Site Preferences and Bond Length Differences in CaAl$_2$Si$_2$-Type Zintl Compounds

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Abstract: The Al$_2$Si$_2^{2-}$ two-dimensional networks in the CaAl$_2$Si$_2$ structure may be derived by a conceptual splitting of the wurtzite lattice and a subsequent reconstruction. The reconstruction suggests some analogies with organic propellanes. The resulting Al$_2$Si$_2^{2-}$ network has two four-coordinate sites, a normal tetrahedral one, and another with a highly distorted local umbrella geometry. A choice is made by Al and Si for one or the other of these sites, a choice whose causes we explore in detail. We begin with a comparison of the energetics of the normal and the "inverted" phase, based on the dispersion of the bands. To avoid destabilizing high dispersion in the filled bands, the more electronegative atoms should occupy the less "dispersive" positions in the crystal. We also examine the Si-Al bonds of the SiAl$_4^{4-}$ "inverted" tetrahedron as isolated from and incorporated into the CaAl$_2$Si$_2$ lattice. When an isolated SiAl$_4^{4-}$ model is flipped from $T_d$ to $C_3v$ geometry, the 1-fold Si-Al bond is weakened more than the 3-fold bond. The reasons for this bring us again close to an organic propellane model. When the SiAl$_4$ motif is incorporated into the lattice, additional inter-unit-cell interaction enhances the difference between the two types of Si-Al bonds. The possibility of an alternative "dimerized graphite"-type structure is also explored.

Zintl's concept$^1$ plays an important role in solid-state chemists' thinking and in their understanding of a large range of crystal structures. In this simple but extremely powerful concept, the electropositive elements are thought of merely as electron donors, donating electrons to the conjoined more electronegative element bonding partners. The latter then comply with the octet rule by receiving those electrons. An example is the NaTl structure,$^1$ in which Na donates one electron to Tl, and the Tl$^-$ moieties, isoelectronic to Pb, therefore similar to C, form the diamond structure. The Na$^+$ cations build another diamond lattice, interpenetrating the Tl$^-$ one. Closely related to the NaTl structure is the LiAlSi$_3$ phase,$^2$ 2. Here the (AlSi)$_3^3$ network forms a zinc-blende structure, and the Li$^+$ ions sit in the center of the tetrahedra formed by the Si atoms.

2 LiAlSi

Though simple and most useful, Zintl's rule is not a universal predictor of molecular structure. It does not give us any hint as to why NaAlSi$_4$ is not isostructural with LiAlSi$_3$ or how the bond length should change when going from one structure to another. More sophisticated theoretical calculations are needed to explain...
New York, 1978. The propellane was first synthesized in Wiberg's many theoretical studies on propellanes. Here is a selection of references on the structural details of these Zintl phases. These can be provided of Ca²⁺ ions are separated by tightly bund AI₂Si²⁻ layers. These layers can in turn be described (and that is all it is for the moment, this is such that the AI atoms become tetrahedral and Si atoms find themselves in the umbrella geometry arising in this paper, with band calculations of the extended Hückel model. Site Preferences in the AI₂Si²⁻ Layer of CaAI₂Si₂. It is useful to examine first the geometrical constraints of the alternative structures. In 8, the AI reside at the center of Si₆ tetrahedra, which happen on a clean Si surface—a reconstruction—and one way to view the CaAI₂Si₂ structure is in a similar way, as indicated in 7 → 8. This way of thinking provides us with a connection between a three-dimensional structure and a two-dimensional lattice. At the moment, this is a paper exercise, but it may be more than that; a line of development in solid-state chemistry is the tailoring of three-dimensional solids into lower dimensional ones and modifying the interfaces between lower dimensional layers to produce desired physical properties.

There is another instructive way to view this structure. Many solid-state phases can be viewed from the point of view of discrete cluster groupings and their progressive condensation. Still other structures may be conveniently imagined as "split" from three-dimensional Zintl networks. The CaAI₂Si₂ structure is such. AI₂Si²⁻ or AlSi²⁻ is isoelectronic to AlN, so one is led to think of the wurtzite lattice. This can be cleaved by "intercalating" Ca²⁺ layers, as shown in 6. The splitting and intercalation prevent vertical bonding between hexagonal Al₂Si₂⁻ layers. Dangling bonds result which will seek for bonding partners. This is what happens on a clean Si surface—a reconstruction—and one way to view the CaAI₂Si₂ structure is in a similar way, as indicated in 7 → 8.

