JOURNAL OF SOLID STATE CHEMISTRY 106, 201–210 (1993)

The Electronic Structure of $DyGe_3$

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Received December 4, 1992; accepted December 23, 1992

IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Recently the crystal structure of a germanium-rich dysprosium germanide ($DyGe_3$) has been reported. Significant bonding interactions are present between the germanium atoms in the structure. One type of germanium forms kinked infinite chains $^1_\infty$[Ge]. The remaining two germanium atoms form dimers, stacked in a two-dimensional array as $^2_\infty$[Ge_2]. $DyGe_3$ raises intriguing questions concerning stability and bonding; these are investigated with the aid of extended Hückel calculations. Ge atoms receive electrons from Dy, and Ge states dominate below the Fermi level. There is an interesting electron balance between the two Ge sublattices. The Ge_2 layers contain one additional electron, making them formally a Ge_2^- double layer; the one-dimensional Ge chains contain two extra electrons, fitting the typical Zintl picture as Ge^{2-}. The Ge_2 double layers exhibit two-center bonding in the pairs, perpendicular to an electron deficient multicenter bonding system within the layers. The latter is responsible for the expected two-dimensional metallic conductivity.

Introduction

The Zintl concept (*1*) has proven immensely useful in understanding bonding in solid state compounds. And it productively guides experimentalists as they synthesize new compounds. As one moves away from alkali or alkaline earth metal salts toward intermetallics, one begins to probe the limits of this simple but heuristically useful concept. This is an area in which delocalized metallic bonding and localized bond formation intersect; the analysis of bonding in such compounds is a challenge to our understanding.

The structure of $DyGe_3$ (*2*) has been determined recently from X-ray and neutron powder diffraction data. $DyGe_3$ crystallizes orthorhombic (space group *Cmcm*) with lattice constants of a = 402.8 pm, b = 2071 pm, and c = 389.97 pm. The structure is shown in Fig. 1.

For some germanides, e.g., low pressure LiGe (*3*), the Zintl concept works well; the Ge^- ions form a three-connected net, as expected for an ion isoelectronic with phosphorus. As we see from the structural discussion in the next section, $DyGe_3$ does not obey simple Zintl counting rules. The bonding characteristics of this germanide are clearly more complicated and are the subject of a molecular orbital investigation in this paper.

The Structure of $DyGe_3$

$DyGe_3$ (Fig. 1) contains double layers of Dy atoms, parallel to the xz plane. The double layer (marked **A** in Fig. 1) may be thought of as being constructed from condensed, nearly trigonal prisms with their pseudo-threefold axis oriented parallel to the a axis. Closest Dy–Dy approaches range from 390.0 to 402.8 pm. One type of Ge

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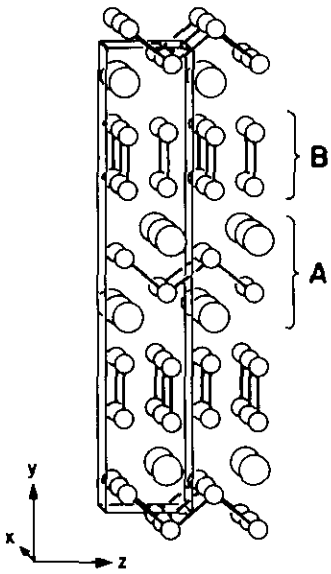


FIG. 1. The crystal structure of $DyGe_3$ with the unit cell outlined. Small spheres are Ge atoms forming double layers (B) and chains enveloped by Dy atoms (A). Bonds drawn between Ge atoms are consistent with the results of our calculations, but additional bonding interactions which exist between adjacent Ge_2 dimers are not drawn.

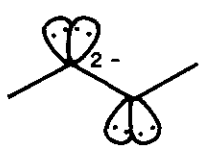
atom is located near the center of these prisms. Each such Ge has two Ge neighbors at a distance of 250.5 pm, forming infinite kinked Ge chains, $^1_\infty$[Ge] (and four plus two Dy neighbors at 294.8 pm and 320.0 pm, respectively). The DyGe double layer alternates along the *y* axis with a double layer of another type of Ge atom (**B** in Fig. 1). The arrangement of the latter Ge atoms may be viewed as a two-dimensional array of Ge pairs, aligned parallel to the *y* axis. Shortest Ge–Ge contacts are 244.2 pm within the dimers and 280.3 pm between adjacent dimers; shortest Ge–Dy contacts are between 299.0 and 301.6 pm. The closest Ge–Ge distance in elemental Ge is 245 pm. Thus the primary Ge–Ge separations in layers **A** and **B** in $DyGe_3$, 250.5 and 244 pm, are clearly bonding contacts. The 280 pm separation between pairs in the two-dimensional layer is also clearly a bonding, albeit weaker, interaction; the identification of pairs within this layer is to some extent arbitrary.

