Donor–Acceptor Layer Formation and Lattice Site Preference in the Solid: The CaBe$_2$Ge$_2$ Structure

Chong Zheng and Roald Hoffmann*

Abstract: The Be$_2$Ge$_2^-$ part of the CaBe$_2$Ge$_2$ structural type is built up of two distinguishable, isomeric layers, the Be and Ge occupying distinct sublattices within one layer and switching their positions in the next layer. A consequence of this differential site occupation is a difference in the dispersions of the Be–Ge bonding and antibonding bands. We define a more dispersive lattice site as being one that engenders more overlap between equivalent sites. In general, if a lattice is made up of several sublattices which differ in dispersivity, and if the lattices may be occupied by atoms of different electronegativity, then depending on the degree of band filling the more electronegative atom will enter or avoid the more dispersive sites. For low band filling the more electronegative atom should enter the more dispersive sites, and for high band filling the more electronegative atoms should be found in the less dispersive sublattice. When Ge is at this site in one layer in CaBe$_2$Ge$_2$ the occupied band is wide and has a higher $\epsilon_0$, transferring electron density to the other layer to form a dielectric material. The high dispersion in the occupied band (mostly of Ge states) is a destabilizing factor within one layer but a better supporter of interaction with an inverted layer in a donor–acceptor mode. The electronegativity and orbital contraction provide tuning for the intra- and interlayer interaction. The orbital of the X element becomes more diffuse when X goes down in the Periodic table, the interlayer interaction favoring the CaBe$_2$Ge$_2$ structure wins out.

The design of organic or inorganic materials with specific desirable physical, especially electronic, properties has benefited much from ideas of molecular donor–acceptor pair proximity or charge transfer. Examples of such inspirations include a proposed molecular diode of donor–acceptor molecules connected by a bond chain molecules, organic ferromagnets of donor–acceptor pairs with the donor (or acceptor) molecule having a stable triplet ground state, and chemical systems built up by donors and acceptors connected by light absorbers capable of photosynthesis, to mention a few. The donor–acceptor concept, when generalized to extended two- or three-dimensional systems, may provide us with a tool to understand bonding in the solid state. We will see in this paper that this is the case for the CaBe$_2$Ge$_2$ structure, where the donor and acceptor are two-dimensional layers.

The CaBe$_2$Ge$_2$ Structure

The CaBe$_2$Ge$_2$ structure, 1, is a variation of another very common phase, ThCr$_2$Si$_2$, 2. The latter phase, into which more than 400 compounds crystallize, 3 consists of layers which are common to many other structures. These layers can be thought of as being "split" from yet another very common structure, CsCl, according to 3. This "splitting" process is imaginary, 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. 4 The "splitting out" viewpoint may also provide us with a correlation between the high occurrence of the ThCr$_2$Si$_2$ structure and that of the CsCl structure.

The layers which build up the AB$_2$X$_4$ compounds crystallizing in the ThCr$_2$Si$_2$ structure have the following feature: the element B forms a square lattice, the element X sits alternately above and below the square lattice holes, 4. In such an arrangement, the element B is at the center of the tetrahedron formed by the X element, and the BX$_4$ tetrahedron propagates into a two-dimensional layer by sharing four of its six edges.

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There are two kinds of \( B_2X_2 \) layers in the \( \text{CaBe}_2\text{Ge}_2 \) structure: one is the same as that in the \( \text{ThCr}_2\text{Si}_2 \) structure and the other is \( 6 \). In \( 6 \) the arrangement is different: it is now the \( X \) element which forms the square lattice, with the \( B \) element sitting alternately above and below the square lattice holes. The two layers are not identical but isomeric. To a first approximation, we may consider \( \text{Ca} \) merely as a two-electron donor (\( \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^- \)) and ignore the interlayer interaction for the time being. The three-dimensional net may be thought of as consisting of two-dimensional identical but isomeric. To a first approximation, we may consider \( \text{Ca} \) merely as a two-electron donor (\( \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^- \)) and ignore the interlayer interaction for the time being. The three-dimensional net may be thought of as consisting of two-dimensional isomeric. To a first approximation, we may consider \( \text{Ca} \) merely as a two-electron donor (\( \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^- \)) and ignore the interlayer interaction for the time being. The three-dimensional net may be thought of as consisting of two-dimensional isomeric. To a first approximation, we may consider \( \text{Ca} \) merely as a two-electron donor (\( \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^- \)) and ignore the interlayer interaction for the time being. The three-dimensional net may be thought of as consisting of two-dimensional isomeric. To a first approximation, we may consider \( \text{Ca} \) merely as a two-electron donor (\( \text{Ca} \rightarrow \text{Ca}^{2+} + 2e^- \)) and ignore the interlayer interaction for the time being. The three-dimensional net may be thought of as consisting of two-dimensional.

