High-throughput ab initio analysis of the Bi–In, Bi–Mg, Bi–Sb, In–Mg, In–Sb, and Mg–Sb systems

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Abstract
Prediction and characterization of crystal structures of alloys are a key problem in materials research. Using high-throughput ab initio calculations we explore the low-temperature phase diagrams for the following systems: Bi–In, Bi–Mg, Bi–Sb, In–Mg, In–Sb, and Mg–Sb. For the experimentally observed phases in these systems we provide information about their stability at low temperatures.
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1. Introduction
Magnesium alloys present an excellent combination of light weight and specific strength compared to steel and aluminum alloys and would offer an opportunity for radical improvement in automotive vehicle design and performance [1,2]. However, for more than fifty years magnesium alloy research has been confined almost exclusively to casting alloys and there has been no equivalent effort in developing wrought magnesium alloys of sufficiently high strength [3]. Both wrought aluminum alloys and wrought magnesium alloys achieve their increased strength levels through the process of precipitation-hardening, also known as age-hardening. In the case of aluminum alloys, the metallurgy of precipitation-hardening has been thoroughly explored and has resulted in the five- and six-element aluminum alloys which form the basis for all aerospace structures [4]. The trial and error research has required an enormous effort over many years to produce the aluminum alloys now in use. This is so because the hardening process depends on the development of stable and metastable phases in the base alloy matrix, a problem particularly difficult for experimental investigation due to long annealing times involved in the phase formation. If the development of greatly increased strength in precipitation-hardenable magnesium alloys followed a similar trial and error path it would require a similar level of effort [5].

Fortunately, the combination of ab initio density functional theory methods and data mining techniques provides an opportunity to dramatically accelerate materials research by efficiently predicting new phases and accurately describing their ground states [6–10]. These theoretical methods are particularly suitable for investigation of low-temperature compounds and can thus play an important role in the development of precipitation-hardenable magnesium alloys.

In this paper we systematically explore the low-temperature phase diagrams for the following six binary alloy systems: Bi–In, Bi–Mg, Bi–Sb, In–Mg, In–Sb, and Mg–Sb. Both Mg–Bi and Mg–Sb systems have the potential to be new age-hardenable magnesium-based alloys. Indium is of interest because it is one of the very few elements with high solubility in magnesium and yet has low electrochemical activity; whereby the relatively high electrochemical activity of magnesium might reasonably be expected to be reduced, albeit at an increase in overall alloy density. The In–Sb and In–Bi systems are included to complete the possibilities for binary alloys among these elements.
The Binary Alloy Phase Diagrams [11] and the Pauling File [12] give a broad review of experimental data on these systems. In most cases the experimental results are complemented by thermodynamic modeling [11–13]. However, to the best of our knowledge, ab initio studies regarding phase stabilities in these systems are scarce [14–16]. To check the completeness of the experimentally known phase diagrams in these systems and provide information on the phase stabilities at low temperatures we have chosen a large library of most common prototypes in binary alloys and calculated ground state energies of these structures with ab initio methods.

We describe the prototype library in the next section, give the details of the ab initio methods used in this study in section “High-throughput first principles calculations”, and present the results for each of the six systems in section “Alloys”.

2. Binary systems and structure prototypes

We make calculations for six alloys, Bi–In, Bi–Mg, Bi–Sb, In–Mg, In–Sb, and Mg–Sb, in 187 crystal structure configurations. Many of these configurations have the same prototype, for example, AB3 and A3B, so the number of distinct prototypes is 109. The various concentrations are listed in Table 1.

<table>
<thead>
<tr>
<th>Compounds composition</th>
<th>Conc. of B (%)</th>
<th>Number of prototypes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A &amp; B</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>A2B &amp; AB2</td>
<td>16.66</td>
<td>3</td>
</tr>
<tr>
<td>A2B &amp; AB3</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>A3B &amp; AB3</td>
<td>25</td>
<td>28</td>
</tr>
<tr>
<td>A2B &amp; A2B2</td>
<td>28.57</td>
<td>1</td>
</tr>
<tr>
<td>A3B &amp; A2B3</td>
<td>33.33</td>
<td>14</td>
</tr>
<tr>
<td>A3B &amp; A2B</td>
<td>37.5</td>
<td>3</td>
</tr>
<tr>
<td>A2B &amp; A2B</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>A4B &amp; A2B3</td>
<td>42.85</td>
<td>1</td>
</tr>
<tr>
<td>AB (&amp; BA*)</td>
<td>50</td>
<td>29 (+3)</td>
</tr>
</tbody>
</table>

The library has 187 structures, and 109 distinct prototypes (* at composition AB; three prototypes have different point groups in atomic positions A and B, so they represent distinct structure types).

