

## Chemical clusters from solid state systems at high temperatures. Interstitials as a means to stability and versatility

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**Abstract** - The reactivity of many "naked" clusters and the means by which these may be isolated as stable "chemical" clusters are briefly considered for the orbitally-rich transition metals, where clusters must be sequestered by coordination with ligands, and for the heavier main group elements that utilize only three p orbitals in bonding. Numerous "naked" clusters with favorable close-shell configurations are known for the latter group both as solids at room temperature and in cluster beams. A few binary transition-metal clusters stable at elevated temperatures are obtained with chloride, sulfide, etc. as ligands. Greater versatility and variety have recently been found for electron-precise clusters that require an interstitial atom Z within  $M_6X_{12}$ -type clusters for stability, as with the  $A_3[Zr_6(Z)X_{12}]X_n$  family and rare-earth-element analogs where 22 different examples of Z and many structure types are known for X = Cl, Br, I. A newer and even broader area of cluster chemistry involves interstitials bonded within chains of confacial octahedra in a variety of polar intermetallic phases that occur in the  $Mn_5Si_3$  structure ( $\sim d[Mn_3Si_3 \cdot Mn_2]$ ), where the large differences in valence state energies of the component atoms generally assure that valence bonding levels on the main-group element are filled first. The electron-rich  $Zr_5Sb_3$  host is found to form  $Zr_5Sb_3Z$  phases with at least 16 examples of Z. Band calculational results for the binary host and for the sulfide are considered. Examples of similar investigations are described for the  $Zr_5Sn_3$ ,  $Zr_5Pb_3$ ,  $La_5Ge_3$ ,  $La_5Pb_3$ , and  $M_5B_3$ , M = Ca, Sr or Ba and B = Sb or Bi. Valence-precise (Zintl) phases are achieved in some  $M_5B_3Z$  compounds from the last two groups.

### INTRODUCTION

Clusters of metal atoms are of great interest in materials chemistry as well as in impinging areas of chemistry and physics. At one end of the spectrum are the "naked" homoatomic clusters studied in the gas phase and at the other, condensed nanoscale to micron-sized particles with considerable potential for catalysis, microdevices, etc. (ref. 1). However, metal clusters seen in beam studies usually exhibit little stability discrimination with respect to size in the range of roughly 5 - 25 or more atoms, many appearing to have more of the character of van der Waals or "jellium" molecules than of "chemical" clusters with well defined, closed shell electronic configurations and high stabilities such as are known in more molecular systems,  $P_4$  and  $C_{60}$  for example (ref. 2). The equilibrium electronic structures of small "chemical" clusters of metals should naturally be better described by molecular orbital rather than by band methods suitable to the bulk. However, it appears likely that few if any metal clusters with these closed shell configurations and relatively high stabilities are achieved in most single component beams because of natural limitations on the valence electron counts that can be achieved. Examples of these same clusters are of course unknown in condensed systems because of their intrinsic reactivity. This article will briefly explore the bases for the above behaviors and some exceptions thereto and then will outline the newer aspects of the more stable "chemical" clusters that may be achieved in binary and ternary systems. A new feature of this chemistry is the added versatility and stability achieved for transition metal cluster halides through manipulation of the cluster electron configurations and thereby the phases formed via the encapsulation of interstitial atoms within the clusters. We will also relate the beginnings of a new cluster chemistry that can be achieved in infinite chain structures of some electron-rich polar intermetallic phases with the  $Mn_5Si_3$  structure and the broad interstitial chemistry that is possible therein.

### NAKED CLUSTERS

Transition metals owe much of their prolific chemistry to the profusion of good bonding orbitals, namely (n-1)d, ns and np, but it is this same orbital abundance that precludes the isolation of small naked transition-metal clusters that are stable in bulk. As an example,

a six-metal cluster with octahedral symmetry will exhibit 7 or 8 good cluster-bonding orbitals and an equal number that are strongly antibonding, but this will still leave about half of the d orbitals unused, roughly nonbonding, and, for most metals, partially occupied by valence electrons. Many of these orbitals will be outward pointing and clearly the source of further reactions, condensation, etc. As a result, transition metal clusters will be stable in dense systems only when these orbitals are fully occupied, as is commonly encountered when the clusters are effectively sheathed by neutral ligands (CO, phosphines, etc.) or, sometimes, anions. The usefulness of the 18-electron rule for each metal atom in so many organometallic examples attests well to these orbital requirements and to the existence of a sharply limited number of electronic configurations of special stability in what we chose to call "chemical" clusters. Naturally, the presence of fewer ligands or anions on a cluster surface can be thought of as furthering the condensation of these clusters through additional metal-metal bonding into larger clusters, oligomers, and so forth. Tantalizingly large clusters may be so achieved, e.g., with  $Rh_{13}$ ,  $Pt_{26}$ , or  $Au_{55}$  units suitably encased by ligands (ref. 3). However, most of the useful ligands in these cases fall into the molecular/organic category, and the upper limits of stability for these clusters are low, seldom exceeding a couple of hundred degrees C.

