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Stabilization and highly metallic properties of heavy group-V hydrides at high pressures

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Compressed hydrides of the heavy group-15 elements Bi and Sb are investigated using *ab initio* methods. While the hydrides of Bi and Sb are known to be quite unstable at one atmosphere, our calculations predict that they can be stabilized at high pressures. Thus, at the composition of XH_3 ($X =$ Bi or Sb), possible Bi hydrides are $BiH_2(Pnma)$ + H beyond 105 GPa and $BiH_3(I4_1/amd)$ beyond 250 GPa; for Sb hydrides, SbH_2 + H hardly appears, and $SbH_3(Pnma)$ is stabilized beyond 150 GPa. All of these hydrides are metallic with very dispersive electronic structures, this being in accordance with the predictions of the Goldhammer-Herzfeld criterion. Superconducting transition temperatures have also been estimated from the extended McMillan equation, and they turn out to be 39 K for BiH_2 at 125 GPa, 65 K for BiH_3 at 270 GPa, and 68 K for SbH_3 at 170 GPa.

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I. INTRODUCTION

Pressure-induced metallization of hydrides is of recent interest mainly because of its physical relevance to superconductivity with possibly high transition temperatures (T_c) [1–3]. The issue has been extensively investigated both by experiment and theory [4–15]. According to the Goldhammer-Herzfeld (GH) criterion [16], the metallization of molecular solids takes place at the density satisfying $4\pi\alpha/(3v_M) = 1$, where α is the average static linear dipole polarizability of a molecule and v_M is the volume per molecule. This rule claims that substances consisting of molecules with high polarizability tend to metallize at low densities. Since the derivation of the GH criterion relies on the Clausius-Mossotti equation, which in turn assumes high symmetry structures and invariant dipole polarizabilities, the criterion should be basically taken to be a rough measure for discussing the possible onset of metallization. However, though less suitable for quantitative estimates, the GH rule actually works as a useful guide when comparing the tendency toward metallization among various molecular solids [17].

High polarizability can sometimes mean that the molecular bonds are not "chemically" tight and, accordingly, that the molecule may be less stable. In other words, the GH criterion might imply that hydrides of lower stability at standard pressures can metallize at correspondingly lower densities. If this is indeed so, then it may be worth considering the hydrides of some notably heavy elements. At standard pressures, hydrides of heavy elements from group 13 to 17 are known to be very unstable and to easily decompose into their constituents. Actually, there was a theoretical study of PbH_4 [10] which predicted that PbH_4 can be a good metal beyond 132 GPa. Experimental data of the polarizability of a PbH_4 molecule is so far not available, but we have made a rough estimate of it on the basis of the Clausius-Mossotti equation and using density functional perturbation theory. The resulting polarizability of a PbH_4 molecule is 7.94 Å^3 (or 53.6 a_0^3 with a_0 being the Bohr radius). It is worth noting that this polarizability is much larger than that of a CH_4 molecule (2.59 Å^3 or 17.5 a_0^3) [18], and CH_4 is predicted to be nonmetallic at least up to 520 GPa according to *ab initio* calculations and when no disproportionation is assumed [19]. Another case similar to PbH_4 is SnH_4, which is likewise unstable at normal conditions and whose polarizability reaches 7.04 Å^3 (47.5 a_0^3). This substance was also shown to metallize at relatively low pressures around 100 GPa from theory [11,12].

In this context, and with the possibility of metallic hydrides now appearing at relatively low pressures, we here investigate the hydrides of Bi and Sb using *ab initio* methods. Typical hydrides of Bi and Sb at ambient pressure are BiH_3 and SbH_3, respectively, and these have the pyramidal structure commonly observed for the other group-15 hydrides (NH_3, PH_3, and AsH_3). Both BiH_3 and SbH_3 exhibit considerable instability at low pressures. Regarding BiH_3 especially, decomposition takes place even below its boiling point (290 K), and only quite recently has experiment succeeded in synthesizing substantial amounts of BiH_3 [20]. According to our preliminary calculations, the largest component of the polarizability tensor of a BiH_3 molecule is about 8.23 Å^3 (55.5 a_0^3) and that of a SbH_3 molecule is 7.50 Å^3 (50.6 a_0^3). These values are, again, much larger than that of a NH_3 molecule, which is 2.19 Å^3 (14.8 a_0^3) [18]. Thus, while NH_3 is predicted to be nonmetallic at least below 500 GPa from *ab initio* calculations [21], the Bi and Sb hydrides are expected to metallize at pressures which lie well within the reach of a diamond anvil cell.

