First-principles calculations of phonon and thermodynamic properties of AlRE (RE = Y, Gd, Pr, Yb) intermetallic compounds

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Abstract
The phonon and thermodynamic properties of aluminum–rare-earth (AlRE, RE=Y, Gd, Pr, Yb) intermetallics with B2-type structure are investigated by performing density functional theory and density functional perturbation theory calculations within the quasiharmonic approximation. The phonon spectra and phonon density of states, including the phonon partial density of states and total density of states, are discussed. Our results demonstrate that the density of states is mostly composed of Al states at high frequency. The temperature dependences of various quantities such as thermal expansion, heat capacities at constant volume and pressure, the isothermal bulk modulus and the entropy are obtained. The electronic contribution to specific heat is discussed, and the present results show that the thermal electronic excitation affecting the thermal properties is inessential.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Aluminum alloys are widely used in aerospace industries, aircraft automotive industries, electronic industries and buildings due to their light weight, good corrosion resistance, reasonably high strength and favorable economics. The addition of rare earth (RE) elements to Al-based metal alloys has received much attention, since it can result in an increase of their wear resistance [1], mechanical properties [2], electrochemical behavior [3], thermal stability [4], etc. Thus, they are important for the design of novel materials and for further scientific and technical investigations. For the development and design of new aluminum alloys, more fundamental physical data on these alloys are needed. Recently, some investigations of AIRE, Al₂RE and Al₃RE systems were performed with first-principles calculations based on density functional theory (DFT) [5–12]. The B2-type AlY is high-temperature stable when the temperature is higher than 1473K [13]. Such metastable phases are also available for AlGd, AlPr, AlYb, etc, intermetallics with B2-type structure [14–16]. Recently, the lattice stability, magnetic properties and solubility of Al–RE binary systems including several structures were studied via first-principles density functional calculations by Gao et al [17] and Mao et al [18], and their calculated phase stabilities at T = 0K show good agreement with experimentally reported ones for a majority of the systems. Srivastava et al [5] investigated the electronic and thermal properties by using the tight binding linear muffin tin orbital method. Tao et al [6, 7] used the projector augmented wave (PAW) method to calculate the elastic...
properties and predicted thermodynamical properties of B2-AIRE intermetallics below 400 K within the Debye-type model. However, accurate calculations of thermodynamic properties for B2-type AIRE intermetallics from the lattice dynamics, i.e. exact phonon spectra, have received only a little attention.

The thermodynamical properties, such as entropy, specific heat, thermal expansion and temperature-dependent equation of state (EOS), of AIRE intermetallics are very important for investigating their properties as well as applications. A simplified method for thermal expansion calculations is in the framework of DFT with a Debye–Grüneisen-based model [19], which is based on the long-wave approximation. This model is useful in calculating the thermal properties at low temperature, and thermodynamic properties of B2-type AIRE intermetallics have been carried out based on this model by Tao et al [7]. A more accurate approach has been made possible by the achievement of density functional perturbation theory (DFPT) from first principles [20], which allowed exact calculations of vibrational frequencies at every point of the Brillouin zone [21]. The vibrational free energy can be obtained using the quasiharmonic approximation (QHA). Moreover, the QHA method lets one take into account the anharmonicity of the potential at first order: vibrational properties can be understood in terms of the excitation of the noninteracting phonon. QHA based on DFPT provided a reasonable description of the thermodynamical properties of many bulk materials below the melting point [21–25], and had been applied with great success to more and more complex materials such as alloys (NiAl2 [26]), perovskite (MgSiO3 [27]) and hexaborides (LaB6 and CeB6 [28]). More recently, we have successfully investigated the thermodynamical properties of NiAl, YAg and YCu [29], and MgRE intermetallics [30] with B2-type structures.

In this paper, we apply first-principles calculations within QHA based on DFPT to study the thermodynamic properties of AIRE (RE=Y, Gd, Pr, Yb) intermetallics with B2-type structures. The phonon spectra and phonon density of states (DOSs), including the phonon partial DOSs (PDOSs) and total DOSs (TDOSSs), have been discussed. Thermal expansions, temperature dependence of isothermal bulk modules, heat capacities at constant volume and constant pressure and the entropy as a function of temperature are presented.

