First-principles prediction of stabilities and instabilities of compounds and alloys in the ternary B-As-P system

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We examine the thermodynamic stability of compounds and alloys in the ternary B-As-P system theoretically using first-principles calculations. We demonstrate that the icosahedral B12As2 is the only stable compound in the binary B-As system, while the zinc-blende BAs is thermodynamically unstable with respect to B12As2 and the pure arsenic phase at 0 K, and increasingly so at higher temperature, suggesting that BAs may merely exist as a metastable phase. On the contrary, in the binary B-P system, both zinc-blende BP and icosahedral B12P2 are predicted to be stable. As for the binary As-P system, As1−xPx disordered alloys are predicted at elevated temperature—for example, a disordered solid solution of up to ~75 at.% As in black phosphorus as well as a small solubility of ~1 at.% P in gray arsenic at T = 750 K, together with the presence of miscibility gaps. The calculated large solubility of As in black phosphorus explains the experimental syntheses of black-phosphorus-type As1−xPx alloys with tunable compositions, recently reported in the literature. We investigate the phase stabilities in the ternary B-As-P system and demonstrate a high tendency for a formation of alloys in the icosahedral B12(As1−xPx)2 structure by intermixing of As and P atoms at the diatomic chain sites. The phase diagram displays noticeable mutual solubility of the icosahedral subpnictides in each other even at room temperature as well as a closure of a pseudobinary miscibility gap around 900 K. As for pseudobinary BAs1−xPx alloys, only a tiny amount of BAs is predicted to be able to dissolve in BP to form the BAs1−xPx disordered alloys at elevated temperature. For example, less than 5% of BAs can dissolve in BP at T = 1000 K. The small solubility limit of BAs in BP is attributed to the thermodynamic instability of BAs with respect to B12As2 and As.

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I. INTRODUCTION

Boron arsenide (BAs) and boron phosphide (BP) with a cubic zinc-blende crystal structure, generally referred to as boron pnictides [Fig. 1(a)], belong to the group of III–V semiconductors, having been of great importance for electronic and optoelectronic applications [1–8]. BAs has recently received special attention, as it has been predicted to be originating from the presence of As vacancies, since the as-synthesized BAs samples were arsenic-deficient [10–12]. At T ∼ 1190 K, BAs irreversibly decomposes into boron subarsenide (B12As2) due to the evaporation of As from BAs [13–15]. As a consequence, considerable efforts are underway to make high-quality macroscopic crystals of BAs, calling for a study of the thermodynamic stability of BAs, having been rarely discussed in the literature [16], and thus deserving further investigation. In a similar fashion, BP decomposes into boron subphosphide (B12P2) upon heating to T ∼ 1500 K. B12As2 and B12P2 are isostructural and can be seen as derivatives of α-rhombohedral boron [Fig. 1(b)]. Owing to their crystal structures, governed by B12 clusters, B12As2 and B12P2 display several highly valued properties [17–19], e.g., high chemical stability, high melting point (Tm > 2300 K), and wide electronic band gap (Eg > 3 eV). As a consequence, the two subpnictides are promising materials for fabrication of betavoltaic cells [20] and high-temperature electronic [21] and thermoelectric devices [22,23]. Furthermore, due to their richness of boron, together with a large thermal neutron absorption cross section of the isotope 10B, the materials have been realized as candidates for solid-state thermal neutron detectors [24].

Since alloying is well known as a process for tuning properties of materials, previous theoretical study of mixing thermodynamics of zinc-blende BAs1−xPx alloys [25] proposed the pseudobinary phase diagram of BAs1−xPx, showing the equilibrium solubility limit of BP in BAs and vice versa, i.e., the miscibility gap, at T ≤ 1168 K. For example, solid solutions of ~18% of BP in BAs and ~18% of BAs in BP were predicted at T = 1000 K. However, it is questionable whether the phase diagram, sketched in Ref. [25], can provide a proper description of the thermodynamic stability of BAs1−xPx alloys at elevated temperature, as the two subpnictides and their constituent elements are not taken into account as competing phases of BAs1−xPx alloys.

In this work, we use a first-principles approach to clarify the thermodynamic stability of compounds/alloys in the ternary B-As-P system. We first consider the thermodynamic stability of the binary B-As and B-P compounds, existing in the ternary B-As-P system as well as binary As1−xPx alloys, against their constituent elements, given by α-rhombohedral boron, black phosphorus [Fig. 1(c)], and gray arsenic [Fig. 1(d)], as well as the relevant binary phases. We then explore, respectively, the mixing thermodynamics of pseudobinary alloys of icosahedral
B_{12}(As_{1-x}P_x)_{x/2} and zinc-blende BAs_{1-x}P_x phases. The thermodynamic stability of all considered phases is determined by the Gibbs free energy as a function of temperature, where the entropy, arising from configurational disorder in the mixing alloys, is derived within the mean-field approximation.

Our investigation reveals that BP and B_{12}P_{2} are both stable compounds in the B-P system, while in the case of the B-As system BAs is found to be thermodynamically unstable against B_{12}As_{2} and gray arsenic, indicating that BAs may merely exist as a metastable phase. As for the binary As-P system, mixing As_{1-x}P_{x} alloys are predicted at elevated temperature—for example, a solid solution of \( \sim 75 \) at.\% As in black phosphorus at \( T = 750 \) K, and a small solubility of \( \sim 1 \) at.\% P in gray arsenic at the same temperature, together with the presence of miscibility gaps. Concerning the ternary B-As-P system, we predict the intermixing of As and P atoms at the diatomic chain sites of the icosahedral phase to form B_{12}(As_{1-x}P_{x})_{x/2} alloys even at room temperature. As for the zinc-blende pseudobinary BAs_{1-x}P_x alloys, we find that only a small amount of BAs can dissolve in BP. For example, less than 5\% of BAs can dissolve in BP at \( T = 1000 \) K.

