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Peierls Distortions in Two and Three Dimensions and the Structures of AB Solids

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Abstract: Two- and three-dimensional analogues of the well-known Peierls distortion in one-dimensional solids can be used to view the structures of the group 6B and 5B elements and their derivative structures. Starting with the simple cubic structure, the β-tin, graphite, gallium, and arsenic structures are easily generated by this route. It is shown how with a large electronegativity difference between A and B the rocksalt structure (a derivative of the simple cubic arrangement) becomes stable for octet systems, the theoretical reasoning being exactly analogous to that used to stabilize square singlet cyclobutadienes by substitution.

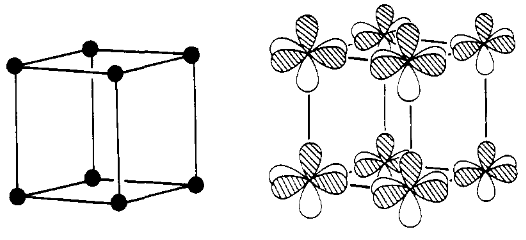
The configurational instabilities associated with both a half-filled band of a solid and a half-filled pair of degenerate orbitals in a molecule are classic structural problems. The first, mainly documented for one-dimensional solid-state systems, is called a Peierls distortion,[2] and the second a Jahn–Teller instability.[3] In both, a symmetric structure distorts so as to remove the zero energy gap between HOMO and LUMO as in Figure 1, where we have used two organic systems as examples. Both are experimentally observed to be distorted away from the symmetrical structure. In the solid state the instability is particularly important since it is often associated with a dramatic change in electronic properties—namely from metal to insulator (or perhaps semiconductor, depending upon the size of the band gap, as is the case in polyacetylene[4]). Almost all the known examples are either strictly or pseudo-one-dimensional systems.[5] In this paper we point out that some simple three-dimensional structures may be regarded as arising via Peierls distortions in two and three dimensions. We also demonstrate that similar tricks may be used to stabilize the undistorted geometries in both molecular and solid-state environments. The results shed new light on the factors determining the structures of AB solids.

Structures Derived from the Simple Cubic Arrangement

In Figure 1b we showed the structural instability in polyacetylene, induced by the half-filled $p\pi$ band. The energy variation for a single chain of equidistant atoms each bearing a single $p\pi$ orbital as a function of the wave vector $\mathbf{k}$ is given[6] by

$$E(\mathbf{k}) = \alpha + 2\beta \cos \mathbf{k}_x a \tag{1}$$

where α and β have their usual meaning within Hückel theory, a is the length of the unit cell along the chain direction (x), and $\mathbf{k}_x$ varies from 0 to π/a. So the bottom of the band has an energy $\alpha + 2\beta$, and the top an energy of $\alpha - 2\beta$. Let us imagine that the simple cubic structure is made up of three similar orthogonal p orbital networks **1**, the only difference from polyacetylene being that we will focus on the dominant $p\sigma$ rather than $p\pi$ interactions between adjacent orbitals.[7] We assume for the sake of argument that two electrons on each center are located in the valence s orbital and do not influence the structural problem, just as in the Rundle–Pimentel scheme[8] for hypervalent molecules. One of the attractions of this model is that the energy dependence on the three-dimensional $\mathbf{k}$ vector may be written down exactly within the framework of tight-binding theory—the solid-state analogue of the LCAO-molecular orbital approach.



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[1] Fellow of the Alfred P. Sloan Foundation and Camille and Henry Dreyfus Teacher–Scholar.

[2] (a) Whangbo, M.-H. *Acct. Chem. Res.*, in press. (b) Peierls, R. E. "Quantum Theory of Solids"; Oxford University Press: London, 1955.

[3] (a) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *A161*, 220. (b) See the discussion in Burdett, J. K. "Molecular Shapes"; Wiley: New York, 1980.

[4] Shirakawa, H.; Ikeda, S. *Polym. J.* **1971**, *2*, 231. Shirakawa, H. Ito, T.; Ikeda, S. *Ibid* **1973**, *4*, 460.

[5] (a) "The Physics and Chemistry of Low Dimensional Solids"; Alcacer L., Ed., Reidel, Davdrecht, Holland, 1980. (b) "Molecular Metals" Hatfield, W. E., Ed., Plenum Press: New York, 1979. (c) Soos, S. G. *Annu. Rev. Phys. Chem.* **1974**, *25*, 21.