Of such prototypes, 67 are chosen from the most common intermetallic binary structures in the Pauling File [12] and the CRYSTMET database [13], plus the common low-temperature compounds (6) reported for the Mg, In, Sb, and Bi systems [11,12]. Such prototypes can be described by their Strukturbericht designation and/or natural prototypes [11,12]: A1, A2, A3, A4, A6, A7, A15, B6, B1, B2, B3, B4, B81, B82, B10, B11, B19, B27, B32, B33 (B7), C7, C, C2, C6, C11b, C14, C15, C15b, C16, C18, C22, C32, C33, C37, C38, C49, D00, D03, D05, D011, D019, D022, D023, D024, D13, D14, D22, D52, D73, D88, D8s, L10, L11, L12, L60, CaIn2, Cr3S3, CuTe, CuZr2, GdSi2 (1.4), Mg2In, Mg3In (hr48, with space group R3m), MoPt2, NbAs (NbP), NbPd3, Ni2In, Ni2Si, Ω (with Ω = 1/4), Pu3Al(Co3V), Ti3Cu4, W5Si3, YCd3, ZrSi2, γ-Ir. The rest of the structures (36) are fcc, bcc, or hcp superstructures. Twelve of these superstructures consist of stacking of pure A and B planes along some common direction [6,17].

3. High-throughput first principles calculations

The high-throughput ab initio method used for this project is fully described in references [6,7]. A summary of the details of the calculations is given below.

UltraSoft Pseudopotential LDA calculations (US-LDA). The energy calculations were performed using density functional theory in the Local Density Approximation (LDA), with the Ceperley–Alder form for the correlation energy as parameterized by Perdew and Zunger [18] and with ultrasoft Vanderbilt type pseudopotentials [19], as implemented in VASP [20]. Calculations are done at zero temperature and pressure, with spin polarization, and without zero-point motion. The energy cutoff in an alloy was set to 1.5 times the larger of the suggested energy cutoffs of the pseudopotentials of the elements of the alloy (suggested energy cutoffs are derived by the method described in [20]). Brillouin zone integrations were performed using at least 3500/(number of atoms in unit cell) k-points distributed on a Monkhorst–Pack mesh [21,22]. With these energy cutoffs and k-point meshes the absolute energy is converged to better than 10 meV/atom. Energy differences between structures are expected to be converged to much smaller tolerances. All structures were fully relaxed.

PAW-GGA calculations. When several structures are in close competition for the ground state, we also performed calculations in the Generalized Gradient Approximation (GGA), with Projector Augmented-Wave (PAW) pseudopotentials, as implemented in VASP [20,23,24]. In general, we expect the PAW-GGA approach to be more accurate than the US-LDA. For the GGA exchange correlation functional, we used the Perdew–Burke–Ernzerhof (PBE) parameterization [25]. Compared to the US-LDA case, we use an increased energy cutoff of 1.75 times the larger of the suggested energy cutoffs for the elements in the system and a finer k-point mesh with at least ~4000/(number of atoms in unit cell).

Symmetries of the pure elements. Our calculations reproduce the correct experimental crystal structures of the pure elements at room temperature. Bi and Sb are most stable in the A7 structure (α-As prototype), while Mg and In have hexagonal closed packed (A3) and face-centered tetragonal (A6) structures, respectively.

Calculation of the formation energies and the convex hull. The formation energy for each structure is determined with respect to the most stable structure of the pure elements. To determine the ground states of a system one needs to find, as a function of composition, the ordered compounds that have an energy lower than any other structure or any linear combination of structures that gives the proper composition.
This set of ground state structures forms a convex hull, as all other structures have an energy that falls above the set of tie-lines that connects the energy of the ground states. In thermodynamical terms, the convex hull represents the Gibbs free energy of the alloy at zero temperature.

4. Alloys

Bi–In (bismuth–indium) (Figs. 1 and 2)

The phase diagram of the Bi–In system is known from experimental investigations and thermodynamic modeling [11,12,26–32]. Three phases are expected to be stable at low temperatures: BiIn–B10, BiIn2–InNi2, and Bi3In5–Cr3B5. However, the evidence for the low-temperature stability of BiIn2 and Bi3In5 is not conclusive [27]. With our US-LDA calculations, we have found that only three phases have negative formation energy. These phases, BiIn–B10, BiIn2–InNi2, and a monoclinic structure with space group C2/m #12 at 50% concentration, have formation energies equal to −17, −5, and −8 meV/atom, respectively. Therefore, the phase diagram calculated in US-LDA has only one stable compound, BiIn–B10; the other two experimentally observed stable phases BiIn2 and Bi3In5 are above the convex hull by 6 and 26 meV/atom, respectively.

