

Articles

Contribution from the Department de Química Inorgànica, Universitat de Barcelona, Diagonal, 647 Barcelona 08028, Spain, and Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

The Electronic Structure of $Ba_7Ga_4Sb_9$, a Compound Seemingly Probing the Limits of the Zintl Concept

Pere Alemany,[†] Santiago Alvarez,[†] and Roald Hoffmann^{*‡}

Received October 3, 1989

In $Ba_7Ga_4Sb_9$, a recently synthesized compound, there is a Ga_4Sb_9 ¹⁴⁻ two-dimensional net that probes the limits of the Zintl concept. It is made up of one-dimensional alternating four- and eight-membered Ga-Sb rings, linked together into a two-dimensional structure by long but bonding Sb-Sb contacts. Band calculations reveal quite localized bonding and a half-filled Sb-Sb σ^* band. A pairing distortion is indicated and should be sought experimentally.

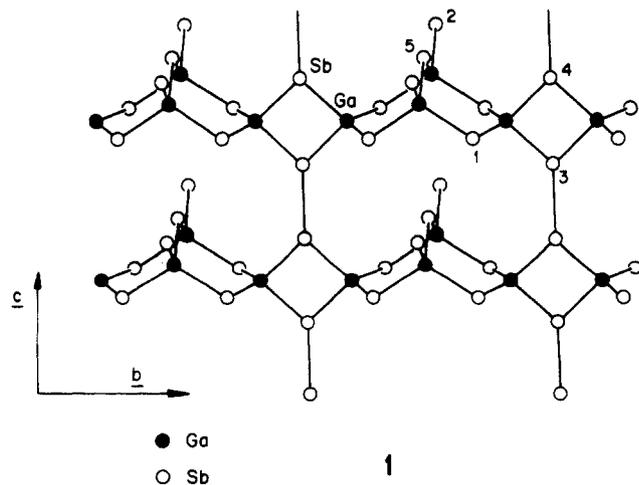
Zintl's concept^{1,2} plays an important role in the description that solid-state chemists give to bonding in a large range of crystal structures. In this simple scheme, electropositive elements act merely as electron donors, donating electrons to their conjoined, more electronegative, bonding partners. The latter elements then form bonds to satisfy the octet rule.

Although tremendously useful in understanding a great variety of crystal structures, Zintl's concept sometimes fails. These limiting cases are inherently interesting in that they inform us of the transition from one bonding type to another. One such compound is $Ba_7Ga_4Sb_9$, which has been synthesized recently by Schäfer, Cordier, and co-workers.³ This compound has a metallic luster, but its electrical properties have not been reported so far. If one tries to assign charges to the Ga and Sb atoms in this compound following Zintl's rule, it is impossible, as we will see, to find a conventional covalent network bearing a charge of -14, necessary to cancel the +14 charges due to the seven Ba^{2+} cations present in the structure.

Our aim is to study the electronic structure of $Ba_7Ga_4Sb_9$, in order to understand the apparently complicated bonding relationships shown by this compound.

Crystal Structure

$Ba_7Ga_4Sb_9$ forms orthorhombic ($Pmnm$) crystals, each unit cell containing two formula units. The Ga_4Sb_9 substructure stands out as a layer (1). Each gallium atom is surrounded approxi-



mately tetrahedrally by four antimony atoms. Four of these

tetrahedra share corners to form an eight-membered Ga_4Sb_4 ring. The shape of this ring allows two of the trans-disposed gallium atoms to share another corner, forming a bridged bicyclic structure. The resulting ring system is analogous to bicyclo[3.3.1]nonane. The Sb atoms that form part of the bicyclic ring system are two-coordinated, while the two remaining Sb atoms bonded to the bridging gallium atoms remain one-coordinated.

It is possible to link the bicyclic ring systems described above into a chain by using the four terminal Sb atoms bonded to the Ga atoms not involved in the bridge. The structure built in this way is a chain formed by alternation of four- and eight-membered Ga-Sb rings running parallel to the b direction of the crystal.

Bonding between the Sb atoms of the four-membered rings of adjacent chains leads to the two-dimensional layer of Ga and Sb atoms shown in 1. The bonding between the antimonys in question, Sb(3) and Sb(4), will emerge as a crucial concern of this paper.

The complete three-dimensional structure of $Ba_7Ga_4Sb_9$ is formed by stacking such Ga-Sb layers. The barium cations occupy octahedral and trigonal-prismatic holes between layers.

