Widespread Interstitial Chemistry of Mn_5Si_3-Type and Related Phases. Hidden Impurities and Opportunities

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The many A_5B_3 phases that exhibit hexagonal Mn_5Si_3-type structures by and large have a nearly unique abilities to bind diverse heteratoms Z in a preformed cavity within a chain of confacial trigonal antiprisms of A. The historical development of this chemistry as interstitially stabilized Nowotny phases and recent research to clarify the necessity for Z and the range of Z possible in certain hosts are described. Some hosts may bind as many as 20 different interstitial Z. Structures, stoichiometric relationships, volume effects, electronic guidelines, anomalies, Nowotny phases that require Z for stability, and a few band calculations are described. The special cases of hosts composed of divalent cations with pnictogens (As−Bi) and tetrels (Si−Pb) and their reactions with H and F are considered. The former Mn_5Si_3-type phase take up some H, but many convert at higher H or F concentrations to the orthorhombic Ca_5Sb_3F-type (formerly β-Yb_5Sb_3) structure. Many of the nominally valence-precise tetrelides with Cr_5B_3 (or other) structures react with H or F to give the new stuffed Cr_5B_3 versions with Z in a tetrahedral cavity (a Ca_5Sn_3F or La_5Pb_3O type). Some early results demonstrate that highly significant reduction of high-temperature corrosion rates of Ti_5Si_3 can be secured for Ti_5Si_3Z, Z = C or O. The number of uninvestigated Mn_5Si_3-type host−interstitial Z systems and the unknown ways in which various Z affect chemical and physical properties in each system are very large.

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Background

Compounds in certain A_5B_3 structure types of widespread frequency can be particularly insidious or remarkable, depending on your viewpoint, in that many can also be synthesized with a range of interstitial (impurity) atoms bound in a preformed cavity. This encapsulation is accompanied by a suitable expansion or contraction of the cavity and cell but without any change in the basic structure or space group. The process obviously provides a novel opportunity to tune the physical and chemical properties of a large set of host compounds within the same structure type. These hosts generally consist of transition metal A combined with a post-transition main-group (or p-element) metal or metalloid B. Although Mn_5Si_3-type phases are far and away the most common and versatile hosts, others may also be workable over smaller ranges of interstitials; in particular, Cr_5B_3 and Yb_5Sb_3 types. Synthetically, this means that the common dependence of investigators on X-ray powder diffraction information for phase and purity identification may be particularly misleading if the "chemical sponge" characteristics of certain binary phases are not appreciated. Accordingly, literature data for the dimensions of a particular Mn_5Si_3-type system from different laboratories or time periods may vary significantly, especially for the evidently common instances in which sizable ranges of different interstitials are possible. These generally include the pervasive impurity atoms C, N, and O.

In many characteristics, the Mn_5Si_3 structure arrangement is virtually unique. The active component in this hexagonal structure ($P6_3/mcm$) is a confacial chain of $A_{6/2}B_{6/2}$ units; that is, a chain of A_6 trigonal antiprisms ("octahedra") that are condensed with like units by sharing basal faces, Figure 1. The shared faces in these condensed units are then each bridged by three B atoms to give what can be described as $^{1}_{\infty}[A_{6/2}B_{6/2}]$ chains. Each of these A atoms (crystallographically A2) has six other A neighbors, two in the shared face and two in each of the two adjoining shared faces. The A atoms likewise have four B neighbors, two around the

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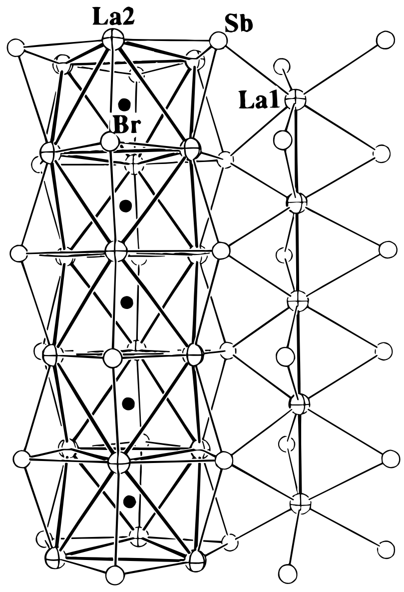

Figure 1. Approximate [110] view of a portion of the hexagonal, stuffed Mn_5Si_3-type structure of La_5Sb_3Br. On the left is the chain of confacial trigonal antiprisms of La2 with the shared faces edge-bridged by Sb, and on the right, the linear chain of La1 atoms at $^1/_3$,$^2/_3$,0, etc. surrounded by the same Sb. The interstitial sites for Z (Br, solid) are centered in the antiprisms.

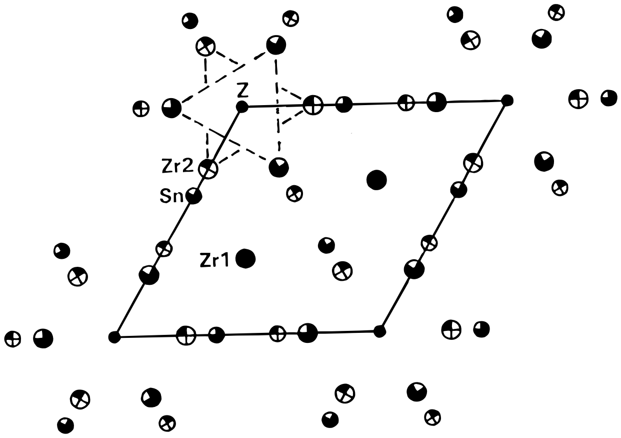

Figure 2. [001] projection of the Zr_5Sn_3Z cell with atoms shaded according to their depth in *z*.[25] Larger circles, Zr; medium, Sn; small, Z. The confacial chains built of Zr2 atoms lie along 0, 0, *z* and the linear Zr1 chains, at $^1/_3$, $^2/_3$, *z* and so forth.

shared face plus one above and one below in the staggered planar A_3B_3 units. The active site for binding of an interstitial atom (*Z*) is the center of each trigonal antiprismatic A_6 unit. The structure actually has a second A-atom "backbone" shown at the right in Figure 1 (formally A1), a parallel linear chain $^1_\infty[A'_2]$ in which the relatively short repeat is one-half of the *c* lattice dimension, the same as for Z. These A′ units also have a B_6 environment but as a twisted trigonal prism. The complete array is shown in [001] projection in Figure 2 in which the atom shadings denote the depth in projection. (The solid Z and A′ occur at both $z = 0$, $^1/_2$.) It will be noted that A−A′ distances can be important too, and all B atoms are also bonded exo to an A vertex in an adjoining antiprismatic chain.

The binary Mn_5Si_3 examples encompass[1] (as A) the alkaline-earth (Ca−Ba) and transition group 3−6 metals combined with post-transition elements (B) of the Al (triel), Si (tetrel), and As (the heavier pnictogen) families (vide infra). There is general electronic consistency regarding the total formal electron transfer from the active metal A to B (in terms of oxidation states) that can be assigned within these combinations, most compounds still being electron-rich after valence bands on the isolated B elements are filled, although none is electron deficient (see later). Thus, the electron-poorer alkaline-earth-metal compounds are generally limited to pnictide compounds, the rare-earth elements R (lanthanides plus La,Y, Sc), to tetrels and beyond (plus a few with Ga−Tl), and electron-richer Ti and V families, to triels and tetrels. A few seemingly irregular combinations of group 3, 4, or 5 metals with Pt, Rh, and Ir may reflect more of Brewer's generalities about the extra stability of compounds formed between early and late transition metals.[2] The W_5Si_3 structure is a notable alternative to that of Mn_5Si_3, especially for Ti and V family elements with Ga and the tetrels, and it is dominant for the 5−3 tetrels of group 6 metals. (The exceptions are probably Z-stuffed Mn_5Si_3 phases.) However, the W_5Si_3 structure type does not seem to have a significant interstitial chemistry, only substitutional. Another structure type, tetragonal Cr_5B_3, has only recently been shown to exhibit a limited interstitial chemistry.

The very wide range of possible $A_3(Z)A'_2B_3$ interstitial compounds of this type has a 2-fold origin: first, there are a great many prospective hosts with the Mn_5Si_3 structure type.[3] Parthé and Rieger classified 93 binaries of this type in 1968,[4] whereas Pearson's 1991 Handbook[1] lists 173 examples. Second, these sources also list a considerable number of Mn_5Si_3Z ternary derivatives in which some amount of a third element is or appears to be bound interstitially in the same structure (Figures 1 and 2). In fact, recent systematic examinations of certain A_5B_3 examples have revealed up to 15 to 20 different Z that may be encapsulated in each, usually in stoichiometric amounts, yet a very large number of other systems remain unexplored in this respect. Of course, different elements might also be segregated between the A (6*g*) and A′ (4*d*) sites too, as in $(Ti_3Mo_2)Si_3$,[5] but neither this type of variation nor mixed interstitials has been explored recently and systematically.