II. METHODOLOGY

A. Computational details

The total energy calculations are performed, based on the density functional theory (DFT), in which the projector augmented wave (PAW) method [26], as implemented in the Vienna \textit{ab initio} simulation package (VASP) [27,28], and the generalized gradient approximation (GGA), proposed by Perdew, Burke, and Ernzerhof (PBE96) [29] for the exchange-correlation functional, are used. A plane-wave energy cutoff is set to 600 eV and the Monkhorst-Pack k-point mesh [30] is chosen for the Brillouin zone integration. For each considered structure, the calculated total energy is converged within an accuracy of 1 meV/atom, with respect to both the energy cutoff and the number of k points, sampling the Brillouin zone. The equilibrium volume at \( T = 0 \) K, denoted by \( V_0 \), for each considered structure is obtained from the minimum point of the total energy curve \( E_0(V) \), calculated for a set of different fixed volumes, where the internal atomic positions and the cell shape are allowed to relax. The tetrahedron method for the Brillouin zone integration, suggested by Blöchl [31], is used for calculating electronic density of states.

Since the standard DFT calculations cannot accurately describe the van der Waals (vdW) interactions between the atomic layers, existing in gray arsenic, black phosphorus, and As_{1-x}P_x alloys, we employ the vdW correction, proposed by Grimme (DFT-D2) [32], to account for the interactions. In general, the use of the vdW correction results in a systematic shift of the total energy, caused by the correction term, added to the standard DFT total energy [32]. We notice that such a shift of the total energy can, somehow, be problematic, when, for example, evaluating the thermodynamic stability of BAs and B_{12}As_{2}, whose total energies are obtained from the standard DFT calculations, with respect to gray arsenic, whose total energy is shifted by the vdW correction term. To avoid such a problem in the present work, the vdW correction is only used for optimizing the crystal structures of gray arsenic, black phosphorus, and As_{1-x}P_x alloys, while the total energies of the optimized structures are all carried out by standard DFT calculations (GGA-PBE96).

In this work, As_{1-x}P_x, and BAs_{1-x}P_x disordered alloys are modeled with the special quasirandom structure (SQS) method [33]. As for the binary As_{1-x}P_x alloys, two types of structures, i.e., black-phosphorus-type and gray-arsenic-type structures, must be considered. The black-phosphorus-type and the gray-arsenic-type As_{1-x}P_x alloys with the compositions \( x = 0.25, 0.50, \) and 0.75 are modeled within 4 \( \times \) 3 supercells (192 atoms) and 4 \( \times \) 4 \( \times \) 2 supercells (192 atoms), respectively, in which As and P atoms are distributed on the lattice sites to mimic a random alloy. The SQS models of zinc-blende BAs_{1-x}P_x alloys are constructed within 4 \( \times \) 3 \( \times \) 3 supercells (288 atoms), where the compositions \( x = 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, \) and 0.875. In this case, all B atoms fully occupy the boron sublattice, while As and P atoms are randomly distributed due to the use of the SQS method on the pnictide sublattice. For modeling the mixing alloys between B_{12}As_{2} and B_{12}P_{2}, we employ a superatom special quasirandom structure (SA-SQS) method [34–36], designed
for modeling configurational disorder in icosahedral boron-rich solids, e.g., boron carbide and boron suboxide, whose crystal structures are analogous to those of boron subphosphides. The SA-SQS models of the mixing alloys include 504 atoms (4×3×3 supercells) and the composition x = 0.167, 0.333, 0.50, 0.667, and 0.833. Detailed explanation of structural modeling of the mixing alloys between B_{12}As_2 and B_{12}P_2 will be further provided in Sec. III C.

B. Thermodynamic stability

In the present work, the thermodynamic stability of compounds and alloys in the ternary B-As-P system, especially As_{1−x}P_x, B_{12}(As_{1−x}P_x)_2, and BAs_{1−x}P_x, with respect to their relevant competing phases is determined by the Gibbs free energy at zero pressure G(T, P = 0):

\[ G(T, 0) = E_0(V_0) - TS_{\text{conf}}(T, V_0). \]

\[ E_0(V_0) \] is the total energy at \( T = 0 \) K, directly obtained from the DFT calculations, and is evaluated at the equilibrium volume \( V_0 \). The term \( TS_{\text{conf}}(T, V_0) \) in Eq. (1) accounts for a contribution arising from the configurational disorder, where \( S_{\text{conf}}(T, V_0) \) is defined as the configurational entropy, and can be reasonably estimated for a random alloy, e.g., As_{1−x}P_x, and BAs_{1−x}P_x alloys, by using the mean-field approach, to be

\[ S_{\text{conf}} = -k_B N \sum_{i=1}^{n} x_i \ln(x_i). \]

\( k_B \) is the Boltzmann constant. \( N \) and \( x_i \) stand for the number of lattice sites, in which the mixing is done, and the concentration of the \( i \)th component of an alloy, involved with the configurational disorder, respectively. We note that for zinc-blende BAs_{1−x}P_x alloys, \( S_{\text{conf}} \) evaluated at \( N \) equal to 1 should be compared with \( E_0(V_0) \) per formula unit, instead of \( E_0(V_0) \) per atom as in the case of As_{1−x}P_x alloys. Note also that the derived \( S_{\text{conf}} \), given in Eq. (2), is volume- and temperature-independent. In the case of the constituent elements and compounds/ alloys, which are fully ordered, \( S_{\text{conf}} \) vanishes.

