaAl$_4$-type derivative structures can be classified according to the type of coordination polyhedron around the transition metal, which can be a tetrahedron or a square pyramid. The tendency of the transition metal to have one or the other coordination polyhedron determines which BaAl$_4$-type derivative structure is formed and explains also the occurrence of the HfFe$_2$Si$_2$ and U$_2$Co$_3$Si$_5$ types – BaAl$_4$-type derivative structures with larger unit cells.

Introduction

The tetragonal BaAl$_4$ structure was originally determined by Andress & Alberti (1935). It was thirty years later that the first ternary BaAl$_4$-type derivative structure was reported for ThCr$_2$Si$_2$ by Ban & Sikirica (1965) and independently for CaAl$_2$Ga$_2$ by Zarechnyuk, Kripyakevich & Gladyshevskii (1965), with more than 250 ternary metallic compounds now being known as isotypic. In the seventies two new

ternary BaAl$_4$-type derivative structures were discovered: the CaBe$_2$Ge$_2$ type (Eisenmann, May, Müller & Schäfer, 1972) and the BaNiSn$_3$ type (Dörrscheidt & Schäfer, 1978). In the course of recent crystallographic studies on rare-earth–transition-metal silicides and related compounds, new ternary phases with powder diffraction diagrams similar to the BaAl$_4$ type were found; the structures of these, however, have not yet been solved. It appeared of interest to derive possible metallic BaAl$_4$-type derivative structures in a systematic manner.*

Description of the BaAl$_4$ structure

A projection of the BaAl$_4$ structure [$I4/mmm$, $Z = 2$, Ba in 2(a), Al in 4(d), Al in 4(e) with $z \sim \frac{3}{8}$] is shown in the bottom right-hand drawing in Fig. 1. The Ba atoms are at the centre of an almost regular 16-atom coordination polyhedron. The Al atoms occupy two kinds of sites which are indicated as t and p in the drawing. All atoms on the tetrahedral (t) sites are surrounded by a tetrahedron of Al atoms and all atoms on the pyramidal (p) sites by five Al atoms in the form of a square pyramid.† In particular, all Al atoms

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* The structure of Nd$_2$O$_2$Te (Raccah, Longo & Eick, 1967) can also be considered, in a larger sense, a BaAl$_4$-type derivative structure, where the Te atom occupies the Ba site and where the Nd and O atoms are arranged in ordered fashion on the Al sites. However, this 'anti-type' structure found with oxide–tellurides, nitride–bismuthides and related ionic compounds will not be discussed further in this paper.

† Considering not only Al but also Ba neighbours, and ignoring the apex of the Al pyramid, the pyramidal sites have also been denoted as antiprismatic sites (Rieger & Parthé, 1969). However, for the ordering discussion only the homonuclear coordination is of interest.

surrounding a t site are on p sites and of the five atoms surrounding a p site, four are on a t site and one is on a p site (apex). Drawings of these coordination polyhedra can be found elsewhere (Braun, Engel & Parthé, 1983). The crystal-chemical formula (Parthé, 1980), of BaAl$_4$ considering only the homonuclear coordination, can be written as

$$BaAl_2^{[+4t]} Al_2^{[+5p]}$$
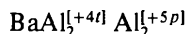
if $5p$ in the square bracket indicates a square pyramid.

Tetragonal BaAl₄-type derivative structures with the same unit cell as BaAl₄

Most of the experimentally known ternary BaAl$_4$-type derivative structures have been found with rare-earth, yttrium, scandium (R) – transition-metal (T) – borides, silicides, phosphides and homologues (M) (see for example Parthé & Chabot, 1983). The R atoms are positioned on the two Ba sites and the T and M atoms are assumed to be arranged in ordered fashion on the eight Al sites (two times two with tetrahedral and four with square-pyramidal coordination) of the BaAl$_4$ structure-type cell.

Considering the possible combinations of distributing the T and M atoms on the eight Al sites, 22 different hypothetical ternary structures can be derived from the BaAl$_4$ type with compositions $RT_{2-x}M_{2+x}$ where $x = 0$, $\pm\frac{1}{2}$, ± 1 and $\pm\frac{3}{2}$.* However, not all of these hypothetical structures are of interest. A study of all experimentally known BaAl$_4$-type derivative structures and of intergrowth structures with BaAl$_4$-type derivative segments in R–T–M systems shows that T–T contacts are excluded. Consequently, from the list of 22 hypothetical structures only those need to be retained where there are no T–T contacts. It is thus necessary to study the Al–Al contacts in the BaAl$_4$ type and to single out those pairs of Al sites which cannot both be occupied by T atoms. The interatomic distances certainly vary with the c/a ratio and the adjustable atom coordinates; however, there are generally two kinds of close Al distances:

(a) Each t-site atom has four neighbouring p-site atoms and vice versa. In the known compounds the distance between these sites corresponds approximately to the sum of the atomic radii of the atoms.

(b) Each p-site atom has one p-site neighbour in the [001] direction forming the apex of the surrounding square pyramid. This distance is also close to the sum of the atomic radii.