The Electron Counting Problem

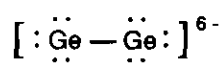
If Dy is 3+, we have three negative charges to dispose over three germaniums. A Zintl viewpoint would complete the octets on the Ge chain (Scheme 1) and the Ge_2 pairs (Scheme 2). This would give $[Ge^{2-}]_n$ and $[Ge^{3-}]_2$, or eight negative charges per three germaniums. Obviously the Ge ions must be oxidized from this formal starting point. But from which Ge sublattice are the electrons removed? And what is the electronic configuration of the Ge substructures? Is the Dy indeed Dy^{3+}? These are some of the puzzles we try to shed light on.

It is clear that one should begin by looking at the isolated sublattices, the $[Ge]_n$ chain and the two-dimensional Ge_2 layer. In the end there will be a common Fermi level in the full lattice, but what occupation should we assume along the way? One possibility is simply to assign one negative charge to each Ge. Another way is to look at each sublattice, and in accordance with an empirical generalization emerging from many studies, to fill the maximum number of bonding levels. We take both points of departure.

Calculations of the electronic structure of $DyGe_3$ were performed with the extended Hückel algorithm (*4*). The electronic structure is built up from fragment Ge sublattices by successive introduction of the Dy atoms with their $4f^9 5d^3 6s^0 6p^0$ electron configuration. Finally the complete structure is reassembled.



SCHEME 1



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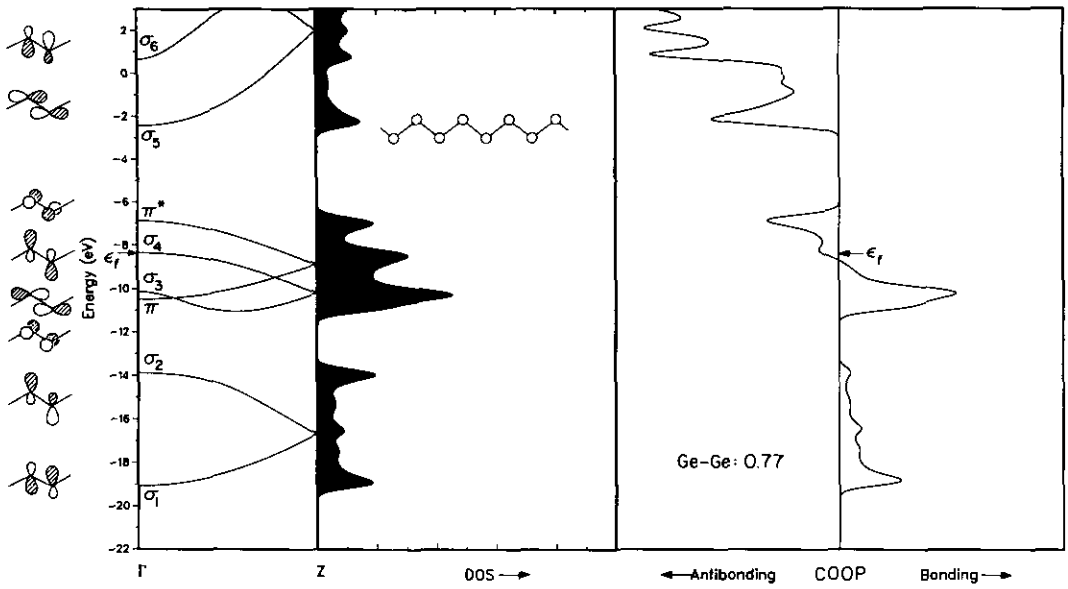


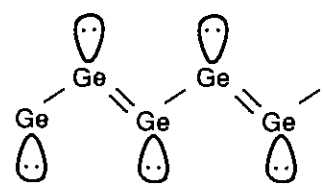
FIG. 2. The band structure, DOS and COOP (from left to right), of a one-dimensional infinite kinked Ge chain. The Fermi level (ε_f) is marked for 10 e^-, i.e., Ge_2^{2-}. Phase relations are shown at Γ. The integrated overlap population is 0.77.

The Kinked Ge-Chain

One type of Ge that is present in the structure forms kinked chains with Ge–Ge distances of 250.5 pm, the Ge chains enveloped by the Dy double layer and well separated from neighboring Ge chains. The electronic structure of an infinite one-dimensional Ge chain with this geometry (no Dy yet) is shown in Fig. 2. For the purposes of the present discussion let us assume five electrons per Ge, i.e., the structure shown in Scheme 1 oxidized by one electron per Ge, or $^1_\infty[Ge^-]$.