To take into account the effect of temperature on the thermodynamic stability of the ordered structures in the binary B-P and B-As systems, we introduce the contribution from the lattice dynamics, given by the Helmholtz free energy \( F_{\text{vib}} \) (\( T, V \)):

\[ F_{\text{vib}}(T, V) = \frac{1}{2} \sum_{q, v} \hbar \omega(q, v, V) \]

\[ + k_B T \sum_{q, v} \ln[1 - \exp(-\hbar \omega(q, v, V)/k_B T)], \]

where \( \hbar \) and \( \omega(q, v, V) \) are the reduced Planck constant and the phonon frequency at the wave vector \( q \) and the band index \( v \), respectively. The phonon frequencies \( \omega \) are calculated within the quasiharmonic approximation, using the PHONOPY package for phonon calculations [52,53], and are thus volume-dependent. The force constants are calculated within fully relaxed supercells, where the total force acting on each atom is less than \( 10^{-6} \) eV/Å, by using the Parlinski-Li-Kawazoe method [54] with a finite displacement of 0.01 Å.

Supercells of different sizes (96–112 atoms) are used for the phonon calculations, depending on compositions in the binary B-P and B-As systems. The supercells are then sampled with \( 21 \times 21 \times 21 \) Monkhorst-Pack k-point grids in order to secure the convergence of the phonon frequencies and thus \( F_{\text{vib}}(T, V) \). The Gibbs free energy \( G(T, P = 0) \) for each ordered structure in the binary B-P and B-As systems, taking into account the influence of lattice vibrations, can thus be evaluated from

\[ G(T, p) = \min_V [E_0(V) + F_{\text{vib}}(T, V) + p V]. \]

We emphasize that the influence of lattice vibrations will only be considered when evaluating the thermodynamic stability of the ordered structures in the binary B-P and B-As systems in the following section, Sec. III A, where \( G(T, 0) \) are calculated from the expression, given in Eq. (4). Instead, the stability of the As_{1−x}P_x, B_{12}(As_{1−x}P_x)_2 and BAs_{1−x}P_x alloys with respect to the relevant competing phases, discussed in Secs. III B to III D, will be evaluated using \( G(T, 0) \), given in Eq. (1), where the influence of lattice vibrations is neglected. This is because \( F_{\text{vib}}(T, V) \) is typically of small importance for isostructural alloys as compared to \( S_{\text{conf}} \). For example, we find that \( G(T, 0) \) of (B_{12}As_{1−x})_2 (B_{12}P_{2−x})_2 alloys, including \( F_{\text{vib}}(T, V) \), differs from that of (B_{12}As_{1−x})_3 (B_{12}P_{2−x})_3 alloys without \( F_{\text{vib}}(T, V) \) by less than 0.5 meV/atom at \( T = 2000 \) K.

III. RESULTS AND DISCUSSION

A. Binary B-P and B-As systems

We first investigate the thermodynamic stability of compounds in the binary B-P and B-As systems. Table I shows a list of structural parameters as well as electronic band gaps, calculated in this work, for the constituent elements and compounds, existing in the binary B-P and B-As systems. We find that our calculated structural parameters of the considered phases are in good agreement with the experiments and previous calculations, confirming the reliability of our calculations. Except for gray arsenic, which is semimetallic, the other phases are predicted to be semiconductors in qualitative accord with the experiments. However, despite being in agreement with the previous calculations, our calculated band gaps are somewhat underestimated, as compared to the experiments. This can be attributed to the use of semilocal functionals, such as LDA and GGA, typically underestimating electronic band gaps.

The stability of B_{12}P_2, BP, B_{12}As_2, and BAs with respect to their constituent elements can be determined by calculating the Gibbs free energy of formation \( \Delta G^{\text{form}} \), in which the Gibbs free energy as a function of temperature for each phase is calculated by using the expression given in Eq. (4). Figure 2 illustrates the convex hulls of the binary B-P and B-As systems at \( T = 0, 300, 500, \) and 800 K. We note that black phosphorus and gray arsenic sublimate at 823 K [55] and 887 K [56], respectively. As can be seen from the convex hull of the B-P system [Fig. 2(a)], both B_{12}P_2 and BP are lying on the hull, confirming their thermodynamic stabilities. On the other hand, the convex hull of the B-As system, as depicted in Fig. 2(b), reveals that B_{12}As_2 is the only stable compound in the B-As system, while BAs, being above the convex hull at \( T = 0 \) K by 77 meV/atom, is thermodynamically unstable against B_{12}As_2 and gray arsenic. We also find that as the temperature...
TABLE I. GGA-PBE96-calculated lattice parameters \((a, b, c)\), angles \((\alpha, \beta, \gamma)\), and electronic band gaps \((E_g)\) of the constituent elements and compounds in the binary B-P and B-As systems, considered in the present work. Note that in this work, the van der Waals (vdW) correction suggested by Grimme (DFT-D2) [32] is used to describe the weak interactions between the layers of P and As for black phosphorus and gray arsenic, respectively, while optimizing their structures. Comparison is made with experiments and previous theoretical calculations.

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<th>(b) (Å)</th>
<th>(c) (Å)</th>
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<th>(\beta) (deg)</th>
<th>(\gamma) (deg)</th>
<th>(E_g) (eV)</th>
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Increases, BAs becomes even more unstable, demonstrated by the increase of \(\Delta G^{\text{form}}\) with respect to the convex hull.

