Bonding in the BaPdSn₃ Structure

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The body-centered BaPdSn₃ structure contains Sn atoms in tetrahedral and square-pyramidal five-coordinate sites, and Pd in square-pyramidal environments. The PdSn₃²⁻ three-dimensional lattice can be formally decomposed into first two-dimensional layers, then into a square Sn lattice with capping Sn and Pd atoms. This geometrical decomposition also serves as a construction principle for building up the electronic structure of this material. Many similarities to BaAl₄ emerge. There is electron deficient multicanter bonding in the layer, normal two-center bonding Sn–Pd between layers. Pd 4d orbitals do not contribute significantly to the bonding.

Since the body centered tetragonal BaAl₄ was first made by Andress and Alberti [1] more than 400 compounds with the same structure have been synthesized [2]. Among these, most have been found in the R₃M₄A₃ ternary system, where R is a rare earth or sometimes an alkaline earth; M, a transition metal; and A, a group 13, 14, or 15 element such as silicon, boron, phosphorus or homologues [3].

There are two different Al sites in the BaAl₄ structure: the tetrahedral sites, so called t-sites, and the pyramidal sites, or p-sites, as shown in 1. Two of the four aluminium atoms in each primitive unit cell occupy the tetrahedral sites and the other two take the pyramidal ones. In the ternary derivatives of BaAl₄ it is the M and A atoms that alternate positions at these sites. There exist seven hypothetical structures possible for such systems with the same unit cell as BaAl₄, if no short M–M contacts are permitted [4]. In fact, three of these have been confirmed experimentally and they are known as the ThCr₂Si₂ type [5], 2a, CaBe₂Ge₂ type [6], 2b, and BaNiSn₃ type [7], 2c. In the ThCr₂Si₂ type structure, the transition metals are almost always located in the tetrahedral sites and the main group elements in pyramidal sites. In the CaBe₂Ge₂ type structure, however, the M and A atoms share t- and p-sites equally. The third BaAl₄ ternary derivative, BaNiSn₃, has its A atoms on all tetrahedral sites, and also on half of the pyramidal sites. The M atoms thus place themselves on another half of the p-sites.

The ternary compounds have many interesting electrical and magnetic properties. The “heavy fermion” material CeCu₂Si₂ [8], and the magnetic properties of the same crystal [9] serve as particular exam-
apes. Many superconducting ternary silicides discovered so far come from the BaAl₄ family: YbPd₃Ge₂, LaPd₃Ge₂, LaNi₃Ge₂ [10] and the low temperature form of YIr₃Si₂ [11] (ThCr₂Si₂ type); the high temperature form of YIr₃Si₂ and LaIr₃Si₂, which have the CaBe₂Ge₂ structure [11]; and LaMSi₃ (M = Ir, Rh) [12], which is of the BaNiSn₃ type, represent all three experimentally found structures described above.

Chemists also have shown their interest in the geometrical deformations, bonding patterns and chemical properties of these lovely crystals. A series of papers describing the ThCr₂Si₂ and CaBe₂Ge₂ type structures has been recently written by one of us and C. Zheng [13]. This work is a continuation of the cited research. BaPdSn₃ [14], a BaNiSn₃ type structure, serves as the main example in the calculations. We proceed by constructing a Sn₃ layer structure from a square lattice of tin atoms with one apical Sn per unit cell, followed by inserting a Pd atom into the adjacent apical site of the opposite face to form a PdSn₃²⁻ layer. Finally, by stacking these layers, we arrive at a three dimensional body-centered tetragonal lattice. With the help of the tight-binding method of the extended Hückel type [15] we are able to show how similar the bonding pattern is to the BaAl₄ structure which was described by Zheng and Hoffmann [16].