To apply the Zintl concept to this compound, we begin with completing octets, thus assigning to each four-coordinate gallium atom a -1 charge, each one-coordinate antimony atom [Sb(2)] a -2 charge, and two-coordinate Sb atoms [Sb(1) and Sb(5)] a -1 charge.

The problem is what to do with Sb(3) and Sb(4). If we look at the Sb(3)-Sb(4) bonds that link the Ga-Sb chains together to form the layer, we find that their separation is 3.296 Å. In the structure of elemental antimony,⁴ Sb-Sb bond distances inside layers are 2.91 Å, while the distance between layers is 3.36 Å. We see that the Sb(3)-Sb(4) bond distance found in $Ba_7Ga_4Sb_9$ is relatively long, if it is to be considered as an Sb-Sb bond, but is 0.06 Å shorter than the Sb-Sb interlayer distance in the elemental structure.

So, we have two possibilities in describing the bonds in $Ba_7Ga_4Sb_9$: either that there is no Sb-Sb bond between chains and consequently each two-coordinate antimony atom of the four-membered ring may be assigned a formal charge of -1, or that there is actually an Sb(3)-Sb(4) bond formed between chains, assigning in this case a formal charge of 0 to each of two three-coordinate antimony atoms.

By considering all the gallium and antimony atoms in the layer, we obtain for the Ga_4Sb_9 unit a formal charge of -13 if we assume a full Sb(3)-Sb(4) bond and of -15 if we neglect it. Neither way is in concordance with the +14 charge assigned to the seven Ba^{2+} cations.

(1) Schäfer, H.; Eisenmann, B.; Müller, W. *Angew. Chem.* 1973, 85, 742.

(2) Schäfer, H. *J. Solid State Chem.* 1985, 57, 97.

(3) Cordier, G.; Schäfer, H.; Stetler, M. Z. *Anorg. Allg. Chem.* 1986, 534, 137.

(4) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 1984.

[†] Universitat de Barcelona.

[‡] Cornell University.

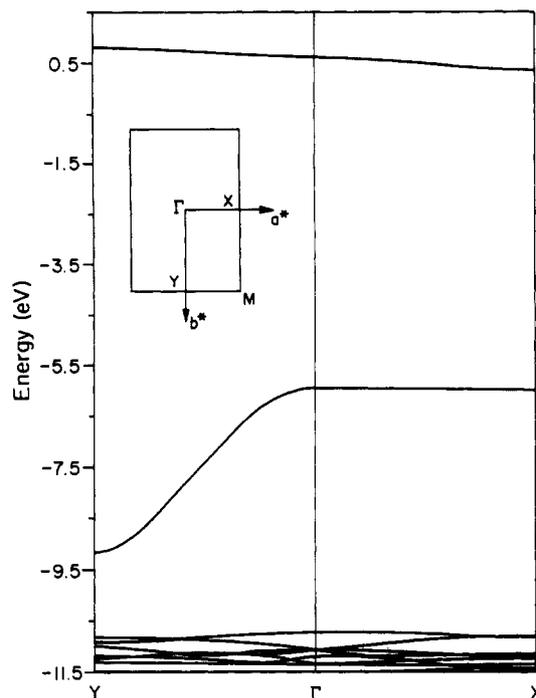


Figure 1. Band structure for a two-dimensional $\text{Ga}_4\text{Sb}_9^{14-}$ layer. The Brillouin zone is shown in the insert.

We study this anomaly here. The detailed band structure of the compound has been calculated, in order to learn where the extra electron [if we think of a full $\text{Sb}(3)\text{-Sb}(4)$ bond] or the electron deficiency (if we neglect the bond) resides in the structure. From the discussion presented above, one might suppose that the critical electrons are to be found in a band that contains the orbitals of the antimony atoms pertaining to the four-membered rings. The problem is to determine which of these orbitals are involved in this band.

Band Structure

Given the layer structure and the apparent absence of strong interactions between the cations and the anionic layers, we have studied a single two-dimensional $\text{Ga}_4\text{Sb}_9^{14-}$ slab. Using the complete three-dimensional structure of the compound, with two $\text{Ga}_4\text{Sb}_9^{14-}$ layers per unit cell, would not provide new information, since interlayer distances are too large to allow important interaction between adjacent layers (shortest $\text{Sb}\cdots\text{Sb}$ distance 4.38 Å). All the band structure calculations were carried out by using the tight-binding approach based upon the extended Hückel method.^{5,6} The parameters used in these calculations are listed in the Appendix.

