First-principles phase stability, magnetic properties and solubility in aluminum–rare-earth (Al–RE) alloys and compounds

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Abstract

First-principles density-functional calculations are used to study the phase stability, magnetic properties and solubilities in aluminum–rare-earth (Al–RE) alloys and compounds. The results are compared with those from potentials with f-electrons treated as valence/core to calculate the phase stability of different Al–RE compounds. Using a small set of test structures, it is found that calculations with potentials with f-electrons in the valence band correctly predict all the known stable phases of Al–RE compounds. It is found that the contribution of magnetism in the compounds is crucial for predicting the correct ground-state Al3RE structures. The calculated magnetic moments are in excellent agreement with experimental values. The RE solubilities in Al are calculated, including both static total energy contributions as well as the free energies associated with atomic vibrations. The vibrational entropy serves to increase significantly the solubilities of RE elements in Al. The calculated solvus curves are in good agreement with the available experimentally measured values.

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1. Introduction

Aluminum–rare-earth (Al–RE) intermetallic compounds have been investigated recently owing to their interesting physical properties as well as the possibility of commercial applications. It is well known that dilute addition of Sc to Al gives the largest per-atom increase in strength to Al, owing to the formation of a high-number-density of L12-ordered, coherent Al3Sc precipitates during aging heat treatment [1]. Alloys involving precipitates of the binary intermetallic compound Al3Sc are of potential interest for high-temperature structural applications, because the low-density of this compound (3.03 mg m−3), its relatively high melting point (1593 K) and the cubic L12 structure of the precipitate may provide some ductility. The addition of RE elements to Al–Sc alloys can significantly decrease the cost of these alloys and may also act to improve high-temperature creep and hardiness properties [2,3]. For example, the heavy RE elements, including Er, Tm, Yb and Lu, substitute for Sc in Al3Sc(L12) precipitates [4], and thus replace substantial quantities of the more expensive Sc. These RE elements also increase the antiphase boundary energy, and the lattice parameter mismatch between the Al3(Sc1−x,REx) precipitates and the α-Al matrix, thus enhancing the elastic interactions with dislocations and thereby improving their high-temperature creep resistance [5,6]. Erbium is the least expensive of the heavy RE that form stable L12 precipitates in α-Al [7,8], and Al3Er has a larger lattice parameter (4.2 nm [9]) than the other Al3RE intermetallics. Erbium is also used to refine grain sizes and thus improve strength at room temperature [10].

The crystal structures of Al–RE compounds exhibit an interesting, complex magnetic behavior and phase stability owing to the presence of RE f-electrons in these compounds.
300 eV to represent the Kohn–Sham wave functions. Unless otherwise specified, all structures were fully relaxed with respect to volume as well as cell-inter- nal atomic coordinates. The convergence of results with respect to energy cutoff and k-points was carefully consid- ered. A plane-wave basis set was used with an energy cutoff of 300 eV to represent the Kohn–Sham wave functions. Where experimental data exist, the present cal- culations for the solvus curves are in good agreement with the experimental data.

2. First-principles computational methodology

The first-principles calculations are based on DFT and employ the plane-wave pseudopotential total energy method as implemented in the Vienna ab initio simulation package (VASP) [16–20]. Projector augmented wave potentials [21] and the generalized gradient approximation of Perdew–Burke–Ernzerhof [22] were used for exchange–correlation. Unless otherwise specified, all structures were fully relaxed with respect to volume as well as all cell-interna- nal atomic coordinates. The convergence of results with respect to energy cutoff and k-points was carefully consid- ered. A plane-wave basis set was used with an energy cutoff of 300 eV to represent the Kohn–Sham wave functions. The summation over the Brillouin zone for the bulk struc- ture, vibrational thermodynamics and solubility in these systems.