Band Dispersion and Its Correlation to Lattice Sites

On going from a discrete molecule to a solid of infinite extent, the energy levels become a continuum indexed by a continuous variable \( k \) (\( k \) is the wave vector, wave node counter, or symmetry label). As in the molecular case, the energy separation between the lowest level (most bonding) and the highest level (most antibonding)—the band width or band dispersion—is determined by the interaction between atoms. In the case of weak interaction, where the interatomic distance is large, the separation between lowest and highest level is small and the energy band has small dispersion. On the contrary, if the interatomic distance is short and the interaction is strong, there will be a big dispersion. The two situations are contrasted in \( 8 \).

In a crystal there might exist several nonequivalent lattice sites. We call a specific lattice site more dispersive if the separation between the equivalent sites of that particular kind is smaller than that of other sites. An example is the two-dimensional layer in \( \text{ThCr}_2\text{Si}_2 \) or \( \text{CaBe}_2\text{Ge}_2 \) structure, \( 9 \), where we emphasize the different lattice sites by deleting the connections between them. Both layers, \( \text{I} \) and \( \text{II} \), are square lattices. But in layer \( \text{I} \) the distance between the lattice sites is shorter than that in layer \( \text{II} \). Thus the lattice sites in layer \( \text{I} \) (which are all equivalent) are more dispersive.

The lattice sites in layer \( \text{I} \) are twice as dense as in layer \( \text{II} \). So when all the sites in layer \( \text{I} \) and two sheets of layer \( \text{II} \) are occupied, the ratio of the number of atoms of site \( \text{I} \) to those at site \( \text{II} \) is \( 1:1 \), as in the case of \( \text{Cr}_2\text{Si}_2 \) or \( \text{Be}_2\text{Ge}_2 \) in \( \text{ThCr}_2\text{Si}_2 \) or \( \text{CaBe}_2\text{Ge}_2 \).

The dispersivity of lattice sites will be reflected in the width of the energy bands, which in turn will affect the energetics of the solids. Given atoms of different electronegativities, the question arises as how to arrange them among different lattice sites so to minimize the lattice energy. This is the so-called "coloring" problem, one aspect of which we will discuss later in this paper. We will now study the donor-acceptor layer formation in the \( \text{CaBe}_2\text{Ge}_2 \) lattice.

Donor–Acceptor Layer Formation in \( \text{CaBe}_2\text{Ge}_2 \) Structures

The layers \( \text{A}, \text{B}, \text{D}, \text{E}, \text{F}, \text{G}, \text{H}, \text{I} \), and \( \text{J} \) in \( \text{CaBe}_2\text{Ge}_2 \) have the stoichiometry \( \text{Be}_2\text{Ge}_2^2- \) or \( \text{BeGe}^2- \). One might think of \( \text{BeGe}^2- \) as the building "bricks" of the layers. \( \text{A} \) and \( \text{B} \) emphasize the diatomic \( \text{BeGe}^2- \) units in the layers \( \text{A} \) and \( \text{D} \). In these layers each \( \text{BeGe}^2- \) monomer pointing "up" is surrounded by 4 others pointing "down" in a square-planar coordination geometry. In \( \text{A} \) the \( \text{Be} \) end of the \( \text{BeGe}^2- \) monomer resides in lattice site \( \text{I} \); in \( \text{D} \) it is the Ge and which occupies lattice site \( \text{I} \).

The typical interatomic distances for a tetrahedral arrangement (\( \text{Be} \) at the center of \( \text{Ge} \) tetrahedron in \( \text{A} \) and \( \text{Ge} \) at the center of \( \text{Be} \) in \( \text{D} \)) are shown in \( 7 \). The \( \text{BeGe}^2- \) distances are the shortest and presumably the strongest in the structure. So it makes sense to focus on the \( \text{BeGe}^2- \) unit as the primary building block, turning on supplemental \( \text{BeBe}, \text{GeGe}, \text{BeGe} \) interlattices and interlayer \( \text{BeGe} \) interactions as perturbations.

A schematic portrayal of the orbital interaction in a \( \text{BeGe}^2- \)
The monomer is given in 12. The more electronegative Ge orbitals lower in energy, interact with Be. The germanium's one s and three p orbitals are pushed down in energy. Correspondingly, the Be orbitals are lifted up by this interaction. Five electrons from Ge and two from Be occupy 7 of the 8 available states in the lower block, mostly of Ge character. The lower block is more dispersive site (central layer I in 9b). This will result in a bigger dispersion in the upper block of the Be–Ge orbitals levels in 12 since that block is more localized on Be, and it is the Be's which are put more in contact by this choice of lattice site. The other choice is to place the Ge end into the more dispersive site, resulting in a bigger dispersion in the lower block in 12, mostly of Ge character. The two situations are contrasted in 13. Please remember that these are schematic drawings. We will soon make them more precise (and complicated) through band calculations.