**Sn Square Lattice and Sn₃ Layer Structure**

The Sn square lattice is shown in 3. The smallest unit cell consists of a single Sn atom. The Sn–Sn distance is 3.44 Å, the same as that measured in the BaPdSn₃ crystal. The electronic structure of a square lattice is well known [17] and the calculated band structure shown in Fig. 1 gives the expected pattern: The lowest s band does not cross the three p bands due to the large separation between tin atoms. The phase relation of the orbitals is as follows: At the Γ point, the center of the Brillouin zone, orbitals carry the same sign at all lattice sites. At the X point, however, they are of the same sign in the y-direction but of opposite sign in the x-direction. At the M point, each orbital has the same sign as its nearest neighbors and opposite sign to the second nearest neighbors. The in-phase combination of s orbitals at Γ is pure σ bonding and leads to lowest energy. The pₓ (or pᵧ) combination at the same point is at higher energy, due to strong σ* antibonding in the x-direction (or the y-direction). The π bonding here is weak and the σ bonding dominates. The highest energy occurs at X for the pᵧ combination. There, the pᵧ orbital is pushed up high because of strong σ* and π* antibonding. The pₓ orbitals, with only π type interactions, have a small dispersion. A schematic drawing of these orbitals at Γ, X and M is presented in Fig. 1 along with the band structure.

Next, we need to construct a band structure for a larger unit cell (two Sn atoms) for such a cell is re-
sponding first Brillouin zones (BZ) in 4c and 4d respectively. The BZ of the large cell is half the size of that for the small unit cell since the large cell itself is twice the size of the small one. \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_1', \mathbf{a}_2' \) are the primitive lattice vectors defined for the big and the small cell respectively, and \( \mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_1', \mathbf{b}_2' \), the corresponding reciprocal lattice vectors. Notice that all the points in the BZ of the small cell are labeled with a prime. On folding, \( \Gamma' \mathcal{N}' \) and \( \Gamma' \mathcal{X}' \) lines in 4d become the \( \Gamma \mathcal{X} \) line in 4c. \( \Gamma' \mathcal{X}' \) and \( \mathcal{M}' \mathcal{X}' \) become \( \Gamma \mathcal{M} \). The resultant band structure is plotted in Fig. 2b. It is exactly what one would obtain if one calculated the bands of the larger unit cell.

Now we add apex Sn atoms to the square lattice. The layer thus constructed is depicted in 5. The distance between an apical Sn and its nearest neighboring atom in the square lattice is 3.05 Å, only a little longer than an ordinary Sn–Sn single bond. So we would expect substantial interaction upon formation

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**Fig. 2.** Band structure of the square lattice of Sn atoms. (A) Before the "folding back" process, (B) after the process. The arrows in (A) indicate the folding directions.
of the layer. Schematic diagrams drawn in Fig. 3 illustrate how energy levels are pushed up or down when local interactions are turned on.

Fig. 3a shows what happens at the $\Gamma$ point. We denote various orbital combinations of the square lattice before interaction as $\psi_x$, $\psi_y$, $\psi_z$, $\psi_x', \psi_y', \psi_z'$, $\psi_x$, $\psi_y$, $\psi_z$ and $\psi_x', \psi_y', \psi_z'$. The $s$, $p_x$, $p_y$ and $p_z$ orbitals of an apical atom are simply labeled $s$, $p_x$, $p_y$, and $p_z$. $s$ and $p_z$ can be imagined to mix with each other and form two hybrids, $h_y$ and $h_y'$. We have no guidance at this

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Fig. 3. Schematic diagrams shown the orbital interactions within a Sn layer: (A) at $\Gamma$ point of the Brillouin zone, (B) at M point. The square lattice orbitals before interaction are always shown at left and the apical tin orbitals, at right.
point as to the precise degree of s and p mixing in these hybrids, so for simplicity let us take the hybrids as 50% s, 50% p. $h_1y$ has the right symmetry to interact with $\psi$, in a $\sigma$ bonding way. As a result, $\psi$, is pushed down and $h_2y$ is pushed up very high. $h_3$, on the other hand, does not interact with any square-lattice orbitals and remains nonbonding. $p_x$ and $p_y$, being of $\pi$ type symmetry, mix with the degenerate pair $\psi_x$, $\psi_y$ and are lifted up in energy. The doubly nodded combinations $\psi_x'$ and $\psi_y'$ do not find any appropriate partners to interact with and stay where they are. The energy levels after interaction are shown in the central part of Fig. 3a.