This research systematically studies the phase stability of different Al–RE compounds and examines the effect of two distinct approaches to treating RE elements. These two approaches involve treating the f-electrons in the valence band versus keeping some of the f-electrons in the core. Non-magnetic and magnetic calculations are compared, and the significant role of spin polarization in predicting the correct ground-state structures of ordered Al3RE phases is shown. The vibrational thermodynamics of stable Al3RE structures and dilute Al–RE solutions are calcu- lated. Combining these static total energies with the vibrational free energies, a systematic series of calculations of the solubility of RE in Al as a function of temperature were performed. Where experimental data exist, the present calcul- 3. Results and discussion

3.1. The stability of the formation of Al–RE compounds

The study began with a test of two different potentials (“standard” with f-electrons in the valence band, and “frozen” with some f-electrons in the core) for the stability of Al–RE compounds by calculating the formation energy of Al–RE compounds in different crystal structures. This section focuses on the Ce–Al, Gd–Al, Yb–Al compounds, since both “standard” and “frozen” potentials are available for these three RE. The following crystal structures of Al–RE compounds were considered: seven Al3RE structures (AuCu3.cP4, Ni3Sn.hP8, Ni3Ti.hP16, BaPb3.hR12, Al3Ho.hR20, Al3Ti.tI8, Al3Zr.tI16), two Al2RE structures (Cu2Mg.cF24, AlB2.hP3), five AlIRE structures (AlCe.oC16, CICs.cp2, BCr.oC8, AlDy.oP16, AlEu.oP20), two AlRE3 structures (Al2Cu.eT12, Co2Si.oP12), and three AlIRE3 structures (Ni3Sn.hP8, AlCe3.mP16, AlCu3.cP4). The calculated results and the reported experimental results are given in Table 1.

For Al–Ce compounds, the experimentally determined stable structures are Al3Ce.hP8, Al2Ce.cF24, AlCe.oC16, AlCe2.oP12 and AlCe3.hP8 (low temperature) [23,24]. It is emphasized that the intermetallic compounds are designated in this section by their stoichiometry and Pearson symbol. The DFT calculations for both potentials correctly showed that Al3Ce.hP8 and Al2Ce.cF24, AlCe.oC16, AlCe3.hP8 structures are the lowest energy structures for each stoichiometry considered. In addition to the qualitative agreement between DFT and experiments for stable structures, good quantitative agreement with experimentally measured formation energies was found. To compare the energetic of the compounds with two-phase mixtures of other compounds, the formation energy results are plotted in the form of convex hull plots in Fig. 1a. The calculated formation energies from the “frozen” potential are slightly more negative, and hence slightly closer to experimental values than those from the standard potential.

The experimentally stable structures of Al–Gd compo- 8onds were Al3Gd.hP8, Al2Gd.cF24, AlGd.oP16 and AlGd2.oP12 [25]. The calculations of the formation energies from both potentials confirmed these stable structures as the lowest energy structures at each stoichiometry. The calculated convex hulls of stable structures are displayed in Fig. 1b, and once again demonstrate excellent qualitative agreement between DFT and experimental formation energies. The results from the two potentials are very
similar, and the formation energies from the standard potential are only slightly lower than those from the frozen potential.

The phase stability of Al–Yb compounds differed significantly from the Al–Ce and Al–Gd systems. There are the only two stable compounds known in the system: Al₂Yb.cF₂⁴ and Al₂Yb.cP₂⁴ [26]. For this system, significant differences were found between the standard and frozen potentials. The calculated formation energies from the standard potential with 7-electrons in the valence band correctly predicted these two stable phases to be the lowest energy structures for each stoichiometry. But the frozen potential calculations incorrectly predicted Al₂Yb.hP₈ to be lower in energy than the observed stable Al₂Yb.cP₂⁴ phase. The formation energies of the stable structures are displayed in a convex hull plot (Fig. 1c).

It was found that the standard potentials gave formation energies in good quantitative agreement with experimental values, whereas the frozen potentials in this case gave formation energies that were significantly too high. Overall, the DFT-calculated formation energies of Al–Ce and Al–Gd compounds from both potentials were very close to the experimental values shown in Fig. 1. And, in the case of Al–Yb, the standard potentials gave quantitatively accurate formation energies. The results from standard potentials also correctly predicted all the experimentally determined stable phases. From the calculations, Al₂RE.cF₂⁴ had the lowest formation energy compared with all other compounds in each system, implying strong stability in this CF₂⁴ structure. This result is in excellent agreement with the experimental observation that, in each of the Al–RE systems discussed, the Al₂RE.cF₂⁴ compound has the highest melting point [27,28]. The results are also in good agreement with previous calculations [15]. Based on the results in Table 1 and Fig. 1, standard potentials (where available) for La, Ce, Gd and Yb are used in all the calculations described below, since these potentials yield more reliable results. For all other RE elements, frozen potentials are used.