Due to the rather small energy differences and overall low formation energies we further investigate the phase diagram with the PAW-GGA potentials, as described in the method section. With PAW-GGA, we find that BiIn–B10 has less negative formation energy, −7 meV/atom and BiIn2–InNi2 becomes stable by having the formation energy of −9 meV/atom, which is 4 meV/atom below the tie-line In ↔ BiIn. The monoclinic structure with space group C2/m #12 at 50% concentration is now unstable having the formation energy of 14 meV/atom. The Bi3In5 phase still has positive formation energy (23 meV/atom) and remains significantly higher than the tie-line InNi2 ↔ InBi (by 31 meV/atom). In summary, our results suggest that at low temperatures BiIn2 may be stable, while Bi3In5 is likely to be unstable.

Bi–Mg (bismuth–magnesium) (Fig. 3)

Only one stable compound has been observed for the Mg–Sb system at low temperatures: αBi2Mg3–La3O2 [11, 12,33–35]. Our calculations confirm the low-temperature stability of this phase with a formation energy of −253 meV/atom (−211 meV/atom with PAW-GGA). We have not found any other stable compounds for this system and thus suggest that the experimental low-temperature part of the diagram is complete.
The off-stoichiometry Mg₅In₂–D₈ₘ phase is not a subject of our investigation, since it requires simulations of off-stoichiometry systems. With our calculations, we find the ordered phase MgIn₃–L₁₂ [12,37] to be stable. Two competing long-period superstructures of MgIn₃–L₁₂, D₀₂₃ and D₀₂₄, are less favorable than the L₁₂ phase by ~3 and ~6 meV/atom, respectively. This suggests that long-range interactions are weak in this system at composition MgIn₃. We confirm the stability of MgIn–L₁₀ (β′′), Mg₂In–β₂, and Mg₃In–β₁ phases (the latter has nearly the same energy per atom as Mg₃In–L₁₂), but find that Mg₅In₂–D₈ₘ lies 5 meV/atom above the tie-line Mg₃In–β₁ ↔ Mg₅In–β₂. Besides this, Mg₂In–β₂ is stable but with a relative stability energy of 4 meV/atom below the tie-line Mg₃In ↔ MgIn, which is within the error of the present calculations. We find a metastable compound, MgIn₂–Cₚ, to be ~3 meV/atom above the tie-line MgIn ↔ MgIn₃. This compound might become stable at higher temperatures and pressures. We recalculate the phase diagram with PAW-GGA potentials and find little difference compared to the US-LDA results: phases Mg₃In–β₁ and Mg₅In–L₁₂ are nearly degenerate, Mg₃In–β₂ is now ~3 meV/atom above the Mg₃In ↔ MgIn tie-line, Mg₅In₂–D₈ₘ is above the Mg₃In ↔ MgIn by ~13 meV/atom, and MgIn₂–Cₚ remains metastable by 7 meV/atom. In summary, our calculations confirm the low-temperature part of the Mg–In diagram known from experiment. The results show that Mg₅In₂–D₈ₘ may not be stable at low temperatures. In addition, we identify a metastable phase, MgIn₂–Cₚ, which might be stable at higher pressures and temperatures.

![Fig. 3. Bi–Mg (bismuth–magnesium) ground state convex hull.](image)

**Bi–Sb (bismuth–antimony)**

No intermediate stable compounds have been reported for the Bi–Sb system and it is considered to be a non-compound forming system [11,12]. Our calculations confirm the absence of any stable phases. The structure with lowest formation energy in the whole range of concentrations is found to be BiSb–B₁ with \( E_f = 21 \text{ meV/atom} \).

**In–Mg (indium–magnesium) (Fig. 4)**

Five ordered compounds have been reported for the system Mg–In at low temperatures [11,12,36–42]: Mg₁₂In₄–L₁₂ (γ'), Mg₆In–L₁₀ (β''), Mg₂In (prototype, β₂, Mg₂Tl in [11]), Mg₃In₂–D₈ₘ (β₃), and Mg₃In (β₁) with Pearson symbol hR₄₈, and space group R₃m (#166) [11,12] (note that β₁ has Pearson symbol hR₁₆ in Massalski [11]). At high temperatures, phase β₁ transforms into the L₁₂ structure.