Discoveries of the interstitial binding characteristics of A_5B_3 compounds with this structure originated in Vienna with Nowotny and co-workers during studies of, first, the silicides and germanides and some aluminides of transition metal groups 4, 5, and 6. These discoveries appeared in the literature between 1954 and 1966.[5−18] Originally, these hosts were identified as $D8_8$ (*Strukturbericht*) structure types and, after 1960, as the Mn_5Si_3 type.[3] Many of the binary compounds were observed to take up B, C, N, and O atoms, and the view was advanced by the Vienna group that many nominally binary $D8_8$ phases in fact *required* some minimum amount of the small nonmetals for stability.[6−12] Compounds with this characteristic thus became labeled "Nowotny phases".[13] It later became clearer that this criterion did not apply to all Mn_5Si_3-type compounds,[14] but the classification persisted.[15] The ternary Nowotny phases as well as the many A_5B_3Z derivatives of stable

A_5B_3 hosts to be described here might be better labeled as "stuffed Mn_5Si_3 types", although $Mo_{4.8}Si_3C_{0.6}$[16] (with deficiencies on the 4*d* Mo sites), Hf_5Sn_3Cu (characterized on the basis of X-ray powder studies),[17] or self-stuffed Ti_5Ga_4[18] have also been cited as parent structures.

Publications since this early period pertained mainly to the existence of new and supposedly binary compounds and some scattered ternary examples, particularly of the rare-earth elements. The lack of definitive answers to several aspects of this chemistry led us to undertake a systematic study of several features, particularly as to (a) whether many empty binary hosts exist and can be obtained pure, in high yield and well-ordered, (b) whether Z incorporation always arises by insertion into the empty cavity in the octahedral chain, as opposed to substitution for or exchange with A or B atoms, (c) what variety of interstitial Z can be encapsulated in particular hosts, and (d) what range of Z stoichiometries, if any, may pertain in representative cases. These studies have over the last dozen years covered, in roughly chronological order, the interstitial chemistry of the hosts Zr_5Sb_3,[19−21] $(Ca,Sr,Ba)_5(Sb,Bi)_3$[22] (this usage of commas means *or*), Zr_5Sn_3,[23,24] Zr_5Si_3,[25] Zr_5Pb_3,[26] La_5Ge_3,[27] an $La_{15}Ge_9Z$ superstructure,[28] and La_5Pb_3.[29] These explorations have recently been extended to La_5Pb_3Z (Cr_5B_3-type)[30] and to various $(Ca,Sr,Ba,Sm,Eu,Yb)_5(As,Sb,Bi)_3$ systems in this or other structures that are usually specific for insertion of hydride or fluoride.[31−33] In general, we did not consider substitutional possibilities within the hexagonal A_5B_3Z systems, as might be achieved when off-composition, at very high temperatures, or when mixed A, B or Z are included. The broad stabilities, flexibilities, and chemical tolerances of this type of "garbage chemistry" and the potential for serious errors have not been generally appreciated or reviewed.

Experimental Considerations

Syntheses of quality materials require considerable development (see especially refs 19, 21, 23, and 24). Naturally, many improvements in experimental materials and methods have come about since the first studies in the 1950s and 1960s, most particularly in regard to containers, X-ray powder and single crystal characterization means, glovebox and other inert atmosphere equipment, furnaces, and, of course, the quality of commercial starting materials. Silica, BN, even graphite containers or dies were utilized in the early days, even though these all could contribute interstitials themselves. Fused silica is a certain source of appreciable H_2O, and thence of O and perhaps H, increasingly with time and at higher temperatures (>700−800 °C) because of recombination of bound OH groups in the glass.[34] Welded tantalum containers (or perhaps niobium with less refractory systems)[35] have proven to be superb, with substantially no involvement evidence in many systems studied (vide supra), at least to 1400 °C. These are usually sealed under high vacuum within a second well-baked SiO_2 jacket (the water concern) for protection from the atmosphere when heated in tube furnaces. (Softening of the jacket enters in above ~1100 °C.) Reactions at higher temperatures have been carried out well to at least 1400 °C in a high vacuum furnace with the container held in a open Ta can (as a getter), or occasionally, to 1600 °C by induction heating in a vacuum. Tantalum becomes brittle when it reacts with most elements via precipitation of new compounds at grain boundaries, and so preservation of its ductility is often a good diagnosis for the noninvolvement of the container. Reactive powder sintering of suitable components in a pressed pellet may be included, and Mo liners between sample and the Ta wall may be useful (vide infra).[36] Although reactions in many systems can start directly with the elements, some more reactive or volatile ones are better introduced as preformed binary compounds (or mixtures), some of which can be produced in SiO_2 at <600 °C. Many of the latter will also be more brittle, which allows grinding and better homogeneity and weighing.

The objective has been to work in as clean systems as possible so as to obtain the best samples (generally single phase), first as binary A_5B_3 and then as A_5B_3Z, both being equilibrated at as low a temperature as possible, ~500−1400 °C, depending of course on phase relationships and diffusivities. All intermediates and products as well as the elements have generally been handled in a good glovebox where the reactants can be weighed to ~5 mg. Although arc-melting may be helpful in earlier stages with very refractory materials (baring material losses), these products should always be annealed to equilibrium as already mentioned. Single-crystal structural studies on whiskers that sometimes grow outward on the buttons on cooling (perhaps at 1500−2500 °C) have often revealed substantial substitutional and vacancy defects,[21,24,36] but these can generally be annealed out at 800−1400 °C if the sample is still homogeneous and on-composition.

Once the characteristics of an empty binary phase A_5B_3 had been established (these exist in all of the systems listed above), ternary syntheses were pursued to establish the range of Z elements that form stoichiometric A_5B_3Z phases in each and their cell dimensions. That Z does bind in the "octahedral" cavity described earlier has been established by modern single-crystal X-ray means for ~20 examples of the types of compounds investigated, without exception (vide infra).[37] Most other ternary combinations have been verified by the indisputable results that can be deduced from powder diffraction data for samples loaded with a A_5B_3Z composition. If the last is stable, a clear Mn_5Si_3-type powder pattern will be seen that is reproducible under different conditions, one that usually makes up at least 95% of the total according to relative intensities and has altered lattice constants and cell volume relative to the binary. (These usually increase except for O, N, and some C that contract the cell.) On the other hand, the instability of the stoichiometric target will mean either that unaltered A_5B_3 lattice constants are found, plus Z, or more often in active metal systems, the result of a reaction of Z with A_5B_3 (usually the A component) to produce some A_xZ phase and the next B-richer $A_{5-x}B_3$ phase as well. A ternary with a substoichiometric limit (i.e., a $A_5B_3Z_{1-y}$ composition) though apparently infrequent in the systems studied, would probably still give a shift in apparent A_5B_3 parameters, but would require further investigations because the uncombined Z might not be seen. Self-interstitials can also be confusing (e.g.,

Zr_5Sb_{3+x}).[21] Only in a very few cases have mixed B, Z interstitial site occupancy been discovered in systems with A_5B_3Z compositions under our conditions, as might occur if some competitive AZ_x phase forms and moves the system off stoichiometry as $A_5B_3(Z_{1-x}B_x)$. (Zr_5Sn_3-Fe is such an example.[24,36]) Scanning electron microscopy (SEM) studies can be valuable in sorting out these problems. Some specifics for problem cases will come up later.

Success with the aforementioned procedures is heavily dependent on excellent diagnoses that can be afforded by X-ray powder patterns. Vital to this are the sharp patterns and good line resolution that are obtained with the self-focusing Guinier technique with a built-in monochomator and thin samples mounted between pieces of cellophane tape and held in the focal plane of the camera under vacuum. This procedure is advantageous also for the small amount of sample required and because of the protection from gaseous impurities that is provided by the tape and vacuum for samples that were presumed at the beginning to be air sensitive. A small amount of standard Si mixed with the samples affords an internal standard, so that the patterns can be scanned, calibrated, and indexed, and the lattice parameters can be refined by least-squares methods fairly easily. Standard deviations so obtained are generally on the order of 1 or 2 parts in 10^4. The detection limit for impurities is ~3−5%, depending on their relative scattering powers, crystallinity, and unit cell sizes and symmetries.

Binary Phases

The number of binary A_5B_3 phases with Mn_5Si_3 structures that have been refined from single-crystal data is large enough that a general absence of stabilizing Z (other than H) is beyond doubt for many systems. In several instances, disproof of the reported or presumed necessity of a stabilizing third element (in a Nowotny phase) has been enabled to a considerable degree through the purer reagents, better containers, etc. now available. For example, Zr_5Sb_3 when first observed seemed to be extremely unstable because it decomposed in (reacted with) air in a half-hour, in contrast to the inertness of Zr_5Sb_5Z, Z = Ni, Cu, Zn,[38] and the volume per atom also seemed too large.[18] However, an increased inertness is common for ternary derivatives, and pure Zr_5Sb_3 is perfectly stable otherwise.[19] Zr_5Al_3 has also been shown to be stable and not to require oxygen.[39] An early conclusion that Zr_5Si_3 was really a ternary phase and always contained small amounts of B, C, N, or O, even 0.3 atom % C,[6,8] was put forth in parallel with similar research on the group 5 and 6 silicides. (The last are all tetragonal W_5Si_3-type compounds that do transform to the hexagonal phases on the addition of fairly small amounts of C, O, etc.[2])

In a case such as Zr_5Si_3, even regularities and trends in unit cell dimensions and volumes (see later) can be very useful in diagnosing relative impurity levels. Cell volumes of 305.1 Å^3 were regularly obtained for the best (single phase) Zr_5Si_3, $Zr_5Si_3C_x$ compositions with $x = 0.5$ and 1.0 gave 0.80(1) to 1.3(1) Å^3 *larger* values, and a Zr_5Si_3O composition had a volume of 301.5 Å^3, 3.6 (1) Å^3 *less* than that of the binary.[25] (The ternary systems all contained 5−20% of the corresponding binary ZrZ_x phase even after annealing at high temperature so the stated Z contents are probably high.) These volume trends with Z are not unusual and parallel those found in other systems (vide infra). In contrast, four literature reports regarding Zr_5Si_3 gave significantly smaller cell volumes, in the range 298−302 Å^3, whereas their nominal 0.2 and 0.3 atom % C samples gave similarly low volumes, 296 and 302 Å^3, showing that significant amounts of other impurities must have been present already.[6,8] At about the same time, Brewer and Krikorian[40] concluded that binary Zr_5Si_3 was stable, but they also noted that the presence of Zr_5Si_3Z components with Z = C, O displaced two other binary phases from the ternary system. These results highlight the effects that unidentified, intrinsic impurities can have in what is one of the more difficult systems we have studied.

