Phase stability of three-dimensional bulk and two-dimensional monolayer As$_{1-x}$Sb$_x$ solid solutions from first principles

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Abstract

The mixing thermodynamics of both three-dimensional bulk and two-dimensional monolayered alloys of As$_{1-x}$Sb$_x$ as a function of alloy composition and temperature are explored using a first-principles cluster-expansion method, combined with canonical Monte-Carlo simulations. We observe that, for the bulk phase, As$_{1-x}$Sb$_x$ alloy can exhibit not only chemical ordering of As and Sb atoms at $x = 0.5$ to form an ordered compound of AsSb stable upon annealing up to $T \approx 475$ K, but also a miscibility gap at $475 \lesssim T \lesssim 550$ K in which two disordered solid solutions of As$_{1-x}$Sb$_x$ of different alloy compositions thermodynamically coexist. At $T > 550$ K, a single-phase solid solution of bulk As$_{1-x}$Sb$_x$ is predicted to be stable across the entire composition range. These results clearly explain the existing uncertainties in the alloying behavior of bulk As$_{1-x}$Sb$_x$ alloy, as previously reported in the literature, and also found to be in qualitative and quantitative agreement with the experimental observations. Interestingly, the alloying behavior of As$_{1-x}$Sb$_x$ is considerably altered, as the dimensionality of the material reduces from the three-dimensional bulk state to the two-dimensional monolayered state—for example, a single-phase solid solution of monolayer As$_{1-x}$Sb$_x$ is predicted to be stable over the whole composition range at $T > 250$ K. This distinctly highlights an influence of the reduced dimensionality on the alloying behavior of As$_{1-x}$Sb$_x$.

Keywords: bulk/multilayer As$_{1-x}$Sb$_x$, monolayer As$_{1-x}$Sb$_x$, phase diagram, mixing thermodynamics, first-principles approach, cluster-expansion formalism, density functional theory

(Some figures may appear in colour only in the online journal)

1. Introduction

Three-dimensional bulk arsenic—As—and antimony—Sb—both crystallize in the rhombohedral A7-type structure ($R3m$) under ambient condition, in which As and Sb atoms, respectively, form the buckled layers periodically stacking in a sequence of ABCABC... [1, 2], as illustrated by figure 1(a). Rather than the stacked layered structures in their bulk phases, arsenene and antimonene, single buckled layers of As and of Sb, respectively, have recently been received considerable interest from the two-dimensional materials research community [3, 4], since they have been demonstrated via several independent studies to exhibit unique properties significantly different from their three-dimensional bulk counterparts and
thus have been expected as promising candidates for fabrication of next-generation thermoelectric [5], piezoelectric [6], optoelectronic and electronic devices [7–10]. In practice, arsenene and antimonene can be prepared either by electrochemical or liquid-phase exfoliation of bulk arsenic and antimony, respectively [11, 12], or by molecular beam or van der Waals epitaxial growth [13, 14].

In spite of the remarkable properties in their pure elemental states, alloying arsenene with antimonene to form a monolayered arsenic antimonide (As$_1$–Sb$_x$) alloy has been suggested as a process to essentially optimize and to further enhance the materials properties for efficient utility of the materials in their future applications—for example, the expected improvement of the thermoelectric performance of As$_1$–Sb$_x$ alloy with respect to that of arsenene and of antimonene [15]. When speaking of the alloy, one should, however, be aware of the fact that in reality the constituent elements of the alloy can at a given temperature and alloy composition display different alloying behaviors, i.e. an ordering tendency to form an ordered structure, a clustering tendency toward phase segregation, and a mixing tendency to form a homogeneous solid solution. Generally, those alloying behaviors are governed by the mixing thermodynamics of the alloy constituents, and to a large extent can affect the alloys properties.

For the three-dimensional bulk As$_1$–Sb$_x$ alloy, it was formerly believed, as demonstrated by the As–Sb phase diagrams existing in the literature [16, 17], that As and Sb form a continuous series of solid solutions of As$_1$–Sb$_x$ over the entire composition range at temperature above 600 K, while a phase separation of a single-phase solid solution of As$_1$–Sb$_x$ into two limiting solid solutions exhibiting different alloy compositions $x$ at lower temperature is still ambiguous. Furthermore, it was not obvious at that time whether or not some chemically ordered compounds of As$_1$–Sb$_x$ alloys were also formed at low temperature [18, 19]. Even though the possible existence of an ordered compound of As$_1$–Sb$_x$ alloy at $x \approx 0.5$ was previously proposed by Ohyama [19] and Bayliss [20], the information about structural characterization of such an ordered structure was not provided in either of their studies.

Recently, Shoemaker et al [21] provided a concrete evidence in their studies that, for the binary As–Sb system, As and Sb atoms can display chemical ordering at the stoichiometric composition of AsSb ($x = 0.5$), leading to a formation of the A7-type ordered structure ($R3m$), as illustrated in figure 1(b). In addition, as demonstrated by the high-temperature diffraction studies [21], the ordered structure of AsSb remains stable, upon annealing, up to 550 K, before undergoing a structural phase transition to a state, in which As and Sb atoms configurationally disorder on the lattice sites. Thus, the existence of the ordered compound for As$_{0.5}$Sb$_{0.5}$ not only gives rise to ambiguity in the previously proposed phase diagram of the binary As–Sb system [16], but it also brings up a question about the alloying behavior of bulk As$_1$–Sb$_x$ alloy, distinctly deserving further clarification. Still, it is obscure whether the alloying behavior of As$_1$–Sb$_x$ would be altered, as the dimensionality of the alloy reduces from the three-dimensional stacked layered structure to the two-dimensional monolayered structure.

To the best of our knowledge, the mixing thermodynamics of the monolayered As$_1$–Sb$_x$ alloy has so far never been investigated both theoretically or experimentally.

In the present work, we use the first-principles cluster-expansion method, combined with the Monte Carlo simulations, to clarify the alloying behavior of As$_1$–Sb$_x$ alloy both in the three-dimensional bulk state and in the two-dimensional mono-layered state as a function of temperature, and also derive their isostructural $T - x$ phase diagrams. We find, for the three-dimensional bulk state, that As$_1$–Sb$_x$ alloy is thermodynamically stable as a homogeneous disordered solid solutions across the whole composition range at $T \gtrsim 550$ K, while a small immiscible region, where two disordered solid solutions of As$_1$–Sb$_x$ of different compositions $x$ thermodynamically coexist, is predicted to appear at 475 K $\lesssim T \lesssim 550$ K. At $T \lesssim 475$ K, bulk As$_1$–Sb$_x$ alloy can display chemical ordering of As and Sb atoms at $x = 0.5$ to form a stable ordered compound of AsSb, as displayed by figure 1(b). Our simulations reveal also a finite solubility range ($0.425 \lesssim x \lesssim 0.525$), in which either of As atoms or of Sb atoms dissolve in the ordered compound of AsSb at 200 K $\lesssim T \lesssim 475$ K. These

Figure 1. (a) A7-type structure of bulk arsenic (As), bulk antimony (Sb) and bulk disordered solid solutions of As$_1$–Sb$_x$. (b) Ordered compound of bulk arsenic antimonide (AsSb), previously observed and reported in [21]. Grey spheres in (a) represent either As or Sb atoms, while green and brown spheres in (b) explicitly denote As and Sb atoms, respectively. Thin black lines in both (a) and (b) outline the conventional hexagonal unit cells of the materials with each containing six atoms.
results are found to efficiently provide answers to the questions concerning the alloying behavior of bulk $\text{As}_1 - \text{Sb}_x$ alloy, and thus yield a good agreement with the experimental observations. As in the case of the two-dimensional mono-layered state, we find that the alloying behavior of $\text{As}_1 - \text{Sb}_x$ distinctly differs from that of the three-dimensional bulk state—for example, a temperature at which a complete closure of a miscibility gap occurs is considerably reduced from $\sim 550$ K in the three-dimensional bulk state to $\sim 250$ K in the two-dimensional mono-layered state. In addition, we suggest that, unlike the bulk state, the two-dimensional mono-layered structure, derived from the stable ordered compound of bulk $\text{As}_1 - \text{Sb}_x$ alloy at $x = 0.5$, may merely exist as a metastable state. These findings highlight an influence of the reduced dimensionality on the mixing thermodynamics of $\text{As}_1 - \text{Sb}_x$ alloy.

2. Methodology

2.1. Cluster expansion method

Following the cluster-expansion (CE) formalism, proposed by Sanchez, Ducastelle, and Grastias [22], the total energy ($E$) of any crystalline solid that is strictly a function of the atomic arrangement on a lattice, or a so-called atomic configuration ($\sigma$) can be formally expanded into a sum over correlation functions $\xi_f^{(n)}(\sigma)$ of specific $n$-site figures $f$ with the corresponding effective cluster interactions (ECIs) $V_f^{(n)}$:

$$E(\sigma) = N \sum_f m_f^{(n)} V_f^{(n)} \xi_f^{(n)}(\sigma).$$

(1)

The factor $m_f^{(n)}$ is defined as the multiplicity of specific $n$-site figures $f$, normalized to the number of atomic sites $N$ within the corresponding atomic configuration $\sigma$. To describe any atomic configuration $\sigma$ of $\text{As}_1 - \text{Sb}_x$ alloy, the spin variable $\sigma_i$ is assigned to take on a value of $+1$ or of $-1$, if the lattice site $i$ is occupied by As atom or by Sb atom, respectively. As a result, any atomic configuration $\sigma$ of $\text{As}_1 - \text{Sb}_x$ alloy can be uniquely specified by a set of spin variables $\{ \sigma_i \}$, and the correlation functions $\xi_f^{(n)}$ can subsequently be determined by the products of the spin variables $\sigma_i$:

$$\xi_f^{(n)} = \frac{1}{m_f^{(n)}} \sum_{\alpha \in f} \prod_{i=1}^{n} \sigma_i,$$

(2)

in which the sum of the product in the parentheses runs over all symmetrically equivalent clusters, $\alpha \in f$. As a consequence, the mixing energy $\Delta E_{\text{mix}}(\sigma)$ of $\text{As}_1 - \text{Sb}_x$ of a given atomic configuration $\sigma$ with As and Sb contents ($x_{\text{As}}$ and $x_{\text{Sb}} = 1 - x_{\text{As}}$) can be written as

$$\Delta E_{\text{mix}}(\sigma) = E(\sigma) - x_{\text{As}} E_{\text{As}} - x_{\text{Sb}} E_{\text{Sb}},$$

(3)

where $E_{\text{As}}$ and $E_{\text{Sb}}$ are the total energies of pure elemental phases of As and Sb, respectively.

It is worth noting that, even though the expansion, expressed in equation (1), is mathematically complete in the limit of inclusion of all possible figures $f$, it must be truncated for all practical purposes. For this particular case, we use the MIT $AB\ initio$ Phase Stability (MAPS) code [23], as implemented in the Alloy-Theoretical Automated Toolkit (ATAT) [24], not only to truncate the expansion in equation (1), but also to determine the ECIs in such a way that equation (1) returns the total energies $E(\sigma)$ of $\text{As}_1 - \text{Sb}_x$ as close to those obtained from first-principles calculations as possible for all configurations $\sigma$, included in the expansion. Further details for implementation of the cluster expansion to determine the ECIs and also to evaluate the mixing thermodynamics of $\text{As}_1 - \text{Sb}_x$ alloy both in the three-dimensional bulk state and in the two-dimensional mono-layered state will be provided and discussed in sections 3.1 and 3.2, respectively.

2.2. First-principles calculations

The first-principles total energy of a given atomic configuration $\sigma$ of the binary $\text{As}_1 - \text{Sb}_x$ alloy is calculated from the density functional theory (DFT), in which the projector augmented wave (PAW) method [25], as implemented in the Vienna $ab\ initio$ simulation package (VASP) [26, 27], is used and the generalized gradient approximation (GGA), as suggested by Perdew, Burke, and Ernzerhof [28], is employed for modeling the exchange-correlation interactions. The valence electron configurations, used for pseudopotentials, are $4s^24p^6$ and $5s^25p^3$ for As and Sb, respectively. The energy cutoff for plane waves, included in the expansion of wave functions, is set to 500 eV, and the Monkhorst–Pack $k$-point scheme [29], is chosen for sampling the Brillouin zone.

As for the three-dimensional stacked layered structure of $\text{As}_1 - \text{Sb}_x$, we use a $15 \times 15 \times 15$ Monkhorst–Pack $k$-point mesh for the Brillouin zone integration. The correction, proposed by Grimme (DFT-D3) [30], to the total energy calculations is also added to account for the weak van der Waals forces existing between the buckled layers. During the calculations, the internal atomic coordinates, volume, and cell shape of bulk $\text{As}_1 - \text{Sb}_x$ are allowed to relax in order to minimize the calculated energy.

In the case of a single buckled layer of $\text{As}_1 - \text{Sb}_x$, the material is presumed as a two-dimensional material. For this reason, the structural models are periodic only in the $x$–$y$ plane and the vacuum distance along the $z$ direction is kept fixed at 25 Å to avoid artificial interactions, arising from the periodic boundary condition. A $21 \times 21 \times 1$ Monkhorst–Pack $k$-point mesh is set for the Brillouin zone integration. While optimizing the structural models to minimize their total energy, the cell shape and volume are allowed to relax only in the $x$ and $y$ directions, while all of the atomic coordinates are allowed to relax in all direction.

We emphasize that, for all DFT calculations, the total energies of bulk and mono-layered $\text{As}_1 - \text{Sb}_x$ are ensured to converge within an accuracy of $1$ meV/atom with respect to both the plane-wave energy cutoff and the density of the $k$-point grids.

2.3. Monte Carlo simulations

To investigate the alloying behavior of $\text{As}_1 - \text{Sb}_x$, we utilize the ECIs obtained from the cluster expansion in canonical Monte Carlo (MC) simulations using the Easy Monte Carlo
Code (EMC2) [31], as implemented in the ATAT [24]. In the present work, the simulation boxes of \(20 \times 20 \times 13\) rhombohedral primitive unit cells (10,400 atoms) and of \(40 \times 40 \times 1\) hexagonal conventional unit cells (3200 atoms) are used for modeling, respectively, the configurational thermodynamics of bulk and mono-layered \(\text{As}_{1-x}\text{Sb}_x\) alloys as a function of temperature and alloy composition. In both cases, the simulations are performed at fixed compositions \(x\), where \(0 \leq x \leq 1\) and \(\Delta x = 0.025\). At each composition, the \(\text{As}_{1-x}\text{Sb}_x\) alloy is cooled from 3000 to 25 K, using simulated annealing, where at each temperature, the simulations include 18,000 (24,000) MC steps for equilibrating the system and then 12,000 (16,000) more steps for obtaining the proper averages of \(\Delta E_{\text{mix}}\) and configurational specific heat \(C_V\) for bulk (mono-layered) \(\text{As}_{1-x}\text{Sb}_x\) at different fixed temperatures and alloy compositions. The configurational thermodynamics of \(\text{As}_{1-x}\text{Sb}_x\) alloy is then evaluated through the Gibbs free energy of mixing, \(\Delta G_{\text{mix}}\), given by

\[
\Delta G_{\text{mix}}(x, T) = \Delta E_{\text{mix}}(x, T) - T \Delta S_{\text{mix}}(x, T),
\]

where the mixing entropy \(\Delta S_{\text{mix}}\) can be obtained from thermodynamic integration of \(C_V\):

\[
\Delta S_{\text{mix}}(x, T) = \Delta S_{\text{MF}}(x) + \int_{\text{from } 0}^{T} \frac{C_V(x, T')}{T} dT'.
\]

The term \(\Delta S_{\text{MF}}\) stands for the mixing entropy per atom of the ideally random solid solution of the alloy, stable in the limit of \(T \to \infty\), and it can thus be derived from the mean-field approach to be

\[
\Delta S_{\text{MF}}(x) = -k_B[x \ln(x) + (1 - x) \ln(1 - x)].
\]

For this particular case, we assume that \(\Delta S_{\text{mix}}(x, T = 3000 \text{ K}) \approx \Delta S_{\text{MF}}(x)\), and thus the thermodynamic integration in equation (5) is performed from this high temperature downwards to the temperature of interest.

3. Results and discussion

3.1. Three-dimensional bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy

In the present section, we consider the configurational thermodynamics of three-dimensional bulk \(\text{As}_{1-x}\text{Sb}_x\) alloys. As a first step, we establish a database of different atomic configurations \(\sigma\) by using an algorithm developed by Hart and Forcade [36] to generate a set of 6104 configurations of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy with up to 12 atoms in the primitive supercell, which is equivalent to six primitive rhombohedral unit cells. We single out approximately a hundred of \(\sigma\) to perform the first-principles calculations on them to obtain their total energies, and include them in the cluster expansion, using the MAPS code as described in section 2.1, to determine initial ECIs, which are subsequently used to predict the total energies of all generated \(\sigma\) using equation (1). We note that the initial ECIs may not do the prediction accurately, and thus its predictive power needs to be improved. To this end, we employ the total energies predicted by the initial ECIs as a guideline to single out a few more tens or hundreds of \(\sigma\), not included in the first expansion, calculate their total energies through the first-principles approach, and consider them, together with those from the first cluster expansion, in the second cluster expansion to re-determine the ECIs. Regarding the down selection of \(\sigma\) to be included in the subsequent cluster expansions, we particularly focus on low-energy \(\sigma\), whose \(\Delta E_{\text{mix}} \lesssim 0.01\) eV/atom. These procedures can be repeatedly performed, until the cluster expansion and thus the ECIs of desired quality are reached.

The final expansion includes 241 \(\sigma\) and employs a total of 33 ECIs, composed of 1 0-site interaction, 1 1-site interaction, 19 2-site interactions and 12 3-site interactions. Concerning the predictive power of the derived ECIs, the final expansion fits the 241 input \(\sigma\) with the cross-validation score of 1.102 meV/atom. Figure 2 displays \(\Delta E_{\text{mix}}\) at \(T = 0\) K of all generated \(\sigma\) of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy, evaluated with respect to their constituent elements, i.e. As and Sb. We note further that, as a complement to the diagram, shown in figure 2, DFT-calculated \(\Delta E_{\text{mix}}\) of ideally random solid solutions of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy with the compositions \(x = 0.25, 0.5, \) and \(0.75\), modeled within 64-atom supercells by using the special quasirandom structure (SQS) method [37], are given for comparison to the cluster expansion method. The diagram reveals that, in addition to the pure elemental phases of As and Sb, bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy forms a stable ordered structure only at \(x = 0.5\) (see figure 1(b) for visualization of the structure), as indicated by the derived ground-state line at 0 K (thick black lines connecting three large filled circles at \(x = 0, 0.5, \) and 1, shown in figure 2). Our prediction of the ordered structure at \(x = 0.5\) is indeed in line with the experimental observation of an ordered compound of AsSb crystallizing in the rhombohedral \(A7\)-type structure (\(R3\)\(m\)), as recently reported by Shoemaker et al [21]. These results also suggest that, at absolute zero, a solid solution of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy, where \(x < 0.5\) (\(x > 0.5\)), will be transformed into and thus stable as a mixture of the ordered compound of AsSb and pure elemental phase of arsenic (antimony) under thermodynamic equilibrium conditions. Table 1 shows the lattice parameters of As, Sb, and ordered AsSb, both calculated in the present work and experimentally measured from previous studies. As can be seen from table 1, the calculated lattice parameters of all three phases differ from the experimental values by less than 2\%, providing evidence of the reliability of our methodological approach in terms of e.g. exchange-correlation approximation.

To investigate the configurational thermodynamics of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy as a function of alloy composition and of temperature, we utilize the ECIs obtained from the final expansion in the canonical MC simulations by using the EMC2 code and then derive the mixing Gibbs free energy \(\Delta G_{\text{mix}}\), as described in section 2.3. Figure 3(a) shows the resulting \(\Delta G_{\text{mix}}\) curves of bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy at some selected temperatures. As can be seen from figure 3(a), \(\Delta G_{\text{mix}}\) exhibits a positive curvature for the whole composition range already at \(T = 600\) K, indicating a formation of a homogeneous solid solution for bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy under thermodynamic equilibrium conditions. By applying common tangent construction to the \(\Delta G_{\text{mix}}\) curve at different fixed temperatures, we outline an isostuctural \(T-x\) phase diagram for bulk \(\text{As}_{1-x}\text{Sb}_x\) alloy, as depicted by figure 3(b). The phase diagram reveals that, at \(T > 550\)
K, a single-phase solid solution of bulk As$_{1-x}$Sb$_x$ alloy, as denoted by α phase, is thermodynamically stable across the entire composition range, while $T \lesssim 550$ K, we observe the existence of both the stable ordered compound at $x = 0.5$ (see figure 1(b)) and clustering of As$_1$-Sb$_x$ alloys of different compositions $x$. As for the latter, a miscibility gap is predicted to exist at 475 K $\lesssim T \lesssim 550$ K. Within such a small immiscible region, bulk As$_{1-x}$Sb$_x$ alloy is thermodynamically stable as a mixture of As-rich and Sb-rich As$_1$-Sb$_x$ solid solutions, as denoted by $\alpha'$ and $\alpha''$ phases, respectively. At $T \lesssim 475$ K, the ordered compound AsSb is predicted to be stable, as denoted by $\alpha''$ phase. Interestingly, at 200 K $\lesssim T \lesssim 475$ K, a finite solubility either of As atoms or of Sb atoms in the $\alpha''$ phase is predicted at 0.425 $\lesssim x \lesssim 0.525$, while at lower temperature the $\alpha^*$ phase is essentially a line compound at $x = 0.5$. We also find that, at a particular composition of AsSb ($x = 0.5$), both As and Sb atoms would lose their chemical long-range order and thus become disordered with the global $R3m$ symmetry at $T > 525$ K, as indicated by a sharp peak in the simulated configurational specific heat of bulk As$_{0.5}$Sb$_{0.5}$ alloy (see figure 4). Our predicted configurational order-disorder transition temperature for bulk As$_{0.5}$Sb$_{0.5}$ alloy is found to be in good agreement with the experimental value of 550 K, as recently observed by Shoemaker et al [21]. We note further that the experimental order-disorder transition temperature of 550 K, reported in [21], well matches our predicted temperature at which a complete closure of the miscibility gap takes place at $x \approx 0.5$ for bulk As$_{1-x}$Sb$_x$ alloy (see figure 3(b)). This is thus in line with our prediction that at $T > 550$ K the alloy is thermodynamically stable as a homogeneous disordered solid solution.

Last but not least, Quensel et al [18] previously studied allemonite—a natural form of As$_{1-x}$Sb$_x$ alloy. Through their analyses, they observed some allemonite minerals were heterogeneous and thus consisted of two phases, by which one of the phases had a composition of about As$_{0.5}$Sb$_{0.5}$. This indeed corresponds to and can be interpreted by the two-phase regions—either ($\alpha^* + \alpha'$) or ($\alpha^* + \alpha''$) depending on the alloy composition $x$—as shown in figure 3(b). Within these regions, bulk As$_{1-x}$Sb$_x$ alloy is stable as a mixture of $\alpha^*$ and $\alpha'$ ($\alpha''$) phases for $x < 0.5$ ($x > 0.5$) under thermodynamic equilibrium conditions. We noted that, in the present work, the influence of lattice vibrations on $\Delta G_{\text{mix}}$ of bulk As$_{1-x}$Sb$_x$ (and also of mono-layered As$_{1-x}$Sb$_x$ in the following section) are neglected. This is because, for isostructural alloys, they are typically of minor importance and often do not yield a
significant impact on the mixing thermodynamics, as compared to the contributions arising from the configurational degree of freedom.

According to the above discussions, we have demonstrated that the uncertainties in the alloying behaviors of bulk As$_{1-x}$Sb$_x$ alloy, as previously reported in the literature through a series of experimental observations, can be well explained by our proposed phase diagram. This thus evidently proves reliability of our used approaches, i.e. the cluster expansion in combination with the canonical Monte Carlo simulations, to determine the mixing thermodynamics for bulk As$_{1-x}$Sb$_x$ alloy.

3.2 Two-dimensional mono-layered As$_{1-x}$Sb$_x$ alloy

The next step is to examine the configurational thermodynamics of two-dimensional mono-layered As$_{1-x}$Sb$_x$ alloys. To do so, we apply the same expansion procedure, as done for bulk of As$_{1-x}$Sb$_x$, to a single buckled layer of As$_{1-x}$Sb$_x$ alloy. For this particular case, we generate a set of 2702 configurations of mono-layered As$_{1-x}$Sb$_x$ with up to 14 atoms in the primitive supercell, which is equivalent to seven primitive hexagonal unit cells. After a few ten iterations of the cluster-expansion procedures, focusing particularly on low-energy $\sigma$, whose $\Delta E_{\text{mix}} \lesssim 0.075$ eV/atom as the down-selection criterion for the included $\sigma$, the final expansion includes 345 $\sigma$ and employ a total of 33 ECIs, composed of 1 0-site interaction, 1 1-site interaction, 19 2-site interactions and 12 3-site interactions. The final expansion fits the input 345 $\sigma$ with the cross-validation score of 0.131 meV/atom, and $\Delta E_{\text{mix}}$ at $T = 0$ K of all generated $\sigma$ of mono-layered As$_{1-x}$Sb$_x$, evaluated with respect to single layers of arsenene and antimonene, are displayed in figure 5. Interestingly, after a full relaxation, a single buckled layer of the ordered As$_{1-x}$Sb$_x$ alloy at $x = 0.5$, as illustrated by figure 1(b), is thermodynamically unstable with respect to its constituent elements, and as a consequence
Figure 5. Ground-state diagram at $T = 0$ K of two-dimensional monolayer As$_{1-x}$Sb$_x$ alloy. Red crosses are the CE-predicted mixing energy $\Delta E_{\text{mix}}$ of the generated 2702 configurations of monolayer As$_{1-x}$Sb$_x$ alloy. Open black circles are the DFT-calculated $\Delta E_{\text{mix}}$ of the selected 345 configurations, included in the final cluster expansion. Thick black lines, connecting two large filled black circles at $x = 0$ and 1, represent the DFT-derived ground-state line of monolayer As$_{1-x}$Sb$_x$ alloy. Filled blue squares stand for the DFT-calculated $\Delta E_{\text{mix}}$ of the ideal random solid solutions of monolayer As$_{1-x}$Sb$_x$ alloy, modeled within 72-atom supercells by the SQS method.

at absolute zero the two-dimensional mono-layered alloy of As$_{1-x}$Sb$_x$ is expected to decompose into arsenene and antimonene across the entire composition range under the thermodynamic equilibrium conditions. This is indeed in contrast to its bulk counterpart, in which the ordered structure is predicted to be stable up to about 500 K. According to the present calculations, the in-plane lattice parameters $a$ of free-standing arsenene, antimonene, and ordered mono-layered As$_{0.5}$Sb$_{0.5}$ are 3.608, 4.113, and 3.861 Å, respectively, which are all in excellent agreement with the theoretical values, previously reported in the literature (<0.3% difference) [6, 15, 38, 39]. Despite being predicted to be unstable, it should be noted that $\Delta E_{\text{mix}}$ of the ordered mono-layered structure at $x = 0.5$ is merely 1.731 meV/atom above the convex hull at $T = 0$ K. The stabilization of the ordered mono-layered As$_{0.5}$Sb$_{0.5}$, including its possible existence, will be further discussed in the following paragraphs.

By utilizing the ECIs, derived from the final expansion, in the canonical MC simulations, we calculate $\Delta G_{\text{mix}}$ of mono-layered As$_{1-x}$Sb$_x$ alloy as a function of alloy composition and temperature. Figure 6(a) shows $\Delta G_{\text{mix}}$ curves at some selected temperatures of mono-layered As$_{1-x}$Sb$_x$ alloy, where $0 \leq x \leq 1$. Unlike its bulk counterpart, the $\Delta G_{\text{mix}}$ curve of two-dimensional mono-layered As$_{1-x}$Sb$_x$ alloy exhibits a positive curvature across the entire composition range at $T \geq 250$ K, and via inspecting their configurational specific heats at different fixed alloy compositions (not shown), we find that the order-disorder transition temperature for mono-layered As$_{1-x}$Sb$_x$ alloy ranges approximately from 100 K to 150 K. These results thus indicate that As and Sb readily mix with each other to form random solid solutions of mono-layered As$_{1-x}$Sb$_x$ alloy across the entire composition range even at a temperature below room temperature, as denoted by $\alpha$ in figure 6(b) illustrating an isostructural $T - x$ phase diagram for two-dimensional mono-layered As$_{1-x}$Sb$_x$ alloy. The diagram reveals the presence of two phase regions, labeled by $\alpha'$ and $\alpha''$, at $T \lesssim 250$ K, in which two solid solutions of mono-layered As$_{1-x}$Sb$_x$ alloy of different compositions $x$ coexist in thermodynamic equilibrium.

Even though the aforementioned ordered mono-layered As$_{0.5}$Sb$_{0.5}$ alloy is not thermodynamically stable against phase separation into arsenene and antimonene, it may be experimentally achieved, for example, via a mechanical or liquid-phase exfoliation of bulk ordered As$_{0.5}$Sb$_{0.5}$ alloy (figure 1(b)) [11, 12], and it is also very likely that the phase separation of the exfoliated ordered mono-layered As$_{0.5}$Sb$_{0.5}$ into its constituent elemental phases is hindered in practice. This is due mainly to a large difference in lattice parameters between arsenene and antimonene, giving rise to a non-negligible constituent strain energy ($\Delta E_{\text{cs}}$) [40, 41], which must accordingly be taken into account for determining the stability of the ordered mono-layered As$_{0.5}$Sb$_{0.5}$ alloy. For this particular case, $\Delta E_{\text{cs}}$ of a given ordered structure $\sigma$ of mono-layered As$_{1-x}$Sb$_x$ alloy is approximately defined by a modification of equation (3):

$$\Delta E_{\text{cs}}(\sigma) = E(\sigma, a_{\sigma}) - x_{\text{As}}E_{\text{As}}(a_{\sigma}) - x_{\text{Sb}}E_{\text{Sb}}(a_{\sigma}).$$ (7)

$a_{\sigma}$ is the equilibrium lattice constant of the mono-layered As$_{1-x}$Sb$_x$ alloy exhibiting a configuration $\sigma$. We observe that $\Delta E_{\text{cs}}$ of the ordered mono-layered As$_{0.5}$Sb$_{0.5}$ alloy under consideration is $-83.49$ meV/atom, considerably lower than $\Delta E_{\text{mix}}$ calculated from the same $\sigma$ ($+1.731$ meV/atom). Such a large contribution from the in-plane strain indicates that the clustering of As and Sb atoms to form arsenene and
antimonene, respectively, is unlikely to be promoted experimentally, and thus the phase separation would never be favored over the ordered structure of mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$ alloy, whose (meta)stability is maintained by the in-plane strain resulting from a large difference in lattice parameters between antimonene and arsenene. Nevertheless, further experimental elaboration is needed to verify this theoretical analysis.

For a comparison purpose, $\Delta E_{\text{mix}}$ of the disordered solid solution of the mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$ approximated at the same level of the in-plane strain to that of the ordered mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$ is $-72.02$ meV/atom, while its $\Delta E_{\text{mix}}$ is $+13.29$ meV/atom. Theoretically, this implies that as $T \to 0$ K, the phase separation of the disordered solid solution of mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$ into antimonene and arsenene is likely to be prohibited in analogy to that of the ordered mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$. It should, however, be noted that at $T = 0$ K, the disordered mono-layered $\text{As}_{0.5}\text{Sb}_{0.5}$ will never be favored over the ordered one due to its relatively higher energy.

Apart from the exfoliation approaches, a single layer of $\text{As}_{1-x}\text{Sb}_x$ alloy may be prepared by epitaxial growth techniques, such as molecular beam epitaxy [13] and van der Waals epitaxy [14]. It is, however, worth noting that by employing these epitaxy methods, the as-synthesized monolayer of $\text{As}_{1-x}\text{Sb}_x$ alloy is expected to be achieved in the form of disordered solid solutions ($\alpha$ phase). This is because the temperature during the synthesis process can reach several hundred Kelvin [13, 14]. One can further expect the $\alpha$ phase of mono-layered $\text{As}_{1-x}\text{Sb}_x$ still persists upon cooling down the alloy to low temperature. As illustrated by our derived phase diagram (figure 6(b)), the two-phase regions ($\alpha' + \alpha''$) are predicted to present at rather low temperature ($T \lesssim 250$ K). As a result, the phase separation of the $\alpha$ phase into $\alpha'$ and $\alpha''$ phases is likely to be hindered by a lack of atomic mobility at such a low temperature. These results suggest that the alloying behavior of two-dimensional mono-layered $\text{As}_{1-x}\text{Sb}_x$ alloy can be to a large extent different from its bulk counterpart, and it should be considered for further theoretical and experimental investigations of two-dimensional mono-layered $\text{As}_{1-x}\text{Sb}_x$ alloy.

4. Conclusion

We utilize a first-principles cluster-expansion method in combination with canonical Monte Carlo simulations to clarify the alloying behavior of crystalline $\text{As}_{1-x}\text{Sb}_x$ alloy, both in the three-dimensional bulk state and in the two-dimensional mono-layered state, as a function of temperature and alloy composition. For the bulk phase, we demonstrate that $\text{As}_{1-x}\text{Sb}_x$ alloy forms a continuous series of disordered solid solutions over the whole composition range at $T > 550$ K, while at lower temperature we observe the existence of both the ordered compound of $\text{AsSb}$ at $x = 0.5$ and clustering of $\text{AsSb}_x$ alloys of different compositions $x$. For the latter, a miscibility gap is predicted to exist within a narrow temperature range from $\sim 475$ K to $\sim 550$ K, in which bulk $\text{As}_{1-x}\text{Sb}_x$ alloy is thermodynamically stable as a mixture of As-rich and Sb-rich $\text{As}_{1-x}\text{Sb}_x$ solid solutions. At $T \lesssim 475$ K, the stable ordered compound of $\text{AsSb}$ is predicted, and interestingly our simulations reveal a finite solubility either of As atoms or of Sb atoms in the ordered compound of $\text{AsSb}$ at $200$ K $\lesssim T \lesssim 475$ K. These results clearly explain the uncertainties in the alloying behavior of bulk $\text{As}_{1-x}\text{Sb}_x$ alloy, previously reported in the literature through a series of experimental observations, thus bringing clarity to the mixing thermodynamics of As and Sb in their bulk phases. We additionally observe a distinct change in the mixing thermodynamics of As and Sb, as the dimensionality of the materials reduces from the three-dimensional bulk state to the two-dimensional mono-layered state. For example, a temperature at which a complete closure of a miscibility gap occurs is considerably reduced from $\sim 550$ K in the three-dimensional bulk state to $\sim 250$ K in the two-dimensional mono-layered state, and the two-dimensional mono-layered structure, derived from the stable
ordered compound of bulk As$_{1-x}$Sb$_x$ alloy at $x = 0.5$, may merely exist as a metastable state. These findings highlight an influence of the reduced dimensionality on the alloying behavior of As$_{1-x}$Sb$_x$.

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