Article

The Thermal Properties of L₁₂ Phases in Aluminum Enhanced by Alloying Elements

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Abstract: The L₁₂ type trialuminide compounds Al₃M possess outstanding mechanical properties, which enable them to be ideal for dispersed strengthening phases for the high-strength thermally stable Al based alloys. Ab-initio calculations based on the density functional theory (DFT) were performed to study the structural, electronic, thermal, and thermodynamic properties of L₁₂-Al₃M (M = Er, Hf, Lu, Sc, Ti, Tm, Yb, Li, Mg, Zr) structures in Al alloys. The total energy calculations showed that the L₁₂ structures are quite stable. On the basis of the thermodynamic calculation, we found that the Yb, Lu, Er, and Tm atoms with a larger atomic radii than Al promoted the thermal stability of the Al alloys, and the thermal stability rank has been constructed as: Al₃Yb > Al₃Lu > Al₃Er > Al₃Tm > Al, which shows an apparent positive correlation between the atomic size and thermal stability. The chemical bond offers a firm basis upon which to forge links not only within chemistry but also with the macroscopic properties of materials. A careful analysis of the charge density indicated that Yb, Lu, Er, and Tm atoms covalently bonded to Al, providing a strong intrinsic basis for the thermal stability of the respective structures, suggesting that the addition of big atoms (Yb, Lu, Er, and Tm) are beneficial for the thermal stability of Al alloys.

Keywords: L₁₂ phases; Al alloy; first-principles calculation; thermal stability

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1. Introduction

The considerable attention that aluminum alloys have received originates from their excellent physical and chemical properties, such as low density, high specific strength, easy processing and molding, excellent electrical conductivity, thermal conductivity, corrosion resistance, etc. Thus, Al alloys are nowadays widely used in the aviation, aerospace, automotive, machinery manufacturing, shipping, and chemical industries [1–3]. However, scientific development and advanced technological projects, e.g., high-speed trains, and large aircraft and spacecraft, put higher requirements in front of the overall performance of aluminum alloys.

The structure of the L₁₂ type compounds Al₃M similarity with the Al matrix leads to a coherent interface, thereby minimizing the surface energy and maximizing the strengthening effect [4]. Recently, the L₁₂-Al₃M structure phase in Al alloy has received great attention since it was reported to improve the strength, toughness, wear resistance, corrosion resistance, fatigue resistance, and high-temperature resistance properties significantly [5,6].

Particularly, this structure was widely used as a high-temperature structural material because of its good thermal stability [7–11]. Al_3Sc is the most extensively studied intermetallic compound because of its thermodynamically stable L_{12} structure, large volume fraction, and moderate coarsening rate [12–14]. However, the high cost of Sc limits its industrial applications. The alloying of RE elements (RE = Er, Tm, Yb, Lu) with Al yields thermodynamically stable L_{12} -phase Al_3RE precipitates, and RE elements are less expensive than Sc. Moreover, the substitution of Sc by RE elements also improved the high-temperature creep and hardness properties of Al_3Sc [15,16]. Thus, Al_3RE alloys are considered to be an important diffusion reinforcing phase for high-temperature applications, and the thermodynamic properties are investigated for understanding and predicting the response, thermal stability, and phase transformation of materials at high temperatures [4,9,15].

Investigations [4] have shown that many elements are potential additives to form the Al_3M phases in Al alloys during aging heat treatment process, such as the four heaviest rare earth elements RE (RE = Er, Tm, Yb, Lu) [17], the Group IVA transition metal elements Ti, Zr and Hf, and other common elements in Al alloys. Previous studies of the L_{12} - Al_3M structure have focused on structural properties, mechanics, and thermodynamic properties (i.e., entropy and enthalpy formation). Zhang et al. [18] performed first-principles calculations on the thermodynamic properties of Al_3Tm and Al_3Lu under high pressure and found that Al_3Tm exhibited better thermal stability than Al_3Lu in the temperature range of 0–1000 K. Li et al. [19] calculated some of the thermal quantities of Al_3Mg and Al_3Sc alloys and confirmed that the quantities exhibited a linear high-temperature behavior at high pressure, eventually converging to an almost constant value at both high pressure and high temperature. Pan et al. [20] investigated the thermal properties and thermoelasticity of L_{12} - Al_3RE (RE = Er, Tm, Yb, Lu). It is found that the thermal properties of Al_3RE are nearly isotropic in the considered temperature range, and the Al_3RE phases can maintain a definite strength at a high temperature.

