



# First-principles solubilities of alkali and alkaline-earth metals in Mg-B alloys

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(Received 17 February 2009; published 3 April 2009)

In this article, we present a comprehensive theoretical study of solubilities of alkali (Li, Na, K, Rb, Cs) and alkaline-earth (Be, Ca, Sr, Ba) metals in the boron-rich Mg-B system. The study is based on first-principles calculations of solutes formation energies in MgB<sub>2</sub>, MgB<sub>4</sub>, MgB<sub>7</sub> alloys and subsequent statistical-thermodynamical evaluation of solubilities. The advantage of the approach consists in considering all the known phase boundaries in the ternary phase diagram. Substitutional Na, Ca, and Li demonstrate the largest solubilities, and Na has the highest (0.5%–1% in MgB<sub>7</sub> at  $T=650$ – $1000$  K). All the considered interstitials have negligible solubilities. The solubility of Be in MgB<sub>7</sub> cannot be determined because the corresponding low-solubility formation energy is negative indicating the existence of an unknown ternary ground state. We have performed a high-throughput search of ground states in binary Mg-B, Mg-A, and B-A systems, and we construct the ternary phase diagrams of Mg-B-A alloys based on the stable binary phases. Despite its high-temperature observations, we find that Sr<sub>9</sub>Mg<sub>38</sub> is not a low-temperature equilibrium structure. We also determine two possible ground states CaB<sub>4</sub> and RbB<sub>4</sub>, not yet observed experimentally.

DOI: [10.1103/PhysRevB.79.134203](https://doi.org/10.1103/PhysRevB.79.134203)

PACS number(s): 61.50.Ks, 74.70.Ad, 81.30.Hd

## I. INTRODUCTION

The interest in magnesium diboride emerged after the discovery of superconductivity in MgB<sub>2</sub> at about  $T_c=39$  K.<sup>1</sup> Attempts to increase  $T_c$  by small additions of alkali [Li,<sup>2–6</sup> Na,<sup>7,8</sup> Rb,<sup>9,10</sup> Cs<sup>9,10</sup>] and alkaline-earth [Be,<sup>11</sup> Ca,<sup>4,7,12,13</sup> Ba<sup>9</sup>] metals to MgB<sub>2</sub>, proved to be unsuccessful. The difficulty was attributed not only to the inability of such solutes to decrease  $T_c$  but also to their low solubility and precipitation in secondary phases. Although a claimed superconductivity at 50 K was reported for the Mg-B-A ( $A=Cs, Rb, Ba$ ) system,<sup>9</sup> attempts to reproduce the results have been so far unsuccessful (for  $A=Cs, Rb$ ).<sup>10</sup> The problem can be attributed to solutes' segregation in grain boundaries and to low solubility in the bulk phase (much lower than reported in Ref. 9).

For consistent interpretation of experimental observations, theoretical studies of solubility in Mg-B of alkali metals and alkaline-earth metal solubilities are therefore necessary. For instance, in Ref. 14, the semiempirical Miedema approach<sup>15</sup> and the Toop's model<sup>16</sup> were used to address the heats of formation of binary alloys Mg-A, B-A, and Mg-B ( $A=Li, Na, Ca$ ). It was proposed that Ca may form stable compounds while Na and Li could lead to metastable or unstable ternary phases in MgB<sub>2</sub>. In Ref. 17, by calculating first-principles formation energies of Li and Na impurities in MgB<sub>2</sub>, and by neglecting the effects of other ground states in the ternary phase diagram solubility calculations, it was concluded that Na should have very low solubility, whereas the solubility of Li should be comparatively higher although modestly diminished by a segregation into a LiB phase.

The present paper is orthogonal to previous studies. We develop a comprehensive theoretical framework to determine the solubilities of alkali metals (Li, Na, K, Rb, Cs) and alkaline earths (Be, Ca, Sr, Ba) in the boron-rich Mg-B system. The study consists of first-principles calculations of solutes formation energies in MgB<sub>2</sub>, MgB<sub>4</sub>, MgB<sub>7</sub> alloys and subse-

quent statistical-thermodynamical evaluations of solubilities with respect to *all known equilibrium states* of the Mg-B-A system. The results help outlining future directions in experimental searches.

The paper is organized as following. In Sec. II, we describe the adopted solubility mechanisms in Mg-B. In Sec. III, we discuss the relevant impurity formation energies in terms of supercell energy calculations and the appropriate ground state(s). In Sec. IV, the approximation for the free energy of Mg-B-A solid solution is formulated. In Sec. V, we present an approach for solubility calculation considering all the ternary ground states. A simple analytical low-solubility approximation is devised. Section VI is devoted to the high-throughput *ab initio* search for ground states in binary Mg-B, Mg-A, and B-A systems, to the ternary phase diagrams of Mg-B-A systems, and to the impurity formation energies determined through the phase boundaries of the systems. The numerical values of solubilities are presented in Sec. VII. Section VIII summarizes the results, draws conclusions, and comments on strategies for future research in this area.

## II. Mg-B-A SOLID SOLUTION

For the description of solubility of alkali and alkaline-earth metal elements  $A$  ( $A=Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba$ ) in the Mg-B system, we consider the disordered solid solutions of  $A$  atoms as interstitial and substitutional impurities in the experimentally reported compounds<sup>18,19</sup> MgB<sub>2</sub>, MgB<sub>4</sub>, and MgB<sub>7</sub>. We consider only substitutions in the magnesium sublattice as boron substitutions have not been observed experimentally.<sup>2–13</sup> The disordered solid solution of  $A$  inside Mg-B is labeled as “(1)” throughout the paper.

While the magnesium-substitutional positions are determined,<sup>19</sup> the “most accommodating” interstitial locations have to be found. The task is implemented with the

TABLE I. Centers and sizes of the symmetrically inequivalent interstitial cages for the  $\text{MgB}_2$ ,  $\text{MgB}_4$ , and  $\text{MgB}_7$  unit cells. Coordinates are presented as fractions of the standard unit cell basis vectors  $(a, b, c)$  (Ref. 19). The radius is the distance from the cage center to the nearest Mg or B atom.  $\nu_i$  indicates the numbers of the symmetrically equivalent cages within the unit cell. The total numbers of distinct geometrical cages before agglomeration upon insertion of an interstitial is reported in brackets.

Structure	$i$	Coordinates (fraction of $a, b, c$ )	Cageradius Å	$\nu_i$
$\text{MgB}_2$	1	0.341, 0.681, 0.000	1.7619	2 (6)
	2	0.006, 0.000, 0.500	1.7616	1 (6)
	3	0.500, 0.500, 0.122	1.6015	6 (6)
$\text{MgB}_4$ ( $\text{Mg}_4\text{B}_{16}$ )	1	0.106, 0.669, 0.412	1.9145	4 (52)
	2	0.375, 0.250, 0.337	1.7836	4 (4)
	3	0.145, 0.632, 0.813	1.7821	8 (24)
	4	0.144, 0.750, 0.925	1.7252	4 (24)
	5	0.225, 0.750, 0.719	1.6322	4 (4)
	6	0.086, 0.015, 0.527	1.6128	8 (8)
$\text{MgB}_7$ ( $\text{Mg}_8\text{B}_{56}$ )	7	0.101, 0.543, 0.261	1.5322	8 (8)
	1	0.000, 0.049, 0.618	2.0050	8 (152)
	2	0.189, 0.250, 0.821	1.8937	8 (24)
	3	0.250, 0.217, 0.750	1.7995	8 (8)
	4	0.243, 0.250, 0.505	1.7888	8 (24)
	5	0.197, 0.250, 0.469	1.7802	8 (24)
	6	0.000, 0.250, 0.150	1.7002	4 (24)
	7	0.012, 0.000, 0.000	1.6995	8 (64)
	8	0.250, 0.062, 0.250	1.6068	8 (40)
	9	0.000, 0.171, 0.788	1.4991	8 (8)
10	0.131, 0.186, 0.119	1.4443	16(16)	

following exhaustive search performed through our software AFLOW.<sup>20,21</sup> Let us consider a quadruplet of no-coplanar atoms, where the first atom belongs to the unit cell and the others are closer than the maximum diagonal of the unit cell to the first atom. A *cage* is defined when the spherical region of space touching all the four atoms of the quadruplet does not contain further atoms inside. An *interstitial* position is found if the cage has its center inside the unit cell. By considering all the possible combinations, the symmetrically inequivalent interstitials can be identified through the calculation of their site symmetry (with the factor group of the unit cell). Note that in unit cells with complex arrangements,

TABLE II. Numbers of atoms  $n, m$  ( $\text{Mg}_n\text{B}_m$ ) in the conventional unit cells (“uc”) (Ref. 19) and in the constructed supercells (“sc”) for  $\text{MgB}_2$ ,  $\text{MgB}_4$ , and  $\text{MgB}_7$ .  $\nu_s$  indicates the number of symmetrically equivalent  $s$ -type Mg atom positions within the corresponding unit cell:  $\sum_s \nu_s = n_{\text{uc}}$ .  $d_{AA}$  and  $d_{BB}$  are the distances between the nearest solutes and nearest solvent atoms (boron-boron in our case) in the supercell.