To verify that the instability of BAs does not arise from the uncertainty of the used exchange-correlation functional, that is, GGA-PBE96, we redetermine the stability of BAs at \(T = 0\) K with respect to \(B_{12}As_2\) and gray arsenic by using the local density approximation (LDA), applying the Ceperly and Alder (CA) [57] exchange correlation, as parametrized by Perdew and Zunger (PZ) [58], as well as the hybrid functional HSE06 [59,60] for the exchange-correlation functionals. We note that, in these two cases, \(\Delta G^{\text{form}}\) is evaluated without considering the influence of lattice dynamics, and the vdW correction is not applied. We find that the result obtained from the use of LDA-CAPZ is more or less the same as that calculated by GGA-PBE96, in which \(\Delta G^{\text{form}}\) of BAs is 66 meV/atom above the convex hull. On the one hand, the \(\Delta G^{\text{form}}\) of BAs estimated by the use of HSE06 is 10 meV/atom above the convex hull. Even though the HSE06-estimated \(\Delta G^{\text{form}}\) is found to be lower than those obtained from LDA-CAPZ and GGA-PBE96, it still does not qualitatively change our findings that BAs is thermodynamically unstable with respect to \(B_{12}As_2\) and gray arsenic.

According to the literature [61], large BP wafers can be synthesized using chemical vapor deposition (CVD). This is in line with our prediction that BP is the stable compound in the B-P system. On the other hand, only tiny millimeter-sized crystalline samples of BAs have so far been achieved in the experiments [5,10,11]. This is probably limited by the thermal decomposition of BAs into \(B_{12}As_2\) due to the evaporation of As from BAs at elevated temperature [13–15], where the atomic diffusion is usually playing a role. We note that previous theoretical studies [12,62,63] demonstrated that BAs...
and black phosphorus, and (b) B\textsubscript{12}As\textsubscript{2} and BAs with respect to disordered As\textsubscript{1} compositions, which are lying on and above the convex hulls at different fixed temperatures, respectively.

The thermodynamic stability of the As\textsubscript{1} models of disordered As\textsubscript{1} arsenic, with the compositions structures, which are those of black phosphorus and gray alloys in this work are considered, based on two types of crystal facts together with our prediction in the present work that is dynamically and mechanically stable. Considering these facts together with our prediction in the present work that BAs is thermodynamically unstable against B\textsubscript{12}As\textsubscript{2} and gray arsenic, we suggest that BAs may either exist as a metastable phase, or be stabilized by unavoidable high concentrations of either As vacancies or B interstitials as As deficiencies were indeed obtained [5,10,11].

B. Mixing thermodynamics of binary As\textsubscript{1-x}P\textsubscript{x} alloys

The next step is to examine the mixing thermodynamics of the As\textsubscript{1-x}P\textsubscript{x} alloys. As described in Sec. II A, the As\textsubscript{1-x}P\textsubscript{x} alloys in this work are considered, based on two types of crystal structures, which are those of black phosphorus and gray arsenic, with the compositions \( x = 0.25, 0.5, \) and 0.75. The models of disordered As\textsubscript{1-x}P\textsubscript{x} solid solutions are constructed within 192-atom supercells by the SQS method [33]. The thermodynamic stability of the As\textsubscript{1-x}P\textsubscript{x} alloys with respect to black phosphorus and gray arsenic is determined by the mixing Gibbs free energy, \( \Delta G_{\text{mix}} \). The Gibbs free energy of the As\textsubscript{1-x}P\textsubscript{x} alloys at each composition \( x \) is evaluated by the expression, given in Eq. (1). Figure 3 illustrates \( \Delta G_{\text{mix}} \) of the ordered and disordered As\textsubscript{1-x}P\textsubscript{x} alloys at \( T = 0 \) K, where the term \(-TS_{\text{conf}}\) on the right-hand side of Eq. (1) vanishes. The positive \( \Delta G_{\text{mix}} \) indicates a driving force for phase separation of both the ordered and disordered As\textsubscript{1-x}P\textsubscript{x} alloys into black phosphorus and gray arsenic.

To consider the stability of the As\textsubscript{1-x}P\textsubscript{x} alloys at \( T > 0 \) K, the mixing Gibbs free energy \( \Delta G_{\text{mix}} \) at \( T = 0 \) K of the disordered As\textsubscript{1-x}P\textsubscript{x} alloys, shown in Fig. 3, is fitted with a cubic spline interpolation and combined with the term \(-TS_{\text{conf}}\) on the right-hand side of Eq. (1) as a driving force for phase separation of both black-phosphorus-type and gray-arsenic-type As\textsubscript{1-x}P\textsubscript{x} disordered alloys at different fixed temperatures, depicted in Fig. 4. We note again that black phosphorus and gray arsenic sublimate at 823 K [55] and 887 K [56], respectively. The phase diagram, obtained by a common tangent construction to the \( \Delta G_{\text{mix}} \) curves of both black-phosphorus-type and gray-arsenic-type As\textsubscript{1-x}P\textsubscript{x} disordered alloys at different fixed temperatures, depicted in Fig. 4. We note again that black phosphorus and gray arsenic sublimate at 823 K [55] and 887 K [56], respectively. The phase
diagram of the $\text{As}_{1-x}\text{P}_x$ alloys, shown in Fig. 4, is plotted with an assumption that the $\text{As}_{1-x}\text{P}_x$ alloys remain solid for the whole temperature range considered.

