Semimetal Clustering in Intermetallic Phases*

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The alkali and alkaline earth metals combine with the semimetals to form not only compounds with salt-like stoichiometries but also numerous compounds in which clustering of the semimetals occurs. Chains, rings, and cages of different lengths and sizes, as well as infinite sheets and porous frameworks are encountered. The constituents of these units are metalloids of the same type that belong to the third, fourth, and fifth main groups, as well as combinations of them. Starting with the ionic formulation, most of these anionic clusters are determined by the (8-N) rule. The principal significance and the limits of these concepts are discussed. © 1985 Academic Press, Inc.

Introduction

The semimetals of the fourth and fifth main groups exhibit structures which are determined by as many covalent bonds as required by the (8-N) rule. When these materials are reacted with alkali or alkaline earth metals, the semimetals acquire electrons from the non-noble metals because of their high electronegativities. If the number of donors is sufficient, the semimetals fill their octet completely and "salt-like" structures are encountered, in which the semimetal atoms are isolated; i.e., they have only non-noble metals as neighbors, with no bonds to other semimetals. If the transferred electrons do not fill the octet,

clustering of the semimetals occurs by forming as many two-electron single bonds as are necessary to form octets for all member atoms. In what follows we will demonstrate the importance as well as the limits of these basic considerations for the interpretation of the stoichiometries and structures of these intermetallic compounds (Zintl phases (*1*)). The discussion is focused mainly on the structural features; due to space limitations it is not possible to cover all related compounds (*1*).

Binary Compounds

In Fig. 1 are summarized the structural patterns hitherto found in the binary element(V) compounds with the non-noble metals. The phosphides are omitted as v. Schnering has recently described in a review article (*2*). Sketched on top of Fig. 1 are the sheet structures of the heavy ele-

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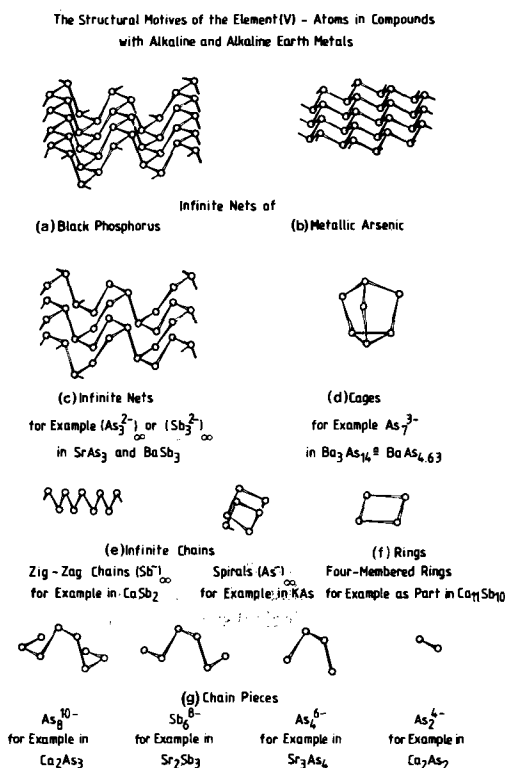
The Structural Motives of the Element(V) - Atoms in Compounds
with Alkaline and Alkaline Earth Metals

Infinite Nets of

(a) Black Phosphorus

(b) Metallic Arsenic

(c) Infinite Nets

for Example $(As_3^{2-})_\infty$ or $(Sb_3^{2-})_\infty$
in $SrAs_3$ and $BaSb_3$

(d) Cages

for Example As_7^{3-}
in $Ba_3As_{14} \triangleq BaAs_{4.63}$

(e) Infinite Chains
Zig - Zag Chains $(Sb^-)_\infty$ Spirals $(As^-)_\infty$
for Example in $CaSb_2$ for Example in KAs

(f) Rings
Four-Membered Rings
for Example as Part in $Ca_{11}Sb_{10}$

(g) Chain Pieces

As_8^{10-}	Sb_6^{8-}	As_4^{6-}	As_2^{4-}
for Example in	for Example in	for Example in	for Example in
Ca_2As_3	Sr_2Sb_3	Sr_3As_4	Ca_2As_2

FIG. 1. The structural features of alkali and alkaline earth pnictides.

ments of the fifth main group, the black phosphorus type (Fig. 1a), and the arsenic type (Fig. 1b). Both contain only three-bonded atoms according to the (8-N) rule.

When alloying with non-noble metals these nets gain electrons, so many bonds are broken as required by the number of electrons brought in. One can demonstrate this feature in the structure of $SrAs_3$ (Fig. 1c) (3, 4). Two As atoms of the formula unit take one electron each of the two Sr electrons. Counting these, they have six electrons in the outer shell, as do the chalcogen atoms in elemental form; therefore, they form only two covalent bonds to complete the octet. The last arsenic atom, having no possibility to obtain electrons from the Sr atoms, must form three bonds, as in the elemental structure itself. Two-dimen-