[6] See, for example: Reitz, J. R. *Solid State Phys.* **1955**, *1*, 2.

[7] The picture doesn't change if $p\sigma$ and $p\pi$ interactions are included too, but the algebraic form of the bands is a little more complex.

[8] Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446; Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.

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$$\begin{array}{lll} p_x & E(\mathbf{k}) = \alpha - 2\gamma \cos \mathbf{k}_x a & \\ p_y & E(\mathbf{k}) = \alpha - 2\gamma \cos \mathbf{k}_y a & (2) \\ p_z & E(\mathbf{k}) = \alpha - 2\gamma \cos \mathbf{k}_z a & \\ & (0 < \mathbf{k}_i < \pi/a) & \end{array}$$

Here γ now represents the Hückel β for the σ interaction of two p orbitals. The difference in sign between eq 1 and eq 2 is simply due to the sign of the overlap integral between adjacent orbitals, negative in **2** positive in **3**, but this makes no difference to the form of the bands. The result is the formation of three degenerate energy bands whose energies are given simply in terms of a one-dimensional **k** vector. In other words, the electronic problem is just the sum of three perpendicular, independent, one-dimensional systems. We will now see how the simple cubic structure will distort depending on how these three perpendicular electronic bands are filled with electrons.

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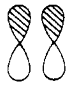

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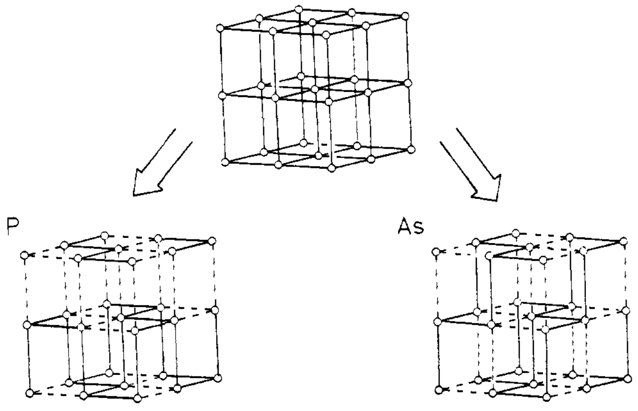
Breaking Three Linkages. With three p electrons per atom, as in the group 5B elements (s^2p^3), by analogy with the one-dimensional case we should expect a distortion away from simple cubic by the fission of alternate linkages along x, y, and z directions. This is just what is found. **4** shows an idealization of the structures of arsenic (A7) and black phosphorus (A17) generated in this way.[9] **5** shows how the half-filled p_x, p_y, and p_z bands are stabilized on such a distortion in an exactly analogous fashion to that shown in Figure 1. Each atom in practice ends up in a trigonal-pyramidal environment. Elsewhere we show[10] that there are 36 distinctly different structures of this type, with this size cell, and that their relative stabilities are determined in a rather interesting way.[11] We may regard all of them as arising via a three-dimensional Peierls distortion. The distortion may be reversed. Under pressure black phosphorus is converted[12] to a simple cubic arrangement which is metallic, as is to be expected from the half-filled band. There is also evidence for similar transformations for the heavier elements of this group[13] which normally crystallize in the arsenic (A7) structure type.



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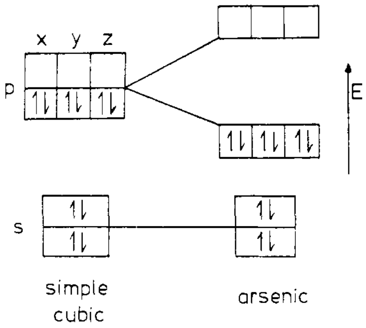

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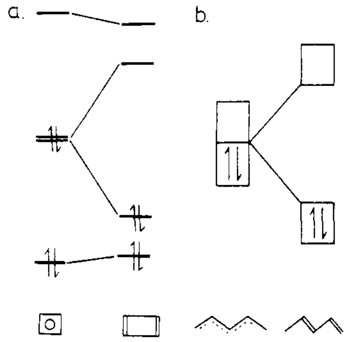
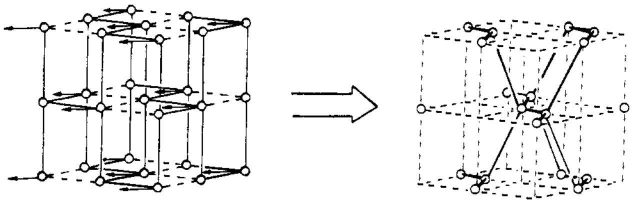