Compound	$n_{\text{uc}}$	$m_{\text{uc}}$	$\nu_s$	$n_{\text{sc}}$	$m_{\text{sc}}$	$d_{BB}$ (Å)	$d_{AA}/d_{BB}$
$\text{MgB}_2$	1	2	1	8	16	1.7811	3.46
$\text{MgB}_4$	4	16	4	4	16	1.7004	2.60
$\text{MgB}_7$	8	56	4,4	8	56	1.7372	3.44

many of the interstitial positions can be extremely close. Thus, an interstitial atom located in any of those close positions would deform the nearby local atomic environment and *relax* to the same final location. Hence, the number of symmetrically inequivalent cages can be further reduced by considering the whole set of positions that would *agglomerate* upon insertion of an interstitial atom, as a single interstitial site. The results of the search are presented in Table I. The table demonstrates that the higher boron contents the larger number of cages and the larger radius of the bigger cage.

### III. FORMATION ENERGIES DEFINITIONS

#### A. “Raw” formation energies

Let us define the so-called raw formation energies  $\mu_i$  and  $\bar{\mu}_s$  (composition unpreserving<sup>22</sup>) as the changes in the energies of the solvent upon introduction of one solute atom  $A$  in the  $i$ th type interstitial or  $s$ th type substitutional positions. In first-principles calculations, the solvent can be replaced by a large supercell (“sc”), so that

$$\mu_i \equiv \mu_i^{(1)}(A) = E_{\text{sc}}[A^{(i)}\text{Mg}_{n_{\text{sc}}}\text{B}_{m_{\text{sc}}}] - E_{\text{sc}}[\text{Mg}_{n_{\text{sc}}}\text{B}_{m_{\text{sc}}}],$$

$$\begin{aligned} \bar{\mu}_s &\equiv \mu_s^{(1)}(A) - \mu^{(1)}(\text{Mg}) \\ &= E_{\text{sc}}[A^{(s)}\text{Mg}_{n_{\text{sc}}-1}\text{B}_{m_{\text{sc}}}] - E_{\text{sc}}[\text{Mg}_{n_{\text{sc}}}\text{B}_{m_{\text{sc}}}], \end{aligned} \quad (1)$$

where  $n_{\text{sc}}$  and  $m_{\text{sc}}$  are the numbers of Mg and B atoms in the supercell;  $\mu^{(1)}(\text{Mg})$ ,  $\mu_i^{(1)}(A)$ , and  $\mu_s^{(1)}(A)$  are the zero-temperature chemical potentials of the Mg atom, and the  $A$  atoms in the  $i$ th interstitial and  $s$ th substitutional positions, respectively.<sup>23</sup>

The conventional unit cells of  $\text{MgB}_2$ ,  $\text{MgB}_4$ , and  $\text{MgB}_7$  are used to construct the appropriate supercells. The supercells are chosen to have solute-solute  $A$ - $A$  distance at least  $\sim 2.5$  times the nearest-neighbor solvent bonds in order to diminish the contribution of the  $A$ - $A$  interactions to the calculated energies. We use  $2 \times 2 \times 2$  unit cells for  $\text{MgB}_2$ , while there is no need to create supercells of  $\text{MgB}_4$  and  $\text{MgB}_7$  since their unit cells are already large enough. Note that boron-boron (B-B) bond is the shortest among the Mg-Mg, B-B, and Mg-B bonds. Table II summarizes the parameters of the supercells and Table III lists the supercell atomic compositions.

#### B. “True” formation energies

The true formation energies (composition preserving<sup>22</sup>) are defined from the raw formation energies (composition unpreserving<sup>22</sup>) as

TABLE III. Interstitial and substitutional supercell atomic compositions ( $x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}}$ ) as functions of the  $n_{\text{sc}}$  (for Mg) and  $m_{\text{sc}}$  (for B) numbers of atoms in the super cell.

	Interstitials	Substitutional
$x_A^{\text{sc}}$	$[1+n_{\text{sc}}+m_{\text{sc}}]^{-1}$	$[n_{\text{sc}}+m_{\text{sc}}]^{-1}$
$x_B^{\text{sc}}$	$m_{\text{sc}}[1+n_{\text{sc}}+m_{\text{sc}}]^{-1}$	$m_{\text{sc}}[n_{\text{sc}}+m_{\text{sc}}]^{-1}$
$x_{\text{Mg}}^{\text{sc}}$	$n_{\text{sc}}[1+n_{\text{sc}}+m_{\text{sc}}]^{-1}$	$n_{\text{sc}}[n_{\text{sc}}+m_{\text{sc}}]^{-1}$

$$E_A^{(i)} \equiv \mu_i - \mu_A^{\text{pure}},$$

$$E_A^{(s)} \equiv \bar{\mu}_s + \mu_{\text{Mg}}^{\text{pure}} - \mu_A^{\text{pure}}, \quad (2)$$

where  $\mu_A^{\text{pure}}$  and  $\mu_{\text{Mg}}^{\text{pure}}$  are the chemical potentials (energies per atom) of A and Mg atoms in pure A and Mg solids at zero temperature, respectively.

### C. Low-solubility formation energies

In Ref. 24, a quantity called “low-solubility formation energy,” was shown to determine the dilute solubility in binary alloys through the temperature exponential factor. The quantity can be generalized to the case of Mg-B-A alloy as (compare with Eq. (29) in Ref. 24),

$$E_{\text{sol}}^\alpha(A) \equiv \Delta E_{\text{sc/at}}^\alpha / x_A^{\text{sc}}, \quad (3)$$

with  $\alpha = (i), (s)$  and

$$\Delta E_{\text{sc/at}}^{(i)} = \frac{E_{\text{sc}}[A^{(i)}\text{Mg}_{n_{\text{sc}}}\text{B}_{m_{\text{sc}}}] - E_{\text{at}}^{\text{mix}}(x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}})}{1 + n_{\text{sc}} + m_{\text{sc}}},$$

$$\Delta E_{\text{sc/at}}^{(s)} = \frac{E_{\text{sc}}[A^{(s)}\text{Mg}_{n_{\text{sc}}-1}\text{B}_{m_{\text{sc}}}] - E_{\text{at}}^{\text{mix}}(x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}})}{n_{\text{sc}} + m_{\text{sc}}}, \quad (4)$$

where  $E_{\text{at}}^{\text{mix}}(x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}})$  is the energy of a the three-phase mixture at the same composition of the supercell (see Table III),

$$E_{\text{at}}^{\text{mix}}(x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}}) = X_1 \frac{E_{\text{uc}}[\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}] - X_2 E_{\text{at}}^{(2)} + X_3 E_{\text{at}}^{(3)}}{n_{\text{uc}} + m_{\text{uc}}}. \quad (5)$$

The coefficients  $X_k$  ( $k=1, 2, 3$ ) are determined from the following linear system of equations,

$$\begin{cases} x_A^{\text{sc}} = X_2 x_A^{(2)} + X_3 x_A^{(3)} \\ x_B^{\text{sc}} = X_1 \frac{m_{\text{uc}}}{n_{\text{uc}} + m_{\text{uc}}} + X_2 x_B^{(2)} + X_3 x_B^{(3)} \\ x_{\text{Mg}}^{\text{sc}} = X_1 \frac{m_{\text{uc}}}{n_{\text{uc}} + m_{\text{uc}}} + X_2 x_{\text{Mg}}^{(2)} + X_3 x_{\text{Mg}}^{(3)}, \end{cases} \quad (6)$$

where  $E_{\text{at}}^{(k)}, x_A^{(k)}, x_B^{(k)}, x_{\text{Mg}}^{(k)}$  ( $k=2, 3$ ) are the energies (per atom) and stoichiometric compositions of the two other ground states that, together with  $\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}$ , form the *convex-hull triangle* containing the point  $(x_A^{\text{sc}}, x_B^{\text{sc}}, x_{\text{Mg}}^{\text{sc}})$  in the ternary phase diagram. For example,  $\text{MgB}_2$ , Mg, and  $\text{LiB}_3$  are the three ground states surrounding  $\text{Mg}_7\text{B}_{16}\text{Li}$  (a supercell of

$\text{MgB}_2$  with a substitutional Li atom) as shown in Fig. 2. The coefficient  $X_k$  ( $k=1, 2, 3$ ) represents the fraction of the  $k$ th phase in the mixture. The quantities  $\Delta E_{\text{sc/at}}^\alpha$  defined in Eq. (4) are the supercell formation energies (per atom) determined with respect to the mixture of ground states.<sup>24</sup>  $E_{\text{sol}}^\alpha(A)$  and  $\Delta E_{\text{sc/at}}^\alpha$  cannot be negative. If they do, the list of ground states is incomplete, and a better phase diagram should be established (the missed ground state can be the supercell itself).<sup>24</sup>

In analogy with binary alloys,<sup>24</sup> the ternary alloy low-solubility formation energy  $E_{\text{sol}}^\alpha(A)$  is shown to determine the solubility of A in the low-solubility limit (Sec. V).

