

## Electronic and Bonding Properties of BaGaGeH: Hydrogen-induced Metal-insulator Transition from the AlB<sub>2</sub>-type BaGaGe Precursor

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Received July 27, 2011, Accepted November 15, 2011

The hydrogenation of AlB<sub>2</sub>-type BaGaGe exhibits a metal to insulator (MI) transition, inducing a puckering distortion of the original hexagonal [GaGe] layers. We investigate the electronic structure changes associated with the hydrogen-induced MI transition, using extended Hückel tight-binding band calculations. The results indicate that hydrogen incorporation in the precursor BaGaGe is characterized by an antibonding interaction of  $\pi$  on GaGe with hydrogen 1s and the second-order mixing of the singly occupied antibonding  $\pi^*$  orbital into it, through Ga-H bond formation. As a result, the fully occupied bonding  $\pi$  band in BaGaGe changes to a weakly dispersive band with Ge *pz* (lone pair) character in the hydride, which becomes located just below the Fermi level. The Ga-Ge bonds within a layered polyanion are slightly weakened by hydrogen incorporation. A rationale for this is given.

**Key Words** : Metal hydride, Zintl phase, Electronic structure

### Introduction

The unexpected discovery of superconductivity at 39 K in MgB<sub>2</sub><sup>1</sup> has attracted much attention to the layer structured compounds with the AlB<sub>2</sub>-type structure because of their potential in the search for non-cuprate superconductors. Ternary silicides Sr(Ga<sub>0.37</sub>Si<sub>0.63</sub>)<sub>2</sub>, Ca(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> and Sr(Al<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> adopt the AlB<sub>2</sub> structure, in which Si and (Ga, Al) atoms are arranged in the hexagonal honeycomb layers, and alkaline-earth metals are intercalated between them, and become superconductors with transition temperatures  $T_c$  of 3.5, 7.8 and 5.1 K, respectively.<sup>2-5</sup> Similar isotopic ternary compounds M(Ga<sub>0.5</sub>Si<sub>0.5</sub>)<sub>2</sub> (M=Ca, Sr, Ba) have also been reported to become superconductors at  $T_c = 4.1-5.2$  K.<sup>4,6</sup>

CaAlSi and SrAlSi have shown some interesting features that the majority of their charge carriers are electrons in contrast to the holes in MgB<sub>2</sub>.<sup>5</sup> The key ingredients to the superconducting properties of MgB<sub>2</sub> are related to the existence of  $\sigma$ p-band holes in negatively charged boron planes.<sup>7</sup> For MAISi the partially occupied  $\pi^*$  band plays a decisive role as the origin of the superconducting properties.<sup>8-10</sup> Furthermore, some compositions MAISi react with hydrogen and form the monohydride MAISiH.<sup>11</sup> Hydrogen may be incorporated in the polymeric anion where it acts as a covalently bonded terminating ligand to a p-block metal atom.

The H incorporation imposes only small changes to the structure of the precursor polyanionic layer. However, electronic structures can be dramatically influenced by the inclusion of H.<sup>11</sup> This offers interesting opportunities for fundamental studies into main group element-H interactions and their consequences to properties of materials. The reversible nature of hydrogen-induced metal-insulator transition provides a compelling basis for technological development in switchable mirror systems.<sup>12</sup> Electronic considerations of

the structure-properties relationship in the case of metal hydrides may lead to a better understanding of the hydrogenation processes, because they are believed to play a dominant role in various niche applications such as hydrogen storage.

In the present work we describe the electronic properties of BaGaGeH, which is a further example of a polyanionic hydride, with an emphasis on structure and bonding principles as well as implications for its physical properties. The precursor phase BaGaGe is not electron precise with respect to the AlB<sub>2</sub>-like structure and displays a metallic behavior, yielding one excess electron per formula unit. The formation of BaGaGeH from BaGaGe precursor causes a metal-insulator transition and turns the precursor into an electron precise Zintl phase with a band gap at the Fermi level. Of particular interest will be the mechanism of the band gap opening in the electronic structure of BaGaGe upon hydrogen uptake. The [Ga-H] entities in BaGaGeH are part of a two-dimensional polyanionic layer where Ga is bonded to Ge atoms. The bonding properties of polyanionic hydrides are virtually unexplored; however, their knowledge would provide valuable insight into the fundamental question of how hydrogen interacts with metals and semimetals. It is thus of importance to study the modification of the crystallographic and electronic properties generated by the formation of the hydride to get a better understanding of the evolution of the physical properties in solid-state materials. The purpose of this paper is to better elucidate the bonding of these two compounds and especially the role of hydrogen.