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* It is assumed here that the derivative structure is tetragonal and consequently the two symmetry-equivalent tetrahedral sites at $z = \frac{1}{4}$ are occupied by one kind of atom only. The same applies for the two tetrahedral sites at $z = \frac{3}{4}$. For the further discussion it is important to know that atoms on tetrahedral sites do not touch each other.

In BaAl$_4$ with $a = 4\cdot566$, $c = 11\cdot250$ Å and $z_{Al} = 0\cdot38$ the shortest distance between Al atoms on t and p sites is $2\cdot74$ Å, and between p and p sites $2\cdot70$ Å. All other Al–Al distances are longer by 18% or more.
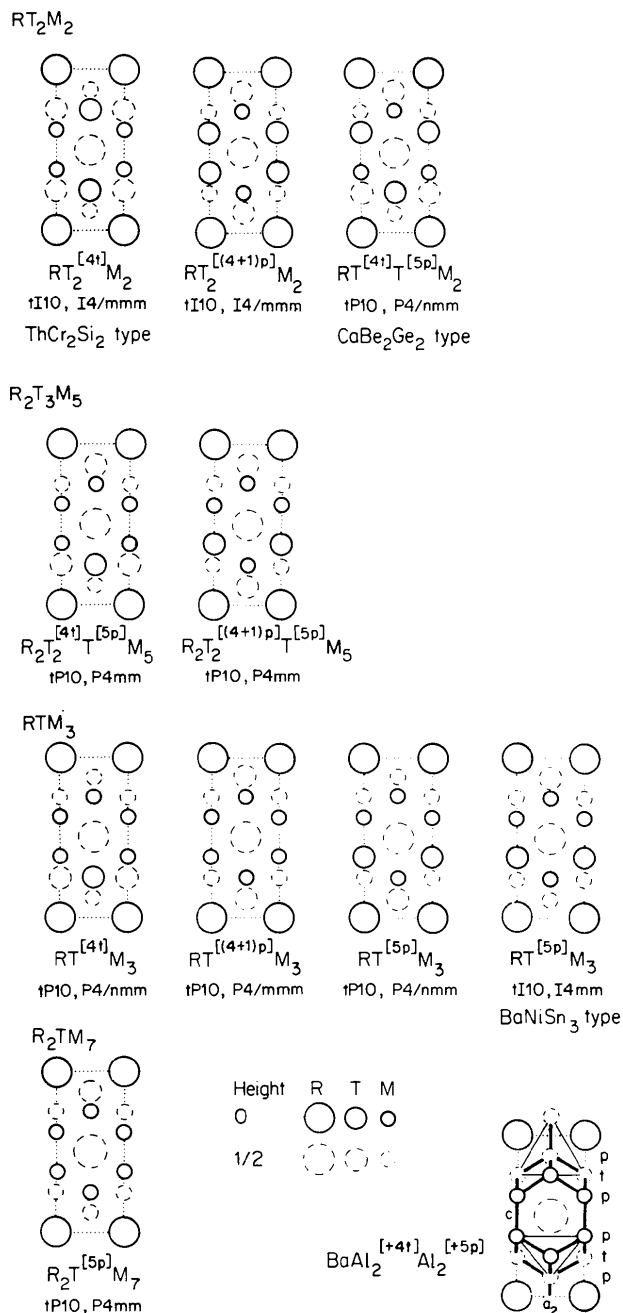

Fig. 1. The ten possible ordered ternary BaAl$_4$ derivative structures with tetragonal symmetry and the same unit cell as BaAl$_4$ having compositions RT_2M_2, $R_2T_3M_5$, RTM_3, and R_2TM_7 (projection along [100]). Only those structures are considered where neighbouring tetrahedral and pyramidal sites are not both occupied by T atoms. In the BaAl$_4$ structure shown at the bottom right the contours of one surrounding tetrahedron and one surrounding square pyramid are outlined with thin lines. Heavy lines indicate the two kinds of short Al–Al distances.

We shall first consider case (*a*) for our further discussion of hypothetical BaAl₄-type derivative structures, *i.e.* omitting structures where neighbouring *p* and *t* sites are both occupied by *T* atoms. There remain then only 10 possibilities for ordered structures, shown in Fig. 1, which have compositions $RT_{2-x}M_{2+x}$ where *x* is now only positive, that is $x = 0, \frac{1}{2}, 1$ and $\frac{3}{2}$. In Fig. 1 the structures are ordered with the *M* content increasing from top to bottom and each structure is characterized by a crystal-chemical formula, the coordination exponent inside the square brackets applying only to the *M* and *T* surroundings of the *T* atoms. On the left are shown the structures with the maximum possible number of *T* atoms in tetrahedral sites, on the right

those with the maximum number of *T* atoms in pyramidal sites. If the *T* coordination exponent is (4 + 1)*p*, the *T* element has four *M* neighbours and one close *T* neighbour (case *b*). Although these structures are not expected to be observed, they have been included in Fig. 1 only because slabs of some of them, cut in such a way that *T–T* contacts are avoided, have been found in intergrowth structures. If these structures with *T–T* contacts on neighbouring *p* sites are omitted only seven hypothetical ternary BaAl₄-type derivative structures remain, of which three have already been found experimentally.