The phase diagram reveals two single-phase regions, as denoted by $\alpha$ and $\beta$, at elevated temperature, as well as the presence of two-phase regions (miscibility gaps). $\alpha$ and $\beta$ phases represent, respectively, the gray-arsenic-type and black-phosphorus-type $\text{As}_{1-x}\text{P}_x$ disordered alloys. According to our prediction, a noticeable amount of $\text{P}$ ($x \geq 0.01$ in our case) can dissolve in gray arsenic to form gray-arsenic-type $\text{As}_{1-x}\text{P}_x$ solid solution ($\alpha$ phase) at $T > 700$ K, while As atoms can dissolve more easily in black phosphorus to form black phosphorus-type $\text{As}_{1-x}\text{P}_x$ solid solution ($\beta$ phase). We find that the degree of solubility of $\text{P}$ atoms in gray arsenic is rather limited. At $T = 1500$ K, ~8 at.% of $\text{P}$ can dissolve in gray arsenic. The degree of solubility of $\text{As}$ atoms in black phosphorus is, on one hand, largely affected by temperature; for example, the solubility of ~4 at.% of $\text{As}$ in black phosphorus at $T = 450$ K increases up to ~83 at.% at $T = 1500$ K. The miscibility gap on the $\text{As}$-rich side, labeled as $\alpha + \beta$, represents a region where $\alpha$ and $\beta$ phases coexist, and is predicted to exist up to high temperature. The region $\beta^+ + \beta^\prime$ is also a miscibility gap, where two $\beta$ phases of different compositions $x$ coexist.

Our prediction of the thermodynamic stability of the $\text{As}_{1-x}\text{P}_x$ disordered alloys is found to be in line with the recent experimental syntheses of the black-phosphorus-type $\text{As}_{1-x}\text{P}_x$ alloys with different and tunable compositions ($0.17 \leq x \leq 1$) at elevated temperature, close to the sublimating points of the materials [64,65]. According to the reports, found in the literature [64,65], the as-synthesized black-phosphorus-type $\text{As}_{1-x}\text{P}_x$ alloys remain metastable at low temperature, presumably due to a lack of atomic mobility of $\text{As}$ and $\text{P}$ atoms. Note that a direct transformation of the black-phosphorus-type $\text{As}_{1-x}\text{P}_x$ alloys to the gray-arsenic-type $\text{As}_{1-x}\text{P}_x$ alloys under high pressure has been reported [66].

C. Mixing thermodynamics of alloys between icosahedral $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$

In this section, we investigate the thermodynamics of mixing between the two boron subpnictides, i.e., $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$, which are isostructural [Fig. 1(b)]. To start with, we explore a possibility for the two subpnictides to configurationally disorder, that is, substitution of $\text{As}$ and $\text{P}$ atoms in the diatomic chains for the icosahedral B atom. Configurational disorder in icosahedral boron-rich solids has recently been highlighted, especially for boron carbide, as it has been predicted to play an important role to the stability and the properties of the material at elevated temperature [34–36]. We consider different kinds of $\text{B}/\text{P}$ and $\text{B}/\text{As}$ substitutional defects in the dilute limit, typically involved with only 2 or 4 atoms, in a fully relaxed $2 \times 2 \times 2$ supercell of $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$, respectively. To keep the global compositions of the two subpnictides fixed as $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$, the substitutional defects are only generated by swapping $\text{P}$ or $\text{As}$ atoms, residing in the diatomic chains with icosahedral B atom in the supercell.

The dilute defect formation energy, $\Delta E_{\text{defect}}$, is calculated by

$$\Delta E_{\text{defect}} = E_{\text{defect}}(V_0) - E_{\text{defect−free}}(V_0),$$

where $E_{\text{defect}}$ and $E_{\text{defect−free}}$ are defined as the total energy of the defective and the defect-free structures, respectively. During the calculations of $E_{\text{defect}}$, the supercell volumes of the defective structures are kept fixed at the equilibrium volume $V_0$ of the defect-free structure and thus only the atomic coordinates within the supercells are relaxed.

We find that the calculated $\Delta E_{\text{defect}}$ falls into a range between 2.4 and 9.6 eV for $\text{B}_{12}\text{P}_2$, while it ranges from 2.8 to 10.4 eV for $\text{B}_{12}\text{As}_2$. Also, the lowest $\Delta E_{\text{defect}}$ of the subpnictides are found to be relatively high, as compared to those of boron carbides, i.e., 0.23 eV and 0.6 eV for $\text{B}_4\text{C}$ [34] and $\text{B}_{13}\text{C}_2$ [35], respectively. We thus conclude that configurational disorder at the atomic level, induced by the substitutional defects, is highly unlikely for the two boron subpnictides.

To construct theoretical models of the mixing alloys between $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$, we employ a superatom special quasirandom structure (SA-SQS) method [34–36]. In this case, a $\text{B}_{12}$ icosahedral cluster, together with a diatomic chain, is treated as a superatom. As a first step, we define two types of superatoms, i.e., $\text{B}_{12}(\text{P-P})$ and $\text{B}_{12}(\text{As-As})$, as shown in Figs. 5(a) and 5(b), respectively. The configuration of superatoms is then modeled in accord with a random alloy pattern, generated by the SQS technique. In the present work, the SA-SQS models of the mixing alloys between $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$ are constructed within $4 \times 3 \times 3$ supercells (504 atoms) with the compositions $x = 0.167, 0.333, 0.50, 0.667$, and 0.833. The theoretical model of the disordered alloys, including the $\text{B}_{12}(\text{As-As})$ and $\text{B}_{12}(\text{P-P})$ superatoms, is denoted by $\text{B}_{12}(\text{As-As})_{1-x}\text{B}_{12}(\text{P-P})_x$. We note that, besides the configurational disorder between the $\text{B}_{12}(\text{As-As})$ and $\text{B}_{12}(\text{P-P})$ superatoms due to the use of SQS method, $\text{P}$ and $\text{As}$ atoms residing in the diatomic chains may intermix, giving rise to $\text{P}$-$\text{As}$ and $\text{As}$-$\text{P}$ chains, which must also be taken into consideration for evaluating the mixing thermodynamics of the alloys.