2. Theory

To study the effects of changing temperature, one has to look at the Helmholtz free energy, incorporating the effects of thermal-electronic excitations and thermal vibrations (phonons). The Helmholtz free energy at temperature $T$ and constant volume $V$ is given by [31, 32]

$$F(V, T) = E_0(V) + F_{el}(V, T) + F_{vib}(V, T),$$

where $E_0(V)$ is the static contribution to the internal energy at volume $V$ and can be easily obtained from standard DFT calculations. $F_{el}(V, T)$ given in equation (1) is the thermal electronic contribution to free energy and is given by

$$F_{el} = E_{el} - TS_{el},$$

Here, the electronic excitation energy $E_{el}$ is given by

$$E_{el}(V, T) = \int_0^\infty n(\varepsilon, V) f(\varepsilon) \varepsilon \, d\varepsilon - \int_0^{\varepsilon_F} n(\varepsilon, V) \varepsilon \, d\varepsilon, \quad (2)$$

where $n(\varepsilon, V)$ is the electronic DOS at energy $\varepsilon$ and volume $V$, $f(\varepsilon)$ is the Fermi–Dirac distribution function and $\varepsilon_F$ represents the Fermi level. The electronic entropy $S_{el}$ is formulated as

$$S_{el}(V, T) = -k_B \int_0^\infty n(\varepsilon, V) [f(\varepsilon) \ln f(\varepsilon) + (1 - f(\varepsilon)) \ln (1 - f(\varepsilon))] \, d\varepsilon, \quad (3)$$

where $k_B$ is the Boltzmann constant. The thermal electronic contribution to free energy is generally considered to be negligible away from the melting point of the material under consideration.

$F_{vib}(V, T)$, equation (1), is the vibrational free energy that comes from the phonon contribution. Within the QHA, $F_{vib}(V, T)$ is given by

$$F_{vib}(V, T) = k_B T \sum_{q, \lambda} \ln \left(2 \sinh \left(\frac{\hbar \omega_{q, \lambda}(V)}{2 k_B T} \right)\right). \quad (4)$$

Here, the sum is over all phonon branches $\lambda$ and over all wave vectors $q$ in the first Brillouin zone, $\hbar$ is the reduced Planck constant and $\omega_{q, \lambda}(V)$ is the frequency of the phonon with wave vector $q$ and polarization $\lambda$, evaluated at constant volume $V$.

The vibrational specific heat $C_V$ at constant volume in the QHA can be obtained from the following equation:

$$C_{V}^{\text{ vib}} = \sum_{q, \lambda} k_B \left(\frac{\hbar \omega_{q, \lambda}(V)}{2 k_B T}\right)^2 \cosh^2 \left(\frac{\hbar \omega_{q, \lambda}(V)}{2 k_B T}\right). \quad (5)$$

The electronic specific heat can be obtained from

$$C_{V}^{\text{ el}} = T \left(\frac{\partial S_{el}}{\partial T}\right)_V \quad (6)$$

and we define the total specific heat at constant volume as $C_V = C_{V}^{\text{ vib}} + C_{V}^{\text{ el}}$. Owing to anharmonicity, the specific heat of a crystal at constant pressure, $C_p$, is different from the specific heat of a crystal at constant volume; $C_V$ goes to a constant which is given by classical equipartition law: $C_V = 3Nk_B$, where $N$ is the number of atoms in the system while $C_p$, which is what experiments determine directly, is proportional to $T$. QHA lets one take into account the anharmonicity of the potential at first order: vibrational properties can be understood in terms of the excitation of the noninteracting phonon. The equilibrium volume at temperature $T$ is obtained by minimizing Helmholtz $F$ with respect to $V$, i.e. $\min_{V}[F(V, T)]$. The volume thermal expansion coefficient is given by

$$\alpha(T) = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (7)$$

and the linear thermal expansion is described as

$$\epsilon(T) = \frac{\alpha(T) - \alpha(T_c)}{\alpha(T_c)} \quad (8)$$
where \(a(T_c)\) is the equilibrium lattice constant \(a(T) = [V(T)]^{1/3}\) at \(T_c = 300\) K.

Then, \(C_p\) can be obtained from \(C_V\) and \(a\) by the equation

\[
C_p = C_V + a^2 B V T, \tag{9}
\]

where \(B(T) = -1/V \partial^2 F/\partial V^2\) is the bulk modulus.