II. COMPUTATIONAL DETAILS

Calculations of enthalpy are carried out by using density functional theory within the generalized gradient approximation [22]. We have used QUANTUM ESPRESSO [23] which utilizes plane-wave basis sets and ultrasoft pseudopotentials [24]. The cutoff radii of the pseudopotentials are 1.27 Å for Bi (with $5d\,6s\,6p$ as valence), 1.11 Å for Sb (with $4d\,5s\,5p$ as valence), and 0.42 Å for H, and the cutoff energy is set at 816 eV. The k-point sets are generated such that the k-point number is nearly equal to $(40\ \text{Å})^3/v_{\text{cell}}$, where v_{cell} is the volume of the unit cell. A Fermi-distribution smearing is used with a temperature of $k_BT = 0.1$ eV. For relativistic effects, we basically take account only of scalar-relativistic terms. In fact, we have observed that spin-orbit effects have almost no influence on the comparison of enthalpy.

Computations of the electron-phonon interaction are performed by using the density functional perturbation theory.

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The numbers of k points and q points (phonon wave vectors) are, respectively, taken to be about $(50\ \text{Å})^3/v_{\text{cell}}$ and $(13\ \text{Å})^3/v_{\text{cell}}$. Here, we chose to use pseudopotentials which treat Bi $5d$ and Sb $4d$ electrons as core electrons. The cutoff radii are accordingly increased to 1.48 Å for Bi (with $6s\,6p$ as valence), and 1.38 Å for Sb (with $5s\,5p$ as valence). When one deals with elemental Bi and Sb at high pressures, where the overlap of the increased cutoff radii is appreciable, these choices actually lead to somewhat lower accuracy. However, so long as the hydride systems are treated, in a manner where the heavy atoms do not come too close to each other (owing to the presence of hydrogen), the use of these pseudopotentials is appropriate. Indeed, relative enthalpies among the hydrides are found to remain accurate at least to below 300 GPa. We have also checked that dealing with the d electrons as core does not significantly influence the band structures; see the Supplemental Material [25], where all-electron results with the full-potential linearized augmented plane-wave method (WIEN2K code [26]) are additionally presented for comparison.

III. STRUCTURES AND ENTHALPIES

The search for stable structures of $X\text{H}_3$ ($X = \text{Bi}$ or Sb) has been carried out by using *ab initio* molecular dynamics. We first prepare several initial structures which contain at most four $X\text{H}_3$ units per primitive cell, basically mimicking the structures proposed for NH_3 [21]. Then, constant-pressure molecular dynamics calculations are performed with the temperature gradually being decreased. The resulting candidate structures were found to contain H_2 pairs for both BiH_3 and SbH_3 at about 150 GPa. Appearance of such H_2 pairs very often suggests that the system considered is unstable to disproportionation or decomposition. Therefore, we have examined in greater detail whether the decomposition into $X\text{H}_2 + \text{H}$ or $X\text{H} + 2\text{H}$ can indeed take place and have found that there is in fact a distinct possibility of the occurrence of $X\text{H}_2 + \text{H}$. The enthalpies of the structures thereby selected are presented in Fig. 1, where the results are given for the composition of $X\text{H}_3$. At low pressures, the completely decomposed system ($X + 3\text{H}$) is stable in accordance with experimental findings at room pressure. In the clamped nuclei approximation (top panels of Fig. 1), the $X + 3\text{H}$ system first transforms into $X\text{H}_2 + \text{H}$ and then into $X\text{H}_3$ for both $X = \text{Bi}$ and Sb as the pressure is steadily increased. One prominent difference between Bi and Sb exists in the pressure range where $X\text{H}_2 + \text{H}$ is stable. Indeed, for static lattice, $\text{SbH}_2 + \text{H}$ marginally appears just around 190 GPa, while $\text{BiH}_2 + \text{H}$ is stabilized in a large pressure region.