### IV. FREE ENERGY OF THE Mg-B-A SOLID SOLUTION

The Gibbs free energy per unit cell (“uc”) of the Mg-B-A solid solution is determined within the mean-field approximation,

$$G_{\text{uc}}^{(1)}[\{c_i, c_s\}, T] = E_{\text{uc}}[\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}] + \Delta g_I + \Delta g_S,$$

$$\Delta g_I = \sum_i \nu_i \{c_i \mu_i + k_B T [c_i \ln c_i + (1 - c_i) \ln(1 - c_i)]\},$$

$$\Delta g_S = \sum_s \nu_s \{c_s \bar{\mu}_s + k_B T [c_s \ln c_s + (1 - c_s) \ln(1 - c_s)]\}, \quad (7)$$

where  $k_B$  is a Boltzmann constant,  $T$  is the temperature, and  $E_{\text{uc}}[\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}]$  represents the energy (enthalpy) of initial  $\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}$  unit cell without A solutes; the summations over  $i$  and  $s$  are with respect to all the inequivalent types of interstitial and substitutional positions in unit cell;  $c_i$  and  $c_s$  are equal to the *site* concentrations of A atoms at each interstitial ( $i$ -) and substitutional ( $s$ -) type, respectively. Thus, we assume that the concentrations in the equivalent positions are equal in the disordered state. The raw formation energies  $\mu_i$  and  $\bar{\mu}_s$  are introduced in Sec. III. The mean-field approximation, although neglecting correlations, should work well when the deviation from stoichiometry is small (see Sec. 19 in Ref. 25). In addition, we neglect solute-solute interactions that might be important especially at high solute concentrations. In conclusion, our model is similar to Wagner-Schottky model of a system of noninteracting particles.<sup>26</sup>

For given concentrations  $\{c_i, c_s\}$ , the total number of atoms per unit cell,  $N_{\text{uc}}^{\text{at}}$ , the total concentrations of A interstitials,  $x_{A(i)}^{(1)}$ , A substitutional,  $x_{A(s)}^{(1)}$ , and the total concentration of A atoms,  $x_A^{(1)}$ , are determined as

$$N_{\text{uc}}^{\text{at}} = \sum_i \nu_i c_i + n_{\text{uc}} + m_{\text{uc}},$$

$$x_{A(i)}^{(1)} = \sum_i \nu_i c_i / N_{\text{uc}}^{\text{at}}, x_{A(s)}^{(1)} = \sum_s \nu_s c_s / N_{\text{uc}}^{\text{at}},$$

$$x_A^{(1)} = x_{A(i)}^{(1)} + x_{A(s)}^{(1)}. \quad (8)$$

At given temperature and concentration  $x_A^{(1)}$ , the Gibbs free energy per atom  $G_{\text{at}}^{(1)}[x_A^{(1)}, T]$  is determined by minimizing Eq. (7) with respect to  $\{c_i\}$  and  $\{c_s\}$ ,

TABLE IV. The formation energies  $\Delta E_{\text{at}}^{\text{bin}}$  [Eq. (27)] for Mg-B, B-A, and Mg-A binary ground states ( $A=\text{Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba}$ ). The symbol (+) indicates possible ground states never observed experimentally ( $\text{CaB}_4$  and  $\text{RbB}_4$ ). The symbol (−) indicates the experimentally observed  $\text{Sr}_9\text{Mg}_{38}$ , which was not confirmed to be a ground states by first-principles calculations.

	$\Delta E_{\text{at}}^{\text{bin}}$ (eV/at.)	Prototype <sup>a</sup>	Spacegroup <sup>b</sup>	Pearson	Ref.
$\text{Li}_3\text{B}_{14}$	−0.219	$\text{Li}_3\text{B}_{14}$	$I\bar{4}2d(122)$	tI160	39
$\text{LiB}_3$	−0.235	$\text{LiB}_3$	$P4/m\bar{b}m(127)$	tP20	40
$\text{Li}_8\text{B}_7$	−0.216	$\text{Li}_8\text{B}_7$	$P\bar{6}m2(187)$	hP15	32
$\text{Be}_3\text{B}_{50}$	−0.032	$\text{Be}_3\text{B}_{50}$	$P4_2/n\bar{m}m(134)$	tP53	41
$\text{Be}_{1.11}\text{B}_3$	−0.096	$\text{Be}_{1.11}\text{B}_3$	$P6/m\bar{m}m(191)$	hP111	42
$\text{MgBe}_{13}$	−0.009	$\text{NaZn}_{13}$	$Fm\bar{3}c(226)$	cF112	43
$\text{NaB}_{15}$	−0.059	$\text{NaB}_{15}$	$Imma(74)$	oI64	44
$\text{Na}_3\text{B}_{20}$	−0.070	$\text{Na}_3\text{B}_{20}$	$Cmmm(65)$	oC46	45
$\text{MgB}_7$	−0.138	$\text{MgB}_7$	$Imma(74)$	oI64	46
$\text{MgB}_4$	−0.152	$\text{MgB}_4$	$Pnma(62)$	oP20	47
$\text{MgB}_2$	−0.151	$\text{AlB}_2$	$P6/m\bar{m}m(191)$	hP3	48
$\text{KB}_6$	−0.043	$\text{CaB}_6$	$Pm\bar{3}m(221)$	cP7	49
$\text{CaB}_6$	−0.423	$\text{CaB}_6$	$Pm\bar{3}m(221)$	cP7	50
$\text{CaB}_4(+)$	−0.410	$\text{UB}_4$	$P4/m\bar{b}m(127)$	tP20	51
$\text{CaMg}_2$	−0.128	$\text{MgZn}_2$	$P6_3/m\bar{m}c(194)$	hP12	52
$\text{RbB}_4(+)$	−0.163	$\text{UB}_4$	$P4/m\bar{b}m(127)$	tP20	
$\text{SrB}_6$	−0.464	$\text{CaB}_6$	$Pm\bar{3}m(221)$	cP7	53
$\text{Sr}_2\text{Mg}_{17}$	−0.055	$\text{Th}_2\text{Ni}_{17}$	$P6_3/m\bar{m}c(194)$	hP38	54
$\text{Sr}_9\text{Mg}_{38}(-)$	−0.070	$\text{Sr}_9\text{Mg}_{38}$	$P6_3/m\bar{m}c(194)$	hP94	55
$\text{Sr}_6\text{Mg}_{23}$	−0.085	$\text{Th}_6\text{Mg}_{23}$	$Fm\bar{3}m(225)$	cF116	56
$\text{SrMg}_2$	−0.114	$\text{MgZn}_2$	$P6_3/m\bar{m}c(194)$	hP12	57
$\text{BaB}_6$	−0.421	$\text{CaB}_6$	$Pm\bar{3}m(221)$	cP7	53
$\text{Ba}_2\text{Mg}_{17}$	−0.072	$\text{Zn}_{17}\text{Th}_2$	$R\bar{3}mh(166)$	hR57	54
$\text{Ba}_6\text{Mg}_{23}$	−0.085	$\text{Th}_6\text{Mg}_{23}$	$Fm\bar{3}m(225)$	cF116	56
$\text{BaMg}_2$	−0.097	$\text{MgZn}_2$	$P6_3/m\bar{m}c(194)$	hP12	57

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 38.

$$G_{\text{at}}^{(1)}[x_A^{(1)}, T] = \min_{\{c_i, c_s\}} [G_{\text{at}}^{(1)}[\{c_i, c_s\}, T]]_{x_A^{(1)}}, \quad (9)$$

$$x_A^{(1)}(n_{\text{uc}} + m_{\text{uc}}) = \sum_i \nu_i c_i (1 - x_A^{(1)}) + \sum_s \nu_s c_s. \quad (12)$$

where

$$G_{\text{at}}^{(1)}[\{c_i, c_s\}, T] = G_{\text{uc}}^{(1)}[\{c_i, c_s\}, T]/N_{\text{uc}}^{\text{at}}. \quad (10)$$

The solution  $\{c_i, c_s\}$  defines the equilibrium distribution of interstitial and substitutional  $A$  solutes in the  $\text{Mg}_{n_{\text{uc}}}\text{B}_{m_{\text{uc}}}$  solvent.

