Phase stability of two-dimensional monolayer $\text{As}_{1-x}\text{P}_x$ solid solutions revealed by a first-principles cluster expansion

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The phase stability of two-dimensional monolayer $\text{As}_{1-x}\text{P}_x$ solid solutions, exhibiting the puckered (α phase) and buckled (β phase) structures are investigated using a first-principles cluster-expansion method. Canonical Monte Carlo simulations, together with harmonic approximation, are performed to capture the influences of thermally induced configurational disorder and lattice vibrations on the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$. We first demonstrate that, as the temperature approaches 0 K, the monolayer $\text{As}_{1-x}\text{P}_x$ displays a tendency toward phase separation into its constituent elemental phases, and thus no stable ordered structures of $\text{As}_{1-x}\text{P}_x$, both α and β phases, are predicted to be thermodynamically stable. We further reveal with the inclusion of the lattice vibrational contributions that $\beta\text{-As}_{1-x}\text{P}_x$ is thermodynamically favored over $\alpha\text{-As}_{1-x}\text{P}_x$ across the entire composition range even at 0 K and increasingly so at higher temperature, and a continuous series of disordered solid solution of $\beta\text{-As}_{1-x}\text{P}_x$, where $0 \leq x \leq 1$, is predicted at the temperature above 550 K. These findings not only indicate that the ordered structures of monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$, frequently studied in the literature, may not exist in nature, but also presumably suggest that monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ is metastable with respect to monolayer $\beta\text{-As}_{1-x}\text{P}_x$.

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I. INTRODUCTION

Owing to their unique and exceptional properties, two-dimensional (2D) monolayers of phosphorus (P) and arsenic (As), known as phosphorene and arsenene, respectively, have recently attracted interest in the 2D materials research community and intensively studied as potential candidates for future nanodevices [1–10]. Among the different allotropic forms, a puckered sheet, denoted by α phase and displayed in Figs. 1(a) and 1(c), has been claimed to be the most stable structure of phosphorene at 0 K [11,12], while a buckled layer, denoted by β phase and displayed in Figs. 1(b) and 1(d), has been reported to be the most stable structure of arsenene [12,13].

Aside from their pristine states, arsenene and phosphorene have often been considered together from the theoretical viewpoint in the form of monolayer $\text{As}_{1-x}\text{P}_x$ [14–17]. In this way, their properties could be effectively fine tuned for relevant applications, as recently demonstrated for three-dimensional (3D) bulk $\beta\text{-As}_{1-x}\text{P}_x$ [18–21]. It should, however, be noted that theoretical investigations on the properties of monolayer $\text{As}_{1-x}\text{P}_x$ in most cases have so far been restricted only to some certain ordered structures [14–17], in which the configurational degree of freedom has been completely neglected. In reality, the alloy constituents can exhibit at a given temperature

and composition different alloying behaviors, i.e., an ordering tendency to form ordered structures/compounds, a clustering tendency toward phase separation, and a mixing tendency to form disordered solid solutions. Those alloying behaviors are, in principle, determined by the mixing thermodynamics of the alloy constituents, and can substantially influence the alloys properties.

To the best of our knowledge, the mixing thermodynamics of monolayer $\text{As}_{1-x}\text{P}_x$ solid solutions, both α and β phases, has so far never been explored. Although the alloying behavior of bulk α - and $\beta\text{-As}_{1-x}\text{P}_x$ solid solutions was previously reported in the literature [22], recent theoretical investigation of bulk and monolayer $\text{As}_{1-x}\text{Sb}_x$ solid solutions has revealed that the mixing thermodynamics of As and Sb in the 2D monolayer state is considerably different from that of their 3D bulk counterparts [23]. This highlights an importance of understanding the mixing thermodynamics of monolayer $\text{As}_{1-x}\text{P}_x$ in order to optimally design the alloy and fully functional it in future applications.