Before moving to the more limited variety of cluster systems that are stable at elevated temperatures, it is worth noting that there is an area of exception to this naked cluster reactivity, and this occurs largely because the constituent elements have a very limited number of good bonding orbitals available. This circumstance applies best to clusters of the post-transition or main-group elements from the silicon, phosphorus and sulfur families in low oxidation states where p orbitals are the principal means for bonding, the increasing s-p separation for elements in the later groups or heavier periods leading to s orbitals that exhibit essentially only nonbonding functions. As in boranes, the three valence orbitals generate strongly bonding, closed shell configurations in several categories; those with  $2n + 2$  electrons in *closo* (regular deltahedral) geometries containing *n* skeletal atoms,  $2n + 4$  electrons in the related *nido* polyhedron where one vertex is missing, etc. Another problem in the isolation of these, as illustrated by the  $Sb_4$  and  $Bi_4$  analogs of  $P_4$ , is that the neutral species inevitably rearrange to the common elemental structures in the condensed state. This tendency can be altered substantially by working with the isoelectronic *ions* so that disproportionation is the limiting reaction, viz.,  $Na_2Bi_4 \rightarrow 2NaBi + 2Bi$ , and by reducing the lattice energy change that favors the decomposition product either through strong complexing of the sodium cations in both binary phases with 2,2,2 crypt, a polyether amine, or by substitution of a large cation, e.g.,  $NR_4^+$ . Examples of such naked clusters, the so-called Zintl anions, that have been isolated in this way include the *closo*  $Sn_5^{2-}$ ,  $Pb_5^{2-}$  and  $TlSn_9^{3-}$ , the *nido*  $Pb_2Sb_2^{2-}$  and  $Sn_6^{4-}$ , and square planar  $Bi_4^{2-}$  (ref. 4). Of course, high temperature stability is lost by these last tricks, but some of these anions, or their isoelectronic analogs, may still be found in a limited number of high temperature systems. Thus,  $Bi_8^{2-}$  and  $Bi_5^{3-}$  can be isolated from molten  $AlCl_4^-$  systems (ref. 5), and some of the smaller or more stable polyanions are found as high melting alkali-metal compounds, viz., as  $As_7^{3-}$  and  $Te_3^{2-}$  as well as the  $P_4$  analogs  $Ge_4^{4-}$ ,  $Sn_4^{4-}$ , etc. (ref. 6).

Naked cluster species with electronic configurations like the boranes and Zintl ions above exhibit stabilities that far exceed those with other electron counts. However, it appears that none of the known, or predictable, closed shell examples cited above can be achieved as neutral or low charged clusters in a beam generated from a single type of atom, except of course for analogs of the long known  $P_4$ . On the other hand, these special "chemical" configurations with their very large stability enhancements can be readily observed in mixed element beams as what have been called "compound clusters", for example, as  $Pb_3Sb_2$ ,  $Pb_2Sb_3^+$  ( $\Delta Sn_5^{2-}$ ),  $Pb_5Sb_4$  ( $\Delta Pb_9^{4-}$ ),  $Cs_5Sn_9^+$  ( $\Delta Sn_9^{4-}$ ) and  $Bi_4In^+$  ( $\Delta Bi_5^{3+}$ ) (ref. 7-10).

### SOLID STATE CLUSTERS BY HIGH TEMPERATURE ROUTES

Inorganic groups that sheath transition metal clusters and render them stable at higher temperatures have traditionally involved the chalcogenides and halides, although examples of the pnictides (As, Sb, etc.) will also be considered later. The classic examples among the chalcogenides are the famous Chevrel phases built from units like  $Mo_6S_8$ , in which a nominal metal octahedron has sulfur strongly bound over each triangular face. Strongly bonding orbitals that remain at each metal vertex cause these to link further, six of the face-capping sulfurs in one cluster also bonding to vertices in six other clusters and vice versa, an arrangement that also provides a Mo-Mo intercluster conduction path and metallicity. Many derivatives such as  $M_xMo_6S_8$  ( $x \leq 4$ ), oligomers  $S(Mo_3S_3)_nS^{m-}$ , and infinite polymer chains  $\frac{1}{2}[Mo_3S_5]$  as well as molybdenum and niobium oxide examples have been discovered and are well described elsewhere (ref. 11-13). Cluster halides of the early transition metals in which interstitials provide an additional versatility represent a still newer chemistry and provide broader insights on cluster stability.

Traditional metal cluster halides are almost always based on transition-metal octahedra that are edge-bridged by 12 halide atoms. The number of binary cluster halides that are possible is relatively low, reflecting a highly restricted range of stable electronic configurations, particularly at elevated temperatures where equilibrium considerations apply. Accordingly,

the known examples involve only  $(\text{Nb,Ta})_6\text{X}_{12}^{2+,3+}$  units for  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , and some  $\text{I}$ , corresponding to clusters with 15 or 16 bonding electrons after the lower lying halogen valence levels are filled. The binary compounds that contain these clusters utilize the additional halide anions in intercluster bridging roles, e.g., in  $\text{Nb}_6\text{Cl}_{14}$ ,  $\text{Ta}_6\text{Cl}_{15}$ , while ternary versions with the same electron counts may be formed with additional alkali-metal halide,  $\text{CsNb}_6\text{Cl}_{15}$  and  $\text{Na}_4\text{Nb}_6\text{Cl}_{18}$  for example. The anion in the last is written more clearly as  $(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6^{4-}$  to show that the last six chlorides are individually bonded at the cluster vertices. Only six structure types and three X:M ratios are known for the lot. An even smaller group of face-capped octahedral cluster halides are known in  $(\text{Nb}_6\text{I}_8)\text{I}_3$  and  $(\text{Mo}_6\text{X}_8)\text{X}_4$  ( $\text{X} \neq \text{F}$ ), but the list can be expanded by including mixed halide-chalcogenide clusters of molybdenum and rhenium (ref. 11, 12).