3.2. Phase stability of ordered Al₃RE compounds

The study next turns to the phase stability of Al₃RE compounds, and specifically examines the effect of spin polarization on the stability of these compounds. The phase stability of Al₃RE is especially interesting, owing to the use of RE elements to replace Sc in Al–Sc alloys, which involve Al₃Sc L1₂ precipitates. To investigate the phase stability of Al₃RE, calculations were performed for all Al–Sc systems, each in four ordered-Al₃RE crystal structures: L₁₂ (Al₃RE.cP₄), DO₁₉ (Al₃RE.hP₈), DO₂₂ (Al₃RE.t₁₈) and DO₃₃ (Al₃RE.h₃₁₆). The formation energies were calculated by two different methods for all RE elements: non-magnetic and ferromagnetic (spin-polarized).

The Al₃RE results are exhibited in Fig. 2, for both non-magnetic and ferromagnetic (spin-polarized) calculations. The experimentally observed stable Al₃RE compounds had the DO₁₉ crystal structure for the early RE metals, with a change in stability to the L₁₂ structure for the late RE metals. This shift in stability from DO₁₉ to L₁₂ was accurately captured from ferromagnetic calculations, but not non-magnetic, demonstrating the critical role of magnetism in the stability of Al₃RE compounds. In the non-magnetic calculations, L₁₂ (Al₃RE.cP₄) always has
the lowest formation energy (except for Al$_3$La), and DO$_{22}$ has the highest formation energy among the four structures investigated: DO$_{19}$ and DO$_{23}$ are intermediate. These non-magnetic results yield an incorrect prediction for the stability of L1$_2$ in Al$_3$RE compounds of early RE elements (before Ho).

The ferromagnetic calculations are, however, significantly different from the non-magnetic calculations. In the ferromagnetic calculations (Fig. 2), the formation energies of DO$_{19}$ are lower than the other three structures from RE = Ce to Ho, and L1$_2$ is lowest in energy for the late RE after Ho. This transition from DO$_{19}$ to L1$_2$ across the RE series in the magnetic calculations corresponds precisely to the crystal structures observed experimentally. Thus, one can conclude that the competition between the stability of DO$_{19}$ and L1$_2$ is due to magnetism in the Al$_3$RE compounds. Interestingly, the curves in Fig. 2 exhibit systematically smooth trends across the majority of the RE series, but there are anomalies at Eu and Yb because of their half-filled and completely filled 4$f$ orbital states.

3.3. Magnetic properties of stable ordered Al$_3$RE

As demonstrated above, the magnetic contributions to the phase stability of Al$_3$RE compounds have a significant effect on the formation energies and lead to stabilization of the DO$_{19}$ structure for the early RE. The calculated magnetic properties of Al$_3$RE compounds are now compared with experimental measurements.

As discussed above, the Al$_3$RE DO$_{19}$ structure is stable from La to Ho, and L1$_2$ is stable thereafter. The magnetic contributions to the formation energies of Al$_3$RE compounds are significant, and even responsible for the stability of DO$_{19}$. The magnetic moments for stable Al$_3$RE are calculated and displayed in Fig. 3. From the calculations, it is found that the average effective magnetic moments of stable DO$_{19}$ Al$_3$RE per RE atom (Fig. 3) are significantly different from those of the pure RE elements and increase through the RE series reaching its maximum value for Ho. These calculated values are in very good agreement with experiments [29, 30]. For the late RE elements, the magnetic moments of Er to Lu were also calculated for the metastable DO$_{19}$ structure, and the results are also displayed in Fig. 3.
## 3.4. Vibrational properties and entropies of Al<sub>3</sub>RE and dilute impurities of RE in Al

The vibrational thermodynamic properties are essential for calculating the temperature dependence of solubilities and nucleation energies of RE elements in Al. To calculate the phonon dispersions for the solubility of a RE in Al, the frozen phonon method was used in 2x2x2 supercells for RE dilute solid-solutions with a 32-atom cubic cell, with the RE atom replacing Al on the central site, 2x2x2 supercells for bulk unit cells for Al<sub>3</sub>RE(DO19), and 3x3x3 supercells for bulk unit cells for Al<sub>3</sub>RE(L12). In this method, a series of total energy differences between atomic configurations with and without a single displaced atom are calculated. This information is used to populate the dynamical matrix, and hence to evaluate the phonon frequencies [31–33]. This research used the harmonic approximation for all vibrational calculations. The first step is to relax the atomic coordinates in the supercells. Then a series of single-point energy calculations are performed on the same supercells with displaced atoms. The energy for the harmonic approximation is given by [34]