Structures

Self-interstitial examples A_5B_{3+x} constitute a special category in these systems. Refined examples (Ti_5Ga_4 types in the limit) include $Ti_5P_{3.15}$,[41] $Zr_5Sb_{3.16}$,[19] $Zr_5Sn_{3.18}$ and Zr_5Sn_4,[23] Zr_5Pb_4,[26] Zr_5Al_4,[42] Nb_5Ga_4,[43] and Th_5Sn_4.[44] The composition limit in the second is $Zr_5Sb_{3.4}$ at ~1050 °C.[19] For those systems in which the phase relationships are known, the A_5B_3−A_5B_4 interval is single phase only at high temperature. This close structural relationship between the 5:3 and 5:4 stoichiometries is still relatively rare, with most A_5B_4 phases having other structures.

The subset of well-established ternary hexagonal $A_5B_3Z_x$ phases for which the presence of Z in the trigonal antiprismatic chains has been confirmed and the metric details established by single-crystal X-ray diffractometer-counter studies is large enough to leave little doubt about the general behavior. These include Zr_5Sb_3(Zn,Si),[21] (Ca,Ba)$_5Sb_3Cl$,[22] Zr_5Sn_3(C,O,Ge,Ga) (the last from a Reitveld powder refinement),[24] Zr_5Sn_3Cu,[45] Zr_5Pb_3Zn,[26] La_5Ge_3Cr,[27] and Ca_5Pb_3(Mn,Fe),[46] plus several $La_{15}Ge_9Z$ (=$La_5Ge_3Z_{1/3}$) superstructures.[28] Numerous other ternaries with the supposed stuffed structure have been reported to agree well with the model on the basis of observed and calculated X-ray powder diffraction intensities. There are often discernible intensity changes with and without Z, although the stoichiometry measure is not quantitative. There is certainly no clear example in which these A_5B_3Z phases contains more than a single interstitial atom per host either stoichiometrically or structurally,[37] although bound C_2^{2-} groups could be imagined, and additional amounts in substitutional defects at high temperature are certainly possible. In general, the three components A, B, and Z are found well segregated after samples have been annealed in a region where some diffusional mobility remains. Thus, the presumption that analytically excess oxygen present in a Nb_5Ir_3O sample was disordered over both Nb and Ir sites[47] (rather than as second phase, NbO, etc.) seems highly improbable. This was not a problem with Nb_5Pt_3O.[48]

Clearly, reexamination of other aspects of the earlier reports would be useful. The question of the ability of a stable binary among the unusual combinations A_5(Rh,Ir,Pt)$_3$ and so forth to take up Z in the usual site is unexplored except as just noted for oxygen. Only one of about a dozen examples of these binaries has been

Table 1. Interstitial Ranges for A_5B_3Z Derivatives of Five Mn_5Si_3-Type Hosts[a]

Zr_5Sb_3											
						—[b]	—	C	—	O	
						—	Al	Si	P	S	
		Fe_x[c]	Co	Ni	Cu	Zn	(Ga)[d]	Ge	As	Se	
		Ru	—	—	Ag		(In)[d]		Sb_x[e]		
Zr_5Sn_3											
						—	B	C	N	O	
						—	Al	Si	P	S	
		Fe_x[c]	Co_x[c]	Ni_x[c]	Cu	Zn	Ga	Ge	As	Se	
		—	—	—				Sn			
Zr_5Pb_3											
						—	—	—	—	—	
						—	Al	Si	P	S	
		Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
					Ag	Cd	In	Sn	Sb	Te	
								Pb			
La_5Ge_3											
						—	B_x[c,e]	C_x[c,e]	N	O	
						—		$Si_{0.75}$[c]	P	S	Cl
Cr	Mn	Fe	Co	Ni	Cu	Zn			As	Se	
		Ru				Cd			Sb		
La_5Pb_3											
							B_x[c,e]	C_x[c,e]	—[c]	—[c]	
								—[c]	P	S	Cl
Cr	Mn	Fe	Co	Ni	Cu	Zn		—[c]	As	Se	
		Ru			Ag			—[c]	Sb		

[a] References 21, 24, 26, 27, and 29. [b] Not investigated. [c] See text. [d] Probable but not quantified. [e] Substoichiometric.

examined by single-crystal means, Ho_5Rh_3, whereas unsolved superstructures were seen for R_5Ir_3, R = Er, Lu.[49] The same structure as well as a superstructure has been reported for $(Zr,Hf)_5Ir_3$, depending on stoichiometry.[50] Deformed 3*c* superstructures were also established for the latter in which the once-linear A'_2 chains undulated.[51]

Ranges and Stoichiometries of Z

Studies of the range of Z possible in each of the hosts Zr_5Sb_3, Zr_5Sn_3, Zr_5Pb_3, La_5Ge_3, and La_5Pb_3 have revealed a surprisingly diverse group of workable Z in each. The flexibility and conformability of the structure and the A_6 cavity to changes in the size and electron count of Z is quite remarkable. The best way to describe these results is to lay out the established Z in a periodic table style for each of these hosts, Table 1. Unless noted, these listings refer to fully stoichiometric phases at equilibrium in each host somewhere in the range 850−1200 °C that are stable with respect to alternate phases. The breadth of Z possible seems even more remarkable when it is noted that the competing A_xZ compound is different for almost every Z in a given period. In most cases, the neighboring blank spaces (unlisted elements) reflect unsuccessful experiments (i.e., none of the target phase formed). Note that the second period Z were not investigated in Zr_5Pb_3, the studies instead demonstrating that notably heavier Z could be bound in the larger host than in Zr_5Sn_3, even though the competitive Zr_xZ compositions presumably remain the same. The interested reader should see the original articles regarding variations and special techniques used in some syntheses (vapor-phase transport, fluxes, etc.). Most phases were successfully obtained via either reactive powder sintering or from arc-melted products after annealing at a comparable temperature. Prior grinding of the latter buttons was sometimes necessary to remove gross inhomogeneities originating with the melting characteristics of the ternary system (e.g., for Zr_5Sn_{3-4}).[23]

Particular problems were encountered with iron in the Zr−Sb and Zr−Sn systems, and with Co, Ni as well in the Zr−Sn system but not in the Zr−Pb system. After several reactions, erratic results, and SEM studies, it became clear that a significant side reaction of Fe is to extract some Zr to form $ZrFe_2$ (doped with Sb or Sn, judging from lattice constants). (This side reaction was the source of the supposed magnetic anomaly found for "Zr_5Sb_3Fe".[52]) Formation of $ZrFe_2$ made the systems Sb- or Sn-richer, and a mixed interstitial compound near $Zr_5Sb_3(Fe_{\sim 1/3}Sb_{\sim 1/3})$ was formed in the former (see ref 36). Studies of the Zr_5Sn_3(Fe,Co,Ni) systems concluded that a $Zr_5Sn_3(Sn_xZ_{1-x})$ product with melting characteristics analogous to those of Zr_5Sn_3−Zr_5Sn_4 existed over about $^1/_3 \leq x \leq 1$. These diverse reaction characteristics may arise from the stability of metal-rich $Zr_5(B)_{3+x}$ self-interstitial phases for both B = Sn, Sb, which also allows a stable ternary, Z-deficient but B-rich, phase to form when Zr_xZ byproducts occur. Reduction of the Sn or Sb content to diminish the mixed interstitial component led instead to substituted W_5Si_3-type phases.[36] Another problem found in these studies can be loss of iron into the Ta container above ∼800 °C, but this can be prevented in solid systems by use of an intervening Mo foil liner. (There are also some alloy systems from which Zr may be lost into the Ta at >1000 °C without similar protection.[24,36])

On the other hand, regularities in cell dimensions (see later) together with several crystal structure determinations have all shown that the equilibrated ternary products generally contain well-segregated A, B, and Z atoms rather than significant amounts of mixed site occupancies or defects. This result was particularly well shown by single-crystal X-ray studies of Zr_5Sb_3Si, Zr_5Sn_3Ge and Zr_5Sn_3Ga, for which the isotypic Zr_5Z_3 phases are also known. In contrast, structures of a few crystals grown at high temperatures, usually on cooling from arc-melting, behaved otherwise, appearing to represent more disordered systems with generally larger cells. For example, such a Zr_5Sb_3Al crystal refined with 72% Al, 28% Sb on the Z site and 13% Al, 87% Sb on the B site assuming full occupancies of both ($R(F) = 1.7\%$). Likewise, Zr_5Sb_3S appeared to contain only 70% S as Z.[21] Interstitial sites in similarly prepared Zr_5Sn_3Al and Zr_5Sn_3Ga samples yielded 112 and 84% Z occupancies, respectively, when refined as only the intended Z.[24]