Several new types of cluster units, as well as a much greater versatility in stoichiometry and structures, have recently been found for the electron-poorer transition metals in groups 3 (rare-earth elements R) and 4 (Zr, Hf). Since the average oxidation state of the metal in an  $\text{M}_6\text{X}_{12}^{m+}$  cluster with a positive charge of  $0 \leq m \leq 3$  (like the group 5 examples above) is +2 to +2.5, analogous clusters composed of these earlier elements would contain only 3 – 6 (R) or 9 – 12 (Zr) metal-metal bonding electrons, significantly below those in any known examples stable at high temperature. The generation of the zirconium clusters with an appreciable negative charge might help, but in fact only those in the rare-earth-metal group seem to form cluster anions. Nature instead provides a new and remarkable way around this shortage of cluster bonding electrons, the encapsulation of an interstitial atom (Z) within the clusters to furnish not only additional electrons but also strong host – Z bonding. The cluster example shown in Fig. 1(a) emphasizes the strong Zr-Z bonding and the halide bonded at each vertex. A considerable range of valence characteristics among the workable Z examples now allows access to a large variety of cluster charge types (compositions), structures and new chemistry, in marked contrast to the small variability known with niobium and tantalum.

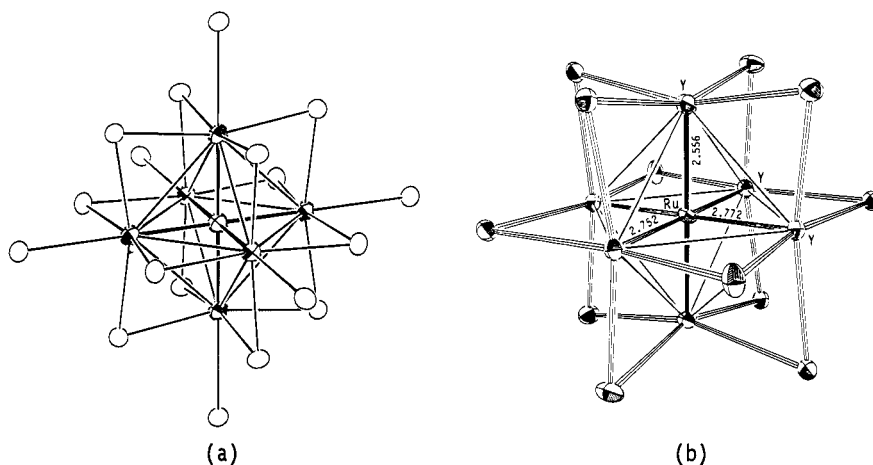


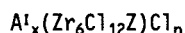
Fig. 1. (a) An example of a centered zirconium cluster  $[(\text{Zr}_6(\text{Z})\text{X}_{12})]\text{X}_6$  with 12 edge bridging and 6 terminal halide atoms. Zr - shaded ellipsoids; Z - crossed, with Zr-Z bonding emphasized; Cl - open ellipsoids. (b) A heavy metal interstitial example in the  $\text{Y}_6\text{I}_{12}\text{Ru}$  cluster (below).

Three relatively distinct families of centered octahedral ( $\text{M}_6\text{X}_{12}$ -type) clusters are encountered: 1) zirconium chlorides, 2) zirconium iodides and, 3) rare-earth-metal iodides. Some of these provide remarkable parallels in host-Z combinations with intermetallic systems to be described shortly. The cluster halide work is quite recent, and only limited amounts have been published, especially for the rare-earth-metal iodides.

#### Centered zirconium chlorides

The breadth of zirconium chloride examples that can be achieved arises from three aspects of bonding orbital conservation. The first comes from internal Zr-Zr and Zr-Z bonding and the variability in the number of valence electrons provided by the interstitials Z that may be accommodated, namely H, Be, B, C or N in a large range of structures or the transition metals Mn, Fe, Co or Ni in just a few. The structural variety arises from two other remarkable features of these (and other) clusters, the dominance of six-metal octahedra, always with twelve edge-bridging halides ( $\text{M}_6\text{X}_{12}$ ), and the evident necessity of bonding some sort of halide at the six metal vertices of each cluster (Fig. 1(a)). As the Cl:Zr ratio increases from 12 to 18, the chloride used for the last type of bonding changes from that

which is also edge-bridging halide in other clusters through chloride that bridges between clusters ( $Zr_6-Cl-Zr_6$ ) to chloride that is bound at only one vertex. Finally, alkali metal cations  $A^+$  may also be accommodated within the cluster network. All three variables allow for a large family with compositions



where examples are known with  $x$  and  $n$  each ranging through all values between zero and six.

Much of the driving force that affords this versatility appears to originate with the need to achieve an optimum electron count within the  $Zr_6Z$  cluster. M.O. calculations show, and experimentation confirms, that this number is about 14 with a main-group Z atom and 18 with a centered transition metal. Two isoelectronic series that exemplify the former class are  $Zr_6Cl_{12}Be$ ,  $Zr_6Cl_{13}B$ ,  $Zr_6Cl_{14}C$ ,  $Zr_6Cl_{15}N$  and  $Zr_6Cl_{13}B$ ,  $RbZr_6Cl_{14}B$ ,  $Rb_2Zr_6Cl_{15}B$ ,  $Rb_3Zr_6Cl_{16}B$ , etc. (The 14-electron count in each case comes from  $6 \cdot 4 + x - (n + 12)$  plus those contributed by Z.) From another viewpoint, the bonding can be thought of in terms of the bonding orbitals and valence electrons that are both contributed by Z to the formation of four strong Zr-Z bonds, together with three filled orbitals ( $t_{2g}$  or  $t_{1u}$ ) in each octahedron that are only Zr-Zr bonding. The transition metal-interstitial examples hold four more electrons because of a nonbonding  $e_g^4$  orbital centered on Z (ref. 14-18). A general description has been given elsewhere (ref. 19).