<table>
<thead>
<tr>
<th>Composition % In</th>
<th>Experimental (Massalski [11])</th>
<th>Ab initio result</th>
</tr>
</thead>
<tbody>
<tr>
<td>~26 to 38.5</td>
<td>Mg₃In (β₁) hR₄₈ R₃m [12] (low T)</td>
<td>Mg₃In–β₁</td>
</tr>
<tr>
<td>28.6</td>
<td>Mg₅In₂–D₈ₘ (β₃)</td>
<td>two-phase region</td>
</tr>
<tr>
<td>~34</td>
<td>Mg₂In (β₂)</td>
<td>Mg₂In stable</td>
</tr>
<tr>
<td>~39 to 59</td>
<td>MgIn–L₁₀ (β''′')</td>
<td>MgIn–L₁₀</td>
</tr>
<tr>
<td>~69.5 to 75.5</td>
<td>Mg₁₂In₄–L₁₂ (γ')</td>
<td>MgIn₃–L₁₂</td>
</tr>
</tbody>
</table>

![Fig. 4. In–Mg (indium–magnesium) ground state convex hull.](image)

**In–Sb (indium–antimony) (Fig. 5)**

The phase diagram of the system In–Sb is based on a single compound αInSb–B₃ [11,12,43–48]. It is well studied at high pressures and temperatures where other modifications of InSb (βInSb, γInSb, and δInSb) have been observed [28,46]. The high-pressure transitions have also been thoroughly studied with ab initio methods [15,16].
At zero pressure our calculations give the formation energy of \(-105\) meV/atom (\(-123\) meV/atom with PAW-GGA) for compound \(\alpha\text{InSb–B3}\) and confirm its low-temperature stability. The \(\text{InSb–B10}\) phase, stable for the similar binary system \(\text{In–Bi}\) at 50\% concentration, is here unstable with the formation energy close to zero. We do not observe any other stable compounds for the \(\text{In–Sb}\) system; the low-temperature experimental characterization of the system is apparently complete.

### In–Sb system

**Low-temperature phases comparison chart**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Experimental (Massalski [11])</th>
<th>Ab initio result</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 Sb</td>
<td>B3</td>
<td>(\alpha\text{InSb–B3} = -105) meV/atom</td>
</tr>
</tbody>
</table>

![Fig. 5. In–Sb (indium–antimony) ground state convex hull.](image)

\(\text{Mg–Sb (magnesium–antimony)}\) (Fig. 6)

Mg and Sb have similar dimensions and satisfy the first Hume-Rothery rule [53] (atomic radius ratio \(R_{\text{Sb}}/R_{\text{Mg}} = 1.09\) [11], less than 15\% difference) to be solid-soluble. However, they have a relatively large difference in electronegativity (\(\Delta\text{EN}_{\text{Sb–Mg}} = 0.7\), greater than 0.4) and do not satisfy the second Hume-Rothery rule [53–55], so there is no solid solubility for Mg in Sb or Sb in Mg. Similarly to the Bi–Mg system the Mg–Sb system has only one stable compound at low temperature: \(\alpha\text{Mg}_3\text{Sb}_2–\text{B5}_2\) [12,11,49,35,50–52]. At high temperatures phase \(\alpha\text{Mg}_3\text{Sb}_2–\text{B5}_2\) undergoes a polymorphic change, as reported in [35]. To our knowledge, there is no information about the stability of \(\alpha\text{Mg}_3\text{Sb}_2–\text{B5}_2\) below 450 °C and it is unclear how far this stable phase extends into the low-temperature region. Our calculations confirm that this compound remains stable at low temperatures having the formation energy of \(-404\) meV/atom (\(-373\) meV/atom with PAW-GGA). No other stable compounds have been found for this system; therefore our results are consistent with the experimental phase diagram at low temperatures.