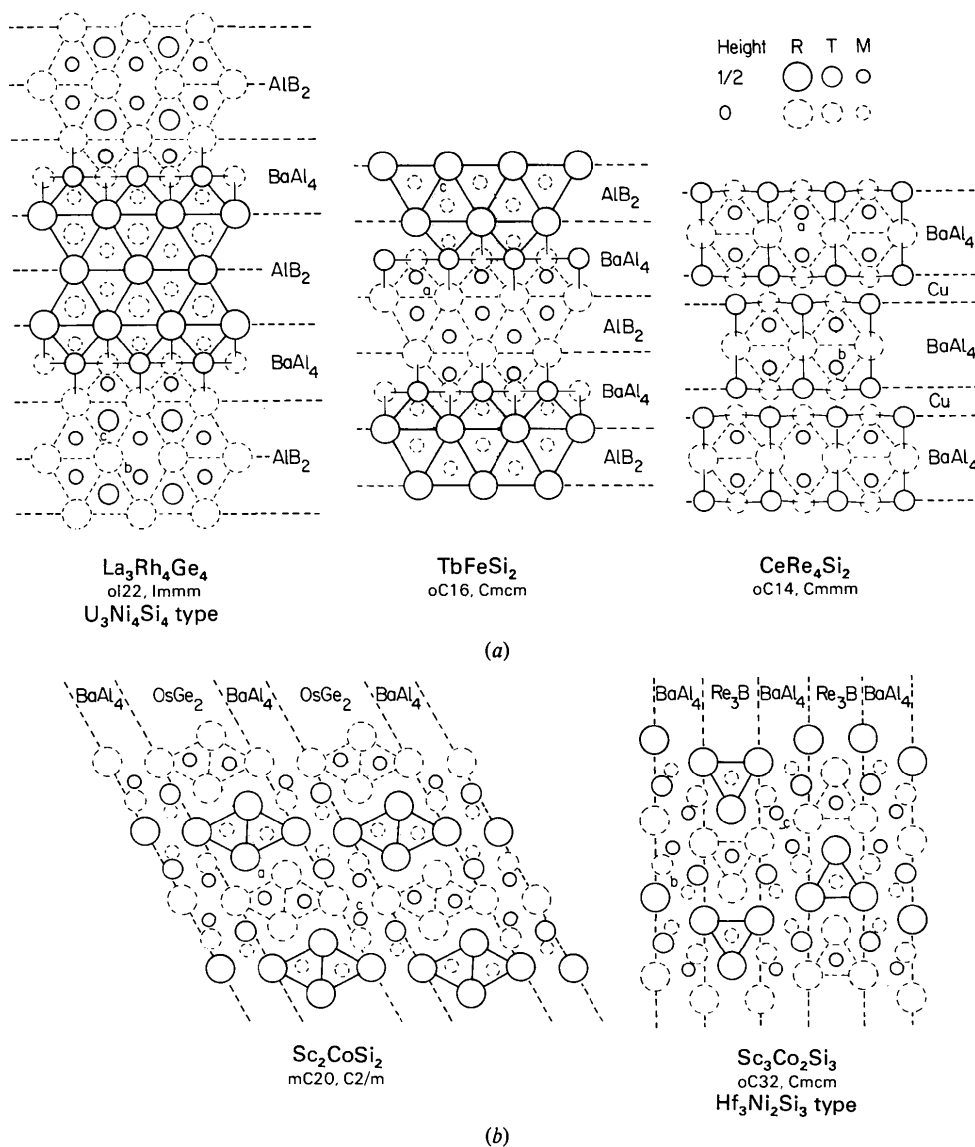The 10 structures shown in Fig. 1 will now be discussed in more detail.

Fig. 2. (*a*) Three intergrowth structures with ternary BaAl₄-type derivative slabs, cut parallel to (001), having an atom ordering as in the ThCr₂Si₂ type. (*b*) Two intergrowth structures with BaAl₄-type derivative slabs, cut parallel to (011), having an atom ordering as in the ThCr₂Si₂ type.

RT₂M₂ compounds: two probable structures and one with T–T contacts

$RT_2^{[4t]}M_2$, *I4/mmm*: this atom arrangement is known as the $ThCr_2Si_2$ type (Ban & Sikirica, 1965). This structure type is widely distributed for RT_2M_2 compounds. According to a recent survey (Parthé & Chabot, 1983) some 200 rare-earth–transition-metal borides, gallides, silicides, and germanides are known.