We now proceed to the three-dimensional lattice. When layers A and D are stacked together to form the BeGe2− framework of the CaBe2Ge2 structure, the Fermi levels of both layers should equalize. To accomplish this, electron transfer from layers D to A should occur, resulting in formation of a dielectric material, shown schematically in 14. Our calculation, to be discussed below, gives a charge transfer of 0.6 e− from D to A per unit cell or 0.3 e− per Be–Ge2 monomer.

It is worthwhile to note that some AB2X3 compounds where B is a transition-metal element crystallize in two phases. The low-temperature phase is the ThCr2Si2 structure consisting of only A layers. The high-temperature phase is the CaBe2Ge2 structure built up from both A and D layers. One can obtain the CaBe2Ge2 form by quenching from high temperature and study its superconducting behavior. The first example was LaIr2Si2, reported by Braun, Engel, and Parthè. Recently this was reported for YIr2Si2. Shelton et al. have measured the superconducting temperatures for both of these compounds, as well as for a series of AB2X3 compounds crystallizing either in the ThCr2Si2 or in the CaBe2Ge2 structure, where A = La, Y, Th, U; B = Ru, Rh, Pd, Os, Ir, Pt; and X = Si, Ge. From this study it seems that the CaBe2Ge2 phase is more likely to be a superconductor. Possibly relevant to this is that there has been some speculation that excitonic superconductors, in which the conducting electron pairs are in one metallic layer mediated by excitons of another dielectric layer, would have higher Tc. Some researchers recently also suggested nonphononic superconductivity; one of the materials is CeCu2Si2 crystallizing in ThCr2Si2 structure. So there are good reasons to examine the structure, both geometric and electronic, of these fascinating materials.

The Electronic Structure of CaBe2Ge2

The starting point is a diatomic BeGe2 monomer. Figure 1 is an interaction diagram for that. In the lower block of the resulting BeGe2 levels there are four orbitals: the lowest 1σ and 2σ are the Be and Ge's orbitals and sp (z is chosen along the Be–Ge axis) hybrid bonding combinations; then come the two degenerate π orbitals. These lower orbitals have bigger coefficients on Ge and thus the electrons occupying these orbitals become on Ge. The LUMO, 3π, as well as the other orbitals above it, has bigger coefficients on Be. We will construct the approximate band structures from these molecular orbitals. The geometry of the layers has been described: each BeGe2 monomer sticking up is surrounded by four other nearest BeGe2 monomers pointing down in the layer. In layer A it is the Be side which resides in the central square lattice site; in layer D the Ge side of the monomer takes this position. Let us begin the construction for layer A. We will embed each BeGe2 MO into the lattice and determine the nature of the dispersion of the band developed from the MO by changing the phase relation between BeGe2 monomer and its four nearest neighbor monomers.

15 shows this process for the lowest BeGe2 MO, 1σ, in layer A. A rule to determine the phase relation is the following: the BeGe2 monomer 1 (pointing up) in 15 is related by a glide plane (reflection in the central square lattice plane and translation along the direction indicated by the arrow) to another nearest neighbor 2. When this symmetry operation is performed, if the phase is the same we in-phase propagation (corresponding to the 1...
Figure 1. An interaction diagram for Be-Ge formed from Be and Ge.

Figure 2. Schematic band structures for Be$_2$Ge$_2$ layer A, plotted from $\Gamma(0,0)$ to $X(1/2,0)$.

Figure 3. Calculated band structures for Be$_2$Ge$_2$ layer A (a) and layer D (b).

We can proceed to work out the approximate band structure derived from other MO's, as Figure 2 shows. Since all the $\sigma$-type orbitals have the same topology, the bands generated from them should behave similarly: they should go up in energy from $\Gamma$ to $X$, as the $1\sigma$ band does. The $\pi$ orbitals go down in energy along the same line in the Brillouin zone for the following reason.