Figure 1. Distortions of symmetric geometries to remove Jahn–Teller and Peierls instabilities: (a) molecular case of square singlet cyclobutadiene, (b) solid-state case of polyacetylene. In both examples the distortion is associated with the filling pattern of π type levels. In this figure and in others like it throughout the paper we have deliberately overemphasized the band splitting in b above. In fact the top and bottom of the split band have probably changed very little in energy but a gap has opened up in the middle.

Breaking Two Linkages. With two p electrons, as in the elements of group 4B (s^2p^2), we only expect to break alternate linkages in two of the three Cartesian directions of the simple cubic structure. **6** shows the idealized result, by leaving all the "vertical" linkages of **4** intact and also something closer to the actual atomic positions expected. The result is simply the (A5) white, or β-tin structure,[14] found for tin under ambient conditions and for silicon and germanium under higher pressures.[13] **7** shows a simple band picture of the distortion. The β-tin structure is closely related to the well-known cubic diamond structure **8** (A4). Here then



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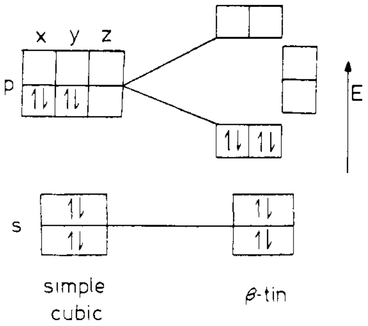

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(9) (a) Geometrically this has been noted by Wells and Adams (Wells, A. F. "Structural Inorganic Chemistry", 4th ed.; Oxford University Press: London, 1975. Adams, D. M. "Inorganic Solids"; Wiley: London 1974). (b) Electronically the problem has been viewed in this way by using soft phonon concepts by Littlewood (Littlewood, P. B. *J. Phys. C* **1980**, *13*, 4855; "Proceedings 4th International Conference Physics of Narrow Gap Semiconductors", Springer-Verlag New York, 1982; *J. Phys. C* **1980**, *13*, 4875.)

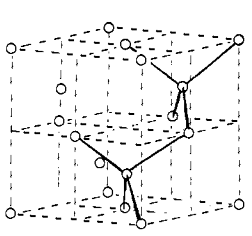
(10) Burdett, J. K.; McLarnan, T. J. *J. Chem. Phys.* **1981**, *75*, 5764.

(11) Burdett, J. K.; Haaland, P.; McLarnan, T. J. *J. Chem. Phys.* **1981**, *75*, 5774.

(12) Jamieson, J. C. *Science (Washington, D.C.)* **1963**, *13.*, 1291.

(13) See, for example: Liu, L. *High Temp.-High Pressures* **1981**, *13*, 387.

(14) As shown in **6** this is a distorted form of the β-tin structure. The real structure is orthorhombic and is elongated along the direction of the zig-zag chains in **6**.



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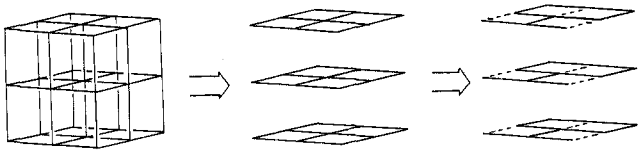
is a two-dimensional Peierls distortion, the result being to leave each atom four-coordinate. Although there is no experimental evidence for such an arrangement for these elements, Cohen and co-workers[15] find by calculation that the simple cubic structure is less stable than the β-tin and diamond structures for silicon and germanium.

Breaking One Linkage. (a) The Graphite Structure. This arrangement may also be viewed in terms of a Peierls type of distortion. Let us take a primitive cubic structure, separate the layers one from another, and distort the resulting 4^4 nets to 6^3 nets (**9**) by breaking every other linkage in one direction only.



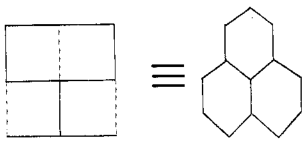


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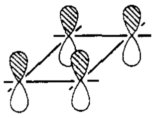
Figure 2 shows the resulting band picture. In (b) we have shown a narrow π band for the p orbitals perpendicular to the 4^4 sheets (**10**). (Recall that until now we have stressed σ interactions only).