We use the extended Hückel tight-binding (EHTB) method<sup>13,14</sup> to determine the influence of hydrogenation on the electronic structure responsible for the metallic behavior of the precursor. The parameters used for all atoms are listed in Table 1. Although the EH method is quite approximate, the analysis of orbital interactions by perturbation theory

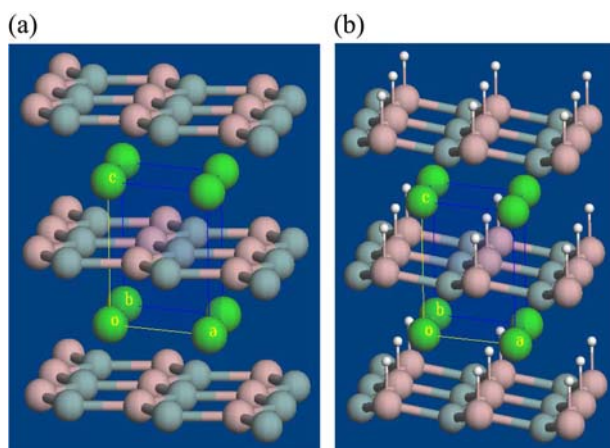
**Table 1.** Extended Hückel parameters

Atom	Orbital	H <sub>ii</sub> (eV)	ζ
Ba	6s	-4.76	1.263
	6p	-2.64	1.263
Ga	4s	-14.58	1.77
	4p	-6.75	1.55
Ge	4s	-16.0	2.16
	4p	-9.0	1.85
H	1s	-13.6	1.3

seems to be reasonably reliable. The CAESAR package<sup>15</sup> was used to calculate the density of states (DOS) and the crystal orbital overlap population (COOP) spectra of pure and hydrogenated BaGaGe structures. While the DOS provides information about the band structure and the distribution of various orbitals in energy, the COOP curves describe the nature of the bonds between constituent atoms, with positive and negative values indicating bonding and antibonding states, respectively.

### Crystal Structure

**BaGaGe.** For the precursor BaGaGe the ordered AlB<sub>2</sub> structure was considered. This compound crystallizes with the SrPtSb structure (space group *P-6m2*), an ordered ternary derivative of the hexagonal AlB<sub>2</sub>-like structure.<sup>16</sup> The crystal structure of the BaGaGe phase can be viewed as planar [GaGe] layers that are stacked above one another along the direction of the *c*-axis, with layers of Ba cations between them (Figure 1(a)). The gallium and germanium atoms occupy the boron positions by an alternate arrangement and form two-dimensionally infinite flat layers of [Ga<sub>3</sub>Ge<sub>3</sub>] hexagons with intralayer Ga-Ge distances of 2.50 Å, only slightly larger than the sum of the Pauling single-bond radii<sup>17</sup> of 2.49 Å for gallium and germanium, indicating strong covalent Ga-Ge bonding within the hexagonal layer. The interlayer Ga-Ga distances of 5.09 Å in BaGaGe may be considered as negligibly weak interactions. Table 2



**Figure 1.** Crystal structures of (a) BaGaGe and (b) BaGaGeH. Green, pink, gray, and white circles denote Ba, Ga, Ge, and H atoms, respectively.

**Table 2.** Crystallographic data for BaGaGe and BaGaGeH<sup>a</sup>

	BaGaGe	BaGaGeH
Space group	<i>P-6m2</i>	<i>P3m1</i>
<i>a</i>	4.3352	4.3344
<i>c</i>	5.0928	5.1895
Ga-Ge	2.50	2.56
Ga-H		1.71
Ba-(Ga, Ge)	3.57	

<sup>a</sup>Lattice parameters and distances in Å are taken from ref 16.

lists the structural parameters and important bond distances from experiment.