sional nets are formed with a wide mesh of 14 atoms, which show a remarkable relation (compare Figs. 1c and a) to the net of the black phosphorus type. Parts of the neutral net have been omitted. However, this similarity is not as significant as one might think: this is demonstrated by the anionic part of the structure of $BaAs_{4.63}$ $\triangleq$ Ba_3As_{14} (Fig. 1d) (5) which shows no direct relation to the elemental structures, although the stoichiometry is comparable to that of $SrAs_3$. Also in this case, the electrons provided by the alkaline earth atoms are not sufficient in number to provide every As atom with one additional electron. Thus, as in $SrAs_3$, three-bonded and two-bonded As atoms occur, forming a cage, so that through charge and bonding all the member atoms complete their octet. The resulting As_7^{3-} anion is isosteric to the well-known P_4S_3 molecule. If the alkali or alkaline earth metals content in the compound is high enough so that every element (V) atom acquires one electron, chains are formed. They may be planar zigzag rows as in $CaSb_2$ or $SrSb_2$ (6, 7) or spirals such as in LiAs (8) or KAs (Fig. 1e). The chains may be closed to form rings, for example, four-membered rings, as found in part of the structure in the $Ca_{11}Sb_{10}$ phase (9) (Fig. 1f). When additional electrons are brought in by increasing the content of non-noble metals, the chains are split into fragments (Fig. 1g). Eight-membered (10), six-membered (11), four-membered pieces (10, 12), and dumbbells (13, 14) have been reported. The structure of Sr_3As_4 (12) is cited as an example in Fig. 2 to demonstrate explicitly the relation between structure and stoichiometry: here one encounters four-membered chains. One can calculate the charge of these by examining the numbers of bonds. The two-bonded arsenic atoms in the middle behave like the element (VI), they therefore have a charge of -1. The terminal atoms are one-bonded, like the halogens; they therefore are assigned a charge of -2.
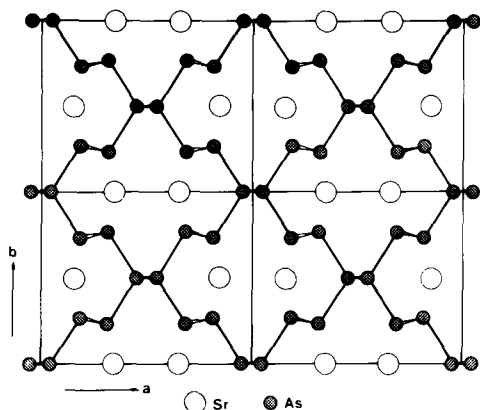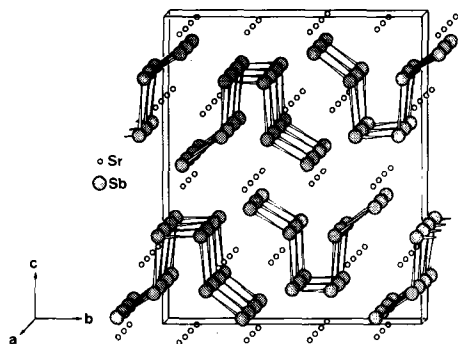
FIG. 2. The structure of SrAs$_3$.

Altogether, a charge of -6 for the whole unit must be compensated by the alkaline earth ions. An analogous explanation holds for the six-membered piece found in Sr$_2$Sb$_3$ (Fig. 3) (11), and for the combination of the eight- and four-membered pieces in Ca$_2$As$_3$ (Fig. 4) (10).

The compounds of the group(IV) elements show analogous structural features, the only difference, being that with the same number of bonds, the charges are higher. The structural patterns, found up to this point, are summarized in Fig. 5. Si$_2^{6-}$ dumbbells analogous to the isoelectronic As$_2^{4-}$ dumbbells are formed in several compounds (15–17). Infinite (Si, Ge, Sn, Pb)$^{2-}$ zigzag chains corresponding to the isosteric

Sb$^-$ chains are observed in many cases (18–20). Also, the structural principles of the element(V) themselves are encountered in suitable compounds. The connection principle of the white phosphorus—P$_4$-tetrahedra—for example, are duplicated as Si$_4^{4-}$ tetrahedra in KSi or BaSi$_2$ (21–23). Si$^-$ and Ge$^-$ nets, isosteric to the neutral As nets, are stacked in several CaSi$_2$ and CaGe$_2$ modifications (24–26), as determined by the kind of the donors between them. Of special interest is the fact that some compounds exhibit connection principles which the group(V) elements themselves do not form but which are encountered in the structures of SrSi$_2$ (27) and LiGe (28). In both cases, and in accord with the (8-N) rule, three-bonded Si$^-$ or Ge$^-$ atoms form frameworks with the cations in the voids (Fig. 6). Apparently, when formed from group(V) element atoms alone, these structures are too loose to be stable.

Two-bonded and three-bonded Si atoms in combination are realized in Ba$_3$Si$_4$ (29). The oligomeric Si$_4$ unit (Fig. 7) can be roughly described as a Si$_4$ tetrahedron with one broken edge. The resulting two triangles with one common side, inclined to each other by an angle of 113°, are surrounded by only Ba atoms. From the (8-N) rule, one calculates a charge of -2 for the two-bonded Si atoms and a charge of -1, for the three-bonded atom. The -6 charge

FIG. 3. The structure of Sr$_2$Sb$_3$.
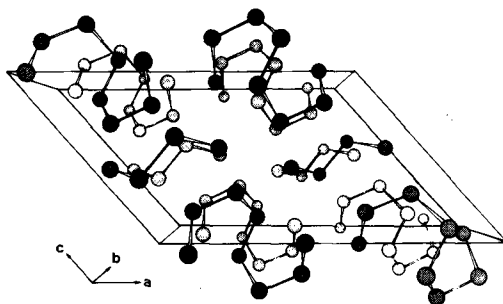
FIG. 4. The arsenic substructure in Ca$_2$As$_3$.

The Structural Motives of the Element (IV) atoms in Compounds
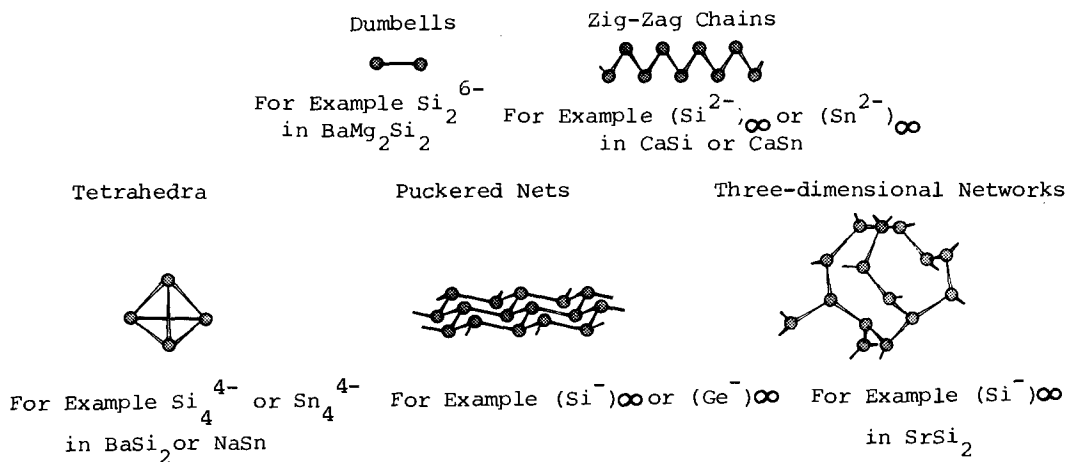with Alkaline and Alkaline Earth Metals