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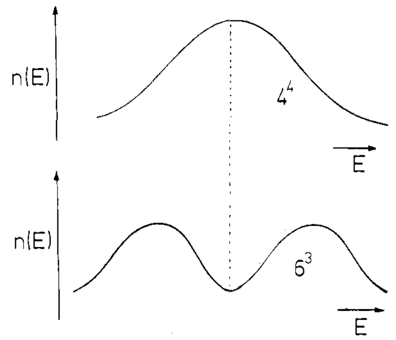
On distortion of the 4^4 net to the 6^3 net the half-filled π band does experience a stabilization which is not adequately shown by the schematic of Figure 2. **11** shows the change in the density of states



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associated with this band. As can be seen, the top and bottom halves of the band stick together (by symmetry at the point K in the Brillouin zone) and as a result graphite is a semimetal.[16] This π band *is* split into two halves in BN where there is an electronegativity difference between the alternate atoms of the net.

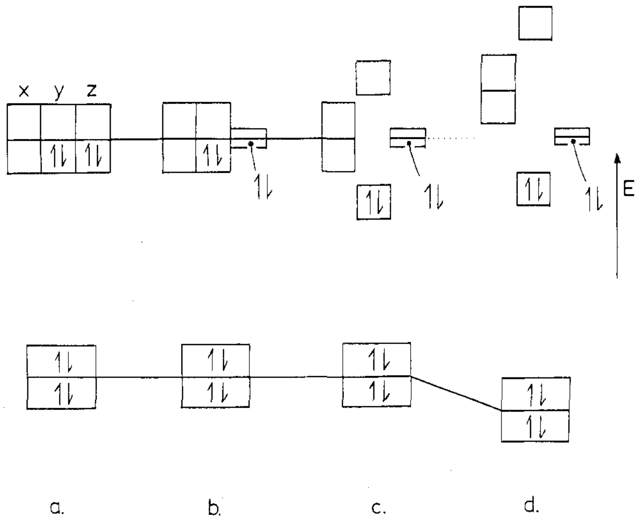
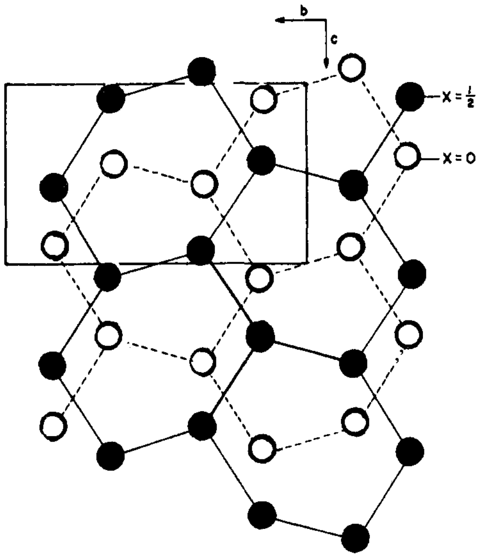


Figure 2. Generation of the band picture of graphite from that of the primitive cubic structure (a). (b) Separation of the layers (**14**) showing a narrower π band for the p orbitals perpendicular to the layers than the σ orbitals within the layers. (c) Peierls type distortion along one direction of the 4^4 net to give the 6^3 net. (d) Effect of sp mixing.

The true state of affairs in graphite is shown schematically in Figure 2d, where mixing between the s band and the in plane p bands is now switched on.[17] This simple model however is clearly insufficient to identify the conditions under which the graphite structure will be favored over the β-tin or diamond structure but does show in an interesting and simple geometric–electronic way how the structure may be generated.

(b) The Gallium Structure. It is a difficult task to relate the structures of the boron allotropes with their preponderance of B_{12} icosahedral units to the geometric possibilities created by a Peierls distortion of the simple cubic structure in one direction. However, rhombohedral 12 boron contains two types of planes stacked on top of each other. The first is a simple graphite-like 6^3 sheet and contains icosahedra with their twofold axes perpendicular to the sheets and the other is a more complex 6434 sheet which contains boron icosahedra with their threefold axes parallel to c. AlB_2 contains 6^3 sheets of boron separating 3^6 nets of aluminum atoms with half the number density and a trigonal-prismatic boron atom coordination. The structure of elemental gallium (**12**) is very easily



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(15) Yin, M. T.; Cohen, M. L. *Phys. Rev.* **1982**, *26*, 5668.