Although the L_{12} - Al_3M structure in Al alloys has attracted great attention and been widely investigated, there are fewer systematic experimental and theoretical studies on the thermodynamic properties of L_{12} - Al_3M structures, and the general rule of judging the thermodynamic properties of different L_{12} - Al_3M structures has not been performed up to now. In fact, structural information, thermodynamic properties, and bonding analysis are difficult to measure experimentally. With the development of computer science and technology, first-principle calculations have started to play an increasingly important role in predicting and analyzing materials' physical and chemical properties.

Encouraged by the special interest of L_{12} - Al_3M structures in potential high strength Al alloys, eleven elements (Er, Tm, Yb, Lu, Sc, Zr, Ti, Hf, Li, Mg, and Si) have been added to the Al matrix to analyze the thermodynamic properties using first-principles calculations systematically. Important physical quantities related to thermal properties, such as enthalpy of formation, Gibbs free energy, thermodynamic entropy, constant-pressure heat capacity, coefficient of thermal expansion, and Grüneisen parameters, are computed to reveal the thermodynamic properties of L_{12} - Al_3M structures. The purpose of the present paper is to show the structural features and the thermodynamic properties of individual L_{12} - Al_3M structures, and to try to propose an effective rule judging whether the additive element is helpful to improve the thermodynamic properties of Al alloys. Finally, we found that the addition of RE elements (Yb, Lu, Er, and Tm) significantly enhances the Al alloy thermal stability. The Al alloy thermal stability exhibits a significant positive correlation with the atomic radii of RE elements, which would positively affect the design and application of Al alloys in technology and industry.

Due to the limitation of small solid solubility and the diffusion coefficient of RE elements in the Al matrix [14,21,22], there are still some difficulties in experimental verification and testing. We believe that our results can provide strong theoretical support for subsequent experiments. We hope to overcome the present knowledge and manufacturing barriers and develop aluminum alloys with superior properties that remain stable under high temperatures.

2. Theoretical Methods

The first-principle calculations were performed using the Vienna ab initio simulation package (VASP) [23], which solves the Kohn–Sham equation using the plane wave total-energy method to obtain the valence electron density and the wave function [24]. The electron–ion interaction was described by the projector augmented wave (PAW) method. It is worth noting that the narrow f-bands in RE compounds are not adequately described by standard local density approximation (LDA) and the generalized gradient approximation (GGA) [25,26] due to strong electronic correlation effects. In order to deal with these insufficiencies, the DFT + U method [27] is often employed, with U used fit to some spectral data. Another approach is to use a hybrid functional introducing a portion of exact Hartree–Fock type exchange into the exchange–correlation functional [28–30]. Both approaches improve the treatment of strongly correlated electrons. However, DFT + U suffers from an ambiguity of the Hubbard U value, while hybrid functionals suffer from extremely demanding computational costs. Generally, the strong correlation of f-electrons have a great influence on the oxide, nitride and insulator systems and they have little influence on the metal system because of the small degree of the electron localization in the metal system [29,31–33]. In this study, the Perdew–Burke–Ernzerh (PBE) version of the GGA [34] was used to treat the exchange–correlation functional. In the VASP calculations, geometric optimization was performed by the conjugate gradient algorithm [35] until the total energy changed to $<10^{-6}$ eV/atom and the Hellmann–Feynman force on the atom [20] was in the range of 10^{-3} eV/Å. To ensure the calculation accuracy, we performed a series of convergence tests and finally set the truncation energy to 400 eV. The Brillouin zone integral used the high-symmetric k-point method in the form of the Monkhorst–Pack method [36], and the k-point separation was $13 \times 13 \times 13$. The linear tetrahedron method with Blöchl corrections [37] was used for static total energy calculations. The PAW_PBE pseudopotentials for each element in this calculation were chosen as Al, Er_3, Hf_pv, Lu_3, Sc_sv, Si, Ti_sv, Tm_3, Yb_2, Li_sv, Mg, and Zr_sv. Thermal properties were calculated by employing the quasi-harmonic approximation (QHA) theory implemented in the PHONOPY code [38]. For phonon calculations, $3 \times 3 \times 3$ supercells and Monkhorst–Pack $3 \times 3 \times 3$ k-point grids were chosen. At the same time, Hessian matrices (second-order derivative matrices) were determined by the density-generalized perturbation theory, using symmetry to reduce the number of displacements.