We proceeded to investigate the effects of zero-point energy (ZPE) of the nuclei within the harmonic approximation (bottom panels of Fig. 1). Here, the ZPE is calculated from the frozen-phonon method by using the Phonopy algorithm [32], where supercells containing at least 64 atoms are used. A major change attributed to the consideration of ZPE is that the transition pressures from $X + 3\text{H}$ to $X\text{H}_2 + \text{H}$ and from $X\text{H}_2 + \text{H}$ to $X\text{H}_3$ are both lowered. Consequently, the stable phases can now be summarized as follows: $\text{Bi} + 3\text{H} \rightarrow [105\,\text{GPa}] \rightarrow \text{BiH}_2(Pnma) + \text{H} \rightarrow [250\,\text{GPa}] \rightarrow \text{BiH}_3(I4_1/amd)$; $\text{Sb} + 3\text{H} \rightarrow [150\,\text{GPa}] \rightarrow \text{SbH}_3(Pnma)$. In Fig. 1(d), the $P2_1/m$ and the $Cmcm$ structures are presented as though they were candidate high-pressure phases of SbH_3 beyond 250 GPa. The two structures, however, have phonon modes whose frequencies are slightly imaginary below about 400 GPa; for the sake of expedience, their ZPE's are estimated just by ignoring the contribution from the imaginary-frequency phonons. Also, we found several other structures (with imaginary-frequency phonons) whose enthalpies are competitive with those of the $P2_1/m$ and the $Cmcm$. Here, we have mentioned only these two structures simply because their primitive cells are among the smallest (eight atoms). Thus, beyond 250 GPa, the search of SbH_3 phases entails some complexities, and so far the structures have not been clearly determined.

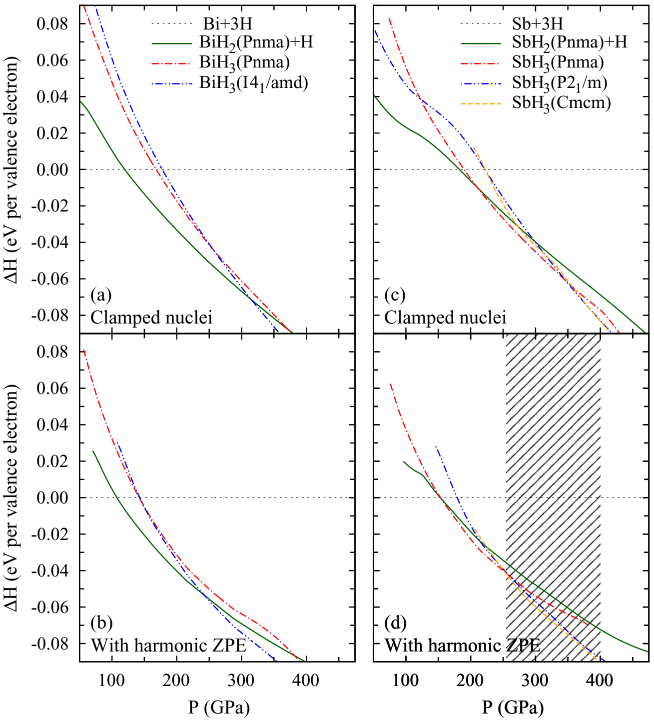
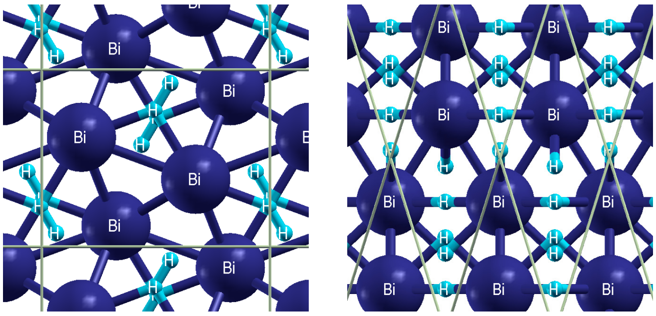
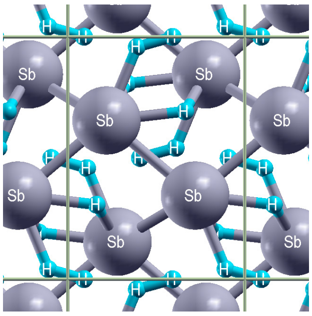


