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Thermal properties and thermoelasticity of $L1_2$ ordered Al_3RE (RE = Er, Tm, Yb, Lu) phases: A first-principles study

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ABSTRACT

Thermal properties and thermoelasticity of $L1_2$ Al_3RE (RE = Er, Tm, Yb, Lu) phases have been studied by first principles calculations combined with density functional perturbation theory and quasi-harmonic approximation. In the temperature range considered, the calculated thermal properties including equilibrium volume, isothermal bulk modulus, Grüneisen parameters for different Al_3RE phases exhibit analogous variation tendency and the numerical values are associated with the atomic radius of RE. The calculated thermal expansion and heat capacity for different Al_3RE are almost indistinguishable from each other. The obtained elastic constants and polycrystalline elastic moduli exhibit gentle softening trends with temperature, and the variation tendency is also very similar. In the temperature range considered, Al_3RE phases are nearly isotropic. The present study would be valuable for future investigation and design of high temperature Al alloys.

1. Introduction

The $L1_2$ type trialuminide compounds Al_3M (where M represents transition or rare earth elements) have increasingly attracted attention due to the outstanding mechanical properties such as high specific strength and elastic moduli [1–7]. Moreover, they also possess low density, high melting points, superior oxidation resistance, sufficient creep resistance, good thermal stability and conductivity [6–11]. Especially, the structural similarity with Al matrix is favorable for a coherent interface, thereby minimizing the surface energy and maximizing the strengthening effect [6]. All these excellent properties enable them as the ideal dispersed strengthening phases for the high-strength thermally-stable Al based alloys.

Investigations [6] have shown that many elements are potential additives to form the coherent $L1_2$ Al_3M phases in Al alloys during aging heat treatment process. Typical additives are the Group IIIA transition metal element Sc, the Group IVA transition metal elements Ti, Zr and Hf, the late rare earth elements RE (RE = Er, Tm, Yb, Lu). Among them, Al_3Sc has been studied extensively due to their superior properties [12–14]. However, the high cost of Sc constrains the application of Al_3Sc. Although neighboring transition metal elements Ti, Zr and Hf seem to be the feasible candidates to substitute for Sc, the Al_3(Ti, Zr, Hf) phases with the $L1_2$ structure are thermodynamically metastable and transform to their respective equilibrium tetragonal $D0_{22}$ or $D0_{23}$ structure at elevated temperature [15]. The rare earth elements RE (RE = Er, Tm, Yb, Lu) could not only form the thermodynamically stable $L1_2$ Al_3RE precipitates after alloying with Al, but also have a lower price than Sc element [16]. In addition, the substitution of RE elements for Sc could also improve high-temperature creep and hardness properties of Al_3Sc [16,17]. Thus, Al_3RE are considered to be the important dispersion strengthening phases of Al alloys for elevated temperature applications [6,16,18].

For high temperature applications of alloys, temperature dependent elastic properties are crucial [19]. Moreover, knowledge of thermoelasticity is also essential for predicting and understanding material response, strength, mechanical stability as well as phase transitions under high temperature [20]. So a great number of investigations of elastic properties at high temperature have been performed [21–35]. Experimental measurements of high temperature elastic properties are extensively performed using various techniques such as resonant ultrasound spectroscopy (RUS) [23–25] and brillouin scattering (BS) [26,27]. Theoretically, first principles calculations combined with other theoretical models are also widely used for predicting thermoelasticity [28–35].

To our best knowledge, no experimental and theoretical investigations on the thermoelasticity for $L1_2$ Al_3RE are performed up to now. Although theoretical investigations of elastic properties for $L1_2$ Al_3RE at 0 K have been reported [1,4], which could not reflect the high temperature mechanical behavior. Encouraged by the special interest of $L1_2$ Al_3RE phases in potential high strength Al alloys, the temperature dependent elastic properties of $L1_2$ Al_3RE are predicted by first principles calculations combined with the quasi-harmonic approximations (QHA) method in the present work. The important thermal properties

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including thermal equilibrium volume, isothermal bulk modulus, thermal expansion, Grüneisen parameter and heat capacity, are studied and compared with available experimental and theoretical data.