The basic geometry is that of the carbon sublattice of polyethylene or polyacetylene (*5*). Due to the symmetry of the chain, all energy bands are folded at the zone boundary (Z). There are two low-lying σ (σ_1, σ_2, mainly *s*) bands, both Ge–Ge bonding, the upper one less so. The π and π^* (p_x for the coordinate system given in Fig. 1) bands are in the same energy range as the bonding σ_3 and σ_4 (p_y and p_z) levels, whereas the antibonding σ^* levels (σ_5, σ_6) are at higher energies.

If we fill all bonding levels, the π (p_x) band contains two electrons. In fact, due to the way the σ_4 and π levels cross, the corresponding antibonding π^* level is slightly occupied and the bonding σ_4 (p_y) level is incompletely filled. The corresponding densities of states (DOS) of these bands are shown in the center of Fig. 2. The bonding and antibonding natures of the above-mentioned bands can be seen from the crystal orbital overlap population (COOP) (*6*) at right in Fig. 2. All bonding levels are filled with 10 electrons per 2 Ge atoms, with an overlap population of 0.77 for the Ge–Ge bond. Neglecting the overlap of σ_4 and π^*, the electronic structure of such a Ge^- polymer would be described schematically as Scheme 3. We do not worry about the



SCHEME 3

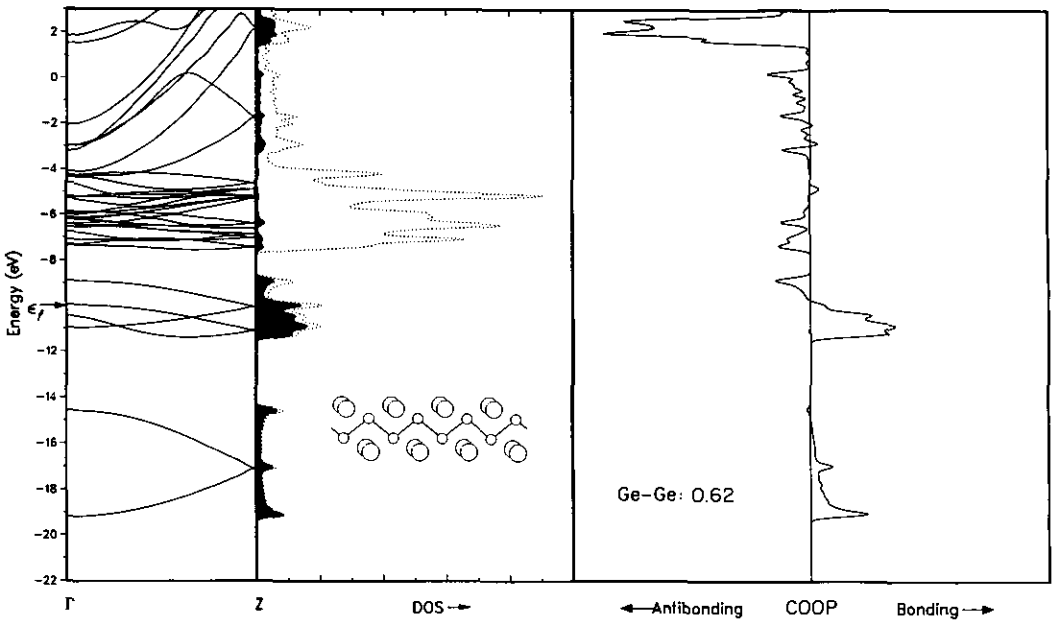


FIG. 3. The band structure, DOS and COOP (from left to right), of a one-dimensional infinite kinked Ge chain enveloped by Dy atoms. This is a model for one sublattice of $DyGe_3$. The contribution of Ge states to the total DOS (dotted lines) is blackened. The Fermi level (ε_f) is marked for $2Dy_2Ge^{5+}$ or "$2Ge^-$." The COOP curve is shown for Ge–Ge bonding, with a calculated overlap population of 0.62.

Peierls distortions implicit in this structure, because the actual band filling in the full $DyGe_3$ structure will differ.

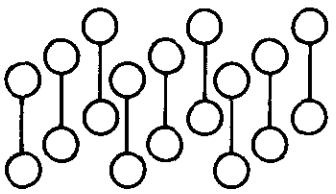
We now introduce the surrounding Dy atoms, studying a model one-dimensional Dy_2Ge chain extracted from layer **A**. In this chain the trigonal prism around each Ge is completed. The 5*d* and 6*s*, 6*p* states of rare earth metals (e.g., Dy) lie higher in energy than the 4*s* and 4*p* states of Ge. Therefore the rare earth ions mix only slightly into the Ge states. The resulting band structure of the infinite Ge chain with its surrounding Dy atoms is shown in Fig. 3 at left. We omit the Dy *f* states from the calculation. The six lowest Ge bands remain qualitatively unaltered, although they are lowered in energy due to bonding Dy–Ge interactions. The DOS (Fig. 3, center) displays the small contributions of Dy states to the Ge states below the Fermi level, which again is chosen for Ge^-, i.e., Dy_2Ge^{5+}. Dy states dominate above the marked Fermi level, separated by a 1-eV gap from Ge states.