In this work, we use the first-principles cluster-expansion approach, combined with the canonical Monte Carlo simulations and the harmonic approximation, to evaluate the phase stability of free-standing monolayers of α - and $\beta\text{-As}_{1-x}\text{P}_x$ solid solutions as a function of temperature T and composition x . We reveal that as $T \rightarrow 0$ K, monolayer $\text{As}_{1-x}\text{P}_x$ exhibits a tendency toward phase segregation into its constituent elemental phases without formation of stable ordered structures of $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$. Furthermore, we demonstrate

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FIG. 1. Top-view visualization of (a) α -phosphorene and (b) β -arsenene. Their side-view images are shown in (c) and (d), respectively.

that the contributions from the lattice vibrations can significantly affect the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$, thus leading to the higher thermodynamic stability of the β phase relative to that of the α phase over the whole composition range even at $T = 0$ K and upon annealing a complete solubility of β -arsenene and β -phosphorene to form a continuous series of disordered solid solution of $\beta\text{-As}_{1-x}\text{P}_x$ with $0 \leq x \leq 1$ is predicted at $T \gtrsim 550$ K. These findings suggest not only that the ordered structures of monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$, frequently discussed in the previous theoretical studies [14–17], may not exist in nature, but also that monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ may merely be metastable with respect to monolayer $\beta\text{-As}_{1-x}\text{P}_x$.

II. METHODOLOGY

A. Cluster-expansion formalism

Following the cluster-expansion (CE) formalism, proposed by Sanchez, Ducastelle, and Grastias [24], the total energy of mixing $\Delta E_{\text{mix}}(\sigma_\tau)$ of a free-standing monolayer of $\text{As}_{1-x}\text{P}_x$ of a given atomic arrangement on a lattice (σ_τ) with As and P contents (x_{As} and $x_{\text{P}} = 1 - x_{\text{As}}$) can be written as

$$\Delta E_{\text{mix}}(\sigma_\tau) = E(\sigma_\tau) - x_{\text{As}}E_{\text{As}}(\beta) - x_{\text{P}}E_{\text{P}}(\alpha), \quad (1)$$

where the subscript $\tau = \alpha$ or β , indicating the phase of a monolayer of $\text{As}_{1-x}\text{P}_x$. $E_{\text{As}}(\beta)$ and $E_{\text{P}}(\alpha)$ are the total energy of the most stable β -arsenene and α -phosphorene, respectively, while $E(\sigma_\tau)$ is defined as the total energy of a monolayer of $\text{As}_{1-x}\text{P}_x$ of a given σ_τ and can be formally expanded into a sum over correlation functions $\xi_f^{(n)}(\sigma_\tau)$ of specific n -site figures f with the corresponding effective cluster interactions (ECIs) $V_f^{(n)}$:

$$E(\sigma_\tau) = \sum_f V_f^{(n)} \xi_f^{(n)}(\sigma_\tau). \quad (2)$$

Even though the expression in Eq. (2) is mathematically complete in the limit of inclusion of all possible f , it has to be truncated for all practical purposes. Here, we use the MIT *ab initio* phase stability (MAPS) code [25], as implemented in the alloy-theoretic automated toolkit (ATAT) [26], to truncate the expansion and to determine the ECIs in such a way that

Eq. (2) returns the total energies $E(\sigma_\tau)$ of $\text{As}_{1-x}\text{P}_x$ as close to those obtained from first-principles calculations as possible for all σ_τ , included in the expansion. Further details for implementation of the cluster-expansion method to determine the ECIs for the monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$ will be provided and discussed in Sec. III A.

B. First-principles calculations

The first-principles total energy of a given configuration σ_τ of the monolayer $\text{As}_{1-x}\text{P}_x$ is calculated from the density functional theory (DFT), in which the projector augmented-wave (PAW) method [27] as implemented in the Vienna *ab initio* simulation package (VASP) [28,29] is used and the exchange-correlation effects are modeled using the generalized gradient approximation [30]. For all DFT calculations, the plane-wave energy cutoff is set to 500 eV, and the Monkhorst-Pack scheme is chosen for sampling the Brillouin zone [31].

Since monolayer α - and $\beta\text{-As}_{1-x}\text{P}_x$ are presumed as 2D materials, the structural models, shown in Fig. 1, are periodic only in the x - y plane and the vacuum distance along the z axis is kept fixed at 35 and 25 Å for α - and $\beta\text{-As}_{1-x}\text{P}_x$, respectively, to avoid artificial interactions, arising from the periodic boundary condition. In order to optimize 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 directions. We also ensure that, for all DFT calculations, the total energies are converged within an accuracy of 1 meV/atom with respect both to the plane-wave energy cutoff and to the density of the $\mathbf{k}$ -point grids. As for the latter, $15 \times 15 \times 1$ and $21 \times 21 \times 1$ Monkhorst-Pack $\mathbf{k}$ -point meshes are set for the Brillouin integration of α - and $\beta\text{-As}_{1-x}\text{P}_x$, respectively.