A similar correlation diagram at the M point is constructed in Fig. 3b. Notice that here orbital combinations of the square lattice before interaction form four degenerate pairs. They are $\psi_x$ and $\psi'_x$; $\psi_y$ and $\psi'_y$; $\psi_x$ and $\psi'_y$; $\psi_y$ and $\psi'_x$ in order of increasing energy. Taking linear combinations of $\psi_x$ and $\psi_y$ yields two orbitals: $\psi(xy)$ and $\psi'(xy)$. $\psi(xy)$, being of $\sigma$ type symmetry, can now interact with $h_1y$ and shifts to higher energy. The other orbital, $\psi'(xy)$ is nonbonding and does not change its position. $p_x$ and $p_y$ orbitals, on the other hand, have the correct symmetry to mix with both $\psi_x$’s and $\psi_y$’s, but interact predominantly with $\psi_x$’s due to their better match in energy.

Fig. 5 shows the contributions to the DOS of the two hybrids. We tried in this context not only $sp_z$ hybrids, 50% $s$, 50% $p_z$, but also different $s$, $p$ mixing ratios. The most informative results were obtained for $h_1y$ being 75% $s$, 25% $p$, and $h_2y$ 25% $s$, 75% $p$. These projections are plotted in Fig. 5. $h_1y$ is split among two bands: its lower part, at $-15 \sim -20$ eV is the contribution to $\psi_{\sigma}$, while its upper part at 6 to 9 eV is $\psi_{\pi}$. The distribution of $h_2y$ is very different. This level is very much localized in a band between $-7$ and $-10$ eV.

The previous discussion has traced the construction of the band structure of the Sn$_1$ part of a layer. But it is not really descriptive of the nature of the
bonding in the layer. To reach a simpler description we note the hypervalent 5-coordination of Sn₅, the resemblance of the square pyramidal units to B₃H₆ [21], and our previous discussion of BaAl₄ [16].

Suppose we begin with a set of four tetrahedral sp³ hybrids at each Sn₅, recognizing its local environment. At the Sn₅, on the other hand, let's just form two sp hybrids as before, leaving the rest two p orbitals unhybridized. The picture we have so far is drawn in 9 (only two squares shown, labelled "Sn" and "Pd").

In the "Sn" square or pyramid there will be bonding between the five Sn’s, above the square lattice, in the “Pd” square we expect orbitals below the square, directed toward the Pd which will eventually come there in the next stage of the construction.

Fig. 4. Band structure of the Sn₅ 2-dimensional layer along 2 directions. The main contributions to the bands are drawn at Γ and M.

What is the nature of the bonding within the “Sn” pyramid? A schematic diagram is indicated in 10. At
Fig. 5. Density of states (DOS) projections of the two sp$_2$ hybrids in a Sn$_3$ layer structure. On the left is the hy$_1$ (75% s, 25% p$_z$) contribution and on the right, the hy$_2$ (25% s, 75% p$_z$) contribution. The dashed line is the total DOS and the dotted line, the integrated hybrid state density.
left are the four symmetry-adapted combinations of the four Sn, sp$^3$ hybrids in the square, at right the Sn$_p$ orbitals. Three bonding combinations, a$_1$+e, or o+$\pi$ result. The six electrons in these three MO's hold together the Sn$_p$ to four Sn$_e$ atoms. This is electron-deficient multi-center bonding, just as one has in B$_3$H$_6$ [21]. In addition we have a non-bonding out-pointing orbital on Sn$_p$, h$_{yz}$, whose presence we have already traced.

Superimposed on this picture of bonding in the “Sn” hollow or pyramid we expect several bands corresponding to Sn, hybrids pointing toward the “Pd” hollow. The delocalized orbitals will hardly follow our penchant for localization, so in the two-dimensional Sn$_3$ network things will be more complicated, delocalized. Still we should see the traces of this localized picture.

A good way to characterize bonding in a periodic network is to examine COOP [22] curves. These are overlap population weighted DOS curves, and they show the average contributions to bonding (in a specified bond) of all the levels in a given energy interval. Such a curve for the Sn$_3$ layer is shown in Fig. 6. The bonding peaks marked $\psi_b$ and $\psi_a$ are the main contributions to Sn$_e$–Sn$_p$ bonding. There are many states, especially around the Fermi level, which do not contribute to such bonding. These are orbitals pointing toward the Pd sites, which we now will begin to populate.