Figure 1 shows the band structure obtained for the two-dimensional $\text{Ga}_4\text{Sb}_9^{14-}$ slab. Γ and Y refer to the usual special k -points of the Brillouin zone for a rectangular two-dimensional net, shown as an insert in Figure 1. In this case the $\Gamma\text{-X}$ direction corresponds to the direction of the chains formed by alternating four- and eight-membered rings, while the $\Gamma\text{-Y}$ direction is parallel to the chain linking $\text{Sb}(3)\text{-Sb}(4)$ bonds.

Prominent in Figure 1 is a single band in the region extending from -9.5 to -5.5 eV. This band is only half-filled for the $\text{Ga}_4\text{Sb}_9^{14-}$ electron count and has very different dispersion relations in the two different directions represented in Figure 1. Along $\Gamma\text{-X}$ the band is very narrow. This holds also for all directions parallel to this (e.g. for the $M\text{-Y}$ direction, not represented in Figure 1). Along the other direction studied, however, the band has a great dispersion. These results indicate that this compound should have substantial anisotropy in its electrical properties, behaving as a pseudo-one-dimensional conductor, the conduction direction being parallel to the $\text{Sb}\text{-Sb}$ bonds.

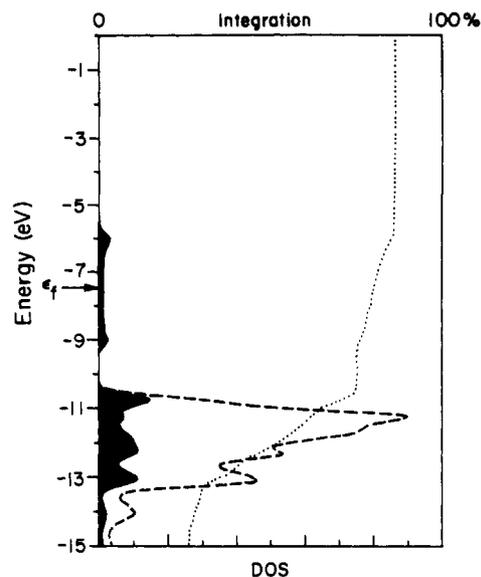


Figure 2. Density of states for a $\text{Ga}_4\text{Sb}_9^{14-}$ layer. The shaded area corresponds to the contribution of the antimony atoms in the four-membered rings to the total DOS (dashed line). The dotted line is an integration of the shaded area.

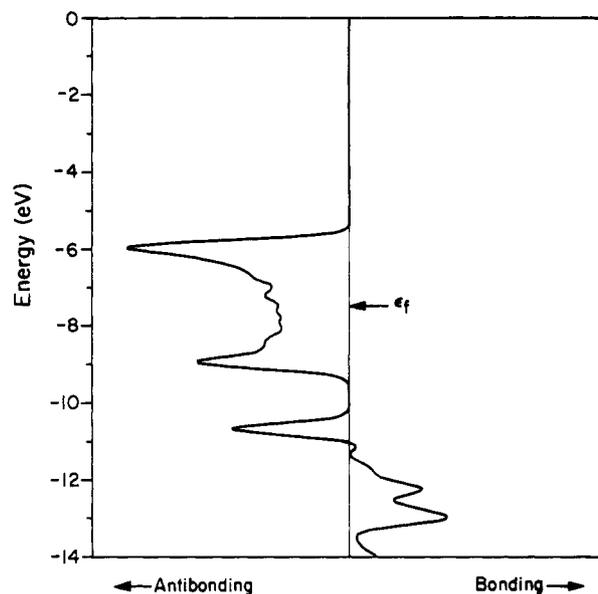
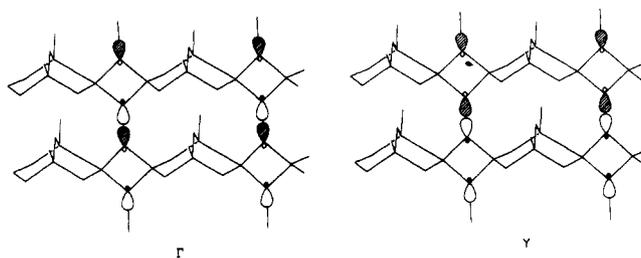


Figure 3. COOP curve for the $\text{Sb}\text{-Sb}$ bonds.

