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

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By devising a novel framework, 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-principle calculations of solutes formation energies in MgB$_2$, MgB$_4$, MgB$_7$ 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$_7$ at $T = 650 - 1000$ K). All the considered interstitials have negligible solubilities. The solubility of Be in MgB$_7$ 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$_3$Mg$_5$ is not a low-temperature equilibrium structure. We also determine two new possible ground states CaB$_4$ and RbB$_4$, not yet observed experimentally.

I. INTRODUCTION

The interest in magnesium diboride emerged after the discovery of superconductivity in MgB$_2$ at about $T_c=39$ K. Attempts to increase $T_c$ by small additions of alkali (Li, Na, K, Rb, Cs) and alkaline earth metals (Be, Ca, Sr, Ba) to MgB$_2$, 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 50K was reported for the Mg-B-A (A=Cs, Rb, Ba) system, attempts to reproduce the results have been so far unsuccessful (for A=Cs, Rb). The problem can be attributed to solutes’ segregation in grain boundaries and to thus 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 semi-empirical Miedema approach and the Toop’s model were used to address the heats of formation of binary alloys Mg-A, B-A, and Mg-B (A=Li, Na, and Ca). It was proposed that Ca may form stable compounds while Na, Li could lead to metastable or unstable ternary phases in MgB$_2$. In Ref. 17, by calculating first-principle formation energies of Li and Na impurities in MgB$_2$, 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 LiB phase.

The present paper is orthogonal to previous studied. 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-principle calculations of solutes formation energies in MgB$_2$, MgB$_4$, MgB$_7$ alloys and subsequent statistical-thermodynamical evaluation 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 Section II we describe the adopted solubility mechanisms in Mg-B. In Section III we introduce the relevant impurity formation energies in terms of supercell energy calculations and the appropriate ground state(s). In Section IV the approximation for the free energy of Mg-B-A solid solution is formulated. In Section 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 Section 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 $A$ ($A=\text{Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba}$) in the Mg-B system, we consider the disordered solid solutions of $A$-atoms as interstitial and magnesium-substitutional impurities in the experimentally reported compounds\cite{18,19} MgB$_2$, MgB$_4$, and MgB$_7$. We do not consider boron substitutions by $A$ because it has not been observed experimentally\cite{2,3,4,5,6,7,8,9,10,11,12,13}. The disordered solid solution of $A$ inside Mg-B is labeled as “(1)” throughout the paper.

While the magnesium-substitutional positions are determined\cite{19}, the “most accommodating” interstitial locations have to be found. The task is implemented with the following exhaustive search performed through our software AFLLOW\cite{20,21}. Let us consider a quadruplet of non-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, many of the interstitials 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 position. 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

“Raw” formation energies

Let us define the so-called “raw” formation energies $\mu_i$ and $\overline{\mu}_s$ (composition unpreserving\cite{22}) as the changes of 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

$$\mu_i \equiv \mu_i^{(1)}(A) = E_{\text{sc}}[\mu_i^{(s)} \mu_{n_{sc}}^{\text{m}_{sc}}] - E_{\text{sc}}[\mu_{n_{sc}}^{\text{m}_{sc}}],$$

$$\overline{\mu}_s = \mu_s^{(1)}(\text{sc}) - \mu_i^{(1)}(\text{sc}) = E_{\text{sc}}[\mu_i^{(s)} \mu_{n_{sc}}^{\text{m}_{sc}}] - E_{\text{sc}}[\mu_{n_{sc}}^{\text{m}_{sc}}],$$

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

The conventional unit cells of MgB$_2$, MgB$_4$, and 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 MgB$_2$, while there is no need to create supercells of MgB$_4$ and 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 I summarizes the parameters of the supercells and Table III lists the supercell atomic compositions.