Dumbells

For Example Si_2^{6-}
in $BaMg_2Si_2$

Zig-Zag Chains

For Example $(Si^{2-})_\infty$ or $(Sn^{2-})_\infty$
in CaSi or CaSn

Tetrahedra

Puckered Nets

Three-dimensional Networks

For Example Si_4^{4-} or Sn_4^{4-}
in $BaSi_2$ or NaSn

For Example $(Si^-)_\infty$ or $(Ge^-)_\infty$

For Example $(Si^-)_\infty$
in $SrSi_2$

FIG. 5. The structural features of alkali and alkaline earth tetrelides.

◉ Si ○ Sr

◉ Ge ○ Li

Three-dimensional Element (IV) Networks in
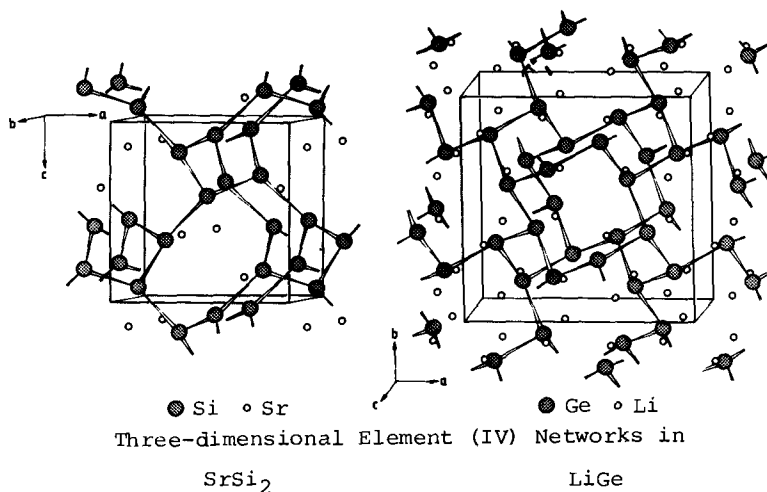
$SrSi_2$

LiGe

FIG. 6. The structures of $SrSi_2$ and LiGe.

of the whole unit is compensated by the three Ba ions.

When group(III) elements are combined with the alkali metals, we must first mention, as a tribute to history, the famous NaTl structure, determined by Zintl (30), who created the basis of the ideas presented. The Tl atoms by themselves form the diamond structure. They form four bonds with each other for which purpose they also need the electrons of the alkali

metals, which are located in the holes of this framework. These binary systems alkali metal/element(III) contain additional phases with very complicated stoichiometries, which are summarized in Table I for the Ga compounds. The Li compounds are excluded because in many cases they show a peculiar behavior with respect to their structures and stoichiometries (58–62). A common feature of all compounds (Table I), is that they contain more group(III) ele-
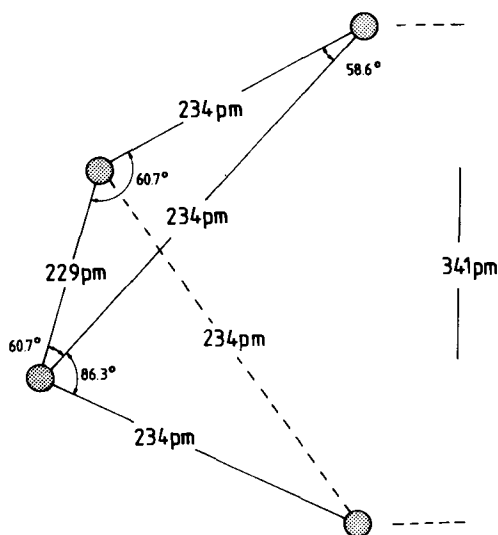
FIG. 7. The isolated Si_4 unit in Ba_3Si_4.

The Ga_{12} - Icosahedra
(Distances in pm)

The Ga_{15} - Cluster
(Distances in pm)

FIG. 8. The Ga clusters in $Na_7Ga_{13}(I)$.

ment atoms than alkali atoms. This fact already makes it clear that the simple interpretation used until now is not appropriate for these compounds. The Ga atoms, which, because of the stoichiometry, gain no electrons from the alkali atoms cannot complete their octet by forming single bonds only; they do not have enough electrons with which to form a sufficient number of bonds. The structures of all these compounds are very complicated forming big cells (31–36). Therefore, we describe here the atomic arrangement of only one compound, Na_7Ga_{13} (31), to illustrate the essential principles. In this structure, the Ga atoms form three characteristic clusters (Fig. 8); two different icosahedra, and a Ga_{15} polyhedron. The arrangement of the icosahedra alone is shown in Fig. 9. Each sphere in this picture symbolizes an icosahedron. One type of these icosahedra is connected to planar sheets perpendicular to a trigonal axis. These sheets may be de-

TABLE I

INTERMETALLIC COMPOUNDS OF GALLIUM WITH ALKALI METALS; INTERPRETATION ACCORDING TO WADE'S RULES WITH (37) DIFFERENT SKELETONS

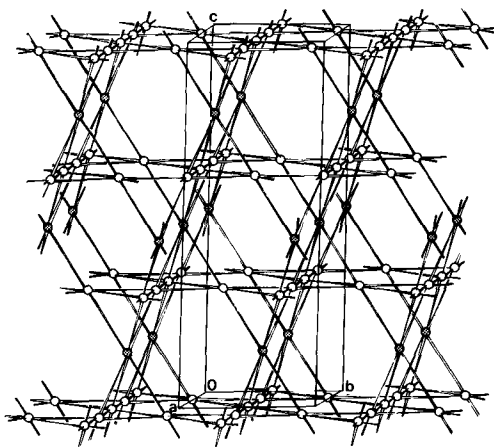|	Skeletons			
	Icosahedra	Octadecahedra	Dodecahedra	Undecahedra
$Na_7Ga_{13}(I)$ (31)	×			×
$Na_7Ga_{13}(II)$ (32)	×			×
$(Na_{22}Ga_{39})$ (34)				
K_3Ga_{13} (33)	×	×		
$RbGa_3$ (35)			×	
$RbGa_7$, $CsGa_7$ (36)	×			

