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Concerning the Different Roles of Cations in Metallic Zintl Phases: $Ba_7Ga_4Sb_9$ as a Test Case

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The question of the different roles of cations in metallic Zintl phases has been examined by taking $Ba_7Ga_4Sb_9$, an electron-rich phase, as a test case. The electronic structure of this solid has been studied by means of a first-principles density functional theory approach and, indeed, the different Ba atoms are found to play very different roles in determining the structural and transport properties of this phase. It is also found that $Ba_7Ga_4Sb_9$ should be an anisotropic metal with both one- and three-dimensional contributions to the Fermi surface so that the system could exhibit a potentially very interesting physical behavior while keeping the metallic properties down to very low temperatures. Suggestions in order to modify the band filling and the physical properties are examined. Although isostructural electron-precise phases may be envisioned, it is predicted that they would be essentially three-dimensional metals.

Introduction

For a long time, it has been common wisdom that electropositive atoms in Zintl phases can be considered, at least formally, as completely transferring their electrons to the clusters or networks of their more electronegative partners. The success in relating the number of electrons with the shape and nature of the anionic subnetworks on the basis of this assumption has been really impressive.[1–3] Very fundamental and simple chemical bonding schemes such as the octet and Wade rules, i.e., approaches that associate chemical stability with structural building blocks (clusters, networks, etc.) having an electronically closed-shell configuration, have provided a useful *ansatz*, leading to a clear and appealing way to understand how the structure and number of electrons in literally hundreds of these phases are interrelated. An almost automatic corollary has been the belief that Zintl phases must usually be semiconductors or insulators. Exceptions have always been known,[4] but they were often seen as accidents, which should not cast a shadow on an already clear and neat picture. For instance, it is assumed that in some rare cases the band gap between the valence and conduction bands can close and lead to "accidental metallic behavior" because of this slight overlap.

The number of Zintl phases that do not follow the "standard" view has been increasingly growing during recent years. Hence, it was felt that a reexamination of the role of the electropositive atoms in the electronic structure of these phases was necessary.[5,6] Indeed, it has been found that they have a much more important role than was assumed in the past. After all, if phases exist in which the anionic network has an electronic excess or deficiency with respect to those predicted by the above-mentioned anion-based approach, it seems quite obvious that the cationic species must compensate in some way for the inherent instability associated with this feature and, thus, be much more than mere "electron suppliers". However, the role of such cations seems, at least

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for the moment, not so easy to grasp in simple terms because of the lack of a real experience concerning the nature of the cation orbitals in their often quite irregular environment. Thus, it is important to study appropriate systems in order to develop a kind of intuitive feeling of the actual role of the electropositive partners in the Zintl phases. In this paper, we briefly comment on one aspect of this question. The structure and transport properties of a system can crucially depend on the interaction between the cationic and anionic networks or not. However, the structure of a phase depends on the whole set of filled levels of the system, whereas the transport or many other properties only depend on a small number of them (i.e., for a metallic conductor, from those in a narrow energy range around the Fermi level). Consequently, if the cations play a role in leading to the stability and structural features of a given phase, this does not necessarily mean that they are also important to understand the transport properties. Parenthetically, to say that cations play a role in understanding some aspect of the structure and/or properties of a material does not mean that *all* cations are active players. It may perfectly be that some cations are decisive in conferring stability to the phase, whereas a different set of cations are those really influencing the details of the conductivity.

In the course of our work on “unusual” Zintl phases, we have found that $Ba_7Ga_4Sb_9$ nicely illustrates this situation. This phase was prepared by Cordier et al.,[7] and it is not possible to distribute the 14 electrons formally given by the Ba atoms in the covalent network of Ga and Sb without contradicting conventional ideas about the relationship between coordination and electron counting. This led to an extended Hückel study by Alemany et al.[8] in which it was found that an “extra” electron was housed in an essentially Sb−Sb antibonding band, which is half-filled. Although the material has metallic luster, something that would agree with this observation, the conductivity has not yet been measured. In principle, occupation of an antibonding band should not be a favorable feature for this phase if there is not some additional aspect, some in which the cations are most likely implicated, that more than outweighs it. However, the role of cations was not explicitly accounted for in that work. As part of our interest in these unusual Zintl phases, we report here a first-principles study of this phase, which we believe provides a clear illustration of the different roles that cations may play in Zintl phases. In addition, as a consequence of this study, $Ba_7Ga_4Sb_9$ reveals as a very interesting material certainly deserving further attention.