The enthalpy, $E(T)$, free energy, $F(T)$, entropy, $S(T)$, and heat capacity, C_v , can be given as follows [39,40]:

$$E(T) = E_{tot} + E_{zp} + k_B T \int \frac{\hbar\omega}{\exp(\hbar\omega/k_B T)} F(\omega) d\omega \quad (1)$$

$$F(T) = E_{tot} + E_{zp} + k_B T \int F(\omega) \ln[1 - \exp(\hbar\omega/k_B T)] d\omega \quad (2)$$

$$S(T) = k_B \left\{ \int \frac{\hbar\omega/k_B T}{\exp(\hbar\omega/k_B T) - 1} F(\omega) d\omega - \int F(\omega) \ln[1 - \exp(\hbar\omega/k_B T)] d\omega \right\} \quad (3)$$

where T is the temperature, E_{tot} is the total energy of the system, E_{zp} is the zero-point vibrational energy, $\hbar$ is the Planck constant, k_B is Boltzmann constant, and $F(\omega)$ is the phonon density of states.

When the relationship between heat energy and volume is expressed within a quasi-harmonic approximation (QHA), the Helmholtz free energy can be written as follows [41,42]:

$$F(V, T) = U_0(V) + F_{vib}(V, T) \quad (4)$$

where $U_0(V)$ is the zero-temperature classical energy, while

$$F_{vib} = \frac{1}{2} \sum_{q,j} \hbar\omega_j(q, V) + k_B T \sum_{q,j} \ln[1 - \exp(-\hbar\omega_j(q, V)/k_B T)] \quad (5)$$

denotes the contribution of vibration to free energy F , $\omega_j(\mathbf{q}, V)$ is the phonon frequency in the j th mode, and $\mathbf{q}$ is the wave vector for a given volume V . The coefficient of linear thermal expansion can be expressed as follows:

$$\alpha(T) = \frac{1}{3B} \sum_{\mathbf{q}, j} \gamma_j(\mathbf{q}) C_{vj}(\mathbf{q}, T) \quad (6)$$

where B is the isothermal bulk modulus and $\gamma_j(\mathbf{q})$ is the Grüneisen parameter in the j th mode, which can be expressed as follows:

$$\gamma_j(\mathbf{q}) = -\frac{d[\ln \omega_j(\mathbf{q}, V)]}{d(\ln V)} \quad (7)$$

and $C_{vj}(\mathbf{q}, T)$, the mode contribution to the specific heat, is defined as follows:

$$C_{vj}(\mathbf{q}, T) = \frac{\hbar \omega_j(\mathbf{q}, V)}{V} \frac{d}{dT} \left[\exp\left(\frac{\hbar \omega_j(\mathbf{q}, V)}{k_B T}\right) - 1 \right]^{-1} \quad (8)$$

From the definition of the specific heat, the total specific heat of the crystal can be obtained from the following equation:

$$C_v(T) = \sum_{\mathbf{q}, j} C_{vj}(\mathbf{q}, T) \quad (9)$$

The thermal Grüneisen parameter is the weighted average of the mode Grüneisen parameters:

$$\gamma_{th} = \frac{1}{C_v(T)} \sum_{\mathbf{q}, j} \gamma_j(\mathbf{q}) C_{vj}(\mathbf{q}, T) = \frac{\alpha K_T V}{C_v} = \frac{\alpha K_S V}{C_p} \quad (10)$$

where C_v and C_p denote the heat capacity at a constant volume and pressure, respectively. K_T and K_S are the isothermal volume modulus and adiabatic volume modulus, respectively. The relationship between C_p and C_v can be expressed as follows:

$$C_p = C_v(1 + \alpha \gamma_{th} T) \quad (11)$$

3. Results and Discussion

3.1. Thermal Properties

The enthalpy of formation (ΔH) of the ordered $L1_2$ - Al_3M ($M = \text{Er, Hf, Lu, Sc, Si, Ti, Tm, Yb, Li, Mg, Zr}$) phase is defined as the energy gain or loss relative to the unstretched volume. It reflects the alloying capability and thermal stability of the corresponding system [43–45] and can be calculated using the following equation [46]:

$$\Delta H(Al_3M) = E(Al_3M) - \frac{3}{4}E(Al) - \frac{1}{4}E(M) \quad (12)$$

where $E(Al_3M)$ is the total energy per unit cell of Al_3M . $E(Al)$ is the average energy of each Al atom in the FCC structure, and $E(M)$ is the average energy of each atom of Er, Hf, Lu, Mg, Sc, Ti, Tm, and Zr in the hexagonal close-packed structure, Li in the body-centered cubic structure, Si in the diamond structure, and Yb in the FCC structure.