Slabs of the $ThCr_2Si_2$ structure cut parallel to (001) and with a thickness corresponding to half the height of one unit cell ($\frac{1}{2}c$) are also found in various structures which can be interpreted as an intergrowth of different structure slabs. $ThCr_2Si_2$-type slabs are found for example in $La_3Rh_4Ge_4$ (Hovestreydt, Klepp & Parthé, 1982) with $U_3Ni_4Si_4$ type, $TbFeSi_2$ (Yarovets & Gorelenko, 1981) crystallizing with a site-exchange variant of the $CeNiSi_2$ type and in $CeRe_4Si_2$ (Bodak, Gladyshevskii & Pecharskii, 1977). These three structures are presented in Fig. 2(a). One should note that, if the slabs cut parallel to (001) have a thickness smaller than the *c* translation period, there might be different ways to label the ternary atom arrangement. For example, the $ThCr_2Si_2$-type slabs with a thickness of $\frac{1}{2}c$ found in $La_3Rh_4Ge_4$ and $TbFeSi_2$ (but not those in $CeRe_4Si_2$) can also be cut from the lower half of the $CaBe_2Ge_2$ type. The absence of *T–T* contacts applies only to the segments with $BaAl_4$-type derivative structure. In the other intergrown segments other ordering principles may exist which could permit *T–T* contacts as can be seen for example in the Cu-type slab in $CeRe_4Si_2$.

In Fig. 2(b) two intergrowth structures are shown where deformed $ThCr_2Si_2$-type slabs have been cut parallel to the (011) plane of the $ThCr_2Si_2$ cell. For Sc_2CoSi_2 (Gladyshevskii & Kotur, 1978) the drawing has been oriented such that the atom positions of the $ThCr_2Si_2$-type slabs may be compared directly with those of the $ThCr_2Si_2$ structure, given in Fig. 1. In $Sc_3Co_2Si_3$ (Gladyshevskii & Kotur, 1978) with $Hf_3Ni_2Si_3$ type, successive $ThCr_2Si_2$-type slabs (separated by Re_3B-type slabs and stacked along [001]) are rotated both with respect to each other and with respect to Fig. 1.

$RT_2^{[(4+1)p]}M_2$, *I4/mmm*: this structure is a site-exchange variant of the $ThCr_2Si_2$ type. In this case, the *T* atoms occupy neighbouring *p* sites; this means there are *T–T* contacts in the [001] direction. No examples have been reported in the literature.

Slabs of the site-exchange variant of the $ThCr_2Si_2$ type with a thickness corresponding to half a *c* translation period ($\frac{1}{2}c$), are found in the intergrowth structure of $CeNiSi_2$ (Bodak & Gladyshevskii, 1970a). This structure type is also occasionally called the $BaCuSn_2$ type (May & Schäfer, 1974). Slabs with a thickness of $\frac{1}{4}c$ occur in the intergrowth structure of $La_3Co_2Sn_7$ (Dörrscheidt & Schäfer, 1980a). In both intergrowth structures, which are presented in Fig. 3, no short *T–T* distances are found.

$RT^{[4t]}T^{[5p]}M_2$, *P4/nmm*: this $BaAl_4$-type derivative was first reported for $CaBe_2Ge_2$ (Eisenmann, May, Müller & Schäfer, 1972) and also occurs in the high-temperature modification of $LaIr_2Si_2$ (Braun, Engel & Parthé, 1983). The structure can be interpreted as being built up by a periodic intergrowth of
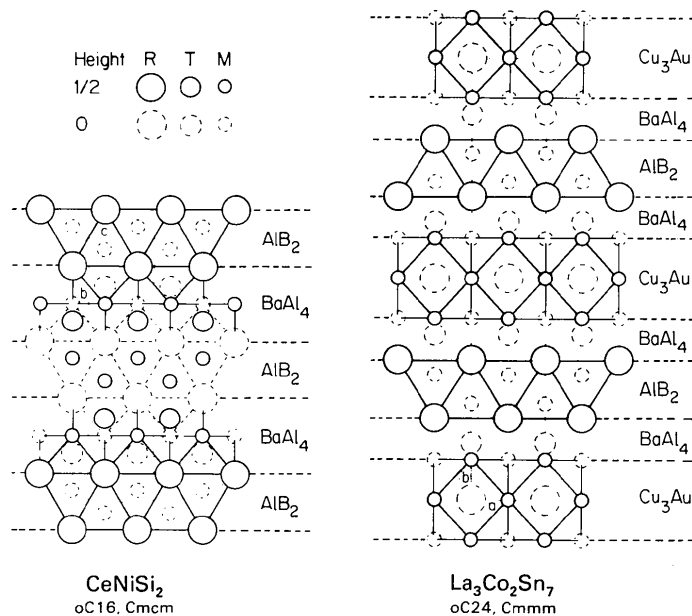

CeNiSi₂
oC16, Cmcm

La₃Co₂Sn₇
oC24, Cmmm

Fig. 3. $CeNiSi_2$ and $La_3Co_2Sn_7$: two intergrowth structures where the slabs denoted $BaAl_4$ are actually built up as in the site-exchange variant of the $ThCr_2Si_2$ type.

ThCr$_2$Si$_2$-type slabs ($\frac{1}{2}c$) and slabs corresponding to its site-exchange variant ($\frac{1}{2}c$). There are no short T–T distances in the [001] direction.