| Structure | Coordinates | Cage radius (Å) | $\nu_i$ |
|-----------|-------------|----------------|--------|
| MgB$_2$   | 0.341, 0.681, 0.000 | 1.7619 | 2 (6) |
|           | 0.006, 0.000, 0.500 | 1.7616 | 1 (6) |
|           | 0.500, 0.500, 0.122 | 1.6015 | 6 (6) |
| MgB$_4$   | 0.106, 0.669, 0.412 | 1.9145 | 4 (52) |
| (Mg$_2$B$_6$) | 0.375, 0.250, 0.337 | 1.7836 | 4 (4) |
|           | 0.145, 0.632, 0.813 | 1.7821 | 8 (24) |
|           | 0.144, 0.750, 0.925 | 1.7252 | 4 (24) |
|           | 0.225, 0.750, 0.719 | 1.6322 | 4 (4) |
|           | 0.086, 0.015, 0.527 | 1.6128 | 8 (8) |
|           | 0.101, 0.543, 0.261 | 1.5322 | 8 (8) |
| MgB$_7$   | 0.000, 0.049, 0.618 | 2.0690 | 8 (12) |
| (Mg$_5$B$_9$) | 0.189, 0.250, 0.821 | 1.8937 | 8 (24) |
|           | 0.250, 0.217, 0.750 | 1.7995 | 8 (8) |
|           | 0.243, 0.250, 0.505 | 1.7888 | 8 (24) |
|           | 0.197, 0.250, 0.469 | 1.7502 | 8 (24) |
|           | 0.000, 0.250, 0.150 | 1.7002 | 4 (24) |
|           | 0.012, 0.000, 0.000 | 1.6905 | 8 (64) |
|           | 0.250, 0.062, 0.250 | 1.6068 | 8 (40) |
|           | 0.000, 0.171, 0.788 | 1.4991 | 8 (8) |
|           | 0.131, 0.186, 0.119 | 1.4443 | 16 (16) |

TABLE I: Centers and sizes of the symmetrically inequivalent interstitial cages for the MgB$_2$, MgB$_4$, and MgB$_7$ unit cells. Coordinates are presented as fractions of the standard unit cell basis vectors (a, b, c). 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.
TABLE II: Numbers of atoms $n, m$ (Mg$_n$B$_m$) in the conventional unit cells ("uc") and in the constructed supercells ("sc") for MgB$_2$, MgB$_4$, and MgB$_7$. $\nu_s$ indicates the number of symmetrically equivalent s-type Mg atom positions within the corresponding unit cell. $d_{AA}$ and $d_{BB}$ are the distances between the nearest solutes and nearest solvent atoms (boron-boron in our case) in the supercell.

| Compound | n$_{uc}$ | m$_{uc}$ | $\nu_s$ | n$_{sc}$ | m$_{sc}$ | $d_{AA}$ (Å) | $d_{BB}$/d$_{sc}$ |
|----------|----------|----------|---------|----------|----------|-------------|----------------|
| MgB$_2$  | 1        | 2        | 1       | 8        | 16       | 1.7811      | 3.46           |
| MgB$_4$  | 4        | 16       | 4       | 4        | 16       | 1.7004      | 2.60           |
| MgB$_7$  | 8        | 56       | 4       | 8        | 56       | 1.7372      | 3.44           |

TABLE III:Interstitial and substitutional supercell atomic compositions ($x^{sc}_A$, $x^{sc}_B$, $x^{sc}_C$) as functions of the $n_{sc}$ (for Mg) and $m_{sc}$ (for B) numbers of atoms in the supercell.

| Interstitials | Substitutional |
|---------------|----------------|
| $x^{sc}_A$    | $x^{sc}_B$     |
| $m_{sc}[1+n_{sc}+m_{sc}]^{-1}$ | $m_{sc}[n_{sc}+m_{sc}]^{-1}$ |
| $x^{sc}_B$    | $x^{sc}_C$     |
| $n_{sc}[1+n_{sc}+m_{sc}]^{-1}$ | $n_{sc}[n_{sc}+m_{sc}]^{-1}$ |

“True” formation energies

The “true” formation energies (composition preserving) are defined from the “raw” formation energies (composition unpreserving) as

$$E^{(i)}_A = \mu_i - \mu^\text{pure}_A,$$

$$E^{(s)}_A = \mu_s + \mu^\text{pure}_A - \mu^\text{pure}_A,$$

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

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]):

$$E^{\alpha}_{\text{sol}}(A) = \Delta E^{\alpha}_{\text{sc/at}}/x^{sc}_A \equiv E^{\alpha}_{\text{sc/at}}(A^{24}),$$