In the case of small concentrations of interstitials, the minimization can be done with the Lagrange multiplier method, obtaining

$$c_i = \left[ 1 + \exp \frac{\mu_i + \mu(1 - x_A^{(1)})}{k_B T} \right]^{-1}, \quad c_s = \left[ 1 + \exp \frac{\mu_s + \mu}{k_B T} \right]^{-1}. \quad (11)$$

where the Lagrange multiplier  $\mu$  is determined from the following equation [derived from Eq. (8)],

## V. SOLUBILITY

According to Nernst's theorem, either a single compound or a phase separation of compounds at correct stoichiometry can be present at equilibrium at zero temperature. At finite temperatures, the composition of phases can differ from stoichiometry through solution because of the entropic promotion (Sec. VII and Ref. 24). At a given temperature, the solubility of  $A$  atoms in a compound is defined as the maximum homogeneously achievable concentration of  $A$  atoms, without the nucleation of a new phase.

To calculate the solubility,<sup>27</sup> we consider the Gibbs free energy  $G_{\text{at}}^{\text{mix}}$  of the mixture of three phases with a given general ("gen") composition  $x^{\text{gen}} \equiv (x_A^{\text{gen}}, x_B^{\text{gen}}, x_{\text{Mg}}^{\text{gen}})$ . The first phase is the substitutional and/or interstitial solid solution

with atomic concentration  $x_A^{(1)}$  of element  $A$  in  $Mg_{n_{uc}}B_{m_{uc}}$ . At zero temperature, the two other phases and  $Mg_{n_{uc}}B_{m_{uc}}$  form a triangle containing the point  $x^{\text{gen}}$  in the ternary phase diagram. At a finite temperature, the free energy  $G_{\text{at}}^{\text{mix}}$  is the generalization of Eq. (5),

$$G_{\text{at}}^{\text{mix}}[x_A^{(1)}, T] \approx X_1[x_A^{(1)}, T]G_{\text{at}}^{(1)}[x_A^{(1)}, T] + X_2[x_A^{(1)}, T]E_{\text{at}}^{(2)} + X_3[x_A^{(1)}, T]E_{\text{at}}^{(3)}, \quad (13)$$

where  $G_{\text{at}}^{(1)}[x_A^{(1)}, T]$  is given by Eq. (9), and the second and third phases are assumed to be stoichiometric, so that their free energies can be approximated by their ground-state energies (enthalpies)  $E_{\text{at}}^{(2)}$  and  $E_{\text{at}}^{(3)}$ , respectively. The approximation does not affect much the results, as we are interested in the small solubility regime of  $A$ . Similarly to Eq. (6), the fractions  $X_k$  are determined by solving the system,

$$\begin{cases} x_A^{\text{gen}} = X_1x_A^{(1)} + X_2x_A^{(2)} + X_3x_A^{(3)} \\ x_B^{\text{gen}} = X_1x_B^{(1)} + X_2x_B^{(2)} + X_3x_B^{(3)} \\ x_{\text{Mg}}^{\text{gen}} = X_1x_{\text{Mg}}^{(1)} + X_2x_{\text{Mg}}^{(2)} + X_3x_{\text{Mg}}^{(3)}, \end{cases} \quad (14)$$

where the second “(2)” and third “(3)” phases are at stoichiometry. In addition, we have

$$\begin{aligned} x_B^{(1)} &= \frac{n_{uc}}{n_{uc} + m_{uc}}(1 - x_A^{(1)}[x_A^{(1)}, T]), \\ x_{\text{Mg}}^{(1)} &= 1 - x_A^{(1)} - x_B^{(1)}, \end{aligned} \quad (15)$$

where  $x_{A^{(i)}}^{(1)}[x_A^{(1)}, T]$  is the equilibrium concentration of  $A$  interstitials in the first phase given by Eqs. (8) and (9) at the chosen total concentration  $x_A^{(1)}$ . The minimization of  $G_{\text{at}}^{\text{mix}}$  with respect to  $x_A^{(1)}$  gives the solubility  $x_A^{(1)}(T)$  in the first phase “(1)”:

$$G_{\text{at}}^{\text{mix}}[x_A^{(1)}(T), T] = \min_{x_A^{(1)}} G_{\text{at}}^{\text{mix}}[x_A^{(1)}, T]. \quad (16)$$

This procedure, equivalent to the common-tangent method, is the generalization of the approach developed in Ref. 24 to the case of ternary alloys. The method is somehow different from that developed in Ref. 28. Although, the regular solution model used in Ref. 28 and the presented ideal solution model coincides in the low-solubility regime, the consideration of only two ground states (“gs”) by the authors of Ref. 28, differs from our approach requiring the knowledge of the whole ternary stability. This is because the disordered Mg-B-A solution does not generally belong to the Mg-B  $\leftrightarrow$  gs<sup>(2)</sup> or Mg-B  $\leftrightarrow$  gs<sup>(3)</sup> lines in the ternary phase diagram. Thus, we have to consider the phase mixture of  $Mg_{n_{uc}}B_{m_{uc}}$ , gs<sup>(2)</sup>, and, gs<sup>(3)</sup> to guarantee accurate estimation of the solubility.

### A. Low-solubility approximation

In order to get the analytical expression for equilibrium solubilities from Eq. (16), further approximations are required: (a) the equilibrium concentration of solute  $A$  is small and (b) only substitutional or interstitial positions of one type  $\alpha$  are occupied (this approximation will be eliminated at the

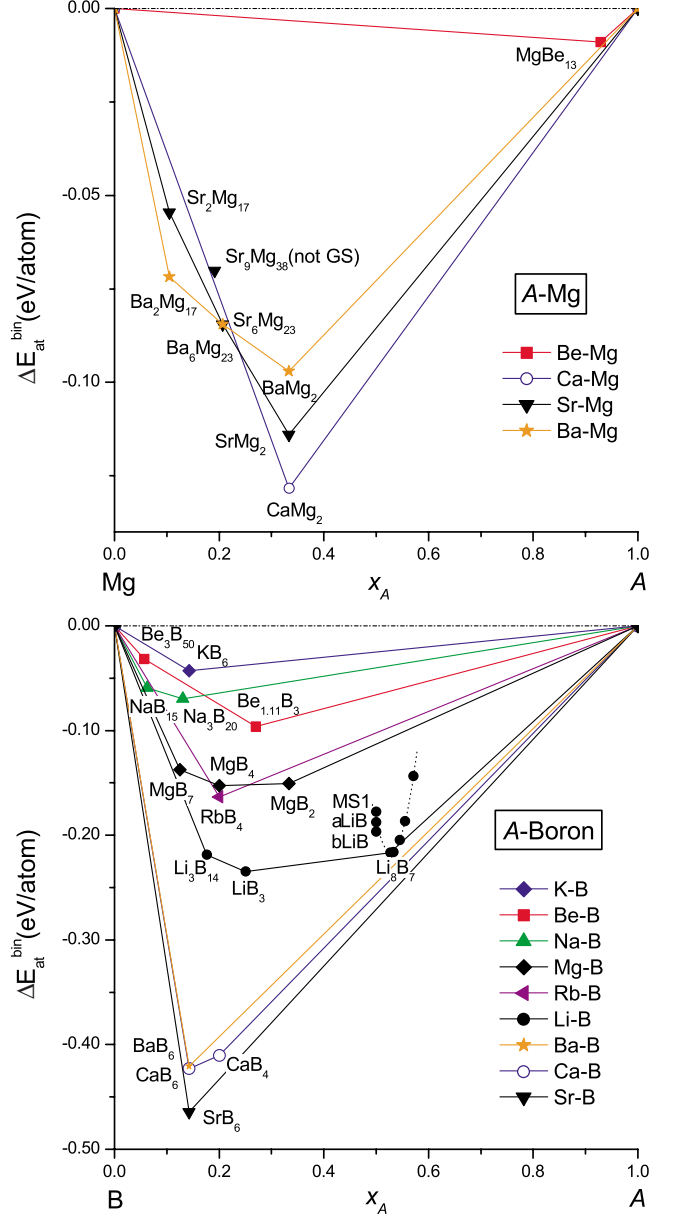


FIG. 1. (Color online) Formation energies  $\Delta E_{\text{at}}^{\text{bin}}$  for Mg-B, B-A, and Mg-A binary ground states ( $A=\text{Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba}$ ) from Table IV. The dashed parabola for the Li-B system indicates the linear chains phases of Ref. 32.

end of section). Hence, from Eqs. (13) and (16) we obtain

$$\frac{\partial G_{\text{at}}^{\text{mix}}}{\partial x_A^{(1)}} \approx \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_A^{(1)}} + X_1 \frac{\partial G_{\text{at}}^{(1)}[x_A^{(1)}, T]}{\partial x_A^{(1)}} = 0, \quad (17)$$

where

$$E_{\text{at}}^{\text{mix}}[x_A^{(1)}, x^{\text{gen}}] = X_1E_{\text{at}}^{(1)} + X_2E_{\text{at}}^{(2)} + X_3E_{\text{at}}^{(3)}, \quad (18)$$

where the fractions  $X_k = X_k[x_A^{(1)}, x^{\text{gen}}]$  are determined from Eqs. (14) and (15). Note that the ca. ( $\approx$ ) in Eq. (17) corresponds to approximation (a) applied to Eqs. (7) and (10),

$$\frac{\partial X_1}{\partial x_A^{(1)}} G_{\text{at}}^{(1)} \approx \frac{\partial X_1}{\partial x_A^{(1)}} E_{\text{at}}^{(1)}. \quad (19)$$