From the density of states (DOS) and the contributions to the DOS by Sb atoms forming the $\text{Sb}(3)\text{-Sb}(4)$ bonds (Figure 2), it is easy to see that the band cut by the Fermi level is mainly formed by orbitals pertaining to these Sb atoms. There is no important contribution from any other atom of the structure to this band.

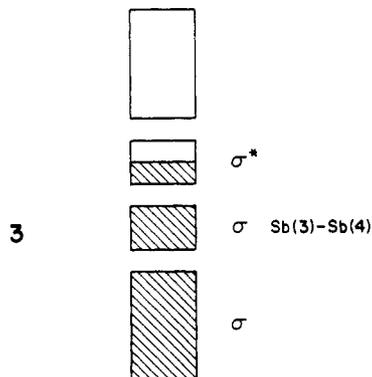
The COOP curve in Figure 3 shows that the band in question is $\text{Sb}\text{-Sb}$ antibonding. The wave functions associated to this band for Γ and Y are shown schematically in 2. We see that it is in fact the $\text{Sb}\text{-Sb}$ σ^* orbital that forms the band.



(5) Hoffmann, R. *J. Chem. Phys.* 1963, 39, 1397.

(6) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 6093.

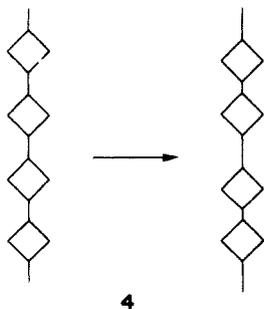
All this is consistent with the structural information and the ambiguities of electron counting. First, the Sb(3)–Sb(4) bond is long (3.296 Å). So one would not expect the σ and σ^* combinations formed from it to be very much split apart in energy (compared to other bonds, here Ga–Sb). Second, if we assume such an Sb(3)–Sb(4) bond, then we have an extra electron per two Sb's over a fully σ -bonded configuration. This electron would enter the Sb(3)–Sb(4) σ^* band, half-filling it. The qualitative argument is shown in 3 and is supported by the calculated band structure.



Given the localized nature of this band, one wonders what the origin of the large dispersion of the band along the $\Gamma \rightarrow Y$ direction is. Is it through-space or through-bond interaction^{7,8} that makes this band wide? The slope of the band is such that the zone center, Γ , is at high energy. The band “runs down”.⁹ This is consistent with a direct, through-space, interaction of the dominant p contributions of the Sb(3)–Sb(4) σ^* bonds. However, there are some pointers in the literature for through-bond interactions also being significant in four-membered rings.¹⁰ We probed the nature of the interaction by a band calculation in which direct interactions between nonbonded Sb(3) and Sb(4) atoms, across the four-membered ring, were deleted. The dispersion of the band in question was much reduced but did not disappear. It thus seems that through-space (cross-ring) and through-bond [using the Ga–Sb bonds bridging the Sb(3) and Sb(4) sites] interactions both count, but the former dominates.

Pairing Distortion

It is well-known that a one-dimensional system with a half-filled band is stabilized by a pairing or Peierls distortion.^{11,12} Because the band in question is localized in the Sb(3)–Sb(4) bonds, the effective distortion is likely to involve a geometry change affecting these bonds. The simplest candidate is 4, in which Sb(3)–Sb(4)



bonds along y are alternately made short and long. We consider

- (7) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.
 (8) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
 (9) Hoffmann, R. *Solids and Surfaces*; VCH Publishers: New York, 1988.
 (10) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.
 (11) Whangbo, M.-H. *Acc. Chem. Res.* **1983**, *16*, 95.
 (12) Peierls, R. E. *Quantum Theory of Solids*; Oxford University Press: London, 1955.

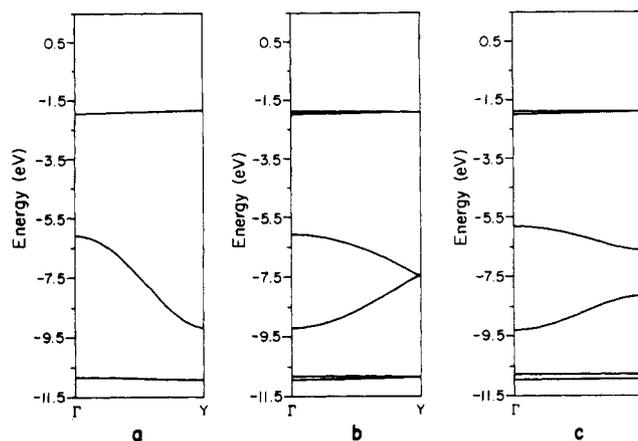
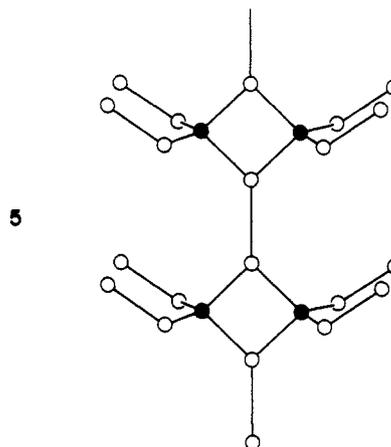