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

$$\Delta E^{(i)}_{\text{sc/at}} = \frac{E^{(i)}_{\text{sc}[A^\alpha \text{Mg}_{n_{sc}} B_{m_{sc}}]}_{\text{sc}}}{1+n_{sc}+m_{sc}} - E^{\text{mix}}_{\text{at}}(x^{sc}_A, x^{sc}_B, x^{sc}_C),$$

$$\Delta E^{(s)}_{\text{sc/at}} = \frac{E^{(s)}_{\text{sc}[A^\alpha \text{Mg}_{n_{sc}} B_{m_{sc}}]}_{\text{sc}}}{1+n_{sc}+m_{sc}} - E^{\text{mix}}_{\text{at}}(x^{sc}_A, x^{sc}_B, x^{sc}_C),$$

where $E^{\text{mix}}_{\text{at}}(x^{sc}_A, x^{sc}_B, x^{sc}_C)$ is the energy of a the three phase mixture at the same composition of the supercell (see Table III).

$$E^{\alpha}_{\text{at}}(x^{sc}_A, x^{sc}_B, x^{sc}_C) = X_1 E^{\alpha}_{\text{uc}}[\text{Mg}_{n_{sc}} B_{m_{sc}}]_{\text{uc}} + X_2 E^{(2)}_{\text{at}} + X_3 E^{(3)}_{\text{at}}.$$

(5)

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

$$\begin{align*}
    x^{sc}_A &= X_2 x^{(2)}_A + X_3 x^{(3)}_A \\
    x^{sc}_B &= X_1 x^{(1)}_B + X_2 x^{(2)}_B + X_3 x^{(3)}_B \\
    x^{sc}_C &= X_1 x^{(1)}_C + X_2 x^{(2)}_C + X_3 x^{(3)}_C
\end{align*}$$

(6)

where $E^{(k)}_{\text{at}}$ ($x^{(k)}_A$, $x^{(k)}_B$, $x^{(k)}_C$) are the energies (per atom) and stoichiometric compositions of the two other ground states that, together with Mg$_{n_{sc}}$B$_{m_{sc}}$, form the convex hull triangle containing the point ($x^{sc}_A$, $x^{sc}_B$, $x^{sc}_C$) in the ternary phase diagram. For example, MgB$_2$, Mg, and LiB$_3$ are the three ground states surrounding Mg$_7$B$_{16}$Li (a supercell of 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 $\Delta E^{\alpha}_{\text{sc/at}}$ defined in Eq. (4) are the supercell formation energies (per atom) determined with respect to the mixture of ground states $^{24}$. $E^{\alpha}_{\text{sol}}(A)$ and $\Delta E^{\alpha}_{\text{sc/at}}$ cannot be negative. If they do, it indicates that the list of ground states is incomplete, and a better phase diagram should be established (the missed ground state can be supercell itself $^{24}$).

In analogy of with binary alloys $^{24}$, the ternary alloy “low-solubility formation energy” $E^{\alpha}_{\text{sol}}(A)$ is shown to determine the solubility of $A$ in the low-solubility limit (Section IV).

IV. FREE ENERGY OF 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:

$$G^{(1)}_{\text{uc}}[\{c_i, c_s\}, T] = E_{\text{uc}}[\text{Mg}_{n_{uc}} B_{m_{uc}}]_{\text{uc}} + \Delta g_t + \Delta g_s,$$

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

$$\Delta g_s = \sum_s \nu_s [c_s \mu_s + k_B T (c_s \ln c_s + (1 - c_s) \ln(1 - c_s))],$$

(7)

where $k_B$ is a Boltzmann constant, $T$ is the temperature, and $E_{\text{uc}}[\text{Mg}_{n_{uc}} B_{m_{uc}}]$ represents the energy (enthalpy) of initial Mg$_{n_{uc}}$B$_{m_{uc}}$ unit cell without A-solutes; the summations over $i$ and $s$ are over 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 $\mu_s$ are introduced in Sec. III. Although, the mean-field approximation neglects correlations, it should work well when the deviation from stoichiometry is small (see Sec. 19 in Ref. 24). In addition, we neglect solute-solute interactions that might be important especially for high solute concentrations. In conclusion, our model is similar to Wagner-Schottky model of a system of non-interacting particles.