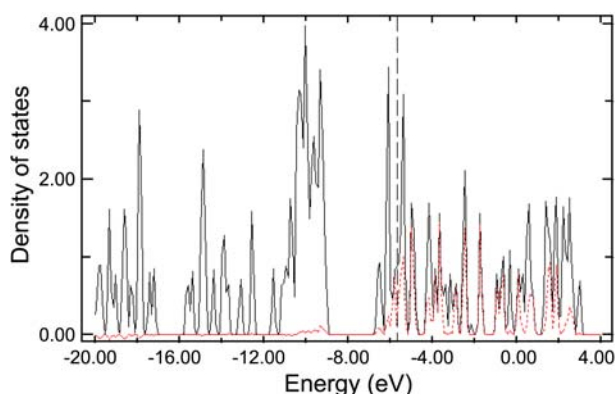
**BaGaGeH.** The structural consequences of the hydrogenation of precursor phase BaGaGe to BaGaGeH are depicted in Figure 1(b). Hydrogenation modifies the lattice parameters, i.e., 4.3352 → 4.3344 Å (-0.02%) for *a* and 5.0928 → 5.1895 Å (1.90%) for *c*. The unit cell shows a small, but anisotropic expansion along with the hydrogen incorporation. This leads to a slight puckering of the two-dimensional polyanion [GaGeH]<sup>2-</sup> layers in which Ga and Ge atoms are arranged in the puckered hexagon layers with three nearest unlike neighbors, separated by the Ba atoms. The arrangement of Ba atoms is not affected at all and the space group symmetry of the hydride is reduced to *P3m1*.<sup>16</sup>

The formation of the hydride BaGaGeH from the precursor BaGaGe proceeds with minor structural changes in the hexagon layer. According to the Zintl concept,<sup>20</sup> Ga and Ge are formally reduced by the electropositive Ba and the coordination of each Ga atom is completed by a hydrogen atom in a distorted tetrahedral fashion. This arrangement fits the electron count of Ga<sup>-</sup>, which is isoelectronic to a group 14 element. The introduction of hydrogen changes the coordination number of Ga from 3 in BaGaGe to 4 in BaGaGeH. Here hydrogen is added to a three-bonded, formally *sp*<sup>2</sup> hybridized Ga<sup>-</sup> entity, which changes into a *sp*<sup>3</sup> hybridized one upon bonding to H. BaGaGeH is apparently charge-balanced when assigning the oxidation states -1 for Ga and Ge and zero for singly bonded H.

For BaGaGe → BaGaGeH the Ga-Ge interatomic distance increases appreciably from 2.50 to 2.56 Å upon puckering of the hexagon layers and the layers move farther apart when terminated by hydrogen. The Ga-H distance is around 1.71 Å from the experimental crystal structure, which is rather large compared to the sum of the corresponding Pauling's covalent radii (1.62 Å). It compares well with the Ga-H distance in the isoelectronic dihydrides SrGa<sub>2</sub>H<sub>2</sub> and BaGa<sub>2</sub>H<sub>2</sub> (1.69 Å).<sup>18</sup> Selected interatomic distances in BaGaGeH are given in Table 2.

### Results and Discussion

To investigate the electronic structure and chemical bonding features that contribute to the structural trends in BaGaGe and BaGaGeH, EHTB band calculations were carried out on observed crystal structures. In spite of the small structural changes, the transition from 9-electron pre-

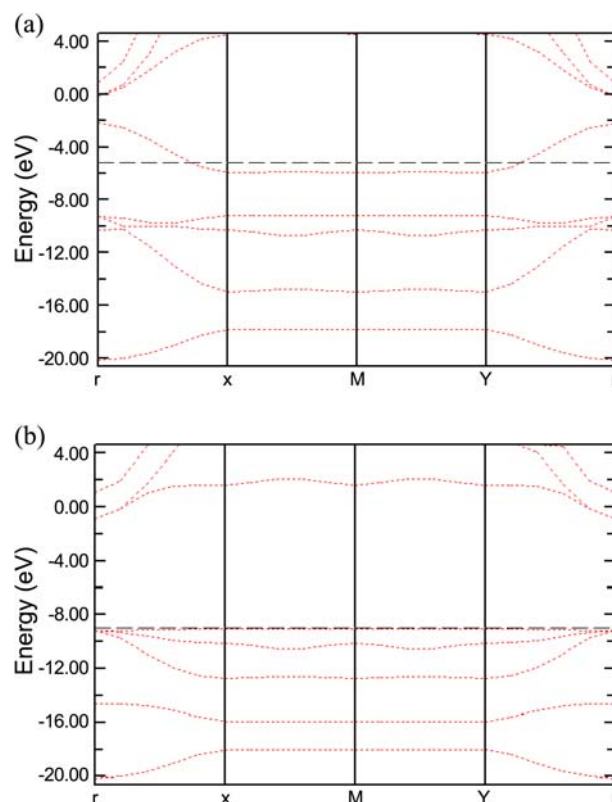


**Figure 2.** Total DOS of BaGaGe (solid line) and the contribution of Ba orbitals to that DOS (dotted line). What is not on Ba is on Ga/Ge. The vertical dashed line indicates the Fermi level.