Electronic Considerations and Limits

A useful viewpoint for qualitative electronic considerations of these systems derives from their polar nature or, similarly, the sizable differences in valence orbital energies between the active or transition-metals A and the post-transition elements B. One therefore expects the valence orbitals (bands) of B in the A_5B_3 phases to be distinctly lower-lying and occupied. Because the latter atoms are always isolated, without any reasonable B−B bonding, their necessary electronic requirements (oxidation states) are easily assigned by the $8 - N$ rule (i.e., Pn^{-3}, Tt^{-4}, etc.). Combination of these with valence electron counts from A then yields useful assessments of the number of excess metallic electrons in an A-dominated conduction band (viz., $4 \cdot 5 - 3 \cdot 3 = 11$ e$^-$ for Zr_5Sb_3; $4 \cdot 5 - 4 \cdot 3 = 8$ e$^-$ for Zr_5Tt_3; and 3 e$^-$ for La_5Ge_3). Electrons necessary to fill valence orbitals on at least the more electronegative (nonmetal) Z will come from this supply. The same electrons are presumably important in the bonding of the more metallic Z as well but the valence orbital levels on these lie higher and cannot be treated so simply. A decrease to zero in the free electron count, that is, to a valence compound, on adding Z is a reasonable limit, although it's not inviolate in other structure types [see the later tetragonal Cr_5B_3-type A_5B_3(H,F) alternatives]. The selection of La_5Ge_3 as one test host was made to see whether the excess electron count of three might be titrated to zero by pnictogen Z, thus giving La_5Ge_3(P,As,Sb) as valence (Zintl) compounds. Semiconduction was verified for the phosphide, and the arsenide was qualitatively similar. Less substantively, all three were dull black rather than with the metallic luster seen with electron-richer or less electronegative Z. For similar reasons, hexagonal $(Ca,Sr,Ba)_5(Sb,Bi)_3Z$ products (as well as some that contain dipositive R elements) are limited to F, Cl, some Br, and H derivatives by the availability of only one excess electron. In such instances, O, S, etc. always give different compositions and structure types.[22,32]

Accordingly, electron-poorer tetrel Z give stoichiometry problems in $La_5(Tt)_3$ hosts ($5 \cdot 3 - 4 \cdot 3 = 3$) and the like because there are insufficient electrons to fill the added Z (Tt) states (bands). Holes in the valence band seem to be disfavored in that such compositions always yield structures that contain Tt dimers instead (viz., Sm_5Ge_4 or Zr_5Si_4 varieties for a number of La_5Ge_3Tt). Likewise, powder sintering of La_5Pb_3 with equimolar amounts of Tt = Si, Ge, and Sn all gave essentially single-phase La_5Pb_3Tt compounds with the Sm_5Ge_4-type structure, the same as occurs for La_5Sn_4 and La_5Pb_4.[53] For $La_5Ge_3C_x$, lattice constant variations with x suggested an upper limit in the range $0.7 < x < 1.0$, with LaC_2 always seen for $x \geq 1.0$. A homogeneous range therebelow appeared to extend to $x \simeq 0.5$ where the phase is in equilibrium with $La_{15}Ge_9C$ ($x = 0.33$) (next section). The variations in lattice dimensions were not sufficiently precise to be very clear about the upper limit and the supposed valence properties. On the other hand, a $La_5Ge_3Si_{0.75}$ limit was clearly seen. Possible La_5Si_3 and La_5Sn_3 hosts have different structures, Cr_5B_3 and W_5Si_3 types, respectively, changes that are not so easily explained. Boron in La_5Ge_3 gave increasing lattice parameters from ~0.3 to ~0.6−0.8 in x and became constant beyond, but with no sign of the expected side product LaB_x up to $x = 1.25$. The changes are again too imprecise to bracket the limiting composition well, but the ideal B need for five electrons would limit stoichiometrically at $x = 0.60$. Sintered cold-pressed pellets of the elements at 1300 °C for $La_5Pb_3C_x$ over $0.25 \leq x \leq 1.0$ in intervals of 0.125 gave a clear break (onset of a two-phase region) in the c lattice length between $x = 0.62$ and 0.75 (i.e., consistent with the ideal limit at $x = 0.75$ for a valence compound). The nature of the still larger Mn_5Si_3-like cell for $x > 0.75$ is unknown; second phases that had other structures were not seen until $x \geq 1.1$. Small changes in dimensions for single phase $La_5Pb_3B_x$ phases over 0.25 to 0.75 in x did not show a clear break. A unique inverse-Th_3P_4-type phase was also seen at $x = 1$, suggesting a B-stabilized $La_4Pb_3B_x$ material, probably off-stoichiometry. Two ternary La_5Pb_3Z systems gave some surprises. Both Z = N and O yielded not a stuffed Mn_5Si_3 structure but the first recognized examples of interstitials in a Cr_5B_3 structure, but one that lacks the customary Pb_2 dimer.[30] The same result has been encountered for R_5Rb_3N (R = Pr, Nd)[33] according to powder pattern data. The smaller tetrahedral cavity available for Z is presumably important in these changes. All of the nitrides should be a valence compounds if the lead dimers are absent. More isotypes will be noted later for alkaline-earth-metal tetrelide hydrides.

A few binary A_5B_3 phases can be designed that could be valence compounds themselves, the pseudo-binary $Ba_3La_2Ge_3$ for example. But the only ones that have been investigated are the more problematic R_5Tr_3 types (trivalent R, triel = Ga, In, Tl) as Mn_5Si_3-types, which could be closed-shell *if* distinct octet ions Tr^{-5} actually exist, as opposed to nominal lone pairs that are delocalized in a conduction band. This is not the case for the metallic R_5Ga_3, R = La, Gd, Y, Ho, Er. The first three (and perhaps all five) are Ba_5Si_3-type (deformed Cr_5B_3) instead, so the zero free-electron state is not tested. However, Y_5Ga_3, Ho_5Ga_3, and Er_5Ga_3 can be quenched to pure samples with an evidently slightly deformed Mn_5Si_5-type structure. Nonetheless, the Y_5Ga_3 phase is metallic or semimetallic ($\rho_{273} \sim 75\ \mu\Omega\cdot$cm) and shows a Pauli-like temperature-independent paramagnetism. Substitutions of some electron-richer Si, Sb, etc. for Ga do give stable Mn_5Si_3-type phases. The temperature dependencies of the resistivities of analogous hexagonal R_5In_3 were about zero, but poorly reproducible. Interstitial derivatives could not be obtained for the hexagonal Ga or In host phase, which is consistent with expectation.[54] These are the only negative results for Z binding in compounds with this structure type.

In contrast, the electron-poor host Ca_5Pb_3 gives a surprising result; that is, the formation of normal-appearing Mn_5Si_3Z-type derivatives with a variety of metal atoms. This result leads us to the presumption that these Z must be electron donors. First, there is some confusion about the nature of the nominal host Ca_5Pb_3 itself. From what has been already said about tetrel derivatives of the early metals, one would expect some degree of Pb−Pb bonding. An early film study of the structure that reported a $\sqrt{3} \times \sqrt{3}$ superstructure related to Mn_5Si_3[55] was incomplete and evidently wrong. A restudy[53] indicated a cell with a new motif, a cation self-interstitial in $Ca_{5.67}Pb_3$ [$Ca_{15}Pb_9(Ca_2)$] plus enough Pb−Pb dimers (at 3.51 Å) to make it closed shell and diamagnetic ($R = 3.2\%$). The distribution of Ca interstitials in two-thirds of the antiprisms is the inverse of that in $La_{15}Ge_9Z$ (vide infra), and there are no electrons left for Ca−Ca bonding within the chains. The synthesis and composition were highly reproducible when the correct phase diagram (which contains Ca_5Pb_3)[56] was used. However, later recognition of the intrinsic problem of hydrogen impurities in commercial calcium (vide infra) led to a brief restudy of its synthesis under dynamic vacuum, and this made clear that the same results were not obtained when hydrogen was pumped off. A thorough restudy is needed.

Notwithstanding these complications, a remarkable return of the stuffed Mn_5Si_3 structure in all details and in high yield was found for Ca_5Pb_3Z compounds with Z = V−Ni, Zn, Cd, Ru (Mn and Fe were refined).[46] This result is remarkable in view of the evident electron-deficiencies of all other $(Ca{-}Ba)_5Tt_3$ phases that lead to structures with Tt−Tt bonds, basically in fulfillment of Zintl−Klemm concepts.[57] The present novel results can be understood well and simply only if the particular Z are acting as two-electron donors. The apparent presence of a more positive Z in the Ca antiprisms is also reflected in significant increases in Ca−Ca distances between and within the shared faces relative to the similar La_5Ge_3Cr, by 0.13 and 0.44 Å, respectively. The Ca−Z distances are likewise relatively large. Similar products were not found for the Sr, Ba, Sn, or Pb analogues. The iron moment in the soft ferromagnet Ca_5Pb_3Fe ($6.3\,\mu_B$) is strikingly larger than those in La_5Ge_3Fe, $La_{15}Ge_9Fe$ (next section) and Fe itself, which are $1.83{-}2.00\,\mu_B$. Likewise, the XPS binding energy of Fe $2p_{3/2}$ in Ca_5Pb_3Fe, 707.2 eV, is notably greater than 705.8 and 705.3 eV in La_5Ge_3Fe and $La_{15}Ge_9Fe$, respectively, the order for increased reduction of iron in the ternary phases. Both are suggestive of an electron loss (oxidation) for iron bound in the unusual Ca_5Pb_3Fe.