FIG. 1. (Color online) Relative enthalpy of Bi hydrides (left) and Sb hydrides (right) for the composition of $X\text{H}_3$ ($X = \text{Bi}$ or Sb), where the ionic system is treated in the clamped nuclei approximation (top) and within the harmonic approximation (bottom). The enthalpy is given per valence electron, the numbers of valence electrons of Bi and Sb being chosen to be 5. The enthalpy of Bi is calculated for the bcc structure [27], that of Sb for the bcc structure [28], and that of H for the $C2/c$ [29], the $Cmca$-12 [29], the $Cmca$ [30], and the Cs-IV ($I4_1/amd$) [31] structures. The hatched area in (d) indicates that low-enthalpy structures without imaginary-frequency phonons have not been found there in this study.

The proposed structures are illustrated in Fig. 2. Paired H_2 units are still apparent for the $Pnma$ BiH_2 and the $Pnma$ SbH_3 phases, but although the appearance of isolated H_2 pairs is sometimes a sign of disproportionation or decomposition as mentioned above, this inference is not valid in these cases. The H_2 pairs observed here are far from isolation and are interacting strongly with Bi or Sb atoms. Indeed, the bond lengths of the H_2 pairs are actually larger than that of a standard hydrogen molecule; it is 0.807 Å in the BiH_2 at 125 GPa, and 0.879 Å in the SbH_3 at 170 GPa. As the pressure is increased, BiH_3 takes



BiH_2 (Pnma, 125 GPa) BiH_3 ($I4_1$/amd, 270 GPa)



SbH_3 (Pnma, 170 GPa)

FIG. 2. (Color online) (Top left) The $Pnma$ structure for BiH_2 at $r_s = 1.70$ (see Ref. [33] for the definition of r_s): $a = 5.905$ Å, $b = 3.159$ Å, $c = 4.577$ Å; Bi at 4c sites (0.174, 0.25, 0.631); H at 4c sites (0.493, 0.25, 0.478) and (0.063, 0.25, 0.173). (Top right) The $I4_1/amd$ structure for BiH_3 at $r_s = 1.55$: $a = 2.851$ Å, $c = 9.098$ Å; Bi at 4a sites (0.0, 0.75, 0.125); H at 4b sites (0.0, 0.25, 0.375) and 8e sites (0.0, 0.25, 0.273). (Bottom) The $Pnma$ structure for SbH_3 at $r_s = 1.58$: $a = 4.19$ Å, $b = 3.249$ Å, $c = 5.755$ Å; Sb at 4c sites (0.219, 0.25, 0.095); H at 4c sites (0.163, 0.25, 0.443), (0.092, 0.25, 0.750), and (0.391, 0.25, 0.792).

on the more symmetric $I4_1/amd$ structure, and then the H_2 units eventually disappear.