The two orbitals $\pi_a$ and $\pi_c$ are plotted in 17 and 18 in a view from above the square lattice. At the $\Gamma$ point, where monomer 1 does not change phase when mapped into monomer 2 by the glide plane, the antibonding character indicated by the arrows in 17a pushes the $\pi_a$ orbital high above the same orbital at the $X$ point. For the $\pi_c$ orbital there are 2 nearest bonding (solid
Projected DOS
Intgrated DOS
Total DOS

Figure 4. Calculated total density of states (dashed lines) and the contributions from the Be-Ge bonding MO's (solid lines) for Be₃Ge₂ layer A (a) and layer D (b). The dotted lines indicate the integrated Be-Ge bonding states.

arrow) and 4 next nearest antibonding (dotted arrow) interactions. It turns out that the antibonding feature wins out. Thus the two bands πₐ and πₜ drop down in energy from Γ to X. Moreover, πₜ is antisymmetric with respect to the plane m perpendicular to the paper and indicated in 17 and 18. But πₐ is symmetric, as are all the other σ orbitals. Hence πₜ has an avoided crossing with one of the σ-type bands.

The reader may wonder why there are only four low-lying bands (mainly Ge) in Figure 2, whereas the true unit cells contain two BeGe units and so eight bands (two s and six p) would be expected. What we have done in the preceding discussion and will continue to do in the remainder of the paper is to utilize maximally the symmetry available, and in particular the glide plane symmetry. The complete band structure may be obtained by “folding back” areas and lines of the larger Brillouin zone for one BeGe per asymmetric unit that we use here into the smaller zone for the true Be₃Ge₂ unit cell.

Figure 3a shows the calculated band structures for the Be₂Ge₂ layer A. The lowest 5 bands have the appropriate features that we indicated schematically in Figure 2: 3 σ-type bands rise up and 2 π-type bands drop down, with an avoided crossing between one of the π bands and a σ band. The electron occupation in BeGe is such that there are 7 electrons per BeGe, or 3.5 filled bands.

The same analysis applies to layer D. However, when we put the Ge side of the Be-Ge- unit into the central square lattice there will be more overlap between these sites for those occupied MO's which have bigger coefficients on Ge. The situation for 1e is shown in 19, in contrast to 15 and 16. The bigger lobe of 1e resides in the central square lattice, enhancing the difference in energy between the Γ and X points. The same is true for all other

Figure 5. Total energy difference between Be₂Ge₂ layer D and layer A as a function of electron count in the unit cell.

Figure 6. Same as in Figure 5, except that the Be-Ge interaction is turned off here.
occupied orbitals: the bonding and the antibonding extremes within each band will both be enhanced. What should happen is indicated schematically in 20, which reproduces Figure 2 and

indicates by arrows the change expected upon putting Ge in the more dispersive site. The most important consequence of this should be a reduction in the band gap.

The calculated band structures for layer D are shown in Figure 3b. Indeed the band gap is decreased. What we have is a layered material in which there is a periodic variation of the band gap in the lattice. Another well-known material with band gap variation is the solid-state superlattice,16 21, which has many interesting physical properties. However, the period of the band gap variation in the superlattice is in the order of 102 Å. A smaller value would increase the tunneling between different layers and reduce the effective band gap difference.16 Furthermore, the charge transfer from donor to acceptor layer by this tunneling effect leaves the valence band in the narrow-gap layer positively charged. Correspondingly, there are less electrons thermally excited into the conduction band. The valence band shifts to a lower energy scale and the conduction band to a higher one, just as a positively charged atom has a bigger (magnitude) ionization potential and a negatively charged one a smaller one (compare H+ with H, for example). Thus the band gap in the donor layer becomes bigger. For the same reason the band gap in the acceptor layer gets smaller. The band gap difference is reduced until the electron transfer is inhibited by the electric field induced by this charge transfer. This is shown schematically in 22.17

A strategy to reduce the interlayer tunneling is to have big cations intercalated between layers A and D in CaBe2Ge2-type compounds. Could organometallic or organic cations serve here? Enhancing the dispersion difference in the occupied bands (see 13) should increase the εf difference which in turn leads to a greater band gap difference. A combination of small atom B and big atom X with large electronegativity difference should be a good choice for this purpose, as long as other chemical requirements are satisfied.

However, solid-state chemistry provides us with more diversified opportunities. For example, two B2X2 layers can be condensed into one,18 23; the layer composition can be changed,19 24; and the interlayer distance may be increased by inserting other layers.20

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It will not be a surprise if some of the interesting physical phenomena unique to a two-dimensional system are observed in one or another of these layered compounds.

Site Preference

As indicated in 13, layer D has a higher Fermi energy and if isolated would be unstable relative to layer A. Figure 4 shows the calculated density of states (DOS) and the contributions to it of the Be-Ge monomer bonding states (the 4 lowest orbitals in Figure 1), for both layers. The higher dispersion in the filled states (in 13b) pushes more Be–Ge bonding states above the Fermi level in layer D than in layer A. This decomposition, the position of the Fermi level, and the calculated total energy per unit cell of the two layers all indicate greater stability for layer A.