Variations in Z Stoichiometries

The question of general variability of $A_5B_3Z_x$ ($x < 1$) has not been thoroughly researched. Certainly the answer very much depends on the temperature applied as well as the system. The results in Table 1 generally pertain to stoichiometric systems just above the lower limit of diffusional equilibrium on time scales of several hours to days. Under these conditions, the observation of substantial deviations from a full Z content was infrequent, but many ternaries have been investigated only at full stoichiometry.

Some earlier experiments tested the question of stoichiometries via reactions with $A_5B_3Z_{0.5}$ compositions, and all produced powder patterns showing two Mn_5Si_3-type compounds with lattice parameters approaching the $x = 0$ and $x = 1$ limits for $A_5B_3Z_x$. These included several Zr_5Sb_3Z and Zr_5Sn_3Z systems with Z = Al, Sn, Cu, Ga, Ge (broad lines with the last three),[21] and La_5Ge_3Z with Z = C, P, Mn, Co, Ni for which the ordered superstructure $La_{15}Ge_9Z_{1.0}$ is the next lower phase.[27] On the other hand, the a dimension of Zr_5Pb_3Cu decreased 10% (0.014(1) Å) of the way to that for Zr_5Pb_3 when $Cu_{0.5}$ was loaded.[29] The case for a variable $La_5Ge_3B_x$ is not too strong but some carbides appear to be nonstoichiometric (vide supra). For Zr_5Sn_3O, for which equilibrium was difficult to obtain, patterns showed significant lattice parameters ranges between those values for the empty binary and the contracted Zr_5Sn_3O. Good data for the sulfide at 1050 °C demonstrated continuous variations only in the c parameter between $\sim S_{0.5}$ and the expanded $S_{1.0}$, the former being in equilibrium with a clearly expanded lower $Zr_5Sn_3S_x$ ($x <\sim 0.2$).

A superstructure that represents an ordered arrangement for $A_5B_3Z_{0.33}$ has been observed for a wide range of $La_{15}Ge_9Z$, Z = Mn−Cu, Ru, C, O and P (with refined structures for Mn−Ni, C, P) and for $La_{15}Sn_9Z$, Z = C, O, from powder data.[28] On the other hand, a $La_{15}Sn_9Z$ superstructure did not form with Ti, V, Cr, Zn, Cd, B, As, Sb, S, Cl, all but the first two of which do form La_5Ge_3Z compounds. (N and Se were not explored.) The new superstructure consists of a $\sqrt{3}a \times \sqrt{3}a \times c$ expansion of the Mn_5Si_3Z version with ordered occupancy of one-third of the interstices in the chains. Voids in the $A_{6/2}B_{3/2}$ chains that lie at the corners of the new cell (the edges of which are long diagonals of the basal plane in the small cell, Figure 2) are all empty whereas the chains now along $^1/_3,^2/_3,z$ and $^2/_3,^1/_3,z$ are half occupied. (Substantially linear chains of La′ remain between these features.) Figure 3 shows the latter, alternately occupied pairs of chains in $La_{15}Ge_7Fe$ in which the long − short cavity height differences for empty and full sites, respectively, are obvious. The same $\sqrt{3} \times \sqrt{3} \times c$ cell as well as a $3c$ version were recognized earlier for $R_5Si_3C_x$ samples, R = Y, Gd, Ho, Er,[58,59] but neither the structures nor the compositions could be resolved. Their samples may not have been at equilibrium. We accordingly presume this structure will occur fairly widely in at least R_5Tt_3Z systems.

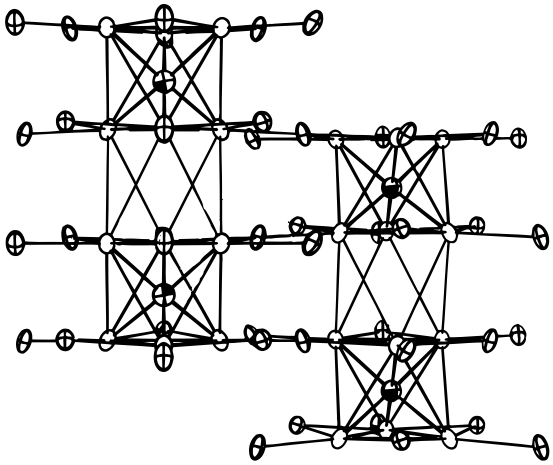

Figure 3. Side (~[110]) view of portions of two-half-occupied chains ($^1/_3$, $^2/_3$, z; $^2/_3$, $^1/_3$, $\bar{z}$) in the superstructure of $La_{15}Ge_9Z$.[28] Note the contraction of the occupied antiprisms that causes the interbridging Ge atoms to be slightly noncoplanar with La_3 faces. Comparable chains along 0, 0, z are free of interstitial atoms.

Nowotny Phases

The numerous A_5B_3Z derivatives of the Mn_5Si_3 structure that form in many systems generally represent increased bonding and stability, certainly in the thermodynamic sense. Although many are derived from known, empty hosts, there are certainly some for which this hexagonal structure is known only as more stable ternaries (i.e., Nowotny phases). For example, the unknown Zr_5As_3 does exist as the analogous Zr_5As_3Z derivatives with Si and Al[60] and doubtlessly with many other Z. A comparable Zr_5In_3Z series exists for Z = Cu, Al, ..., whereas the binary host is unknown.[24] Likewise, La_5Sn_3 (W_5Si_3 type) gives two hexagonal oxides, La_5Sn_3O and $La_{15}Sn_9O$, and the first result pertains to the analogous silicide and germanide as well.[25] The tetragonal-to-hexagonal transition between these two La−Sn phases cannot be reversed by temperature alone, so a simple phase transition at constant composition cannot be the explanation. Likewise, although R_5Si_3 for

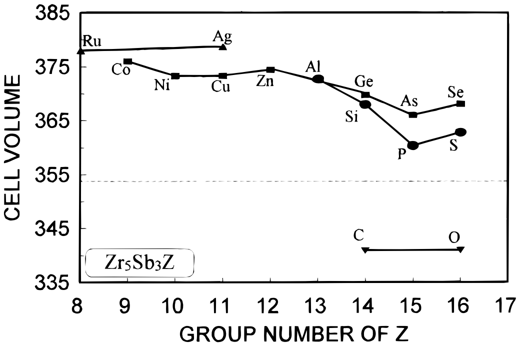

Figure 4. Unit cell volumes (Å^3) of Zr_5Sb_3Z as a function of the group of Z, arranged by the period of Z.[21] The dashed line marks the volume of empty Zr_5Sb_3. (Standard deviations are all ≤ 0.2 Å^3.)

R = La−Nd exist with a Cr_5B_3-type structure (or, probably, the distorted Ba_5Si_3 version), and Sm−Lu, in the Mn_5Si_3 type, only the neodymium compound in the former group transforms to a hexagonal stuffed Mn_5Si_3 structure when reacted as $R_5Si_3C_{0.5}$.[61] Clearly, a sizable group of other Nowotny phases exist according to early work from the Vienna group. For example, the $(V,Nb,Ta)_5(Si,Ge)_3$ collection of binaries all occur as W_5Si_3 or Cr_5B_3 structure types, yet additions of C especially (or N) were found to convert the lot to stuffed Mn_5Si_3-type phases.[1] The Z limits were generally not sought or described quantitatively, but the amount of C reported necessary to achieve the change was sometimes rather small, ≤ 1 atom %. The same is true of $Mo_5(Si,Ge)_3$ and $(Nb,Ta)_5Ga_3$ with C.[10] Oxygen was reported to not be effective for this group of transformations,[6] perhaps because smaller tetrahedral interstices would be more suitable (e.g., in the Cr_5B_3-type ternary).

Volumes and Proportions

Some of the systematic changes associated with the binding of Z in various hosts can be seen well when A_5B_3Z cell volumes are laid out in a periodic table manner, in parallel with Table 1. Of course, these are only approximate measures of the size and effect of Z since the intra- and interchain A−B and A−A bond lengths and the height-to-edge proportions of the filled antiprisms (also seen indirectly in *c*/*a* ratios) may change from one Z to the next. The latter factors have been clearly sorted out only for those ternary compounds for which crystal structures have been refined.

Figures 4 to 7 contain plots of unit cell volumes versus the group of Z arranged according to period of Z for the Zr_5Sb_3Z,[21] Zr_5Sn_3Z,[24] Zr_5Pb_3Z,[26] and La_5Ge_3Z[27] systems, respectively. These hosts contain progressively fewer free electrons (11, 8, 8 and 3, respectively) and therefore show less binding. Horizontal lines on each figure mark the volumes of the empty hosts, except that for Zr_5Pb_3 is off-scale (368.5 Å^3).

One of the most striking effects in these results is the contraction of all cells on binding O, N where studied, and C in Zr_5Sb_3 and, marginally, in Zr_5Sn_3. (Second period Z were not studied for Zr_5Pb_3.) These results clearly reflect particularly significant increases in bonding and stability. All other Z give volume increases, but this should not be taken to mean that larger Z are poorly bound, only that they are intrinsically larger. We generally found larger volume increments for compounds with Z from the third period and beyond than had been reported earlier for the same systems. This difference presumably reflects a decreased co-mixture of small adventitious impurity Z.