The calculated COOP again shows that about 10 electrons (per $(Dy_2Ge)_2$) are needed to fill all Ge bonding energy states (Fig. 3, at right). The 10-electron Fermi level (ε_f) for the Ge chain is lowered slightly (relative to the pure Ge chain), due to the influence of the surrounding Dy atoms.

We reiterate at this point that we do not yet know how many electrons are to be put into the substructure; only when we study the other Ge sublattice and the full structure does the precise degree of oxidation become apparent.

The Ge_2 Layer

Two Ge atoms in the $DyGe_3$ structure form dimers that are aligned in a two-dimensional array, to form a double layer which deviates slightly from tetragonal symmetry, the Ge–Ge–Ge angles being 91.8° and 88.2°, respectively. The layer is shown in Scheme 4. Ge–Ge separations are 244.1 pm within a Ge dimer (between the layers) and 280.3



SCHEME 4

pm between adjacent dimers. An idealized Ge_2 layer, adapted from the $DyGe_3$ structure, is considered first. For the construction of the band structure of a two-dimensional double layer (Fig. 4) we use the reciprocal space notation of the tetragonal system.

The band structure of the Ge_2 layer (Fig. 4) contains two low-lying, mainly s bands (with significant p orbital mixing). The phase relations of these orbitals at the Γ' point indicate bonding and antibonding characteristics. The bonding within each dimer is marked by a strong Ge–Ge σ bond, represented by the lowest band in Fig. 4, a result of strong s, p_y orbital mixing (*7*). Higher in energy are two lone pair combinations and a σ level that is antibonding within the pair. The part of the band formed from this orbital that is bonding between pairs comes quite low in energy. The p_x and p_z orbitals mix to yield two times two bands, bonding and antibonding, with respect to the dimer.

The levels of a diatomic Ge_2 molecule are shown schematically below (Scheme 5). Above the Ge–Ge σ bond we have two lone pair combinations (symmetric and antisymmetric, in order of increasing energy), a π

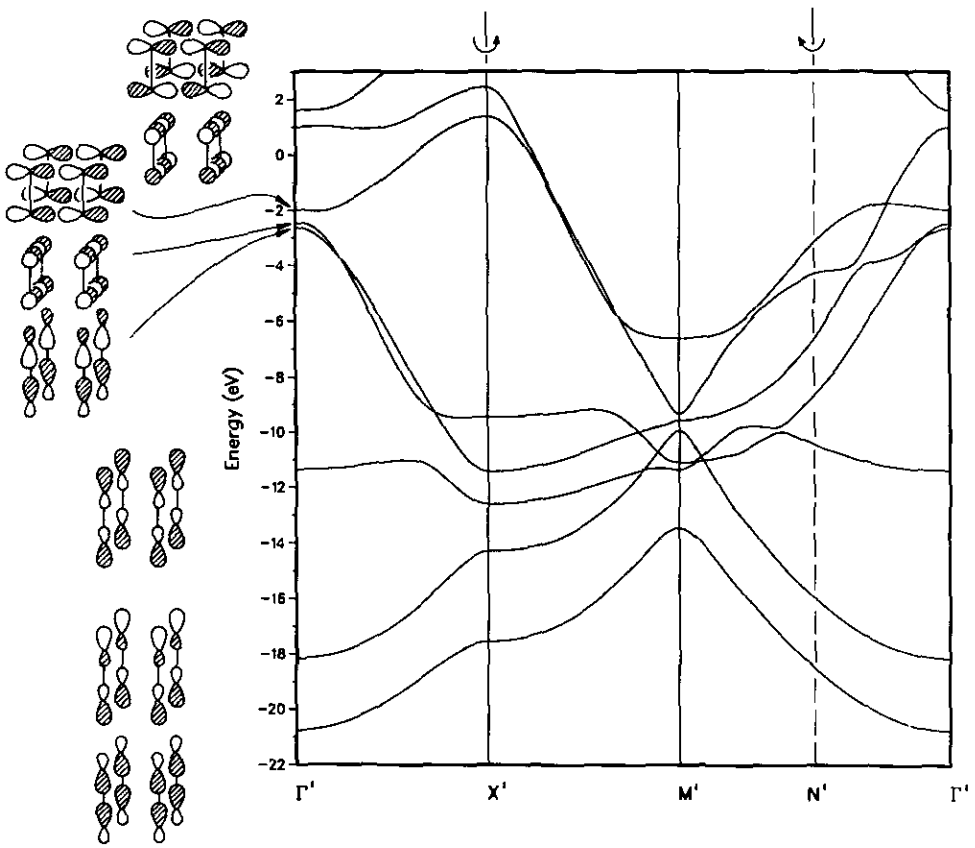
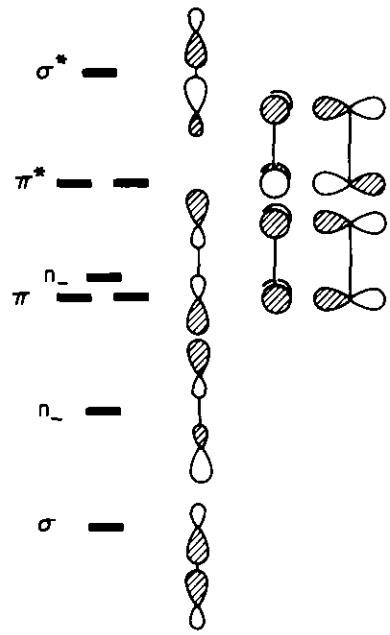