It should be stated that in some previous experimental studies on RT_2M_2 compounds the atom arrangement corresponding to the ThCr$_2$Si$_2$ structure type was assumed *a priori* without any tests for its site-exchange variant or the CaBe$_2$Ge$_2$ type. It might be worthwhile to reinvestigate whether certain of the supposedly ThCr$_2$Si$_2$-type compounds perhaps crystallize with the CaBe$_2$Ge$_2$ type. Here can be mentioned, for example, the RPt$_2$Si$_2$ phases, for which the space group $I4/mmm$ was first given (Mayer & Yetor, 1977), but later studies (Ballestracci & Astier, 1978) revealed a *primitive* tetragonal lattice.

Slabs of the CaBe$_2$Ge$_2$ type can also be found in intergrowth structures, as for example in ScNi$_2$Si$_3$ (Kotur, Bodak & Gladyshevskii, 1978), presented in Fig. 4.

$R_2T_3M_5$ compounds: one probable structure and one with T–T contacts

$R_2T_2^{[4t]}T^{[5p]}M_5$, $P4mm$: there are no T–T contacts in this structure; it has, however, not yet been reported in the literature. Instead, $R_2T_3M_5$ compounds with an orthorhombic BaAl$_4$-type derivative structure are known, with a unit-cell volume four times larger than that of BaAl$_4$, which will be discussed below.

$R_2T_2^{[(4+1)p]}T^{[5p]}M_5$, $P4mm$: this second structure with composition $R_2T_3M_5$ has a T–T contact in the [001] direction. No examples are known.

RTM_3 compounds: three probable structures and one with T–T contacts

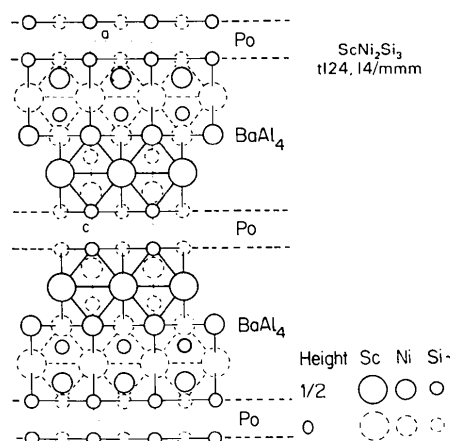$RT^{[4t]}M_3$, $P4/nmm$: there are no T–T contacts, but no example is known.

$RT^{[(4+1)p]}M_3$, $P4/mmm$: there are T–T contacts in this structure. No examples are known. However, slabs with the thickness of one c translation are found in the intergrowth structure of Ce$_3$Ni$_2$Si$_8$ (Stepien, Lukaszewicz, Gladyshevskii & Bodak, 1972), presented in Fig. 5. We note that no short T–T distances occur in this intergrowth structure.

$RT^{[5p]}M_3$, $P4/nmm$: no T–T contacts, but again no examples are known.

$RT^{[5p]}M_3$, $I4mm$: this is the second structure with the same crystal-chemical formula; however, there is a larger separation between the T atoms. This atom arrangement is known as BaNiSn$_3$ type (Dörrscheidt & Schäfer, 1978). It is found, for example, with LaIrSi$_3$ (Engel, Braun & Parthé, 1983).

RTSi$_3$ compounds with BaAl$_4$-type derivative structure have been reported for CeCoSi$_3$ (Bodak & Gladyshevskii, 1970b) and EuNiSi$_3$ (Mayer & Felner, 1977); however, without further information it is impossible to assign their structures to this type or any other RTM_3 type.

R_2TM_7 compounds: only one probable structure

$R_2T^{[5p]}M_7$, $P4mm$: no example for an ordered structure is known as yet. But here should be mentioned the rare-earth nickel gallides studied by Grin' (1982) with homogeneity ranges which in most cases include the compositions RTM_3 and R_2TM_7. He assumes that Ga atoms occupy the tetrahedral sites and a mixture of Ni and Ga atoms all pyramidal sites. The space group was
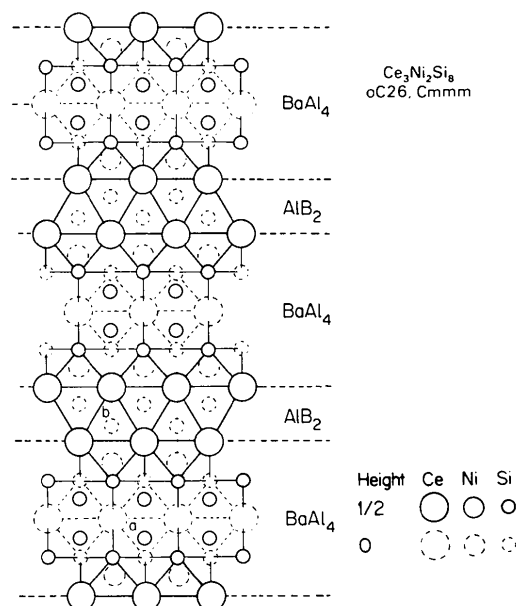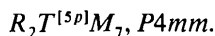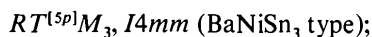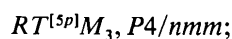

