

Paper

Formation energies of lithium intercalations in AlSb, GaSb and InSb

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By using the *ab initio* norm-conserving pseudopotential method, the lithium intercalations in AlSb, GaSb and InSb have been studied. The formation energies, changes of volumes, electronic structures and charge densities of the lithium interactions in zinc blende-type antimonides Li_xMSb ($M = \text{Al, Ga, In}$) are presented. Our calculations show that during lithium insertion in MSb the lithium intercalation formation energy per lithium atom are all around 2.0 eV. The volume expansions of AlSb, GaSb and InSb due to lithium insertions are relatively large, which might imply that the limit of Li intercalation in antimonides should be small.

Introduction

In recent years, a considerable interest in antimonides MSb ($M = \text{Al, Ga, In}$) has been found to develop due to their potential applications as anode materials in rechargeable lithium batteries.^{1–6} The zinc blende-type structure compounds such as antimonides drive their properties from exhibiting enormous theoretical Li storage capacities and showing an increased long-term cycling stability, when compared with binary lithium–other metal alloys such as Li–Al, Li–Si and Li–Sn.^{7,8} Lithium intercalation in MSb has been studied extensively with a variety of experimental and theoretical techniques. To our best knowledge, no unified picture of the intercalation process has emerged and a number of contradictory results have been reported. For example, in the topotactic reaction of Li/InSb ($x\text{Li} + \text{InSb} \leftrightarrow \text{Li}_x\text{InSb}$), the maximum electrochemical insertion x had been reported to be 2.³ However, another experimental study found x to be 0.27.⁵ Although the crystalline structure of AlSb and GaSb are identical to that of InSb, all with a zinc blende-type structure, both Li/AlSb and Li/GaSb cells provide significantly inferior capacities to the Li/InSb cell.² In the present study, results from the density-functional theory calculations on the Li intercalations in AlSb, GaSb and InSb are presented. The formation energies of Li intercalation, volume changes of the unit cell, changes in electronic structures and charge densities due to the lithium interactions are also presented. It is believed that the theoretical calculation could help us to understand the micro-mechanism of intercalation processes, save experimental expense and reveal some useful implications.

Theoretical calculations

The calculations were performed within the framework of density functional theory. We have used the well-established *ab initio* norm-conserving pseudopotential method with the mixed-basis expansion of the wave-function. The mixed-basis method was originally developed by Louie, Ho and Cohen⁹ and is now also a well-established method in solid state physics. Its code has been constantly updated, *e.g.*, ref. 10 and 11. The exchange and correlation effects were treated using local density approximation (LDA) and a Ceperley–Alder formula for the exchange–correlation potential was employed.¹² The mixed-basis set consisted of plane waves and Bloch sums of numerical local orbitals which were constructed from atomic valence pseudo-wavefunctions. The plane wave kinetic energy

cutoff up to 15.5 Ry was adopted which is found to be sufficient to converge the total energy of the unit cell to within 0.01 eV. Brillouin-zone k -point sampling was performed using the Monkhorst–Pack¹³ grid with a $6 \times 6 \times 6$ mesh, which has been shown to converge the total energy to within 0.01 eV. For some of the configurations of lithium insertions in interstitial sites of MSb ($M = \text{Al, Ga, In}$), atomic relaxations were possible and their equilibrium atomic positions had been achieved by using the calculated Hellmann–Feynman forces as a guide in the processes of the adjustment of the atomic configurations (until the H–F force on each atom was less than 1 mRy a.u.^{–1}).

In the present calculation, the lithium intercalation in the interstitial sites of AlSb, GaSb and InSb were supposed to keep the zinc blende structure of antimonides unchanged. Then, the formation energy of lithium intercalation in MSb ($M = \text{Al, Ga, In}$) can be defined as

$$E = \frac{1}{x} [E_{\text{tot}}(\text{MSb}, \Omega_0) + xE(\text{Li}_{\text{atomic}}) - E_{\text{tot}}(\text{Li}_x\text{MSb}, V_0)]$$

which is the total energy differences between systems with and without lithium insertions. The $E_{\text{tot}}(\text{MSb}, \Omega_0)$ and $E_{\text{tot}}(\text{Li}_x\text{MSb}, V_0)$ are the total energies of MSb without lithium and that of Li_xMSb with lithium intercalations, respectively. The Ω_0 and V_0 are their corresponding equilibrium unit cell volumes. The x represents the amount of lithium intercalation, *e.g.*, for the limit of $x = 2$ the corresponding compounds are Li_2MSb ($M = \text{Al, Ga, In}$), all interstitial sites in the zinc blende-type MSb are then occupied by lithium atoms. The $E(\text{Li}_{\text{atomic}})$ in the formula denotes the atomic energy of a free lithium atom, which is -5.27 eV calculated by our pseudo-potential. In the formula, the formation energy has been divided by x , which represents the averaged formation energy per Li atom. After lithium intercalations in MSb, the volume of the systems will expand and the ratio of volume expansion of the system is defined as