\[
H = \frac{1}{2} \sum_i M_i [u(i)]^2 + \frac{1}{2} \sum_{ij} U(i,j) u(i) u(j)
\]

where \(M_i\) is the mass of atom \(i\), \(u(i)\) is the displacement away from its equilibrium position, and \(U(i,j)\) is the tensor of the force constants from the displacement of atom \(j\) to the force on atom \(i\). The Helmholtz free energy of the system is given by [35]

\[
F = E^* + N k_B T \int_0^\infty \ln \left( 2 \sinh \left( \frac{h v}{2 k_B T} \right) \right) g(v) dv
\]

where \(E^*\) is the total energy of the system at \(T = 0\) K at its equilibrium position, \(h\) is Planck’s constant, \(N\) is the number of atoms in the supercell, and \(g(v)\) is the phonon density of states (DOS). The vibrational entropies for Al<sub>3</sub>RE(DO19) and Al<sub>3</sub>RE(L12) were calculated for a dilute solute-solution of a RE in a face-centered cubic (fcc) Al supercell. Fig. 4 compares the phonon DOS for Al<sub>3</sub>RE in the stable DO19 and metastable L12 structures for the early RE elements, Ce and Gd. The strong well-defined phonon peaks at lower frequencies are observed for the L12 and DO19 structures, but there is more weight to these low-frequency peaks in the L12 structure for both Al<sub>3</sub>Ce and Al<sub>3</sub>Gd. This larger proportion of low-frequency phonon states in L12 leads to a larger vibrational entropy, and hence narrows the free energy difference between these structures at finite temperatures. Fig. 5 shows the phonon DOS for a series of Al<sub>3</sub>RE L12 compounds, with RE = Ce, Gd, Er or Yb. The low-frequency L12 phonon peaks shift slightly toward lower frequencies, moving from Al<sub>3</sub>Ce to...
Al₃Gd → Al₃Er → Al₃Yb. This shift corresponds to the Al–RE bonding, which becomes stronger in L1₂ Al₃RE as the RE atomic number increases. The partial phonon DOS of a single RE impurity in fcc Al is presented in Fig. 6. The DOS peaks shift from high frequency to low frequency. The shift is responsible for the stronger Al–RE bonding and smaller lattice parameter misfits in going from Ce to Yb. The calculated vibrational formation entropies of Al₃RE (both DO₁₉ and L₁₂) and a dilute RE in Al are presented in Table 2. The formation entropies are the entropy of the compound or solution relative to the composition-weighted pure elements. It is next demonstrated that these vibrational entropies make a significant contribution to the RE solubility in Al.

3.5. Solubility of RE in Al

The solubility of a RE element in Al is a very important property for the addition of a RE into different Al alloys, such as Al–Sc and Al–Mg alloys. There are very limited data and previous experimental or theoretical results on this topic. Only two experimental points for Yb and Er solubility have been reported [36]. It was recently demonstrated that accurate calculations of solubility in Al alloys are possible from DFT, provided that the important role of vibrational entropy is included [37–40]. These RE solubilities are calculated from first principles, and the calculated values are compared with the two experimental data points. The solubility limits of a RE in Al can be calculated employing the ideal-solution equation if the Al₃RE phase is treated as a line compound and the solid-solution phase is treated as dilute. The solvus boundary between the bulk Al and ordered Al₃RE phases is given by the following expression:

\[ c_s(T) = \exp \left[ \frac{\Delta G(Al_3RE)}{k_B T} \right] \]

where \( \Delta G(Al_3RE) \) is the Gibbs free energy of formation per RE atom for Al₃RE, and \( \Delta G(Al_3RE) \) is the solution free energy per RE atom for a dilute RE in Al. \( \Delta H \) and \( \Delta S \) are the corresponding enthalpy and (non-configurational) entropy contributions to the Gibbs free energy of formation for \( \Delta G(Al_3RE) \) and \( \Delta G(Al_3RE) \). Note that the entropy

![Fig. 6. Partial phonon spectra of dilute RE in Al.](image)