Equations (14) and (15) lead to

$$\frac{\partial X_k}{\partial x_A^{(1)}} \approx -X_1 \frac{\partial X_k}{\partial x_A^{\text{gen}}}, \quad (20)$$

and through Eq. (18),

$$\frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_A^{(1)}} \approx -X_1 \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_A^{\text{gen}}}. \quad (21)$$

By using the expression of  $G^{(1)}$  from Eq. (7), we have

$$\frac{\partial G_{\text{at}}^{(1)}}{\partial x_A^{(1)}} \approx \mu_\alpha + k_B T \ln \frac{c_\alpha}{1 - c_\alpha}, \quad (22)$$

where the ca. ( $\approx$ ) corresponds to approximation (a).<sup>29</sup>

Equation (17) can be solved with respect to  $c_\alpha$  with the help of Eqs. (21) and (22) as

$$c_\alpha = \left[ 1 + \exp \frac{E_{\text{sol}}^\alpha(A)}{k_B T} \right]^{-1} \approx \exp \left( - \frac{E_{\text{sol}}^\alpha(A)}{k_B T} \right) \Big|_{k_B T \ll E_{\text{sol}}^\alpha(A)}, \quad (23)$$

where

$$\begin{aligned} E_{\text{sol}}^\alpha(A) &= \mu_\alpha - \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_A^{\text{gen}}} \\ &= \frac{1}{x_A^{\text{gen}}} \left[ E_{\text{at}}^{(1)} + \mu_\alpha x_A^{\text{gen}} - \left( E_{\text{at}}^{(1)} + \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_A^{\text{gen}}} x_A^{\text{gen}} \right) \right] \\ &= \frac{1}{x_A^{\text{gen}}} [E_{\text{at}}^{(1)}(x^{\text{gen}}) - E_{\text{at}}^{\text{mix}}(x^{\text{gen}})]. \end{aligned} \quad (24)$$

Both Eqs. (3) and (24) define the same quantity: the low-solubility formation energy,  $E_{\text{sol}}^\alpha(A)$ , determining the low solubility of  $A$  solutes in  $\alpha$ -type positions. In addition, by using Eq. (8) (Ref. 29) the total equilibrium concentration of solute  $A$  in the phase (1) becomes

$$x_A^{(1)} \approx \frac{\nu c_\alpha}{n_{\text{uc}} + m_{\text{uc}}}, \quad (25)$$

where  $c_\alpha$  is determined by Eq. (23).

Approximation (b) can be relaxed if the various types of substitutional and interstitial positions are occupied independently. This is expected to be true in the low solute concentration limit. Thus, the expression (25) can be integrated through the various types of positions, leading to

$$x_A^{(1)} \approx \frac{\sum_i \nu_i c_i + \sum_s \nu_s c_s}{n_{\text{uc}} + m_{\text{uc}}}, \quad (26)$$

where  $c_i$  and  $c_s$  are obtained from a set of Eq. (23), by using the corresponding  $E_{\text{sol}}^{(i)}(A)$  and  $E_{\text{sol}}^{(s)}(A)$  for each type of defects.

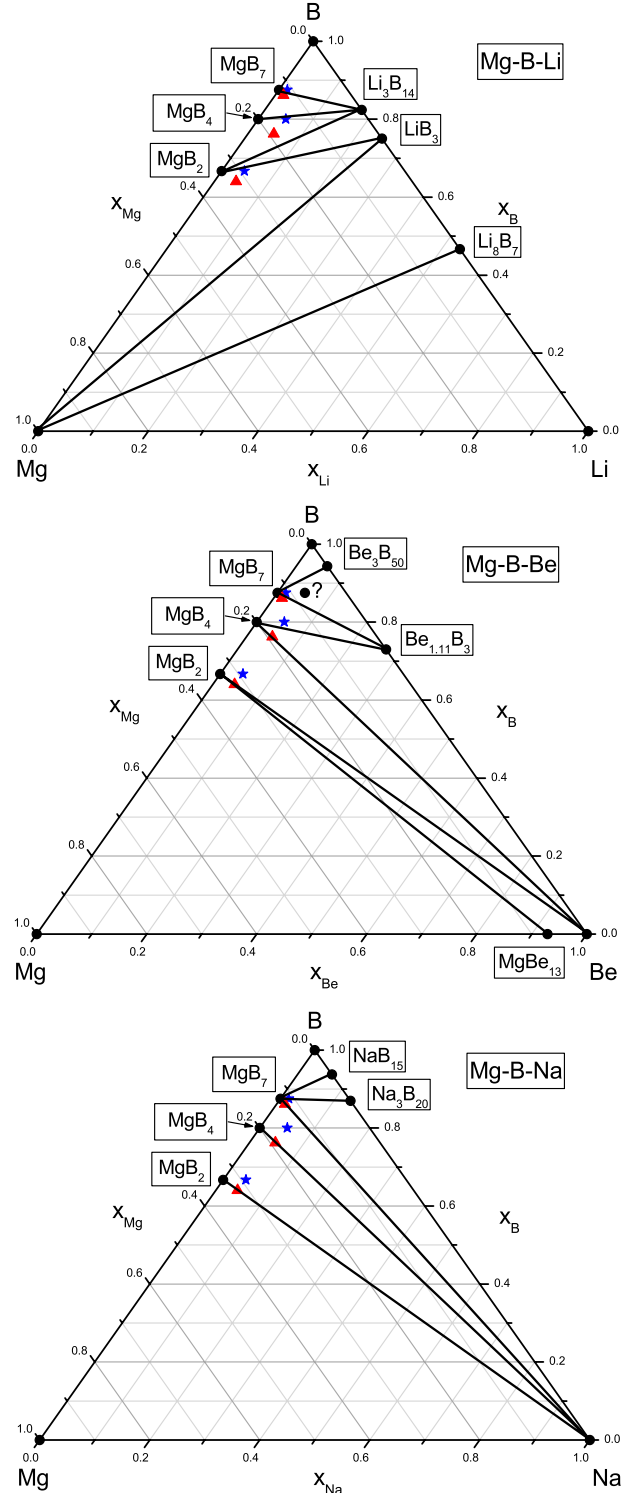


FIG. 2. (Color online) The ternary ground-state phase diagrams of Mg-B- $A$  alloys ( $A$ =Li, Be, Na). The filled circles represent known ground states. The blue stars and red triangles represent the substitutional ( $\text{Mg}_7\text{B}_{56}A$ ,  $\text{Mg}_3\text{B}_{16}A$ ,  $\text{Mg}_7\text{B}_{16}A$ ) and interstitial ( $\text{Mg}_8\text{B}_{56}A$ ,  $\text{Mg}_4\text{B}_{16}A$ ,  $\text{Mg}_8\text{B}_{16}A$ ) supercells, respectively. Each supercell has been constructed from the most appropriate Mg-B compound ( $\text{MgB}_2$ ,  $\text{MgB}_4$ , or  $\text{MgB}_7$ ). The question mark in the Mg-B-Be system indicates the existence of new possible ternary ground state(s) (Sec. VI).