For given concentrations $\{c_i, c_s\}$, the total number of atoms per unit cell, $N_{uc}$, 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

$$N_{uc} = \sum_i n_{uc} \mu_i + n_{uc} \mu_s, \quad x_{A(i)}^{(1)} = \sum_i \nu_i c_i / N_{uc}, \quad x_{A(s)}^{(1)} = \sum_s \nu_s c_s / N_{uc}, \quad x_{A}^{(1)} = x_{A(i)}^{(1)} + x_{A(s)}^{(1)}. \quad (8)$$

At given temperature and concentration $x_{A}^{(1)}$, the Gibbs free energy per atom $G_{at}^{(1)}[x_{A}^{(1)}, T]$ is determined by minimizing Eq. (6) with respect to $c_i$ and $c_s$:

$$G_{at}^{(1)}[x_{A}^{(1)}, T] = \min_{\{c_i, c_s\}} \left[ G_{at}^{(1)}[\{c_i, c_s\}, T] \right]_{x_{A}^{(1)}}^2, \quad (9)$$

where

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

The solution $\{c_i, c_s\}$ defines the equilibrium distribution of interstitial and substitutional A-solutes in the Mg$_{nuc}$B$_{muc}$ 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. 3):

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

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 formation of a new phase.

To calculate the solubility, we consider the Gibbs free energy $G_{at}^{\text{mix}}$ of the mixture of three phases with a given general (“gen”) composition $x_{\text{gen}}^{(1)} = (x_{A}^{\text{gen}}, x_{B}^{\text{gen}}, x_{\text{Mg}}^{\text{gen}})$. The first phase is the substitutional and/or interstitial solid solution with atomic concentration $x_{A}^{(1)}$ of element $A$ in Mg$_{nuc}$B$_{muc}$. At zero temperature, the two other phases and Mg$_{nuc}$B$_{muc}$ form a triangle containing the point $x_{\text{gen}}^{(1)}$ in the ternary phase diagram. At a finite temperature, the free energy $G_{at}^{\text{mix}}$ is the generalization of Eq. (5):

$$G_{at}^{\text{mix}}[x_{A}^{(1)}, T] \simeq X_1[x_{A}^{(1)}], T]G_{at}^{(1)}[x_{A}^{(1)}, T] +$$

$$X_2[x_{A}^{(1)}, T]E_{at}^{(2)} + X_3[x_{A}^{(1)}, T]E_{at}^{(3)} \quad (13)$$

where $G_{at}^{(1)}[x_{A}, T]$ 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) $E_{at}^{(2)}$ and $E_{at}^{(3)}$, 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:

$$\begin{cases}
X_{\text{gen}}^{\text{A}} = X_1 x_{A}^{(1)} + X_2 x_{B}^{(2)} + X_3 x_{\text{Mg}}^{(3)} \\
X_{\text{gen}}^{\text{B}} = X_1 x_{B}^{(1)} + X_2 x_{B}^{(2)} + X_3 x_{\text{Mg}}^{(3)} \\
X_{\text{gen}}^{\text{Mg}} = X_1 x_{\text{Mg}}^{(1)} + X_2 x_{\text{Mg}}^{(2)} + X_3 x_{\text{Mg}}^{(3)}
\end{cases} \quad (14)$$

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

$$x_{A}^{(1)} = \frac{n_{uc}}{n_{uc} + n_{muc}} (1 - x_{A}^{(1)}[x_{A}^{(1)}, T]), \quad (15)$$

$$x_{B}^{(1)} = 1 - x_{A}^{(1)} - x_{B}^{(1)},$$

where $x_{A}^{(1)}[x_{A}^{(1)}, T]$ is the equilibrium concentration of A-interstitials in the first phase given by Eqs. (8) at for chosen total concentration $x_{A}^{(1)}$. The minimization of $G_{at}^{\text{mix}}$ with respect to $x_{A}^{(1)}$ gives the solubility $x_{A}^{(1)}(T)$ in the first phase “(1)”: $G_{at}^{\text{mix}}[x_{A}^{(1)}, T] = \min_{x_{A}^{(1)}} G_{at}^{\text{mix}}[x_{A}^{(1)}, T]. \quad (16)$

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 coincide 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 solution does not generally belong to the Mg-B-→gs(2) or Mg-B-→gs(3) lines in the ternary phase diagram. Thus, we have to consider the phase mixture of Mg$_{\text{nucl}}$B$_{\text{nucl}}$, gs(2), and gs(3) to guarantee accurate estimation of the solubility.