FIG. 9. The arrangement of the Ga_{12} icosahedra in $Na_7Ga_{13}(I)$ (different spheres correspond to the different icosahedra).

scribed as Kagomé nets which are staggered and connected by the additional icosahedra in the same manner as the Cu atoms in the intermetallic phase $MgCu_2$, which is the most common of the Laves phases. The large voids, filled in the $MgCu_2$ structure with the Mg atoms, contain the Ga_{15} polyhedra. The sodium atoms are located between—not in—these large polyhedra. The fact that the large clusters are empty shows immediately that arguments in favor of a close packing of atoms—which are so powerful for the interpretation of

other classes of intermetallic compounds—do not apply here. Covalent bonds with fixed orientations are apparently essential for this loosely packed structure. For the interpretation it is useful to examine the boron compounds, where similar structural principles are involved. For the stability of such boron icosahedra Wade (38) on the basis of theoretical consideration, postulated a characteristic electron number of 26 for the B_{12} skeleton; we adopt this number for the Ga_{12} icosahedron, as well. For the rare Ga_{15} polyhedron such characteristic numbers are lacking, so that we must assume covalent single bonds for the entire polyhedron, except for the top symmetric triangle, where relatively long Ga–Ga distances of 284.6 pm occur (Fig. 8) for which we postulate a closed two-electron three-center bond. This scheme involves 21 covalent single bonds and one two-electron three-center bond, which require 44 electrons altogether. In addition, all bonding between these clusters, which we call "exobonds," must be taken into account as Wade has done. All atoms in the Ga_{15} polyhedra have those exobonds. Of the 12 Ga icosahedra in the cell only 9 involve exobonds at all atoms. The remainder—three icosahedra—have only 6 exobonds. A total of 792 electrons are necessary for such a Ga structure (Table II). Inside the cell there are

TABLE II

THE VALENCE ELECTRONS PER CELL OF $Na_7Ga_{13}(I)$

|	
Ga_{12} skeleton electrons	$26 \times 12 = 312$
Ga_{12} "exobond" electrons	$12 \times 9 + 6 \times 3 = 126$
Ga_{15} skeleton electrons	$(21 \times 2 + 2) \times 6 = 264$
Ga_{15} "exobond" electrons	$15 \times 6 = 90$
Sum of the bonding electrons for the Ga substructure	792
Number of the valence electrons of the atoms in the cell	$234\ (Ga) \times 3 + 126\ (Na) \times 1$ 828
	$\Delta 36$
18 free electron pairs at the Ga atoms of the 3 icosahedra with no "exobonds"	$3 \times 6 \times 2 = 36$
Ionic formulation: $Na_7Ga_{13} \rightarrow 7\ Na^+ + (Ga_{13}^{7-})_\infty$	
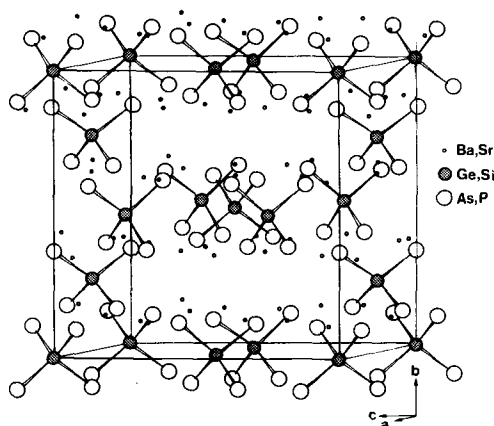
FIG. 10. The Ba_4SiAs_4 structure type.

234 Ga atoms and 126 sodium atoms, which involve 828 valence electrons. At first glance, there appear to be 36 more electrons than are necessary. But remembering the three icosahedra with six Ga atoms that are not exo-bonded, the whole system follows the scheme of Wade, if every Ga atom of these is assigned one nonbonding electron pair, as has been found in many other compounds. Thus there is good reason to characterize these Ga compounds with the unusual composition by the ionic designation of 7 $Na^+(Ga_{13})_n^{7-}$ (*31*) as has been done in the former case for the true Zintl phases. In this case as well the Ga structure as a whole needs the electrons of the alkali atoms to form its complicated cluster structure. The same ideas also apply to the other compounds listed in Table II, investigated both in Darmstadt and in Montpellier, France, by Dr. Belin (*33–37*).