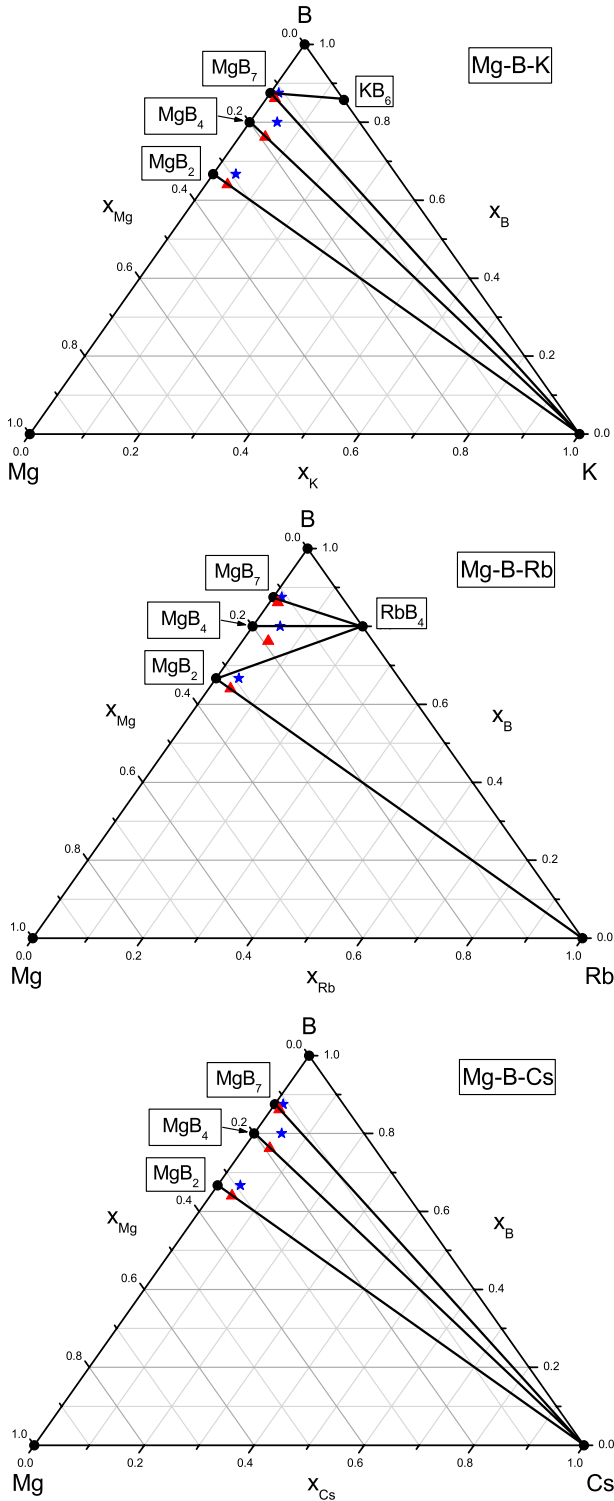


FIG. 3. (Color online) The ternary ground state phase diagrams of Mg-B-A alloys ( $A=K, Rb, Cs$ ).

VI. FIRST-PRINCIPLES CALCULATIONS

The first-principles calculations of energies are performed by using our high-throughput quantum calculations framework AFLOW (Refs. 20 and 30–32) and the software VASP.<sup>33</sup> We use projector augmented waves (PAW) pseudopotentials<sup>34</sup> and exchange-correlation functionals as

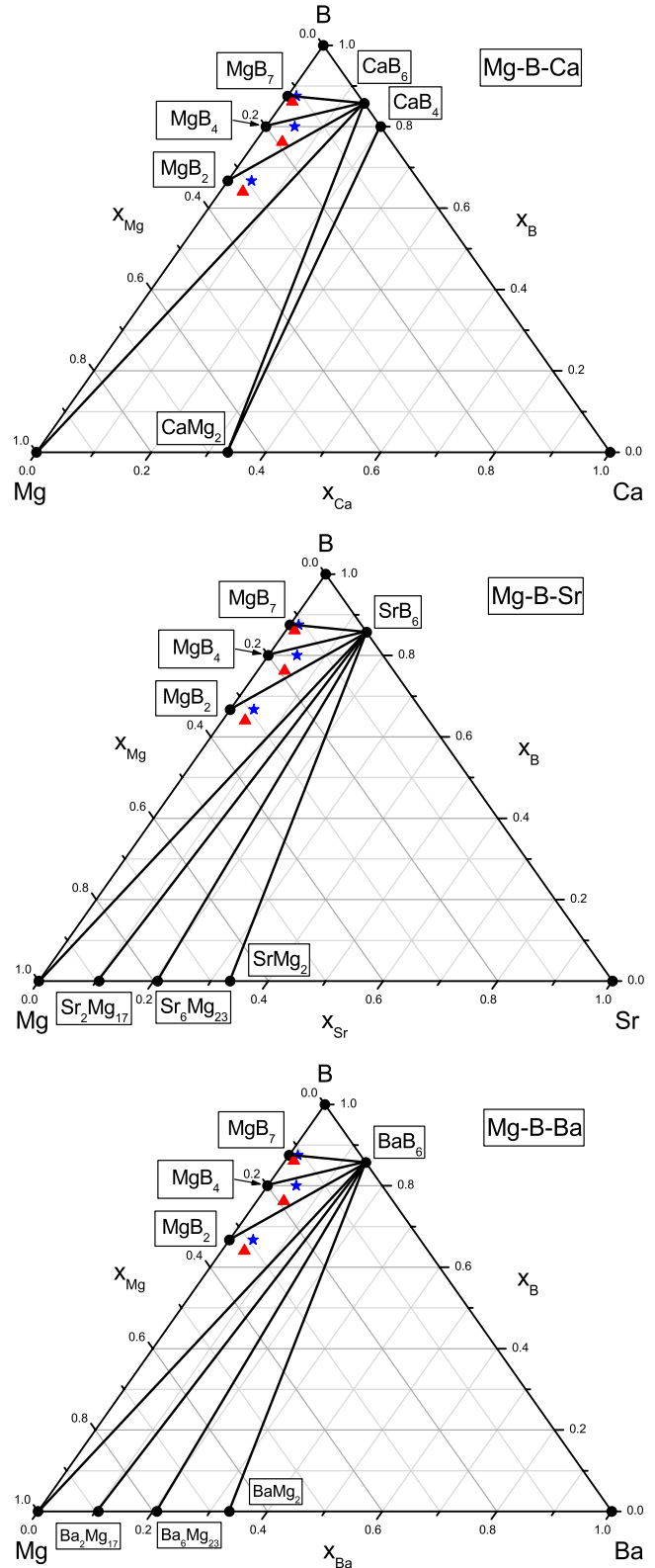


FIG. 4. (Color online) The ternary ground-state phase diagrams of Mg-B-A alloys ( $A=Ca, Sr, Ba$ ).

parameterized by Perdew and Wang<sup>35</sup> for the generalized gradient approximation (GGA). Simulations are carried out without spin polarization (not required for the elements under investigation), at zero temperature, and without zero-

TABLE V. Interstitial (i) and substitutional (s) quantities for alkali and alkaline-earth solute elements  $A$  in  $\text{MgB}_2$ ,  $\text{MgB}_4$ , and  $\text{MgB}_7$  compounds: “raw” formation energies  $\mu_i$ ,  $\bar{\mu}_s$  [Eq. (1)], “true” formation energies  $E_A^{(i)}$ ,  $E_A^{(s)}$  [Eq. (2)] and low-solubility formation energies  $E_{\text{sol}}^{(i)}$ ,  $E_{\text{sol}}^{(s)}$  [Eq. (3)]. In each case, the presented value is the lowest one among all the possible interstitial or substitutional positions.

A	(eV)	$\text{MgB}_2$		$\text{MgB}_4$		$\text{MgB}_7$	
		(i)	(s)	(i)	(s)	(i)	(s)
Li	$\mu_i, \bar{\mu}_s$	0.542	-0.111	0.234	-0.109	-0.959	-0.055
	$E_A^{(i,s)}$	2.444	0.310	2.136	0.312	0.943	0.366
	$E_{\text{sol}}^{(i,s)}$	2.716	0.574	2.654	0.686	1.657	0.506
Be	$\mu_i, \bar{\mu}_s$	-2.665	-0.876	-0.506	-0.710	-1.577	-2.100
	$E_A^{(i,s)}$	1.042	1.350	3.201	1.516	2.130	0.126
	$E_{\text{sol}}^{(i,s)}$	1.054	1.21	3.201	1.256	2.181	-0.557
Na	$\mu_i, \bar{\mu}_s$	5.623	1.839	2.409	1.285	1.999	0.869
	$E_A^{(i,s)}$	6.932	1.666	3.718	1.113	3.308	0.697
	$E_{\text{sol}}^{(i,s)}$	6.944	1.526	3.718	0.802	3.308	0.147
K	$\mu_i, \bar{\mu}_s$	7.022	4.674	2.984	3.001	3.453	2.077
	$E_A^{(i,s)}$	8.061	4.232	4.023	2.559	4.492	1.635
	$E_{\text{sol}}^{(i,s)}$	8.073	4.092	4.023	2.248	4.492	0.838
Ca	$\mu_i, \bar{\mu}_s$	2.833	-0.295	1.042	-1.107	1.251	-1.941
	$E_A^{(i,s)}$	4.751	-0.732	2.960	-0.671	3.169	-1.504
	$E_{\text{sol}}^{(i,s)}$	6.364	1.747	4.993	1.218	5.453	0.358
Rb	$\mu_i, \bar{\mu}_s$	9.463	6.572	3.733	3.957	4.751	3.312
	$E_A^{(i,s)}$	10.393	6.021	4.663	3.406	5.681	2.761
	$E_{\text{sol}}^{(i,s)}$	10.406	5.981	4.862	3.460	6.047	2.477
Sr	$\mu_i, \bar{\mu}_s$	5.514	1.761	1.334	0.221	2.149	-0.960
	$E_A^{(i,s)}$	7.138	1.618	2.958	0.364	3.773	-0.817
	$E_{\text{sol}}^{(i,s)}$	9.042	3.802	5.282	2.544	6.348	1.331
Cs	$\mu_i, \bar{\mu}_s$	4.663	8.436	4.559	5.064	6.488	5.131
	$E_A^{(i,s)}$	5.523	7.815	5.419	4.444	7.349	4.510
	$E_{\text{sol}}^{(i,s)}$	5.536	7.675	5.419	4.134	7.349	3.411
Ba	$\mu_i, \bar{\mu}_s$	2.450	3.959	1.365	1.084	3.118	0.335
	$E_A^{(i,s)}$	4.373	3.518	3.288	1.525	5.041	0.777
	$E_{\text{sol}}^{(i,s)}$	5.971	5.99	5.306	3.400	7.309	2.624

point motion. All structures are fully relaxed (shape and volume of the cell and internal positions of the atoms). The effect of lattice vibrations is omitted. Numerical convergence to within about 1 meV/atom is ensured by enforcing a high energy cutoff (414 eV) and dense 4500  $k$ -point meshes.