**Low-solubility approximation**

In order to get the analytical expression for equilibrium solubilities from Eq. (10), 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 end of section). Thus, from Eqs. (13,16) we obtain:

$$\frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}} \approx \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}} + X_{1} \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}}, \quad (17)$$

where

$$E_{\text{at}}^{\text{mix}}[x_{A}^{(1)}, x_{\text{gen}}] = X_{1} E_{\text{at}}^{(1)} + X_{2} E_{\text{at}}^{(2)} + X_{3} E_{\text{at}}^{(3)}, \quad (18)$$

and the fractions $X_{k} = X_{k}[x_{A}^{(1)}, x_{\text{gen}}]$ come from Eqs. (14,15). Note that the *circa* ($\approx$) in Eq. (17) corresponds to approximation (a) applied to Eqs. (7,10):

$$\frac{\partial X_{1}}{\partial x_{A}^{(1)}} G_{\text{at}}^{(1)} \approx \frac{\partial X_{1}}{\partial x_{A}^{(1)}} E_{\text{at}}^{(1)}.$$

Equations (14,15) lead to:

$$\frac{\partial X_{k}}{\partial x_{A}^{(1)}} \approx -X_{1} \frac{\partial X_{k}}{\partial x_{A}^{(1)}} \quad (20)$$

and through Eq. (15):

$$\frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}} \approx -X_{1} \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}}. \quad (21)$$

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 *circa* ($\approx$) corresponds to approximation (a).

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

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

where

$$E_{\text{sol}}^{(1)}(A) = \mu_{\alpha} - \frac{\partial E_{\text{at}}^{\text{mix}}}{\partial x_{A}^{(1)}} \quad (24)$$

Both Equations (24) and (3) define the same quantity: the low-solubility formation energy, $E_{\text{sol}}^{(1)}(A)$, determining the low-solubility of $A$-solutes in $\alpha$ type positions. In addition, by using Eqs. (5)-(23) the total equilibrium concentration of solute $A$ in the phase (1) becomes

$$x_{A}^{(1)} \approx \frac{\mu_{\alpha}}{n_{\text{uc}} + m_{\text{uc}}}, \quad (25)$$

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, expression (25) can be integrated out through the various types of positions, leading to

$$x_{A}^{(1)} \approx \sum_{i} \nu_{i} c_{i} + \sum_{s} \nu_{s} c_{s} n_{\text{uc}} + m_{\text{uc}}, \quad (26)$$

where $c_{i}$ and $c_{s}$ are obtained from a set of Eq. (23), by using the corresponding $E_{\text{sol}}^{(1)}(A)$ and $E_{\text{sol}}^{(s)}(A)$ for each type of defects.

**VI. FIRST-PRINCIPLES CALCULATIONS**

The first-principles calculations of energies are performed by using our high-throughput quantum calculations framework AFLOW20,30,31,32 and the software VASP. We use projector augmented waves (PAW) pseudopotentials24 and exchange-correlation functionals as parameterized by Perdew and Wang25 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-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 cut-off (414 eV) and dense 4,500 k-point meshes.

**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.

Based on the knowledge of the binary systems, we built 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]).