Ternary Compounds

When two semimetals are combined with alkali or alkaline earth metals a large number of compounds can be prepared, which again are intimately related to the salts. To discover the essential principles one starts with those compounds for which one can perceive direct analogies to complex salts. In Fig. 10 the structure of Ba_4SiAs_4 is outlined. There are discrete $SiAs_4^{8-}$, $GeAs_4^{8-}$, or GeP_4^{8-} and SiP_4^{8-} tetrahedra (*39–41*) whose charges are compensated by the alkaline earth cations. One may call these *ortho*-phosphido- or *ortho*-arsenido-silicates or germanates, because the O^{2-} ions in the ordinary silicate SiO_4^{4-} have been replaced by As^{3-} or P^{3-} ions. From the number of bonds one can also calculate the charges. Ge or Si atoms, four bonded, are assigned zero charge, in accord with the (8-N) rule. The P or As atoms form only one bond and therefore behave like the halogen elements; they are given two electrons, and one obtains a total of eight negative charges as mentioned above. Such isolated tetrahedra are also formed with element(III) atoms in combination with group(IV) or group(V) semimetals. This is demonstrated in the compound $Ca_{14}AlSb_{11}$ (Fig. 11) (*42*). Together with the isolated Sb^{3-} ions one also encounters linear Sb_3 groups and $AlSb_4$ tetrahedra in the structure. These units (Fig. 12) are far apart, separated only by Ca ions. The unexpected stoichiometry can be explained by the $AlSb_4$ tetrahedra, which are assigned a charge of nine in conformity with their isosterism to the simple AlO_4^{5-} anion. Again, the O^{2-} ions are replaced by Sb^{3-} ions. To explain the linear Sb_3 group, one has to add up seven negative charges. The linearity results from the electron pair distribution shown in Fig. 12. The terminal antimony atoms have completed octets, but the central one has a decet. According to Gillespie the five electron pairs are arranged in a trigonal bipyramid in which the equatorial sites are occupied by the nonbonding, the free pairs. With these groups we reformulate this compound in accordance with the structural units as
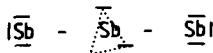
$$Ca_{14}AlSb_{11} \rightarrow 14\ Ca^{2+}$$
$$+ AlSb_4^{9-} + 4\ Sb^{3-} + Sb_3^{7-}$$
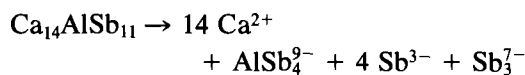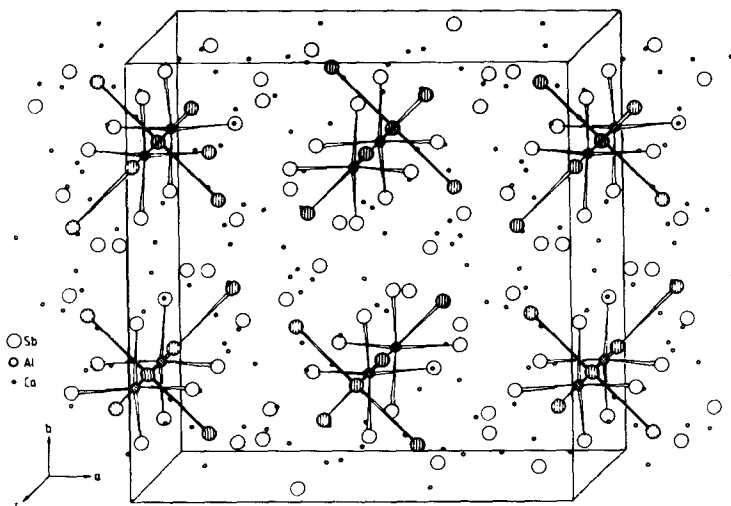
FIG. 11. The structure of $Ca_{14}AlSb_{11}$.
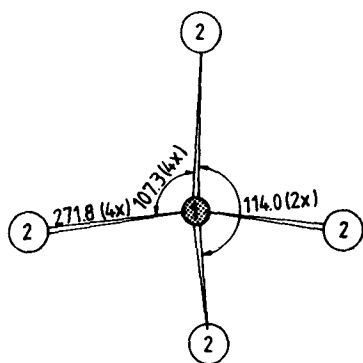
$AlSb_4^{9-}$ - Tetrahedra, Isosteric to AlO_4^{5-}

(Distances in pm, Angles in Degrees)
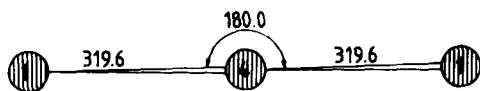
The Sb_3^{7-} - Anion

Electronic Configuration

$$|\overline{Sb} - \overline{\underline{Sb}} - \overline{Sb}|$$

In Accordance to the Structural Units found:

$$Ca_{14}AlSb_{11} \longrightarrow 14\ Ca^{2+} + AlSb_4^{9-} + Sb_3^{7-} + 4\ Sb^{3-}$$
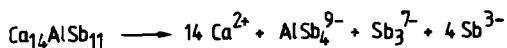
FIG. 12. Anionic units in $Ca_{14}AlSb_{11}$ (in addition to isolated Sb^{3-} anions).

Of the many compounds, related to the above units we select only some examples, to demonstrate the broad applicability of these ideas even to condensed, oligomeric and polymeric units—anionic clusters or polyanions, as one would say in the case of the salts. The examples are chosen according to the increasing degree of polymerization.

In the compound Ba_3AlSb_3 two $AlSb_4$ tetrahedra share a common edge, forming a $Al_2Sb_6^{12-}$ anion (Fig. 13) (43, 44). Al, as a member of the third main group, forms only the observed four bonds, if it is provided one extra electron, so that it becomes isosteric the elements of the fourth main group. The Sb atoms at the common edge form two bonds and behave like elements of the sixth main group; thus, each of them also acquired one extra electron. The terminal Sb atoms form only one bond as the halogens do; so two extra electrons must be added. A total of 12 charges for this unit must be compensated by the Ba ions. This kind of anion structure not only is known in other salts such as the isosteric $Ge_2S_6^{4-}$ or $P_2S_6^{2-}$ ions, but one also finds this connection principle in the isosteric neutral Al_2Cl_6 molecule.
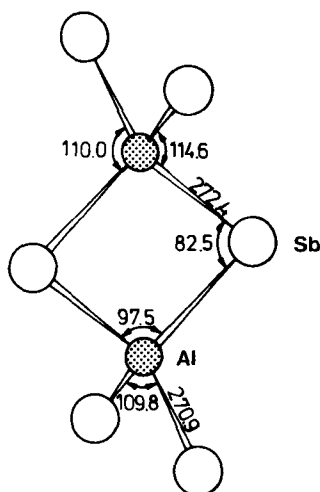
FIG. 13. The $Al_2Sb_6^{12-}$ anion in Ba_3AlSb_3 (distances in pm, angles in degrees).