Computational Details

First-principles calculations for $Ba_7Ga_4Sb_9$ were carried out using a numerical atomic orbitals density functional theory (DFT) approach,[9] which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[10−12] The use of atomic orbitals instead of plane waves greatly facilitates a chemical analysis of the results. We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew et al.[13] Following recent first-principles work on Bi- and Ba-containing intermetallic phases,[14] only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[15] factorized in the Kleinman−Bylander form.[16] Nonlinear partial core corrections to describe the exchange and correlations in the core region were used for Sb, Ga, and Ca.[17] We have used a split-valence double-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 100 meV.[18] The 3d electrons of Ga, the 5p and 5d electrons of Ba, and the 3d electrons of Ca were treated as valence electrons. The energy cutoff of the real-space integration mesh was 150 Ry. The Brillouin zone was sampled using a grid of $5 \times 5 \times 5$ *k* points.[19] Spin polarization was found to have no influence on the electronic structure of this phase. Except otherwise stated, we have used the experimental crystal structure because the calculated forces for the different atoms were not found to be significant.

Results and Discussion

A. Crystal Structure. The crystal structure of $Ba_7Ga_4Sb_9$ is orthorhombic and contains Ga_4Sb_9 layers perpendicular to the *a* direction (see Figure 1a,c). Successive layers are shifted by $b/2 + c/2$ so that the unit cell is built from two identical layers. Every layer is made of a series of condensed $GaSb_4$ tetrahedra (see Figure 1b), four of which lead to a Ga_4Sb_{11} bicyclic unit analogous to bicyclo[3.3.1]nonane. By sharing the two opposite pairs of Sb atoms, these units lead to Ga_4Sb_9 chains along the *b* direction. Relatively long but nonnegligible Sb−Sb contacts (Sb3−Sb4: 3.296 Å) interconnect the successive chains along the *c* direction, resulting in the Ga_4Sb_9 layers. Between these layers, three different types of Ba atoms (Ba1, Ba2, and Ba3; see Figure 1a,c) reside. Loosely speaking, whereas two types of Ba atoms (Ba1 and Ba2) can be considered as residing in the interlayer region, another one (Ba3) resides inside the layers. Thus, just from simple geometric inspection, one may suspect that different cations can play very different roles. Both Ba1 and Ba2 make relatively short Ba···Sb contacts with two different layers (this is more clearly seen in Figure 1c), thus providing some link between them.

B. Electronic Structure: Partially Filled Bands and Ba Contributions. The Ga_4Sb_9 layers contain two monocoordinated (Sb2), five bicoordinated (Sb1 and Sb5), and two tricoordinated (Sb3 and Sb4) Sb atoms as well as four tetracoordinated Ga atoms, which, for electron-counting

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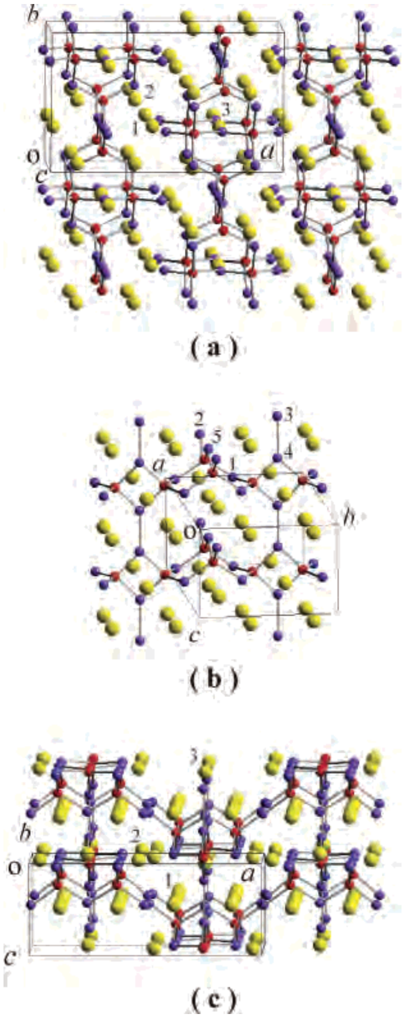

Figure 1. Crystal structure of $Ba_7Ga_4Sb_9$: (a) view approximately along the *c* direction; (b) view approximately along the *a* direction emphasizing the topology of the Ga_4Sb_9 layer; (c) view approximately along the *b* direction. The blue, red, and yellow spheres correspond to Sb, Ga, and Ba, respectively. The labeling of the Ba atoms is shown in parts a and c, and that of the Sb atoms is shown in part b.