TABLE IV: The formation energies $\Delta E_{\text{bin}}$ (Eq. (27)) for Mg-B, B-A, and Mg-A binary ground states ($A=$Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba). The symbol (+) indicates possible ground states never observed experimentally (CaB$_6$, K, Ca, Rb, Sr, Cs, Ba). The symbol (-) indicates the experimentally observed Sr$_9$Mg$_{38}$, which was not confirmed to be a ground state by first-principle calculations.

| $\Delta E_{\text{bin}}$ (eV/atom) | Prototype[27] | Space group[27] | Pearson | Ref. |
|----------------------------------|---------------|----------------|---------|------|
| Li$_3$B$_{14}$                   | -0.219        | Li$_3$B$_{14}$ | tI160   | 39   |
| LiB                              | -0.235        | LiB            | tP20    | 40   |
| Li$_3$Be                          | -0.216        | Li$_3$Be       | P6/mmm(187) | hP15 | 41   |
| Be$_2$B$_{10}$                   | -0.032        | Be$_2$B$_{10}$ | P6/mmm(134) | tP53 | 42   |
| Be$_{11}$B$_3$                    | -0.096        | Be$_{11}$B$_3$ | P6/mmm(191) | hP111 | 43   |
| Mg$_2$Be$_{13}$                  | -0.009        | NaZn$_{13}$   | Fm3c(226) | cF112 | 44   |
| NaB                              | -0.059        | NaB$_{15}$    | Imma(74) | oI64 | 45   |
| Na$_3$B$_{20}$                   | -0.070        | Na$_3$B$_{20}$ | Cmcm(65) | oC46 | 45   |
| Mg$_8$B$_7$                      | -0.138        | Mg$_8$B$_7$   | Imma(74) | oI64 | 46   |
| Mg$_4$B$_4$                      | -0.152        | Mg$_4$B$_4$   | Pnma(62) | cP20 | 47   |
| Mg$_2$B$_2$                      | -0.151        | Mg$_2$B$_2$   | P6/mmm(191) | hP3 | 48   |
| KB$_6$                           | -0.043        | CaB$_6$       | Pn3m(221) | cP7 | 49   |
| Ca$_6$B$_6$                      | -0.423        | Ca$_6$B$_6$   | Pn3m(221) | cP7 | 49   |
| Ca$_4$B$_4$                      | -0.410        | UB$_4$        | P4/mmm(127) | tP20 | 50   |
| Ca$_2$B$_2$                      | -0.128        | Mg$_2$Zn$_2$  | P6$_3$/mcm(194) | hP12 | 51   |
| Rb$_6$B$_4$                      | -0.163        | UB$_4$       | P4/mmm(127) | tP20 | 52   |
| Sr$_6$B$_6$                      | -0.464        | CaB$_6$       | Pn3m(221) | cP7 | 53   |
| Sr$_2$Mg$_{17}$                 | -0.055        | Th$_2$Ni$_{17}$ | P6$_3$/mmc(194) | hP38 | 54   |
| Sr$_9$Mg$_{38}$                 | -0.070        | Sr$_9$Mg$_{38}$ | P6$_3$/mcm(194) | hP94 | 55   |
| Sr$_9$Mg$_{38}$                  | -0.085        | Sr$_9$Mg$_{38}$ | P6$_3$/mcm(194) | hP94 | 55   |
| Sr$_9$Mg$_{38}$                 | -0.114        | Mg$_2$Zn$_2$  | P6$_3$/mcm(194) | hP12 | 57   |
| Ba$_6$B$_6$                      | -0.421        | CaB$_6$       | Pn3m(221) | cP7 | 58   |
| Ba$_2$Mg$_{17}$                 | -0.072        | Zn$_{17}$Th$_2$ | R3m(166) | hK57 | 59   |
| Ba$_2$Mg$_{23}$                 | -0.085        | Th$_2$Mg$_{23}$ | Pn3m(221) | cF116 | 60   |
| Ba$_2$Mg$_{23}$                 | -0.097        | Mg$_2$Zn$_2$  | P6$_3$/mcm(194) | hP12 | 61   |

The existence of the ground states for a given binary $A$-$B$ system is based on binary bulk formation energy, which, for each phase $\phi$ with stoichiometry $A_xB_{2x}$, is determined with respect to pure $A$ and $B$ energies $E_{\text{at}}(A)$ and $E_{\text{at}}(B)$ as

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

(27)

The results are presented at Table IV and in Figure 1. For each element $A$, the reference energy is chosen to be the lowest among the pure fcc, bcc and hcp energies. The reference energy for boron is taken to be $\alpha$-boron (Refs. [19, 31, 59, 60, 61]).