cursor BaGaGe to electron precise 10-electron hydride BaGaGeH gives rise to drastic changes in the electronic structure. We address this issue in terms of the energy bands, density of states, and crystal orbital overlap populations.

The chemical bonding in BaGaGe is characterized by intralayer bonds between Ga and Ge within the flat  $[\text{Ga}_3\text{Ge}_3]$  hexagons. The Ga-Ga interlayer distances are 5.09 Å. The  $[\text{GaGe}]$  layers are completely separated from each other and the orbital interactions between the layers along the  $c$ -axis take place slightly *via* the intervening large Ba cations. States contributed by these cations are of higher energy and thus nearly empty (see Figure 2). As expected from the Zintl-Klemm concept, Ba loses its valence electrons almost entirely, and the orbital contributions of Ba are largely restricted to the virtual DOS region; below the Fermi level, the Ba mixing is quite small. Consequently, the Ba atom would contribute two electrons to the  $[\text{GaGe}]$  sublattice which should be formally written as  $[\text{GaGe}]^{2-}$ . In this paper, we may neglect the interlayer interactions and simplify our calculations by employing the two-dimensional (2D)  $[\text{GaGe}]^{2-}$  polyanionic layers.

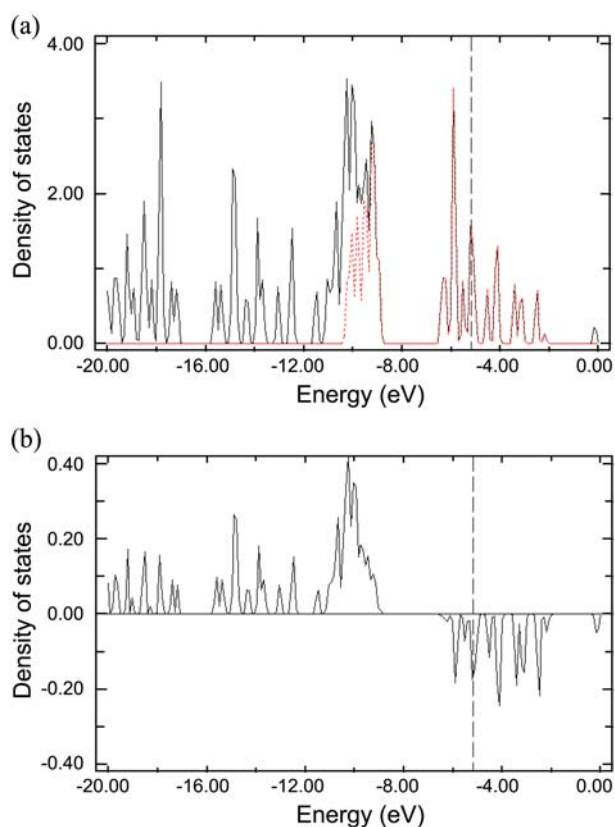
We start our discussion with BaGaGe. The band structure of this material is shown in Figure 3(a). The  $s$ ,  $px$ , and  $py$  orbitals of Ga and Ge form three bonding  $\sigma$  bands which are occupied and three vacant antibonding  $\sigma^*$  bands, since there is only one Ga-Ge layer per cell. These hybridized  $sp^2$  orbitals participate in strong covalent  $\sigma$  states, forming 2D honeycomb network bonds. It is also notable that there is more Ge character than Ga in each of these three bonding bands, implying a polar  $\sigma$  bond. This is not surprising since Ge is more electronegative than Ga. The lowest-lying  $\sigma$  band is essentially composed of Ga  $s$  and Ge  $s$  orbitals. The next two  $\sigma$  bands have mixed character of mainly Ga and Ge  $p$  orbitals. The remaining two occupied bands are of  $pz$  character of both Ga and Ge ( $pz$  is the  $p$  orbital directed along the  $c$  axis, while  $px$  and  $py$  are directed in the Ga-Ge plane). The Ga and Ge  $pz$  orbitals give rise to two  $\sigma$  bands, one bonding and one antibonding. Due to the different energies of Ga and Ge  $p$  orbitals, the bonding  $\pi$  band has a larger Ge  $pz$  contribution, while the antibonding  $\pi^*$  band has