Fig. 4. ScNi$_2$Si$_3$: an intergrowth structure where the slab denoted BaAl$_4$ is built up as in the CaBe$_2$Ge$_2$ type.
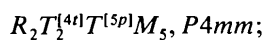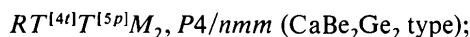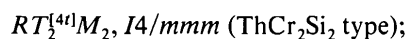

Fig. 5. Ce$_3$Ni$_2$Si$_8$: an intergrowth structure. The slab denoted BaAl$_4$ is cut from the $RT^{[(4+1)p]}M_3$ structure (shown in Fig. 1) in such a way that no short T–T distances occur.

given as $I4/mmm$ and the diffraction pattern was said to correspond to the $ThCr_2Si_2$ type or its site-exchange variant. Since the other experimental evidence indicates that neighbouring pyramidal sites are never both occupied by T elements, these nickel gallides need to be reinvestigated. However, since Ni and Ga only differ by three electrons it will be difficult to determine the atomic ordering.

In summary, the seven probable tetragonal $BaAl_4$-type derivative structures without T–T contacts and with unit cells as for $BaAl_4$ are:

$RT_2^{[4t]}M_2$, $I4/mmm$ ($ThCr_2Si_2$ type);

$RT^{[4t]}T^{[5p]}M_2$, $P4/nmm$ ($CaBe_2Ge_2$ type);

$R_2T_2^{[4t]}T^{[5p]}M_5$, $P4mm$;

$RT^{[4t]}M_3$, $P4/nmm$;

$RT^{[5p]}M_3$, $P4/nmm$;

$RT^{[5p]}M_3$, $I4mm$ ($BaNiSn_3$ type);

$R_2T^{[5p]}M_7$, $P4mm$.
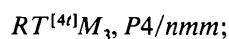
Discussion

The seven probable tetragonal $BaAl_4$-type derivative structures have been derived from the theoretically possible ordering variants of the $BaAl_4$ type by omitting all those with T–T contacts. The absence of T–T contacts is also characteristic of intergrowth structures where slabs occur with atom arrangements as in $BaAl_4$-type derivative structures. It can be mentioned that the absence of T–T contacts has also been a guide-line for the interpretation of the atom ordering in ternary rare-earth structures built up of centred trigonal prisms (Parthé, Chabot & Hovestreydt, 1983).

For composition RT_2M_2 two possible structures are found for which the T coordination differs: in the $ThCr_2Si_2$ type all T are on tetrahedral sites, whereas in the $CaBe_2Ge_2$ type half of the T are on pyramidal sites. The tendency of the T atoms to prefer tetrahedral or pyramidal sites cannot be predicted as yet. It may change with temperature or with the nature of the M atoms. For example, $LaIr_2Si_2$ has a low-temperature modification with $ThCr_2Si_2$ type, but a high-temperature modification with $CaBe_2Ge_2$ type (Braun, Engel & Parthé, 1983). According to Hofmann & Jeitschko (1983) the rare-earth–nickel (palladium) pnictides have the $ThCr_2Si_2$ type if $M = P$, As, but the $CaBe_2Ge_2$ type if $M = Sb$, Bi.

For composition RT_2M_2 and with a tetragonal unit cell as in $BaAl_4$, it is impossible to find an atom arrangement where all T atoms are on pyramidal sites and where there are no T–T contacts. There exists, however, the orthorhombic $HfFe_2Si_2$ type (Yarmolyuk, Lysenko & Gladyshevskii, 1976) with 20 atoms per

unit cell and found, for example, with $ScFe_2Si_2$ (Gladyshevskii, Kotur, Bodak & Skvorchuk, 1977) where also the second half of the T atoms has a (deformed) pyramidal coordination of M atoms. The $HfFe_2Si_2$ type and the $CaBe_2Ge_2$ type (now projected along [110]) are presented in Fig. 6. As compared to the $CaBe_2Ge_2$ type all atoms are displaced in the $HfFe_2Si_2$ type – in particular, the T atoms originally at $z = \frac{1}{4}$. Instead of a tetrahedral M coordination in the $CaBe_2Ge_2$ type the T atoms now have a distorted pyramidal coordination with the ideally square-planar base of the pyramid now considerably deformed. The occurrence of the $HfFe_2Si_2$ type seems thus to be related to the strong tendency of *all* T atoms to have a pyramidal coordination of M atoms.

To complete the series of possible $BaAl_4$-type derivative structures for composition RT_2M_2 three more structure types have to be mentioned which have not yet been found with RT_2M_2 compounds.