All experimentally observed phases are confirmed except for Sr$_9$Mg$_{38}$ (P6$_3$/mcm). We also find two possible new phases, CaB$_4$ and RbB$_4$, both P4/mmm (#127) and with UB$_4$ prototype (CaB$_4$ was previously identified in ab initio online database[21]). The formation energies for Ba$_2$Mg$_{17}$, Ba$_2$Mg$_{23}$, BaMg$_2$, and CaMg$_2$ are similar to those of Ref. [62] (reported as -0.079 eV, -0.089 eV, -0.088 eV, and -0.126 eV, respectively). The small differences can be explained on the basis of different GGA pseudopotentials (PW91 versus PBE) and different energy cut-offs (414 eV versus 360 eV). Our results can not be compared with the thermodynamic discussion based on the semi-empirical Miedema method reported in Ref. [14], because...
we include further 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 and 3. Note that in each phase diagram, the red triangles and blue stars represent the supercells with one interstitial or substitutional A atom, respectively. In the interstitial case, the supercells belong to the lines Mg$_n$B$_m$$\leftrightarrow$A, while in the substitutional case, the supercells belong to the lines parallel to Mg$\leftrightarrow$A and intersecting the Mg$_n$B$_m$ (constant B concentration).

Formation energies numerical results

The calculated parameters of the model (“raw” $\mu_i$, $\mu_s$ (Eq. 1), “true”- $E_i^{(i)}$, $E_s^{(s)}$ (Eq. 2) and low-solubility $E_i^{(i)}$, $E_s^{(s)}$ (Eqs. 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 $E_{sol}^{(i,s)}$ 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$_3$B$_{50}$ $\leftrightarrow$ Be$_{11,1}$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 systems. 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. (d) 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$_2$ have the lowest formation energies (0.147 eV, 0.358 eV, 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 formation energies $E_{sol}^{(i,s)}(A)$ generally demonstrate a similar behavior as functions of $A$. Exceptions are $E_A^{(i,s)} < 0$ for $A=$Ca and Sr and $E_{sol}^{(i,s)}(A) < 0$ for $A=$Be. The difference is due to the consideration of all the known ground states for the determination of $E_{sol}^{(i,s)}$ and not only pure Mg, B and A (as for $E_A^{(i,s)}$).

### Table V: Interstitial (i) and substitutional (s) quantities for alkali and alkaline earth solute elements $A$ in MgB$_2$, MgB$_4$, and MgB$_7$ compounds.

| A    | MgB$_2$  | MgB$_4$  | MgB$_7$  |
|------|----------|----------|----------|
|      | $(i)$    | $(s)$    | $(i)$    | $(s)$    |
| Li   | 0.542    | -0.111   | 0.234    | -0.149   | 0.3959   | 0.0555   |
| Be   | -2.665   | -0.876   | -0.506   | -0.710   | -1.577   | -2.100   |
| Na   | 5.623    | 1.350    | 3.201    | 1.516    | 2.130    | 0.126    |
| K    | 7.022    | 4.674    | 2.984    | 3.001    | 3.453    | 2.077    |
| Ca   | 2.833    | -0.295   | 1.042    | -1.107   | 1.251    | -1.941   |
| Rb   | 9.463    | 6.372    | 3.733    | 3.957    | 4.751    | 3.312    |
| Sr   | 9.514    | 4.705    | 4.198    | 3.864    | 6.787    | 4.331    |
| Cs   | 4.663    | 8.436    | 4.559    | 5.064    | 6.488    | 5.131    |
| Ba   | 2.450    | 3.959    | 1.365    | 1.084    | 3.118    | 0.335    |

FIG. 4: (color online) The ternary ground state phase diagrams of Mg-B-A alloys ($A=$Ca, Sr, Ba).
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\(_2\) is \(\sim 0.5-1\%\) at \(T = 650 - 1000\) K. (b) The substitutional solubility of Be in MgB\(_2\) cannot be determined because the corresponding formation energy \(E_{\text{sol}}^{(s)}\) (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 \(E_{\text{sol}}^{(b)}\) (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 \(E_{\text{sol}}^{(i)}\) (Table V and Fig. 5), all the 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 MgB\(_2\) agree with previous experimental observations.\(^{3,4,5,6,13}\) We did not find any sign of nonvanishing solubilities of Rb, Cs and Ba in the MgB\(_2\) alloy even at high annealing temperature in disagreement with the reported experimental data of Ref. 3. However, our negligible Rb and Cs solubility in bulk MgB\(_2\) are in agreement with the experimental conclusion made in Ref. 16 where the author suggest that Rb and Cs dopants most likely segregate in grain boundaries.