(16) See, for example; Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. Soc. London Ser. A* **1979**, *A366*, 23.

(17) The arsenic structure is very simply related to that of graphite by puckering the planar 6^3 nets of the latter geometry. It is easy to see this electronically by manipulating the diagrams of **2** and Figure 2. A discussion of the graphite → arsenic process is given by Burdett and Lin (Burdett, J. K.; Lin, J.-H. *Acta Crystallogr., Sect. B* **1982**, *B28*, 408.

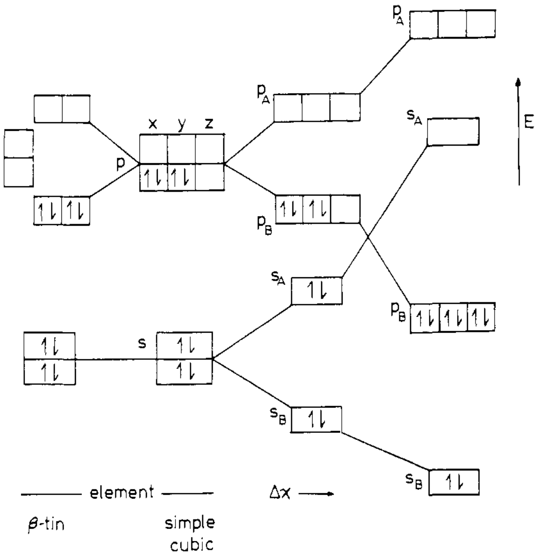
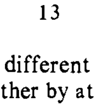


Figure 3. Change in energy of the simple cubic levels as the structure is distorted geometrically to the β-tin structure (left) and as the electronegativity difference ($\Delta\chi$) between A,B atoms of the rocksalt structure is increased (right). The bands in this exceedingly simplified picture are labeled s_A, p_B etc., although it is understood that anywhere other than the far right-hand side of the diagram the two will be mixed together.

generated by breaking alternate linkages of the 4^4 net along one Cartesian direction. The result is 6^3 graphite-like networks of distorted hexagons lying perpendicular to x, each shifted with respect to the one below so that the gallium coordination is three from within the sheet, two from above and two from below, a total of seven. In contrast to graphite, the sheets are bound together by strong covalent forces. Heine and Weaire[18a] have also studied the gallium structure and conclude that "the lattice vectors move so as to increase the band gaps", which of course is just the result of a Peierls type of distortion we have described.[18b]

Stabilization of the Parent Structure

Although the square cyclobutadiene molecule of Figure 1 is configurationally unstable, substituted cyclobutadienes have been made.[1] It is instructive to follow through the theoretical strategy behind the stabilization of the square geometry.[20] In our discussion above we identified the degenerate pair of orbitals as the culprit for the instability of this arrangement. However, a small distortion or perturbation will remove the degeneracy but not the instability, because now the two orbitals will couple together via a second-order Jahn–Teller mechanism and the distortion will continue.[21] Only when the HOMO and LUMO are well separated in energy will the square-planar structure become stabilized. The best way of doing this[20] is to make the substitution **13** where



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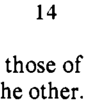

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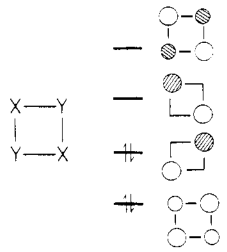
there are now two different groups, those of one type being separated from each other by atoms of the other. The C–C distances within the ring are equal in these compounds. In the so-called "push–pull" compound $C_4(Et_2N)_2(CO_2Et)_2$ with the pattern **13**, for example, the ring CC distances are all 1.45 Å within experimental error.[19c] The orbital picture now looks like **15**. The



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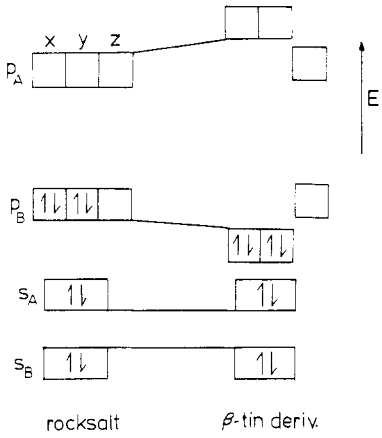
alternative substitution **14** is much less effective in opening up a good HOMO–LUMO gap in the molecule. Figure 3 shows how a similar strategy allows eventual stabilization of the rocksalt structure (this is just the simple cubic arrangement but with alternate A,B atoms along x, y, z directions) for the case of eight electrons per atom pair (AB). With a large electronegativity difference between A and B there is now a substantial HOMO–LUMO gap.