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then pack together (11) to form the layer. For an ideal tetrahedral arrangement, the Si-Si contact is $2^{1/2}$ times as long as the Al--Al separation, as shown in 12a. In the layer derived from 9 $\rightarrow$ 10, the situation is reversed, 12b.

Imagine the Al$_2$Si$_2^{2-}$ layer built up from Al-Si- dinuclear monomers, emphasized by the bold lines in 13. The schematic interaction diagram for the diatomic is shown in Figure 1. When the more electronegative Si interacts with Al, its orbitals are pushed down, resulting in four low-lying orbitals in the dinuclear unit which are mainly descendants of the one s and three p orbitals of Si. The eight valence electrons of the AlSi$^{2-}$ unit reside in these four Al-Si bonding orbitals, with an energy gap between the four low-lying orbitals and another four high-lying orbitals, mainly of Al character, and Al–Si antibonding.

On to the solid state: When these AlSi$^{2-}$ units are arranged in the Al$_2$Si$_2^{2-}$ layer as in 13, the shorter Al--Al contact indicated in 12a should result in a greater dispersion of those bands concentrated on Al. These constitute the upper block of the Al$_2$Si$_2^{2-}$ layer. In contrast, the occupied lower block of the AlSi$^{2-}$ diatomic unit should generate bands of lesser width, due to the larger separation between the Si atoms in the Al$_2$Si$_2^{2-}$ layer.

Figure 1. Schematic interaction diagram of Al and Si$^{2-}$ to form Al–Si$.^{2-}$

Figure 2. Schematic picture showing the difference in the filled and unfilled band dispersion between the normal, a, and the inverted, b, Al$_2$Si$_2^{2-}$ layers.

Figure 3. Density of states (dashed lines) and the Si contribution to it (solid lines) of the normal, a, and the inverted, b, Al$_2$Si$_2^{2-}$ layers. The dotted lines are integrated Si states, indicating that more than 70% of the Si states is filled in the normal Al$_2$Si$_2^{2-}$ layer, a, but less than 60% of the Si states is below the Fermi level in the inverted one, b.

The situation is shown schematically in Figure 2a. The inverted layer, 10, will have the greater dispersion in the lower, occupied, mainly Si block bands (Figure 2b). This is a consequence of the coupling overlap being mainly Si–Si, the
The situation becomes clear now: the bigger dispersion in the completely filled lower block in the inverted Al₁₂Si₂⁻ layer in Figure 2b is the solid-state equivalent of a filled shell or four-electron repulsion. The result is a higher Fermi energy and a destabilization relative to the normal Al₁₂Si₂⁻ structure.

We will discuss the band structure of CaAl₁₂Si₂ below, but let us anticipate the result by extracting some of the conclusions relative to the present discussion. Figure 3 shows the calculated density of states (DOS) for both layers 9 and 10. The solid lines indicate the contribution of Si, states to the total DOS; what is left over under the dashed lines is to be assigned to Al. It is quite clear that in the inverted layer represented by Figure 3b, these mainly Si states have greater dispersion.

We should also mention here a significant point made by one of the reviewers: There may also be an electrostatic, Madelung energy contribution to the preference for net 8 over 10. In 8, the negative Si atoms are nearer to the Ca²⁺ sheets; in 10, it would have been the relatively positive Al atoms.

Inequivalent Bonds at Si. On going from wurtzite to Al₁₂Si₂⁻, the aluminum environment remains tetrahedral, but the coordination geometry at Si changes drastically, from tetrahedral to "umbrella", as shown in 14. There are two kinds of bonds, which we will call "handle" (the unique axial one) and "rib" (three such). The experimental observation is that the handle bond is longer than the rib bond in all CaAl₁₂Si₂ compounds except some in which there is a transition metal at the Al position with a d⁵ configuration. We will treat the transition-metal cases in a separate contribution.