The obtained low solubilities of Li and Sr in MgB\(_2\) differ from experimental values (solubility up to 30% in Refs. 2,3,6,9). This discrepancy can be attributed to segregation of Li and Sr in the grain boundaries as was concluded for Rb and Cs in Ref. 16. 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 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 MgB\(_2\).

In Ref. 17, qualitative conclusions about high solubility of Li and low solubility of Na in 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 MgB\(_2\), the Li-solubility is still very low (Sec. VI).

It should be emphasized that our model is 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 solubility remaining from the initial specimen preparation at higher temperature. Besides, the segregation of defects into grain-boundaries, especially in multicrystalline samples prepared through non optimal cooling dramatically affect 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 MgB$_2$, the solute atoms would concentrate and nucleate such phases, and this may be misinterpreted as a high solubility in MgB$_2$ phase. Furthermore, a new equilibrium ternary phase would result in an increase of impurities formation energies and, correspondingly, in a decrease of solubility. Numerical approximations in the first-principles are not expected to affect the values of solubility: i.e. typically for $\delta E_{val} \sim 30 \text{ meV/atom}$, $\delta x_{(1)} \sim 2 \times 10^{-4}$. 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 approach is in taking into account all known ternary ground states rather than just pure solids. Based on the approach, we propose an analytical low-solubility approximation that can be used for high-throughput calculations of solubilities in alloys.

Combining the developed approach with first principle 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 the largest solubilities, with Na in MgB$_2$ reaching 0.5-1% at $T = 650 \sim 1000$ K. All the considered interstitial scenarios lead to negligible solubilities. The solubility of Be in MgB$_7$ can not be determined with 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 also present a high-throughput search of ground states in binary Mg-B, Mg-A, and B-A alloys ($A=$Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba). Ternary phase diagrams Mg-B-A are constructed based on of the determined phases. Sr$_3$Mg$_{58}$ is not an equilibrium ground state despite its high temperature validations. Two new ground states CaB$_4$ and RbB$_4$ are found.

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**TABLE VI: Calculated equilibrium interstitial $x_{A}^{(1)}$ (i) and substitutional $x_{A}^{(s)}$ (s) A-solute concentrations at temperatures $T = 300$, 650, and 1000 K, in MgB$_2$, MgB$_3$, and 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 $E_{val}^{(s)}$ (see Eq. (2)) is negative implying that the ground state(s) list is not complete.**

| $A$ | $T$ (K) | $x_{A}^{(1)}$ | $x_{A}^{(s)}$ |
|-----|---------|---------------|---------------|
| Li  | 300     | 0             | 0             |
|     | 650     | 1.3×10$^{-5}$ | (1.2×10$^{-5}$) |
|     | 1000    | 4.5×10$^{-4}$ | (4.3×10$^{-4}$) |
| Be  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 1.8×10$^{-5}$ | (1.8×10$^{-5}$) |
| Na  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 3.6×10$^{-6}$ |                 |
| K   | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
| Ca  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
| Rb  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
| Sr  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
| Cs  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
| Ba  | 300     | 0             | 0             |
|     | 650     | 0             | 0             |
|     | 1000    | 0             | 0             |
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As shown in Sec. V, the low-solubility formation energy $E_{\text{sol}}^{(s)}(\text{Na}) = 1.53$ eV rather than "true" formation energy $E_{\text{Na}}^{(s)} = 1.67$ is more accurate for corresponding solubility characterization when the system is miscible. The 0.14 eV difference between $E_{\text{Na}}^{(s)}$ and $E_{\text{sol}}^{(s)}(\text{Na})$ suggests that the effect of other ground state (MgB$_4$, see Fig. 2) on the formation energy and subsequently on the solubility is not negligible.