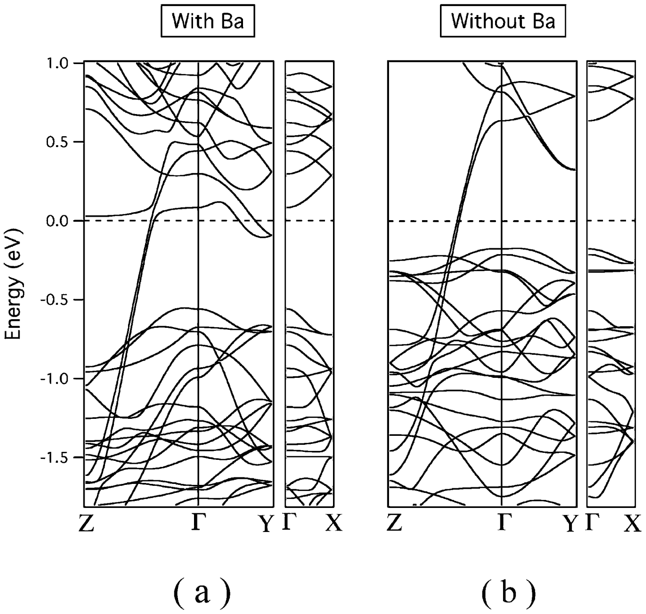

Figure 2. Calculated band structure for $Ba_7Ga_4Sb_9$ (a) and $(\square^{2+})_7(Ga_4Sb_9)^{14-}$. The dashed line refers to the Fermi level, and $\Gamma = (0, 0, 0)$, $X = (^1/_2, 0, 0)$, $Y = (0, ^1/_2, 0)$, and $Z = (0, 0, ^1/_2)$ in units of the orthorhombic reciprocal cell vectors.

purposes, can be considered as Sb^{2-}, Sb^{-}, Sb^{0}, and Ga^{-}, respectively. Thus, the formal charge of the repeat unit of the layers is 13−, one electron short from the 14− provided by the seven Ba atoms, assuming a complete transfer. Thus, at least formally, $Ba_7Ga_4Sb_9$ can be considered as a Zintl phase with an electronic excess. Understanding the possible interrelationship between this feature and the potential metallic character with the long Sb3−Sb4 interchain contacts and the cation−anion interactions on the basis of first-principles calculations is the goal of the present work.

Shown in Figure 2a is the calculated band structure for $Ba_7Ga_4Sb_9$ along the three main directions of the reciprocal lattice. All bands pair up at the X and Y points because there are two identical layers related by nonsymmorphic symmetry elements parallel to the *a* and *b* directions. The crucial feature of this figure is that two pairs of bands cross the Fermi level. One of the pairs is a very dispersive one along c^* (see the $\Gamma \rightarrow Z$ direction in Figure 2a). Analysis of the character of the wave functions along this line (notice a weakly avoided crossing near the Fermi level) as well as the Sb3/Sb4 projected density of states of Figure 3 clearly shows that this band is heavily based on the Sb3 and Sb4 atoms, as found in the previous extended Hückel analysis by Alemany et al.[8] However, there is a second pair of bands crossing the Fermi level along b^* that is heavily based on the Ba atoms. This is an important difference from the previous study because, besides showing clearly the involvement of cations in the electronic structure of the material, it also changes the shape of the Fermi surface and, thus, the predicted and so far unstudied transport properties of the material. Let us consider these two questions separately.