IV. ELECTRONIC STRUCTURES AND SUPERCONDUCTIVITY

The densities of states (DOS) are presented in Fig. 3. Each DOS curve suggests that the system is close to a nearly free-electron metal. As a result, the DOS at the Fermi energy is rather large in every phase. The dispersive electronic properties are indeed remarkable when compared with other metallic hydrides of relatively light elements proposed so far [4,8,13–15,17]. The highly metallic characters fit well with the aforementioned guide from the GH relation that these substances are inclined to metallize at low densities. To check this point for BiH_2 (in addition to BiH_3 and SbH_3), we estimated the polarizability of BiH_2. Since a BiH_2 unit has an odd number of electrons, we looked into Bi_2H_4 instead of BiH_2. Then, the largest component of the polarizability tensor turned out to be 24.50 $Å^3$ (165.3 a_0^3). This value is quite high, perhaps reflecting in part the fact that the Bi_2H_4 unit is somewhat large, possessing as it does six atoms. All these findings, together with those on PbH_4 [10] and SnH_4 [11,12], suggest that the heavy hydrides have a strong tendency

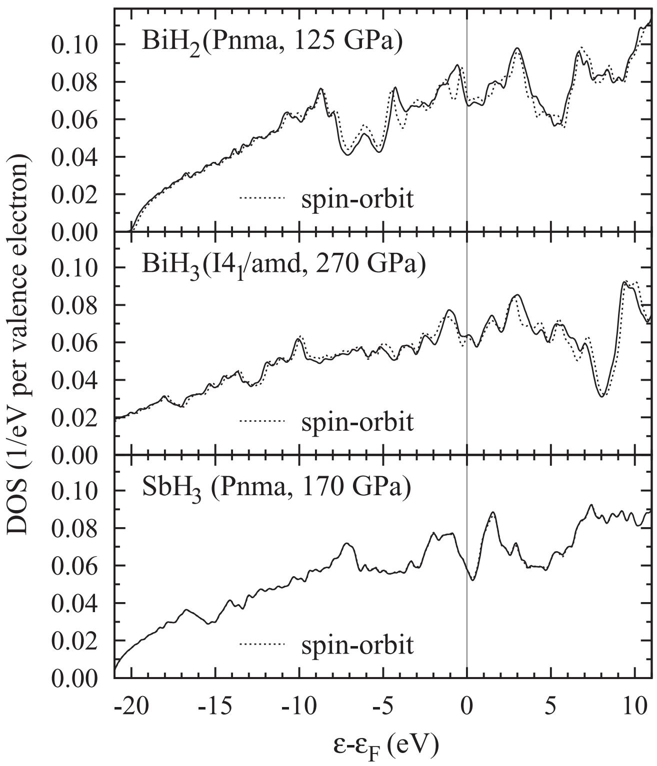


FIG. 3. The DOS per valence electron of the $Pnma$ structure for BiH_2 at $r_s = 1.70$ (top), the $I4_1/amd$ structure for BiH_3 at $r_s = 1.55$ (middle), and the $Pnma$ structure for SbH_3 at $r_s = 1.58$ (bottom). The dotted line shows the DOS with spin-orbit interactions included. [The spin-orbit effects for SbH_3 are almost invisible in the present scale.]

to become good metals. The effects of spin-orbit interaction on the electronic structures have also been examined. While spin-orbit interactions do not affect the DOS of SbH_3, they bring about little in the way of changes to those of BiH_2 and BiH_3. Yet, since their electronic structures are intrinsically dispersive, the changes do not lead to any significant decrease of the DOS at the Fermi energy.

Figure 4 shows the density of phonon modes D_{ph} and the Eliashberg function α^2F scaled by $2/\omega$. The three structures possess no imaginary phonon frequencies and are, therefore, mechanically stable. As mentioned, there exist H_2 pairs in the BiH_2 and SbH_3 structures. The phonon modes corresponding to the stretching motions of these H_2 pairs are found to be from 3000 to 3100 cm^{-1} in the BiH_2 at 125 GPa, and from 2100 to 2500 cm^{-1} in the SbH_3 at 170 GPa. Notice that these frequencies are much lower than those of the stretching modes observed in pure hydrogen (the vibron) at corresponding pressures: The frequency of the softest (Raman-active) vibron in hydrogen is about 4100 cm^{-1} at 125 GPa and 3950 cm^{-1} at 170 GPa [34,35]. This fact again indicates that the H_2 pairs formed in the BiH_2 and the SbH_3 are significantly affected by surrounding heavier (Bi or Sb) atoms. The continua of D_{ph} below about 300 cm^{-1} consist almost only of Bi or Sb components, and the other phonon modes of H components. Thus, the plots of $2\alpha^2F/\omega$ show that both H and the heavier (Bi or Sb) atoms contribute to the electron-phonon coupling. The influence of the phonon modes attributable to heavier-atomic