More common is the connection principle found in the stoichiometrically analogous compound Ca_3AlAs_3 (43) (Fig. 14). $AlAs_4$ tetrahedra are connected by common corners to infinite chains, such as often found in the isosteric polyphosphates (i.e.,
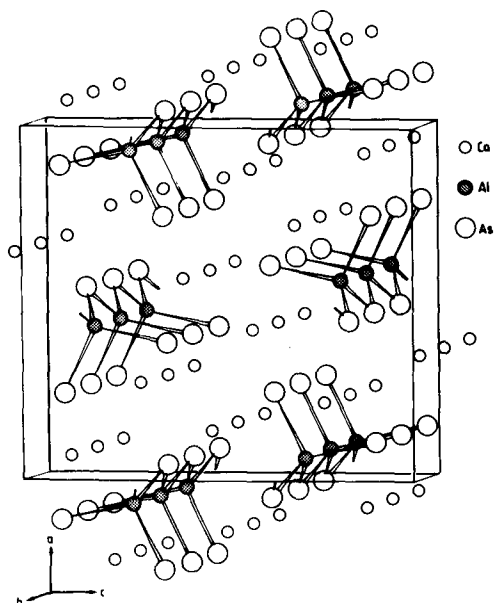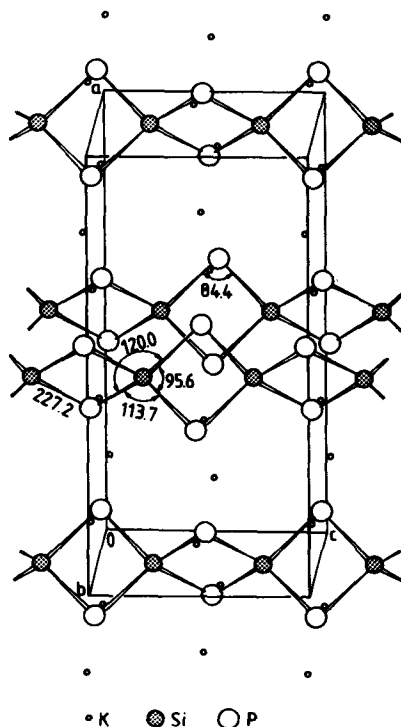

FIG. 14. The structure of Ca_3AlAs_3.

• K   ⊗ Si   ○ P

FIG. 15. The SiP_2 chains in K_2SiP_2.

PO_3^- chains) or polysilicates (i.e., SiO_3^{2-} chains). Again, if one calculates the charge on the basis of the bonds formed, one will find agreement with the number of compensating Ca ions.

Chains are also formed if such tetrahedra are connected by common edges. This is demonstrated in the structure of K_2SiP_2 (45) or K_2GeAs_2 (Fig. 15). SiP_4 tetrahedra are linked together by common edges, as in the famous structure of SiS_2. The substitution of sulfur S^0 by P^- anions yields isosteric chains, whose charges are compensated by potassium ions. The crystals of this compound have the same characteristic mechanical properties as those of SiS_2: namely, they split like a broom, if one touches them too strongly at one end.

Anionic sheet structures we observed for cases such as $Ca_3Al_2As_4$ (Fig. 16) (46). $AlAs_4$ tetrahedra are connected by common
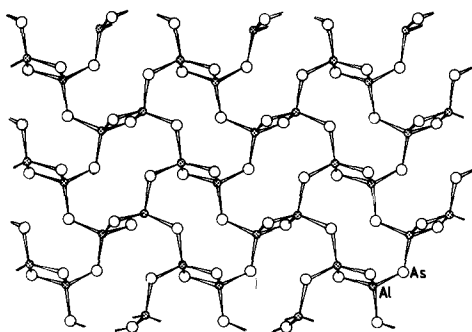
FIG. 16. The $AlAs_2^{3-}$ net in $Ca_3Al_2As_4$, isosteric with the $GaSe_2^-$ net in $CaGa_2Se_4$.

corners and edges to two-dimensional nets of the formula $(AlAs_2^{3-})_n$; the Ca ions are located between them. In this case one can find direct analogous chalcogenides with the same structural features as, for example, in $CaAl_2S_4$ or $CaGa_2Se_4$ (47). The $(GaSe_2^-)_n$ or $(AlSe_2^-)_n$ nets are isosteric and completely identical in regard to the connection principle. Naturally, the stacking must be different because the number of alkaline earth ions compensating the charge is quite different.

A three-dimensional framework of corner-connected $AlGe_4$ tetrahedra is formed in $Ca_3Al_2Ge_3$ (48). As shown in Fig. 17, the $AlGe_4$ tetrahedra are connected to a framework in such a way, that three corners of each tetrahedron are joined to three others, and one corner, to two other tetrahedra.
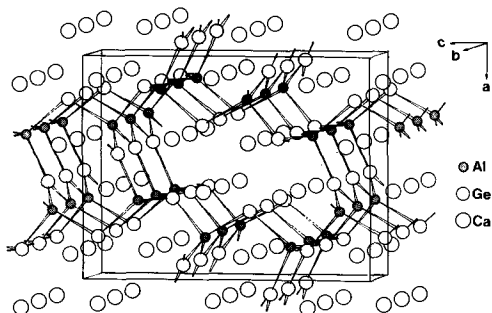
Using the (8-N) rule, one assigns one negative charge each to the four-bonded aluminum atoms, because they behave like the element(IV). The three-bonded Ge atoms require one negative charge because they are isosteric to the element(V); the two-bonded Ge atoms have two negative charges because they behave like the element(VI) atoms. Thus in the Al,Ge partial lattice we obtain a total of six negative charges per formula unit, which are compensated by the Ca^{2+} ions located in the tunnel-like channels of this framework. This colorful array of anions will be further broadened by anions with a formal lower oxidation state of the central atoms. These are analogs to compounds such as the subphosphates or dithionates. Figure 18 shows, as an example, the structure of the silvery compound $Ba_6Sn_2P_6$ (49). Two trigonal SnP_3 pyramids are connected by a Sn–Sn single bond in staggered position to a Sn_2P_6 octahedron. Counting the number of bonds and using the (8-N) rule one assigns
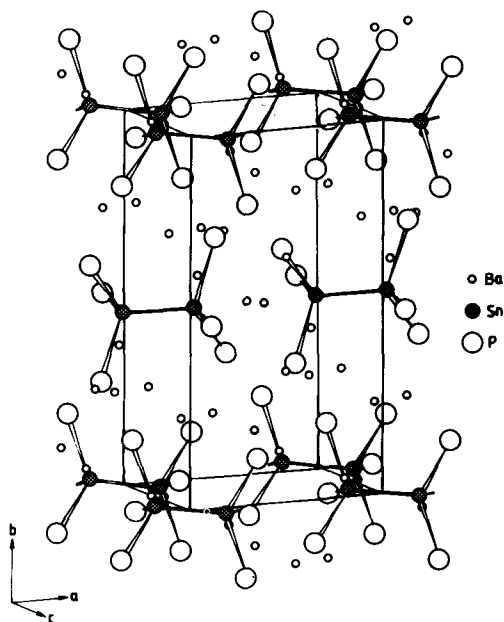

FIG. 17. The structure of $Ca_3Al_2Ge_3$.