C. Canonical Monte Carlo simulations

To investigate the phase stability of the heterogeneous 2D monolayer $\text{As}_{1-x}\text{P}_x$ alloy system, we employ the ECIs derived from the cluster expansions of monolayer α - and $\beta\text{-As}_{1-x}\text{P}_x$ in canonical Monte Carlo (MC) simulations *via* the easy Monte Carlo (EMC2) [32], as implemented in the ATAT[26]. For this particular case, the simulation boxes of $34 \times 25 \times 1$ orthorhombic unit cells (3400 atoms) and of $40 \times 40 \times 1$ hexagonal unit cells (3200 atoms) are used for modeling the phase stability of monolayer α - and $\beta\text{-As}_{1-x}\text{P}_x$, respectively, as a function of temperature and alloy composition x , where $0 \leq x \leq 1$ and $\Delta x = 0.025$. At each composition, the α (β) phase of monolayer $\text{As}_{1-x}\text{P}_x$ is cooled from 3000 to 25 K, using simulated annealing $\Delta T = 25$ K and at each temperature, the simulations include 27 000 (24 000) MC steps for equilibrating the system and then 18 000 (16 000) more steps for obtaining the proper averages of $\Delta E_{\text{mix}}^\tau$ and configurational specific heat C_V^τ at different fixed temperatures and alloy compositions. The phase stability of monolayer $\text{As}_{1-x}\text{P}_x$ is then evaluated *via* the mixing Gibbs free energy $\Delta G_{\text{mix}}^\tau$, defined by

$$\Delta G_{\text{mix}}^\tau(x, T) = \Delta E_{\text{mix}}^\tau(x, T) - T \Delta S_{\text{mix}}^\tau(x, T), \quad (3)$$

where $\tau = \alpha$ or β denoting, respectively, the α or β phase of monolayer $\text{As}_{1-x}\text{P}_x$, while the mixing entropy $\Delta S_{\text{mix}}^\tau$ can be

obtained from thermodynamic integration of C_V^τ :

$$\Delta S_{\text{mix}}^\tau(x, T) = \Delta S_{\text{mix}}^{\text{MF}}(x) + \int_\infty^T \frac{C_V^\tau(x, T')}{T'} dT'. \quad (4)$$

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

$$\Delta S_{\text{mix}}^{\text{MF}}(x) = -k_B[x \ln(x) + (1-x)\ln(1-x)]. \quad (5)$$

Here, we assume $\Delta S_{\text{mix}}^\tau(x, T = 3000 \text{ K}) \approx \Delta S_{\text{mix}}^{\text{MF}}(x)$, and as a result the thermodynamic integration in Eq. (5) is performed from this high temperature downward to the temperature of interest.

D. Harmonic approximation of lattice vibrations

It should be noted that $\Delta G_{\text{mix}}^\tau$, expressed by Eq. (3), has been evaluated without explicitly taking into account the impact of lattice vibrations. However, Aierken *et al.* [33] recently showed through their theoretical work on monolayer phosphorene that a structural phase transition from α - to β -phosphorene can be triggered by the influence of lattice vibrations. This is expected to have a direct consequence also on the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$. In order to demonstrate the influence of the lattice vibrations on the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$, the mixing Helmholtz free energy, arising from the lattice vibrations and denoted by $\Delta F_{\text{vib-mix}}^\tau$, is introduced as an additional contribution to $\Delta G_{\text{mix}}^\tau$.

In this work, $\Delta F_{\text{vib-mix}}^\tau$ is obtained at the level of harmonic approximation using the finite-displacement method, as implemented in the PHONOPY package for phonon calculations [34,35], in which the force constants are calculated within $4 \times 4 \times 1$ orthorhombic primitive unit cells (64 atoms) for α phase and $4 \times 4 \times 1$ hexagonal primitive unit cells (32 atoms) for β phase using the Parlinski-Li-Kawazoe method with an atomic displacement of $0.01 \text{ \AA}$ [36]. As a result of the used harmonic approximation, the Helmholtz vibrational free energy F_{vib}^τ of monolayer $\text{As}_{1-x}\text{P}_x$ at a given τ as a function of composition x and temperature T can be written as

$$F_{\text{vib}}^\tau(x, T) = \frac{1}{2} \sum_{\mathbf{q}, \nu} \hbar \omega^\tau(\mathbf{q}, \nu, x) + k_B T \sum_{\mathbf{q}, \nu} \ln\{1 - \exp[-\hbar \omega^\tau(\mathbf{q}, \nu, x)/k_B T]\}. \quad (6)$$