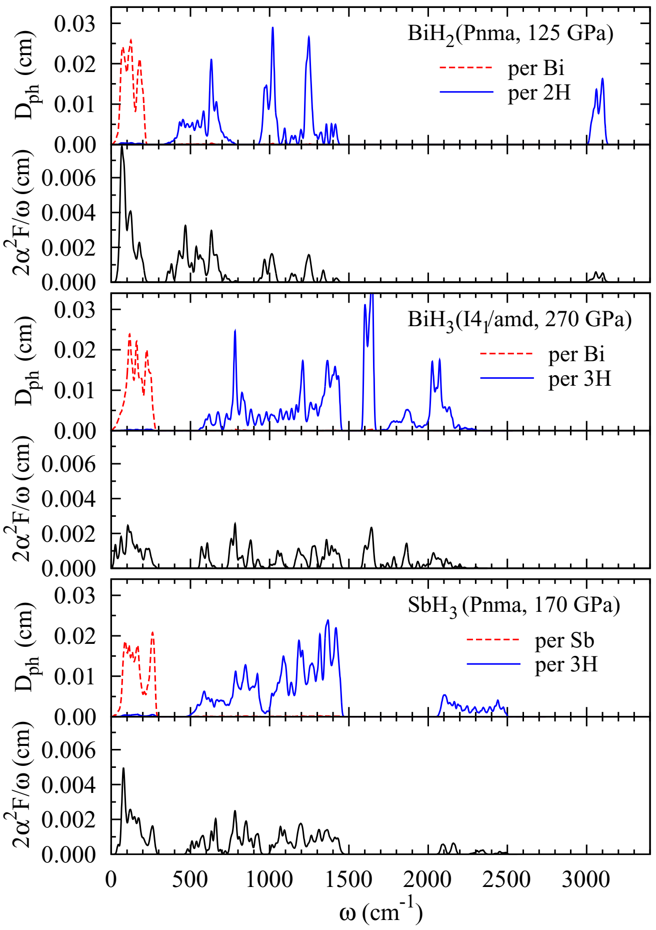


FIG. 4. (Color online) The densities of phonon modes D_{ph} and the Eliashberg function multiplied by $2/\omega$ (i.e., $2\alpha^2F/\omega$). (Top two panels) For the *Pnma* structure for BiH_2 at $r_s = 1.70$; $\lambda = 1.24$ and $\omega_{\log} = 422$ K. (Middle two panels) For the $I4_1/amd$ structure for BiH_3 at $r_s = 1.55$; $\lambda = 1.07$ and $\omega_{\log} = 905$ K. (Bottom two panels) For the *Pnma* structure for SbH_3 at $r_s = 1.58$; $\lambda = 1.25$ and $\omega_{\log} = 731$ K.

motions on the Eliashberg function is especially crucial in BiH_2, where sharp peaks of $2\alpha^2F/\omega$ can be found at very low frequencies. Although the peaks help increase the electron-phonon coupling parameter λ, they drastically decrease $\langle \log \omega \rangle$ since $2\alpha^2F/\omega$ is the weight function for calculating $\langle \log \omega \rangle$. Indeed, the average $\omega_{\log} (= \exp[\langle \log \omega \rangle])$ for the BiH_2 is 422 K, which is somewhat low in comparison with those of the BiH_3 (905 K) and the SbH_3 (731 K).