PdSn$_2^{-2}$ Layer Structure

We are now ready for building up a two dimensional layer structure of PdSn$_2^{-2}$, as indicated in 11. There are two types of lattice sites: the tetrahedral site within the square lattice and the pyramidal site at the apical positions. The unit cell is drawn in 12. It contains two t-site Sn atoms, which we denote as Sn$_t$ as before; a p-site tin, Sn$_p$, and a p-site palladium, Pd$_p$. A total number of twenty-four electrons is associated with each unit cell. The local environment

![Figure 6](image-url)  
Fig. 6. Crystal Orbital Overlap Population (COOP) curve for the Sn$_e$–Sn$_p$ bond in a Sn$_3$ layer. The arrow indicates the Fermi level.
of Snₚ and Pdₚ is what we see in 13: a set of square pyramids with their apices pointing alternately up and down. Each Snₚ and Pdₚ sits on top of a square pyramid and has a close contact with four basal tins (Snₚ). Later, when forming a three dimensional structure, a Snₚ-Pdₚ bond will be introduced and these atoms will eventually be five-coordinate. The picture here is very similar to the Al₂²⁻ layer structure in the BaAl₄ crystal [16], except that here the downward apex is occupied by a different type of atom.

The similarity between BaAl₄ and BaPdSn₃ can be pushed a little further. If the Pd were taken as neutral and approximately d¹⁰, and if the d electrons of Pd were not participating in the bonding, then PdSn₃²⁻ is a 4 atom-14 electron unit, just as Al₂²⁻. But is it safe to say that the Pd d electrons indeed have little contribution to the local bonding? Density of states projection of the 4d levels, plotted in Fig. 7, gives a definite answer. It is obvious that the energy levels are, to a great degree, localized at a value of ~ -12 eV. Other calculations indicate that this is a common feature present in BaNiSn₃ type structures [23]. There is a small crystal field splitting of the d band, but it is too small to show up on the scale of Fig. 7. Actually the crystal field splitting, as small as it is, is an inverse one, stabilizing dₓᵧ [24] relative to the other orbitals. This is a consequence of the Sn orbitals being at higher energy than the metal d set, the reverse of the usual ligand-metal orbital energy ordering.

The essential, quasilocalized features of the bonding are shown in Fig. 8. The left-hand side of Fig. 8 reproduces 10. We will not repeat the argument: there is delocalized multi-center bonding in the “Sn” hollow, using six electrons, plus an out-pointing lone pair on Snₚ. Similar constructions apply to the “Pd” hollow. The only difference now is that the hybrids at Pd are higher in energy, and so are the Pd 5p orbitals. There are still three bonding orbitals (a₁⁺e, a₁+π), and in addition one has the relatively non-interacting Pd 4d set and a now empty, down-pointing hybrid at Pd. The total electron count of 24 is now the right one for PdSn₃²⁻. Of these 24 electrons, 10 are in the Pd 4d, 12 in Sn-Sn and Sn-Pd delocalized bonding, 2 in the Sn lone pair.

This is a localized picture, highly simplified. On going to the delocalized picture shown schematically at right side of 14, energy levels are broadened into bands. The inter-cell interactions are strong enough to destroy the locally imposed small gap between the highest occupied and the lowest unoccupied levels indicated at left of 14. A partial overlap of these bands should result.

To see whether the above analysis gives a qualitatively correct representation we show here the calculated band structure along two symmetry lines, ΜΓ and ΓX, in Fig. 9. There is indeed an overlap between the 12th and 13th band.
Fig. 8. Schematic diagrams of the local interactions in the PdSn$_2^-$ layer structure. The left-hand side shows the orbital interactions of the an apical Sn with the square lattice, and the right-hand side gives a similar picture for an apical Pd.