### A. Ground states determination

The calculation of solubility of  $A$  in Mg-B compounds requires the knowledge of the relevant ground states in the ternary Mg-B- $A$  system. The systems under investigations have not been well characterized experimentally or theoretically, and only the binary Mg-B, B- $A$ , and Mg- $A$  systems have been studied. Hence, we performed additional high-throughput searches to determine if further ground states exist in the three binary systems.<sup>20,30–32</sup> Based on the knowledge of the binary systems, we built<sup>36</sup> the ternary ground state phase diagrams for Mg-B- $A$ , with the expectation that no missed ternary ground state is relevant to the solubility of  $A$  (Ref. 37).

The existence of the ground states for a given binary  $A$ - $B$  system (where  $A$  and  $B$  are two generic elements) is based on binary *bulk* formation energy, which, for each phase  $\phi$  with stoichiometry  $A_{x_A}B_{x_B}$ , is determined with respect to pure  $A$  and  $B$  energies  $E_{\text{at}}(A)$  and  $E_{\text{at}}(B)$  as

$$\Delta E_{\text{at}}^{\text{bin}}(\phi) \equiv E_{\text{at}}(\phi) - x_A E_{\text{at}}(A) - x_B E_{\text{at}}(B). \quad (27)$$

The results are presented at Table IV and in Fig. 1. For each element  $A$ , the reference energy is chosen to be the lowest among the pure fcc, bcc, and hcp energies.<sup>58</sup> The reference energy for boron is taken to be  $\alpha$ -boron (Refs. 19, 31, and 59–61).

All experimentally observed phases are confirmed except for  $\text{Sr}_9\text{Mg}_{38}$  ( $P6_3/mmc$ ). We also find two possible new phases,  $\text{CaB}_4$  and  $\text{RbB}_4$ , both  $P4/mbm$  (No. 127) and with  $\text{UB}_4$  prototype ( $\text{CaB}_4$  was previously identified in an *ab initio* online database<sup>51</sup>). The formation energies for  $\text{Ba}_2\text{Mg}_{17}$ ,  $\text{Ba}_6\text{Mg}_{23}$ ,  $\text{BaMg}_2$ , and  $\text{CaMg}_2$  are similar to those of Ref. 62 (reported as -0.079, -0.089, -0.088, and -0.126 eV, respec-



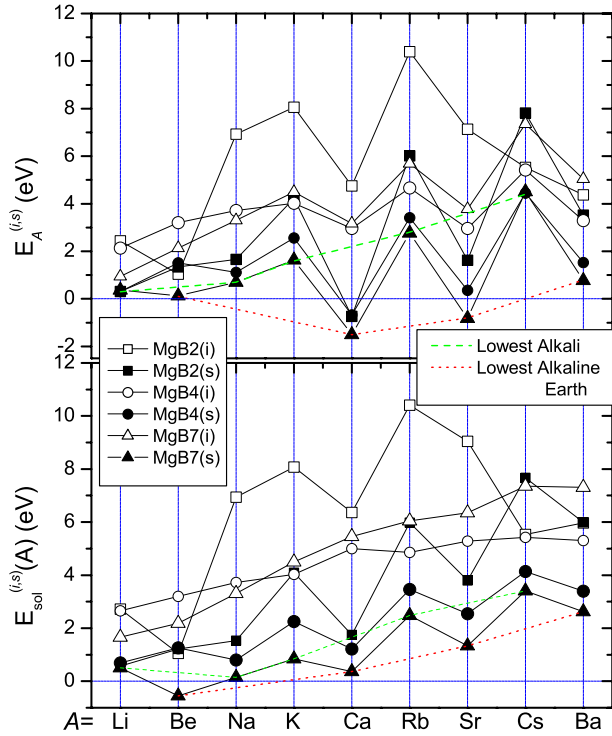


FIG. 5. (Color online) Representation of the formations energies from Table V. Dashed (green) and dotted (red) lines connect the lowest formation energies for alkali and alkaline-earth elements, respectively.

tively). The small differences can be explained on the basis of different GGA pseudopotentials (PW91 versus PBE) and different energy cutoffs (414 versus 360 eV). Our results cannot be compared with the thermodynamic discussion based on the semiempirical Miedema method reported in Ref. 14, because we include additional ground-state prototypes other than those used in the heat of formations fitting in Ref. 14.

The calculated ternary ground-state phase diagrams for Mg-B-A alloys are depicted in Figs. 2–4. Note that in each phase diagram, the triangles and stars represent the supercells with one interstitial or substitutional A atom, respectively. In the interstitial case, the supercells belong to the lines  $Mg_nB_m \leftrightarrow A$ , while in the substitutional case, the supercells belong to the lines parallel to  $Mg \leftrightarrow A$  and intersecting the  $Mg_nB_m$  (constant B concentration).

### B. Formation energies numerical results

The calculated parameters of the model (“raw”  $\mu_i$ ,  $\bar{\mu}_s$  [Eq. (1)], “true”- $E_A^{(i)}$ ,  $E_A^{(s)}$  [Eq. (2)] and low-solubility  $E_{sol}^{(i)}$ ,  $E_{sol}^{(s)}$  [Eq. (3)] formation energies) are presented in Table V and in Fig. 5.

The values of the low-solubility energies reported in Table V suggest the following. (a) Only  $E_{sol}^{(s)}$  for substitutional Be in  $MgB_7$  was found to be negative, indicating the existence of unknown ground state(s) within the triangle  $MgB_7 \leftrightarrow Be_3B_{50} \leftrightarrow Be_{1,11}B_3$ . This fact is summarized by the question mark in Fig. 2. (b) Generally, the substitutional systems have lower formation energy than the interstitial sys-

tems. Exceptions are Be, Cs, and Ba in  $MgB_2$ ; (c) although oscillating, the formation energies tend to increase with the element number, as shown in Fig. 5. Regular oscillations are observed for all substitutional systems starting with Na. The lower and higher boundaries of such correspond to alkaline earth and alkali elements, respectively. (d) Na, Ca, and Li substitutionals in  $MgB_7$  have the lowest formation energies (0.147, 0.358, and 0.506 eV, respectively), resulting in high solubility (Sec. VII). (e) In general for substitutional systems, the higher boron contents the lower formation energy (except Li and Be). (f) The corresponding true  $E_A^{(i,s)}$  and low-solubility  $E_{sol}^{(i,s)}(A)$  formation energies generally demonstrate a similar behavior as functions of A. Exceptions are  $E_A^{(s)} < 0$  for  $A=Ca$  and  $Sr$  and  $E_{sol}^{(s)}(A) < 0$  for  $A=Be$ . The difference is due to the consideration of all the known ground states in the determination of  $E_{sol}^{(i,s)}$  and not only the pure Mg, B and A references (as for  $E_A^{(i,s)}$ ).

In Ref. 17, for Li-Mg-B the formation energies were obtained from first principles for interstitial and substitutional Li in boron-rich  $MgB_2$  (3.00 and 0.27 eV, respectively). These results are different from our low-solubility formation energies  $E_{sol}^{(i)}(Li)=2.72$  eV and  $E_{sol}^{(s)}(Li)=0.57$  eV (see Table V), because only the hexagonal  $\alpha$ -LiB phase was considered as a ground state in Ref. 17 and the other boron-rich phases were reported to be unstable (the  $\alpha$ -LiB was refined in Ref. 32 by variational minimization of the Li and B concentrations as  $Li_8B_7$ ). However, in our high-throughput framework, we found  $LiB_3$  and  $Li_3B_{14}$  to be stable,<sup>63</sup> and the appropriate analysis of the formation energies should be done with respect to the triangle  $MgB_2 \leftrightarrow LiB_3 \leftrightarrow Mg$  as shown in Fig. 2. In the low-solubility limit of Li, since the supercell composition is close to  $MgB_2$ , the lever rule of phase decomposition of the mixtures does not cause significant errors if the energies are calculated with respect to other references, and therefore the results of Ref. 17 are somehow similar.