$$\frac{V_0 - \Omega_0}{\Omega_0} \times 100\%$$

The structure evolution of MSb during lithium insertion or extraction might be very complicated in real systems, we here deal with only the systems when the crystal structures of MSb keep unchanged during lithium intercalation or extraction.

A cubic unit cell (4 formula units) of the zinc blende-type structure was employed in the present calculation. The

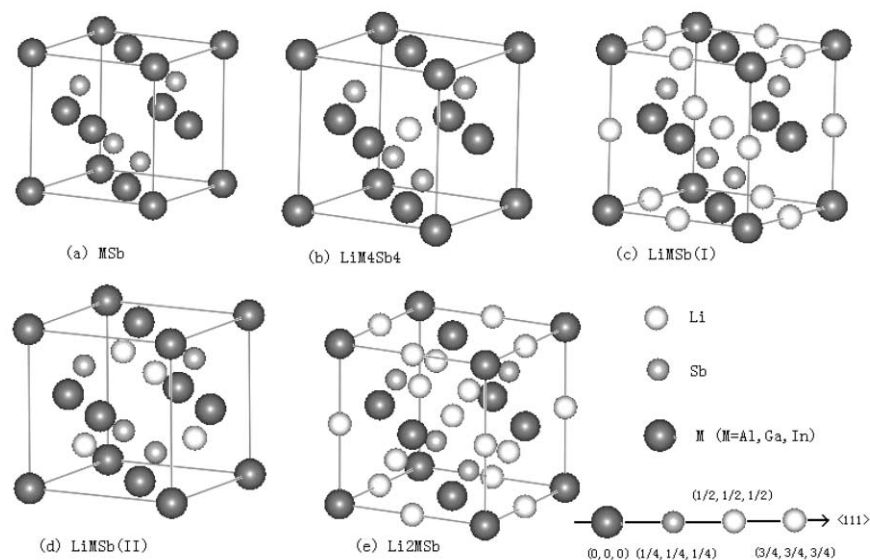


Fig. 1 Crystalline structures of (a) MSb, (b) LiM₄Sb₄, (c) LiMSb (I), (d) LiMSb (II), and (e) Li₂MSb, with M = Al, Ga, In.

calculated lattice parameters are 6.08, 5.95 and 6.30 Å, respectively, which are in good agreement with the experimental values of 6.14 Å for AlSb,¹⁴ 6.10 Å for GaSb¹⁵ and 6.48 Å for InSb,¹⁵ respectively. These lattice parameters are adopted throughout the calculations of lithium intercalations in MSb. In the zinc blende structure there are two types of interstitial sites which can both in principle accommodate lithium atoms, shown in Fig. 1(b) and Fig. 1(d). The positions of the two types of interstitial sites can be represented by $\tau_3 = (1/2, 1/2, 1/2)a$ (Fig. 1(b)) and $\tau_4 = a(3/4, 3/4, 3/4)a$ (Fig. 1(d)) together with their equivalent lattice sites, where a is the lattice constant. The interstitial sites and insertion configurations are shown in Fig. 1(a)–(e).

Results and discussion

The lithium intercalation formation energies together with the volumes of the unit cell, lattice constants and ratio of volume expansions of AlSb, GaSb and InSb due to Li insertions are listed in Table 1. It shows that the lithium intercalation formation energy per lithium atom is around 2.0 eV for all the intercalation configurations concerned. At small amount of lithium intercalation, *i.e.* $x = 1/4$, the expansion of the cell volumes are small, around 2, 6 and 5% for AlSb, GaSb and InSb, separately. At the maximum amount of lithium