To account for the presence of the $\text{P}$-$\text{As}$ and $\text{As}$-$\text{P}$ diatomic chains, we define two more types of superatoms, i.e., $\text{B}_{12}(\text{P-As})$ and $\text{B}_{12}(\text{As-P})$, as shown in Figs. 5(c) and 5(d), respectively, and include them, together with the former two types of superatoms, in modeling the disordered mixing alloys, denoted by $\text{B}_{12}(\text{As-As})_{1-x}\text{B}_{12}(\text{P-P})_x$. This time, the SA-SQS models of the $\text{B}_{12}(\text{As-As})_{1-x}\text{B}_{12}(\text{P-P})_x$ alloys are made, by which the concentrations of each superatomic species at each composition $x$ are given in a way that maximizes the configurational entropy $S_{\text{conf}}$, given in Eq. (2), which is a random distribution of $\text{As}$ and $\text{P}$ atoms on the diatomic chain sites. We note also that, within

FIG. 5. Four types of superatoms, defined for modeling the mixing alloys between $\text{B}_{12}\text{P}_2$ and $\text{B}_{12}\text{As}_2$: (a) $\text{B}_{12}(\text{P-P})$, (b) $\text{B}_{12}(\text{As-As})$, (c) $\text{B}_{12}(\text{P-As})$, and (d) $\text{B}_{12}(\text{As-P})$. White, gray, and red spheres represent $\text{B}$, $\text{P}$, and $\text{As}$ atoms, respectively.
the superatom framework, \( N \) and \( x_i \) in Eq. (2) are defined, instead, as the number of superatomic sites in a supercell and the concentration of the \( i \)th superatomic species, respectively. The concentrations of the four superatomic species, used for the SA-SQS modeling of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) disordered alloys with the composition \( x = 0.167, 0.333, 0.5, 0.667, \) and 0.833, are summarized in Table II.

By inspecting the optimized structural parameters and the electronic band gaps of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) disordered alloys, we find that both properties follow Vegard's law very well. The intermixing of As and P atoms at the diatomic chain sites is found to have a minimal impact on the structural and electronic properties of the mixing alloys, as can be seen from the almost identical lattice parameters and the band gaps between the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys (not shown).

The thermodynamic stability of \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys are first examined at \( T = 0 \) K by calculating \( \Delta G_{\text{mix}} \) with respect to seven possible competing phases; these are \textalpha-rhombohedral boron, black phosphorus, gray arsenic, \( \text{B}_{12}\text{P}_{2} \), BP, \( \text{B}_{12}\text{As}_{2} \), and BAs. Regardless of \( x \), both \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys are thermodynamically unstable against phase decomposition into \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \). As a result, it is sufficient to from now on evaluate \( \Delta G_{\text{mix}} \) of \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys with respect only to their constituent compounds, i.e., \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \). Then the discrete data sets of \( \Delta G_{\text{mix}} \) evaluated at different fixed temperatures, are fitted with the cubic spline interpolation on a grid of \( \Delta T = 0.01 \). Figure 6 illustrates the \( \Delta G_{\text{mix}} \) curves at \( T = 0 \) K of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys. A few selected ordered structures of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys with \( x = 0.5 \), modeled within the smaller 14-atom and 28-atom supercells as well as an \([\text{B}_{12}(\text{P}−\text{As})]_{0.5}\)[\(\text{B}_{12}(\text{As}−\text{P})\)]_{0.5} alloy, consisting only of the mixed chain units in a 504-atom supercell, are also considered and included in Fig. 6. As can be seen from Fig. 6, none of the configurations, considered in the present work, is found to be stable with respect to \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \), as indicated by the positive \( \Delta G_{\text{mix}} \). Interestingly, \( \Delta G_{\text{mix}} \) of \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\), where the As and P atoms intermix at the diatomic chain sites, is found to be lower than that of \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) for a whole composition range. As \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) possesses twice as much \( S_{\text{conf}} \) as does either \([\text{B}_{12}(\text{P}−\text{As})]_{0.5}[\text{B}_{12}(\text{As}−\text{P})]_{0.5}\) or \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) for all \( x \) listed in Table II, it is predicted to be a favorable disordered state and is stable against a phase separation into \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \) at elevated temperature.

By drawing the common tangents to a set of \( \Delta G_{\text{mix}} \) curves of \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) at different fixed temperature, we sketch out a \( T-x \) phase diagram of \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\), as depicted by Fig. 7. The obtained phase diagram exhibits a miscibility gap at \( T \lesssim 913 \) K, in which a solid solution of \( \text{B}_{12}\text{As}_{1-x}\text{P}_x \), denoted by \( \alpha \), is stable as a mixture of two \( \text{B}_{12}\text{As}_{1-x}\text{P}_x \) phases of different compositions \( x \). Interestingly, the intermixing of As and P atoms at the diatomic chain sites to form \( \text{B}_{12}\text{As}_{1-x}\text{P}_x \) disordered alloys is predicted even at room temperature. We note that in general the mean-field approach used in the present work to estimate \( S_{\text{conf}} \) in Eq. (2), typically results in an overestimation of the maximum \( T \) for the boundary between a single-phase region (\( \alpha \)) and a miscibility gap (\( \alpha' + \alpha'' \)), and thus it should be taken as an upper limit. Since boron subnictides are usually synthesized at \( T \gtrsim 1300 \) K [19,21,24,67–69], one can, based on our prediction, expect the intermixing of As

### Table II. Concentrations of the four superatomic species, used for the SA-SQS modeling of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) disordered alloys within 4\( \times \)4\( \times \)3 supercells (504 atoms) with the compositions \( x = 0.167, 0.333, 0.5, 0.667, \) and 0.833.