The overall cell volume ranges for the zirconium systems lie between 11% (Sb) and 8% (Sn,Pb). The *c*/*a* ratios, which vary from 2.3% (Pb) to 3.4%(Sn,Sb), are smaller for most interstitials than for the host (the cavities reapportion) except for chalcogen and some pnictogen Z for which the *c*/*a* ratios increase appreciably. The latter effects have been taken to result from repulsions between the more anionic Z, as these are generally separated in these structures by <3.0 Å (*c*/2). Otherwise, changes within periods more-or-less follow trends in metallic/covalent radii. The eight examples of zirconium compounds for which single-crystal data were refined illustrate two themes when Z becomes bound [for Si, Zn with Sb; C, O, Ga, Ge (Sn); Zn, Pb (Pb)]. For larger Z, *d*(Zr−Zr) in the Zr_6 antiprisms increases about twice as much in the shared (bridged) faces as between them (vertical in Figure 1) (e.g., 0.40−0.46 versus 0.18−0.20 Å, respectively, in the Ga, Ge structures). On the other hand, the small C and O atoms contract the Zr_6 cavity radii by 0.08 and about 0.11 Å, respectively, affecting the lengths of both antiprism edges to yield *d*(Zr-Z) values that are 0.11−0.16 Å less than standard radii. The Zr−Sn separations behave as if the tin atoms provide a semirigid matrix, the tin being closer to the Zr2 chains and further from the linear (Zr1) string with larger Z, and vice versa when small Z are bound.

The molar volume of the La_5Ge_3 host (Figure 7) is about one-third greater than those of the zirconium examples, and the *c*/*a* ratio (0.679) is 12% greater. The ranges of ΔV and $\Delta(c/a)$ are notably larger as well, almost twice for the latter. These and other properties generally seem to reflect a more weakly bound host, presumably because of the larger cation and a lower free-electron count. These trends continue for the alkaline-earth metal pnictides. The larger increases in *V* in La_5Ge_3Z across the three heavy periods are new and characteristic and may reflect the more polar systems. Only one ternary structure (Cr) has been refined, where the expansion of the already large cavity is small, only 0.04 and 0.11 Å in the edges.

The volume effects in the $La_{15}Ge_9Z$ superstructures (vide supra) are remarkably small, spanning only ∼9 out of ∼475 Å^3 among O, C...Cu, Ru for the subcell equivalent of La_5Ge_3. The *d*(La−Z) range is very small too, only 2.67−2.70 Å, and the trends are hard to understand. These properties would appear to reflect a substantial size-buffering effect from the predominant empty cavities.

Finally, the combination of large host atoms and reduced bonding by excess electrons results in only very small volume and *c*/*a* trends in the La_5Pb_3Z series (not shown); that is, only 7 and 14%, respectively, of those for the corresponding germanides. In other words, the partial molar volumes of Z are very small, most of the needed volume already being present in the host. These trends continue with the electron poorer $(Ca-Ba)_5(Sb,Bi)_3$, with only one excess electron.

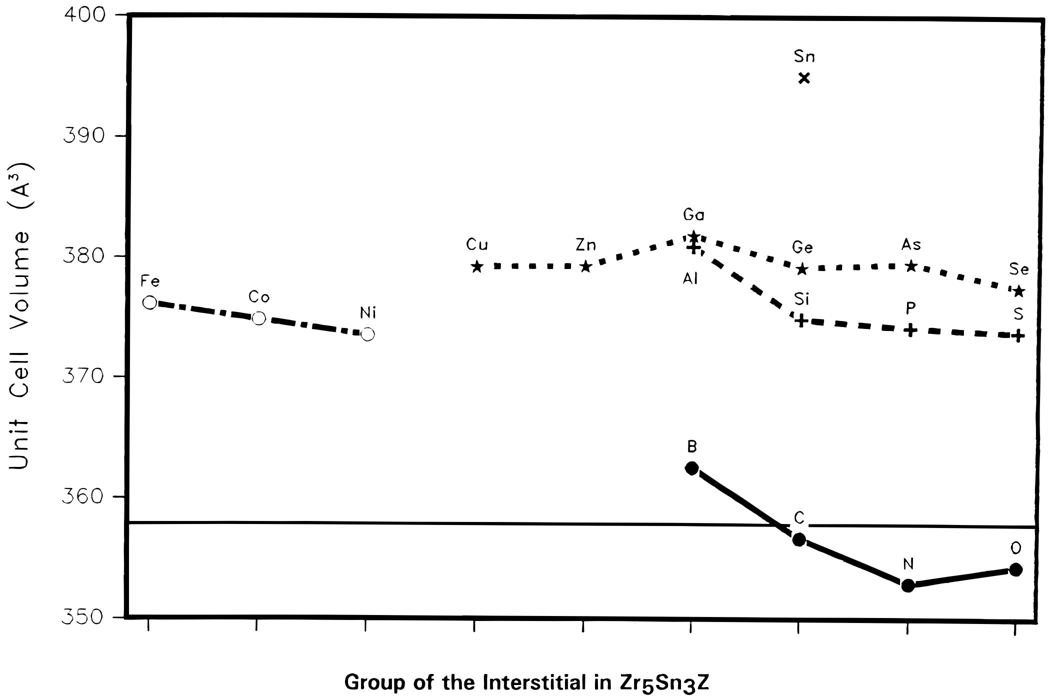

Figure 5. Unit cell volumes of Zr_5Sn_3Z as a function of the group of Z and organized by period of Z. Key: (●) 2^{nd} period; (+) 3^{rd}; (★) 4^{th}; (×) 5^{th}.[24] The solid horizontal line marks the volume of Zr_5Sn_3. The data for Fe, Co, Ni (O) pertain to mixed interstitials (see text).

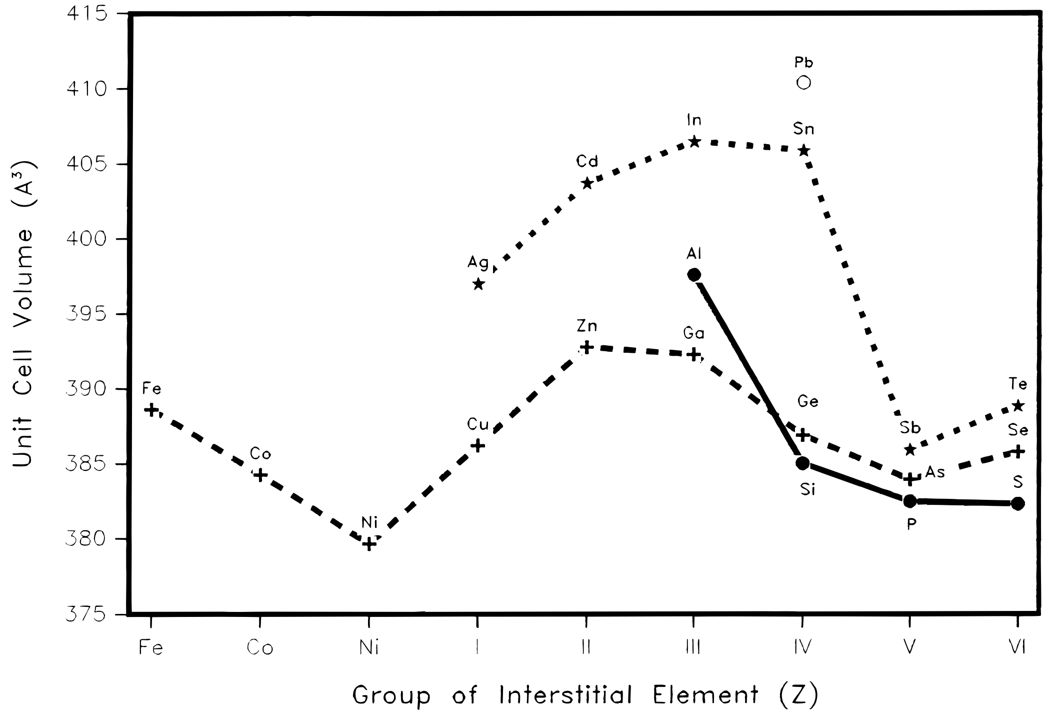

Figure 6. The cell volumes of Zr_5Pb_3Z as a function of the group of Z, ordered in the period of Z.[29] Second-period Z were not studied. Key: (●) 3^{nd} period; (+) 4^{rd}; (★) 5^{th}; (O) 6^{th}). The volume of empty Zr_5Pb_3 is off the bottom of the scale, 368.5 Å³.

Hosts with One or No Extra Electrons

A large amount of comparative chemistry can be realized in 5−3 systems involving divalent cations with the pnictogens [viz., for $(Ca,Sr,Ba,Sm,Eu,Yb)_5(As,Sb,Bi)_3$[32]], all of which nominally have only one extra electron per formula unit. This and size appear to restrict Z to the observed F, Cl, some Br, and H. The chemistry problems for these systems that are already in the literature are exacerbated by the presence of major but unrecognized amounts of H impurities in good commercial Ca, Sr, Ba (5−20 atom % by one estimate[31]) and the invisibility of it by X-ray diffraction. The contamination by H appears to arise from the combined retention when these metals react with traces of water and the lack of its separation on vacuum distillation under the usual conditions. It turns out that the smaller lattice constants reported in the literature for many binary Mn_5Si_3-type phases in this family originate

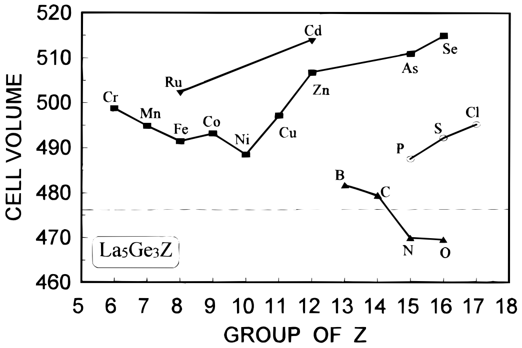

Figure 7. Cell volumes (Å^3) of La_5Ge_3Z as a function of the group of Z and ordered by the period of Z.[27] The dashed baseline is for empty La_5Ge_3. The data for B and C pertain to fractional occupancies (see text).

with unrecognized interstitial H.[33] In fact, the predominance of the stable impurity phases $A_5Pn_3H_x$ in both structure types (vide infra) during earlier studies of many of the A_5B_3 combinations already mentioned obscured until very recently the existence of the complex neighboring $Ca_{16}Sb_{11}$ phase, for which isotypes are now known to occur in 12 other systems: Ca−As,Bi; Sr−As,Sb,Bi; Ba−Sb,Bi; Eu−As,Sb,Bi; and Yb−Sb,Bi.[62] We suspect that H can be a significant interstitial in the electron-richer Mn_5Si_3-type phases considered earlier, especially those with smaller A, but these have not been investigated in any breadth.

