

The Most Populous of All Crystal Structure Types—the Tetragonal $BaAl_4$ Structure

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The $BaAl_4$ ($ThCr_2Si_2$) $I10$ structure, MN_2X_2 , is not only the most populous of all known structure types, being adopted by some 400 phases, but is representative of a new group of metallurgically important structures that do not adhere to classifications of Cu-type close packings or tetrahedral close packings. The structure can be described by a square pyramidal framework of N and X atoms which by edge-sharing from slabs in (001) planes, the slabs being interconnected by $X-X$ bonds along [001] (in perhaps 10% of the phases no [001] $X-X$ bonds exist). This framework creates tetragonal hexagonal prismatic voids, that enclose the large M atoms. The average observed $N-X$ and [001] $X-X$ distances are interpreted in a model that shows that the framework, which is responsible for structural stability, accounts for almost all of the valency electrons provided by N and X . The M atoms (diameters 3.1 to 5.1 Å) are accommodated in the voids of the framework according to the principles of geometrical packing, apparently without size restriction. In some cases $M-N$ or $M-X$ interactions are shown to control the variable a , c , and z_X structural parameters, but they only very modestly influence the $N-X$ distances of the framework. Some comparison with the Cu_2Sb $IP6$ structure is made. © 1985 Academic Press, Inc.

1. Introduction

(i) The $BaAl_4$ Structure

The $BaAl_4$ $I10$ structure type, MN_2X_2 (also variously referred to as the $ThCr_2Si_2$ and $CaAl_2Ga_2$ types), is the most populous of all known structures, there being some 400 phases attributed thereto (1). The structure is described in space group $I4/mmm$ with Ba (M) in $2(a)$ $0,0,0$; $Al(1)$ (N) in $4(d)$ $0, \frac{1}{2}, \frac{1}{2}$; and $Al(2)$ (X) in $4(e)$ $0,0,z$ with $z = 0.380$ (ideally $z = \frac{3}{8}$); $a = 4.566$, $c = 11.278$ Å. The three occupied site-sets lead to many ordered ternary phases with the structure.

The large M atoms are surrounded by a

dicapped tetragonal hexagonal prism of 18 N and X atoms (see Fig. 5 below) and there are four possible equatorial connections to other M atoms which cap the four hexagonal faces. The N atoms are surrounded by a tetrahedron of X atoms which is generally somewhat squashed in the [001] direction, and there also may be connections between N and M . The X atoms of the tetrahedra are always separated by distances greater than D_X , the diameter of the X atom. The X atoms are surrounded by a square pyramid of 4 N in (001) and one X atom along [001]. In addition there are generally also connections between X and M .

One method of determining convex coordination polyhedra of a structure is by the

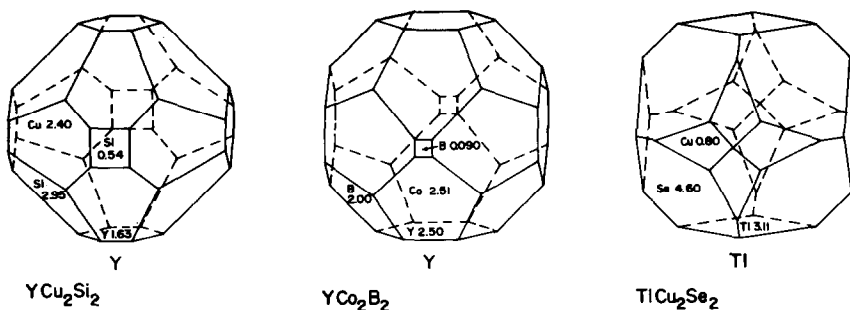


FIG. 1. Comparison of the *Wirkungsbereiche* about the *M* components for the YCu₂Si₂, YCo₂B₂, and TiCu₂Se₂ phases. Indicated on the various faces are the atom that the face separates from the central *M* atom, and the area of the face. The calculations were carried out by the *Potenzeben* construction of (3).

Dirichlet (2) construction of bisecting lines joining possible neighbors of an atom by planes normal to the line. The polyhedron enclosed by these planes (now called *Wirkungsbereich*) defines which atoms are neighbors and which are excluded (no planes in the polyhedron). For reference we show in Figs. 1 and 2 *Wirkungsbereich* about atoms in several phases with the BaAl₄ structure. Of particular interest are those surrounding the *M* atom (corresponding to the tetragonal hexagonal prism, Fig. 5, below), since this is a polyhedron now found in several structures, e.g., ThMn₁₂ *tI*26, Ga₆LaNi_{0.6} *tP*16, and Ce₅Mg₄₁ *tI*92. It

is also found in the Cu₂Sb *tP*6, La₂Sb *tI*12, and Ca₂Sb *tI*12 structures with axial ratio *c/a* or *c/2a* less than about 1.80, where it contains two atoms displaced + and - from its center along [001].

Some eight different variants of the structure can be defined depending on whether the most important interatomic distances (4 *M-M*, 8-4 *M-N*, 8-4 *M-X*, 4 *N-N*, 4-4 *N-X*, and 1 *X-X* along [001]) are longer or shorter than the appropriate radius sums, say, for CN12. However, we consider that only two of these lead to significant differences in structure: the major group of phases in which the [001] *X-X* distances, *d*_{*X-X*}, are less than the diameter of the *X* atom, *D*_{*X*} (*X-X* dumbbells), and those in which this distance is anything up to 2 Å or more, greater than *D*_{*X*}.

The variety of atoms that have been reported variously to occupy the three sites in the BaAl₂ structure is remarkable (Table I) and it portends reasons of stability and availability which do not depend *per se* on group, period, or valency electrons of the components, but rather on geometry.

The BaAl₄ structure, first determined by Andress and Albertini (4), has recently attracted attention. For example, Parthé *et al.* (5) have discussed structural aspects, particularly substitutional replacements, *M_xN_yX_z* and relationships to other struc-

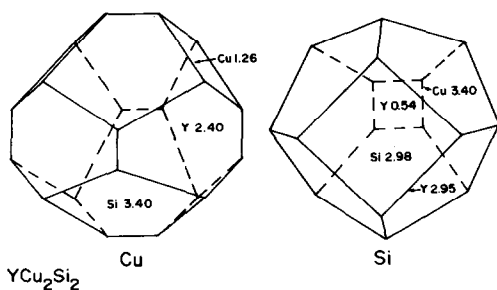


FIG. 2. *Wirkungsbereiche* about the *N* and *X* components for the YCu₂Si₂ phase. That about the *M* component is shown in Fig. 1. Indicated on the various faces are the atom that the face separates from the central Cu or Si atom and the area of the face. The calculations were carried out by the *Potenzeben* construction of (3).

TABLE I
TYPES OF ATOMS THAT OCCUPY THE *M*, *N*, AND *X* SITES OF THE BaAl₄ STRUCTURE

	<i>M</i> Site	<i>N</i> Site	<i>X</i> Site
	Alkali metals	Transition metals	Short-Period elements B, Al, Si, P, S
	Alkaline earths	Noble metals	B Group elements, Ge, Sn, Pb, Se, Te, etc.
	A and B Group metals, e.g., Sc, Y, Tl, Sb, Bi, Te	B Group metals, Zn, Cd, etc.	
	Rare earths	A Group metals, Mg, Al, Ga, In	Actinides
	Actinides	Nitrogen	
Range of <i>CN</i> ₁₂ diameters, Å	Transition metals 3.12–5.09	1.76–3.33	1.96–3.60

tural types. Such relationships can be derived formally as “splitted” variants from space group subrelations as indicated in Table II that shows tetragonal variants of the structure which also have 10 atoms per cell.

Kiseleva and Savitskii (6) have discussed predictions of phases with the BaAl₄ structure. Prediction criteria involve atomic and (apparently) phase properties operated on by computer. Contrary stability criteria so