Fig. 9. Calculated energy bands for the PdSn$_2^-$ 2-dimensional layer along two symmetry lines. The overlap between the 12th and the 13th bands is emphasized by the heavy lines.
DOS curves for palladium 5p, and 5p, plotted in Fig. 10 are consistent with the bonding picture in Fig. 8. The two main peaks appearing at about \(-7.0 \sim -9.0\) eV and \(7.0 \sim 12.0\) eV are the contributions to \(\pi\) ("Pd") and \(\pi^*\) ("Pd") respectively (cf. Fig. 8, right). \(-70\%\) of states being in \(\pi^*\) ("Pd") and only \(-30\%\) in \(\pi\) ("Pd"). This clearly follows what one would expect to happen in an isolated molecule: the antibonding orbital has more contribution from the atomic orbital of higher energy. It is not surprising to see the same phenomenon exhibited in the DOS projection of tin p, and p, also illustrated in Fig. 10. Around \(-10 \sim -11\) eV are now the states contributed to \(\pi\) ("Sn"). They are about 2\sim 3 eV lower in energy than the corresponding ones of \(\pi\) ("Pd"). For \(\pi^*\) ("Sn"), the difference is roughly \(-5 \sim -6\) eV.

Further evidence in support of the argument given in Fig. 8 is to be found in the palladium sp, contribution to the total DOS. This is plotted in Fig. 11. At left is a DOS projection of hy\(_1\) (Pd) [25], the hybrid that points toward the base of the pyramid. \(-20\%\) of its states go into bonding \(\sigma\) ("Pd") and \(-60\%\), into antibonding \(\sigma^*\) ("Pd"). Compared with hy\(_1\) (Pd), the DOS curve of hy\(_2\) (Pd) looks very different. A narrow band between \(-4\) and \(-5\) eV characterizes the non-bonding behavior of this orbital. Not only this. The density of states projections of a, c and b, show agreement with our qualitative considerations outlined above.

The localized bonding pattern of Fig. 8 is confirmed by the COOP curves, Fig. 12. The Sn–Sn, bonding in the PdSn\(_{2}\) layer is nearly identical to that in the Sn\(_3\) sublattice described earlier. The Sn–Pd overlap population also has \(\sigma\) and \(\pi\) peaks, but as Fig. 8 would suggest, these occur at different energies from the Sn–Sn bonding maxima. In addition there is a weak contribution to Sn–Pd bonding from the Pd d band at \(-12\) eV.

![Fig. 10. The p, and p, contributions (shaded area) to the total density of states (dashed lines): (A) 5p, 5p, of an apical tin atom, (B) 5p, 5p, of an apical palladium atom. Dotted lines are the integrated 5p, and 5p, states.](image-url)
Fig. 11. The projected density of state of the Pd\(_p\) hybrids. (A) hy\(_1\) (75\% s, 25\% p\(_p\)), (B) hy\(_2\) (25\% s, 75\% p\(_p\)) in the PdSn\(_{2}^+\) layer structure. The dashed line is the total DOS and the dotted line, the integrated hybrid states. The Fermi energy is indicated in the figure.

Fig. 12. COOP curves for the PdSn\(_{2}^+\) two dimensional lattice: (A) Sn\(_1\)–Sn\(_p\) contact, (B) Sn\(_1\)–Pd\(_p\) contact. The arrows indicate the Fermi level.
PdSn$_3^{2-}$ Three Dimensional Structure

At this stage we turn on interaction between layers. All we do is to stack the PdSn$_3^{2-}$ layers. The process is displayed in 15. Each Pd$_p$ now has a close contact with a Sn$_p$ atom from another layer. The Pd$_p$–Sn$_p$ distance is short (2.636 Å), so a strong interaction between the two is expected. hy$_2$ (Sn), having its big lobe pointing upwards (positive z-direction), overlap nicely with hy$_2$ (Pd), the Pd hybrid pointing downwards. What we obtain is a normal two-center, two-electron σ-type bond, 16. Everything else should be little changed because the intralayer interactions remain essentially unchanged. There is going to be some charge transfer, and charge should flow from Sn$_p$ to Pd$_p$ since hy$_2$ (Sn) was originally filled and hy$_2$ (Pd) was empty.