To the left of the s_A–p_B crossing in Figure 3 there is still an orbital degeneracy problem, and in this region where the p_A–p_B separation may not be large a sizable second-order stabilization of the occupied orbitals may occur. The distortion to the β-tin structure is still an obvious way to lower the energy of the system as in **16** (CdTe is found under pressure in the β-tin derivative



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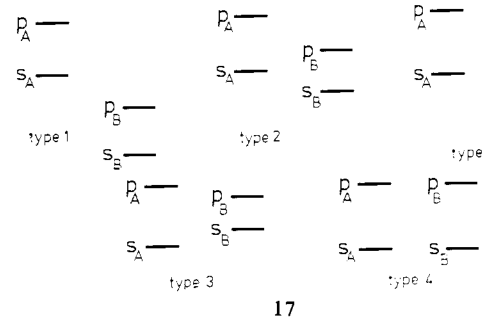
structure[13]). Around the crossing point itself, our very simple model with s–p separability is clearly inappropriate since heavy s–p mixing is certain to occur and strongly influence the choice of structure. All the traditional ideas of structure and bonding suggest that at this point along the abscissa of Figure 3, the likelihood of tetrahedrally coordinated geometries such as those of wurtzite (the derivative structure of hexagonal diamond) and sphalerite (the derivative structure of cubic diamond). These two structures are simple distortions of the β-tin arrangement (**6**, **8**). If the various possibilities of the s,p level orderings are categorized as in **17**, a very general prediction would be that the rocksalt



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[18] (a) Heine, V.; Weaire, D. *Solid State Phys.* **1970**, *24*, 249. (b) Strictly speaking, the argument of Heine and Weaire corresponds to a second-order rather than a first-order Jahn–Teller type of distortion although their argument is couched in the language of pseudopotential theory. The notion of stabilizing molecules by distortions which open up HOMO–LUMO gaps and solids by distortions which increase the band gaps is a valuable theoretical idea to use to understand the structure of both finite and infinite molecules.

[19] (a) Lloyd, D. *MTP Int. Rev. Sci. Org. Chem., Ser. One* **1973**, *3*. (b) Gompper, R.; Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 824. (c) Lindner, H. J.; von Gross, B. *Ibid.* **1971**, *10*, 491.

[20] Hoffmann, R. *J. Chem. Soc. D* **1969**, 240.

[21] See, for example, the discussion by Pearson (Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2104).

structure should only be found for type 1 systems, and the β-tin and typical tetrahedral structures for types 2–4 and those type 1 systems which lie closest to type $1^{1}/_{2}$. In practice, results very close to these are actually found.

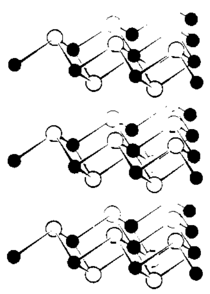
In an earlier study,[22] which explored the use of structural sorting maps to identify the features that determined crystal structure, we pointed out that there were strong correlations between observed structure type for these octet systems and the relative ordering of valence s and p levels, estimated by use of reciprocal pseudopotential radii of Bloch and Schatteman[23b] or of Zunger and Cohen.[24] *Without exception all* the rock salt examples are of type 1. Virtually all the sphalerite examples are of types 2, 3 (only two examples GaSb, BeTe), and 4 (the elements themselves). SiC and CuCl (type 1) are the only exceptions. Materials found on the boundary lines of structure maps (e.g., CuBr, AgI, ZnS, HgSe, MgTe) which are polytypic are generally of type $1^{1}/_{2}$. All examples with the wurtzite structure (with the exception of the borderline MgTe) are of type 1 and reflect the traditional observation that wurtzite examples are more "ionic" than sphalerite ones.