FIG. 4. Band structure of a nearly square layer of Ge_2 dumbbells. Phase relations are drawn at the Γ' point. A folding is indicated by arrows, by flipping $\Gamma'X'$ over $X'M'$, and $\Gamma'N'$ over $N'M'$, to obtain the new ΓM and ΓX directions for the large lattice.



SCHEME 5

and π^* level, and, finally, the σ^*. These pair levels are clearly recognizable in the band structure of the two-dimensional layer (Fig. 4)—they are propagated in a way typical for a simple two-dimensional square lattice (*4*).

The corresponding DOS and COOP curves are shown in Fig. 5. As the COOP shows, different electron counts maximize bonding between pairs (dotted line in COOP) and within pairs (solid line in COOP). With eight electrons (per Ge_2 unit) all bonding states between pairs are filled and antibonding states are slightly occupied. A similar situation occurs for the bonds within the Ge_2 dumbbells, but with nine electrons. Ten electrons per Ge_2 appears to be an unreasonably high electron count for the double layer—both bonds are weakened.

It is interesting to think about these electron counts maximizing bonding in the layer of pairs in terms of the levels of an isolated dimer. In such a pair (see Scheme 5), maximum bonding is achieved by filling the three σ or lone pair levels plus π, a total of 10 electrons, as in N_2. In the layer the maximal intrapair bonding occurs for a smaller electron count. This is a consequence of some *intra*pair antibonding combinations (derived from π^* and σ^*) coming to low energy as a result of bonding *inter*pair interactions.

From the band structure in Fig. 4, it is clear that for maximum bonding six electrons should occupy the three low-lying σ orbitals. Next we occupy mainly π ($p_{x,z}$) orbitals that are bonding with respect to the dimer and the layer, respectively, to reach a total of eight electrons per Ge_2. For this electron count we compute overlap populations of about 0.73 (in the dimer) and 0.22 (between adjacent dimers). With one additional electron the overlap populations remain nearly unaltered (0.71 and 0.20). Note that both σ (p_y) and π ($p_{x,z}$) orbitals contribute to bonding in the layers and in the dimers.

If we want to look at the influence of the Dy atoms capping the Ge_2 layer alternatively from above and below, we have to consider a larger unit cell. There is a simple relationship between the primitive square lattice and the centered square lattice that is present in the structure of $DyGe_3$. The two lattices and the corresponding reciprocal spaces are shown in Scheme 6. The first Brillouin zone (BZ) of the large cell is half as big as the first BZ of the small cell, because of the increase in the area of the unit cell in real space.

The transition to the large lattice can be accomplished by folding (*8*) the band structure (or reciprocal space) of the small lattice. If we fold the reciprocal space along the dashed line marked in the band structure of the small lattice (or first BZ), the band structure of the large lattice (or first BZ) is obtained. The folding superimposes the $\Gamma'N'$ and $N'M'$ lines and the $\Gamma'X'$ and the $X'M'$ lines, respectively, to form the ΓM and ΓX direction of the large lattice (*9*). The resultant band structure has twice as many bands in every direction.