intercalation, *i.e.* $x = 2$, the expansion of the cell volume increases largely, reaching 29% for AlSb, 44% for GaSb and 29% for InSb, separately. These results indicate that the limit of Li intercalations in antimonides should be small, which is consistent with the experimental study showing a $x = 0.27$ limit for the lithium intercalation in Li/InSb cell.⁵ At the amount of lithium intercalation $x = 1$, which corresponds to compounds LiMSb (M = Al, Ga, In), the computed formation energies of lithium intercalation indicated a strong preference of lithium atoms staying at τ_3 sites rather than the τ_4 sites, with a formation energy larger by 0.12 eV per Li for AlSb, 0.03 eV per Li for GaSb and 0.21 eV per Li for InSb. While Li atoms placed at τ_3 sites result in a larger increase of the cell volume than Li atoms placed at τ_4 sites. The local environments of Li atoms for the two types of interstitial sites within MSb are quite different. At the τ_3 position the Li atom coordinates with four nearest neighbor Sb atoms, while at the τ_4 site the Li atom has four nearest neighbor M (M = Al, Ga, In) atoms. When there is only one Li atom at the $\tau_3 = (0.5, 0.5, 0.5)a$ site of the unit cell (then $x = 1/4$), the nearest neighbor Sb atoms has been found to relax from $(0.25, 0.25, 0.25)a$ to $(0.248, 0.248, 0.248)a$ and $(0.247, 0.247, 0.247)a$ in AlSb and GaSb, respectively.

It is important to study the charge transfers and electronic structures of MSb (M = Al, Ga, In) after the lithium intercalations. As an example, the electronic density contour

Table 1 Lattice constants, unit cell volumes, formation energies of lithium intercalations and ratio of volume expansion of AlSb, GaSb and InSb due to Li insertions

Molecular formula (Li _x MSb)	Amount of lithium intercalation, x	Lattice constants/Å	Volume/Å ³	Ratio of volume expansion (%)	Lithium intercalation formation energy/eV Li atom ⁻¹	Crystal structure
AlSb	0	6.08	56.17	—	—	Fig. 1(a)
LiAl ₄ Sb ₄	1/4	6.13	230.48	2.58	1.90	Fig. 1(b)
LiAlSb (I)	1	6.39	65.34	16.33	2.02	Fig. 1(c)
LiAlSb (II)	1	6.35	64.04	14.00	1.90	Fig. 1(d)
Li ₂ AlSb	2	6.63	72.74	29.50	2.23	Fig. 1(e)
GaSb	0	5.95	52.75	—	—	Fig. 1(a)
LiGa ₄ Sb ₄	1/4	6.07	223.24	5.80	1.82	Fig. 1(b)
LiGaSb (I)	1	6.41	65.72	24.57	2.11	Fig. 1(c)
LiGaSb (II)	1	6.30	62.64	18.74	2.08	Fig. 1(d)
Li ₂ GaSb	2	6.73	76.25	44.54	2.35	Fig. 1(e)
InSb	0	6.30	62.60	—	—	Fig. 1(a)
LiIn ₄ Sb ₄	1/4	6.41	263.31	5.15	1.98	Fig. 1(b)
LiInSb (I)	1	6.69	74.70	19.32	2.19	Fig. 1(c)
LiInSb (II)	1	6.63	72.98	16.58	1.98	Fig. 1(d)
Li ₂ InSb	2	6.87	81.05	29.48	2.34	Fig. 1(e)