The calculated lattice constants (a_0), enthalpy of formation (ΔH), volume (V_0) per atom, and lattice mismatch δ of $L1_2$ structures at 0 K are listed in Table 1. The lattice mismatch δ can be defined as $\delta = \frac{|a_{Al_3M} - a_{Al}|}{a_{Al}} \times 100\%$, where a_{Al_3M} and a_{Al} are the lattice constants of the $L1_2$ - Al_3M and pure Al, respectively. The results show that the lattice mismatches between different $L1_2$ -structured precipitate phases and Al matrixes are no more than 6.27%. Generally, the lattice mismatch implies a larger stability. Meanwhile, a negative enthalpy of formation reflects that the precipitation process is exothermic, and

the smaller the enthalpy of formation value, the more stable the phase. Therefore, the calculated results of lattice mismatches and enthalpy both indicate that the ordered $L1_2$ - Al_3M phase shows excellent stability in the Al matrix.

Table 1. The Solute atomic radius ($\text{\AA}$) and calculated lattice constants, a_0 ($\text{\AA}$), formation enthalpy, ΔH ($\text{kJ}\cdot\text{mol}^{-1}$), volume per atom, V_0 ($\text{\AA}^3 \text{atom}^{-1}$), and lattice mismatch, δ (%), of $L1_2$ structures at 0 K.

Structures	Solute Atomic Radius ($\text{\AA}$)	Lattice Constants, a_0 ($\text{\AA}$)		ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)		V_0 ($\text{\AA}^3 \text{atom}^{-1}$)	δ (%)
		This work	Literature	This work	Literature		
Al bulk	1.431 [47]	4.038	4.039 [48]	–	–	16.474	–
Al_3Er	1.757 [47]	4.232	4.215 [49]	–39.949	–40.000 [49]	18.950	4.80
Al_3Hf	1.564 [47]	4.090	4.081 [50]	–35.341	–37.300 [50]	17.108	1.29
Al_3Li	1.520 [47]	4.025	4.025 [48]	–9.452	–9.439 [48]	16.308	0.32
Al_3Lu	1.734 [47]	4.269	4.206 [49]	–38.916	–38.920 [49]	19.453	5.72
Al_3Mg	1.600 [47]	4.138	4.146 [51]	–0.898	–1.060 [51]	17.710	2.48
Al_3Sc	1.630 [47]	4.103	4.106 [48]	–43.649	–43.826 [48]	17.308	1.61
Al_3Ti	1.448 [47]	3.978	3.977 [48]	–35.422	–34.579 [48]	15.735	1.49
Al_3Tm	1.746 [47]	4.221	4.200 [49]	–39.321	–39.000 [49]	18.805	4.53
Al_3Yb	1.940 [47]	4.291	4.200 [49]	–16.312	–17.000 [49]	19.753	6.27
Al_3Zr	1.600 [47]	4.107	4.106 [48]	–44.210	–44.018 [48]	17.323	1.71

Figure 1 shows the temperature dependence of the Gibbs free energy, $F(T)$, and entropy, $S(T)$, of Al and $L1_2$ - Al_3M structures. The graphs in narrower temperature ranges, i.e., 0–400 K and 0–200 K, are presented for better insight. The Gibbs free energy gradually decreases, while the entropy exhibits an increase with the temperature. As illustrated in Figure 1a, the Gibbs free energies of all the $L1_2$ structures decrease slowly in the temperature range from 0 to 400 K. In contrast, the decrease is significant in the temperature range of 400–1000 K. Further investigation shows that the doping atoms Yb, Lu, Er, and Tm combine with Al atoms to form $L1_2$ structures, decreasing the Gibbs free energy of Al alloys. Remarkably, the Gibbs free energy of Al_3Yb is the smallest in the entire temperature range (0–1000 K), indicating that the alloy shows the best thermal stability. However, Hf, Mg, Zr, Li, Sc and Ti atoms do not improve the stability of the Al alloys. The Gibbs free energies of the Al_3M phases varied with temperature in the following order: $Al_3Yb < Al_3Lu < Al_3Er < Al_3Tm < Al < Al_3Hf < Al_3Mg < Al_3Zr < Al_3Li < Al_3Sc < Al_3Ti$, which shows that the Yb, Lu, Er and Tm elements would improve the thermal stability of Al alloys.

The entropy of the system exhibits a distinct behavior. Entropy is considered to be a measure of disorder, and it never decreases because isolated systems spontaneously evolve toward thermodynamic equilibrium, which is the state of maximum entropy (minimum energy). As shown in Figure 1b, the entropy significantly increases with the temperature in the range of 0–400 K, while its growth rate gradually slows down at higher temperatures. Some of the $L1_2$ phases, i.e., Al_3M ($M = Yb, Lu, Er, \text{ and } Tm$), increase the entropy of the Al alloy system at different temperatures. The slope of the curve for Al_3Yb is the largest in the entire temperature range, implying that the Al_3Yb structure exhibits the highest thermal stability. The change of entropy of the Al_3M phases with temperature is arranged in the following order: $Al_3Yb > Al_3Lu > Al_3Er > Al_3Tm > