

# $M_2X$ Intermetallics: Nonmetal Insertion in a h.c.-Like Metallic Distribution

J. Y. Pivan\*<sup>1</sup> and R. Guérin†

\*Laboratoire de Physicochimie Analytique et Théorique, E. N. S. C. Rennes, and †Laboratoire de Chimie du Solide et Inorganique Moléculaire, U. M. R. 6511, Campus de Beaulieu, Avenue du Général Leclerc, 35042 Rennes Cédex, France

Received April 28, 1997; in revised form September 15, 1997; accepted September 18, 1997

A simple structural model is proposed on the basis of an ideal hexagonal close-packing  $(AB)^\infty$  of the metal atoms  $M$ . The metalloid atoms  $X$ , located in an ordered manner in the metallic planes with the stacking sequence  $..(A)^\infty..$  or  $..(B)^\infty..$ , generate two types of elementary units called units  $U_I$  and  $U_{II}$ . These units are hexagonal prisms with the fundamental vectors  $a_0, b_0, c_0$  and the elementary volume  $V_0$ . When the exclusive occurrence of  $U_I$  (or  $U_{II}$ ) only yields 6-prismatic and triangular sites of metalloid atoms  $X$ , additional tetrahedral and pyramidal sites of  $X$  atoms are present when units  $U_I$  and  $U_{II}$  exist simultaneously. The structures of compounds with the general formula  $M_2X$  ( $M = 3d, 4d, 5d$  and (or)  $4f, 5f$  elements,  $X = B, P, As, Sb, Si, Ge, \dots$ ) are described in terms of intergrowth mechanisms. Binary, ternary, or even quaternary structures of compounds, with  $M/X$  ratios equal or close to two, appear as superstructures of the elementary units. Insofar as no ordering is considered along the stacking direction, the vectorial combinations of the fundamental vectors in the form  $A = h \cdot a_0 + s \cdot b_0$ ,  $B = k \cdot a_0 + t \cdot b_0$ ,  $C = c_0$  result in supercells with the volume  $V = (h \cdot t - k \cdot s) \cdot V_0$ . The attainable symmetry (hexagonal, tetragonal, orthorhombic, monoclinic, ...) strongly depends on the particular values of the integers  $h, s, k, t$ . The criteria of occurrence of various series of compounds are presented together with their crystallographic features and structural relationships are emphasized. Moreover, the model demonstrates that numerous compounds with the predicted unit cell parameters should be obtained in each crystal system. © 1998

Academic Press

## INTRODUCTION

Numerous binary, ternary, and even quaternary intermetallic compounds have been reported recently with the general chemical formula  $M_2X$  or  $(M, M')_2X$  ( $M$  and  $M'$  are specified precisely below in the text) (1) and a short stacking vector within the range 3.3–4 Å. The main characteristics of these compounds are:

— The  $M$  subset consists of transition elements with rather small Goldschmidt metallic radius for 12-coordination ( $r \leq 1.5$  Å) (2) and Pauling electronegativity higher than 1.5. They are mainly 3d elements (V to Ni) and more infrequently 4d or 5d elements (Nb, Mo, Ru, Rh, Ta, Pd, Pt). The  $M$  elements typically occupy pyramidal ( $5M \rightarrow X$  bonds) tetrahedral ( $4M \rightarrow X$  bonds), and (or) triangular ( $3M \rightarrow X$  bonds) sites of metalloid atoms  $X$ . Numerous three-dimensional  $M$ – $M$  bondings occur with bond distances slightly longer than those found in pure metals so that these compounds are metallic conductors with resistivity values ca.  $10^{-5}$  Ω cm or higher.

— The  $M'$  subset consists of less electronegative elements ( $\chi$  values  $< 1.5$ ) with Goldschmidt metallic radius larger than 1.5 Å, typically scandium, zirconium, hafnium, lanthanoid elements, and uranium. In relation to their electronegativity and their atomic size, the  $M'$  elements occupy the largest sites available, i.e., 6-prismatic ( $6M \rightarrow X$  bonds) and (or) pyramidal ( $5M \rightarrow X$  bonds)  $X$  sites. In a general way, the magnetic properties only depend on the nature of the  $M'$  elements and as no  $M'$ – $M'$  distances shorter than, say 3.3 Å, occur in the structures, the  $(M, M')_2X$  compounds are Pauli paramagnets ( $M' = Sc, Zr, Hf, \dots$ ) or Curie–Weiss paramagnets ( $M'$  with localized f electrons) with ordering temperature below 10 K.

— The electronegativity values (Pauling's scale) of  $X$  atoms range from 2.1 (phosphorus) to 1.8 (silicon) and the  $X$  atoms solely occupy tricapped trigonal prismatic sites of metal atoms ( $9X \rightarrow (M, M')$  bonds). No  $X$ – $X$  bondings occur in the structures reported up to now. When the electronegativity values of the  $X$  subset (P, As, Si, ...) are compared to those of the  $M$  and  $M'$  subsets, the  $M_2X$  and  $(M, M')_2X$  compounds are actually intermetallic in character. Hereafter,  $M$  and  $M'$  atoms will not be distinguished and the  $(M, M')_2X$  compounds will be named for reason of simplification  $M_2X$ .

The different structures will be discussed by considering that the metal atom arrangement is very close to the ideal h.c. stacking, that is the structures will be described without

<sup>1</sup>To whom correspondence should be addressed.

taking into account the slight atomic displacements that actually occur in the true structures.

Different authors have previously underlined the structural homogeneity of this wide family of  $M_2X$  intermetallics through various models (3–8). A few years ago, we reported on a classification scheme (3) to describe and predict structure types in pnictide and silicide chemistry which was built from fundamental units found in the hexagonal  $Fe_2P$  set of structures, namely (1:0), (1:6:3), (3:10:6), and (6:15:10) units.

A new crystal chemical approach is given in the present paper by considering that the preceding units result from a special distribution of the  $X$  atoms in the planes of the metallic h.c.-like packing. Indeed, the nonmetal  $X$  atoms are exclusively located either in the  $A$  or the  $B$  metallic planes and this distribution of the metal  $M$  and nonmetal  $X$  atoms generates hexagonal slabs with the composition  $M_2X$  and the thickness  $c_0$ . The slabs are stacked along  $\mathbf{c}_0$  and the stacking sequence depends on how they are piled up. In the model presented hereafter, only compounds with identical slabs will be discussed, that is, compounds with stacking vector  $\mathbf{c}_0$  and the  $X$  atoms piled up with the sequence  $(A)^\infty$  or  $(B)^\infty$ .

### GENERAL FEATURES OF THE MODEL

The metal atoms  $M$  are packed together with the  $..(AB)^\infty..$  sequence (h.c.p.) and the  $X$  atoms are located in an ordered manner either in the  $A$  or  $B$  plane. This peculiar ordering leads to the fundamental units named units  $U_I$  and  $U_{II}$  (Fig. 1). These elementary units, which are differentiated from each other by the location of the  $X$  atoms, consist of hexagonal prisms with the fundamental vectors  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ ,  $\mathbf{c}_0$ ,<sup>2</sup>  $\gamma_0 = 120^\circ$ , and the volume  $V_0 = (\mathbf{a}_0 \wedge \mathbf{b}_0) \cdot \mathbf{c}_0$  whatever the location of  $X$  atoms. Each unit contains two  $M$  and one  $X$  atom so that the elementary volume  $V_0$  is associated with the formula  $M_2X$ .

$M_2X$  and related compounds with a  $M/X$  ratio close to 2, the coordination polyhedra and crystallographic features of which are given in the preceding section, can be described from an infinite number of combinations of the  $U_I$  and  $U_{II}$  units and explained as superstructures with the lattice vectors  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$ .<sup>2</sup> The vectors  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  are combinations of the fundamental vectors  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ , and  $\mathbf{c}_0$  expressed as  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$ , and  $\mathbf{C} = f_3(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$  (Table 1, Part 1). The magnitudes of the vectors  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ ,  $\mathbf{c}_0$ ,  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  are denoted below by  $a_0$ ,  $b_0$ ,  $c_0$ ,  $A$ ,  $B$ , and  $C$  and

<sup>2</sup>Bold  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ ,  $\mathbf{c}_0$ ,  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  represent vector quantity  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ ,  $\mathbf{c}_0$ ,  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  while the corresponding  $a_0$ ,  $b_0$ ,  $c_0$ ,  $A$ ,  $B$ , and  $C$  represent vectorial magnitudes. This will be the rule hereafter in the paper.

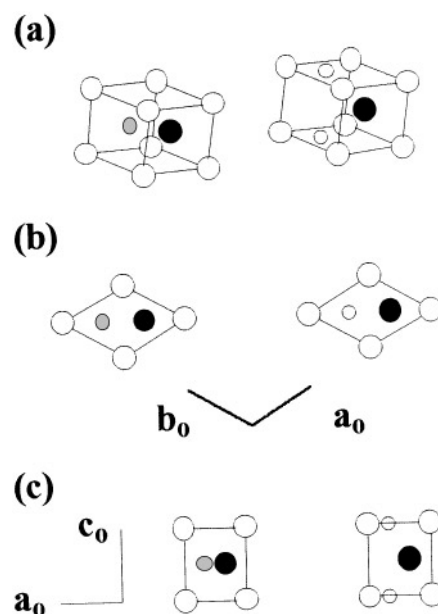


FIG. 1. Different views of the fundamental hexagonal units  $U_I$  and  $U_{II}$ : 3D view (a), view along  $[001]$  (b), and view along  $[010]$  (c). Large circles are metal atoms, small circles are nonmetal atoms.

the interaxial angles by  $\alpha_0$ ,  $\beta_0$ ,  $\gamma_0$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  with  $\alpha_0 = \beta_0 = 90^\circ$ ,  $\gamma_0 = 120^\circ$ . It is worth noting from the crystallographic data reported in literature that the ratio  $a_0/c_0$  is near unity.

However, given the structural features reported for  $M_2X$  and related compounds ( $\mathbf{A}$  and  $\mathbf{B}$  only depend on  $\mathbf{a}_0$  and  $\mathbf{b}_0$  while  $\mathbf{C}$  is a straightforward function of  $\mathbf{c}_0$ ), it is most convenient to consider  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0)$ , and  $\mathbf{C} = f_3(\mathbf{c}_0)$  with the  $\mathbf{C}$  vector parallel with  $\mathbf{c}_0$ . When considering superstructures along  $\mathbf{c}_0$ , the  $f_1$ ,  $f_2$ , and  $f_3$  functions reduce to the vectorial combinations  $\mathbf{A} = h \cdot \mathbf{a}_0 + s \cdot \mathbf{b}_0$ ,  $\mathbf{B} = k \cdot \mathbf{a}_0 + t \cdot \mathbf{b}_0$ ,  $\mathbf{C} = l \cdot \mathbf{c}_0$ , with the corresponding volume  $V = l \cdot (h \cdot t - k \cdot s) \cdot V_0$  (Table 1, Part 2, section 2<sub>1</sub>). If no superstructures occur along  $\mathbf{c}_0$ , the linear combinations limit to  $\mathbf{A} = h \cdot \mathbf{a}_0 + s \cdot \mathbf{b}_0$ ,  $\mathbf{B} = k \cdot \mathbf{a}_0 + t \cdot \mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$  (Table 1, Part 2, section 2<sub>2</sub>). The only structures to be discussed herein are such as  $\mathbf{C} = \mathbf{c}_0$  with the unit cell volume  $V = (h \cdot t - k \cdot s) \cdot V_0$  and when we recall that the volume  $V_0$  is associated with one elementary unit  $M_2X$ , it is easily proved that  $(h \cdot t - k \cdot s)$  units are present in a structure with the volume  $V$ . The corresponding compound is therefore  $M_{2(h \cdot t - k \cdot s)}X_{(h \cdot t - k \cdot s)}$  with  $(h \cdot t - k \cdot s)$  ranging from 1 to  $\infty$ . Particular values of the coefficients  $h$ ,  $k$ ,  $s$ , and  $t$  impose the symmetry (Table 2) which will be hexagonal, monoclinic, orthorhombic, and (or) tetragonal depending on the  $\gamma$  angle between the vectors  $\mathbf{A}$  and  $\mathbf{B}$  and their relative lengths.

**TABLE 1**  
**Vectorial Relations to Describe  $M_2X$  Compounds from the Hexagonal Prism with Fundamental Vectors  $\mathbf{a}_0$ ,  $\mathbf{b}_0$  and  $\mathbf{c}_0$**

**Part 1, General case:**  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$ ,  $\mathbf{C} = f_3(\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0)$

$$\mathbf{A} = h.\mathbf{a}_0 + s.\mathbf{b}_0 + u.\mathbf{c}_0 \text{ with } A = [(h^2 + s^2 - h.s).a_0^2 + u^2.c_0^2]^{1/2},$$

$$\mathbf{B} = k.\mathbf{a}_0 + t.\mathbf{b}_0 + v.\mathbf{c}_0 \text{ with } B = [(k^2 + t^2 - k.t).a_0^2 + v^2.c_0^2]^{1/2},$$

$$\mathbf{C} = m.\mathbf{a}_0 + n.\mathbf{b}_0 + l.\mathbf{c}_0 \text{ with } C = [(m^2 + n^2 - m.n).a_0^2 + l^2.c_0^2]^{1/2},$$

$\alpha$ ,  $\beta$ , and  $\gamma$  are obtained from the analysis of the scalar products  $\mathbf{A.B}$ ,  $\mathbf{C.A}$ , and  $\mathbf{B.C}$  together with the vector products  $\mathbf{A} \wedge \mathbf{B}$ ,  $\mathbf{C} \wedge \mathbf{A}$ , and  $\mathbf{B} \wedge \mathbf{C}$ .

$$V = (\mathbf{A} \wedge \mathbf{B}).\mathbf{C} = [l.(h.t - s.k) + 2/3^{1/2}[n.(u.k - h.v) + m.(s.v - u.t)]. V_0 \text{ with } V_0 = (\mathbf{a}_0 \wedge \mathbf{b}_0).\mathbf{c}_0$$

**Part 2, Particular cases ( $\alpha = \beta = 90^\circ$ ) with  $\mathbf{C}$  along  $\mathbf{c}_0$**

**Section 2<sub>1</sub>,**  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{C} = f_3(\mathbf{c}_0)$

$$\mathbf{A} = h.\mathbf{a}_0 + s.\mathbf{b}_0, A = (h^2 + s^2 - h.s)^{1/2}.a_0, \mathbf{B} = k.\mathbf{a}_0 + t.\mathbf{b}_0, B = (k^2 + t^2 - k.t)^{1/2}.a_0, \mathbf{C} = l.\mathbf{c}_0, C = l.c_0$$

$$\mathbf{A.B} = A.B.\cos(\gamma) = (h.k + s.t - \frac{1}{2}(h.t + s.k)).a_0^2, \mathbf{A} \wedge \mathbf{B} = A.B.\sin(\gamma) = (h.t - s.k).\sin(\gamma_0).a_0^2$$

$$V = (\mathbf{A} \wedge \mathbf{B}).\mathbf{C} = l.(h.t - s.k).V_0$$

**Section 2<sub>2</sub>,**  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{C} = f_3(\mathbf{c}_0)$

$$\mathbf{A} = h.\mathbf{a}_0 + s.\mathbf{b}_0, A = (h^2 + s^2 - h.s)^{1/2}.a_0, \mathbf{B} = k.\mathbf{a}_0 + t.\mathbf{b}_0, B = (k^2 + t^2 - k.t)^{1/2}.a_0, \mathbf{C} = \mathbf{c}_0, C = c_0$$

$$\mathbf{A.B} = A.B.\cos(\gamma) = (h.k + s.t - \frac{1}{2}(h.t + s.k)).a_0^2, \mathbf{A} \wedge \mathbf{B} = A.B.\sin(\gamma) = (h.t - s.k).\sin(\gamma_0).a_0^2$$

$$V = (\mathbf{A} \wedge \mathbf{B}).\mathbf{C} = (h.t - s.k).V_0$$

*Note.*  $\alpha_0, \beta_0, \gamma_0, \alpha, \beta$ , and  $\gamma$  are defined as in the "International Tables for Crystallography" (8) relative to the vectors  $\mathbf{a}_0, \mathbf{b}_0, \mathbf{c}_0, \mathbf{A}, \mathbf{B}$ , and  $\mathbf{C}$ . The vectorial magnitudes are denoted by  $a_0, b_0$ , and  $c_0$  with  $a_0 = b_0 \sim c_0$ ,  $A, B$ , and  $C$  and  $h, k, l, m, n, s, t, u, v$  are integers.

## STRUCTURAL EXAMPLES

### (a) Structures with 6-Prismatic and 3-Triangular Sites of $X$ -Atoms Exclusively

If only  $U_I$  (or  $U_{II}$ ) units are present in a structure, that means that the  $X$  atoms are exclusively located in one plane and the metal atoms are solely in 6-prismatic and 3-triangular sites of  $X$  atoms. The corresponding compound  $M_2X$  is formulated as  $M_1^{\text{pr}}.M_1^{\text{tri}}.X$  with a unit cell volume exactly  $V_0$ . If so, the different sites of metalloid atoms are so different in size that they cannot accommodate only one kind of metal atoms. Indeed, the only compounds reported today which show such a special ordering are ternary hexagonal  $MM'X$  compounds with  $M$  and  $M'$  very different in size and electronegativity. Representatives are the phosphide  $\text{YbPtP}$  (unit cell parameters  $a = 4.077 \text{ \AA}$  and  $c = 3.777 \text{ \AA}$ , space group  $P\bar{6}m2$ ) (10) and its isostructural compounds. The h.c.-like packing of the (Yb, Pt) atoms is readily seen from the projections onto the (001) and (100) planes in Fig. 2. In this structure, the metallic distribution is actually of h.c. type: the exclusive location of the P atoms in the Pt planes only yields polyhedra with 3-fold symmetry along the stacking direction. The more electronegative and smaller Pt atoms are in the triangular sites ( $3M \rightarrow X$  bonds) while the less electronegative and larger Yb atoms are in the 6-prismatic sites ( $6M \rightarrow X$  bonds). The P atoms are surrounded by 6 Yb and 3 Pt atoms in a tricapped trigonal prismatic coordination ( $9X \rightarrow M$  bonds).

### (b) Structures with 5-Pyramidal and 4-Tetrahedral Sites of $X$ -Atoms Exclusively

When  $U_I$  and  $U_{II}$  units occur together in a structure, boundary zones are observed in which the  $X$  atoms are located at the same time in the  $A$  and  $B$  metallic planes. Such an ordering of the  $X$  atoms generates tetrahedral and pyramidal sites within the boundary zone as can be seen from Fig. 3. The tetrahedral and pyramidal sites do not possess 3-fold symmetry according to the stacking direction, so slight displacements from the ideal h.c. location are found within the zone. These atomic displacements result purely and simply from energetical arguments in that the metal atoms are stabilized when placed at the center of gravity of the sites. Accordingly, as observed for most of the structures reported today, the main deviations from the ideal h.c. packing strongly depend on the presence of tetrahedral and pyramidal sites. These deviations are involved sometimes in the formation of metallic clusters, e.g.,  $\text{ZrRuP}$  (11).

Particular orderings of  $U_I$  and  $U_{II}$  units result in the exclusive occurrence of pyramidal and tetrahedral sites. The corresponding compounds are formulated as  $M_1^{\text{pyr}}.M_1^{\text{tet}}.X$  and binary structures are attainable in that the available sites are not very different in size. The structures of binaries  $\text{Fe}_2\text{P}$  (12),  $\text{Fe}_2\text{As}$  (13), and  $\text{Co}_2\text{P}$  (14) (Fig. 4) result from such special distribution. Nevertheless, numerous isostructural ternary compounds  $MM'X$  ( $M$  and  $M'$  as transition

TABLE 2  
Vectorial Relations to Describe M<sub>2</sub>X without Superstructures along c<sub>0</sub>

Linear combinations in consideration.  $\mathbf{A} = h\mathbf{a}_0 + s\mathbf{b}_0$ ,  $\mathbf{B} = k\mathbf{a}_0 + t\mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$

$$A = (h^2 + s^2 - h.s)^{1/2}.a_0, B = (k^2 + t^2 - k.t)^{1/2}.a_0, C = c_0$$

$$\mathbf{A} \cdot \mathbf{B} = (h.k + s.t - \frac{1}{2}(h.t + s.k)).a_0^2, \mathbf{A} \wedge \mathbf{B} = (h.t - s.k).\sin(\gamma_0).a_0^2$$

$$V = (\mathbf{A} \wedge \mathbf{B}) \cdot \mathbf{C} = (h.t - s.k).V_0$$

The integers  $h, k, s$ , and  $t$  are obtained from analysis of the scalar and vector products.

(a) Hexagonal symmetry,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

$$\cos(\gamma) = -\frac{1}{2}, \sin(\gamma) = 3^{1/2}/2 \text{ and } A = B \neq C \text{ implies that } (h^2 + s^2 - h.s) = (k^2 + t^2 - k.t).$$

$$V = (h.t - s.k).V_0 = (h^2 + s^2 - h.s).V_0 = (k^2 + t^2 - k.t).V_0.$$

The integers  $h, k, s, t$  must satisfy the condition  $k.(s - h) = s.t$ .

(b) Orthorhombic and (or) tetragonal symmetry.  $\alpha = \beta = \gamma = 90^\circ$ .

$$\cos(\gamma) = 0, \sin(\gamma) = 1. \text{ The 4-fold axis along } \mathbf{A} \text{ or } \mathbf{B} \text{ for tetragonal symmetry.}$$

$$\mathbf{A} \cdot \mathbf{B} = 0, \mathbf{A} \wedge \mathbf{B} = (h.t).\sin(\gamma_0).a_0^2, V = (h.t).V_0$$

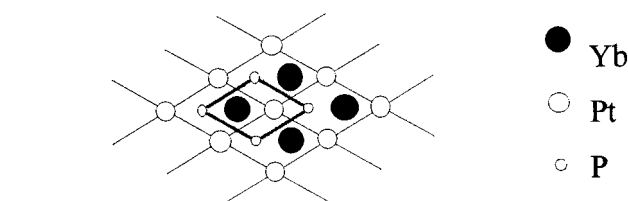
The integers  $h, k, s$ , and  $t$  must satisfy the condition  $2.s = h$  with  $k = 0, t > 0$ .

(c) Monoclinic symmetry.  $\alpha = \beta = 90^\circ$ ,  $\gamma = \text{any value}$ .

2-fold axis along  $\mathbf{A}, \mathbf{B}$ , or  $\mathbf{C}$ . (more likely along  $\mathbf{C}$ )

The integers  $h, k, s$ , and  $t$  do not verify the conditions (a) and (b).

elements) are known, which have been intensively studied by Fruchart *et al.* (7). These authors showed that the metal site preference over the 5-pyramidal and 4-tetrahedral sites depend on the relative atomic sizes and electronegativity values of the metal.



(a) Yb<sup>6-p</sup>·Pt<sup>3-t</sup>·P : U<sub>I</sub><sup>1∞</sup>.

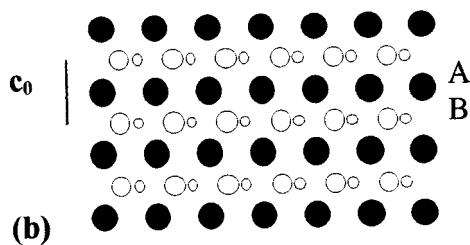


FIG. 2. Structure of the ternary phosphide YbPtP with its h.c.-like packing of metal atoms: view along [001] (a) and along [010] direction (b). The unit cell is emphasized. The stacking sequence of the P atoms is (B)<sup>∞</sup>.

(c) Structures with 6-Prismatic, 5-Pyramidal, 4-Tetrahedral, and 3-Triangular Sites of X-Atoms

The ordering of the  $X$  atoms in the  $A$  or  $B$  metallic planes governs the number and the distribution of the prismatic, pyramidal, tetrahedral, and triangular sites of metalloid atoms. According to the preceding sections, the structures undergo localized deformations all the more because pyramidal and tetrahedral sites are present. A great number of structures for  $M_2X$  compounds ( $M = 3d, 4d, 5d$ , and (or)  $4f, 5f$  elements,  $X = B, P, As, Sb, Si, Bi, Ge, \dots$ ) reported

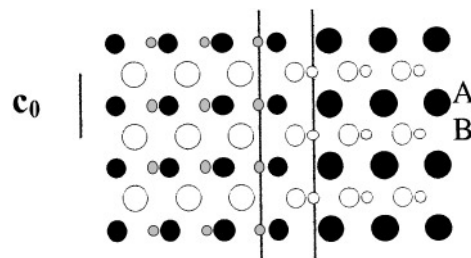
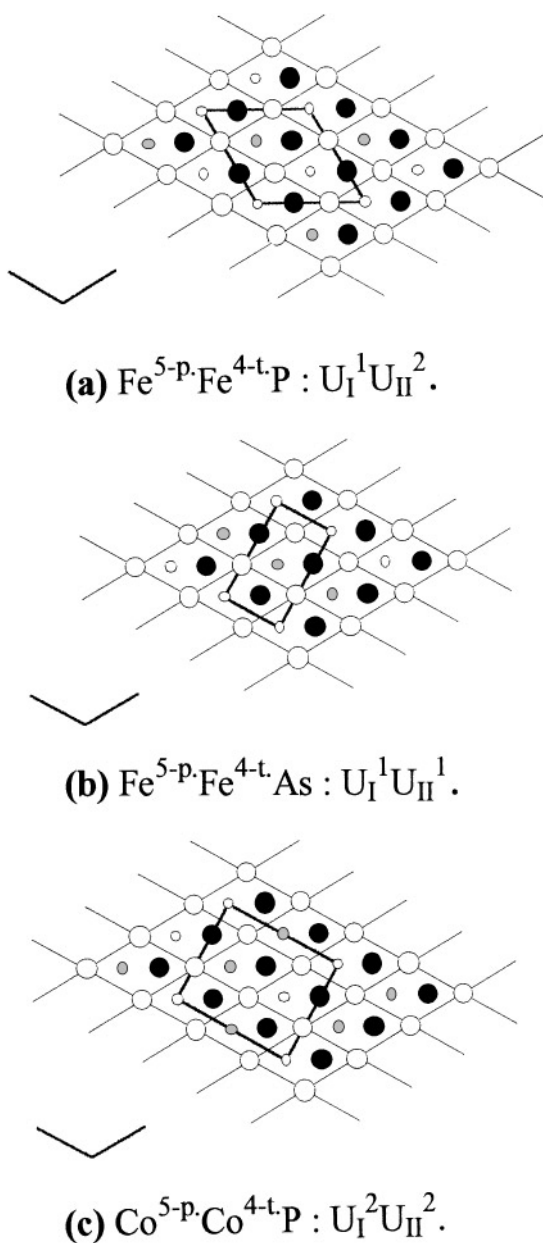


FIG. 3. Boundary zone resulting from the intergrowth of units  $U_I$  and  $U_{II}$  viewed along the [010] direction. The stacking sequence of the  $X$  atoms is (A)<sup>∞</sup> on the left-hand side and (B)<sup>∞</sup> on the right-hand side. Pyramidal and tetrahedral  $X$  sites can exist only within the zone emphasized by the vertical lines.



**FIG. 4.** Structures of the binaries  $\text{Fe}_2\text{P}$  (a),  $\text{Fe}_2\text{As}$  (b), and  $\text{Co}_2\text{P}$  (c) in projection onto the (001) plane. Large circles are metal atoms (Fe, Co); small circles are nonmetal atoms (As, P). For each figure, the number of  $\text{U}_I$  and  $\text{U}_{II}$  units per unit cell and the distribution of metal atoms in the different  $X$  sites are given (6-p., 5-p., 4-t., and 3-t. hold for trigonal prismatic, pyramidal, tetrahedral, and triangular coordination, respectively). Full and open circles are translated from each other by half a translation period of the projection direction. The different unit cells are emphasized.

up to now appear therefore as intermediate between that of  $\text{YbPtP}$  (6-prismatic and triangular sites, formula  $M_1^{\text{pr}}\text{-}M_1^{\text{tri}}\text{-}X$ ) and those of  $\text{Fe}_2\text{P}$ ,  $\text{Fe}_2\text{As}$ , and  $\text{Co}_2\text{P}$  (pyramidal and tetrahedral sites, formula  $M_1^{\text{pyr}}\text{-}M_1^{\text{tet}}\text{-}X$ ). The general formula of these intermediate structures is  $M_{m(\text{VI})}^{\text{pr}}\text{-}M_{m(\text{V})}^{\text{pyr}}\text{-}X_n$ ,

where  $m(\text{VI})$ ,  $m(\text{V})$ ,  $m(\text{IV})$ , and  $m(\text{III})$  are the respective number of metal atoms in 6-prismatic, 5-pyramidal, 4-tetrahedral, and 3-triangular sites of  $X$  atoms and  $n$  is the number of  $X$  atoms per cell. By considering there are as many  $M \rightarrow X$  as  $X \rightarrow M$  bonds, the geometric rule  $6 \cdot m(\text{VI}) + 5 \cdot m(\text{V}) + 4 \cdot m(\text{IV}) + 3 \cdot m(\text{III}) = 9 \cdot n$  together with  $2 \cdot n = m(\text{VI}) + m(\text{V}) + m(\text{IV}) + m(\text{III})$  allows us to count the metal atoms in the different  $X$  sites (15).

*$M_2X$  compounds with hexagonal symmetry.* The  $\gamma$  angle is  $120^\circ$  and the coefficients  $h$ ,  $k$ ,  $s$ , and  $t$  must satisfy the condition  $k \cdot (s - h) = s \cdot t$  from simple scalar and vector products analysis (Table 2). Various vectorial combinations which satisfy this criterion are listed in Table 3. The ratio  $V/V_0$  indicates how many elementary units  $M_2X$  are expected for the different members. When the vectorial combinations involved are analyzed more accurately, one can see that structures are described by combinations of the same kind (see, for example, the strongest reflection  $(hk1)$ ). These structures are members of common subsets as we have previously reported (3).

So, the structures with  $\mathbf{A} = h \cdot \mathbf{a}_0 - \mathbf{b}_0$ ,  $\mathbf{B} = \mathbf{a}_0 + t \cdot \mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$  ( $t = h + 1$ ,  $h \geq 1$ ) constitute the  $\text{Fe}_2\text{P}$  set with the general formula  $M_{2(h^2 + h + 1)}X_{(h^2 + h + 1)}$ , the structures defined by  $\mathbf{A} = h \cdot \mathbf{a}_0$ ,  $\mathbf{B} = t \cdot \mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$  ( $t = h$ ,  $h \geq 1$ ) are the limiting terms ( $\text{WC}$ ,  $\alpha\text{-UCr}_6\text{P}_4$ ,  $\text{Zr}_4\text{Co}_{13}\text{Si}_9$ , ...) described previously and so on.

The first members in the series are given in projection on the (001) plane in Fig. 5 and the validity of the model is readily seen from the curves in Fig. 6. The model confirms the rule  $A = a_0 \cdot K^{1/2}$  (4) by putting  $K = (h \cdot t - s \cdot k)$ . However, the  $V$  vs  $(h \cdot t - s \cdot k)$  curves show that the different members in the hexagonal series divide into two groups with different elementary volumes  $V_0$ . The first group has an elementary volume  $V_0$  of about  $44 \text{ \AA}^3$  while the smaller value  $V_0$  of about  $36 \text{ \AA}^3$  is found for the second group. This elementary volume decrease between the two groups can be explained by considering either that the atomic volumes of the elements are on average smaller or that the number of atoms per elementary unit is lower. If so, the metal/nonmetal ratio will be  $M/X = 2$  in the first case (stoichiometric compounds) and  $M/X \neq 2$  in the second case (defective compounds). This involves that the volume  $V_0$  is associated with the stoichiometric elementary formula  $M_2X$  in the first case and the defective formula  $(M_{1-\varepsilon}\square_\varepsilon)_2X$  (metal deficit) or  $M_2X_{1-\varepsilon}$  (nonmetal deficit) in the second. From careful examination of the structure types reported in literature, it appears that a volume  $V_0$  of about  $36 \text{ \AA}^3$  corresponds to metal defective compounds  $(M_{1-\varepsilon}\square_\varepsilon)_2X$ . As a consequence, metal vacancies are present in the structures of the second group (e.g.,  $\square\text{WC}$ : elementary formula  $(\text{W}_{0.5}\square_{0.5})_2\text{C}$ ,  $\varepsilon = 0.5$ ;  $\square_2\text{Cr}_{12}\text{P}_7$  ( $\varepsilon = 1/7$ ),  $\square\text{LiCo}_6\text{P}_4$  ( $\varepsilon = 1/8$ ),  $\square\text{Zr}_4\text{Co}_{13}\text{Si}_9$  ( $\varepsilon = 1/18$ ),  $\square_6\text{Rh}_{20}\text{Si}_{13}$  ( $\varepsilon = 3/13$ ),  $\square_6\text{U}_2\text{Mo}_{30}\text{P}_{19}$  ( $\varepsilon = 3/19$ ), ...)

TABLE 3  
Series of M<sub>2</sub>X Compounds with Hexagonal Symmetry

$h - s$	$\mathbf{A} = h.\mathbf{a}_0 + s.\mathbf{b}_0$	$\mathbf{B} = k.\mathbf{a}_0 + t.\mathbf{b}_0$	$(hk1)^{*a}$	$V/V_0$	Structure type
1	$\mathbf{a}_0$	$\mathbf{b}_0$	101	1	YbPtP (9), MoP (16), WC (17)
2	$\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 2.\mathbf{b}_0$	111	3	Fe <sub>2</sub> P (12)
	$2.\mathbf{a}_0$	$2.\mathbf{b}_0$	201	4	LiCo <sub>6</sub> P <sub>4</sub> (18)
3	$2.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 3.\mathbf{b}_0$	211	7	Cr <sub>12</sub> P <sub>7</sub> (19), Zr <sub>2</sub> Fe <sub>12</sub> P <sub>7</sub> (20)
	$3.\mathbf{a}_0$	$3.\mathbf{b}_0$	301	9	Zr <sub>4</sub> Co <sub>13</sub> Si <sub>9</sub> (21)
4	$2.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 4.\mathbf{b}_0$	221	12	Hf <sub>2</sub> Co <sub>4</sub> P <sub>3</sub> (22), Ho <sub>5</sub> Ni <sub>19</sub> P <sub>12</sub> (23)
	$3.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 4.\mathbf{b}_0$	311	13	Rh <sub>20</sub> Si <sub>13</sub> (24), Zr <sub>6</sub> Ni <sub>20</sub> P <sub>13</sub> (25)
	$4.\mathbf{a}_0$	$4.\mathbf{b}_0$	401	16	"Ln <sub>9</sub> Ni <sub>26</sub> P <sub>22</sub> " (26)
5	$3.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 5.\mathbf{b}_0$	321	19	UCo <sub>5</sub> Si <sub>3</sub> (27), U <sub>2</sub> Mo <sub>30</sub> P <sub>19</sub> (28)
	$4.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 5.\mathbf{b}_0$	411	21	Ln <sub>12</sub> Rh <sub>30</sub> P <sub>21</sub> (29)
	$5.\mathbf{a}_0$	$5.\mathbf{b}_0$	501	25	U <sub>9</sub> Co <sub>37</sub> Si <sub>25</sub> (21)
6	$3.\mathbf{a}_0 - 3.\mathbf{b}_0$	$3.\mathbf{a}_0 + 6.\mathbf{b}_0$	331	27	?
	$4.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 6.\mathbf{b}_0$	421	28	?
	$5.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 6.\mathbf{b}_0$	511	31	Sm <sub>20</sub> Ni <sub>42</sub> P <sub>31</sub> (30)
	$6.\mathbf{a}_0$	$6.\mathbf{b}_0$	601	36	?
7	$4.\mathbf{a}_0 - 3.\mathbf{b}_0$	$3.\mathbf{a}_0 + 7.\mathbf{b}_0$	431	37	?
	$5.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 7.\mathbf{b}_0$	521	39	U <sub>6</sub> Co <sub>30</sub> Si <sub>19</sub> (31)
	$6.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 7.\mathbf{b}_0$	611	43	Ho <sub>20</sub> Ni <sub>66</sub> P <sub>43</sub> (32), Tb <sub>30</sub> Ni <sub>56</sub> P <sub>43</sub> (30)
	$7.\mathbf{a}_0$	$7.\mathbf{b}_0$	701	49	?
8	$4.\mathbf{a}_0 - 4.\mathbf{b}_0$	$4.\mathbf{a}_0 + 8.\mathbf{b}_0$	441	48	?
	$5.\mathbf{a}_0 - 3.\mathbf{b}_0$	$3.\mathbf{a}_0 + 8.\mathbf{b}_0$	531	49	U <sub>6</sub> Mo <sub>74</sub> P <sub>49</sub> (33)
	$6.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 8.\mathbf{b}_0$	621	52	?
	$7.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 8.\mathbf{b}_0$	711	57	La <sub>18</sub> Rh <sub>96</sub> P <sub>51</sub> (34)
	$8.\mathbf{a}_0$	$8.\mathbf{b}_0$	801	64	?
9	$5.\mathbf{a}_0 - 4.\mathbf{b}_0$	$4.\mathbf{a}_0 + 9.\mathbf{b}_0$	541	61	?
	$6.\mathbf{a}_0 - 3.\mathbf{b}_0$	$3.\mathbf{a}_0 + 9.\mathbf{b}_0$	631	63	?
	$7.\mathbf{a}_0 - 2.\mathbf{b}_0$	$2.\mathbf{a}_0 + 9.\mathbf{b}_0$	721	67	U <sub>20</sub> Co <sub>102</sub> Si <sub>66</sub> (21)
	$8.\mathbf{a}_0 - \mathbf{b}_0$	$\mathbf{a}_0 + 9.\mathbf{b}_0$	811	73	?
	$9.\mathbf{a}_0$	$9.\mathbf{b}_0$	901	81	?

Note.  $\mathbf{A} = h.\mathbf{a}_0 + s.\mathbf{b}_0$ ,  $\mathbf{B} = k.\mathbf{a}_0 + t.\mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$ . The integers  $h$ ,  $k$ ,  $s$ , and  $t$  conform to  $k.(s - h) = s.t$ . The volume of the members is such as  $V/V_0 = (ht - s.k)$ .

<sup>a</sup>The  $(hk1)$  plane is the strongest reflection from X-ray diffraction studies.

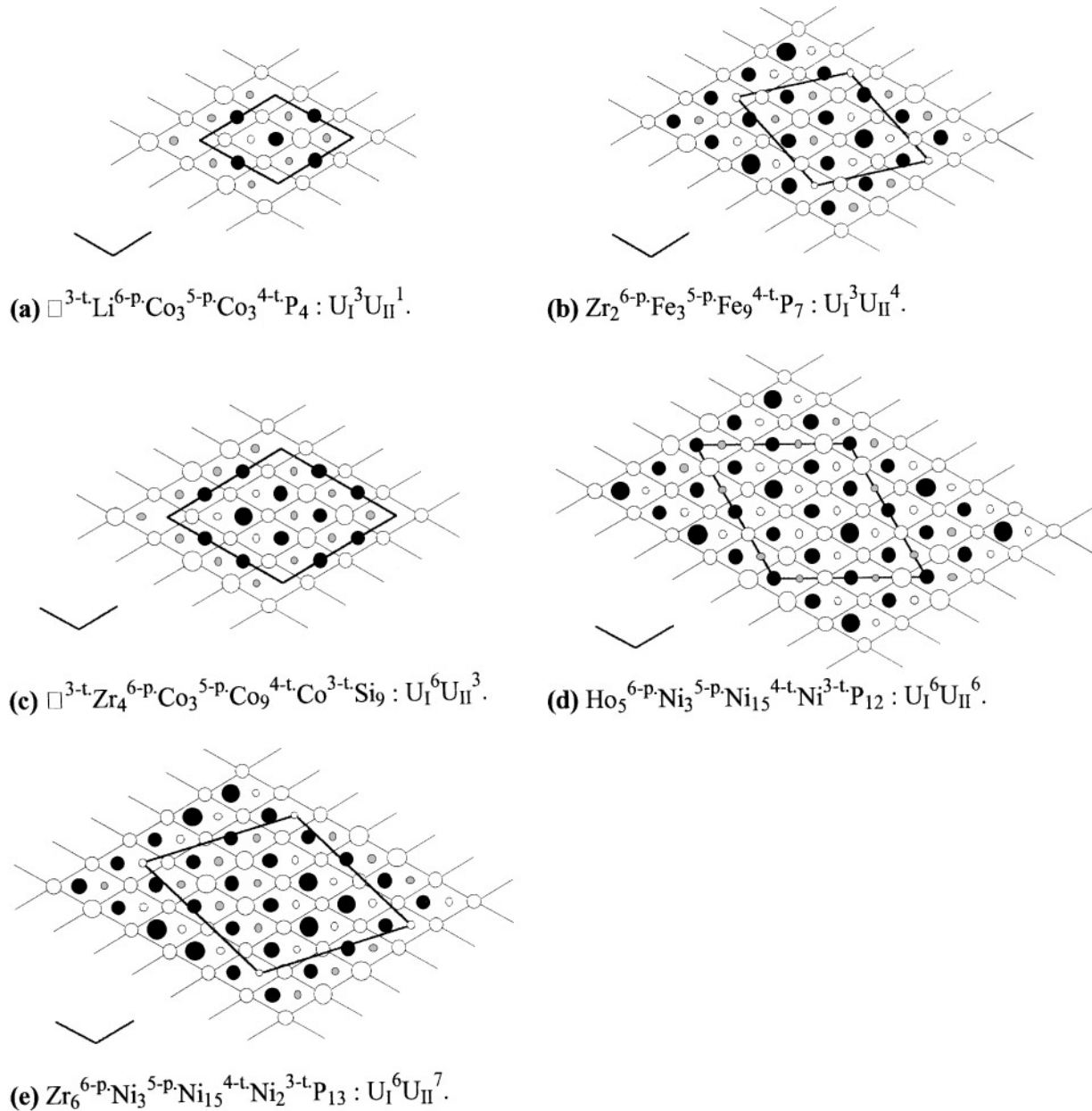
h.c. packing are all the less important because the  $\varepsilon$  value in the elementary formula decreases. Moreover, it is worth noting that the lower the overall electronegativity of the metallic sublattice, the smaller the volume  $V_0$ .

*M<sub>2</sub>X compounds with tetragonal, orthorhombic, and monoclinic symmetry.* Although possible orthorhombic, tetragonal, and especially monoclinic structures are by far much more numerous, few structural examples are reported today. The interaxial angles are 90° for tetragonal and orthorhombic symmetry which implies that the 6-fold axis along the  $\mathbf{c}_0$  direction does not hold. Since the 6-fold symmetry is a manifold of 3- or 2-fold symmetry, only 2- or 3-fold axes can exist along the  $\mathbf{c}_0$  direction. As a consequence, the 4-fold axis for the tetragonal compounds is necessarily perpendicular to the  $\mathbf{c}_0$  direction as it is actually found for the tetragonal iron arsenide Fe<sub>2</sub>As.

Provided that judicious choice of fundamental vectors is made (i.e., for example  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{B} = f_2(\mathbf{b}_0)$ , and  $\mathbf{C} = \mathbf{c}_0$ ,

orthorhombic and (or) tetragonal symmetry are attainable if the coefficients  $h$ ,  $k$ ,  $s$ , and  $t$  verify  $2.s = h$  with  $k = 0$ ,  $t > 0$ . Various vectorial combinations satisfying this criterion are listed in Table 4 together with the expected crystallographic data for the different members. Examples of tetragonal and orthorhombic structures are given in projection onto the (001) plane in Fig. 7. As previously mentioned, the ratio  $a_0/c_0$  (or  $b_0/c_0$ ) in the basic hexagonal prism is near unity so tetragonal symmetry has to be expected when  $\mathbf{B} = \mathbf{b}_0$ .

When the  $h$ ,  $k$ ,  $s$ , and  $t$  do not satisfy the conditions mentioned above, the monoclinic symmetry is obtained. To our knowledge, the only compounds with such a symmetry are the ternary phosphite UCr<sub>5</sub>P<sub>3</sub> (35) and related compounds and the defective quaternary arsenide LaZr<sub>2</sub>Ni<sub>4</sub>As<sub>4</sub> (36) with the 2-fold axis along  $\mathbf{c}_0$  (Fig. 8). The unit cell vectors of UCr<sub>5</sub>P<sub>3</sub> are  $\mathbf{A} = 2.\mathbf{b}_0$ ,  $\mathbf{B} = 3.\mathbf{a}_0 + \mathbf{b}_0$ , and  $\mathbf{C} = \mathbf{c}_0$  ( $h = 0$ ,  $k = 3$ ,  $s = 2$ ,  $t = 1$ ) with the respective magnitudes  $A = 2.a_0$ ,  $B = 7^{1/2}.a_0$ , and  $C = c_0$ . The expected values ( $B/A$ ,  $C/A$ , and  $C/B$  ratios of 1.376, 0.532, and 0.386 and



**FIG. 5.** Idealized structures for the first members of the hexagonal series of  $M_{-2}X$  ( $X = \text{P}, \text{Si}$ ) compounds given in projection onto the (001) plane: the first terms are  $\text{YbPtP}$  and  $\text{Fe}_2\text{P}$  structures (see Fig. 2 and Fig. 4),  $\text{LiCo}_6\text{P}_4$  (a),  $\text{Zr}_2\text{Fe}_{12}\text{P}_7$  (b),  $\text{Zr}_4\text{Co}_{13}\text{Si}_9$  (c),  $\text{Ho}_5\text{Ni}_{19}\text{P}_{12}$  (d), and  $\text{Zr}_6\text{Ni}_{20}\text{P}_{13}$  (e). Large circles represent the less electronegative and larger metal atoms, medium circles represent the more electronegative and smaller metal atoms, and small circles are nonmetal atoms. Full and open circles are translated from each other by half the translation vector of the projection direction (same remarks as for Fig. 4).

$\gamma$  angle of  $100.05^\circ$ ) compare well with the experimental ones (respectively,  $1.359$ ,  $0.455$ ,  $0.335$ , and  $100.36^\circ$ ). In the same manner,  $\text{LaZr}_2\text{Ni}_4\text{As}_4$  is described by  $\mathbf{A} = -\mathbf{a}_0 + 2\mathbf{b}_0$ ,  $\mathbf{B} = 3\mathbf{a}_0 + 2\mathbf{b}_0$ , and  $\mathbf{C} = \mathbf{c}_0$  ( $h = -1$ ,  $k = 3$ ,  $s = 2$ ,  $t = 2$ ) with the respective magnitudes  $A = 7^{1/2}.a_0$ ,

$B = 7^{1/2}.a_0$ , and  $C = c_0$ . The experimental values (angle of  $97.56^\circ$ ,  $B/A$ ,  $C/A$ , and  $C/B$  ratios of  $0.98$ ,  $0.402$ , and  $0.411$ ) are close to those calculated (respectively,  $97.41^\circ$  and  $1$ ,  $0.378$ , and  $0.378$ ). These latter examples are a further confirmation of the adequacy of the model presented.

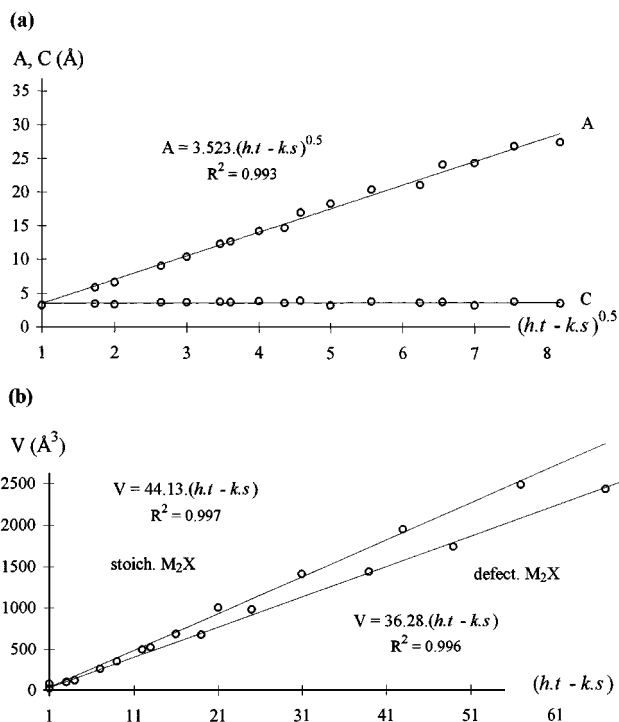


FIG. 6. Experimental unit cell parameters  $A$  and  $C$  ( $h.t - k.s$ )<sup>1/2</sup> (a) and volumes  $V$  ( $h.t - k.s$ ) (b) for the hexagonal series of  $M_2X$  compounds. The  $a_0$  value ( $a_0 = 3.523 \text{ \AA}$ ) and  $V_0$  values ( $V_0 = 44.13 \text{ \AA}^3$  and  $V_0 = 36.28 \text{ \AA}^3$  for stoichiometric and defective compounds, respectively) have been obtained from linear regression. The values of the regression coefficients  $R^2$  confirm the validity of the model.

## CONCLUSION

A generalized crystal chemical model to describe numerous structure types in pnictide, silicide, ... chemistry has been presented by considering hexagonal elementary units of volume  $V_0$  with composition  $M_2X$  and the fundamental vectors  $\mathbf{a}_0$ ,  $\mathbf{b}_0$ , and  $\mathbf{c}_0$ . Insofar as no superstructures are considered along the  $\mathbf{c}_0$  direction, the resulting structures described herein by the vectors  $\mathbf{A} = f_1(\mathbf{a}_0, \mathbf{b}_0)$ ,  $\mathbf{B} = f_2(\mathbf{a}_0, \mathbf{b}_0)$ , and  $\mathbf{C} = \mathbf{c}_0$  consist of identical  $M_2X$  slabs stacked along  $\mathbf{c}_0$ . The metal atoms are piled up in the sequence  $\dots(AB)^\infty\dots$  (h.c. packing) while the nonmetal atoms are ordered in the metallic planes in the stacking sequence  $\dots(A)^\infty\dots$  or  $\dots(B)^\infty\dots$  leading to the two different units  $U_I$  and  $U_{II}$ . The structures of numerous compounds have been described in terms of intergrowth mechanisms of these two units. The model presented herein clearly shows that further investigations must lead to new  $M_2X$  compounds and provides the theoreticians with a useful tool to achieve band structure calculations.

Moreover, if  $\mathbf{C} = l\mathbf{c}_0$  ( $l > 1$ ), related structures can be explained from the same fundamental units intergrown to form slabs (e.g., hexagonal  $\text{Ni}_2\text{In}$ -type  $\mathbf{C} = 2\mathbf{c}_0$ , hexagonal  $\text{TbNiP}$ -type  $\mathbf{C} = 4\mathbf{c}_0$  (1)). But this possibility induces that at least one of the slabs is rotated by  $180^\circ$  around the 3-fold axis of the slab. The different possibilities of slab stacking give rise to the formation of numerous structures as polytypes. This will be discussed in a later paper.

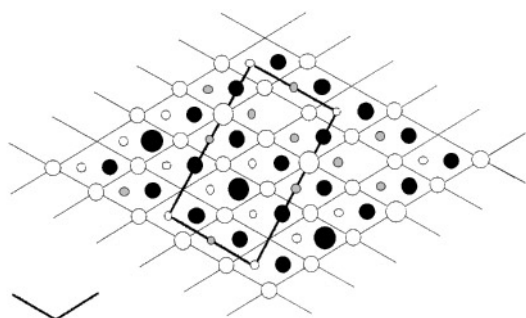
TABLE 4  
Series of Tetragonal and (or) Orthorhombic  $M_2X$  Compounds

$s.t$	$\mathbf{A} = s.(2\mathbf{a}_0 + \mathbf{b}_0)$	$\mathbf{B} = t.\mathbf{b}_0$	$A/B$		Symmetry		Structure type
			th.	exp. <sup>a</sup>	th.	exp. <sup>a</sup>	
1	$2\mathbf{a}_0 + \mathbf{b}_0$	$\mathbf{b}_0$	1.732	1.647	T	T	$\text{Fe}_2\text{As}$ (12)
2	$2\mathbf{a}_0 + \mathbf{b}_0$	$2\mathbf{b}_0$	0.866	0.854	O	O	$\text{Co}_2\text{P}$ (13)
	$4\mathbf{a}_0 + 2\mathbf{b}_0$	$\mathbf{b}_0$	3.464		T		?
3	$2\mathbf{a}_0 + \mathbf{b}_0$	$3\mathbf{b}_0$	0.577		O		?
	$6\mathbf{a}_0 + 3\mathbf{b}_0$	$\mathbf{b}_0$	5.196		T		?
4	$2\mathbf{a}_0 + \mathbf{b}_0$	$4\mathbf{b}_0$	0.433	0.419	O	O	$\text{Pd}_{-12}\text{Mn}_{-4}\text{Ge}_8$ (37)
	$4\mathbf{a}_0 + 2\mathbf{b}_0$	$2\mathbf{b}_0$	1.732	1.712	O	O	$\beta\text{-UCr}_6\text{P}_4$ (38)
	$8\mathbf{a}_0 + 4\mathbf{b}_0$	$\mathbf{b}_0$	6.928		T		?
5	$2\mathbf{a}_0 + \mathbf{b}_0$	$5\mathbf{b}_0$	0.346	0.346	O	O	$\text{CoNbB}$ (39)
	$10\mathbf{a}_0 + 5\mathbf{b}_0$	$\mathbf{b}_0$	8.660		O		?
6	$2\mathbf{a}_0 + \mathbf{b}_0$	$6\mathbf{b}_0$	0.289		O		?
	$4\mathbf{a}_0 + 2\mathbf{b}_0$	$3\mathbf{b}_0$	1.154	1.145,	O	O	$\text{YCo}_5\text{P}_3$ (40),
				1.158	O	O	$\text{HoCo}_3\text{P}_2$ (41),
	$6\mathbf{a}_0 + 3\mathbf{b}_0$	$2\mathbf{b}_0$	2.598	2.839	O	O	$\text{UNi}_5\text{Si}_3$ (42)
	$12\mathbf{a}_0 + 6\mathbf{b}_0$	$\mathbf{b}_0$	10.392		T		?

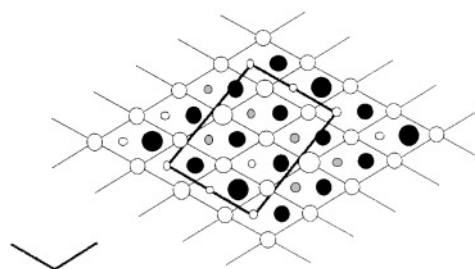
Note.  $\mathbf{A} = s.(2\mathbf{a}_0 + \mathbf{b}_0)$ ,  $\mathbf{B} = t.\mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$ ,  $t > 0$  with  $A = 3^{1/2}.s.a_0$ ,  $B = t.a_0$ ,  $C = c_0$ . The volume is  $V/V_0 = 2.s.t$ . and the ratio  $A/B = 3^{1/2}.(s/t)$ . Note that the combinations  $\mathbf{A} = 2\mathbf{a}_0 + \mathbf{b}_0$ ,  $\mathbf{B} = \mathbf{b}_0$ ,  $\mathbf{C} = \mathbf{c}_0$  with the volume  $V = 2.V_0$  describe the "orthohexagonal" unit cell of iron arsenide  $\text{Fe}_2\text{As}$ .

<sup>a</sup>th. means theoretical, exp. means experimental and the symbols O and T hold for orthorhombic and tetragonal symmetry, respectively.

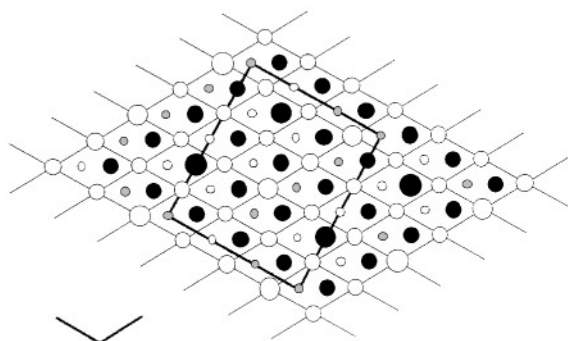




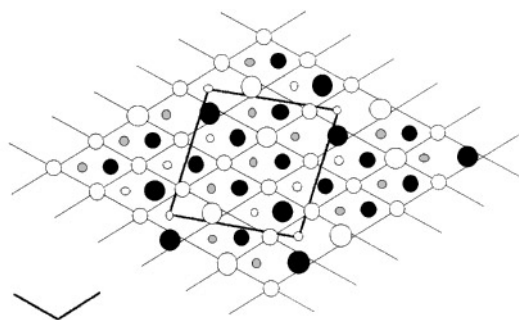
(a)  $\beta\text{-U}_6\text{P}_4 : \text{U}_I^4\text{U}_{II}^4$ .



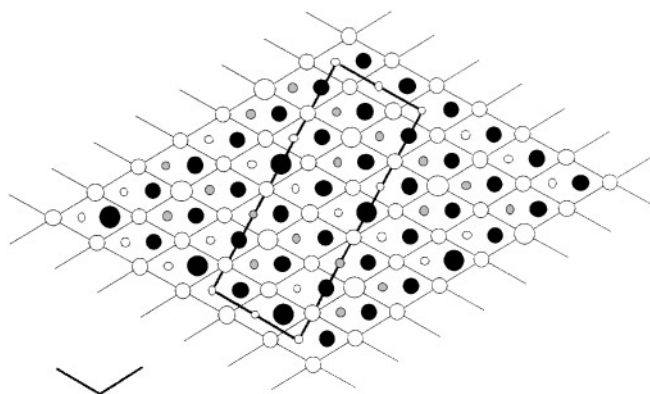
(a)  $\text{U}_6\text{P}_3 : \text{U}_I^3\text{U}_{II}^3$ .



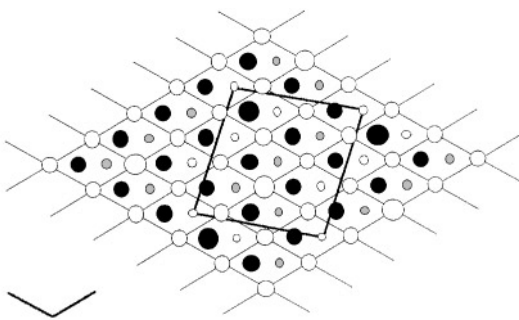
(b)  $\text{Y}_6\text{Co}_4\text{P}_3 : \text{U}_I^6\text{U}_{II}^6$ .



(b)  $\text{La}_6\text{Zr}_1\text{Zr}_1\text{Ni}_4\text{As}_4 : \text{U}_I^4\text{U}_{II}^4$ .



(c)  $\text{U}_6\text{Ni}_1\text{Ni}_4\text{Si}_3 : \text{U}_I^6\text{U}_{II}^6$ .



(c)  $\text{M}'_6\text{M}'_2\text{M}'_5\text{X}_4 : \text{U}_I^4\text{U}_{II}^4$ .

**FIG. 7.** Idealized structures for members of the tetragonal and orthorhombic series of  $M_2X$  compounds given in projection onto the (001) plane. First members are  $\text{Fe}_2\text{As}$  and  $\text{Co}_2\text{P}$  structures (see Fig. 4); Other members correspond to  $\beta\text{-UCr}_6\text{P}_4$  (a),  $\text{YCo}_3\text{P}_3$  (b), and  $\text{UNi}_5\text{Si}_3$  (c) (same remarks as for Figs. 4 and 5).

**FIG. 8.** Idealized structures of the monoclinic variants  $\text{UCr}_5\text{P}_3$  (a) and  $\text{LaZr}_2\text{Ni}_4\text{As}_4$  (b) given in projection onto the (001) plane. In case of the  $\text{LaZr}_2\text{Ni}_4\text{As}_4$  structure, the metallic deficit is related to zirconium atoms in octahedral sites as previously reported (36). The corresponding stoichiometric structure is given in (c) (same remarks as for Figs. 4 and 5).

## REFERENCES

1. Yu. B. Kuz'ma and S. Chykhrij, "Handbook on the Physics and Chemistry of Rare Earths," (K. A. Gschneidner, Jr and L. Eyring, Eds.), Vol. 23, p. 285, Elsevier Science, Amsterdam, 1996. [See references therein]
2. F. Laves, in "Theory of Alloys Phases," A. S. M., Cleveland, Ohio, 1956.
3. J. Y. Pivan, Thèse d'Université, University of Rennes, France, 1985.
4. Ya. P. Yarmolyuk and L. G. Aksel'rud, *Kristallografiya* **28**, 1111 (1983).
5. R. Madar, V. Ghetta, E. Dharhi, P. Chaudouet, and J. P. Sénateur, *J. Solid State Chem.* **66**, 73 (1987).
6. J. Y. Pivan, R. Guérin, and M. Sergent, *J. Solid State Chem.* **68**, 11 (1987).
7. R. Fruchart, *Ann. Chimie. Fr.* **7**, 563 (1982).
8. J. Roy-Montreuil, Thèse d'Etat, University of Orsay, France, 1982.
9. N. F. M. Henry and K. Lonsdale (Eds.), "International Tables for Crystallography," Vol. I, 2nd ed., The Kynoch Press, Birmingham, 1965.
10. G. Wenski and A. Mewis, *Z. Kristallogr.* **174**, 200 (1986).
11. R. Müller and R. N. Shelton, *J. Less Common Met.* **92**, 177 (1983).
12. S. Rundqvist and F. Jellinek, *Acta Chem. Scand.* **13**, 425 (1959).
13. M. Elander, G. Hägg, and A. Westgren, *Ark. Kem. Mineral. Geol. B* **12**, 1 (1936).
14. S. Rundqvist, *Acta Chem. Scand.* **14**, 1951 (1960).
15. E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, and R. Gladyshevskii, in "Gmelin Handbook of Inorganic and Organometallic Chemistry, 8th ed.," Springer-Verlag, Berlin, 1993. [see references therein]
16. S. Rundqvist and T. Lundström, *Acta Chem. Scand.* **17**, 37 (1963).
17. E. Parthé and V. Sadagopan, *Monatsh. Chem.* **93**, 263 (1962).
18. R. Buschmann and H. U. Schuster, *Z. Naturforsch. B, Chem. Sci.* **46**, 699 (1991).
19. H. K. Chun and G. B. Carpenter, *Acta Crystallogr., Sect. B* **35**, 30 (1979).
20. E. Ganglberger, *Monatsh. Chem.* **99**, 557 (1968).
21. E. I. Gladyshevskii and Yu. N. Grin, *Sov. Phys. Kristallogr.* **26**(6), 683 (1981).
22. E. Ganglberger, *Monatsh. Chem.* **99**, 566 (1968).
23. J. Y. Pivan, R. Guérin, and M. Sergent, *Inorg. Chem. Acta* **109**(3), 221 (1985).
24. I. Engström, *Acta Chem. Scand.* **19**, 1924 (1965).
25. R. Guérin, E. H. El Ghadraoui, J. Y. Pivan, J. Padiou, and M. Sergent, *Mater. Res. Bull.* **19**, 1257 (1984).
26. V. S. Babizhets'ky, S. I. Chykhrij, S. V. Oryshchyn, and Yu. B. Kuz'ma, *Zh. Neorg. Khim.* **37**, 2660 (1992).
27. Ya. P. Yarmolyuk, L. G. Aksel'rud, and E. I. Gladyshevskii, *Kristallografiya* **23**, 942 (1978).
28. R. Brink and W. Jeitschko, *Z. Kristallogr.* **178**, 34 (1987).
29. J. Y. Pivan and R. Guérin, *J. Less Common Met.* **120**, 247 (1986).
30. S. I. Chykhrij, V. S. Babizhet'sky, S. V. Oryshchyn, and Yu. B. Kuz'ma, *Kristallografiya* **38**, 262 (1993).
31. Ya. P. Yarmolyuk, L. G. Aksel'rud, V. S. Fundamenskii, and E. I. Gladyshevskii, *Sov. Phys. Kristallogr.* **25**, 97 (1980).
32. J. Y. Pivan, R. Guérin, and M. Sergent, *Mater. Res. Bull.* **20**, 887 (1985).
33. R. Brink and W. Jeitschko, *Z. Kristallogr.* **182**, 46 (1988).
34. J. Y. Pivan, R. Guérin, O. Peña, J. Padiou, and M. Sergent, *Mater. Res. Bull.* **23**, 513 (1988).
35. W. Jeitschko, R. Brink, and P. G. Pollmeier, *Z. Naturforsch. B* **48**, 52 (1993).
36. E. H. El Ghadraoui, J. Y. Pivan, and R. Guérin, *J. Solid State Chem.* **78**, 262 (1989).
37. G. Venturini, B. Malaman, J. Steimetz, and B. Roques, *Mater. Res. Bull.* **16**, 715 (1981).
38. W. Jeitschko and R. Brink, *Z. Naturforsch. B* **47**, 192 (1992).
39. I. Krypyakevich, Yu. B. Kuz'ma, V. Voroshilov, G. B. Shoemaker, and D. P. Shoemaker, *Acta Crystallogr., Sect. B* **27**, 257 (1971).
40. U. Meisen and W. Jeitschko, *J. Less Common Met.* **102**, 127 (1984).
41. W. Jeitschko and U. Jakubowski, *J. Less Common Met.* **110**, 339 (1985).
42. G. Aksel'rud, V. I. Yarovets, O. I. Bodak, Ya. P. Yarmolyuk, and E. I. Gladyshevskii, *Sov. Phys. Kristallogr.* **21**, 210 (1976).