T_c as a function of the Coulomb parameter μ^* is shown in Fig. 5, where the T_c is calculated from the McMillan formula [36] but along with the Allen-Dynes corrections [37]. For $\mu^* = 0.13$ [3] the estimated T_c's of the BiH_2 (125 GPa), BiH_3 (270 GPa), and SbH_3 (170 GPa) are 39, 65, and 68 K, respectively. As expected from the behavior of the Eliashberg functions in Fig. 4, the T_c of the BiH_2 is a little lower than those of the other two. Nevertheless, even the lowest T_c is considered to be rather high for superconductivity driven by electron-phonon coupling, with the required pressure being far below 150 GPa. One of the important prerequisites for accurate prediction of T_c within the framework used here is that the typical bandwidths of electronic structures are much larger than the phonon energy scale [38]. Note that this condition is well satisfied for the three phases as found in their nearly free-electron characters (Fig. 3); this is irrespective of the fact that their phonon energy scales are about ten times as large as those of typical phonon-mediated superconductors.

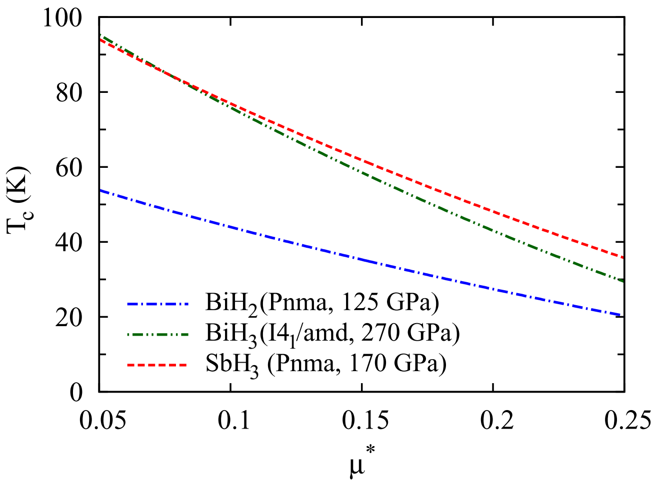


FIG. 5. (Color online) Superconducting transition temperatures T_c of the *Pnma* structure for BiH_2 at $r_s = 1.70$, the $I4_1/amd$ structure for BiH_3 at $r_s = 1.55$, and the *Pnma* structure for SbH_3 at $r_s = 1.58$ as a function of μ^*. The T_c is calculated from the McMillan equation (with the Allen-Dynes corrections, see text).

V. CONCLUSIONS

In summary, using *ab initio* calculations, we have investigated the behavior of Bi and Sb hydrides at high pressures. While Bi and Sb hydrides are quite unstable at ordinary pressures, our calculations have shown that $BiH_2(Pnma) + H$, $BiH_3(I4_1/amd)$, and $SbH_3(Pnma)$ are stabilized above 105, 250, and 150 GPa, respectively, at the composition of XH_3 ($X =$ Bi or Sb). All the hydrides are good metals, and quite dispersive electronic structures are observed with a high density of states at the Fermi energy. The estimated superconducting T_c's are about 40–70 K according to the McMillan's formula augmented with the Allen-Dynes correction. The highly metallic characters are consistent with the rough estimate of the tendency toward metallization based on the GH criterion. A similar discussion from the GH criterion is indeed applicable to PbH_4 [10] and SnH_4 [11,12] and might also be to other heavy hydrides; for example, the calculated polarizabilities of TlH_3, PoH_2, and TeH_2 are likewise high reaching 8.26, 8.56, and 7.09 Å^3 (55.7, 57.8, and 47.8 a_0^3), respectively.

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[1] J. J. Gilman, Phys. Rev. Lett. **26**, 546 (1971).

[2] N. W. Ashcroft, J. Phys. Condens. Matter **16**, S945 (2004).

[3] N. W. Ashcroft, Phys. Rev. Lett. **92**, 187002 (2004).

[4] I. Goncharenko, M. I. Eremets, M. Hanfland, J. S. Tse, M. Amboage, Y. Yao, and I. A. Trojan, Phys. Rev. Lett. **100**, 045504 (2008).

[5] M. I. Eremets, I. A. Trojan, S. A. Medvedev, J. S. Tse, and Y. Yao, Science **319**, 1506 (2008).