References:
Figure 7. Band structures of the Al$_2$Si$_2$ layer. Main contributions at the Γ point are indicated.

Table I lists a selection of main group element compounds in this structure type. The bond length difference between rib (1X) and handle (3X) bonds is clearly seen.

Let us try to understand the origins of this bond length differential. Since the local environment changes in a significant way only around Si, let us model the solid-state process by an umbrella flipping in a cluster, SiAl$_4^{x-}$.

Figure 4 is a Walsh diagram for this process. On the left-hand side of Figure 4, we see the levels of an undistorted SiAl$_4$ tetrahedron. The five orbitals shown are (in increasing energy) one $a_1$ orbital, a bonding combination of Si s and Al s orbitals; three degenerate $t_2$ orbitals, bonding combinations between Si p and Al, mainly s orbitals; and one unfilled $a_1$ orbital, mainly a bonding combination between Si s and Al p orbitals.

The three degenerate $t_2$ orbitals are not drawn with the conventional choice of linear combinations for the degenerate orbital (15). That choice is appropriate to a subsequent deformation

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maintaining an $S_s$ axis, e.g., to $D_{2d}$. What we require here is preparation for a deformation which preserves a 3-fold axis, e.g., to $C_3v$. The appropriate combinations are 16, 17, and 18. 16 is concentrated along one bond; 17 and 18 are perpendicular to that bond. If the symmetry is lowered to $C_{3v}$, a, and maintaining an of the Si p$_z$ orbital, as shown in 15.8 decreases from 109.5° to 70.5°, additional bonding is provided between the handle and the rib Al atoms. This extra stabilization operates through the e orbitals, in which the p orbitals of the handle Al point toward the rib Al's and result in good overlap between them. The overlap population in 21 confirms this observation. The energetic difference is very small, with the $C_{3v}$ more stable than the $T_d$ geometry by 2 kcal/mol in our calculation.

Wiberg and co-workers have performed ab initio calculations on the umbrella bending for methane.29 For $\theta = 90^\circ$, the umbrella handle bond length ($r_1 = 1.114 \text{ Å}$) is longer than the umbrella rib one ($r_2 = 1.080 \text{ Å}$), in agreement with our SiAl-Si expectations based on overlap populations. On moving to the two-dimensional infinite slab, local molecular orbitals develop into bands. We have to speak not of individual levels but of densities of states. But the essential local features will be maintained in the extended solid. For example, the extended solid equivalent of the overlap population for the SiAl-Si layer, the COOP curves,30 which we will discuss later, will show that around the Fermi level (or HOMO), there is an antibonding feature in the vertical (1X) Si-Al bond and the overlap population for that bond is smaller than that of the rib (3X) Si-Al bond. This is exactly the same as in the discrete cluster SiAl-Si case. We will see, however, that there are some novel features added in the extended material.

The resulting overlap populations are shown in 21. Note the weaker handle bond. In fact, both types of bonds are weakened relative to the tetrahedron. This is consistent with the predominant destabilization of 2a$_1$ with $\theta$ (see Figure 4). However, when $\theta$ decreases from 109.5° to 70.5°, additional bonding is provided between the handle and the rib Al atoms. This extra stabilization

Table I. Some AB$_2$X$_2$ Compounds assuming the CaAlSi Structure

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<th>compound</th>
<th>bond length, Å</th>
<th>ref</th>
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mostly 3p, with some Al admixture.

The eight filled orbitals of the repeating dimer Si2Al22- (22b) are shown in Figure 6. Substantial second-order mixing changes the orbitals significantly from just being in- and out-of-phase combinations of the dinuclear monomer unit in Figure 5. The lowest orbital 1a1 is the in-phase combination of the lowest s orbitals of each unit. The out-of-phase combination, however, will build into the molecular orbital some antibonding character between the two Si-Al units. To alleviate this, the σ s orbitals will mix in some π character from the Si-Al σ orbitals of higher energy, thus forming 1b1u. The counterpart of 1b1u is 2a1, at higher energy. 1b2g and 1b2u are the descendants of Si-Al σ* orbitals, mixed to some extent with the Si-Al σ-π* orbitals. lb1u and 1b2u are derived from Si-Al π* orbitals (perpendicular to the plane of the paper).