To discuss the influence of the cations on the bonding (i.e., the structural features), it is more convenient to look at the density of states of the material (see Figure 3). Its main contributions are the following: (a) a peak centered at −17 eV (not shown in the figure) corresponding to the 3d Ga levels, (b) a peak centered at −14 eV (not shown in Figure 3) associated with the 5p Ba levels, (c) a contribution centered around −8.5 eV that is mainly associated with the 5s Sb levels, (d) a contribution centered at −6 eV that may be described as the 4s Ga contribution (although these levels mix quite heavily with 5p Sb orbitals), and (e) a series of peaks collapsing into a wide contribution associated with the 5p Sb and 4p Ga levels. As expected, the Fermi level is very near to a deep minimum in the density of states, which would correspond to the “right” Zintl count. Around the Fermi level, the contributions of the Ba, Ga, and Sb orbitals are 34%, 24%, and 42%, respectively, and those of the individual Sb atoms are 8.3% (Sb1), 4.1% (Sb2), 13.6% (Sb3), 14,4% (Sb4), and 1.6% (Sb5). Taking into account that there is just one Sb3 and one Sb4 atom per unit cell (but four Sb1 and two Sb2 atoms), these values make it clear that in the region around the Fermi level (i.e., the region determining the transport properties) (a) the Sb contribution

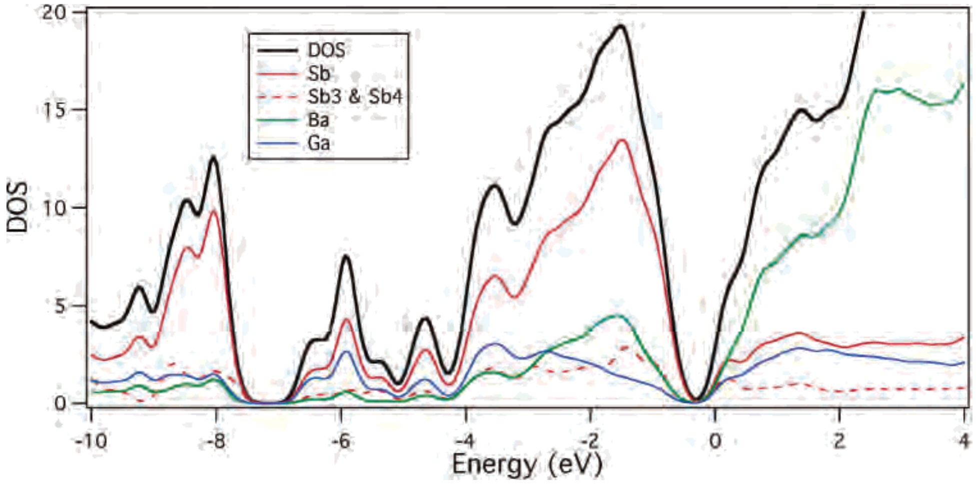

Figure 3. Calculated density of states (DOS) for $Ba_7Ga_4Sb_9$ as well as local contributions of the Sb, Ga, Ba, and Sb3/Sb4 atoms.

is dominated by those of the Sb3 and Sb4 atoms and (b) the Ba contribution is very heavy, almost as large as that of Sb.

Of more interest at this point is, however, the cations contribution to the filled part of the density of states. Except for the region of the peak associated with the 4s Ga levels, the Ba contribution is of the same order as that of the Ga atoms (near the minimum, it is even clearly larger). Taking into account the stoichiometry and the fact that these contributions are not associated with mostly Ba bands, this observation makes it clear that the cations have a very large contribution to the covalent bonding in this phase. The calculated Mulliken charges for Ba1, Ba2, and Ba3 are +0.40, +0.41, and +0.27, respectively. Although one must be cautious toward Mulliken charges, these values are quite far from those expected for Ba mainly acting as an electron donor and clearly show that Ba atoms definitely have an important participation in the covalent bonding of the structure. As a matter of fact, these charges are almost the same as those calculated for $Ba_5In_4Bi_5$, an electron-deficient Zintl phase for which it has been recently shown[5b] that the Ba atoms are strongly involved in covalent interactions with the Bi atoms, leading to a three-dimensional network. In the present structure, all Ba atoms are also implicated in large and positive Ba−Sb overlap populations (0.155, 0.143, 0.127, 0.113, ...), indicating very substantial Ba−Sb bonding interactions, something that is consistent with the large Ba contribution in the filled density of states and, thus, the small positive charges. Just to make this fact even more clear, we have calculated the Mulliken charges for the Sb atoms of $Ba_7Ga_4Sb_9$ using (a) the actual crystal structure and (b) the same structure in which the Ba atoms have been removed and replaced for a 2+ charge uniformly distributed while keeping the same total number of electrons. As expected, the Sb charges are smaller when the Ba atoms are not included in the calculation; the differences are 1.01 (Sb1), 1.42 (Sb2), 0.80 (Sb3), 0.82 (Sb4), and 1.06 (Sb5). Because the calculated differences are essentially the result of covalent interactions with the Ba atoms, it is clear that the Sb2 atoms are those more implicated in these interactions, the Sb1 and Sb5 atoms follow, and the Sb3 and Sb4 atoms are those less implicated.