[6] T. A. Strobel, A. F. Goncharov, C. T. Seagle, Z. Liu, M. Somayazulu, V. V. Struzhkin, and R. J. Hemley, Phys. Rev. B **83**, 144102 (2011).

[7] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, Nature (London) **525**, 73 (2015).

[8] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).

[9] M. Martinez-Canales, A. R. Oganov, Y. Ma, Y. Yan, A. O. Lyakhov, and A. Bergara, Phys. Rev. Lett. **102**, 087005 (2009).

[10] P. Zaleski-Ejgierd, R. Hoffmann, and N. W. Ashcroft, Phys. Rev. Lett. **107**, 037002 (2011).

[11] G. Gao, A. R. Oganov, P. Li, Z. Li, H. Wang, T. Cui, Y. Ma, A. Bergara, A. O. Lyakhov, T. Iitaka, and G. Zou, Proc. Natl. Acad. Sci. USA **107**, 1317 (2010).

[12] J. S. Tse, Y. Yao, and K. Tanaka, Phys. Rev. Lett. **98**, 117004 (2007).

[13] G. Gao, H. Wang, A. Bergara, Y. Li, G. Liu, and Y. Ma, Phys. Rev. B **84**, 064118 (2011).

[14] K. Abe and N. W. Ashcroft, Phys. Rev. B **88**, 174110 (2013).

[15] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, Sci. Rep. **4**, 6968 (2014).

[16] K. F. Herzfeld, Phys. Rev. **29**, 701 (1927).

[17] K. Abe and N. W. Ashcroft, Phys. Rev. B **84**, 104118 (2011).

[18] See, for example, P. G. Jasien and G. Fitzgerald, J. Chem. Phys. **93**, 2554 (1990) and references therein.

[19] G. Gao, A. R. Oganov, Y. Ma, H. Wang, P. Li, Y. Li, T. Iitaka, and G. Zou, J. Chem. Phys. **133**, 144508 (2010).

[20] W. Jerzembeck, H. B. Bürger, L. Constantin, L. Margulès, J. Demaison, J. Breidung, and W. Thiel, Angew. Chem., Int. Ed. Engl. **41**, 2550 (2002).

[21] C. J. Pickard and R. J. Needs, Nat. Mater. **7**, 775 (2008).

[22] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11; J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[23] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009).

[24] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.92.224109 for the effects of the pseudopotential treatment on the band structures.

[26] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria 2001).

[27] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 425 (1942); P. Schaufelberger, H. Merx, and M. Contrè, High Temp.-High Press. **4**, 111 (1972); K. Aoki, S. Fujiwara, and M. Kusakabe, J. Phys. Soc. Jpn. **51**, 3826 (1982); Y. Akahama, H. Kawamura, and A. K. Singh, J. Appl. Phys. **92**, 5892 (2002).

[28] K. Aoki, S. Fujiwara, and M. Kusakabe, Solid State Commun. **45**, 161 (1983).

[29] C. J. Pickard and R. J. Needs, Nat. Phys. **3**, 473 (2007).

[30] B. Edwards, N. W. Ashcroft, and T. Lenosky, Europhys. Lett. **34**, 519 (1996).

[31] K. Nagao, H. Nagara, and S. Matsubara, Phys. Rev. B **56**, 2295 (1997).

[32] A. Togo, F. Oba, and I. Tanaka, Phys. Rev. B **78**, 134106 (2008).

[33] Here, r_s is defined by $v_e = (4\pi/3)r_s^3 a_0^3$, where v_e is the volume per valence electron, and a_0 is the Bohr radius. The number of valence electron is chosen to be 5 for Bi and Sb.

[34] P. Loubeyre, F. Occelli, and R. LeToullec, Nature (London) **416**, 613 (2002).

[35] C.-S. Zha, Z. Liu, and R. J. Hemley, Phys. Rev. Lett. **108**, 146402 (2012).

[36] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[37] P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).

[38] A. B. Migdal, Sov. Phys. JETP **7**, 996 (1958).