However, site preference is a function of band filling. As 13 indicates, the same factor that favors the more dispersive site for the less electronegative atom for CaBe$_2$Ge$_2$ would operate in the opposite direction were the band less than half filled.

To put it another way: for situations such as that occurring in CaBe$_2$Ge$_2$ and summarized schematically in the approximate band structure of 13 (a lattice is made up of several sublattices which differ in dispersivity), for low band fillings bonding will be maximized and dispersivity favored while for high band fillings dispersivity is destabilizing. This is nothing but the usual contrast between two-electron two-orbital stabilization vs. four-electron two-orbital destabilization that we encounter repeatedly as a determinant of structure and reactivity in discrete molecules.

Returning to our specific CaBe$_2$Ge$_2$ case, we plot the energy difference between layers A and D as a function of electron count in Figure 5. There indeed layer D is more stable for very low electron filling, but for the normal filling of 14 electrons per unit cell, layer A is more stable than layer D by about 6.7 eV per unit cell (2 Be–Ge units) from our extended-Hückel calculation.

It should be noted that this conclusion as to the effect of band filling and dispersivity on site preference is quite independent of the interaction of the two nonequivalent lattices with each other. If the distance between Be and Ge layers is stretched over a large range, still curves such as Figure 5 are obtained. Figure 6 is such an illustration, where we have deleted the Be-Ge interaction in the 2-dimensional layer.

In many other examples, molecular and extended structures, the site preference is well-determined for a given electron count and two elements of different electronegativity.
particularly interesting result is that of Burdett et al., who applied the moment method to the coloring problem and concluded that

$$A - B - B \leftrightarrow B - A - B$$

for a half-fitted band the structure in which the A-B interaction is maximized is favored over that where the A-A and B-B interactions are maximized, when the fourth moment $\mu_4$ dominates. While these site preferences are highly illuminating, we still need to understand the CaBe$_2$Ge$_2$ structure, and this is approached in the next section.

**Interlayer Interaction in CaBe$_2$Ge$_2$**

The site preference arguments of the previous section allow us to predict the sorting of atoms of different electronegativity among nonequivalent sites of a B$_2$X$_2$ layer. And so we can understand the preferred isomerism in ThCr$_2$Si$_2$ structures. But in CaBe$_2$Ge$_2$, Be and Ge occupy both the more dispersive and the less dispersive sites. We have shown that layer D is unstable against layer A, thus the extra stabilization in the real structure must come from interlayer interaction. We would like to understand this.

Figure 31 shows the schematic interlayer interactions when the A layers are stacked to form the ThCr$_2$Si$_2$ structure. The Ge's on the outside of the layers interact with each other and the lower block in the band structures will become wider, the upper part being of Ge-Ge antibonding character. Figure 7 shows the COOP curves for this Ge-Ge bond, and the antibonding features immediately below the Fermi level are there as we expected. Perhaps a word is in order about the crystal orbital overlap population (COOP) curves. These are really overlap population weighted densities of states and gauge the bonding capabilities of all the energy levels in a given energy interval. They are the solid-state analogue of an overlap population, with positive values indicating bonding and negative ones antibonding.

The general feature of X-X pairing in the ThCr$_2$Si$_2$ structure type is an important aspect of bonding in this class. We refer the reader to a detailed discussion of the problem elsewhere.

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(27) Schäfer, H., to be published.

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The situation where the A and D layers are stacked together to form the CaBe$_2$Ge$_2$ structure is depicted in figure 32. The empty upper block representing Be in layer D interacts with the filled lower block characterizing Ge in layer A, resulting in a typical stabilizing donor-acceptor interaction scheme. The donor states in A are stabilized and the acceptor states in D are pushed up in energy. But the lower block in D and the upper block in A remain unchanged, since Ge of D and Be of A are in the central layer and out of interaction distance. Figure 8 shows the COOP curve for this Be-Ge bond responsible for the A-D interlayer interaction. It is of bonding character below the Fermi level, as 32 suggested. Thus there are two factors competing: the small dispersion in the lower block in 13 favors layer A by itself and A-A stacking, while the donor-acceptor interaction in 32 favors the simultaneous
presence and bonding of A and D layers. Which effect dominates depends on the electronegativity and orbital diffuseness difference between B and X in AB₂X₂ compounds. Our extended-Hückel calculations for CaBe₂Ge₂ (really with Si parameters for Ge, see Appendix) do not capture this balance correctly—they prefer the A + A stacking to A + D. Nevertheless, both bonding components mentioned above are present; so we are prompted to think in greater depth about the factors influencing the relative magnitude of the band dispersion and donor-acceptor interactions. Some structure systematics point to an important role of the position in the Periodic table of the B and X elements.