<table>
<thead>
<tr>
<th>SA-SQS Model</th>
<th>Composition ( x )</th>
<th>( \text{B}_{12}(\text{P-P}) )</th>
<th>( \text{B}_{12}(\text{As-As}) )</th>
<th>( \text{B}_{12}(\text{P-As}) )</th>
<th>( \text{B}_{12}(\text{As-P}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{B}<em>{12}\text{As}</em>{2})<em>{1-x}(\text{B}</em>{12}\text{P}_{2})_x)</td>
<td>0.167</td>
<td>0.167</td>
<td>0.833</td>
<td>0.139</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>0.333</td>
<td>0.333</td>
<td>0.667</td>
<td>0.222</td>
<td>0.222</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.667</td>
<td>0.667</td>
<td>0.333</td>
<td>0.222</td>
<td>0.222</td>
</tr>
<tr>
<td></td>
<td>0.833</td>
<td>0.833</td>
<td>0.167</td>
<td>0.139</td>
<td>0.139</td>
</tr>
<tr>
<td>((\text{B}<em>{12}\text{As}</em>{1-x}\text{P}_x)_2)</td>
<td>0.167</td>
<td>0.028</td>
<td>0.694</td>
<td>0.139</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>0.333</td>
<td>0.111</td>
<td>0.445</td>
<td>0.222</td>
<td>0.222</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.667</td>
<td>0.445</td>
<td>0.111</td>
<td>0.222</td>
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<tr>
<td></td>
<td>0.833</td>
<td>0.694</td>
<td>0.028</td>
<td>0.139</td>
<td>0.139</td>
</tr>
</tbody>
</table>

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**FIG. 6.** Mixing Gibbs free energy (\( \Delta G_{\text{mix}} \)) curves of the \((\text{B}_{12}\text{As}_{2})_{1-x}(\text{B}_{12}\text{P}_{2})_x\) and \((\text{B}_{12}\text{As}_{1-x}\text{P}_x)_2\) alloys, evaluated with respect to \( \text{B}_{12}\text{P}_{2} \) and \( \text{B}_{12}\text{As}_{2} \) at \( T = 0 \) K.
and P atoms at the diatomic chain sites, i.e., a formation of \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \), when synthesizing a mixture between \( \text{B}_{12}\text{P}_2 \) and \( \text{B}_{12}\text{As}_2 \). Such an intermixing of As and P atoms in \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \) is also expected to possibly quench to room temperature, at which \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \) stays as a metastable state due to a lack of atomic diffusion at low temperature, due to strong interatomic covalent bonds in icosahedral boron-rich solids. Recently, \( \text{B}_{12}\text{As}_2 \) has been suggested as a candidate for thermoelectric applications at high temperature [22,23]. Alloying \( \text{B}_{12}\text{As}_2 \) with \( \text{B}_{12}\text{P}_2 \) to form \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \) should lower the thermal conductivity of the material, thus probably improving their thermoelectric properties. This is due to the large mass difference between As and P atoms, giving high alloy phonon scattering by the disordered chains. As far as we are aware, an experimental synthesis of a mixture between \( \text{B}_{12}\text{P}_2 \) and \( \text{B}_{12}\text{As}_2 \) still awaits realization.

D. Thermodynamic stability of pseudobinary \( \text{BA}_{1-x}\text{P}_{x} \) alloys and B-As-P ternary phase diagrams

In this section, we explore the mixing thermodynamics of the pseudobinary \( \text{BA}_{1-x}\text{P}_{x} \) alloys. Due to the thermodynamic instability of BAs against a phase separation into \( \text{B}_{12}\text{As}_2 \) and gray arsenic as demonstrated in Sec. III A and the presence of binary \( \text{As}_{1-x}\text{P}_x \) and ternary \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \) alloys found in Secs. III B and III C, the thermodynamic stability of the pseudobinary \( \text{BA}_{1-x}\text{P}_{x} \) alloys cannot just be determined with respect to their constituent compounds, i.e., BAs and BP, as previously reported in the literature [25]. Instead, all relevant competing phases, including their constituent elements, \( \text{As}_{1-x}\text{P}_x \), and \( \text{B}_{12}(\text{As}_{1-x}\text{P}_x) \) alloys, must also be taken into

FIG. 8. Calculated ternary phase diagrams of B-As-P at (a) \( T = 0 \) K, (b) \( T = 500 \) K, (c) \( T = 800 \) K, and (d) \( T = 1000 \) K. The black circles represent the stable phases, while the black thick lines connecting two black circles indicate the thermodynamic stability of a series of single-phase disordered solid solutions.
consideration. In this case, the total energy $E_0(V_0)$ of the pseudobinary disordered $\text{BAs}_1-x\text{P}_x$ alloys, calculated at discrete grids at $x = 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875,$ and $1$, are fitted with a cubic spline interpolation and combined with the term $-TS_{\text{conf}}$, analytically evaluated on a grid of $\Delta E = \frac{1}{144}$ to obtain the Gibbs free energy $G(T,0)$. The thermodynamic stability of the pseudobinary $\text{BAs}_1-x\text{P}_x$ alloys is determined by the mixing Gibbs free energy $\Delta G_{\text{mix}}$ with respect to all relevant competing phases, considered in this work, and is then illustrated through ternary phase diagrams of B-As-P plotted at $T = 0, 500, 800,$ and $1000 \text{ K}$, as displayed in Fig. 8.

Besides the disordered $\text{BAs}_1-x\text{P}_x$ alloys, we also explore a possibility of the pseudobinary $\text{BAs}_1-x\text{P}_x$ alloys to form ordered structures at low temperature. In this case, we consider eleven different ordered structures of the zinc-blende $\text{BAs}_1-x\text{P}_x$ alloys with the compositions $x = 0.125, 0.25, 0.50, 0.75,$ and $0.875$, modeled within smaller cells, ranging from a $1 \times 1 \times 1$ unit cell (8 atoms) to a $2 \times 2 \times 2$ supercell (64 atoms). These ordered structures of the $\text{BAs}_1-x\text{P}_x$ alloys are then included, when plotting the ternary phase diagram of B-As-P at $T = 0 \text{ K}$.