2. Theory and computational methods

The key procedure for thermoelastic calculations is to compute the second derivatives of Helmholtz free energy F with respect to the applied strain. For given volume V and temperature T, Helmholtz free energy $F(V,T)$ can be written as:

$$F(V,T) = E_0(V) + F_{el}(V,T) + F_{vib}(V,T) \tag{1}$$

where $E_0(V)$ is the 0 K static total energy, which can be directly calculated by first principles calculations. $F_{el}(V,T)$ is the thermal electronic contribution, which can be calculated by integrating the electronic density of states (EDOS) using the Fermi–Dirac distribution [30]. $F_{vib}(V,T)$ is the vibrational contribution, which can be calculated from the phonon density of states (PDOS) as follows:

$$F_{vib}(V,T) = \int_0^{\infty}\left[\frac{\hbar\omega}{2} + k_B T\,\ln\left(1 - e^{-\hbar\omega/k_B T}\right)\right]g(\omega,V)d\omega. \tag{2}$$

Herein, the magnetic and configuration contributions to the free energy are not taken into account, as the $L1_2$ structure is thermally stable and the magnetic moments of RE (RE = Er, Tm, Yb, Lu) are nearly close to zero [16]. Within the QHA scheme, the partial anharmonic effects caused by volume expansion are taken into account, the intrinsic anharmonic effects caused by the phonon-phonon interaction are neglected [36]. The vibrational frequencies at different volumes are renormalized [36]. At any given volume, the calculated vibrational free energy $F_{vib}(V,T)$, together with E_0 and $F_{el}(V,T)$, yield a Helmholtz free energy surface in volume-temperature space. The equilibrium volume V_T as a function of temperature T can be obtained by fitting the Helmholtz free energy at different volume to Vinet equation of states (EOS). The temperature dependent elastic constants $C_{ij}(T)$ are then calculated. The calculation details have been described elsewhere [28,30,31]. Note that the elastic constants calculated from this approach correspond to isothermal conditions. To compare with experimentally measured adiabatic elastic constants, the isothermal elastic constants are required to convert into adiabatic elastic constants by the following formulas [31]: $B_S = B_T \times (1 + \alpha\gamma T)$, $C_{11}^S = C_{11}^T + \alpha B_T \gamma T$, $C_{12}^S = C_{12}^T + \alpha B_T \gamma T$ and $C_{44}^S = C_{44}^T$, where α is the volume thermal expansion coefficient, B_T is the isothermal bulk modulus from by EOS fitting, γ is the so-called Grüneisen parameter which can be calculated by $\gamma = d\ln\omega/d\ln V$. The super S and subscripts T stand for adiabatic and isothermal condition, respectively. These thermal properties can be derived from the free energy as a function of temperature using the thermodynamic laws.

All calculations were performed based on the density functional theory (DFT) as implemented the Vienna *ab initio* simulation package (VASP) [37]. The electron-ion interaction was described by the projector augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) [38] was used to treat the exchange-correlation functional. After convergence testing, the cut-off energy for plane wave basis was set as 320 eV. The geometry optimization was performed by conjugate gradient algorithm [39] until the total energy changes were $<10^{-5}$ eV/atom and the Hellmann-Feynman forces [40] on atoms were within 10^{-3} eV/Å. The linear tetrahedron method with Blöchl corrections [41] was used for static total energy and electronic DOS calculations. Although two sets of PBE potentials for RE elements are present in VASP package, in the present work the frozen versions of RE_3 pseudopotentials were used and spin polarization was considered in all calculations. As for phonon calculations, the $3 \times 3 \times 3$ supercells and Monkhorst–Pack $2 \times 2 \times 2$ k-point grids were chosen. The force constants were obtained by using the density functional perturbation theory (DFPT) [42] implemented in the VASP code. The phonon vibrational frequencies were then calculated by the PHONOPY code [43]. To obtain the accurate force constants, the convergence criteria for total energy and forces of ionic relaxation were set as 10^{-8} eV/atom and 10^{-6} eV/Å, respectively.