The energy difference between layers A and D arises from the inequality between the lower block band dispersions in 13. Thus reducing the degree of this inequality should decrease the energy difference between A and D layers. The dispersion inequality in turn derives from the difference of overlaps within a given sublattice. What we should have for this purpose is a set of orbitals which have bigger overlaps between site 11's in 9 (4.02 Å apart for CaBe₂Ge₂) than the overlaps between site 1's (2.84 Å for CaBe₂Ge₂). This is not easy to arrange, for most overlaps do not scale in this way. The only candidate that comes to mind is a p–p overlap of type 33.

For every p orbital there is a range of distances over which while \( d_1 > d_2 \), \( S_{pp}(d_1) > S_{pp}(d_2) \). The range in question depends on the contraction (exponent) of the orbitals, the more diffuse the orbital the greater the distance of maximum overlap. Figure 9 shows the effect of varying the principal quantum number while keeping the effective \( Z \) constant in a Slater orbital with \( Z_{eff} = 1.38 \). For \( n = 5 \) the maximum overlap occurs around 3.6 Å and is greater at 4.0 Å than at 2.8 Å. This is a good situation for a CaBe₂Ge₂ structure with a lattice constant \( a \sim 4 \) Å. Figure 10 shows the DOS of A and D layers and the B–X bonding contribution for \( n = 5 \). Compared with Figure 4, the occupied B–X bonding states are reduced from 70% to 54% for layer A due to the site II overlap. For layer D they decrease from 57% to 47%, a smaller reduction. 34 and 35 show the B–X overlap populations for \( n = 3 \) and \( 5 \), respectively. In the \( n = 5 \) case the overlap populations for both A and D layers are nearly equal, and the energy difference between them is reduced to 5.2 eV. There is also a substantial overlap population developed between Ge's at site II for \( n = 5 \).
Figure 11 is a plot showing both the energy difference between layers A and D and the stabilization energy difference between the ThCr$_2$Si$_2$ and CaBe$_2$Ge$_2$ structures as a function of the principal quantum number $n$. The stabilization energy is defined as the difference between the energy sum of the reactant layers and the energy of the composite three-dimensional structure, per unit cell. The energy difference between A and D favors A and the interlayer stabilization energy prefers A + D stacking. As $n$ increases the A, D energy difference becomes smaller and the latter factor, the interlayer stacking, wins out. Their sum, the dotted curve, eventually goes into the CaBe$_2$Ge$_2$ structure region.

Table I lists a selection of some AB$_2$X$_2$ compounds adopting the CaBe$_2$Ge$_2$ structure with $\sim 14$ electrons per unit cell. In all these compounds, X has a bigger principal quantum number. An interesting study of the compounds BaMg$_2$X$_2$ (X = Si, Ge, Sn, Pb) by Eisenmann and Schäfer shows this trend: As $n$ of the ThCr$_2$Si$_2$ to CaBe$_2$Ge$_2$ type, 36.

There are quite a few AB$_2$X$_2$ compounds crystallizing in the CaBe$_2$Ge$_2$ structure where B is a transition metal; Table II lists a selection. Some of these exhibit polymorphism, the high-temperature phase being the CaBe$_2$Ge$_2$ phase. Most of the compounds in Table II have a 29–32 electrons per unit cell, or 9–12 electrons excluding the filled d shell. Thus they have fewer s,p electrons than do the compounds in Table I. Another striking feature is that the X element in Table II is more electropositive in most of the cases. But when the X element is more electropositive its principal quantum number is more likely to be smaller than that of the T element. The structural determinations for most of the compounds in Table II were based on powder patterns. It would be interesting to see the single-crystal structures, since it is not unlikely that the transition metal will play the role of a more electronegative element, as Zn does in CaZn$_2$Al$_2$.7 There Zn is more electronegative and has a bigger principal quantum number.