TABLE II
THE *tI*₁₀ AND *tP*₁₀ “SPLITTED” DERIVATIVES OF THE BaAl₄ STRUCTURE

(i)	<i>I4/mmm</i> → <i>I4mm</i>	Examples
	2(<i>a</i>) 000 → 2(<i>a</i>) 00z (<i>z</i> = 0)	Ba La
	4(<i>d</i>) 0 1/2 1/4 → 4(<i>b</i>) 0 1/2 z (<i>z</i> ~ 1/4)	Sn Si
	4(<i>e</i>) 00z → 2(<i>a</i>) 00z (<i>z</i> ~ 0.42)	Sn Si
	4(<i>e</i>) 00z → 2(<i>a</i>) 00z (<i>z</i> ~ 0.66)	Ni Ir
(ii) and (iii)	<i>I4/mmm</i> → <i>P4/mmm</i> → <i>P4mm</i>	
	2(<i>a</i>) 000 → 1(<i>a</i>) 000 → 1(<i>a</i>) 00z	
	2(<i>a</i>) 000 → 1(<i>d</i>) 1/2 1/2 1/2 → 1(<i>b</i>) 1/2 1/2 z	
	4(<i>d</i>) 0 1/2 1/4 → 4(<i>i</i>) 0 1/2 z → 2(<i>c</i>) 1/2 0z	
	4(<i>d</i>) 0 1/2 1/4 → 4(<i>i</i>) 0 1/2 z → 2(<i>c</i>) 1/2 0z	
	4(<i>e</i>) 00z → 2(<i>g</i>) 00z → 1(<i>a</i>) 00z	
	4(<i>e</i>) 00z → 2(<i>g</i>) 00z → 1(<i>a</i>) 00z	
	4(<i>e</i>) 00z → 2(<i>h</i>) 1/2 1/2 z → 1(<i>b</i>) 1/2 1/2 z	
	4(<i>e</i>) 00z → 2(<i>h</i>) 1/2 1/2 z → 1(<i>b</i>) 1/2 1/2 z	
(iv)	<i>I4/mmm</i> → <i>P4/nmm</i>	Examples
	(origin at center 2/ <i>m</i>)	
	2(<i>a</i>) 000 → 2(<i>c</i>) 1/4 1/4 z (<i>z</i> ~ 3/4)	Ca La
	4(<i>d</i>) 0 1/2 1/4 → 2(<i>a</i>) 3/4 1/4 0	Be Ir
	4(<i>d</i>) 0 1/2 1/4 → 2(<i>b</i>) 3/4 1/4 1/2	Ge Si
	4(<i>e</i>) 00z → 2(<i>c</i>) 1/4 1/4 z (<i>z</i> ~ 3/8)	Be Ir
	4(<i>e</i>) 00z → 2(<i>c</i>) 1/4 1/4 z (<i>z</i> ~ 1/8)	Ge Si

obtained lead to the prediction that the phase concerned does not take the ThCr₂Si₂ structure. Results are shown for the silicon phases of alkaline earths, Y, Zr, Hf, rare earths, and actinides with transition metals, noble metals, and Zn. Most predictions are favorable and many of these are confirmed by observation. Nine unfavorable predictions can be counted, and there are a number of cases where no prediction is made, which we do not understand. Of the nine unfavorable predictions, the authors note three confounded by reports of the phase with the ThCr₂Si₂ structure, and to these we add another case. If violation of unfavorable predictions is to be the test of the method, then the present record is 4:9. Pearson and Villars (7) have discussed control of cell dimensions in 10 almost complete series of phases MN₂X₂, with *M* = rare earth, *N* = Mn, Fe, Co, Ni, or Cu, and *X* = Si or Ge, as further noted in Section 2(i).

(ii) *Sphere Packings and Framework Descriptions of the Structure*

The structures of metals and intermetallic phases generally result from satisfaction of sphere packings. The Cu-type close packings and tetrahedral close packings are two examples of sphere packings long recognized in important metallurgical structure types. The BaAl₄ structure and, e.g., the Cu₂Sb *tP6* and AsPd₃Tl *tP7* types are examples of several structures now recognized as metallurgically important since they are adopted by 100 or more phases. However, such structures do not adhere to the classifications of close-packed or tetrahedrally close-packed structures. They are examples of heterogeneous sphere packings (atoms occupying two or more Wyckoff sites and having different diameters (8)) about which very little is known on a systematic basis since the possibilities are boundless. In contrast all possible cases of homogeneous sphere packings (atoms on

one Wyckoff site only) have been defined by Fischer (9-12) for the cubic and tetragonal classes. The difficulty does not result from recognizing the heterogeneous sphere packings involved in these structures of intermetallic phases, but in demonstrating that the observed structure is more satisfactory for components of given sizes than some other structure, or indeed than the same structure with different axial ratios and values of variables atomic coordinates (see, e.g. (13)—phases with the MoSi₂ *tI6* structure).

TABLE III

THREE POSSIBLE FRAMEWORK DESCRIPTIONS OF THE BaAl₄ STRUCTURE, THE CELL BEING TAKEN IN AN *F* SETTING

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- (a) $t(1/2\ 0)\ 1/4\ 1/4\ [P_{22}[\cdot\ 4t_{4\times 4e}] + C]$
 (b) $b.\ .00\ 1/4\ P_{222}[5py_{4e}] + F$
 (c) $F[\cdot\ 18\ dctr_{4\times 6l}]$

Explanatory Notes

- (a) $t(1/2\ 0)$ specifies the translation between one slab of tetrahedra and those above and below along [001];
 $1/4\ 1/4$ specifies the origin of the lattice complex P_{22} ; P_{22} is the lattice complex which centers the tetrahedra of *X* atoms
 $4t$ indicates the tetrahedra of *X* atoms and indicates their centering by *N* atoms; $4e$ indicates their connectivity by sharing 4 edges
 C is the symbol for the *M* atoms
- (b) $b.\ .$ indicates the relationship between the slabs of pyramids (orientation symmetry)
 $00\ 1/4$ specifies the origin of the lattice complex P_{222} , about which the square pyramids of *N* and *X* are located
 $5py$ indicates the square pyramids of *N* and *X* atoms; $4e$ indicates their connectivity by sharing 4 edges
 F represents the *M* atoms
- (c) F specifies the lattice complex about which the dicapped tetragonal hexagonal prisms are centered
 $18\ dctr$ indicates the dicapped tetragonal hexagonal prisms of *N* and *X* atoms; \cdot indicates the centering of these polyhedra by *M* atoms
 $4 \times 6l$ indicates the face sharing of the four hexagons forming the tetragonal prism faces
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Framework descriptions of structures are basically an expression of sphere packings (8). Their derivation has its inception in the lattice complexes of the individual atomic sites of the structure. The lattice complex symbols for the atoms on the $2(a)$, $4(d)$, and $4(e)$ sites of the $BaAl_4$ structure are, respectively, F , P'_2 , and F'_{2z} (14), which indicate that it is derived from the cubic Heusler alloy structure, $AlCu_2Mn$ $cF16$ (F , P'_2 , F') in which the Mn atoms are replaced by a dumbbell of $X-X$ atoms along $[001]$. However, this formal relationship has little significance in relation to the framework descriptions that can be derived for the $BaAl_4$ structure. The three obvious framework descriptions are given in Table III and illustrated in Figs. 3 to 5. That based on slabs of

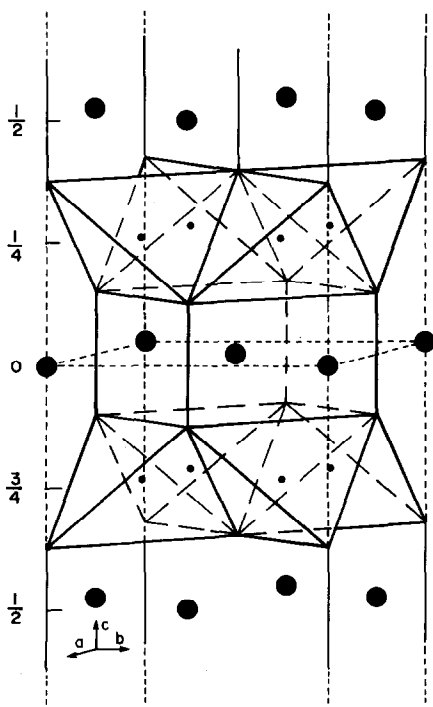


FIG. 3. The tetrahedral framework of X atoms in the $BaAl_4$ structure. The tetrahedra are centered by N atoms and form edge-sharing slabs in (001) planes that are interconnected by $[001]$ $X-X$ bonds. M sites are indicated by large black dots and N sites by small black dots.

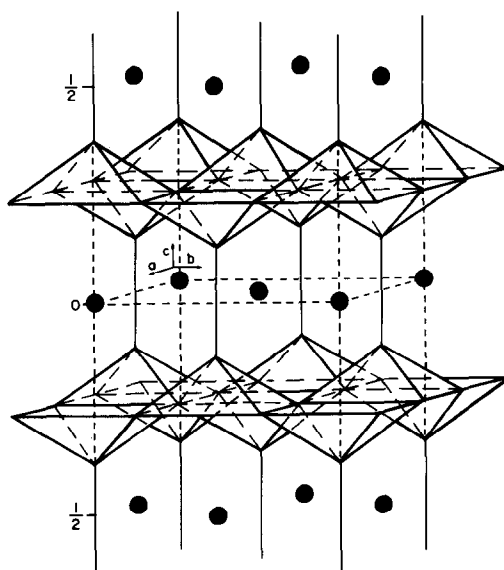


FIG. 4. The square pyramid framework of N and X atoms in the $BaAl_4$ structure. The square pyramids form edge-sharing slabs in (001) planes that are interconnected by $[001]$ $X-X$ bonds. M sites are indicated by black dots.

X tetrahedra in (001) planes, centered by N and interconnected by $X-X$ bonds along $[001]$ ((a) in Table III) has little metallurgical significance since the $X-X$ distances along the edges of the tetrahedra considerably exceed D_X . That based on slabs of square pyramids in (001) planes that are formed by one X and four N atoms and interconnected by $X-X$ bonds along $[001]$ ((b) of Table III) is metallurgically important since the N and X atoms are almost invariably in close contact. This framework also creates the tetragonal hexagonal prismatic voids that enclose the M atoms, and which are the basis of the third framework description ((c) of Table III).

The square pyramidal framework of N and X atoms interconnected by $[001]$ $X-X$ bonds constitutes a heterogeneous sphere packing. As discussed in the next section, the distance between the N and X atoms related, say, to the $CN12$ radius sums, appears to display a remarkable constancy

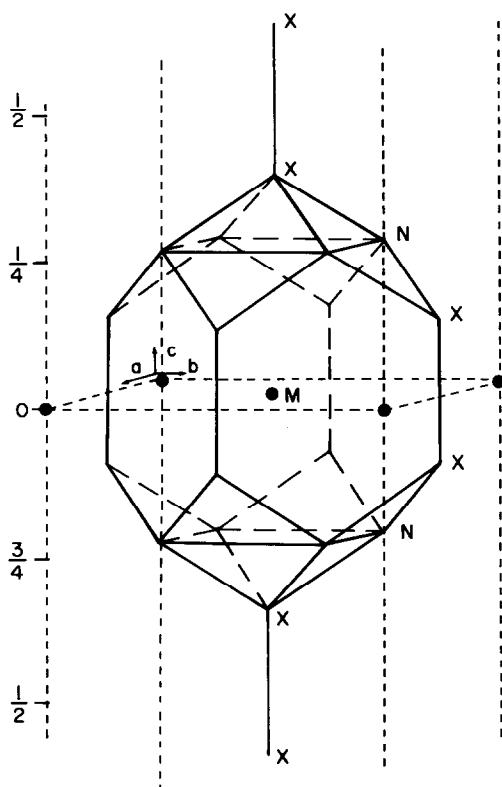


FIG. 5. The tetragonal hexagonal prism framework of N and X atoms in the $BaAl_4$ structure. N and X sites are indicated and M sites are shown by black dots.

when compared to the range of diameters of M atoms contained in its tetragonal hexagonal prismatic voids (Table I). This suggests a particular role of the square pyramidal framework in accounting for the stability of the structure, that transcends the triviality that the N and X atoms comprise four-fifths of the atoms in the structure. Indeed, experience shows that even in slightly complex structures, one cannot assume that the major component(s) will control the structure. For example, in the $MgCu_2$ *cF24* structure, MN_2 , the cell dimensions may be controlled entirely by the minor (larger) component, M , only by the major component, N , or by both together, depending on the particular elements involved in the structure (15). In the Th_2Zn_{17} *hR19* structure, M_2N_{17} , where

the larger M atoms comprise less than 11% of the atoms, it is found that in arrays in the basal plane of the hexagonal cell, they strongly influence the a dimension, yet in arrays running along the $[001]$ direction, they have virtually no influence on the c dimension of the cell (16). Such detailed differences in behavior would not be expected on the assumption that the major component(s) alone necessarily control a structure.

When discussing interatomic distances we generally refer to the $CN12$ diameters of atoms using radii determined from the elements by Teatum *et al.* (17).