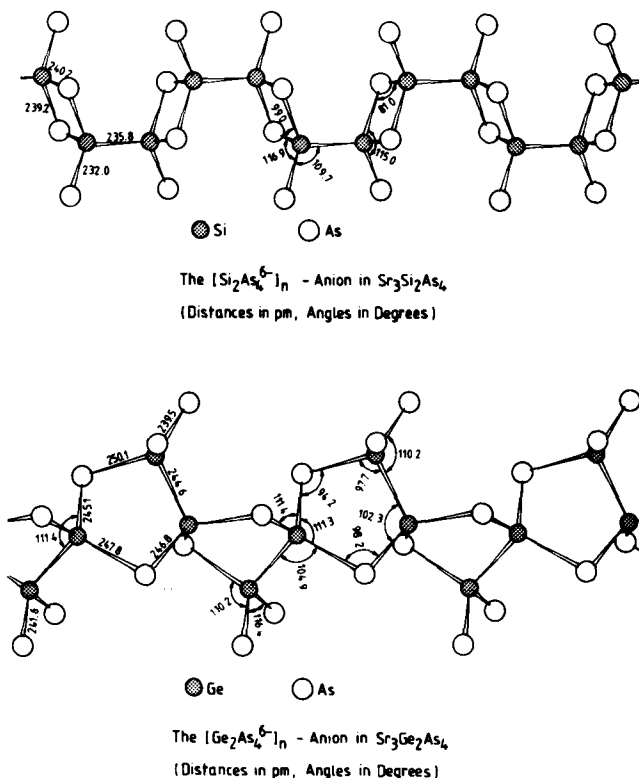FIG. 18. The structure of $Ba_6Sn_2P_6$.

The $[Si_2As_4^{6-}]_n$ – Anion in $Sr_3Si_2As_4$

(Distances in pm, Angles in Degrees)

The $[Ge_2As_4^{6-}]_n$ – Anion in $Sr_3Ge_2As_4$

(Distances in pm, Angles in Degrees)

FIG. 19. The chains in the $Sr_3Si_2As_4$ and $Sr_3Ge_2As_4$ structures.

12 negative charges for this unit, which is isosteric to anions such as $S_2O_6^{2-}$, $P_2O_6^{4-}$, or $Si_2Te_6^{6-}$.

Such units can polymerize, as well. Condensation variants have been found for different combinations of elements. In Fig. 19 are drawn two connecting modes forming $SiAs_2^{3-}$ or $GeAs_2^{3-}$ chains. For the $Sr_3Si_2As_4$ structure type the octahedral (Si_2As_6) units are connected by common edges in such a manner that four-membered rings are formed by two As and two Si atoms (50). More often, the connection principle of the $Sr_3Ge_2As_4$ structure type is observed. Again one encounters X_2B_6 octahedra now sharing common edges such that five-membered rings containing 3 Ge and 2 As atoms are formed. Presumably, these are more stable because in this configuration the

bonding angles are closer to the ideal tetrahedral angle for the element (IV) atoms (50–52).

An essential feature of all these subcompounds is the correlation with dumbbells, i.e., a bonding between atoms of the same kind. But nature does not limit its possibilities to two atoms. This can be shown by means of the structures of the metallic compound $Ba_3Si_4P_6$ (53) (Fig. 20). There are infinite cis–trans chains of Si atoms, which bear Si–P cluster units as shown in Fig. 21. These cluster-carrying chains are further connected to each other by P atoms, so that wave-like sheets result between which the Ba ions are located (Fig. 20). They occur in proper number, which one can calculate from the number of bonds formed in these sheets using the (8-N) rule. Solely the Si_4P_5
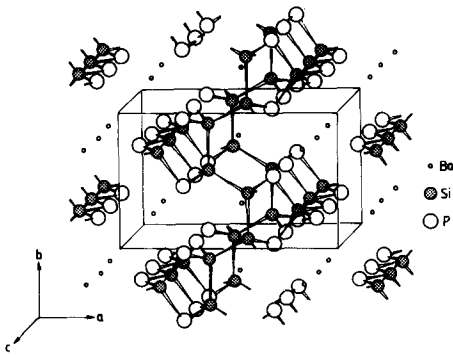
FIG. 20. Perspective drawing of the structure of $Ba_3Si_4P_6$.

FIG. 22. Segment of the AsGe framework in the $BaGe_2As_2$ structure.

cluster in Fig. 21 is isosteric to the P_4S_5 molecule, in which the S atoms are substituted by P, and the P atoms, by Si.

Cis–trans chains are also observed in $BaGe_2As_2$ (54). They run crosswise in the structure, as is demonstrated in part in Fig. 22. These chains are linked together by As atoms to a framework (Fig. 23) in which large tubular channels occur, within which the Ba atoms are located. Again, the stoichiometry can be easily understood on the basis of the structure found by counting the number of bonds and using the (8-N) rule.