The vibrational contribution to the entropy of the crystal is given by

\[
S_{vb} = -k_B \sum_{q,\lambda} \ln \left( \frac{2 \sinh \frac{\hbar \omega_{q,\lambda}(V)}{2k_BT}}{\coth \frac{\hbar \omega_{q,\lambda}(V)}{2k_BT}} \right) - \frac{\hbar \omega_{q,\lambda}(V)}{2k_BT}, \tag{10}
\]

### 3. Computational details

In this work, the static energy and the thermal electronic contribution to the Helmholtz free energy are computed by using first-principles calculations in the framework of DFT. We employed the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) [33, 34] exchange-correlation functional as implemented in the VASP code [38, 39]. The ion–electron interaction is described by the full potential frozen-core projector augmented wave (PAW) method [38, 39], with an energy cutoff of 600 eV for plane waves. The Brillouin zones of the unit cells are represented by the Monkhorst–Pack special \(k\)-point scheme [40]. We used as a sample a \(21 \times 21 \times 21\) \(k\)-point mesh in the full Brillouin zone giving 726 irreducible \(k\)-points to calculate the initial structures and electronic DOS. The radial cutoffs of the PAW potentials of Al, Y, Gd, Pr and Yb were 1.40, 1.81, 1.58, 1.64 and 1.74 Å, respectively. The 3s and 3p electrons for Al, the 4s, 4p, 4d and 5s electrons for Y and the 4f and 6s electrons for Gd, Pr and Yb were treated as valence and the remaining electrons were kept frozen. The thermal electronic energies and entropies are evaluated using one-dimensional integrations from the self-consistent DFT calculations of electronic DOS using Fermi–Dirac smearing as shown in equations (2) and (3). In order to deal with the possible convergence problems for metals, a smearing technique is employed using the Methfessel–Paxton scheme [41], with a smearing of 0.05 eV.

The vibrational free energy was obtained from first-principles phonon calculations by using Phonopy [25, 42, 43], which can support the VASP interface to calculate force constants directly in the framework of DFPT [44]. Phonon calculations were performed by the supercell approach. Since the chosen supercell size strongly influences the thermal properties, we compare the vibrational free energies of a \(3 \times 3 \times 3\) supercell with those of a \(5 \times 5 \times 5\) supercell at 300 and 1000 K, and find that the energy fluctuations between \(3 \times 3 \times 3\) and \(5 \times 5 \times 5\) supercells are less than 0.01%. Hence, we chose the \(3 \times 3 \times 3\) supercell with 54-atom to calculate phonon dispersions. We carried out DFPT calculations on this 54 atoms supercell using PBE-GGA exchange-correlation effects and \(7 \times 7 \times 7\)-point grid meshes for Brillouin zone integrations.

In order to obtain the equilibrium lattice volume as a function of temperature, we have calculated total free energy at temperature points with a step of 1 K from 0 to 1200 K at 13 volume points. At each temperature point, the equilibrium volume \(V(T)\) and isothermal bulk moduli \(B(T)\) are obtained by minimizing free energy with respect to \(V\) by fitting the integral form of the Vinet EOS [45] at \(p = 0\). These procedures applied to AlY are demonstrated in figure 1, where the Helmholtz free energy \(F(V, T)\) as a function of unit cell volume at different temperatures is shown. \(C_p\) has been calculated by polynomial fittings for \(C_V\) and by numerical differentiation for \(\partial V/\partial T\) to obtain \(a(T)\).

### 4. Results and discussions

#### 4.1. Phonon spectra and density of states

We calculated the phonon frequency using the DFPT with the force-constant method [46] with forces calculated using VASP. The calculated phonon spectra of AlY, AlGd, AlPr and AlYb, which are calculated by using \(3 \times 3 \times 3\) supercells, are displayed in figure 2. Owing to the crystal symmetry, the spectra curves are shown along the high-symmetry direction \(G–X–M–Γ–R\) of the Brillouin zone. These dispersion curves have a common framework. Since the B2-type intermetallics contain two atoms per primitive cubic unit cell, there are three acoustical branches and three optical branches. Our results clearly show the degeneration of two transverse–acoustical modes and two transverse–optical (TO) modes in the \(G–X\) and \(G–R\) directions. At the \(G\) point, the degeneration of longitudinal–optical and TO modes is obtained, so there are no polarization effects in the B2-type AlRE intermetallics.
Figure 2. Phonon-dispersion curves of (a) AlY, (b) AlGd, (c) AlPr and (d) AlYb.

Figure 3. Phonon TDOS and PDOS of (a) AlY, (b) AlGd, (c) AlPr and (d) AlYb. The solid curves, dashed curves and dotted curves represent the phonon TDOS, PDOS of RE (RE = Y, Gd, Pr, and Yb) states and PDOS of Al states, respectively. The PDOS indicates that the DOS is mostly composed of Al states at high frequency and RE states at low frequency.