2. Structural Stability and Availability

The z_X parameters of some 140 phases with the $BaAl_4$ structure have been determined so that interatomic distances involving the X atoms can be calculated.¹ Such calculations reveal a notable constancy of the differences of the $N-X$ distances, d_{N-X} , and the appropriate radius sums, $R_N + R_X$. The observed distances for the 140 phases average 0.228 Å shorter than the radius sums taken for $CN12$. No particular difference in this shortening is noticed for phases in which the $[001]$ $X-X$ distances, d_{X-X} , are less than D_X , or are considerably greater than D_X . For phases with $d_{X-X} < D_X$, the observed $[001]$ $X-X$ distances average 0.218 Å less than D_X for $CN12$, although the individual distances are more variable than the $N-X$ distances.

Although it may be argued that constancy of the $N-X$ distances relative to the radius sums is only to be expected since N and X comprise four-fifths of the atoms in the structure, it is nevertheless an impressive feature as seen on comparing the range

¹ Calculated with Pauling's (18) equation $R(1) - R(n) = 0.3 \log n$, where n equals valency divided by coordination number. It should be stressed that these calculations refer to the *average*, not the individual behavior of the phases.

of $R_N + R_X$ values with the range of D_M values found in the structure—particularly as the four $N-X$ and one [001] $X-X$ neighbor distances comprise the tetragonal hexagonal prismatic voids that house the M atoms. Compare LiCu_2P_2 and BaMg_2Ge_2 , the z values and axial ratios of which, are very similar. For CN12 , D_M increases by 1.362 Å ($D_{\text{Li}} = 3.124$ Å, $D_{\text{Ba}} = 4.486$ Å) whereas $R_N + R_X$ increases by only 0.413 Å ($R_{\text{Cu}} + R_{\text{P}} = 2.558$ Å, $R_{\text{Mg}} + R_{\text{Ge}} = 2.971$ Å). Nevertheless, the difference between $R_{\text{Cu}} + R_{\text{P}} - d_{\text{Cu-P}} = 0.210$ Å and $R_{\text{Mg}} + R_{\text{Ge}} - d_{\text{Mg-Ge}} = 0.173$ Å is insignificant. In part, accommodation of the large M atom is achieved by expansion of the [001] $X-X$ distance, since $D_{\text{P}} - d_{\text{P-P}} = 0.421$ Å for LiCu_2P_2 and $D_{\text{Ge}} - d_{\text{Ge-Ge}} = 0.055$ Å for BaMg_2Ge_2 . Even when a different mechanism of accommodating the large M atom is apparent as in BaMn_2Sb_2 , since c/a is much larger, z is smaller and there are no [001] Sb-Sb bonds ($D_{\text{Sb}} - d_{\text{Sb-Sb}} = -0.682$ Å), $R_{\text{Mn}} + R_{\text{Sb}} - d_{\text{Mn-Sb}} = 0.129$ Å has a value not greatly different to those of LiCu_2P_2 and BaMg_2Ge_2 .

(i) *Phases in which [001] $X-X$ Bonds Occur*

We shall now examine further the role of the square pyramidal framework in phases in which [001] $X-X$ bonds occur.

First we examine the shortening of the $N-X$ and [001] $X-X$ distances compared to the CN12 radii sums in relation to the number of valency electrons provided by the N and X atoms. Here we take the 20 phases (that have [001] $X-X$ bonds and the z_X values of which have been determined) which do not contain a transition metal, so that valencies V_X and V_N , are known with certainty. Since X is bonded to one X and four N if we assume $V_X/5$ electrons are used per X bond and $V_N/5$ electrons per N bond, the calculated shortenings¹ of the $N-X$ and [001] $X-X$ bonds relative to the CN12 radius sums is 0.228 Å, embarrassingly close

to the observed *average* values of 0.228 and 0.227 Å, respectively, for the 20 phases. In this calculation the $N-X$ bonds have the same strength whether the valencies of N and X are both three, or whether N is two and X is four.

There are some 285 phases in which N is a transition metal and 41 of these with [001] $X-X$ bonds and X of valency four have z values determined. For these phases the average shortening of the $N-X$ and [001] $X-X$ distances, compared to the CN12 radii sums is 0.240 and 0.162 Å, respectively. Assuming (with Teatum *et al.* (17)) that the transition metals have six valency electrons in the structures from which their CN12 radii were determined, these shortenings correspond to X using 0.62 electrons in the $X-X$ bond and 3.38 in its $N-X$ bonds, whereas the transition metals contribute 5.0 electrons to the $N-X$ bonds.