**Figure 3.** Band structures of (a) the  $[\text{GaGe}]^{2-}$  layer of BaGaGe and (b) the  $[(\text{GaH})\text{Ge}]^{2-}$  layer of BaGaGeH. Horizontal dashed lines indicate the Fermi level.

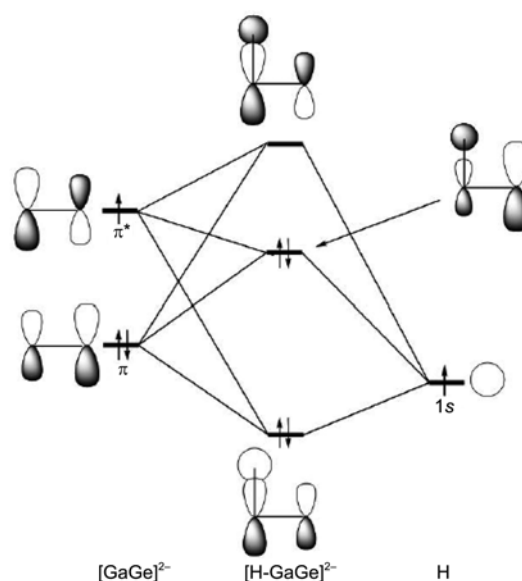
a larger Ga  $pz$  contribution. As a consequence of the weaker  $\pi$  interactions, the  $\pi$  bands are weakly dispersive. The bonding  $\sigma$  and  $\pi$  bands are located below the Fermi level ( $E_F$ ) and not energetically separated. For main group  $\text{AlB}_2$  systems an electron precise situation with all bonding bands filled is attained in eight-electron systems. For the nine-electron BaGaGe system, assuming a formal charge transfer from the electropositive component Ba to the atoms forming the hexagon layer, the Ga  $pz$ -based  $\pi^*$  band becomes partially occupied. The Ga-Ge bond has some of a partial double bond character. Figures 4(a) and 4(b) illustrate DOS and COOP curves for BaGaGe, respectively. The occupied region below the Fermi level displays significant contributions from Ga and Ge atoms: (a) bonding  $\sigma$  bands between  $-20$  and  $-10$  eV, (b) bonding  $\pi$  band between  $-10$  and  $-9$  eV, and (c) antibonding  $\pi^*$  band around  $E_F$ . A deep minimum in the DOS curve at about 1 eV below  $E_F$  corresponds to a valence band filling of 8 electrons per formula unit, which matches the top of the Ga-Ge bonding states shown in the COOP curve.

Next we consider the band structure of the hydride BaGaGeH, which is shown in Figure 3(b). We find the H  $1s$  derived band and in particular, an indirect band gap at the Fermi level ( $E_g = 7.86$  eV). The large gap obtained is not very realistic because our calculations used default valence energy values for the atoms. Although the EH method is quite approximate, the analysis of orbital interactions by perturbation theory is reasonably reliable. This type of cal-



**Figure 4.** (a) Total DOS (solid line) and Ga *pz* and Ge *pz* contributions to it (dotted line), and (b) Ga-Ge COOP in a [GaGe]<sup>2-</sup> layer of the BaGaGe structure.