### Mg–Sb system

**Low-temperature phases comparison chart**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Experimental (Massalski [11])</th>
<th>Ab initio result</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 Sb</td>
<td>D5(_2)</td>
<td>(\text{Mg}_3\text{Sb}_2–\text{D5}_2 = -404) meV/atom</td>
</tr>
</tbody>
</table>

![Fig. 6. Mg–Sb (magnesium–antimony) ground state convex hull.](image)

5. Summary

The results of our systematic ab initio study of the six binary systems Bi–In, Bi–Mg, Bi–Sb, In–Mg, In–Sb,
and Mg–Sb suggest that the experimentally known low-temperature phase diagrams for these alloys are complete. Fig. 7 gives an overview of existing low-temperature compounds in the six binary systems with the corresponding calculated formation energies. In addition, we list the calculated and measured atomic volumes for the experimentally observed compounds in these systems (see Table 2), which are needed, in particular, for evaluation of precipitate volume fractions and precipitation-growth modeling [56,57].

The cell parameters of our fully relaxed structures are described with the expected degree of accuracy for the applied DFT flavors: the bond lengths are within 1%–2% and the atomic volumes are within ∼5% compared to the reported experimental values. The discrepancies follow the applied DFT flavors: the bond lengths are within 1%–2% compared to the experimental values (at room temperature) taken from the Pauling File [12]. The relative volume deviation

\[ \delta_{\text{vol}}(x) = \frac{V_x}{xV_A + (1-x)V_B} - 1, \quad (1) \]

where \( V_A \), \( V_B \), and \( V_x \) are atomic volumes for pure elements \( A \), \( B \), and an intermediate compound \( A_xB_{1-x} \) at concentration \( x \).

Table 2
Comparison of atomic volumes for the experimentally observed compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atomic volume (Å³/atom)</th>
<th>Deviation ( \delta_{\text{vol}}(x) ) (see Eq. (1)) (%)</th>
<th>LDA</th>
<th>GGA</th>
<th>exp</th>
<th>LDA</th>
<th>GGA</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>21.6</td>
<td>22.8</td>
<td>23.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn2</td>
<td>21.2</td>
<td>22.9</td>
<td>22.4</td>
<td>-4.7</td>
<td>-4.8</td>
<td>-6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn</td>
<td>21.8</td>
<td>23.6</td>
<td>23.2</td>
<td>-2.2</td>
<td>-2.5</td>
<td>-3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn2</td>
<td>21.6</td>
<td>23.5</td>
<td>22.5</td>
<td>-3.8</td>
<td>-4.0</td>
<td>-6.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn2</td>
<td>21.5</td>
<td>23.7</td>
<td>23.0</td>
<td>-5.9</td>
<td>-6.1</td>
<td>-6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn3</td>
<td>22.9</td>
<td>25.5</td>
<td>24.3</td>
<td>-2.9</td>
<td>-3.6</td>
<td>-3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>24.2</td>
<td>27.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BiIn2</td>
<td>26.7</td>
<td>29.8</td>
<td>28.5</td>
<td>-2.5</td>
<td>-3.2</td>
<td>-1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BiIn</td>
<td>26.7</td>
<td>29.9</td>
<td>28.9</td>
<td>-3.7</td>
<td>-3.8</td>
<td>-3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BiIn2</td>
<td>28.2</td>
<td>31.2</td>
<td>30.0</td>
<td>-2.5</td>
<td>-3.3</td>
<td>-1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi2Mg3</td>
<td>33.5</td>
<td>36.8</td>
<td>35.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi2Mg3</td>
<td>26.7</td>
<td>28.7</td>
<td>28.0</td>
<td>1.5</td>
<td>0.9</td>
<td>-0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg3Sb2</td>
<td>21.6</td>
<td>22.9</td>
<td>23.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>29.0</td>
<td>31.8</td>
<td>30.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>InSb</td>
<td>33.2</td>
<td>36.8</td>
<td>34.0</td>
<td>24.6</td>
<td>23.5</td>
<td>21.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>24.2</td>
<td>27.7</td>
<td>26.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The volumes calculated in the LDA and GGA (at zero temperature) are compared to the experimental values (at room temperature) taken from the Pauling File [12]. The relative volume deviation \( \delta_{\text{vol}}(x) \) is defined in the text.

Using the calculated ground state energies we complement experimental information on the stability of several phases in the limit of low temperature and zero pressure: phase \( \alpha\text{Mg}_3\text{Sb}_2-B5\) is stable, phase \( \text{Mg}_5\text{In}_2-D8_\gamma \) may not be stable and phase \( \text{Bi}_3\text{In}_5 \) is likely to be unstable. We find that compound \( \text{MgIn}_2-C_\gamma \), not observed experimentally, is metastable but very close to stability and could therefore exist at different temperatures and pressures or form during the precipitation-hardening. Further theoretical investigation of these structures and search for other (meta)stable phases at finite temperatures and pressures should include thermodynamic effects.

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