We would like to see how well these qualitative considerations check out in a full calculation. Fig. 13 shows projected density of states for hy$_2$ (Sn) and hy$_2$ (Pd) [26]. Most of the hy$_2$ (Sn) states (~70%) go into σ whereas σ$^*$ takes up about same amount from hy$_2$ (Pd). This is what one would expect from 16; the bonding molecular orbital is close in energy to hy$_2$ (Sn) and should therefore be more Sn-like.

hy$_2$ (Pd), being higher in energy, contributes mainly to σ$^*$ antibonding, making the σ$^*$ region Pd-like. Note the nice resonance between hy$_2$ (Pd) and hy$_2$ (Sn) contributions in the σ band region.

DOS contributions of the other orbitals, namely the Sn$_p$ square net orbitals, the Pd d block, the Sn$_p$ and Pd$_p$ π orbitals, are all essentially unchanged upon stacking to the three-dimensional structure.

The band structure of 3-dimensional PdSn$_3^{2-}$ is shown in Fig. 14. No detailed discussion is necessary — the resemblance to the 2-dimensional layer of Fig. 9 is clear. The σ and σ$^*$ bands, labelled at Γ and M, are the only new feature, and they cause a minor perturbation of the band structure via some avoided crossings. The overlap between the 12th and 13th bands (bold face) remains. The material should be metallic.

The population analysis shows a flow of 0.35 electrons from Sn$_p$ to Pd$_p$. The relevant COOP curves are drawn in Fig. 15. The Pd$_p$–Sn$_p$ and Sn$_p$–Sn$_{p}$ curves are nearly unchanged relative to the two-dimensional case. The Pd$_p$–Sn$_p$ COOP curve shows maximal contributions where we have identified the σ and σ$^*$ bands. The Fermi level, as usual, comes in a position that maximizes bonding. One interesting aspect of the calculations is that we get a positive overlap population, 0.096, between formally nonbonded tetrahedral site tin atoms. This is to be compared to an overlap population of 0.356 for Sn$_p$–Sn$_p$. From our experience the positive sign and magnitude of
the Sn–Sn overlap population are indicative of real bonding.

To summarize: the PdSn$_3^{2-}$ framework is held together by twenty-four electrons per unit cell. 12 of these are involved in multi-centered bonding between basal Sn atoms (Sn$_x$) and the $p$-site atoms, Sn$_p$ and Pd$_p$. The other two, being used to form a strong $\sigma$-type bond, hold the layers together. The ten 4d electrons, on the other hand, contribute very little to any bonding.
Fig. 15. Crystal Orbital Overlap Population curves for the 3D PdSn$_2$ in the BaPdSn$_3$ structure. (A) the Pd$_p$–Sn$_s$ bonding, (B) the Sn$_p$–Sn$_s$ bonding and, (C) the Pd$_p$–Sn$_p$ bonding. The Fermi level is indicated by the arrows.
Other BaNiSn₃ Type Structures

Listed in Table I are a number of selected compounds with the BaNiSn₃ type structure. All have 24 electrons per unit cell. We have calculated the band structures for BaNiSn₃ and LaIrSn₃ [12, 27] along one or two symmetry lines, but do not present the details here. In general there are great similarities to the PdSn₃⁻ electronic structure presented above. There are differences in the extent of band overlap at the Fermi level, and some of these compounds may be semiconductors.

Table I. Some RMA₃ structures.

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Appendix

The extended Hückel approach in the tight-binding method [15] was employed in all calculations.

Table II lists the parameters used for Sn and Pd. The geometry of BaIrSn₃ was taken from the experimental data. A set of 28 or 40 k points was selected in the irreducible wedge in the Brillouin zone [28] for the DOS and COOP calculations.

Table II. Parameters used in the extended Hückel calculations.

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ᵃ Coefficients used in the double ζ expansion of the d orbitals.

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[19] See, for example: J. K. Burdett, Prog. Solid St. Chem. 15, 173 (1984); Ref. [16, 17].
[23] DOS projections of d orbitals for LaIrSi, and BaNiSn, give the same feature.
[24] The orbital is d_yz with our choice of coordinates, but corresponds to d_{x^2-r^2} in the conventional octahedral field, where the ligands are placed along the x and y axes.
[25] Here again we have chosen sp^3 hybrids with x ≠ 1. hy_1 is 75% s, 25% p, and hy_2 25% s, 75% p.
[26] Both these hybrids are taken as 25% s, 75% p in the projections.