# First-principles study of thermodynamic properties and solubility of aluminum-rare-earth intermetallics

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## ABSTRACT

Thermal properties of several $L1_2$ $Al_3RE$ (RE = Y, Dy, Ho, Er, Tm and Lu) intermetallic compounds are studied using the first-principles phonon calculations. The thermal expansions, the heat capacities at constant pressure, and the isothermal bulk modulus at finite temperatures are obtained from the quasiharmonic approximation. Based on thermodynamic properties, we calculate the solubility of RE elements in Al. We find that the solubility limits increase when the atomic number of RE element decreases from Lu to Y. Dy and Y have the low price and high solubility limits, adding Dy and Y to Al–Sc alloys can reduce the production costs of Al-based alloys. It is meanwhile, Y and Dy have high strengthening capability and much better oxidation resistance, and they are probably the better candidates as potential additions to dilute Al–Sc alloys among several RE elements investigated.

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## 1. Introduction

Because of their good physical properties, such as high special strength, light weight and welding properties, aluminum based alloys have been used in sports, transportation, and aerospace industries [1–3]. But the poor mechanical properties make their applications restrained at high temperatures [4]. The addition of appropriate scandium to aluminum based alloys can form $L1_2$-ordered, coherent $Al_3Sc$ precipitates during aging heat treatment [5]. These precipitates can improve effectively ductility and increase the creep resistance in coarse-grained aluminum based alloys [6–14]. However Sc is very expansive, this limits the industrial applications of Al–Sc alloys. But some rare earth elements (RE) are cheaper than Sc. So some scientists want to replace Sc with other solute elements, such as V, Ti, Hf, Zr and rare earth (RE) elements [15–29]. Similar to Sc, these rare-earth elements (RE = Dy, Ho, Er, Tm, Yb and Lu) exhibit an Al–$Al_3RE$ eutectic reaction, with $Al_3RE$ exhibiting a stable $L1_2$ crystal structure [28–32]. These intermetallic phases can improve the creep resistance of Al–Sc alloys by impeding dislocation climb over precipitates [33–35]. Unlike Sc, however, those rare earth elements have small

solubility in Al, even at the eutectic temperatures [36–38]. Up to now, the investigations of solubility of RE elements in Al are relatively few. Dalen et al. reported that the maximum Er and Yb solid-solubility in Al, as measured by 3-D APT, for Er and for Yb at 640 and at 625 °C, respectively [27]. The phase fraction of precipitates that can form in a solid solution is dependent on the solute solubility at given temperature. The knowledge of the solubility limits is very important for identifying the appropriate processing pathways for synthesizing alloys with desired microstructures. Despite their importance, these solubility limits are very difficult to determine by experimental measurements [39]. The calculation of solute solubility from first principles is a very accurate solution. Ozolins et al. [40] demonstrated that the first-principles calculation can accurately predict the solubility curve for the Al–Sc system. Subsequently, with the first-principles method, researches calculated the solubility curves for other Al based alloys, including Al–Cu [41], Al–Si [42], Al–Er, Al–Yb [17], Al–Li [16], Mg–Nd and Mg–La [43]. There are very limited data of previous experimental or theoretical study on the solubility of RE elements in Al. Our present work aims at systematic study on solubility in Al–RE intermetallic compounds. It is necessary to research systemically solubility of RE elements in Al. These solubility results can be used to guide the efficient utilization and design of RE substitutions for Sc in Al–Sc alloys. Because the vibrational thermodynamics is crucial for a first-principles calculation of solubility, we also report the thermal properties of $L1_2$ Al–RE intermetallic compounds.

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## 2. Computational methods

The first-principles calculations are based on density functional theory (DFT) and employ the plane-wave pseudopotential total energy method as implemented in the Vienna ab initio simulation package code (VASP) [44–46]. A plane-wave basis set is employed within the framework of the projector augmented wave (PAW) method [47,48]. The Perdew–Burke–Ernzerhof (PBE) [49] exchange–correlation functional for the generalized-gradient approximation (GGA) is used. The structures are relaxed without any symmetry constraints for $Al_3RE$ (L1$_2$) intermetallic compounds. The Brillouin zones of the unit cells are represented by the Monkhorst–Pack special $k$-point scheme with $15 \times 15 \times 15$ grid meshes. Spin polarization is considered in all calculations. The cutoff energy of 300 eV has been tested to be sufficient for convergence. The convergences of the energy and force are set to $1.0 \times 10^{-5}$ eV and $1.0 \times 10^{-4}$ eV Å$^{-1}$. The PAW GGA pseudopotentials of Al, Sc, Y_sv, RE_3 (RE = Tb, Dy, Ho, Er, Tm and Lu), are used in present calculations.

The vibrational thermodynamic properties are essential for calculating the temperature dependence of the solubility. In order to obtain the vibrational thermodynamic properties, we carry out the phonon calculation by the supercells approach. Real-space force constants of supercells are calculated by the density-functional perturbation theory (DFPT) implemented in the VASP code. Phonon frequencies are calculated from the force constants with the PHONOPY code [50]. For the QHA calculations, we use the supercells containing $3 \times 3 \times 3$ unit cells for $Al_3RE$ phase. The supercells comprise 108 atoms. For $Al_nRE$ ($n$ = 31), we use a $2 \times 2 \times 2$ face-centered cubic cell with 32 atoms and a RE atom replaces an Al atom on the central site.