Some differences ensue from avoided crossings. For example, the fourth and fifth

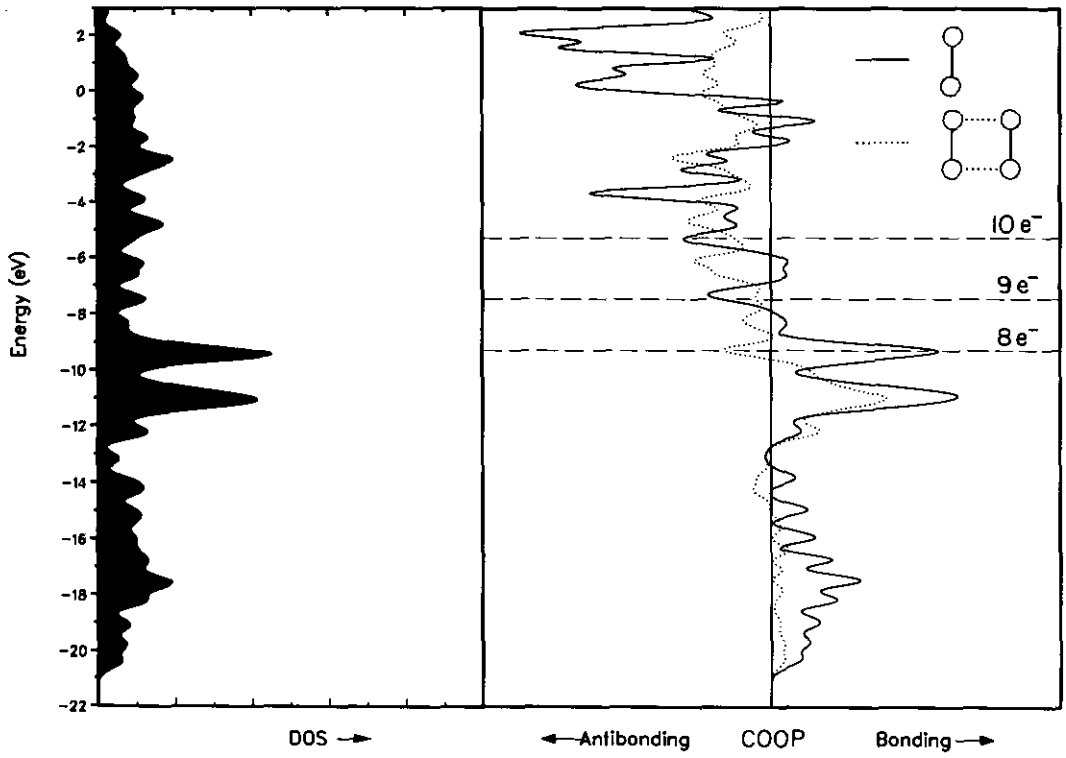
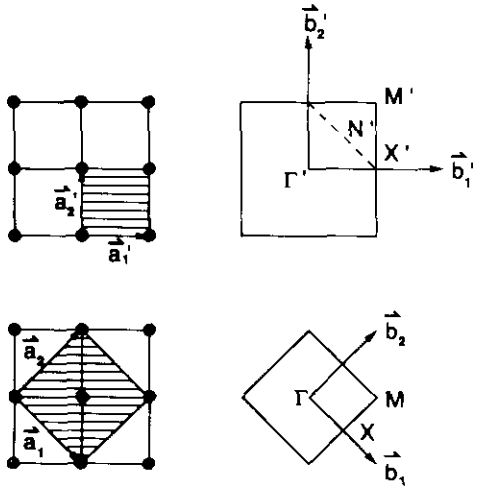


FIG. 5. DOS and COOP of a nearly square layer of Ge_2 dumbbells. Different electron populations are shown as dashed lines in the COOP.

bands between Γ′ and X′ in Fig. 4 should, upon folding, cross the sixth and seventh bands between X′ and M′. As the orbital drawings in Fig. 4 indicate, the fourth and the fifth band are antisymmetric (a) and symmetric (s), respectively, with respect to the horizontal mirror plane (m_y), and so are bands 7 (a) and 6 (s). Therefore the corresponding bands do not cross, after folding.



SCHEME 6

In the model layer (and the full structure) Dy atoms alternately cap every double layer of Ge atoms from above and below, as sketched in Fig. 6. When the Dy atoms are considered, the m_y mirror plane is no longer present and the bands can mix to a greater extent. Note the strong contribution of Dy states at and above the Fermi level, which is marked for $DyGe_2^+$ (10 electrons per Ge_2) Fig. 6, center). The band structure in Fig. 6 (left) exhibits obvious traces of the (unfolded) band structure of the smaller unit of the Ge double layer (Fig. 4). Again, some low-lying Ge bands are stabilized in energy as a result of bonding interactions with Dy atoms.