#### Centered zirconium iodides

The zirconium cluster iodides seem to be somewhat more flexible than the chlorides in both the size of Z that can be accommodated and deviations from the optimum electron count. Both effects probably originate with the larger size of iodide (matrix effect) (ref. 17). The list of known interstitials in a periodic table format is as follows:

				B	C	N
				Al	Si	P
					Ge	
Cr	Mn	Fe	Co			

These all occur with either  $Zr_6I_{12}$  or  $Zr_6I_{14}$  compositions and structures, in contrast to the chlorides, and without incorporation of the heavier transition metals, in contrast to the following rare-earth-metal systems. The different interstitial sizes that are accommodated in this group is surprising, corresponding to a range of 0.27 Å (11%) in  $\bar{d}(Zr-Z)$ , which produces a difference of 0.38 Å in  $\bar{d}(Zr-Zr)$  (ref. 20-22).

#### Centered rare-earth-metal iodides

Examples of centered clusters for group 3 metals (R) exhibit a somewhat different collection of structure types appropriate to their electron-poorer status, forming  $R_6X_{12}Z^{3-}$  anions for example, and with an even more surprising variety of interstitials than before. Iodides are again the more prolific. Only the small scandium is known to exhibit some variety of Z within the chloride clusters (B, N), whereas yttrium chlorides seem to be quite sterile as far as centered clusters are concerned. On the other hand, iodide clusters, typically sampled for but likely not limited to  $R = Y, Pr$  or  $Gd$ , occur in  $R(R_6I_{12}Z)$  or  $R_6I_{10}Z$  structures for

					B	C (C <sub>2</sub> )
Mn	Fe	Co	Ni	Cu		
	Ru	Rh	Pd			
Re	Os	Ir	Pt			

(ref. 23-26). The main-group Z possibilities have not been thoroughly researched beyond the gadolinium halide carbides (ref. 12). The tetragonally compressed  $Y_6I_{12}Ru$  example is shown in Figure 1(b) without the interconnecting iodides that are bonded at all vertices.

#### Condensed clusters

Condensed examples involve clusters that share opposite metal edges (and halogens), and these are found in a number of binary systems, for example, as infinite chains in  $(Gd,Y)_2Cl_3$ , double chains in  $Sc_7Cl_{10}$ , and infinite double metal sheets in  $Zr(Cl,Br)$ , as discussed before (ref. 13, 27). More examples occur only as interstitial compounds, including some in hitherto supposed binaries that are really ternaries like  $Sc_5Cl_8(C,N)$  and  $Sc_4Cl_6(B,N)$ . Recent examples include  $Y_4I_2C$  (single chains), a portion of which is shown in Fig. 2, and  $Y_6I_7C_2$  (double chains) (ref. 28). The binary zirconium monohalides in which cluster chains have been condensed into double metal sheets have an extensive interstitial chemistry as well, involving H, B, C, N, or O but not heavier examples (yet) (ref. 13). Rare-earth-metal monohalide analogs with H, B, C, etc. are also found but now only as the ternary phases (ref. 12). Tetrahedral interstices are available in these layered monohalide structures as well and are utilized by H, N or O.

A striking feature in all of this chemistry is the predominance of only six-metal-atom cluster halides. Surprisingly, no larger cluster units have been found except in the chain

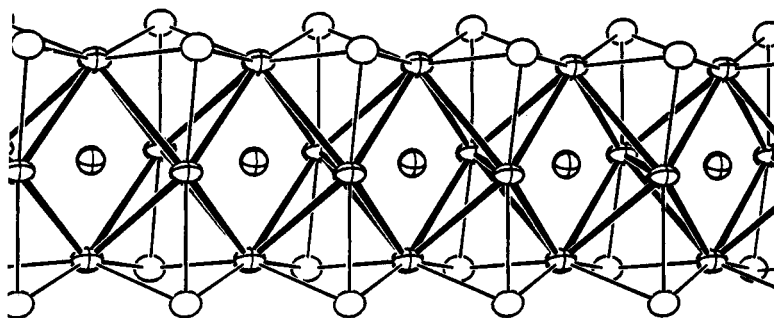


Fig. 2. A portion of the infinite cluster chain in  $Y_4I_5C$ . Note that the chain is constructed of carbon-centered  $Y_6I_{12}C$  clusters that have been condensed through sharing of opposite metal edges and adjoining halides. The Y-C bonding is not shown (ref. 28).

and sheet condensation products just noted; even isolated or condensed tetrahedra are very rare. In other words, the larger halide-sheathed  $Zr_{13}$  cluster (close-packed 3-7-3) must be unstable with respect to the  $Zr_6X_{12}$  unit plus zirconium metal. The smaller six-atom cluster may be favored by strong, polar Zr-X bonding in an effective space-filling result together with energetically better bonding in the bulk metal, as will be discussed elsewhere (ref. 29).