In addition to these compounds, where bonds occur in the semimetal sublattice between equal but more electropositive elements the opposite case is observed as well. Direct bonds can also be formed be-
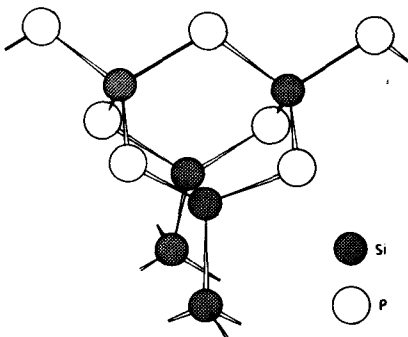
tween the more electronegative atoms. This has been demonstrated, for example, for the metallic compound $Ca_5Al_2Sb_6$ (Fig. 24) (46). Again there are $AlSb_4$ tetrahedra connected by common corners to chains, as in Ca_3AlAs_3 (Fig. 14). But in this case two of those chains are connected by common Sb_2 groups to double chains, running parallel to each other in the structure. Sheets formed by analogous structure elements are found in the silvery compound $Na_7Al_2Sb_5$ (Figs.
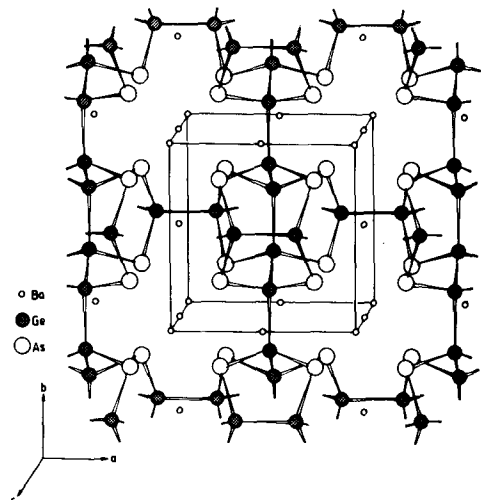

FIG. 21. The Si_4P_5 cage in $Ba_3Si_4P_6$.
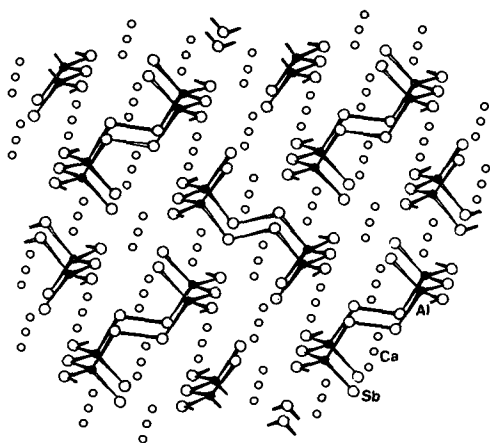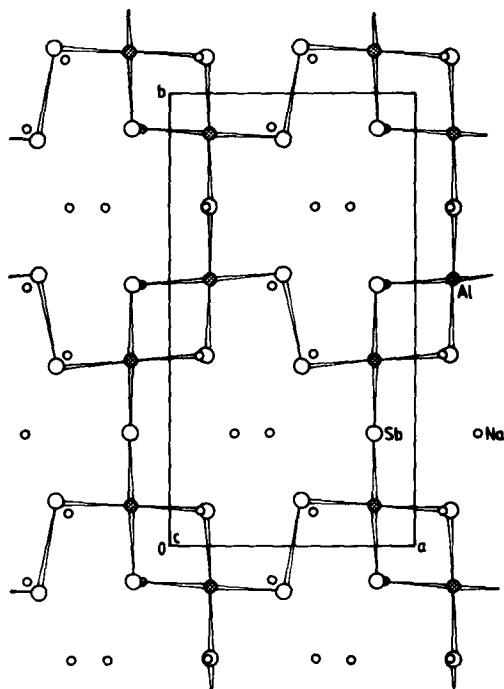

FIG. 23. The $BaGe_2As_2$ structure.

FIG. 24. The structure of $Ca_5Al_2Sb_6$.

FIG. 26. Perspectivic drawing of the Al_2Sb_5 nets in $Na_7Al_2Sb_5$.

25 and 26) (55). $AlSb_4$ tetrahedra, linked by common edges and corners to chains, are connected by Sb_2 dumbbells to two-dimensional nets between which the sodium ions are located. The compound $Na_2Al_2Sb_3$ oc-

curs in the same ternary system (56). In this compound the Al and Sb atoms again form a sheet (Fig. 27). To understand the principle it is useful to concentrate first on the net with distorted Al_3Sb_3 hexagons as meshes. The fourth bonds of the tetrahedrally coordinated Al atoms are saturated by Sb_2 clips. To every clip belong four Al atoms, with their free valences pointing to one side. These "ansa" handles are pointed alternatively in "up" and "down" positions as shown in a projection parallel to the sheet in Fig. 28. This complicated structure also is in conformity with our explanation; electrons are transferred from the alkali metals to the semimetals in numbers sufficient to satisfy the octet rule.

All these compounds referred to here are deeply colored or have metallic luster. They are semiconductors or even poor metallic conductors. However, according to

FIG. 25. Projection of the Al, Sb nets in $Na_7Al_2Sb_5$.
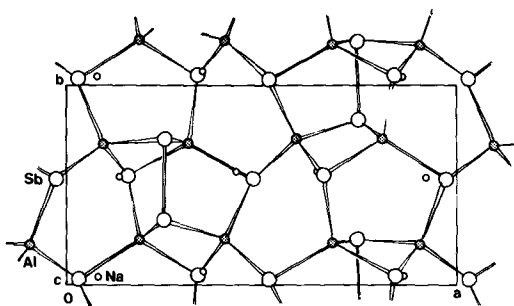
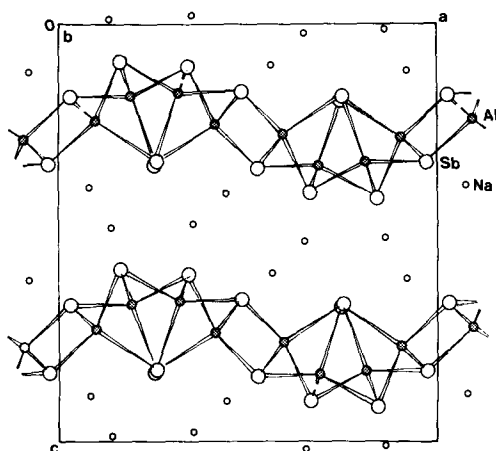FIG. 27. View onto the Al, Sb nets in $Na_2Al_2Sb_3$.

FIG. 28. Projection of the Al, Sb sheets along the *b* axis.

their structures and stoichiometries—which are interpreted in terms of salt-like formation in which there occur clustered semimetals functioning as anions that retain the (8-N) rule—they represent transition forms between the metallic and ionic state. They open up a wide field of new substances which require new bonding concepts for the intermetallic phases. Because of their high reactivity they also are promising substances as starting materials for new molecular compounds in the chemistry of the main group elements.

Acknowledgments

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