A second compound relevant to these discussions was originally reported as orthorhombic β-Yb_5Sb_3,[63] the α-type being Mn_5Si_3. However, it proved impossible to find a direct way to interconvert some of these supposed polymorphs in closed binary systems, Ca_5Sb_3 for example,[22] again suggesting that a composition variable was involved as well. The syntheses of Ca_5Sb_3F and Ca_5Bi_3F, nominally isotypic with β-Yb_5Sb_3 but with F in a nominal tetrahedral cavity, showed the way.[22] Comparative synthesis attempts in high vacuum versus in sealed SiO_2 jackets revealed that all eight compounds reported to have the β-Yb_5Sb_3 structure can be obtained only in sealed systems and are really hydrides in what is better called the Ca_5Sb_3F structure.[31,32] The same tetrahedral cavity may encapsulate either H or F in some systems. With intermediate H contents, many hexagonal Mn_5Si_3-type $(A^{II})_5(Sb,Bi)_3H_{\sim x}$ phases are in equilibrium with the corresponding orthorhombic $(A^{II})_5(Sb,Bi)_3H_{1-x}$. The cell volumes observed for each structure type in such equilibrium mixtures relative to those of the pure binaries with $x = 0$ or 1 allow the relative H concentration ranges in each type to be estimated and thence the relative stabilities. Bonding of hydride in the tetrahedral hole in the Ca_5Sb_3F-type compounds is logically favored, and octahedral site binding in $Mn_5Si_3(H)$ versions destabilized, by small A and, to a lesser degree, larger Pn. This translates to Ca ≥ Yb > Sr ≥ Eu for the stability of the former orthorhombic hydride phases. Only Ca and Sr with Sb and Bi form the fluoride isotype; Yb was not investigated in this respect. Conversely, the hexagonal $Ba_5(Sb,Bi)_3H_x$ and $Sm_5Sb_3H_x$ systems show the largest volume (and presumably x) decrements (i.e., 2.8 to 0.8%). In parallel, orthorhombic (F-type) hydrides do not form in the latter three systems under normal pressures, and the same is true for the hexagonal arsenides of Ca, Sr, Eu, and Yb where the volume changes are comparable (i.e., 3.0 to 0.6%). (Ba−As and Sm−As only form other phases in this region.[32])

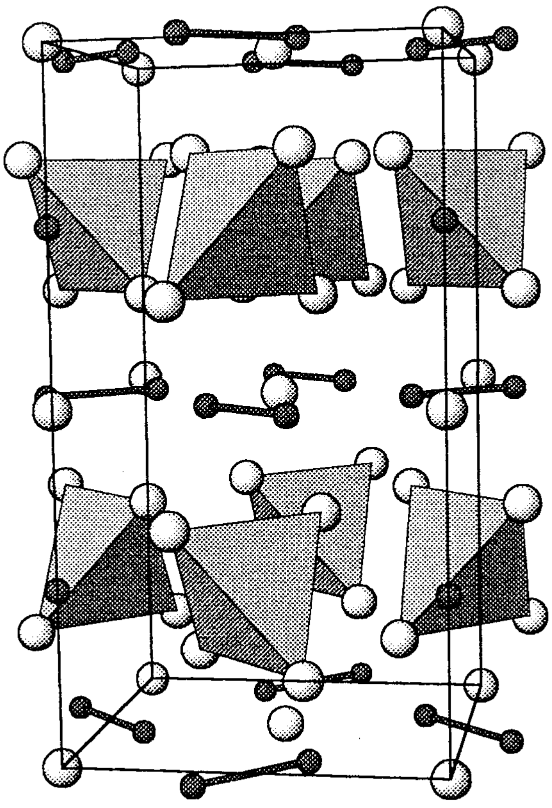

Figure 8. ~[100] view of the tetragonal $Ca_5Sn_3(F,H)$ structure (stuffed Cr_5B_3, $\vec{c}$ vertical).[33] Large spheres respresent calcium, small spheres are tin, and the F or H atoms lie within the outlined Ca_4 tetrahedra.

A more iconoclastic result as far as valence compounds are concerned is generated by the fact that many Cr_5B_3-type phases found in $(A^{II})_5Tt_3$ systems also take up H (or F) without a structure change.[33] The classical parent structure for this family would be formulated as $(A^{+2})_5Tt^{-4}Tt_2^{-6}$, a nominal Zintl (valence) compound ($5\cdot 2 - 4 - 6 = 0$), so that oxidation by H or F would not be expected. Single-crystal X-ray and powder neutron diffraction studies on Ca_5Sn_3Z phases prepared with Z = H, D, and F have confirmed the location of Z in tetrahedral cavities within a Cr_5B_3-like matrix, as shown in Figure 8. This is now termed the tetragonal Ca_5Sn_3F-type structure, a stuffed Cr_5B_3 version. This Z location is also as found earlier for the electron-richer $La_5Pb_3(O,N)$, but the Pb dimers are dissociated in this instance.[30] This Ca_5Sn_3F-like (stuffed Cr_5B_3) chemistry is rather plentiful. The following insert lists such compounds in two categories.

B: Systems that form both empty Cr_5B_3- and filled Ca_5Sn_3F-type phases with H (and usually F when tested);

N: Systems that contain binary compounds with other compositions and structures, but form ternary Ca_5Sn_3F-like phases with H, F (Nowotny phases).

	Si	Ge	Sn	Pb
Ca	**B**	**B**	**N**	
Sr	**B**	**B**	**B**	**N**
Ba	**B**	**B**	**N**	**N**
Eu	**B**	**B**	**N**	
Yb			**N**	

The Ba_5Si_3 data actually pertain to the parent type of a distorted Cr_5B_3 version that is probably more widespread than realized because it usually cannot be recognized in powder patterns. Four of the six N examples have been erroneously reported before as binary compounds. Most of the unlisted $Yb_5(Si,Ge)_3$ phases exist with Mn_5Si_3-type structures with and without H, the cations evidently being trivalent.[33]

The lack of adherence of these compounds to simple valence concepts apparently arises from the fact that some of the highest-energy electrons in these binary $A_5(TtTt_2)$ compounds are screened and delocalized and the hosts are already metallic. In these cases, oxidation to form low-lying H^- or F^- states simply ties up one of the high-lying electrons. The source of the effect evidently lies with the π^* electrons on Tt_2^{6-} ions, which are isoelectronic with halogen X_2 with $\sigma_g^2\pi_u^4\pi_g^{*4}$ p-electron configurations. As might be expected, extended Hückel calculations verify that the π^* orbitals lie the highest, just below E_F, and that E_F moves down into the π^* band on oxidation as low-lying H^- or F^- states are introduced. Consistent with this, the Tt_2 bonds in several structures are observed to shorten on H or F uptake.[33] Again, the early predominance of these A_5Tt_3H impurities appears to have obscured the existence of eight truly binary Cr_5B_3-type compounds (B) as well as four examples of $Ca_{31}Sn_{21}$ ($Pu_{31}Pt_{20}$) and $Yb_{36}Sn_{23}$ phases with oligomeric tetrelide anions.[64] The semiconducting hydride $Ba_5Ga_6H_2$ is a Nowotny phase of sorts, formerly being incorrectly formulated as $(Ba^{5+})_5Ga_6^{8-}(e^-)_2$,[65] and so is $Ba_{21}Ge_2O_5H_{24}$.[66]

Band Calculations

Rudimentary EHMO calculations of densities-of-states (DOS) for the hexagonal hosts Zr_5Sb_3,[21] La_5Ge_3,[27] and Ca_5Bi_3[34] and their adducts highlight some of the ideas and principles already incorporated in the text. A fairly common feature is the moderately fixed bonding ("glue") in the host before and after encapsulation of Z. The electron-rich and strongly bonded Zr_5Sb_3 exhibits a clear gap between a Zr−Sb-based valence band and a largely zirconium conduction band, with E_F well up in the latter. Addition of S generates a low lying band composed of Zr2 d and S p states, an appropriately lower E_F, and a sizable decrease in the Zr2 − Zr2 bond populations within the chain. Other less bonding Zr2 states are pushed higher, Zr2 is clearly oxidized as Zr1 becomes relatively more reduced, and the band gap remains. On the other hand, introduction of a late 3d metal as Z produces a Zr2 − Z 3d band that falls (more-or-less) in the lower part of the conduction band together with Zr2 − Z 4s states in the region of the former valence-conduction band gap. Thus, the simplicity of the former qualitative interpretation of bonding of a more electronegative Z no longer exists.