Table I. Some AB$_2$X$_2$ Compounds Crystallizing in the CaBe$_2$Ge$_2$ Structure

<table>
<thead>
<tr>
<th>AB$_2$X$_2$</th>
<th>diff in principal quantum number $n$</th>
<th>diff in electronegativities $x$</th>
<th>no. of electrons per unit cell</th>
<th>ref</th>
</tr>
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<tbody>
<tr>
<td>CaBe$_2$Ge$_2$</td>
<td>2</td>
<td>0.4</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>BaZn$_2$Sn$_2$</td>
<td>1</td>
<td>0.3</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
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<td>3</td>
<td>1.0</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
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<td>0.2</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td>REL$_2$Sb$_2$</td>
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<td>1.1</td>
<td>15</td>
<td>26</td>
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<td>13</td>
<td>20</td>
</tr>
<tr>
<td>CeCu$_2$Sn$_3$</td>
<td>1</td>
<td>0.1</td>
<td>13</td>
<td>27</td>
</tr>
</tbody>
</table>

For s and p electrons. Thus $n = 4$ for Cu and Zn. $^a$ Values are from Allred (Allred, A. L. Inorg. Nucl. Chem., 1961, 17, 215) assuming normal oxidation state. $^b$ Including d electrons. Assuming $\text{Ln}^{3+}$, Th$^4+$, and all the rare earth elements are in a $+3 \text{ oxidation state.} ^c \text{A} = \text{alkaline earth or rare earth metal.} ^{\text{RE}} \text{ = rare earth.} ^{\text{X}} \text{ = P, As.} ^{\text{T}} \text{ = Ni, Pd.}

There are quite a few AB$_2$X$_2$ compounds crystallizing in the CaBe$_2$Ge$_2$ structure where B is a transition metal; Table II lists a selection. Some of these exhibit polymorphism, the high-temperature phase being the CaBe$_2$Ge$_2$ phase. Most of the compounds in Table II have a 29–32 electrons per unit cell, or 9–12 electrons excluding the filled d shell. Thus they have fewer s,p electrons than do the compounds in Table I. Another striking feature is that the X element in Table II is more electropositive in most of the cases. But when the X element is more electropositive its principal quantum number is more likely to be smaller than that of the T element. The structural determinations for most of the compounds in Table II were based on powder patterns. It would be interesting to see the single-crystal structures, since it is not unlikely that the transition metal will play the role of a more electronegative element, as Zn does in CaZn$_2$Al$_2$.7 There Zn is more electronegative and has a bigger principal quantum number.

Table II. Some Transition-Metal AT$_2$X$_2$ Compounds Crystallizing in the CaBe$_2$Ge$_2$ Structure

<table>
<thead>
<tr>
<th>AT$_2$X$_2$</th>
<th>diff in quantum number $n$</th>
<th>diff in electronegativities $x$</th>
<th>no. of electrons per unit cell</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaIr$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.3$</td>
<td>29</td>
<td>10</td>
</tr>
<tr>
<td>YIr$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.3$</td>
<td>29</td>
<td>11</td>
</tr>
<tr>
<td>LaPt$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.4$</td>
<td>31</td>
<td>12</td>
</tr>
<tr>
<td>ThIr$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.3$</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>ThPt$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.4$</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>UIr$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.2$</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>ThIr$_2$Ge$_2$</td>
<td>$-2$</td>
<td>$-0.2$</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>ThPt$_2$Ge$_2$</td>
<td>$-2$</td>
<td>$-0.3$</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>UIr$_2$Ge$_2$</td>
<td>$-2$</td>
<td>$-0.2$</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>UPt$_2$Ge$_2$</td>
<td>$-3$</td>
<td>$-0.4$</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>HoIr$_2$S$_3$</td>
<td>$-3$</td>
<td>$-0.4$</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>LaPt$_2$Ge$_2$</td>
<td>$-2$</td>
<td>$-0.3$</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>LaSb$_2$F$_4$</td>
<td>$1-0$</td>
<td>$0.2-0.1$</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>Ag$_2$Sb$_2$F$_4$</td>
<td>$0$</td>
<td>$-0.1$</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Ag$_2$B$_2$F$_4$</td>
<td>$1$</td>
<td>$-0.2$</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>RERh$_2$X$_6$</td>
<td>$-2$</td>
<td>$-0.1$</td>
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</tr>
<tr>
<td>REIr$_2$Ge$_2$</td>
<td>$-2$</td>
<td>$-0.2$</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>SrAu$_2$Sn$_3$</td>
<td>$-1$</td>
<td>$-0.5$</td>
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<td>36</td>
</tr>
<tr>
<td>BaAu$_2$Sn$_3$</td>
<td>$-1$</td>
<td>$-0.3$</td>
<td>32</td>
<td>36</td>
</tr>
</tbody>
</table>

Values are from Allred (Allred, A. L. Inorg. Nucl. Chem., 1961, 17, 215) assuming normal oxidation state. Including d electrons. Assuming $\text{Ln}^{3+}$, Th$^4+$, and all the rare earth elements are in a $+3 \text{ oxidation state.} ^c \text{A} = \text{alkaline earth or rare earth metal.} ^{\text{RE}} \text{ = rare earth.} ^{\text{X}} \text{ = P, As.} ^{\text{T}} \text{ = Ni, Pd.}