How many electrons should be put into

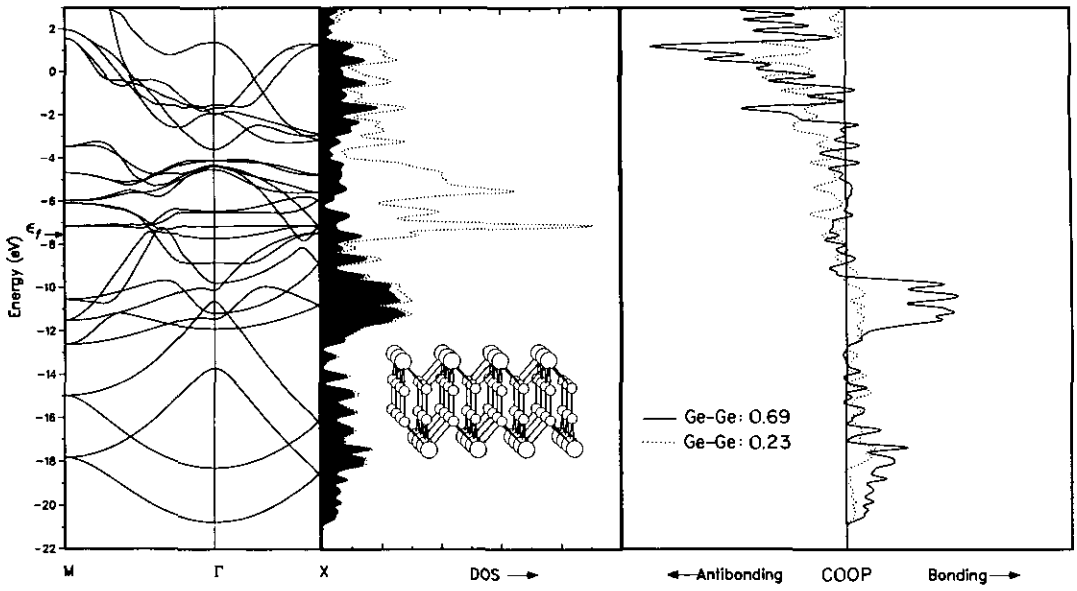


FIG. 6. The band structure, DOS and COOP (from left to right), of a $DyGe_2$ layer. Contributions of Ge to the total DOS (dotted lines) are black. The Fermi level (ϵ_f) is marked for $DyGe_2^+$ or "Ge_2^{2-}." Ge–Ge overlap populations are shown as solid lines within the pairs, and as dotted lines between pairs.

these bands? The $DyGe_3$ structure contains Ge chains and Ge_2 layers with a total of 15 valence electrons per formula unit. The Ge atoms in the chain were tentatively considered as Ge^-. From this starting point 10 electrons are left for the bands of the Ge_2 layer. After the small layer is folded, the unit cell contains two Ge_2 molecules, with their orbitals (and whatever Dy orbitals mix in below ϵ_f) occupied with 20 electrons. This leads to an occupation of antibonding Ge–Ge states (Fig. 6, at right), which, however, are Dy–Ge bonding. With nine electrons in the $DyGe_2$ layer, we maximize overlap populations between Ge atoms. Note that the 10-electron Fermi level of this substructure is substantially higher than that of the Dy_2Ge sublattice.

The Electronic Structure Of $DyGe_3$

The two Ge substructures in $DyGe_3$ are well separated from each other and do not interact directly. Therefore, the DOS contributions of the separately calculated Ge substructures, namely a chain (Fig. 3) and a layer (Fig. 6) of Ge atoms surrounded by their Dy neighbors, are consistent with the total Ge DOS of the $DyGe_3$ structure (Fig. 7). Ge atoms provide the majority of states to the total DOS below the Fermi level because Dy is more electropositive and the corresponding electronic states are mainly at higher energies. Nevertheless, Dy ions interconnect the Ge fragments. There is significant orbital mixing, with bonding Dy–Ge and even bonding Dy–Dy interactions.

Initially all bonding energy states of the Ge chain were filled with five electrons per Ge and the remaining 10 electrons were put into the Ge_2 layer. As we saw, this leads to an unreasonably high Fermi level for the Ge_2 layer compared with the Ge chain. Also, Ge–Ge antibonding states are occupied for the Ge_2 layer.

A calculated DOS of the complete structure shows the balance that is struck. Some electrons are shifted from the two-dimensional Ge_2 sublattice to the chains. With the Fermi energy near -8.5 eV, the antibonding π^* states of the Ge chain (Fig. 2 or 3, at right) are filled.