We find that, with the exception of BP, both ordered and disordered $\text{BAs}_1-x\text{P}_x$ alloys are thermodynamically unstable at $T = 0 \text{ K}$. As can be seen from Fig. 8(a), the pseudobinary $\text{BAs}_1-x\text{P}_x$ alloys are predicted, depending on the composition $x$, to either decompose into $\text{B}_12\text{P}_2$, BP, and gray arsenic, or decompose into $\text{B}_2\text{P}_2$, $\text{B}_12\text{As}_2$, and gray arsenic. At this temperature, neither $\text{As}_1-x\text{P}_x$ nor $\text{B}_12(\text{As}_1-x\text{P}_x)_2$ alloys are thermodynamically stable, as discussed previously in Secs. III B and III C. At $T = 500 \text{ K}$, the stability of the $\text{BAs}_1-x\text{P}_x$ alloys, except BP, is still not predicted, as shown in Fig. 8(b). At this temperature, the phase decomposition of the $\text{BAs}_1-x\text{P}_x$ alloys into the relevant competing phases becomes much more complex due to the intermixing of As and P atoms between $\text{B}_12\text{As}_2$ and $\text{B}_2\text{P}_2$, resulting in a formation of the $\text{B}_12(\text{As}_1-x\text{P}_x)_2$ alloys, stable as a single-phase solid solution at either $x < 0.19$ or $x > 0.83$, as indicated by the black thick lines in Fig. 8(b) (see also Fig. 7). The $\text{BAs}_1-x\text{P}_x$ alloys are, on the other hand, predicted to be thermodynamically stable as a single-phase solid solution at $T = 500 \text{ K}$ with $x \geq 0.88$, as also indicated by the black thick line in Fig. 8(b) (see also Fig. 4).

A prolongation of the black thick lines in Figs. 8(c) and 8(d) with respect to Fig. 8(b) indicates an enlargement of the single-phase regions of both the $\text{As}_1-x\text{P}_x$ and $\text{B}_12(\text{As}_1-x\text{P}_x)_2$ alloys, as the temperature increases from 500 to 800 and 1000 K, respectively. According to our prediction, a small solubility of BAs in BP is possible at $T \lesssim 800 \text{ K}$, in which up to $\sim 1.4\%$ of BAs can dissolve in BP at $T = 800 \text{ K}$, as can be seen from Fig. 8(c), while the solubility limit of BAs in BP increases to $\sim 4.2\%$ at $T = 1000 \text{ K}$ [see Fig. 8(d)]. We note that the ternary phase diagrams, shown in Fig. 8, are plotted without taking into account the influence of lattice vibrations, and the mixing Gibbs free energy $\Delta G_{\text{mix}}$ is evaluated by deriving the contribution from the configurational entropy $S_{\text{conf}}$ within the mean-field approximation, in general resulting in an underestimation of the stability of the disordered alloys. Consequently, one would expect that the calculated solubility limit of BAs in BP is to a small degree underestimated. In line with our findings, an experimental synthesis of the pseudobinary $\text{BAs}_1-x\text{P}_x$ alloys has never been reported in the literature.

IV. CONCLUSION

In conclusion, we investigate, using first-principles calculations, the thermodynamic stability as a function of temperature of different compounds and alloys in the ternary B-As-P system, in which the Gibbs free energy is determined within the mean-field approximation for the configurational entropy. We find that, in contrast to BP, the zinc-blende BAs is thermodynamically unstable with respect to the icosahedral $\text{B}_12\text{As}_2$ and gray arsenic even at low temperature and increasingly so at elevated temperature. As a result, BAs may merely exist as a metastable phase, thus limiting a synthesis of high-quality macroscopic crystalline BAs in experiments. As for the binary As-P system, $\text{As}_1-x\text{P}_x$ disordered alloys are predicted at elevated temperature—for example, a solid solution of $\sim 75 \text{ at.}\%$ in black phosphorus at $T = 750 \text{ K}$, and a small solubility of $\sim 1 \text{ at.}\%$ in gray arsenic at the same temperature, together with the presence of miscibility gaps. The calculated large solubility of As in black phosphorus explains the experimental syntheses of black-phosphorus-type $\text{As}_1-x\text{P}_x$ alloys with tunable compositions, recently reported in the literature [64,65].

By investigating the mixing thermodynamics of alloys between the icosahedral $\text{B}_12\text{As}_2$ and $\text{B}_2\text{P}_2$, we predict an intermixing of As and P atoms at the diatomic chain sites, readily forming $\text{B}_12(\text{As}_1-x\text{P}_x)_2$ disordered alloys even at room temperature and filling the miscibility gap at $T > 900 \text{ K}$. The thermodynamic instability of BAs against a phase decomposition into $\text{B}_12\text{As}_2$ and pure arsenic phase also highlights the importance of including other relevant competing phases in the ternary B-As-P system, e.g., gray arsenic and $\text{B}_12(\text{As}_1-x\text{P}_x)_2$ alloys, apart from BAs and BP, when considering the mixing thermodynamics of the pseudobinary $\text{BAs}_1-x\text{P}_x$ alloys. In contrast to previous calculations, our prediction reveals that only a small amount of BAs can dissolve in BP to form $\text{BAs}_1-x\text{P}_x$ alloys. For example, a small solubility of BAs up to $\sim 4.2\%$ in BP is predicted at $T = 1000 \text{ K}$.

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