Before this section is concluded, it is important to have a hint on the strength of the Sb3−Sb4 interactions. To do so, it is useful to be reminded of the structure of 2,2′,5,5′-tetramethyldistibole,[20] which displays a typical one-dimensional structure in which there are chains of distibine units with Sb−Sb bond lengths of 2.835 Å (for comparison, note that the sum of the covalent radii of the Sb atoms is 2.76 Å and the Sb−Sb distance in elemental Sb is 2.90 Å)[21] separated by Sb−Sb contacts of 3.625 Å. Although these interdistibine contacts are long, they are nonnegligible and, in fact, because of the good orbital orientation, they are responsible for strong interactions along the chains, which are at the origin of the thermochromic effect of this material as well as in other distibine chains.[22] The Sb3−Sb4 distance in $Ba_7Ga_4Sb_9$ is 3.296 Å, which is between the two Sb−Sb distances in 2,2′,5,5′-tetramethyldistibole. Thus, we have calculated the Sb−Sb overlap populations for the two solids. Those associated with 2,2′,5,5′-tetramethyldistibole are 0.295 and 0.077, whereas that for Sb3−Sb4 in $Ba_7Ga_4Sb_9$ is only 0.051. In view of the actual Sb−Sb distances, this result is somewhat surprising. However, when the Ba atoms are removed from the calculation while keeping the same total number of electrons, the calculated overlap population for Sb3−Sb4 increases to 0.105, something that is more expected. Consequently, if it were not for the Ba mixing in the filled region of the density of states associated with the bonding Sb3−Sb4 levels, which necessarily decreases the strength of this bond, the overlap population would suggest an Sb−Sb interaction, corresponding approximately to a half-bond, as expected from the formal electron counting. The Ba atoms decrease the interchain Sb3−Sb4 interactions not only by providing extra electrons to fill an antibonding Sb−Sb level but also by mixing into the associated bonding levels. In view of this analysis, a description of the anionic network of $Ba_7Ga_4Sb_9$ as a series of slightly coupled Ga_4Sb_9 chains seems more appropriate that that based on Ga_4Sb_9 layers.

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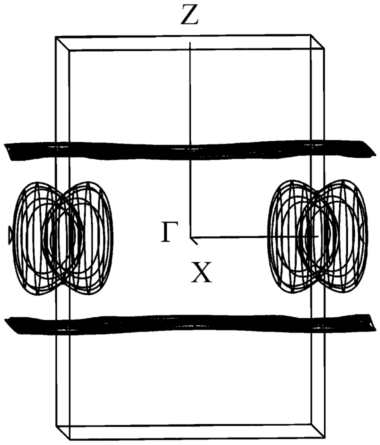

Figure 4. Calculated Fermi surface for $Ba_7Ga_4Sb_9$.

It is clear that the unfavorable electronic situation created by the extra electron formally brought to the anionic network must be outweighted by some stabilizing effect. This is the role of the Ba atoms, which by strongly mixing into the filled part of the density of states provide an extra stabilization that is nothing more than extensive Ba−Sb covalent bonding. Thus, $Ba_7Ga_4Sb_9$ is another example of a phase in which even if the composition cannot lead to a maximum stabilization of the anionic network, as usually happens in traditional Zintl phases, the system finds the cation distribution that maximizes their participation in the covalent bonding of the structure and compensates for the energetic consequences of the electronic excess[23] (or defect[5b]). Before considering the different roles of the three Ba atoms on the stability of this phase, let us now look at its conductivity.