These calculations provide one interpretation of the *average* interatomic distances in a number of phases. They indicate that the N and X atoms contribute most of their valency electrons to the $N-X$ framework (and [001] $X-X$ connections)—there are very few left for $M-N$ and/or $M-X$ interactions even though these distances *may* be close to or even closer than, the appropriate radius sums.

This observation parallels the results of calculations, for individual phases, of the apparent number of valency electrons that would be required to satisfy the observed interatomic distances and which considerably exceed the number provided by the component atoms. Indeed, this is a situation frequently observed in phases whose structures satisfy geometrical packings of the metallic atoms, rather than directed valency bondings per se (see, for example, Debray (19)). It also recalls the observation in Section 1(i), where it was observed that the variety of components that could occupy each of the three sites in the structure (Table I) portended geometrical packings.

Indeed here we see a hybrid structure where valency bonding controls the $N-X$ framework and [001] $X-X$ connections and geometrical packings involve accommodation of the M atoms.

First, the distinction we make here is not entirely "a straw man." For example, in the Cu₂Sb *tP6* structure, the low near-neighbor coordination numbers in phases MX_2 and $MX'X''$ with axial ratio $c/a > 2.0$ suggest a structure dominated by valency bonding. Indeed, the apparent number of valency electrons required to account for the near-neighbor distances equals, within about one electron, the number provided by the component atoms. On the other hand in phases $M'M''X$ with $c/a < 1.80$ and containing a large M atom, where features of geometrical packings are apparent, the apparent number of valency electrons required to account for the near-neighbor distances definitely exceeds those provided by the component atoms.

Second, we examine the results of Pearson and Villars (7) in the context of these observations. They found for 10 series of Mn_2X_2 phases (M = rare earth, N = Mn, Fe, Co, Ni, or Cu, X = Si or Ge) as M changed and N and X were held constant that:

First, $R_M + R_N - d_{M-N} = \text{constant}$ for the two series of Mn phases and $R_M + R_X - d_{M-X} = \text{constant}$ for the eight series of Fe, Co, Ni, and Cu phases indicating that the cell dimensions were controlled by $M-N$ contacts in the first case and $M-X$ contacts in the second. Second, $R_N + R_X - d_{N-X}$ values for all ten series lay in a very narrow band as a function of D_M , but the d_{N-X} values increased by about 0.1 Å as D_M was increased by 0.28 Å. The [001] d_{X-X} also increased with D_M but generally at a slower rate than d_{N-X} (in the Cu series d_{X-X} decreased). Thus we note (on the assumption that z_X is constant in each series) that there is a modest expansion of the $N-X$ framework as M increases in size.

Finally, it should be noted that Pearson and Villars (20) found generally that in phases where the M component was not a rare earth, the $N-X$ contacts had a greater and the $M-N$ and $M-X$ contacts had a lesser influence on the variation of the cell dimensions in a series of phases as the M component changed and N and X remained the same.

(ii) Phases in which there are no $X-X$ Bonds along [001]

Table IV lists 25 phases for which z values are determined in which the [001] $X-X$ distance definitely exceeds D_X for CN12. It is apparent from the table that no uniform conditions govern this phenomenon. For example, the M component may be a very large atom, but it may also be among the smallest M components known (Sb). The condition is found in many phases of bar-

TABLE IV
PHASES FOR WHICH z HAS BEEN DETERMINED AND FOR WHICH THE SEPARATION OF THE X ATOMS ALONG [001], d_{X-X} , IS GREATER THAN D_X , THE DIAMETER OF X FOR CN12