$\omega^\tau(\mathbf{q}, \nu, x)$ is the phonon frequency at the wave vector $\mathbf{q}$ and the band index ν . $\hbar$ and k_B are the reduced Planck constant and the Boltzmann constant, respectively. Since F_{vib}^τ is linear in composition x for a given phase τ and temperature T , F_{vib}^τ for each particular phase τ is evaluated only for arsenene ($x = 0$) and for phosphorene ($x = 1$). Thus, for a given temperature T and phase τ , F_{vib}^τ of monolayer $\text{As}_{1-x}\text{P}_x$, where $0 < x < 1$, is obtained from linear interpolation between the two end points of the composition space. Note that to ensure the convergence of the phonon calculations, the supercells of arsenene and phosphorene are fully relaxed, in which the forces acting on

each atom within the supercells are less than $10^{-6} \text{ eV/\AA}$, and the sufficiently dense Monkhorst-Pack $\mathbf{k}$ -point grids of $35 \times 35 \times 35$ are used to sample the supercell for deriving ω^τ and F_{vib}^τ of monolayer $\text{As}_{1-x}\text{P}_x$.

III. RESULTS AND DISCUSSION

A. Cluster expansions of monolayer α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$ solid solutions

In this work, the cluster expansions of α and β phases of $\text{As}_{1-x}\text{P}_x$ are performed separately from each other. First, a database of different atomic configurations σ_τ of monolayer $\text{As}_{1-x}\text{P}_x$ must be established. To this end, we employ an algorithm developed by Hart and Forcade [37] to generate 3502 σ_α and 3002 σ_β with, respectively, up to 16 atoms and 14 atoms in the primitive supercell. For the α (β) phase, we single out around a hundred of $\sigma_{\alpha(\beta)}$, calculate their total energy using first-principles approach, and include them in the cluster expansion to determine ECIs, which are accordingly used to predict $E(\sigma_{\alpha(\beta)})$ for all generated $\sigma_{\alpha(\beta)}$ by using Eq. (2). Since the initial ECIs may not do the prediction accurately, its predictive power needs to be improved. We thus utilize $E(\sigma_{\alpha(\beta)})$ predicted by the initial ECIs as a guideline to single out a few more tens or hundreds of $\sigma_{\alpha(\beta)}$, not included in the first expansion, perform first-principles calculations to obtain their energies, and include them, together with those from the first expansion, in the second expansion to determine the ECIs. These procedures can be iterated, until the cluster expansion of desired quality is reached for both α and β phases of monolayer $\text{As}_{1-x}\text{P}_x$.

The final expansion of α (β) phase of $\text{As}_{1-x}\text{P}_x$ includes 389 (361) $\sigma_{\alpha(\beta)}$ and employs a total of 39 (37) ECIs. That is, apart from the zero-site and one-site interactions, the ECIs obtained from the expansion of the α (β) phase are composed of 26 (23) two-site interactions and of 11 (12) three-site interactions. Also, the final expansion of the α (β) phase fits the included 389 (361) $\sigma_{\alpha(\beta)}$ with the cross-validation score of 0.430 (0.281) meV/atom, ensuring the predictive power of the derived ECIs. Figures 2(a) and 2(b) illustrate ΔE_{mix} at $T = 0 \text{ K}$ of α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$, respectively, both evaluated with respect to α -phosphorene and β -arsenene. As a complement to the diagrams, shown in Fig. 2, DFT-calculated ΔE_{mix} of the random solid solutions of α - $\text{As}_{1-x}\text{P}_x$ (β - $\text{As}_{1-x}\text{P}_x$) with the compositions $x = 0.25, 0.50$, and 0.75 , modeled within 64-atom (72-atom) supercells by using the special quasirandom structure (SQS) method [38], are given for comparison to the results derived from the CE method.