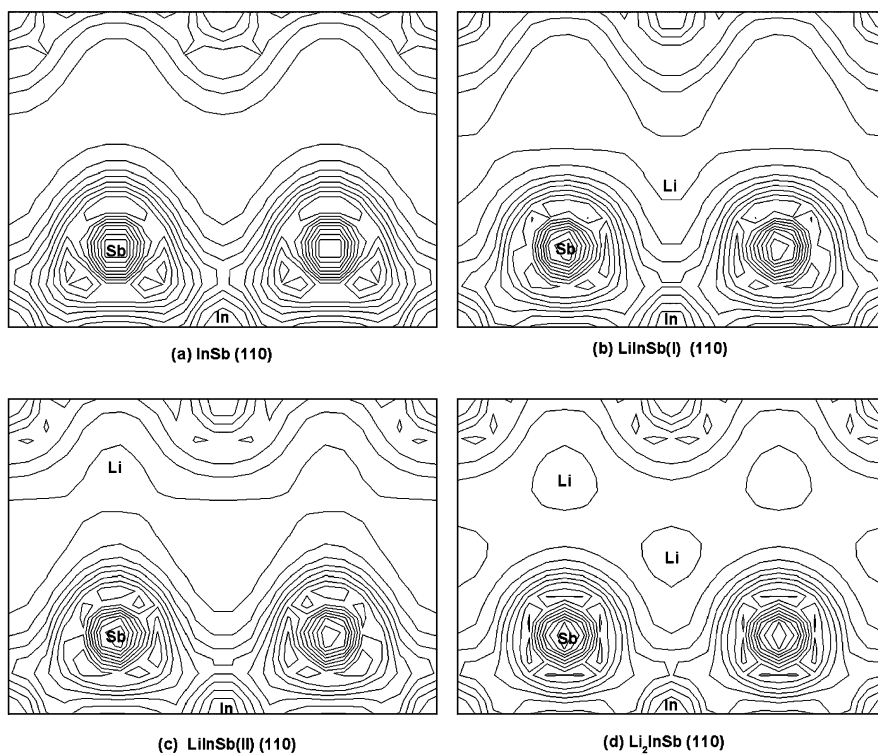


Fig. 2 Contour plots of charge density along (110) plane for (a) InSb, (b) lithium intercalated LiInSb (I), (c) lithium intercalated LiInSb (II) and (d) lithium intercalated Li₂InSb.

plots on the (110) planes of InSb and those of lithium intercalated Li_xInSb are shown in Fig. 2. The valence electrons on intercalated lithium atoms are found to donate to the host material. Fig. 2(a) is for the bulk InSb which is a covalently-bonding semiconductor and a strong covalent character for the In–Sb bonding can be seen. From Fig. 2, we can see that the electronic charge density between In and Sb atoms decreases when Li atoms are intercalated in the InSb. And from Fig. 2(b)–2(d), a more and more significantly decreases of electronic charge densities between In and Sb atoms can be seen. This indicates that lithium intercalations have screened somewhat the In–Sb interaction, and therefore the strength of In–Sb covalent bonding decreases when Li intercalation increases. At the maximum limit of amount of lithium intercalation, the corresponding compound is Li₂InSb, and the electronic charge density around the Sb and In atoms is more circular, as seen from Fig. 2(d), which might indicate that the In–Sb covalent bonding does not exist in Li₂InSb. These features are also found in the Li intercalations in AlSb and GaSb.

As a representative example, the band structure and

electronic density of states (DOS) of Li₂InSb are shown in Fig. 3. Because of the lithium intercalations in the semiconductor InSb, the Li₂InSb is now metallic. The intercalated Li atoms donated their electrons to the lattice, showing that more bands relative to InSb are filled, however, leaving the whole band structure of InSb relatively less perturbed. From their electronic density of states, we found that the electrons at the Fermi level of Li₂InSb consisted of s electrons of Li atoms together with mainly 5p electrons of Sb atom and partly 5s and 5p electrons of In. This is consistent with the picture that In–Sb covalent bonding might no longer exist in Li₂InSb as intercalated lithium atoms screened seriously the interactions between In and Sb atoms.

In summary, the *ab initio* norm-conserving pseudopotentials and a mixed-basis method have been employed to investigate the lithium intercalations in the antimonides AlSb, GaSb and InSb. The formation energies of lithium intercalations, the changes of volume, their band structures, electronic density of states and charge density contour plots for the lithium intercalated antimonides Li_xMSb (M = Al, Ga, In) are calculated and analyzed. Our results show that the lithium

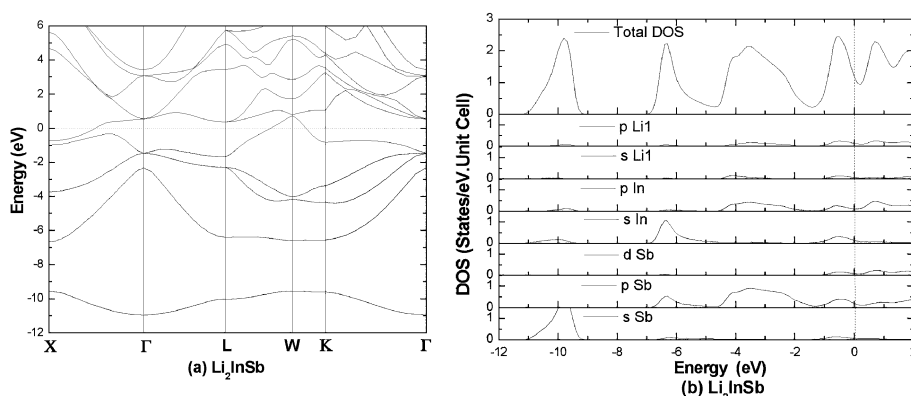


Fig. 3 Band structure and electronic density of states of Li₂InSb (Fermi level set as the energy reference point, shown as dotted line).

intercalation formation energy per lithium atom is around 2.0 eV for all the intercalation configurations. The volume expansions of AlSb, GaSb and InSb due to lithium insertions are all relatively large, the volume increasing order is GaSb > AlSb ~ InSb, which might imply that the limit of Li intercalation in antimonides should be small.

Acknowledgements

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