Substantially all of the halide compounds discussed above are obtained in >90% yield from reactions of the components in welded niobium or tantalum containers at  $750^\circ - 950^\circ C$  for 1 - 4 weeks. Their high thermodynamic stabilities relative to alternate products make virtually quantitative yields common, which in turn provide useful assessments that the stoichiometries have been correctly deduced. An attempt to insert an unsuitable Z accordingly gives only a binary, and often rather ordinary, phase,  $ZrCl$ ,  $ZrI_3$ ,  $YI_3$  and  $PrI_2$ , for example.

### POLAR INTERMETALLICS

Our inquiry regarding both clusters and their interstitial chemistry now extends beyond halides and chalcogenides to transition-metal-rich compounds of the pnictides, As, Sb and Bi particularly but also even further to compounds of Si, Ge, Sn, and Pb. These compounds do not involve any major changes in concepts, although the last two types are apt to be a good deal less familiar. All compounds formed between one of the earlier transition metals (M) and one of these main-group (B) nonmetals, metalloids, or neighboring metals possess some common characteristics regarding electronic and bonding features, namely those that arise because of sizable differences in valence state ionization energies (~electronegativities) of the two types of atoms. As a result, the main-group elements in all of these will be the major components of low lying (and therefore filled) valence p bands, and strong heteroatomic M-B bonding therewith will contribute greatly to the stability of these compounds. Although it would be simplistic and misleading to identify all of the antimonides for example as "salts", their polar nature does make the foregoing electronic relationship very probable. The metal-rich phases of interest generally contain isolated main group elements and therefore exhibit no B-B bonding, so particularly simple (8-N) valence expectations apply to these anions. (Use of the term "anion" naturally refers to the polarity, not the presence of something approaching a "free" ion.)

Phases that are rich in the transition-metal component will likely also exhibit significant M-M bonding. Valence electrons that remain after the predominantly main group element (B) valence states (bands) are filled will occur in a conduction (or metal valence) band that has major contributions from electropositive metal (M). Just how far to the left in the periodic table the main-group element can lie and still have the compound exhibit no overlap between the filled, nominally B, valence band and the metal conduction band remains to be determined. However, we can anticipate that the more electropositive metals and many of the main-group metals or metalloids will form what we have termed "polar intermetallics", compounds in which strong heteroatomic bonding and the above valence generalities apply (ref. 30).

The change from halide to chalcogenide to pnictide clusters or other arrays requires, all other things being equal, an increased number of electrons to meet the valence requirements of the anions, or a decrease in the relative number of anions. For the same structural unit and approximate electron count, the chalcogenide analog of a halide cluster should in the

first case be found for a later transition metal, as is observed (Mo vs Nb), although a simultaneous change from a  $M_6Y_{12}$ - to a  $M_6Y_8$ -type cluster and thus in the optimum electron count also pertain. Continuation of this trend to give isolated cluster pnictides of the platinum metals evidently does not occur; instead, another variable comes into play. Alternate ways to compensate for an electron count per cluster that is too low are through the inclusion of an interstitial, as we have seen, or via cluster condensation in the presence of fewer anions. The latter seems to apply regularly to metal-rich pnictides of the first four transition-metal groups with their paucity of valence electrons. Increases in anion polarizability (-formal charge, covalency) are probably also important in these results. Of course, these "explanations" are not sufficient to predict phase stability. Nonetheless, what is found may often be viewed as the result of condensation of small, often six-metal, clusters through sharing of vertices, edges or faces into, most often, infinite arrays. Sometimes the condensation is so extensive that the sense of a simple cluster is virtually lost. The variety of possibilities has been thoroughly discussed by Simon (ref. 11). An interstitial chemistry comparable to that in the halides described above does not seem to have been investigated (or stumbled upon) for most of the pnictides (or chalcogenides) other than for a few hydrides. One major exception is compounds with the  $Mn_5Si_3$  structure, and a broad one it is.

### The $Mn_5Si_3$ structure

Compounds in  $Mn_5Si_3$  structure have long been known or suspected to take up interstitials, carbon and oxygen most often, or even to require the same for stability (ref. 31-34). Very few quantitative studies of structure or composition have appeared in support of these ideas, however. The breadth of the binary  $M_5B_3$  phases that form with this structure and appear to be candidates is remarkable as well, some 155 by one count (ref. 33), in phases that encompass transition (M) metals from groups 2 through 6 together with main-group elements (B) involving all members of the boron, carbon and nitrogen families. Pearson's handbook has 264 entries for this structure type when mixed systems are included (ref. 35). It would be surprising indeed if other metal-rich structures involving many of these same or neighboring elements, chalcogenides in particular, did not also exhibit a similar interstitial chemistry.

The important structural features of the  $Mn_5Si_3$  arrangement are illustrated in Fig. 3 for the particular case of  $Zr_5Sb_3$  (ref. 30). The hexagonal structure contains two types of infinite metal chains. Fig. 3(a) depicts a portion of the chain of confacial (face-sharing) metal octahedra  $Zr_{6/2}Sb_{6/2}$  that lies along 0,0,z in the unit cell, and in Fig. 3(b), the linear chain of metal ( $Zr_2$ ) that occurs along  $1/3, 2/3, z$  and  $2/3, 1/3, z$  and is reminiscent of those in the A15 structure. The two chain types are not as isolated and the bonding is not as anisotropic as implied by these views; the antimony (or B) elements that bridge edges of the shared faces of the octahedra (left) are the same as those that are six-coordinate about zirconium (M) atoms on the linear chain (right). In fact, the Zr-Zr distances between the chains are comparable to those within the shared octahedra, though the interchain overlap population (~ bond strength) is not as large. The confacial chain is very similar to those in Chevrel phase derivatives involving  $\Delta[Mo_3(Ch)_3]$  units (Ch = chalcogenide); in fact, the structure of  $KMo_3S_3$  can be derived from that of  $Mn_5Si_3$  by replacing pairs of atoms in the linear ( $Zr_2$ ) chains by single potassium ions.