The orthorhombic $BaNi_2Si_2$ type (Dörrscheidt & Schäfer, 1980b) with $a \simeq b = \sqrt{2}a_{BaAl_4}$, $c = c_{BaAl_4}$ is a deformation variant of the $ThCr_2Si_2$ type. In Fig. 7 both structure types are presented, the $ThCr_2Si_2$ in a projection along [110]. In $BaNi_2Si_2$ the transition element is at the centre of a Si tetrahedron as in $ThCr_2Si_2$ but the tetrahedron is now deformed. The Si atom on the former pyramidal site has no contact with the Si atom forming, in $ThCr_2Si_2$, the apex of a surrounding pyramid.
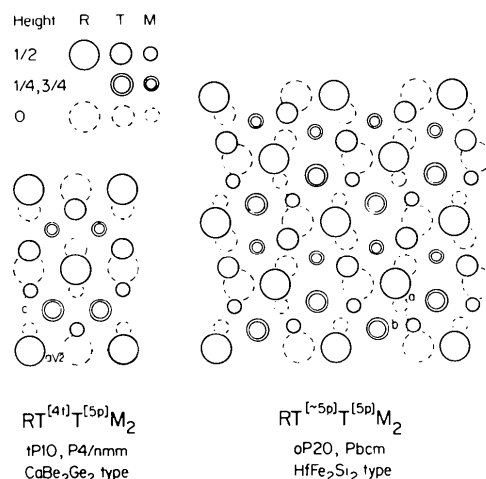

Height   R   T   M

1/2

1/4,3/4

0

$RT^{[4t]}T^{[5p]}M_2$
tP10, P4/nmm
$CaBe_2Ge_2$ type

$RT^{[\sim5p]}T^{[5p]}M_2$
oP20, Pbcm
$HfFe_2Si_2$ type

Fig. 6. The $CaBe_2Ge_2$ type, projected along [110], compared with the $HfFe_2Si_2$ type. In the $CaBe_2Ge_2$ type the T atoms in the lower half of the unit cell have tetrahedral M coordination, while those in the upper half of the unit cell are surrounded by a square pyramid of M atoms. In the $HfFe_2Si_2$ type, however, all T atoms have a pyramidal coordination. For half of the T atoms the pyramid is quite regular (those with $\frac{1}{4} < x < \frac{3}{4}$), but it is strongly deformed for the other half.

The second type is the tetragonal BaMg$_2$Sn$_2$ type (Eisenmann & Schäfer, 1974) with $a = a_{BaAl_4}$ and $c = 2c_{BaAl_4}$. This structure, shown in Fig. 8, can be considered as halfway between the ThCr$_2$Si$_2$ and CaBe$_2$Ge$_2$ types. It can be constructed from two ordered BaAl$_4$-type cells, stacked one on top of the other, one built as ThCr$_2$Si$_2$ and the second as CaBe$_2$Ge$_2$.*

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* By analogy with the above-mentioned structure change of rare-earth–transition-metal pnictides, the BaMg$_2$M$_2$ compounds with M = Si, Ge, Sn and Pb systematically change their structure with a change of the period of the main-group element. BaMg$_2$Si$_2$, BaMg$_2$Ge$_2$ crystallize with ThCr$_2$Si$_2$ type, and BaMg$_2$Pb$_2$ with CaBe$_2$Ge$_2$ type (Eisenmann & Schäfer, 1974).
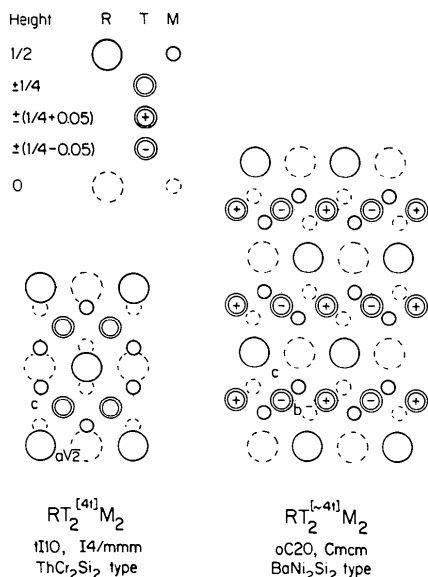
Fig. 7. The tetragonal ThCr$_2$Si$_2$ type (projected along [110]) compared with the orthorhombic BaNi$_2$Si$_2$ type, a deformation variant.
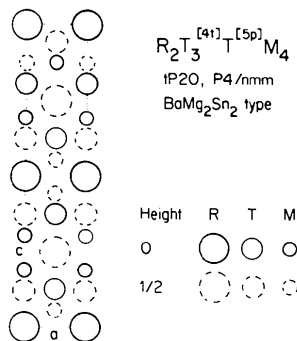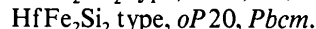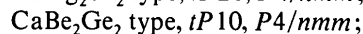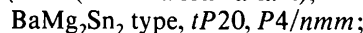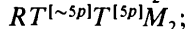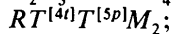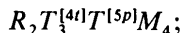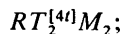

Fig. 8. The BaMg$_2$Sn$_2$ type, a possible RT_2M_2 structure type constructed of ThCr$_2$Si$_2$- and CaBe$_2$Ge$_2$-type cells stacked on top of each other. To allow a better comparison with the ThCr$_2$Si$_2$- and CaBe$_2$Ge$_2$-type cells shown in Fig. 1, the origin of the BaMg$_2$Sn$_2$-type cell has been shifted by 00$\frac{1}{8}$.