## 3. Results and discussion

### 3.1. The ground states properties of Al–RE intermetallics

In order to calculate the equilibrium lattice constants and bulk modulus of each material, the total energy is calculated by variation of the cell volume. Equilibrium lattice constants, bulk modulus $B_0$ and pressure derivation of bulk modulus $B_0'$ are found by fitting the data of energy vs. volume to the Vinet equation of state (EOS) [51]. In Table 1, we summarize our calculated structural properties (lattice constants, bulk modulus and its pressure derivative) of $Al_3RE$ compounds. Our calculated results of lattice parameters for $Al_3RE$ are accord well with the previously experimental and theoretical ones, respectively [52–57]. The small errors of the equilibrium lattice parameter are less than 1%. When we analyzed these results of $B_0$ and $B_0'$, we also find there is a good agreement between our results and the previously theoretical investigations. The bulk moduli close to each other, suggesting that the compressibility is similar.

The formation enthalpy ($\Delta H$) of the several $Al_3RE$ intermetallics compounds is calculated by using following expression [58]:

$$\Delta H = E_{tot}^{AB} - \left[ cE_{form}^{A} + (1-c)E_{form}^{B} \right] \quad (1)$$

where $E_{tot}^{AB}$ refers to the total energy of intermetallic compound per atom, $E_{form}^{A}$ and $E_{form}^{B}$ are the single atomic energies of $A$ and $B$ pure constituents, respectively, in the solid states, $c$ refers to the fractional concentration of the constituent $A$. The obtained $\Delta H$ calculated from Eq. (1) are also presented in Table 1. From Table 1 we can see that formation enthalpy of several compounds is close to experimental and calculated data in the references [52,59,60]. Further analysis is done and it is found that formation enthalpy of these compounds is all negative, which means that the structure of these phases can exist and be stable.

### 3.2. Thermodynamic properties

The thermal properties of solids can be calculated from their phonon density of states. Within the framework of the quasi-harmonic approximation (QHA), the phonon contribution to the vibrational free energy $F_{ph}$ is given by

$$F_{ph}(T) = \frac{1}{2}\sum_{q,v} \hbar\omega_{q,v} + k_B T \sum_{q,v} \ln[1 - \exp(-\hbar\omega_{q,v}/k_B T)] \quad (2)$$

Here, the sum is over $3n$ phonon branches and over all wave vectors $\boldsymbol{q}$ in the first Brillouin zone, $n$ is the number of atoms of per unit cell, $k_B$ is the Boltzmann constant, $\hbar$ is the reduced Planck constant, and $\omega_{\boldsymbol{q}v}(V)$ is the frequency of the phonon with wave vector $\boldsymbol{q}$ and band index $v$, evaluated at constant volume $V$. The vibrational entropy is described by

$$S = -k_B \sum_{q,v} \ln[1 - \exp(-\hbar\omega_{q,v}/k_B T)]$$
$$- \frac{1}{T}\sum_{q,v} \frac{\hbar\omega_{q,v}}{\exp(\hbar\omega_{q,v}/k_B T) - 1} \quad (3)$$

And the heat capacity $C_V$ is given by

$$C_V = \sum_{q,v} k_B \left(\frac{\hbar\omega_{q,v}}{k_B T}\right)^2 \frac{\exp(\hbar\omega_{q,v}/k_B T)}{[\exp(\hbar\omega_{q,v}/k_B T) - 1]^2} \quad (4)$$

When pressure is $p$ = 0, the Gibbs free energy $G$ can be written as

$$G = E_0(V) + F_{ph}(T;V) \quad (5)$$

The coefficient of volume thermal expansion is given by

$$\alpha(T) = \frac{1}{V}\left(\frac{dV(T)}{dT}\right) \quad (6)$$

And the linear thermal expansion is described by

$$\varepsilon(T) = \frac{a(T) - a(T_C)}{a(T_C)} \quad (7)$$

where $a(T_C)$ is the equilibrium lattice constants at $T_C$ = 300 K. Where $C_P$ is the specific heat at constant pressure, it can be calculated with the relationship: $C_P = C_V + \alpha^2 BVT$, where $B$ is the bulk modulus.

For cubic crystals, there is only one independent lattice parameter. Thus, the thermodynamic calculations are performed by varying the lattice parameter from $0.95a$ to $1.05a$ in a step of $0.01a$. The calculations are preformed by varying at 11 volume points. Using data of $F(V, T) - V$, we fit the Vinet equation of state (EOS) at $P$ = 0. The corresponding equilibrium volumes and isothermal bulk moduli are obtained simultaneously from the Vinet EOS [51].

The phonon spectrum curves and phonon DOS (density of state) of the several intermetallic compounds, which are calculated by using $3 \times 3 \times 3$ supercells, are shown in Fig. 1a. The shape of phonon spectrum curves is similar. We give out the phonon spectrum curves of $Al_3Dy$ along the high symmetry Γ–X–M–Γ–R directions and the corresponding phonon density of states are also displayed in Fig. 1a. The unit cell of $Al_3Dy$ contains 4 atoms, which gives rise to a total of 12 phonon branches, which contains 3 acoustic modes and 9 optical modes. On the right side of phonon dispersion curves, the total and partial density of phonon states (PHDOS) are displayed. This low frequency region belongs to the acoustic phonon modes, and comes from hybridization between Al and Dy atoms. This high frequency region results from optical phonon modes, and is dominated by the movements of the Al atoms. Fig. 1b gives the total phonon DOS curve of other intermetallic compounds. The shape of phonon DOS curves is similar. The phonon DOSes of $Al_3RE$