ulation has proved to be very useful in understanding of the electronic structure and bonding of many low-dimensional solids. We note the highest one of mixed Ga *pz*, Ge *pz*, and H *s* orbital character of the five valence bands. The lowest-lying band in BaGaGeH stems from Ga *s* and Ge *s* orbitals and displays the same topology and range of energy as in BaGaGe. The next band in energy has a large H *s* contribution and a sizable Ga *pz* and Ge *s* contribution and accounts for the great majority of the H *s* character seen in the valence bands. It is identified as Ga-H bonding band. It is the orbital interaction between a single hydrogen 1s (*1<sub>SH</sub>*) and the  $\pi$  and  $\pi^*$  on GaGe that is responsible for a good part of the Ga-H bonding. The overlap between these orbitals is non-zero. This leads to a three-orbital interaction problem between the orbitals of  $\sigma$  symmetry with respect to rotation about the Ga-H internuclear axis. The linear combinations of the orbitals *s*,  $\pi$  and  $\pi^*$  lead to three  $\sigma$ -type molecular orbitals (MOs). The orbital interaction diagram for the electronic structure change induced by hydrogenation of BaGaGe is indicated schematically in Figure 5. In this picture there is a substantial covalent bond between Ga and H. Concerning the energetic ordering of the three  $\sigma$  MOs, the lowest lying orbital is composed mainly of the hydrogen 1s. The substantial bonding contributions from  $\pi$  and  $\pi^*$  on GaGe are involved in the MO. This MO generates the second band in Figure 3(b). In turn, the highest occupied molecular orbital (HOMO) has an energy intermediate

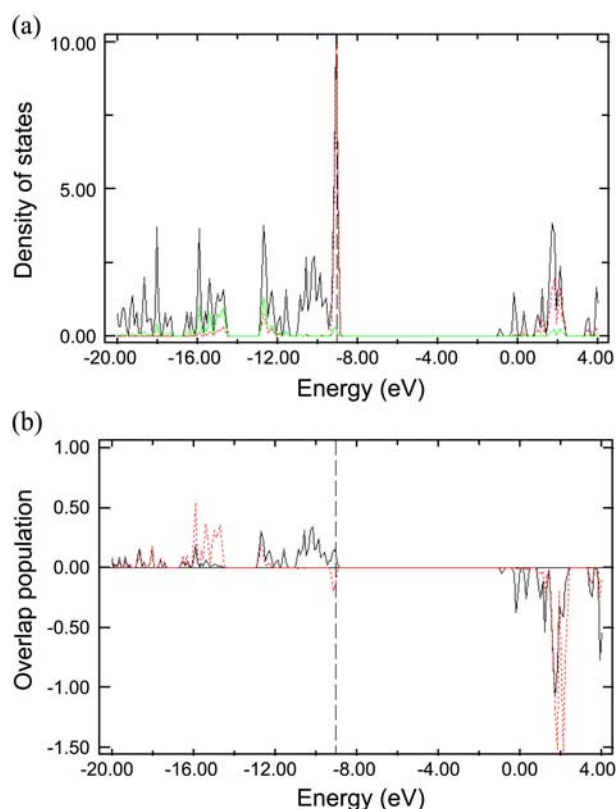


**Figure 5.** Simplified orbital interaction diagram for [H-GaGe]<sup>2-</sup>.

between the two  $\pi$  and  $\pi^*$ . For HOMO, the second-order mixing<sup>19</sup> of  $\pi^*$  occurs as a result of the primary antibonding interaction of  $\pi$  with *1<sub>SH</sub>*. *1<sub>SH</sub>* mixes into  $\pi$  in an antibonding way since *1<sub>SH</sub>* lies lower in energy than  $\pi$ . Within the fragment GaGe,  $\pi^*$  mixes into  $\pi$  with the second-order contribution when the mixing into lower lying  $\pi$  orbital occurs *via* an even lower lying *1<sub>SH</sub>* orbital. Since this mixing is important, the  $\pi$  orbital, interacting in an antibonding way with H 1s, becomes in part Ga-H antibonding and Ga-Ge bonding in the vicinity of the Fermi level. Note that the second-order orbital mixing leads to a HOMO energy stabilization by diminishing a negative overlap between H and Ga and thus creating more localized lone pair electron states of Ge. This suggests that Ge obtains one electron from Ba so that there are two electrons in its *pz* orbital, which then is the origin of HOMO. The fully occupied bonding  $\pi$  band has a very small dispersion of Ge *pz* lone pair character in the hydride. Compared to the  $\pi$  band in BaGaGe, the Ge *pz* lone-pair band in BaGaGeH is raised in energy and becomes located at the top of the valence bands. The relevant DOS and COOP curves are seen in Figure 6. We conclude that hydrogen incorporation in BaGaGe is characterized by the second-order mixing of the partially occupied antibonding  $\pi^*$  orbital into an antibonding interaction of  $\pi$  with *1<sub>SH</sub>*, through Ga-H bond formation, and thus HOMO has been pushed down in energy and is now less antibonding between H and Ga than before. The two remaining occupied bands correspond to the two upper bonding  $\sigma$  bands in BaGaGe, based on the *px* and *py* orbitals of Ga and Ge. There is practically some H *s* character to the bottom of these bands.