It is interesting to compare these results with other measures of the energetic location of the s,p orbitals on A and B, using indices which are combinations of the s,p (and in one case d) pseudopotential radii. The structure map of Bloch and Schatteman,[23b] using the parameters R_{CT} and $\bar{R}_H$ show an excellent separation (one error) of sphalerite examples from those of wurtzite and rocksalt for $\Delta R_{CT} \sim 0.18$. Zunger's map,[25] which uses R_σ, R_π, does not show such a good resolution using a *single* parameter, but for $R_\pi \sim 0.43$ the rocksalt examples are broadly separated from examples with the sphalerite or wurtzite structures. In our earlier work[22] a T_1 parameter of about 1.25 is sufficient to resolve (three errors) examples with four-coordination from those with six (rocksalt structure). For our purposes here we don't need to know in detail what functions these indices (ΔR_{CT}, R_σ, etc.) actually represent. All of them are based on theoretical models of one sort or other (T_1 for example measures[22] the stabilization energy associated with s_A–s_B and p_A–p_B interactions), but basically they are a quantitative measure of the energetic locations of the four sets of levels (s and p) on the atoms A and B. Experimental measures of the crossover from four- to six-coordination come from two places. The Phillips–Van Vechten scheme[26] from dielectric and structural data and Shirley and co-workers XPS studies[27] both give measures of the "ionicity" of the AB system. The boundary between four- and six-coordination occurs quite sharply at an ionicty of about 0.7.[28] (The numerical value of the critical ionicity is slightly different on the two schemes.) These collected observations show quite dramatically the freezing out of the undistorted, substituted structure (rocksalt) as the electronegativity difference between A and B is increased, just as in the molecular case and in keeping with the ideas behind Figure 3.

For systems with 10 electrons, our simple ideas are less useful. As the electronegativity difference between A and B increases, the bond alternation distortion which produces the arsenic or black phosphorus structure for the elements and for systems with small AB electronegativity differences is also that which we might expect at large electronegativity differences by mixing s,p orbitals together. The result is a tetrahedral solid with a lone pair occupying one coordination position. Phrased differently, at the right-hand side of Figure 3, for 10 electrons, the high-lying s_A band is occupied and distortion routes which lower its energy by mixing with the empty p_A band will be important, as we have stressed elsewhere.[29] Contrary to the eight-electron case therefore, we have not stabilized the undistorted structure by substitution. Arsenic and black phosphorus derivative structures are found for types 1, 2, and 4. GeTe and SnTe (type 2 and type $1^{1}/_{2}$, respectively) are examples of the former and (Ge,Sn)(S,Se), all of type 1, are examples of the latter.[30] Where thee electronegativity difference is very large, e.g., InCl, TlF, PbO, TlI, such type 1 systems have structures which are distorted rocksalt variants. Only for the lead chalconides (PbX; X = S, Se, Te) with intermediate electronegativity differences is the rocksalt structure found as the zero-temperature/zero-pressure structure, and its observation is usually ascribed to the inert electron pair on the lead atom.[31]

Other Systems

Several structures which contain fragments of the rocksalt structure can be viewed as derivatives of geometrical arrangements produced via a Peierls type of distortion of the primitive cubic geometry. For example, is is easy to see how the cadmium halide structure with the local geometry shown in **18** is a natural distortion of the simple cubic structure for a system where the p_x, p_y, p_z bands are two-thirds full. The analogy can be made with the trimerization of the one-dimensional chain containing a band two-thirds full of electrons (**19**). Each cadmium atom sits at the center of three such perpendicular systems and is thus six-coordinate. Each halide sits at the ends of three such chains and is therefore pyramidally three-coordinate (**18**). Some other structures which may be viewed along the same lines include those of the layer structures of In_3Te_4 and Bi_2Te_3 and the more fragmented structures of Sb_2Se_3. All of these represent examples where, like GeTe and GeS, the electronegativity difference between the constituents ensures that the bands are split apart in energy. In some cases however, the levels of the constituents are close enough together (e.g., Bi and Te) such that the situation is pseudoelemental.



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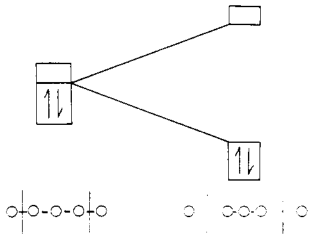

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