C. Conductivity and Different Roles of the Ba Atoms. As mentioned above, there are two pairs of bands crossing the Fermi level. Because the analysis of the density of states around the Fermi level evidenced a strong involvement of the Ba levels in this region, we have carried out a calculation using the same structure in which the Ba atoms have been removed from the calculations in the same way as described above. As shown in Figure 2b, the pair of bands crossing the Fermi level around Y has completely disappeared, whereas the very dispersive one is kept. Because of the absence of the second partially filled pair of bands, the dispersive pair is half-filled and consequently the physical situation has been strongly altered. We are exactly in the scenario of the previous study by Alemany et al.,[8] in which the cations were not considered. Consequently, the Ba atoms have also a key role in determining the conductivity of this phase.

The calculated Fermi surface is shown in Figure 4. There are two almost superposed very flat sheets perpendicular to the c^* direction, which, thus, will be responsible for one-dimensional metallic conductivity along the *c* direction. These two sheets are associated with the bands strongly concentrated on the Sb3 and Sb4 atoms. The Fermi surface has a second contribution associated with a pair of closed three-dimensional electron pockets centered around Y. These electron pockets are mostly associated with the Ba atoms and, as a consequence of their three-dimensional shape, will lead to a three-dimensional metallic conductivity. As a result, $Ba_7Ga_4Sb_9$ is predicted to be an anisotropic three-dimensional metal with best conductivity along the *c* direction even if the Ga_4Sb_9 chains are along the *b* direction. This makes this phase very interesting because the two almost planar sheets of the Fermi surface make it susceptible to an electronic instability of the charge-density wave type, which would destroy these planar components of the Fermi surface, leading to a resistivity anomaly.[24] However, the existence of the Ba-centered closed electron pockets would keep the three-dimensional carriers and thus the metallic conductivity after the anomaly. Because the Fermi surface of Figure 4 is just the superposition of the two components, there would be a very strong change in the character of the metallic conductivity around the transition from anisotropic with better conductivity along *c* to very isotropic.

Let us recall that, because of the closed pockets, the strongly dispersive pair of bands is less than half-filled and, consequently, the nesting vector is not given by a simple fraction, i.e., $q \sim 0.45c^*$. This means that if a charge-density wave occurs in this material, leading to a resistivity anomaly, the associated structural modulation must be incommensurate with the lattice. The driving force for a structural modulation is weaker for incommensurate distortions,[25] and thus it would be very interesting to carry out low-temperature studies in order to see if the instability really occurs. If this is so, then $Ba_7Ga_4Sb_9$ would be a potentially very interesting material because the usual isotropic metallic behavior would coexist with an incommensurate charge-density wave and interesting physical scenarios can be envisioned. Low-temperature magnetoresistance, transport, and X-ray diffuse scattering studies would be worthwhile doing.

To understand the involvement of the different Ba atoms in the conductivity, we show in Figure 5 the calculated band structure when every one of the three different types of Ba atoms is separately removed from the calculations without changing the electron count, as discussed above. It is clear that the Ba1 atoms have practically no effect on the band structure around the Fermi level and that the Ba3 atoms have a minor effect in slightly changing the shape of the Ba-based pair of bands. In terms of the Fermi surface, the Ba1 atoms do not play any role in leading to the actual Fermi surface; the Ba3 atoms have only some influence in slightly changing the shape of the closed electron pockets, but this has no qualitative physical consequences. The Ba2 atoms, however, are essential in leading to the actual electronic structure around the Fermi level and, thus, to the transport properties and potentially very interesting low-temperature behavior of $Ba_7Ga_4Sb_9$. When the wave functions of the Ba-based partially filled bands are looked at in detail, it appears that