Figure 4. (a) Band structure for the one-dimensional model (5). (b) The same, considering a doubled unit cell. (c) Band structure for the one-dimensional model after a pairing distortion in which the Sb–Sb bond distance is modified by ± 0.1 Å.

in this section a one-dimensional model for the $\text{Ga}_4\text{Sb}_9^{14-}$ structure viewed along the Sb–Sb bond direction. This model, shown in 5,



bered ring by hydrogen atoms, forming in this way a one-dimensional $\text{Ga}_2\text{Sb}_6\text{H}_4^{7-}$ chain. The band structure obtained for this model compound (Figure 4, left) essentially reproduces the behavior of the original two-dimensional $\text{Ga}_4\text{Sb}_9^{14-}$ layer in the Γ – Y direction. To prepare for a pairing distortion, we double the unit cell. This just folds back the bands as shown in the middle panel in Figure 4. After the pairing distortion defined in 4 [the Sb(3)–Sb(4) distance is changed by ± 0.1 Å], the band structure of the right side of Figure 4 is obtained. It is clear from this that the pairing distortion opens a gap at the Fermi level, stabilizing the structure. The density of states curves in Figure 5 show how the contribution of the lower band (the filled one) appears after the pairing distortion is centered mainly on the Sb–Sb pair with the longer bond. Increasing the distance produces a stabilization, derived from the loss of antibonding character in that band. The upper band is mostly localized in the shorter Sb–Sb bond. Another way to visualize the same effect is by looking at the COOP curves for the two different Sb–Sb bonds, shown in Figure 6.

A plot of the total energy of the structure vs the extent of the distortion (Figure 7) shows that the minimum-energy structure is obtained with 2.6 and 4.0 Å Sb–Sb distances for the short and long Sb–Sb pairs, respectively. Although the extended Hückel method is not expected to be very accurate for bond distances, Figure 7 clearly predicts the distorted structure to be more stable.

Discussion

The Fermi surface of a partially filled metallic band is defined as the boundary surface of wave vectors that separate the wave vectors leading to filled band levels from those leading to unfilled

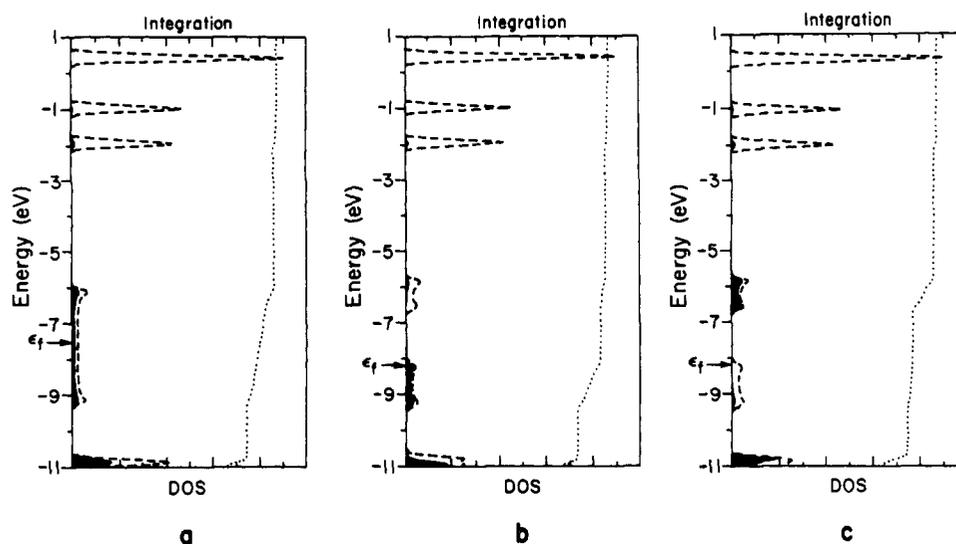


Figure 5. (a) Density of states for the undistorted one-dimensional model. The shaded area corresponds to the projection of the antimony atoms forming one of the two Sb-Sb pairs. (b) Density of states after the pairing distortion. The shaded area represents the contribution of the antimony atoms forming the long Sb-Sb pair. (c) Density of states after the pairing distortion. The shaded area represents the contribution of the antimony atoms forming the short Sb-Sb pair.