When the Al2Si22- lattice is constructed from the SiA1AlSi motif, 22b, these MO's will develop into bands. For example, the 1a1 can be propagated into the lattice in either an in-phase way, corresponding to the r point in the Brillouin zone, or in an out-of-phase way, corresponding to the M point in the Brillouin zone. The in-phase propagation of course, stabilizes the crystal orbital by building up bonding character between the MO's of different unit cells, as indicated by the arrow in 23. The out-of-phase propagation clearly destabilizes the crystal orbital, as also indicated by the arrow in 24. So going from Γ to M, this band should rise in energy.

The behavior of each band as a function of k could be developed in a similar way. The actual band structure that results is plotted in Figure 7, for the line Γ→M. The main contributions to each band at the Γ point are specified in Figure 6.31 As we have concluded above, the lowest band, mainly composed of the 1a1 orbital, goes up in energy from Γ to M. The other bands are not all in the same energy order as in Figure 6, a consequence of substantial inter-cell interaction and mixing between these orbitals. An example of what happens follows: If the 1b1u orbital in Figure 6 were to propagate in an in-phase way, corresponding to the Γ point in the Brillouin zone, antibonding character would build up between the 1b1u orbitals in adjacent unit cells, as shown in 25.

However, when another 2b1u orbital of higher energy, the descendant of the Si-Al π* orbitals, is propagated throughout the lattice, it is bonding which is built up between unit cells, as shown in 26. 25 and 26 will mix, maximizing inter-unit-cell bonding, at the cost of loss of intra-unit-cell vertical bonding.

Figure 8 shows the contribution of the π* to the total DOS. As we can see, the mixing of this locally Al-Si antibonding level into occupied bands is substantial. π* mixes into the occupied bands in a similar way. A consequence of this mixing in π* and π* is some accumulation of Si-Al antibonding character (in the handle or vertical or 1X bond) around the Fermi level.

Figure 9 shows the COOP curves for the vertical (solid line) and the tilted (dotted line) Si-Al bonds. Indeed an antibonding bump is observed in the vertical Si-Al COOP, near the top of the p bands.

The computed overlap populations in the solid are shown in 27, and these should be compared with the cluster model 21. There is a reasonable correspondence between the extended solid

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(31) Orbitals of different symmetries of the Al2Si22- motif (D3h) can mix at the Γ point, because the Γ point has different symmetry.
values (computed for equal Si–Al distances but reflected in the observed distance inequalities) and the cluster model for the solid.

There are several consequences of a weakened vertical bond and the specific way in which it is weakened. First of all, it is possible to intercalate small ions into this Al₂Si₁₉ layer, shown in 28 for LnLi₃P₂. This material can be thought of as LnLi'Li₃P₂ in which Li' intercalates into a CaAl₂Si₁₉-type LnLi₂P₂ structure. Other compounds of this type are LnLi₃Cu₃P₂.\(^{33}\)

Note that Si–Al vertical antibonding character is concentrated near the top of the p band (Figure 9). Oxidation of the layer should then shorten the vertical Si–Al bond. There are some such compounds, with 15 electrons per unit cell.\(^{33}\) However, no single crystal study is yet available for these. It would also be interesting to intercalate some valence fluctuator,\(^{34}\) for example) instead of Ca, the oxidation or reduction of which might affect the bonding in the host lattice. A compound, GdAl₂Si₂, with 17 electrons has been made.\(^{26}\) The extra electron probably resides in the Gd d band, providing the observed metallic behavior, as indicated schematically in 29.