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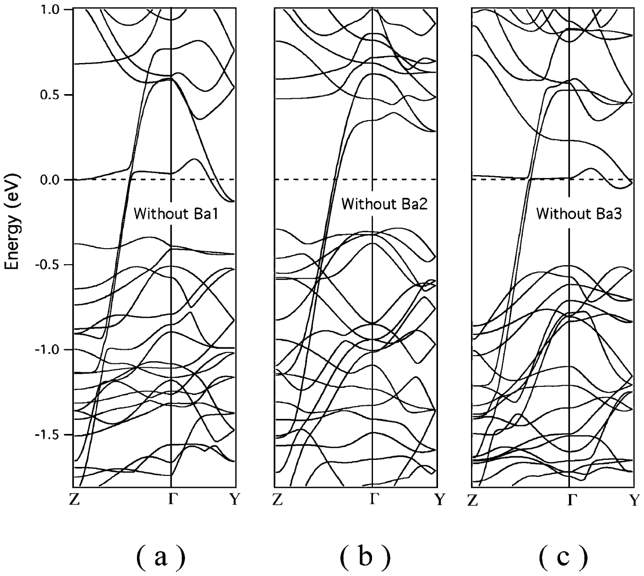

Figure 5. Calculated band structure for $Ba_7Ga_4Sb_9$ in which only the Ba1 (a), Ba2 (b), and Ba3 (c) cations were removed from the calculations without changing the electron count, as discussed above. The dashed line refers to the Fermi level, and $\Gamma = (0, 0, 0)$, $Y = (0, {}^1/_2, 0)$, and $Z = (0, 0, {}^1/_2)$ in units of the orthorhombic reciprocal cell vectors.

the major interactions leading to these closed electron pockets implicate the s orbitals of the Ba2 atoms and the p orbitals of the monocoordinated Sb2 atoms.

D. Substitutions at the Ba3 Site and Implications for the Zintl-Type Approach. Because the electron excess of this phase is of one electron per formula unit and the degeneracy of the Ba3 position is also one, the possibility of creating a “normal” Zintl phase with this structure immediately comes to the mind. In principle, it would suffice to work with a quaternary system in which the Ba3 positions were filled by a monovalent cation of the appropriate size, for instance, K (Pauling radius of 1.33 Å vs 1.35 Å for Ba^{2+}).[21] As noted before, just from geometrical inspection, it is clear that the Ba1 and Ba2 atoms must play a different structural role than Ba3. The analysis of the overlap populations suggests that even if the Ba and Sb atoms lead to a complex three-dimensional network of interactions, the Ba1 and Ba2 atoms are mostly engaged in strong interactions with Sb1 and Sb2 whereas the Ba3 atoms are involved in strong interactions with Sb5 (and Sb1). Thus, roughly speaking, the Ba1 and Ba2 atoms are those providing the interconnection between different Ga_4Sb_9 chains of different “layers”, whereas the Ba3 atoms are those providing the link between Ga_4Sb_9 chains of the same “layer”. Under such circumstances, the possibility of making some tuning of the properties of this structure through a second mechanism appears. It may be possible to change the electronic structure by modifying the size of the cation at the Ba3 position because this could influence the interchain contacts along the *c* direction, i.e., the Sb3−Sb4 contacts, and thus modifying the width of the strongly one-dimensional band. However, to progress along this line, it is necessary to see if the main factors controlling the structure of this phase are the interchain interactions through Ba1/Ba2, those through Ba3, or a combination of both. Only in the first case would it be possible to reason about the possible changes in a rigid-band approach.

To test this point, we have carried out structural optimizations for $Ba_7Ga_4Sb_9$ and the three phases $Ba_6KGa_4Sb_9$, $Ba_6CaGa_4Sb_9$, and $Ba_6NaGa_4Sb_9$, generated from the former by replacing K, Ca, and Na for Ba at the Ba3 site. Essentially, it was found that the structure is quite rigid and not significantly affected by these substitutions at the Ba3 site. For instance, the K replacement led to changes of less than 0.35% in the cell constants, whereas the maximum change amounts to 1.5% for the *c* parameter in both the Na and Ca replacements. The change in the Sb3−Sb4 distance, which may modulate dispersion of the wide one-dimensional pair