Analysis of the chemical bonding in BaGaGeH implies that structure can be readily rationalized from a different point of view, using the classic Zintl formalism.<sup>20</sup> It provides an overly simplistic, yet not unrealistic electron count. Each Ga atom within the corrugated layers formally receives one extra electron to carry a charge of -1. Four-bonded (4b) Ga





**Figure 6.** (a) Total DOS (black line) and H *s* (green line), Ga *pz* and Ge *pz* (red line) contributions to it, and (b) COOP for the Ga-Ge (solid line) and Ga-H (dotted line) bonds in a [(GaH)Ge]<sup>2-</sup> layer of the BaGaGeH structure.

atoms are in tetrahedral coordination and nicely follow the octet rule. Three-bonded (3b) Ge atoms also need one extra electron to complete its valence shell, the formal oxidation state for Ge in that structure would be “-1”, which leaves two electrons per formula unit in the lone pair orbital. The puckered hexagonal nets would be formulated as [(4b)Ga<sup>-</sup>H](3b)Ge<sup>-</sup> = [(GaH)Ge]<sup>2-</sup>, which is optimized for 10 valence electrons. The divalent Ba cations separate these puckered layers and counterbalance the charges. Thus, the hydride possesses an electron precise polyanion [(GaH)Ge]<sup>2-</sup> and one should expect BaGaGeH to be a closed-shell compound. The bonding between Ga and Ge atoms is then considered being of two-center two-electron  $\sigma$  type, indicating that the Ga-Ge bond is slightly weakened by hydrogen incorporation. The integrated overlap populations up to the Fermi level are Ga-Ge 0.71, Ga-H 0.52.

In contrast, Ga-Ge bonding in the graphitic layers of the AlB<sub>2</sub> precursor has some  $\pi$  contribution from the fully occupied bonding and partially occupied antibonding  $\pi$  bands. This accounts for considerably shorter Ga-Ge distances than in BaGaGeH (2.50 vs. 2.56 Å). In BaGaGe the corresponding overlap population is Ga-Ge 0.75. However, the bonding and antibonding characters of the  $\pi$  and  $\pi^*$  bands are weakened by the polarity of the Ga-Ge bond. Formally the nine-electron BaGaGe phase represents an electron excess system with respect to eight electron main-group AlB<sub>2</sub> compounds where only the  $\pi$  bonding band is

occupied. With the incorporation of hydrogen, the polyanionic hydride represents an electron-precise insulator. The hydrogen induced metal-nonmetal transition is confirmed by the electrical resistivity measurements for BaGaGe/BaGaGeH.<sup>16</sup>

## Conclusion

We analyzed the crystal structure and electronic structure changes associated with the hydrogen-induced metal-insulator transition in the BaGaGe precursor. This transition is caused by the small structural change between the AlB<sub>2</sub>-type precursor and the hydride where hydrogen is exclusively attached to Ga. The band-gap opening in the hydride originates from the second-order mixing of the partially occupied antibonding  $\pi^*$  orbital in the metallic precursor [GaGe]<sup>2-</sup> into an antibonding interaction of the occupied  $\pi$  orbital with 1s<sub>H</sub>. This mixing contributes significantly to the covalent Ga-H bonding by diminishing a negative overlap between H and Ga and thus creating more localized lone pair electron states of Ge. The present work shows that the crystal orbitals with substantial Ga-Ge  $\pi^*$  orbital contribution drop just below the Fermi level through the secondary orbital mixing to provide the rationale for its semiconducting character. According to the Zintl-Klemm electron counting scheme, the pyramidal environment surrounding Ga and Ge atoms in puckered [Ga<sub>3</sub>Ge<sub>3</sub>] hexagons is well suited for [GaH]<sup>-</sup> and Ge<sup>-</sup>. This leads to an electron precise formulation (Ba)<sup>2+</sup>[GaH]<sup>-</sup>Ge<sup>-</sup>, which accounts for the nonmetallic properties of this material.

**Acknowledgments.** This work was supported by the Kyungshung University Research Grant in 2011.

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