The phonon DOS including the PDOS and the TDOS are shown in figure 3. Sampling a $51 \times 51 \times 51$ Monkhorst–Pack grid for phonon wave vectors $q$ is found to be sufficient to obtain the mean relative error in each channel of phonon DOS. The phonon band gap of AlY starts at 5 THz, while those of AlGd, AlPr and AlYb start at less than 4 Hz. Among the four intermetallics, AlY and AlYb have the greatest and lowest values of the maximum value of acoustic modes, respectively, since the atomic mass of Y is lightest and that of Yb is heaviest in the four calculated RE elements. The flat regions
Table 1. The equilibrium lattice constants \( a_0 \), the isothermal bulk modulus \( B_0 \) and the pressure derivatives of the isothermal bulk modulus \( B'_0 \) at \( T = 0 \) K for AIRE (RE=Y, Gd, Pr, Yb) in our calculation in comparison with the previous calculated results and the experiment.

|       | Y   | Gd  | Pr  | Yb  |
|-------|-----|-----|-----|-----|
| \( a_0 \) (Å) | 3.606, 3.605\(^b\), 3.759\(^b\) | 3.635, 3.634\(^a\), 3.7208\(^a\) | 3.760, 3.759\(^a\), 3.82\(^d\) | 3.699, 3.697\(^a\) |
| \( B_0 \) (GPa) | 62.84, 63.70\(^a\) | 62.54, 61.72\(^a\) | 54.18, 55.11\(^a\) | 38.72, 39.11\(^a\) |
| \( B'_0 \) | 3.97, 3.99\(^a\) | 3.79, 3.81\(^a\) | 3.86, 3.92\(^a\) | 4.24, 4.30\(^a\) |

\(^a\) Tao et al [6].
\(^b\) Dagerhamn [13].
\(^c\) Baenziger and Moriarty [15].
\(^d\) Kripjakevich and Zaluckjj [16].

Figure 4. Isothermal bulk moduli \( B \) as a function of temperature.

of phonon-dispersion curves, which correspond to the peaks in the phonon PDOS, indicate localization of the states, i.e. they behave like ‘atomic states’ [25]. In the four intermetallics, the DOSs are mostly composed of Al states above the phonon band gap since its atomic mass is much lighter than those of the RE elements (RE=Y, Dy, Pr, Tb).

4.2. Bulk properties and thermal expansion

The calculated results of the equilibrium lattice constants \( a_0 \), the isothermal bulk modulus \( B_0 \) and the pressure derivatives of the isothermal bulk modulus \( B'_0 \) at \( T = 0 \) K for AIRE (RE=Y, Dy, Pr, Tb) intermetallics together with the previous calculated results [6] and the available experimental values [13, 15, 16] are shown in table 1. Our calculated results for the equilibrium lattice constants at \( T = 0 \) K show excellent agreement with previous theoretical and experimental results. For the isothermal bulk modulus \( B_0 \) and the pressure derivatives of the isothermal bulk modulus \( B'_0 \) at \( T = 0 \), which are obtained from the Vinet EOS, the present results are within 1.7% error from the previous calculated values obtained from Rose’s EOS [6]. The temperature-dependent isothermal bulk modulus \( B(T) \) is shown in figure 4. Among the four intermetallic compounds in the temperature range 0–1200 K, light RE AlY and heavy RE AlYb have the highest and lowest bulk moduli, respectively, that is, AlY is the most incompressible and AlYb is the most compressible. With increasing temperature, the differences among the bulk moduli remain almost unchanged. The overall observation is that the \( B_T \) of the intermetallics decreases with increasing temperature and approaches linearity at higher temperature and zero slope around zero temperature.

As shown in figure 1, the equilibrium volume at any temperature corresponds to the minimum values of the fitted thermodynamic functions. The thermal expansion is observed as an increase in the equilibrium volume. The linear thermal expansion \( \epsilon \) defined by equation (8) as a function of the four AIRE intermetallics is shown in figure 5(a). The linear expansions of the four compounds are found to be AlYb > AlY > AlGd > AlPr, and those of AlY and AlGd are nearly equivalent. The coefficients of the volume thermal expansion \( \alpha \) as a function of temperature are shown in figure 5(b). With increasing temperature, the thermal expansion grows rapidly up to \( \sim 200 \) K, and the slopes become smaller and nearly constant at high temperatures except for AlYb. In addition, \( \alpha \) can be used to estimate the anharmonic effects according to the Grüneisen relation \( \alpha = \gamma C_v / V B_T \), and the Grüneisen parameter \( \gamma = -d \ln \rho / d \ln V \). In QHA, the phonon frequencies at given lattice parameters are independent of temperature. In a real crystal, this is not the case. The accuracy of QHA applied to AI(RE=Al, Y, Gd, Pr, Yb) can be verified by experiment in the future.