![Fig. 7. DFT calculated solubilities of Al₃Ce: (a) the impact of vibrational entropy on the solubilities of DO₁₉; (b) the solubilities of stable DO₁₉ and metastable L₁₂.](image)

<table>
<thead>
<tr>
<th>RE</th>
<th>( \Delta S ) (kJ/solute atom)</th>
<th>Solubility ( \Delta H ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute RE</td>
<td>DO₁₉ Al₃RE</td>
<td>L₁₂ Al₃RE</td>
</tr>
<tr>
<td>Ce</td>
<td>0.228</td>
<td>−3.425</td>
</tr>
<tr>
<td>Pr</td>
<td>−0.757</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>−0.765</td>
<td></td>
</tr>
<tr>
<td>Pm</td>
<td>−0.779</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>−0.785</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>−0.808</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>0.330</td>
<td>−2.654</td>
</tr>
<tr>
<td>Tb</td>
<td>−0.825</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>−0.838</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>−0.849</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>0.463</td>
<td>−3.065</td>
</tr>
<tr>
<td>Tm</td>
<td>−0.888</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>0.497</td>
<td>−3.489</td>
</tr>
<tr>
<td>Lu</td>
<td>−0.906</td>
<td></td>
</tr>
</tbody>
</table>

contribution $\Delta S$ specifically includes only non-configura-
tional entropy, as the configurational entropy is already ac-
tioned for in the derivation of Eq. (1). From Table 2 it is
found that the enthalpy contribution decreases (reducing
solubility) and the contribution from vibrational entropy
decreases (except Ce) as RE atomic number increases, from
Gd to Lu. The calculations showed that the contribution of
vibration entropies to solubility is significant and cannot be
neglected. Fig. 7a shows the calculated stable DO$_{19}$ Al$_3$Ce
solubility in Al with and without vibration entropy. The
contribution of vibrational entropy enhances the RE solu-
Bility. Fig. 7b shows the solubilities of stable DO$_{19}$ and
metastable L1$_2$ Al$_3$Ce in Al. From this figure, one can see
that, as expected, the metastable L1$_2$ has much higher sol-
ubility than DO$_{19}$ structures and is less stable than DO$_{19}$.
But, Fig. 7b serves to illustrate how DFT calculations
may be used to compute the solvus curves easily for meta-
stable phases, which are often difficult to obtain experi-
mentally. Fig. 8 shows the solubilities of a series of RE
elements, Ce, Gd, Er and Yb, as functions of temperature.
The solvus curves are for the stable phases: DO$_{19}$ for Al$_3$Ce
and Al$_3$Gd, and L1$_2$ for Al$_3$Er and Al$_3$Yb. The solubility
decrees as the RE atomic number increase from Ce to
Yb. The two experimentally determined solubility points
of Er and Yb are just slightly below the calculated solu-
ility lines, and demonstrate that the DFT calculations are
quite accurate for these solubilities. These solubility results
can be used to guide the efficient utilization and design of
RE substitution of Sc in Al–Sc alloys.

4. Conclusion

This paper systematically studied the phase stability,
magnetic property and solubility of aluminum rare-earth
compounds based on bulk thermodynamics (both static
total energies and vibrational free energies) by first-princi-
ples calculations, leading to the following conclusions.

1. Standard potentials with $f$-electrons treated as valence
band electron correctly predict that all the stable phases
of Al–RE compounds and frozen potentials (with some
$f$-electrons in the core) are also in good agreement with
experiments, except for one compound, Al$_3$Yb.eP4.
2. Magnetic contributions of the RE elements and com-
pounds have a significant impact on the formation
energy of ordered Al$_3$RE compounds, and are respon-
sible for the stability of the observed DO$_{19}$ phases for the
early Al$_3$RE compounds. The spin polarized calculations
correctly predict the ground state of ordered
Al$_3$RE: DO$_{19}$ is stable from La to Ho, L1$_2$ stable
thereafter.
3. The calculated magnetic moments increase from 0.6 to
6.2 $\mu_B$ per RE atom in DO$_{19}$ structures from La to
Ho, which are in excellent agreement with experiments.
4. The vibrational entropy plays an important role in the
solubility of RE in Al. The calculated solubility of RE
decreases as the RE atomic number increases. The calcu-
lated solvus curves of Er and Yb are in very good agree-
ment with experimental values.

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