### Interstitial derivatives

Many single crystal studies have now settled the questions of the amounts of interstitials incorporated and where they go - in the rather obvious octahedral cavities in the chain on the left (small circle, Fig. 3(a)) and often at full occupancy (ref. 36). This confirms what had been estimated earlier in other systems, largely on the basis of powder diffraction and lattice constants.

Syntheses of both the binary  $M_5B_3$  hosts and ternary  $M_5B_3Z$  compounds containing interstitial Z have generally been aimed at achieving quantitative yields so that the stoichiometries are clear, the high sensitivity of Guinier powder diffraction being routinely employed for the yield determination. Traditional methods of arc melting ( $\approx 3000^\circ C$ ) followed by annealing as well as powder sintering have been employed most frequently, although metal-fluxed and vapor-phase-transport reactions have also been useful. Temperatures of  $900 - 1200^\circ C$  are typically necessary to get equilibrium. Self interstitials in phases like  $Zr_5Sb_{3+x}$ ,  $0 \leq x \leq 0.4$ , or  $Zr_5Sn_4$  are sometimes found (the fully occupied example is called the  $Ti_5Ga_4$  structure). Lattice constant changes produced by self-(B)interstitials may sometimes mimic those produced by foreign (Z) elements, so more than a qualitative change in lattice dimensions may be necessary to establish the formation of a given ternary phase. The wide range of main-group elements that form the binary phases also means that some B-Z interchange may occur in some systems, particularly at arc temperatures, but ordering seems to be achieved fairly regularly on annealing.

The chemistry and valence properties of these extended cluster systems are significantly more variable than for the fairly electron-precise cluster and extended cluster halides noted above. On the other hand, the local Zr-Z bonding interactions should be rather similar. As might be anticipated from the earlier remarks regarding the valence

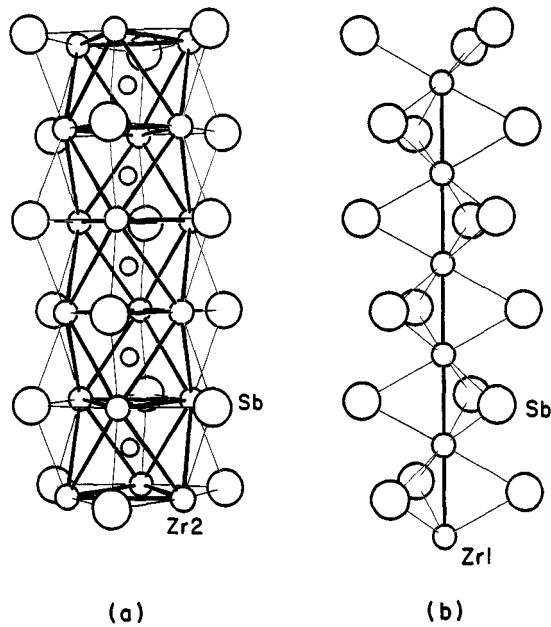


Fig. 3. The separate chains in the  $Mn_5Si_3$  type structure, as determined for  $Zr_5Sb_3$  (ref. 30). Antimony - large circles, zirconium - medium circles, interstitial Z - small circles. The confacial chain of zirconium(2) octahedra in (a) contains the interstitial site for Z. The antimony atoms about the linear zirconium(1) chain in (b) are the same as those sheathing the octahedral chain in (a).

characteristics of "polar intermetallics", many of these host  $M_5B_3$  phases are metallic, and we shall keep track not on the cluster-centered bonding electron population but on the total number of electrons in the conduction band in the hosts and in the ternary products with Z. Thus  $Zr_5Sb_3$  has  $5 \cdot 4 - 3 \cdot 3 = 11$  electrons per formula unit in the conduction band, a quantity that we designate as  $n$ . The ability to tune these systems so as to either approach or achieve the  $n = 0$  state through choice of the host or Z, or both, has also been investigated in several systems. The  $n = 0$  limit naturally represents the formation of a valence compound (Zintl phase), conventionally a semiconductor. Resistivity studies relating to this end point are underway. Distortions in low- $n$  systems that might be of a Peierls or other character and lead to band splitting have not been seen; on the other hand, fractional occupancy by Z in an ordered manner does lead to some interesting superstructures (ref. 36,37).