According to Pecharskii, Pankevitch & Bodak (1982) the compound CeNi$_{2.35}$Sb$_{1.65}$ supposedly crystallizes with an orthorhombic deformation variant of the BaAl$_4$ type (*Immm*, $a \simeq b = a_{BaAl_4}$, $c = c_{BaAl_4}$). Since the Ni and Sb atoms assume no ordered arrangement on the Al sites this structure will not be discussed further.

Thus, five ordered BaAl$_4$ derivative structure types are possible for RT_2M_2 compounds; these are listed below in the order of increasing percentage of T atoms with pyramidal coordination:

$RT_2^{[4t]}M_2$;	ThCr$_2$Si$_2$ type, $tI10, I4/mmm$;
	BaNi$_2$Si$_2$ type, $oC20, Cmcm$
	(deformation variant);
$R_2T_3^{[4t]}T^{[5p]}M_4$;	BaMg$_2$Sn$_2$ type, $tP20, P4/nmm$;
$RT^{[4t]}T^{[5p]}M_2$;	CaBe$_2$Ge$_2$ type, $tP10, P4/nmm$;
$RT^{[\sim 5p]}T^{[5p]}M_2$;	HfFe$_2$Si$_2$ type, $oP20, Pbcm$.
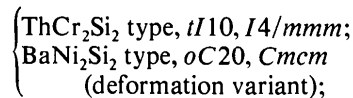
For composition $R_2T_3M_5$ only one ordered structure is probable with a unit cell as in BaAl$_4$. In this case two T atoms are on tetrahedral sites and one T is on a pyramidal site. It is possible, however, to construct a BaAl$_4$-type derivative structure with a larger orthorhombic cell with two T atoms on pyramidal sites and one T atom only on a tetrahedral site. This structure is known as U$_2$Co$_3$Si$_5$ type (Akselrud, Yarmolyuk & Gladyshevskii, 1977) and has been found with Sc$_2$Co$_3$Si$_5$ (Kotur & Bodak, 1980) and R_2Rh$_3$Si$_5$ compounds (Chevalier, Lejay, Etourneau, Vlasse & Hagenmuller, 1982). It is shown in Fig. 9 together with
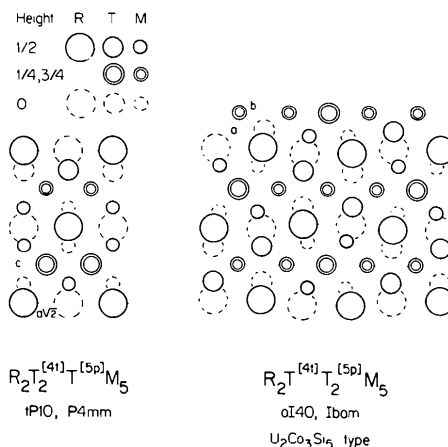

Fig. 9. Two BaAl$_4$-type derivative structures with composition $R_2T_3M_5$: the tetragonal structure of Fig. 1 without T–T contacts (now projected along [110]) and the orthorhombic U$_2$Co$_3$Si$_5$-type structure. The T atoms in the lower half of the tetragonal structure have a tetrahedral surrounding of M atoms; however, those in the upper half have a square pyramidal coordination. In the orthorhombic structure only the T atoms at $\pm(\frac{1}{4}0\frac{1}{4})$ and $\pm(0\frac{1}{4}\frac{1}{4})$ have a tetrahedral coordination; all eight other T atoms/unit cell are surrounded by a square pyramid of M atoms. In the U$_2$Co$_3$Si$_5$ type some of the Si atoms are slightly displaced from the ideal position. They approach more closely the Co atoms on the tetrahedral sites.

the $R_2T_2^{[4t]}T^{[5p]}M_5$, $P4mm$ structure of Fig. 1 (now projected along [110]). The orthorhombic cell with $a = c_{BaAl_4}$, $b = 2\sqrt{2}a_{BaAl_4}$, $c = \sqrt{2}a_{BaAl_4}$ has a volume four times larger than the BaAl$_4$ cell. The reason for the formation of this orthorhombic structure with this composition is obviously the tendency of the T atoms to have a pyramidal coordination. This is better satisfied with the larger orthorhombic structure as compared to the structure with the smaller tetragonal cell.

For composition RTM_3 one structure is possible with T atoms in tetrahedral coordination and two structures with T atoms in pyramidal coordination. In the latter case, the BaNiSn$_3$ type should be preferred if the T atoms tend to be as far apart as possible.

For composition R_2TM_7 only one structure is possible with T atoms in pyramidal coordination.

Further experimental studies are necessary to verify the existence of the different BaAl$_4$-type derivative structures and to clarify the conditions for their occurrence.

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