4.3. Specific heat and entropy

Once the phonon spectrum over the entire Brillouin zone is available, the vibrational heat capacity at constant volume \( C^\text{vib}_V \) can be calculated by using equation (5), while the electronic contribution to heat capacity at constant volume \( C^\text{el}_V \) can be obtained from the electronic DOS by using equation (6). Then, the specific heat at constant pressure \( C_p \) can be computed by equation (9). For comparison, both \( C_p \) values, including electronic contribution and not, are plotted. We display these results in figure 6. At high temperature, \( C^\text{vib}_V \) tends to the classical constant value \( 6 R \) (\( R \) is the molar gas constant), and \( C^\text{el}_V \) and \( C_p \) still increase. Considering thermal electronic contributions to specific heat, we find that \( C^\text{el}_V \) lets \( C_p \) suffer a little shift and can be negligible. This character can be understood from the electronic DOS at the Fermi level \( n(\epsilon_F) \). AIRE intermetallics have low electronic DOS near the Fermi level and the Fermi levels occur at a valley in the curves of electronic DOS [6]. Obviously, \( C^\text{el}_V \) is much smaller than the value \( C_p - C_V = \alpha^2 B V T \). Hence, the electronic excitations affecting the thermal properties are inessential. Compared with our previous study of MgRE intermetallics [30], the electronic specific heat cannot be negligible since the Fermi level for MgRE intermetallics occurs above a peak in the electronic DOS [47] and the electronic excitations affecting the thermal properties are remarkable. Whether we consider
Figure 5. (a) Temperature dependence of the linear thermal expansion $\epsilon(T)$ for AlRE (RE=Y, Gd, Pr, Yb); (b) the coefficients of volume thermal expansion $\alpha$ for AlRE (RE=Y, Gd, Pr, Yb) as a function of temperature.

Figure 6. Temperature dependence of heat capacity of (a) AlY, (b) AlGd, (c) AlPr and (d) AlYb. Solid and dashed curves denote the calculated $C_p$, including the electronic contribution and not, respectively. Dotted and dot-dashed curves show vibrational and electronic $C_V$, respectively.

The entropy as a function of temperature is an important thermodynamic quantity in thermodynamic modeling. The calculation results of entropies for the four B2-type structures of AlRE are shown in figure 8. It can be clearly seen that the entropies of the four compounds increase with temperature. In the temperature range 0–1200 K, the overall observation is that the order of the entropy $S$ is AlY < AlGd < AlPr < AlYb. At the temperature 300 K, the calculated values of entropy for AlY, AlGd, AlPr and AlYb are 67.48, 74.87, 77.93 and 85.03 J mol$^{-1}$ K$^{-1}$.

5. Conclusions

The phonon and thermodynamic properties, such as the thermal expansions, the heat capacities at constant volume and constant pressure, the isothermal bulk modulus and the entropy as a function of temperature, of AlRE (RE=Y, Gd, Pr, Yb) intermetallics with B2-type structure are investigated by DFT and DFPT within the QHA. The phonon
Figure 7. The specific heat at constant volume $C_v$ for AIRE (RE= Y, Gd, Pr, Yb) as a function of temperature below 200 K.

Figure 8. The entropy $S$ for AIRE (RE= Y, Gd, Pr, Yb) as a function of temperature.

spectra and phonon DOSs, including the phonon PDOSSs and TDOSs, have been discussed. Our results demonstrate that the DOSs are mostly composed of Al states at high frequency and composed of RE (RE= Y, Gd, Pr, Yb) states at low frequency. In the calculated temperature range 0–1200 K, AlY is the most incompressible and AlYb is the most compressible. The differences of the isothermal bulk moduli among the four intermetallics remain almost unchanged with increasing temperature. The thermal expansions of the four compounds are found to be AlYb > AlY > AlGd > AlPr, and those of AlY and AlGd are nearly equivalent. The specific heats and entropy increase with temperature, while $C_{V,p}$ tends to a constant and $C_p$ maintains positive slopes at high temperature. The electronic contribution to the specific heat is discussed, and the presented results show that the thermal electronic excitation affecting the thermal properties is inessential.

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