#### $Zr_5Sb_3$ host: $n = 11$

The amazing ability of the  $Zr_5Sb_3$  host to bond interstitial atoms with a wide range of chemical properties is summarized by the following list of those that have been incorporated (ref. 37):

					Al	C		O
Co	Ni	Cu	Zn	Ga	Si	P		S
		Ag			Ge	As		Se
						Sb		

The majority of the  $Zr_5Sb_3Z$  products have been identified on the basis of the formation of single phase samples with appropriate and reproducible shifts in Guinier-based lattice parameters following stoichiometric reactions by powder sintering or vapor phase transport. Several single crystal studies have naturally been much more informative about both dimensional changes within the host and the stoichiometry. On the other hand, the occurrence of self interstitials in the solution  $Zr_5Sb_{3+x}$ ,  $0.0 \leq x \leq 0.4$  ( $x \neq 1$ ), correlates with an apparent ease of mixed Sb-Z interstitial formation in single crystals grown under arc-melting conditions. For example, an early report of the formation of  $Zr_5Sb_3O_x$  (ref. 31) probably pertained to a  $Zr_5Sb_{3+x}$  sample instead, since an authentic oxide sample exhibits significantly smaller dimensions than the binary solution. The system with  $Z = Fe$  is particularly complicated by both self interstitials with antimony and an antimony-poorer ternary phase (ref. 36).

The densities-of-states results from an extended-Hückel band calculation for the  $Zr_5Sb_3$  host are shown in Figure 4. This emphasizes the valence characteristics already anticipated in a general way. Projections of the Sb 5p and Zr 4d orbital contributions show that all of the antimony 5p (and 5s) bonding and nonbonding states occur in a low lying valence band(s) while only the Zr1 (linear chain) and Zr2 (chain of octahedra) atoms (Fig. 3) make significant contributions to the conduction band. The formation of an interstitial derivative from this will in a general sense utilize some of the electrons and zirconium orbitals in the (approximately nonbonding) conduction band to form Zr-Z bonds while retaining with little alteration the dimensions and strong valence bonding of the host.

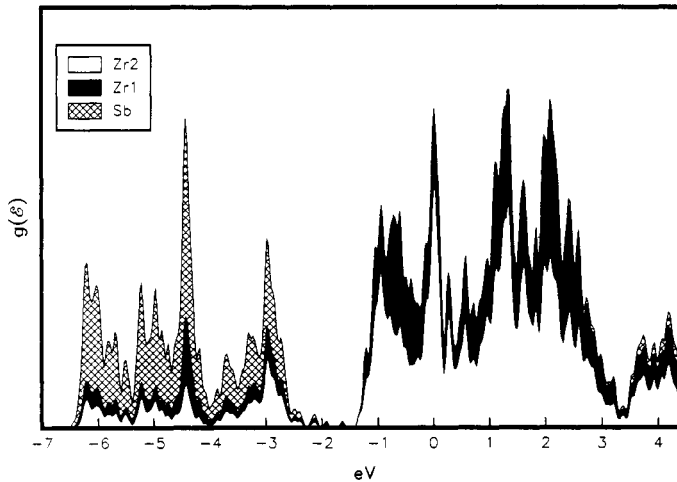


Fig. 4. The densities-of-states results for  $Zr_5Sb_3$  (extended-Hückel calculation, 24 k points,  $E_F = 0$ ) with the Zr 4d and Sb 5p orbital contributions projected out. The Zr2 and Zr1 atoms are in the confacial and linear chains, (a) and (b), respectively, in Fig. 3. Other atomic orbitals are unimportant in this region.

Figure 5 shows for comparison the comparable calculational result for  $Zr_5Sb_3S$ . As generalized above, the principal result is the loss of two electrons (and some Zr 4d states) from the conduction band and the appearance of S 3p (and some more Zr 4d) bonding states that overlap the lower energy part of the antimony valence band. (The Sb 5s and S 3s levels appear at higher binding energies ( $\sim -20$  eV) and are relatively unimportant.) Calculated overlap populations emphasize the gain of Zr-Z bonding and the loss of what was only modest Zr-Zr bonding in the confacial chains in forming the sulfide. On the other hand, the overlap populations for Zr-Sb, Zr1-Zr1 and Zr1-Zr2 interactions and all Zr-Sb distances are virtually unchanged in the process. In general, the greatest dimensional changes on interstitial inclusion show up as a lateral expansion of the shared faces of the host chain, while the Zr1-Zr1 distances along the linear chain and, therewith, the c axis exhibit much less increase, perhaps because this dimension is more determined by strong bonding in this chain. The driving force for these reactions seems to derive, as with the earlier isolated cluster examples, from the formation of strong Zr-Z bonds, but with the necessary valence electrons required coming from the conduction band supply. The Zr-Z bonding levels for all of the Z examples listed above will naturally not lie within the Sb 5p ( $\sim$ Zr) valence band as described above for sulfur.

#### **$Zr_5Sn_3$ , $Zr_5Pb_3$ hosts: $n = 8$**

The tin system at equilibrium near  $1100^\circ\text{C}$  contains only the line phases  $Zr_5Sn_3$  and  $Zr_5Sn_4$ , although homogeneous samples near  $Zr_5Sn_{3.3}$  that contain interstitial tin can be obtained by arc melting. Segregation of samples into  $\sim Zr_5Sn_3$  and  $\sim Zr_5Sn_{3.3}$  compositions induced by temperature gradients during arc melting was apparently responsible for an earlier report of the formation of two distinct phases with this structure (ref. 38). The list of Z elements accommodated by  $Zr_5Sn_3$  is similar to that given for antimony, viz,

					B	C	N	O
					Al	Si	P	S
Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
			Ag			Sn		