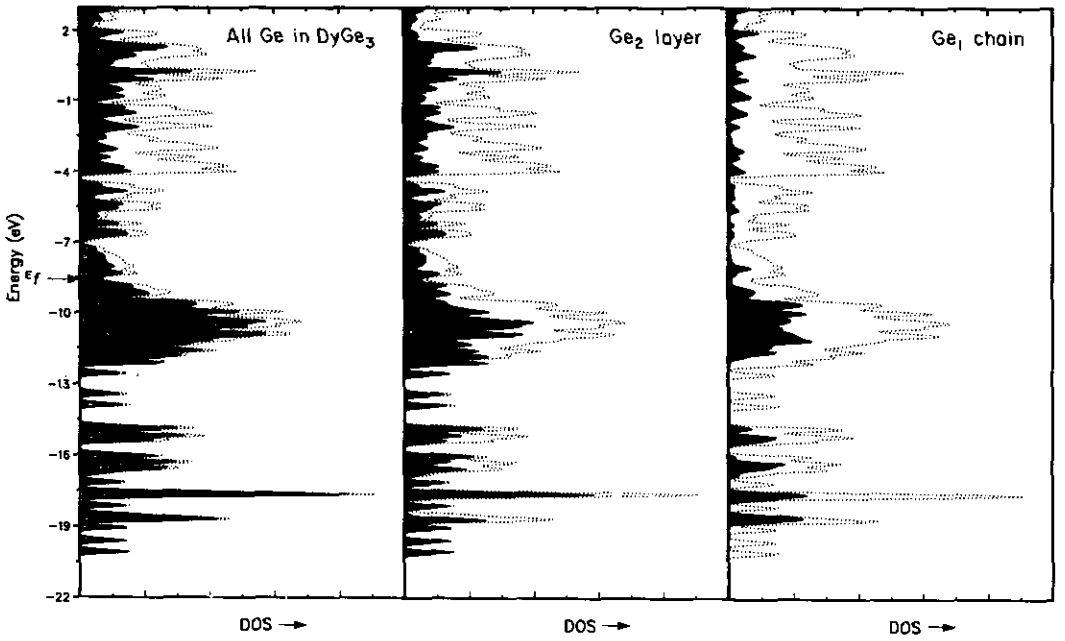
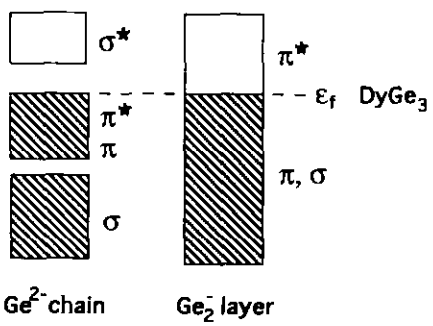


FIG. 7. Contributions of Ge states (black) to the total DOS of $DyGe_3$ (dotted lines), at left, and the individual DOS contributions of Ge atoms forming the layers (center) and the chains (right), to the total DOS. The Fermi level for $DyGe_3$ is marked as ε_f.

A schematic electron occupation picture of the substructures is shown in Scheme 7, after electron transfer from the Ge_2 layer into the Ge chain (*10*).

As a result of the equalization of the Fermi levels of the substructures, the π^* orbitals in the Ge chain become occupied. We get a 12-electron (per two Ge atoms) chain that follows the Zintl rule. This makes the Ge chain atoms formally Ge^{2-}, isoelectronic with a sulfur chain. The resulting Ge–Ge overlap populations calculated in the full $DyGe_3$ structure are 0.61 for Ge atoms forming the chains (Ge–Ge distance 250.5 pm). Structurally, and possibly electronically, these chains compare with the kinked boride chains in CrB (*11*) and FeB (*12*).



SCHEME 7

For an isolated Ge double layer a total number of eight electrons gives maximum overlap populations for bonds between pairs, and a total number of nine electrons gives maximum overlap populations for the bonds within a pair. When the Dy atoms are included, the bonding between pairs is increased if nine electrons are present.

Only one additional electron is formally present in the Ge_2 layer, making it a nine electron double layer (Ge_2^-). Relatively large overlap populations between the Ge dimers (Ge–Ge = 244.2 pm) of 0.70 are the result of a two-center two-electron bond strengthened by π bonding interactions. The π orbitals are mainly responsible for electron deficient multicenter bonding between

adjacent dimers (Ge–Ge = 280.3 pm) with overlap populations of 0.37. Related layered structures and their possible distortions are discussed in (*13*).

While the formal division of electrons is Ge^{2-} and Ge_2^-, there is, of course, substantial orbital mixing of Dy states. The actual computed charge distribution is $Dy^{1+}Ge^{0.6-}(Ge_2)^{0.4-}$.

The band structure of $DyGe_3$ exhibits several bands crossing the Fermi level parallel to the axial directions of the xz plane. Parallel to the y direction, bands are very flat, with an almost 3 eV band gap. These results mark the importance of Ge–Ge bonding in the Ge layers along the xz plane of the structure. The π and π^* bands of this sublattice are responsible for the expected electronic conductivity of $DyGe_3$.

Appendix

The extended Hückel approach, within a tight-binding scheme, was employed in all calculations. Since parameters for Dy were not available, Sm values were used. Sm and Ge parameters were obtained from the literature (*14*, *15*).

Acknowledgments

H.-J.M. thanks the Deutsche Forschungsgemeinschaft, Federal Republic of Germany, for support of this research. The work at Cornell was supported by NSF Grant CHE8912070. We thank Jane Jorgenson for her expert drawings.

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9. This folding is not exactly correct for the orthorhombic layer in the real lattice as it is for a tetragonal lattice. The p_x and p_z bands are not degenerate at Γ as a result of the slight deviation from tetragonal symmetry (Fig. 4).
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