3. Results and discussion

The calculated ground state properties are listed in Table 1, together with available experimental and theoretical results [1,4,6]. Despite slightly larger lattice constants of Al_3RE phases than the experimental data due to the overestimation from GGA functional itself, the GGA results are still in good agreement with the other theoretical data [1, 4].

The calculated elastic properties for Al_3RE at 0 K also agree well with the previous results [1,4] except for Al_3Yb. The slightly large differences may be due to Yb_2 potentials [1,4]. All the calculated elastic constants of Al_3RE phases satisfy the mechanical stability criteria for cubic crystals: $C_{11} + 2C_{12} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$ [44], indicating Al_3RE phases are mechanical stable. The Cauchy pressure C_{12}–C_{44} values of Al_3RE phases are negative, implying the directional (covalent) bonding features [45]. In addition, the G/B values of Al_3RE phases are larger than 0.57, indicating the brittleness of these phases [46].

3.1. Thermal properties

The thermal equilibrium volume (V_T), isothermal bulk modulus (B_T), linear thermal expansion coefficient (α_L), Grüneisen parameter (γ) and heat capacity (C_P, C_V) are the fundamental thermodynamic parameters, which are also required for the following conversion from isothermal to adiabatic elasticity constants. As described in Section 2, thermal equilibrium volume V_T and isothermal bulk modulus B_T as a function of temperature for Al_3RE can be obtained by fitting free energies at different volumes to the Vinet equation of states, and the calculated results are shown in Fig. 1(a) and (b), respectively. From Fig. 1(a), it can be seen that the calculated equilibrium volume V_T of all Al_3RE phases exhibit similar increasing trends with temperature, the numerical values of thermal equilibrium volumes for Al_3RE phases in the temperature range 0 K–900 K exhibit the sequence $Al_3Er > Al_3Tm > Al_3Yb > Al_3Lu$, which is similar to the order of RE radii $r_{Er} > r_{Tm} > r_{Yb} > r_{Lu}$.

From Fig. 1(b), the calculated isothermal bulk moduli of Al_3RE phases decrease slowly at low temperature and then rapidly and linearly above 200 K. The decreasing tendencies are similar for these four Al_3RE phases. In contrast to the Fig. 1(a), the calculated bulk moduli of the Al_3RE phases from 0 K to 900 K exhibit opposite order of RE radii,

Table 1
The calculated ground state properties, including lattice constants a, elastic constants (C_{11}, C_{12}, C_{44}), bulk modulus B, shear modulus G, Young's modulus E and G/B values.

	a (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)	G (GPa)	E (GPa)	G/B
Al_3Er	4.232	159.59	36.33	62.64	77.42	62.24	147.25	0.804
	4.215[a]	160.05[b]	36.52[b]	60.95[b]	77.70[b]	61.28[b]	145.56[b]	
	4.235[b]	165.83[c]	33.57[c]	65.46[c]	77.66[c]	65.73[c]	153.79[c]	
	4.232[c]							
Al_3Tm	4.223	159.26	37.17	62.64	77.87	62.10	146.99	0.797
	4.203[a]	160.92[b]	37.03[b]	61.17[b]	78.33[b]	61.48[b]	146.19[b]	
	4.221[b]	166.04[c]	34.39[c]	65.51[c]	78.27[c]	65.64[c]	153.89[c]	
	4.220[c]							
Al_3Yb	4.212	158.27	38.01	61.76	78.10	61.11	145.39	0.782
	4.200[a]	126.00[b]	24.77[b]	56.69[b]	58.51[b]	54.17[b]	124.19[b]	
	4.295[b]	126.90[c]	25.25[c]	60.30[c]	59.13[c]	56.31[c]	128.57[c]	
	4.291[c]							
Al_3Lu	4.204	157.83	38.90	61.53	78.54	60.70	144.79	0.773
	4.187[a]	159.85[b]	38.43[b]	60.44[b]	78.90[b]	60.54[b]	144.64[b]	
	4.206[b]							

[a] Experimental data from Ref. [3].
[b] Calculated results from Ref. [4].
[c] Calculated results from Ref. [1].