(35) Venturetti, G.; Méot, M.; Francois, M.; Malaman, B.; Marché, J. F.; McRae, E.; Roques, B., to be published.
Tautomeric Instability of 10-Deoxydaunomycinone
Hydroquinone

David J. Brand1 and Jed Fisher*1

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and Lipids Research, The Upjohn Company, Kalamazoo, Michigan 49001. Received August 5, 1985

Abstract: 10-Deoxydaunomycinone and daunomycin are reduced by excess sodium dithionite, under anaerobic conditions, to 10-deoxydaunomycinone hydroquinone. This hydroquinone is not stable, having an approximate rate constant (in 48% MeOH, 52% H2O, 10 mM Tris-HCl, 10 mM Tris base) for its disappearance of 2 × 10−6 s−1. This disappearance results from a number of tautomeric equilibria, which transform this hydroquinone into more stable species. Typically, eight products in addition to 10-deoxydaunomycinone are detected by reverse-phase liquid chromatographic analysis of the product mixture. Thus far seven of these products have been identified and characterized. Three of the products are diastereomers of (2R)-2-acyetyl-1,2,3,4,4a,12a-hexahydro-2,6,11-trihydroxy-7-methoxy-5,12-naphthacenediene (4% of the product) and (2R)-2-acyetyl-1,2,3,4-tetrahydro-2,6-dihydroxy-7-methoxy-5,12-naphthacenediene (4% of the product), which take place from the reduction of the 12-deoxydaunomycinone by the excess dithionite present in the mixture. The effect of Fe(III) ion chelation on the anaerobic dithionite reduction of both daunomycin and 10-deoxydaunomycinone is examined. A modest rate increase for the tautomization of the hydroquinone is observed for the anaerobic dithionite reduction of the 10-deoxydaunomycinone-Fe(III) chelate, whereas little effect is observed for the daunomycin-Fe(III) chelate. This surprising diversity of materials may account for the abundance of aglycon metabolites found in vivo (many as yet uncharacterized), may prove of value in the synthetic elaboration of anthracyclines, and is likely to be representative of the hydroquinone behavior of the p-dihydroxyanthracyclines of the rhodomycinone, isorhodomycinone, and pyromycinone families.

Daunomycin (1a) and adriamycin (1b) are among the most useful of the antitumor antibiotics.1 Nevertheless the discovery of the chemical attributes of these molecules responsible for their antibiotic efficacy has proven an extraordinarily difficult problem. Several theories of surprising dissimilarity remain at this time, all of which have experimental evidence in their support.2, 3 The focus of one of these theories2 centers on the ability of these molecules to enter into redox chemistry by virtue of their quinone moiety. In the presence of a suitable redox enzyme (generally

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Table III. Extended-Hückel Parameters

<table>
<thead>
<tr>
<th>orbital</th>
<th>H(_{\alpha}) (eV)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>2(\sigma)</td>
<td>−10.0</td>
</tr>
<tr>
<td></td>
<td>2(\pi)</td>
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</tr>
<tr>
<td>Si (Ge)</td>
<td>3(\sigma)</td>
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<td></td>
<td>3(\pi)</td>
<td>−9.2</td>
</tr>
<tr>
<td>Ca</td>
<td>4(\sigma)</td>
<td>−7.0</td>
</tr>
<tr>
<td></td>
<td>4(\pi)</td>
<td>−4.0</td>
</tr>
</tbody>
</table>

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Acknowledgment. This research was supported by the National Science Foundation through Grant CHE 8406119 and Grant DMR 82172702 to the Materials Science Center at Cornell University. C. Z. would like to thank Professor H. Schäfer and Dr. B. Eisenmann of T. H. Darmstadt for stimulating discussions. We are grateful to J. Burdett and the reviewers for helpful comments, to Cora Eckenroth for the typing, and the Jane Jorgensen and Elisabeth Fields for the drawings.

Appendix

The extended-Hückel method38 was used in all calculations. Si parameters were used to mimic Ge since no reliable Ge parameters were available. The parameters are assembled in Table III. The geometry was chosen such that Be (Ge) in layer A (D) is at the center of an ideal Ge (Be) tetrahedron. Be-Ge (Ge-Ge) = 2.83 Å, Be-Ge = 2.45 Å. A 28K point set39 was used for the 2-dimensional layer and a 30K point set for the 3-dimensional structure. The calculations were repeated for the 3-dimensional structure with Ca. We found that the calculations with and without Ca were essentially the same.

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1 University of Minnesota.
2 The Upjohn Company.