Finally, the reconstruction process 7–8, where the local environment change is shown in 30, is not the only one. The other possibility is 31, similar to the intramolecular recombination to tricyclo[2.2.2]octane, i.e., [2.2.2]propellane of the bicyclic di-radical. The resulting structure is of a "dimerized" graphite net type, 32. Our calculation shows that the two structures 30b and 31b have approximately the same energies for Al₂Si₁₉\(^{2-}\). However, the closer contact between Si atoms in 31b results in a negative overlap population, shown in 33a, compared to the structure 30b whose overlap populations are depicted in 33b. The negative overlap population in 33a is due to the closed-shell repulsion

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between Si atoms, formally Si$^{4+}$. However, when the electro-

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negativity difference between the B (open circle) and the X (black circle) atoms is decreased, the repulsion should be minimized. So a stoichiometry of B$^+_1$B$^-_2$ (or X$^+_1$X$^-_2$) should increase the pos-

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sibility of the "dimerized" graphite structure 32.

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Appendix

The extended Hückel method$^{15}$ was used in all calculations. Table II lists the parameters used for Al and Si. The geometry is chosen such that Si is at the center of an idealized Al$_4$ tetra-
hedron with Si–Al = 2.45. A 30 k-point set is used in the irre-
ducible wedge in the Brillouin zone$^{15}$ to calculate average prop-
erties.

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Ligand Effects on the Electronic Structure, Spectra, and Electrochemistry of Tetracarbonyl Carbonyl Clusters

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Abstract: Self-consistent field $X\alpha$ calculations using the discrete variational method (SCF-$X\alpha$-DV) have been performed for Co$_4$(CO)$_{12}$ (I) and the Ca symmetry model clusters ($\eta$-C$_6$H$_6$)Co$_4$(CO)$_9$ (II), Co$_4$(CO)$_6$(PH$_2$)$_2$CH (III), and ($\eta$-

C$_6$H$_6$)Co$_4$(CO)$_6$(PH$_3$)$_2$CH (IV) to explore the effect of phosphine and arene ligands on cluster electronic structures. Density of states plots have been used to simplify analysis of bonding trends in these complex clusters. The cluster core charge varies from 3.11, to 2.58, to 2.41, to 1.80 e along the I–IV series. Charge on the apical Co is least positive in the arene-capped cluster II while basal cobalts are least positive in IV. Ionization potential calculations support qualitative Hückel studies that suggested ($\eta$-C$_6$H$_6$)M fragments bind more strongly to other metal centers than isolobal (M(CO)$_3$) fragments. Electronic absorption spectra of I, ($\eta$-MeC$_6$H$_5$)Co$_4$(CO)$_9$ (V), Co$_4$(CO)$_9$(tripod) (VI) (tripod = (PH$_2$)$_2$CH), ($\eta$-MeC$_6$H$_5$)Co$_4$(CO)$_6$(tripod) (VII), and ($\eta$-

C$_6$Me$_5$)Co$_4$(CO)$_6$(tripod) (VIII) exhibit low-energy features between 1000 and 400 nm. Arene-capped clusters exhibit an extra low-energy absorption and calculations for the models II and IV assign this to a HOMO–LUMO transition that resembles intramolecular charge transfer from the apical to basal cobalt atoms. All substituted cobalt clusters V–IX (IX = ($\eta$-[2.2]-paracyclophane)Co$_4$(CO)$_9$(tripod)) exhibit reversible 1e reductions by cyclic voltammetry. Only clusters VI and VII display reversible 1e oxidations. Redox potentials correlate well with calculated tetracobalt core charges for the model systems I–IV but do not correlate well with HOMO or LUMO energies. Effects of apical and basal substitutions on redox potentials in the tetracarbonyl clusters are shown to be additive. This supports the notion of delocalized cluster bonding. For this reason cluster core charges better reflect gross properties of the cluster rather than HOMO or LUMO energies of localized two-electron orbitals.

Electronic structures of dinuclear metal complexes have been thoroughly studied, resulting in well-characterized one-dimen-
sional metal–metal interactions. An understanding of the elec-
tronic structure of larger clusters, beyond electron counting rules, has not yet been achieved. Trinuclear clusters, which exhibit two-dimensional metal–metal interactions, have been the most extensively studied class of large clusters. Calculations for triang-
ular M$_3$(CO)$_9$ (M = Ru, Os) complexes using extended Hückel theory (EHT)$^3$ and the self-consistent field $X\alpha$ discrete

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