The distinctively lower conduction electron count present in the host La_5Ge_3 and the elongation of the structure along *c* give significant changes. E_F naturally lies in the lower part of the conduction band, but large La−Ge bond dispersion, particularly in the edge-bridging functions on the chain, closes up any potential gap (not shown). Antibonding La2−La2 interactions occur within the shared faces that were absent in Zr_5Sb_3, and these distances lengthen less on inclusion of interstitial P. The La1−La1 contacts are only weakly bonding throughout and not important in dimensionality, rather their separation more-or-less follows the remaining structural matrix. Added P opens up a narrow gap in the DOS, with the appearance of a P p contribution in a lower band, as seen in Figure 9, while more antibonding La2 features move up. La2(z)−La2(z) interactions are greatly reduced by their bonding to P instead (i.e., La2 is oxidized). Inclusion of Fe instead is again a good deal less classical. A narrow unsplit Fe d band fills any gap around E_F, whereas broader La−Fe 4s bonding states fall near the top of the valence band.

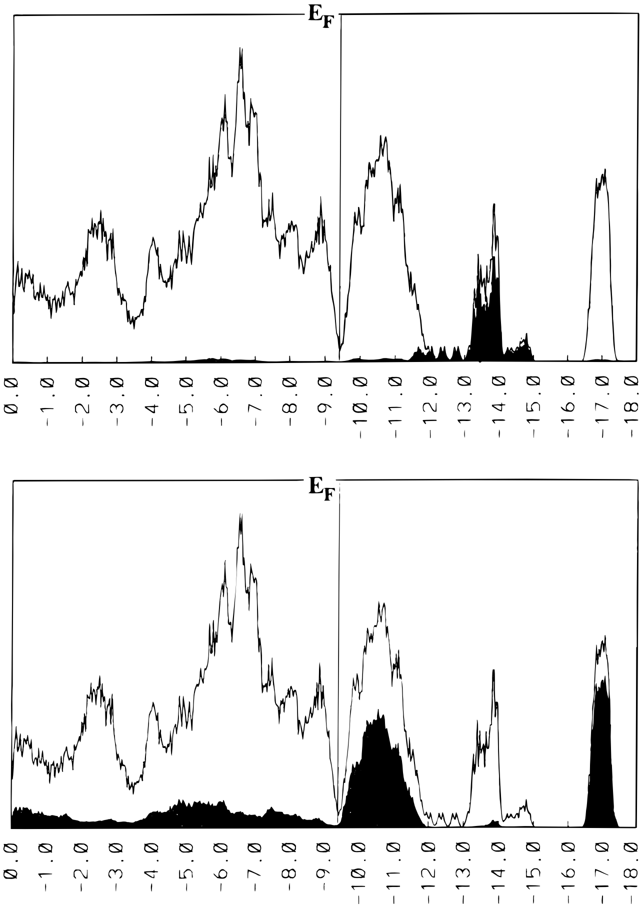

Figure 9. Energy (eV) vs total densities-of-states (DOS) for the valence compound La_5Ge_3P.[27] The P p and Ge s, p states are projected out in the top and bottom portions, respectively.

Finally, a calculation (according to an X-ray study) on the apparently empty Ca_5Bi_3 (Mn_5Si_3-type) gives a clear signal that interstitial bonding is present. As shown in Figure 10, a small half-filled band composed mostly of Ca−Ca bonding (and Ca−Bi antibonding) states is found centered on E_F within a fairly sizable gap. This feature originates with contraction of Ca_6 cavities in the calcium chain by unseen hydrogen and highlights evidently under-utilized Ca bonding. The band disappears on the correct hydrogen insertion with the development of the low-lying hydride band, as shown.[32]

Related Interstitial-Metal Cluster Units in Halides

As an aside, it is worthwhile noting that a somewhat similar, yet quite different, interstitial chemistry occurs

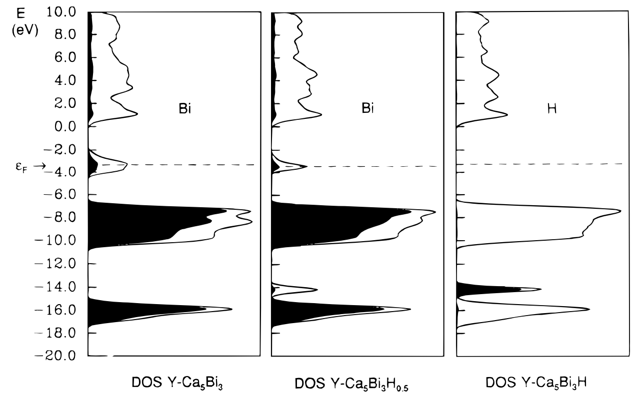

Figure 10. Total DOS for the host Ca_5Bi_3 (Y or Ca_5Sb_3F-type) with the indicated atom contributions projected out.[32] Left: for the empty binary as determined by X-ray crystallography, with the unfilled bonding states at E_F; center and right, the results when $H_{0.5}$ and $H_{1.0}$ are included.

for many Z-centered, but usually isolated, octahedral metal cluster halides (X) of both zirconium and many of the rare-earth metals, typically with $M_6(Z)X_{12+n}$ stoichiometries and in a wide variety of structures.[67] In these cases, the Z atoms are essential to stability, and clusters without Z (as are known for Nb, Ta, etc.) do not occur for these electron-poorer metals. The list of the 14 Z that can be inserted into zirconium cluster halides of some type is somewhat like that in Zr_5Sn_3Z (Table 1) except for the absence of the later fourth period p-elements, whereas related rare-earth metal cluster systems expand Z considerably to include the later 4d and 5d metals. The local interactions within these M_6Z clusters must be fairly similar to those described here, but the halide clusters are electron-precise, or nearly so, and the compounds are semiconductors. These units are in effect more oxidized by the 12 to 18 surrounding halides than are the intermetallic A_5B_3 and, characteristically, the M−Z distances are often appreciably less than standard values, by up to 0.3 Å. It's a chemically small world!

Opportunities and Possible Applications

We have heretofore laid out the results of recent explorations of a few Mn_5Si_3-type systems and what appear to be some of the guiding principles. Clearly a great many of the 175+ possible hosts for this sort of chemistry are yet to be examined, including nearly all of those derived from transition metal groups 5 and 6 (vanadium and chromium families). One can only pretend to imagine what may be discovered. Many A_5B_3Z systems appear to allow substantial variations in the nature of Z within the same host and structure type. These forecast parallel but largely unexplored changes in intrinsic chemical and physical properties within each closely related family, the studies to date touching only on equilibrium characteristics as they relate to identification and classification. Furthermore, we can surmise that doping A_5B_3 with Z will also affect transport properties of these intermetallic "solvents", as is implied by the reduced reactivity of many phases with air after doping. Such changes have much more to do with dynamics, nucleation, and mechanical properties far from ambient conditions and in a fairly unfamiliar world to chemists.

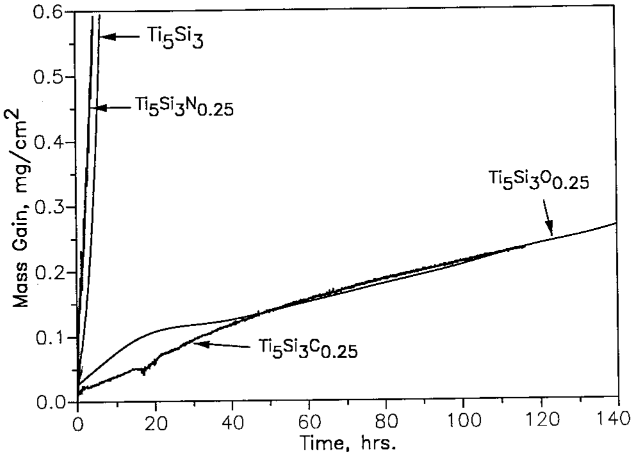

Figure 11. Oxidation (mass gain) of Ti_5Si_3 and of $Ti_5Si_3Z_{0.25}$, Z = C, N, O, in zero air at 1000 °C. Note the substantial reduction of oxidation on encapsulation of C or O (but not N).[68]

Fortunately, some quite spectacular results regarding the reduced corrosion of certain A_5B_3Z phases have recently appeared from the group of Akinc, also at Ames Laboratory, building on known corrosion-resistant characteristics of silicides.[68] The rates of oxidation of Ti_5Si_3 (Mn_5Si_3 type) alone and after doping interstitially to $Ti_5Si_3Z_x$, Z = B, C, N, O, $0.25 \leq x \leq 0.75$, have been studied under the conditions of "zero air" and 1000−1300 °C. Direct analyses for all of the listed Z elements and separate crystal structure refinements have verified the levels and the expected location of Z.[69] As shown in Figure 11, decreases in the rate of oxidation (mass gain) at 1000 °C are quite dramatic, especially for Z = C, O, whereas boron is somewhat less effective, and nitrogen seems to have no value. The C, O advantages persist at 1300 °C. In general, the rates of corrosion of Ti_5Si_3 are reduced by at least a factor of 10^3 through the encapsulation of C or O interstitials. Reduction of the mobility of titanium and thence oxidation through tighter bonding by the interstitial is believed to be important in these remarkable changes. The absence of a nitrogen effect is a mystery.

Clearly there are a large number of possible systems in which the effects of diverse interstitials on all sorts of properties might be studied. As with these corrosion studies, many will depend on properties that have not been touched on in our explorations of equilibria and structures. The opportunities seem manifold.

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