According to our calculations, β -arsenene is found to be thermodynamically stable relative to α -arsenene, in which the energy difference between them at $T = 0 \text{ K}$ is $\sim 36.5 \text{ meV/atom}$ [see Fig. 2(a)]. In contrast to arsenene, phosphorene is predicted to be thermodynamically stable in the α phase, whose total energy at $T = 0 \text{ K}$ is only slightly lower than that of the β phase by $\sim 1 \text{ meV/atom}$ [see Fig. 2(b)]. These results are in line with the previous theoretical studies of monolayer arsenene [12–14] and phosphorene [11,12,33] in terms of both their stable allotropic forms and the difference in total energy between the α and β phases. The diagrams, displayed in Fig. 2, additionally

FIG. 2. Ground-state diagram at $T = 0$ K of a monolayer of (a) α - $\text{As}_{1-x}\text{P}_x$ and (b) β - $\text{As}_{1-x}\text{P}_x$, both determined with respect to β -arsenene and α -phosphorene. Red crosses are the CE-predicted energies of mixing ΔE_{mix} of all generated configurations. Open black circles are the DFT-calculated ΔE_{mix} of the selected configurations, included in the final cluster expansions. Thick black lines, connecting two large filled black circles at $x = 0$ and 1, in (a) and (b) represent the DFT-derived ground-state lines of α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$, respectively, while filled blue squares stand for the DFT-calculated ΔE_{mix} of the completely random solid solutions of α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$, both modeled by the SQS method.

reveal that ΔE_{mix} of monolayer α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$, evaluated with respect to α -phosphorene and β -arsenene, are positive for all generated σ_α and σ_β , including those modeled by the SQS approach. This indicates a tendency toward phase separation at $T = 0$ K of 2D monolayer $\text{As}_{1-x}\text{P}_x$, both α and β phases, into α -phosphorene and β -arsenene under thermodynamic equilibrium conditions. We note further that, as far as we are aware, no stable ordered structures of α - $\text{As}_{1-x}\text{P}_x$ or β - $\text{As}_{1-x}\text{P}_x$ have been observed in experiment. This covers not only the 2D monolayer phases of $\text{As}_{1-x}\text{P}_x$, but also its 3D bulk phases, which is accordingly in line with the present prediction.

Furthermore, we find that our optimized in-plane lattice parameters of phosphorene and arsenene (both α and β phases), given in Table I, are in good agreement with the theoretical values previously reported in the literature ($<0.2\%$ difference) [13,33,39], whereas the lattice parameters of monolayer

α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$ solid solutions, obtained from the SQS method, slightly deviate from the Vegard's law ($<0.5\%$) (see Fig. 3).

B. Phase stability of monolayer α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$ solid solutions

To investigate the phase stability of the free-standing monolayer α - and β - $\text{As}_{1-x}\text{P}_x$ solid solutions as a function of temperature T and alloy composition x , we utilize the ECIs obtained from the final cluster expansions, discussed in the previous section, in the canonical MC simulations using the EMC2 code to derive $\Delta G_{\text{mix}}^\alpha$ and $\Delta G_{\text{mix}}^\beta$, as described in

FIG. 3. Calculated lattice parameters of (a) monolayer α - $\text{As}_{1-x}\text{P}_x$ and (b) monolayer β - $\text{As}_{1-x}\text{P}_x$ random solid solutions as a function of alloy composition x . The dashed lines indicate the Vegard's law for the solid solutions of monolayer α - $\text{As}_{1-x}\text{P}_x$ and β - $\text{As}_{1-x}\text{P}_x$.

TABLE I. Calculated lattice parameters of phosphorene and arsenene (both α and β phases). Comparison is made with the theoretical values, previously reported in the literature.

	a (Å)	b (Å)	Reference
α -phosphorene	3.303	4.617	This work
	3.298	4.625	[33]
	3.300	4.620	[39]
β -phosphorene	3.278		This work
	3.277		[33]
	3.280		[39]
α -arsenene	3.687	4.778	This work
	3.677	4.765	[13]
	3.690	4.770	[39]
β -arsenene	3.611		This work
	3.607		[13]
	3.610		[39]

FIG. 4. The mixing Gibbs free-energy curves $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ of the monolayer $\text{As}_{1-x}\text{P}_x$ alloy, calculated with respect to β -arsenene and α -phosphorene, at $T = 150, 300, 450$, and 600 K without taking into account the influence of lattice vibrations $\Delta F_{\text{vib-mix}}^{\alpha}$ and $\Delta F_{\text{vib-mix}}^{\beta}$.

Sec. II C. Since the monolayer $\text{As}_{1-x}\text{P}_x$ alloy may exist either in α phase, in β phase, or in both phases at a given temperature and alloy composition under thermodynamic equilibrium conditions, $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves, calculated with respect to β -arsenene and α -phosphorene, must be drawn together to describe the phase stability of the monolayer $\text{As}_{1-x}\text{P}_x$. Initially, we consider the case, in which the influence of lattice vibrations is not taken into account. Figure 4 displays $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves at some selected temperatures of the monolayer $\text{As}_{1-x}\text{P}_x$, where $0 \leq x \leq 1$. By applying the common-tangent construction to $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves at different fixed temperatures, we outline a phase diagram for monolayer $\text{As}_{1-x}\text{P}_x$, as shown in Fig. 5. The diagram is composed not only of a single-phase region, labeled by β phase, but also of two-phase regions or miscibility gaps, as denoted by $(\beta + \alpha)$ and $(\beta' + \beta'')$. Here, the notations α and

FIG. 5. Phase diagram of monolayer $\text{As}_{1-x}\text{P}_x$, derived from the Monte Carlo simulated $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves at constant temperatures without the contributions arising from the lattice vibrations.

FIG. 6. The mixing Gibbs free-energy curves $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ of the monolayer $\text{As}_{1-x}\text{P}_x$ alloy, including the vibrational contributions $\Delta F_{\text{vib-mix}}^{\alpha}$ and $\Delta F_{\text{vib-mix}}^{\beta}$, respectively, and calculated with respect to β -arsenene and α -phosphorene, at $T = 150, 300, 450$, and 600 K.

β , including β' and β'' , stand for α -phosphorene and solid solutions of monolayer $\beta\text{-As}_{1-x}\text{P}_x$, respectively. According to our prediction, the two-phase region of $(\beta' + \beta'')$, existing at $375 \text{ K} \lesssim T \lesssim 550 \text{ K}$, denotes a region where two solid solutions of monolayer $\beta\text{-As}_{1-x}\text{P}_x$ of different alloy compositions x coexist in thermodynamic equilibrium, while the two-phase region, denoted by $(\beta + \alpha)$ and existing at $T < 375 \text{ K}$, represents a region, where a solid solution of As-rich monolayer $\beta\text{-As}_{1-x}\text{P}_x$ coexists with α -phosphorene. On the other hand, the miscibility gap of $(\beta + \alpha)$, predicted to exist at $T > 375 \text{ K}$ in the P-rich region ($x > 0.925$), indicates a mixture between P-rich monolayer $\beta\text{-As}_{1-x}\text{P}_x$ solid solution and α -phosphorene, both stable under thermodynamic equilibrium condition. At a given temperature T , the equilibrium compositions x of monolayer $\beta\text{-As}_{1-x}\text{P}_x$ solid solutions within the two-phase regions, both $(\beta + \alpha)$ and $(\beta' + \beta'')$, can be obtained by using the lever rule.

We note that, without the impact of lattice vibrations, a noticeable solubility of P atoms in β -arsenene to form a solid solution of monolayer $\beta\text{-As}_{1-x}\text{P}_x$ (β phase) in the As-rich region is predicted at $T > 250 \text{ K}$ (see Fig. 5). On the other hand, a solubility of As atoms in α -phosphorene to form a solid solution of monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ is not predicted even at high temperature beyond the sublimating temperatures at ambient pressure of α -phosphorene and β -arsenene, i.e., 823 K [40] and 887 K [41], respectively. However, as stated in Sec. II D, Aierken *et al.* [33] suggested that the lattice vibrations can induce a structural phase transition in phosphorene, and it is thus expected to have a significant impact on the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$. To quantify the effect of lattice vibrations on the phase stability of monolayer $\text{As}_{1-x}\text{P}_x$, we redetermine $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves by, respectively, taking into consideration the vibrational contributions $\Delta F_{\text{vib-mix}}^{\alpha}$ and $\Delta F_{\text{vib-mix}}^{\beta}$, as discussed in Sec. II D.

Figure 6 displays $\Delta G_{\text{mix}}^{\alpha}$ and $\Delta G_{\text{mix}}^{\beta}$ curves at some selected temperatures, in which the influence of lattice vibrations is taken into account. Our results indicate that, by

FIG. 7. Phase diagram of monolayer $\text{As}_{1-x}\text{P}_x$, derived from the $\Delta G_{\text{mix}}^\alpha$ and $\Delta G_{\text{mix}}^\beta$ with the addition of the corresponding vibrational contributions, i.e., $\Delta F_{\text{vib-mix}}^\alpha$ and $\Delta F_{\text{vib-mix}}^\beta$, respectively, at constant temperatures.

including the contributions arising from the lattice vibrations, β -phosphorene is thermodynamically favored over α -phosphorene already at $T = 0$ K and increasingly so at higher temperature, while α -arsenene is predicted to be thermodynamically stable with respect to β -arsenene at $T \gtrsim 2000$ K, which is considerably higher than the sublimating temperature of the material. This consequently results not only in a disappearance of the two-phase regions of $(\beta + \alpha)$, but also in formation of a continuous series of solid solutions of monolayer $\beta\text{-As}_{1-x}\text{P}_x$ or the β phase across the whole composition range at $T \gtrsim 550$ K, as can be seen from Fig. 7 illustrating a phase diagram of monolayer $\text{As}_{1-x}\text{P}_x$, derived from the $\Delta G_{\text{mix}}^\alpha$ and $\Delta G_{\text{mix}}^\beta$ with the addition of the corresponding vibrational contributions, i.e., $\Delta F_{\text{vib-mix}}^\alpha$ and $\Delta F_{\text{vib-mix}}^\beta$, respectively, at constant temperatures.

With the inclusion of the vibrational contributions, it should, however, be emphasized that in Ref. [33], at $T = 0$ K and $x = 1$, $\Delta G_{\text{mix}}^\beta$ is only slightly higher than $\Delta G_{\text{mix}}^\alpha$ by less than 1 meV/atom, and thus α -phosphorene is predicted to transform into β -phosphorene at $T > 135$ K. This is in contrast to this work, where at $T = 0$ K and $x = 1$ $\Delta G_{\text{mix}}^\beta$ is readily lower than $\Delta G_{\text{mix}}^\alpha$ by ~ 1 meV/atom, indicating the higher thermodynamic stability of β -phosphorene relative to that of α -phosphorene. The difference in temperature at which β -phosphorene is thermodynamically stable with respect to α -phosphorene between this work and Ref. [33] may be attributed to the effect of the thermal lattice expansion, which has been neglected in this work. Even though the relative stability between α and β phases of phosphorene at $T \leq 135$ K, predicted here, is different from that of Ref. [33], it is rather obvious that at $T > 135$ K monolayer $\beta\text{-As}_{1-x}\text{P}_x$ is thermodynamically favored over monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ across the whole composition range, as demonstrated in Fig. 6.

Although α phase of monolayer $\text{As}_{1-x}\text{P}_x$ is never stable from thermodynamic consideration with respect to β phase, a large solid solubility of As atoms in bulk α -phosphorus to form a bulk solid solution of $\alpha\text{-As}_{1-x}\text{P}_x$, in which the arsenic content can be as high as 80 at.% ($x \approx 0.2$), was theoretically

predicted at elevated temperature [22] and also in line with the experimental syntheses of bulk $\alpha\text{-As}_{1-x}\text{P}_x$ with highly tunable compositions ($0.17 \lesssim x \lesssim 1$), conducted by Liu *et al.* [18] and Osters *et al.* [42]. On the other hand, a solubility of P atoms in β -arsenic to form a bulk solid solution of $\beta\text{-As}_{1-x}\text{P}_x$ is rather small ($x < 0.1$) even at temperature above the sublimating temperature of the materials [22]. This thus opens up a route to fabricate monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ in a metastable state from the bulk counterpart by using the exfoliation methods, as demonstrated by Liu *et al.* [18]. In comparison with 3D bulk $\text{As}_{1-x}\text{P}_x$, our results on 2D monolayer $\text{As}_{1-x}\text{P}_x$ derived here evidently suggest that the alloying behavior of 2D monolayer $\text{As}_{1-x}\text{P}_x$ can be different from its 3D bulk counterparts, which should be considered in its future studies.