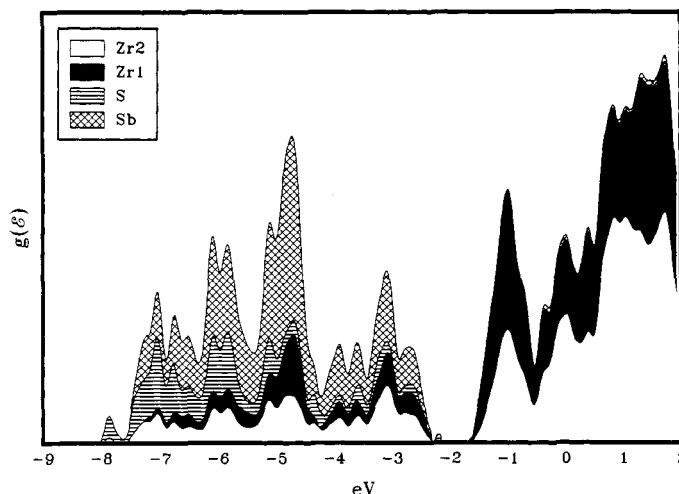


Fig. 5. The densities-of-states results for  $Zr_5Sb_3S$  with Zr 4d, Sb 5p and S 3p orbital contributions projected out. The sulfur bonding and nonbonding p states overlap the valence band of the host; compare Fig. 4.

Further examples will doubtlessly be found, but the majority of the omissions in this table represent negative results. The  $Zr_5Pb_3$  host systems have been investigated less thoroughly, but the behavior seems similar, with the following positive results for Z:

Mn	Fe	Co		Cu	Zn	Al	Si	S
				Ag		Ga	Ge	Se
						In		Te
							Pb	
								Sb

#### $La_5Ge_3, La_5Pb_3$ hosts: $n = 3$

The lanthanum systems are still under exploration, but several aspects are already in evidence. Expanded  $Mn_5Si_3$  structures readily result for  $La_5Ge_3Z$  with Z = Fe, Ru, Co, Ni, Cu, B, C, P or As, and new supercells occur with some metals for ordered, fractional Z. Likewise, the lead analog forms isostructural compounds with B, C, Mn, Fe, Ru, Co, Ni, Cu, Sb or Bi. It is interesting that binary La-Fe compounds are unknown.

Reactions of these  $La_5(Ge,Pb)_3$  ( $n = 3$ ) hosts with equimolar amounts of Z = Si, Ge, Sn (and Z = Pb for B = Ge), all of which require four more valence electrons, uniformly give a quantitative yield of  $La_5(Ge,Pb)_3Z$  in the  $Sm_5Ge_4$  structure. (Whether there is ordering of Ge or Pb and Z is not known.) This result is in complete accord with valence expectations already outlined since occupation of the valence levels of both the main group element (B) and Z should produce  $n = -1$ , i.e., with one hole in the valence band. The usual consequence of this possibility is the same as with many other Zintl phases (ref. 6), the formation of B-B (B-Z or Z-Z) dimers equal in number to one-half the number of potential holes, and this is exactly what the  $Sm_5Ge_4$  structure represents. A phase with an interstitial occupancy of 0.75 or less which would still allow retention of the  $Mn_5Si_3$  structure ( $n \geq 0$ ) does not appear to be stable for Z = Si, Ge. The occupancy with Z = B, C is not clear at this time.

#### $M_5B_3$ hosts: $n = 1$

Finally, the same  $Mn_5Si_3$  structure is known to result for most members of the family  $(Ca, Sr, Ba)_5(As, Sb, Bi)_3$ . A few also exhibit the relevant  $\beta$ - $Yb_5Sb_3$  type structure - below. All of these  $M_5(Sb, Bi)_3$  examples have recently been found to also form isostructural chlorides  $M_5(Sb, Bi)_3Cl$  ( $n = 0$ ) and, for the three examples studied, bromides as well. The volume increases observed on chloride formation are only one-fourth (with calcium) to one-half (barium) of the standard value for a chloride ion, indicating how much of the cavity is already available in the binary phase. Again, the principal dimensional change appears to be in the shared face of the octahedral chain. The compounds  $Ce_5(Sb, Bi)_3$  ( $n = 3$ ) also form analogous chlorides and bromides ( $n = 2$ ). The 5:3 alkaline-earth-metal compounds with B = Si, Ge, etc. ( $n = -2$ ) occur in the  $Cr_5B_3$  structure with B-B dimers, in complete analogy with the lanthanum examples cited above.

It was noted above that some of these alkaline-earth-metal binaries form a relatively complex  $\beta$ - $Yb_5Sb_3$  structure as well. A suitable, preformed but small interstitial cavity and

one valence electron are also available in the known or hypothetical examples of this structure type for the binary calcium phases, and the fluorides  $\text{Ca}_5(\text{Sb,Bi})_3\text{F}$  with this structure can also be synthesized (but not  $\text{Ba}_5\text{Sb}_3\text{F}$ ). Appropriate amounts of iodide, oxide or sulfide all form Zintl phases with other structures (ref. 39).

Both fluoride and chloride are plausible impurities in the alkaline-earth-metal samples that were available in past decades, and so earlier reports on the  $\text{A}_5\text{B}_3$  binary compounds may have actually pertained to the ternary halides. Unfortunately, lattice dimensions are the only practical means of comparison, and some of the older values were not very accurate. However, in a larger context, there are probably many reported phases that unknowingly contained, or were stabilized by, adventitious impurities in similar roles. Whether there are such chemical and structural roles for essential interstitials in important alloy systems is generally unknown but a tantalizing prospect.

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