For Na-Mg-B, it can be shown that the substitutional Na formation energy in magnesium-rich  $MgB_2$  (1.74 eV) obtained in Ref. 17 is equivalent to our “true” formation energy for substitutional Na in  $MgB_2$  ( $E_{Na}^{(s)}=1.67$  eV, see Table V). The observed small numerical difference between two results can be attributed to the different energy cutoffs for the basis set (414 versus 312 eV).<sup>64</sup>

## VII. SOLUBILITY RESULTS

Solubility results are presented in Table VI (the low-solubility approximation values are shown in brackets). We report only values larger than  $10^{-6}$  (Li, Na, Ca, and K). The values on Table VI suggest the following. (a) Na is the only element which has a substantial solubility: Na in  $MgB_7$  is  $\sim 0.5$ –1% at  $T=650$ –1000 K. (b) The substitutional solubility of Be in  $MgB_7$  cannot be determined because the corresponding formation energy  $E_{sol}^{(s)}$  [see Eq. (3)] is negative implying that the ground state list is not complete. Thus the approach of Sec. V is not applicable. (c) In agreement with their lowest formation energies  $E_{sol}^{(s)}$  (Table V and Fig. 5), substitutional Li, Na, and Ca experience the largest solubilities among all studied systems; (d) due to their considerably high formation energies  $E_{sol}^{(i)}$  (Table V and Fig. 5), all the

TABLE VI. Calculated equilibrium interstitial  $x_{A(i)}^{(1)}$  (i) and substitutional  $x_{A(s)}^{(1)}$  (s)  $A$ -solute concentrations at temperatures  $T=300, 650,$  and  $1000$  K, in  $\text{MgB}_2, \text{MgB}_4,$  and  $\text{MgB}_7$  compounds. The values obtained within the low-solubility approximation are reported in brackets. Zeros are used for values smaller than  $10^{-6}$ . For Be “ $\Delta E < 0$ ” indicates that the corresponding formation energy  $E_{\text{sol}}^{(s)}$  [see Eq. (3)] is negative implying that the ground state(s) list is not complete and the approach of Sec. V is not applicable.

	$x_{A(i,s)}^{(1)}$	$\text{MgB}_2$		$\text{MgB}_4$		$\text{MgB}_7$	
		$T$ (K)	(i)	(s)	(i)	(s)	(i)
Li	300	0	0	0	0	0	0
	650	0	$1.3 \times 10^{-5}$ ( $1.2 \times 10^{-5}$ )	0	0	0	$9.9 \times 10^{-6}$ ( $9.9 \times 10^{-6}$ )
	1000	0	$4.5 \times 10^{-4}$ ( $4.3 \times 10^{-4}$ )	0	$6.9 \times 10^{-5}$ ( $7.0 \times 10^{-5}$ )	0	$2.6 \times 10^{-4}$ ( $2.6 \times 10^{-4}$ )
Be	300	0	0	0	0	0	$\Delta E < 0$
	650	0	0	0	0	0	$\Delta E < 0$
	1000	0	0	0	0	0	$\Delta E < 0$
Na	300	0	0	0	0	0	$2.1 \times 10^{-4}$ ( $2.1 \times 10^{-4}$ )
	650	0	0	0	0	0	$4.4 \times 10^{-3}$ ( $4.2 \times 10^{-3}$ )
	1000	0	0	0	$1.8 \times 10^{-5}$ ( $1.8 \times 10^{-5}$ )	0	$1.0 \times 10^{-2}$ ( $0.96 \times 10^{-2}$ )
K	300	0	0	0	0	0	0
	650	0	0	0	0	0	0
	1000	0	0	0	0	0	$3.6 \times 10^{-6}$
Ca	300	0	0	0	0	0	0
	650	0	0	0	0	0	$1.1 \times 10^{-4}$ ( $1.0 \times 10^{-4}$ )
	1000	0	0	0	0	0	$1.0 \times 10^{-3}$ ( $0.96 \times 10^{-3}$ )
Rb	300	0	0	0	0	0	0
	650	0	0	0	0	0	0
	1000	0	0	0	0	0	0
Sr	300	0	0	0	0	0	0
	650	0	0	0	0	0	0
	1000	0	0	0	0	0	0
Cs	300	0	0	0	0	0	0
	650	0	0	0	0	0	0
	1000	0	0	0	0	0	0
Ba	300	0	0	0	0	0	0
	650	0	0	0	0	0	0
	1000	0	0	0	0	0	0

investigated interstitial systems have negligible solubilities. (e) The low-solubility approximation and the general theory agree within 5%.

The calculated negligible solubilities of Be, Na, Ca in  $\text{MgB}_2$  agree with previous experimental observations.<sup>4,7,8,11–13</sup> We did not find any sign of nonvanishing solubilities of Rb, Cs, and Ba in the  $\text{MgB}_2$  alloy even at high annealing temperature in disagreement with the reported experimental data of Ref. 9. However, our negligible Rb and Cs solubility in bulk  $\text{MgB}_2$  are in agreement with the

experimental conclusion made in Ref. 10 where the authors suggest that Rb and Cs dopants most likely segregate in grain boundaries.

The obtained low solubilities of Li and Sr in  $\text{MgB}_2$  differ from experimental values (solubility up to 30% in Refs. 2–6 and 13). This discrepancy can be attributed to segregation of Li and Sr in the grain boundaries as was concluded for Rb and Cs in Ref. 10. In particular, the value of  $E_{\text{sol}}^{(s)}=3.8$  eV for Sr is too large for non-negligible bulk solubility. For Li in  $\text{MgB}_2$  the calculated formation energy  $E_{\text{sol}}^{(s)}=0.57$  eV is not

very large and it is the smallest among the investigated solutes in  $\text{MgB}_2$ . In Ref. 17, qualitative conclusions about high solubility of Li and low solubility of Na in  $\text{MgB}_2$  were made based on a large difference between the corresponding formation energies. Our numerical results demonstrate that, despite much lower formation energy of Li in comparison with Na in  $\text{MgB}_2$ , the Li solubility is still very low (Sec. VI).

It should be emphasized that we consider the alloy in thermodynamical equilibrium which can be difficult to reach at low temperatures and the experimental equilibrium solubility tends usually to be overestimated. In fact, the formation of metastable and/or unstable states which are subsequently frozen at low temperatures, can make solubility measurements very challenging. In such scenarios, the measured solubility may correspond to spinodal concentration rather than actual binodal concentration or simply characterize the frozen out of equilibrium solution remaining from the initial specimen preparation at higher temperature. Besides, the segregation of defects into grain boundaries, especially in multicrystalline samples prepared through nonoptimal cooling, dramatically affects the amount of frozen defects and solutes.

Although in our study we did not perform an extensive search over the configurational space of ternary alloy, if a new ternary phases were present near  $\text{MgB}_2$ , the solute atoms would concentrate and nucleate such phases, and this may be misinterpreted as a high solubility in  $\text{MgB}_2$  phase. Furthermore, a new equilibrium ternary phase would result in an increase in impurities formation energies and, correspondingly, in a decrease in solubility. Numerical approximations in the first principles are not expected to affect the values of solubility: i.e., typically for  $\delta E_{\text{sol}} \sim 30$  meV/atom,  $\delta x_A^{(1)} \sim 2 \times 10^{-4}$ . Lattice vibrations and solute-solute interactions are neglected because they are not expected to play important roles at low temperatures and low solute concentrations.

### VIII. CONCLUSIONS

In the present paper, we present an approach to study the solubilities in ternary alloys. The advantage of the ap-

proach consists in considering all the known ternary ground states rather than just the pure references. Furthermore, we propose an analytical low-solubility approximation that can be used for high-throughput calculations of solubilities in alloys.

Combining the developed framework with first-principles calculations, we have determined the formation energies and solubilities of alkali (Li, Na, K, Rb, Cs) and alkaline earth (Be, Ca, Sr, Ba) metals in the Mg-B system. It is found that the considered metals have low solubilities in the boron-rich Mg-B alloy. Substitutional Na, Ca, and Li experience the largest solubilities, with Na in  $\text{MgB}_7$  reaching 0.5%–1% at  $T=650$ – $1000$  K. All the considered interstitial scenarios lead to negligible solubilities. The solubility of Be in  $\text{MgB}_7$  cannot be determined within our model because the corresponding low-solubility formation energy is negative implying that the existing ground states list must be augmented through a more extensive search over the configurational space.

We have also presented a high-throughput search of ground states in binary Mg-B, Mg-A, and B-A alloys ( $A = \text{Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba}$ ). Ternary phase diagrams Mg-B-A are constructed based on of the determined phases.  $\text{Sr}_9\text{Mg}_{38}$  is not an equilibrium ground state despite its high temperature validations. Two new ground states  $\text{CaB}_4$  and  $\text{RbB}_4$  are found.

### ACKNOWLEDGMENTS

We acknowledge Mike Mehl, Igor Mazin, and Wahyu Setyawan for fruitful discussions. This research was supported by ONR (Grants No. N00014-07-1-0878 and No. N00014-07-1-1085) and NSF (Grant No. DMR-0639822). We thank the Teragrid Partnership (Texas Advanced Computing Center, TACC) for computational support (Grant No. MCA-07S005).

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