C. Possible existence of ordered solid solutions of monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$

Although ordered structures/compounds of monolayer $\alpha\text{-As}_{1-x}\text{P}_x$ and $\beta\text{-As}_{1-x}\text{P}_x$ have been demonstrated in Sec. III A to be thermodynamically unstable even at $T = 0$ K with respect to phosphorene and arsenene (see Fig. 2), they might exist in metastable states. This could be attributed to a significant difference in the lattice parameters (a and b) between phosphorene and arsenene of up to $\sim 11\%$ (see Table I), giving rise to a non-negligible *constituent strain energy* (ΔE_{cs}) [43,44], which must accordingly be taken into consideration for determining the stability of the ordered monolayer $\text{As}_{1-x}\text{P}_x$. For this particular case, ΔE_{cs} of a given σ_τ of monolayer $\text{As}_{1-x}\text{P}_x$ is defined by a modification of Eq. (1):

$$\Delta E_{\text{cs}}(\sigma_\tau) = E(\sigma_\tau, a_{\sigma_\tau}) - x_{\text{As}}E_{\text{As}}(a_{\sigma_\tau}) - x_{\text{P}}E_{\text{P}}(a_{\sigma_\tau}), \quad (7)$$

where a_{σ_τ} is the optimized lattice constants of monolayer $\text{As}_{1-x}\text{P}_x$ exhibiting a configuration σ_τ . For example, we consider the lowest energy σ_β of $\beta\text{-As}_{0.5}\text{P}_{0.5}$, as included in Fig. 2(b). We find that its ΔE_{cs} is -40.56 meV/atom, which is somewhat lower than ΔE_{mix} evaluated from the same σ_β ($+14.38$ meV/atom). Such a large contribution from ΔE_{cs} implies that clustering of As and P atoms to form arsenene and phosphorene, respectively, is unlikely to take place in an actual experiment, and consequently, the metastability of the ordered monolayer $\beta\text{-As}_{0.5}\text{P}_{0.5}$ under consideration might be maintained supposedly by the in-plane strain, induced by the difference in lattice parameters between the elemental phases. One should, however, also be aware of a possibility of incoherent phase separation, in which an alloy, whose constituent phases have very different lattice parameters and/or different crystal structures, could phase separate into its constituent phases. According to our analysis, an access to the (possibly metastable) ordered structures of monolayer $\text{As}_{1-x}\text{P}_x$ can be rather limited and they might be achieved in practice only at low temperature. As a consequence, the ordered structures of monolayer $\text{As}_{1-x}\text{P}_x$ (both α and β phases), regularly considered in the previous theoretical studies [14–17], may not exist in nature, while fabrication of monolayer $\text{As}_{1-x}\text{P}_x$ by using, for example, epitaxial growth [45,46], chemical vapor deposition [47], and pulse laser deposition [48] techniques, in which the operation temperature can reach several hundred Kelvin, can lead to the formation of disordered solid

solutions, in particular β -As_{1-x}P_x, under the thermodynamic equilibrium conditions. Phase separation of the as-synthesized disordered solid solutions of monolayer β -As_{1-x}P_x into the relevant competing phases upon cooling down is, however, likely to be hindered due to a lack of atomic diffusion at low temperature.

IV. CONCLUSION

We employ the cluster-expansion technique, combined with the canonical Monte Carlo simulations and the harmonic approximation, to investigate the phase stability of monolayer As_{1-x}P_x in the α and β phases. Our findings show that, as $T \rightarrow 0$ K, the monolayer As_{1-x}P_x displays a tendency toward phase segregation into its constituent elemental phases without formation of stable ordered compounds/structures both of α -As_{1-x}P_x and of β -As_{1-x}P_x. We further find from thermodynamic consideration that β -As_{1-x}P_x is favored over α -As_{1-x}P_x across the entire composition range even at $T = 0$ K and increasingly so at higher temperature, and a complete closure of a miscibility gap takes place at $T \sim 550$ K at which monolayer β -As_{1-x}P_x with $0 \leq x \leq 1$ is stable as a single-phase disordered solid solution in thermodynamic equilibrium. Evidently, these findings not only demonstrate

that the ordered structures of monolayer As_{1-x}P_x (both α and β phases), frequently discussed in the previous studies [14–17], may not exist in nature, but also suggest that monolayer α -As_{1-x}P_x recently fabricated in experiments *via* exfoliation of bulk α -As_{1-x}P_x [18] is metastable with respect to monolayer β -As_{1-x}P_x.

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