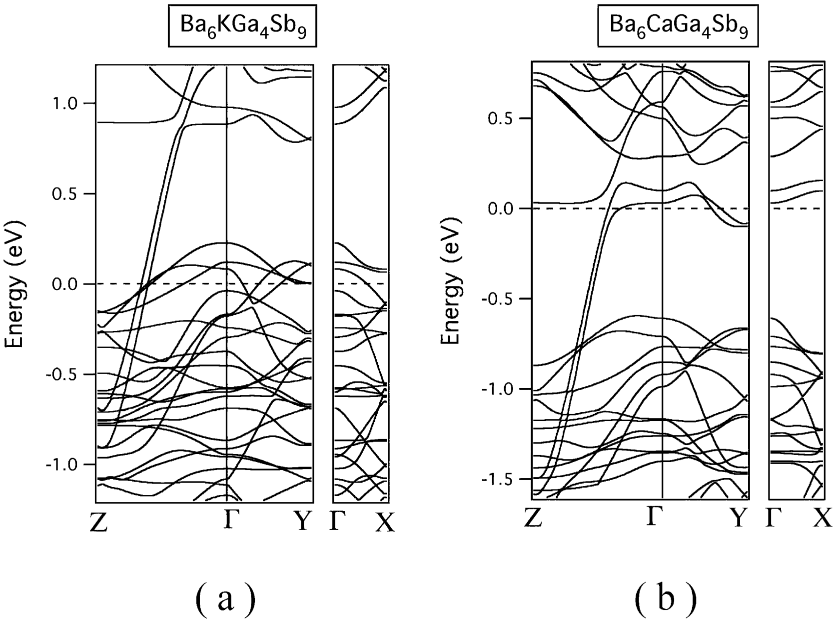

Figure 6. Calculated band structure for $Ba_6KGa_4Sb_9$ (a) and $Ba_6CaGa_4Sb_9$ (b). The dashed lines refer to the Fermi level, and $\Gamma = (0, 0, 0)$, $X = ({}^1/_2, 0, 0)$, $Y = (0, {}^1/_2, 0)$, and $Z = (0, 0, {}^1/_2)$ in units of the orthorhombic reciprocal cell vectors. The optimized structures have been used.

of bands is only 1.0−1.6%. Thus, we conclude that the Sb−Ba interactions implicating the Ba1 and Ba2 atoms already dominate the structural arrangement of the Ga_4Sb_9 chains in a way that leaves space for another cation that may comfortably sit in the hole created by one Sb5 atom of a chain and the four Sb1 atoms of the next chain (see Figure 1b,c). Thus, we conclude that a rigid-band approach must be appropriate when considering substitutions at the Ba3 site of this phase.

Because the interchain Sb3−Sb4 contacts created in that way are short enough so as to lead to a strongly dispersive one-dimensional band that overlaps substantially with the top of the valence bands, it is clear that when using a monovalent cation to fill the Ba3 positions, i.e., when there is one electron less per formula unit to fill the bands of the system, there will be no gap at the Fermi level. Instead, the Fermi level will occur at the upper part of the valence bands (see Figure 6a) and thus the system will be a three-dimensional metal even if on the basis of traditional Zintl counting arguments one could have expected a band gap and insulating behavior. As shown in Figure 6b, replacement of Ca for Ba at the Ba3 position leaves the partially filled bands practically unaltered. Interestingly, replacement of a divalent cation by a monovalent cation considerably reduces the role of the low-dimensional component of the metallic conductivity, making the system essentially three-dimensional (and thus probably destroying the potentially interesting low-temperature physics) even keeping the structure unaltered. We thus conclude that phases with the $Ba_7Ga_4Sb_9$ structure with different cations at the Ba3 position should be stable metals until very low temperatures (and thus it would also be interesting to look for superconductivity) although the anisotropy and the metallic behavior as a function of the temperature may be strongly different. This feature makes the study of $Ba_7Ga_4Sb_9$ and other phases with this structure very interesting.

Concluding Remarks

The present work provides a further example of the importance of taking into account the cations when trying to understand the bonding and transport properties of Zintl phases. A wealth of information concerning the structure and properties can be obtained when their participation on the electronic structure is carefully analyzed on the basis of reliable first-principles approaches. Through the analysis of $Ba_7Ga_4Sb_9$, we have shown that, although every cation plays a definite structural role, the transport properties may be decided by just a small subset of the cations, which are those to be considered in trying some tuning of their transport properties. It turns out that $Ba_7Ga_4Sb_9$, a phase with a peculiar structure but whose physical properties have not yet been studied, may lead to a family of materials with very appealing and different physical behavior.

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