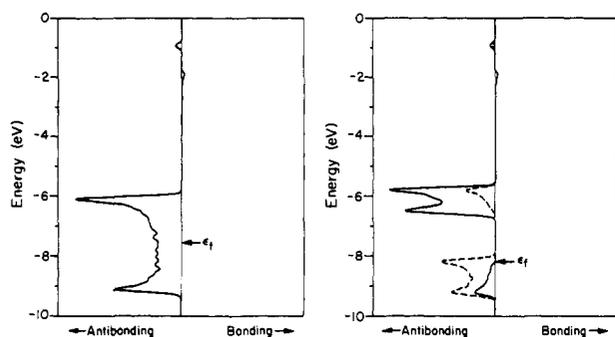


Figure 6. (a) Left: COOP curve for the Sb-Sb pairs in the undistorted one-dimensional model. (b) Right: COOP curves for the Sb-Sb pairs in the distorted structure. The solid line represents the overlap population for the short Sb-Sb pair; the dashed line represents the COOP curve for the long Sb-Sb pair.

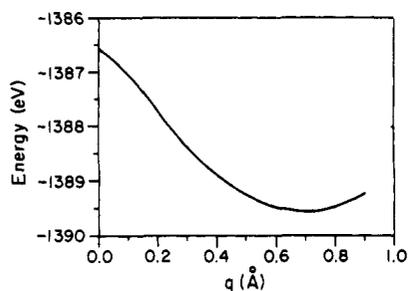
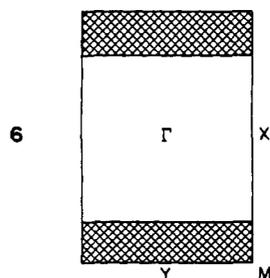


Figure 7. Energy variation with extent of pairing. The distortion is defined taking $d' = d \pm q$ for the antimony pairs. The bonding distance in the undistorted structure is $d = 3.29 \text{ \AA}$.

band levels. The Fermi surface obtained for Ga₄Sb₉¹⁴, shown in 6, consists of two separated pieces. Thus, Ba₇Ga₄Sb₉ is expected



to be a pseudo-one-dimensional metal with better electrical conductivity along the crystallographic c direction (ΓY in k -space).

Table I. Parameters Used in Extended Hückel Calculations

	orbitals	H_{ii} , eV	ζ
Ga ¹⁴	4s	-14.58	1.77
	4p	-6.75	1.55
Sb ¹⁵	5s	-18.8	2.323
	5p	-11.7	1.999
H ⁵	1s	-13.6	1.3

According to the calculations, the metallic state should suffer a pairing distortion, leading to opening of an energy gap at the Fermi level. The distorted structure would be stabilized relative to the original one. The experimental structure, determined by X-ray diffraction, seems not to be distorted at room temperature. However, high-temperature factors for the relevant atoms were found for this and a related Ba₇Al₄Sb₉ structure.¹³ These are being reinvestigated.¹³ It would be very interesting to study the electrical and magnetic properties of these materials and their dependence on temperature. These measurements could probe the predicted existence of a metal-to-insulator transition associated with the pairing distortion described above. Another possibility is a charge density wave (CDW) that would open up an energy gap at the Fermi level by a mechanism based on electron-electron repulsion minimization.

Acknowledgment. P.A. is gratefully indebted to the Ministerio de Educación y Ciencia for a grant of the Plan Nacional de Nuevos Materiales. The research at Barcelona was supported by the CICYT through Grant PB86-0272. Collaboration between Cornell and Barcelona groups was made possible by a Cooperative Research Grant in Basic Science, CCB86/4004/88, from the U.S.-Spanish Joint Committee for Scientific and Technological cooperation.

Appendix

The extended Hückel method^{5,6} was used in all calculations. Table I lists the parameters used for Ga, Sb, and H in these calculations.

The Sb-H bonding distance for the one-dimensional model is taken from SbH₃, and its value is 1.7 \AA .⁴

(13) Cordier, G. Private communication.

(14) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759.

(15) Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3872.