Phase	$D_X - d_{X-X}$ (Å)	Phase	$D_X - d_{X-X}$ (Å)
BaRh ₂ B ₂	-2.113	BaMn ₂ P ₂	-1.175
LaCo ₂ B ₂	-0.594	BaFe ₂ P ₂	-1.283
YCo ₂ B ₂	-0.323	BaZn ₂ P ₂	-1.125
SrAu ₂ Si ₂	-0.305	SrFe ₂ P ₂	-0.874
CaAu ₂ Si ₂	-0.128	SrCo ₂ P ₂	-0.865
(CeMn ₂ Si ₂	-0.067)	CaFe ₂ P ₂	-0.150
CeNi ₂ Si ₂	-0.229		
NdMn ₂ Si ₂	-0.127	BaMn ₂ As ₂	-0.965
(YCr ₂ Si ₂	-0.020)	(SrNi ₂ As ₂	-0.054)
(ThCr ₂ Si ₂	-0.028)	KFe ₂ As ₂	-1.309
		KRh ₂ As ₂	-1.100
(BaMn ₂ Ge ₂	-0.009)	BaMn ₂ Sb ₂	-0.682
SrCo ₂ Ge ₂	-0.159		
SrNi ₂ Ge ₂	-0.091	TiCo ₂ S ₂	-1.415
(EuCu ₂ Ge ₂	-0.010)	TiFe ₂ Se ₂	-1.204
		TiCu ₂ Se ₂	-1.111
SbN ₂ Th ₂	-0.637		
BiN ₂ Th ₂	-0.654		
TeN ₂ Th ₂	-0.466		

ium. For example, in BaMn_2Sb_2 with $z = 0.3659$, the Sb-Sb distance is 0.682 \AA greater than D_{Sb} for *CN12*, but there are also many phases of barium where it does not occur, for example, in BaMn_2Sn_2 and BaAg_2Sn_2 , both with $z = 0.376$, where the Sn-Sn distances are, respectively, 0.154 and 0.275 \AA shorter than D_{SnIV} for *CN12*.

The phenomenon does not seem to be very prevalent in phases of Si and Ge, and even if the $[001] d_{X-X}$ distance exceeds D_X , it does so to a much smaller extent than in phases of P, As, Sb, S, and Se. Nevertheless, for example, there are also several phases of phosphorus in which $d_{\text{P-P}}$ is notably smaller than D_P .

The breaking of the $[001] X-X$ bonds has little influence on the $N-X$ distances. For the phases listed in Table IV, the average shortening of the $N-X$ distances relative to the radius sums for *CN12* is 0.251 \AA compared to 0.228 \AA for all phases. Indeed, an increased shortening is to be expected since electrons not used in $X-X$ bonds are available for $N-X$ bonds.

(iii) Conclusions

From these observations we see the $N-X$ framework (and $[001] X-X$ connections) established by valency bonding, which uses most of the electrons provided by the N and X atoms, as the feature that provides structural stability. In creating also the tetragonal hexagonal prismatic voids it provides packing for the large M atoms, apparently without any size restrictions, accounting for the wide availability of the structure. Although the large number of adherents of the structure results in part from the multiplicity of the rare earths and the transition metals, it is nevertheless noted that size restrictions are found in structures adopted by rare earths (see, e.g., (21-23) of many possible references) and Group restrictions are found in structures formed by transition metals (see, e.g., (24, 25) of many possible references). The BaAl_4 structure is adopted

by transition metals from the Cr to the Ni Group, apparently without this restriction.

$N-X$ distances relative to the radius sums may remain constant, or vary modestly while accommodating M atoms of various sizes. This accommodation can be achieved by changing the height-to-base ratio of the square pyramids, by rather modest changes of the distances between the X atoms along $[001]$, or by eliminating the $[001] X-X$ bonds—all by suitable adjustment of a , c , and z without greatly altering the average $N-X$ distances of the framework. Such adjustments may be controlled by specific interactions involving the M atoms (e.g., $M-N$, $M-X$) as in the phases studied in (7). Close $M-M$, $M-N$, or $M-X$ distances that may be observed in phases with the structure should be regarded as resulting from "geometrical packings," rather than directed chemical bonding.

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Note added in proof. In the first submission of this paper, the suggestion was made that measurement of electron transport and other physical properties, particularly of single crystals, would indicate whether our model of the framework had any validity. Recently, such a paper has appeared (26). The authors concluded that TiCu_2Se_2 has one hole per formula unit at the top of the valency band which has predominantly Se $4p$ character. Expressing this result in terms of our calculations, we calculate a shortening of 0.278 \AA for the Cu-Se distance relative to $R_{\text{Cu}} + R_{\text{Se}}$ for *CN12*. The observed shortening is 0.265 \AA .

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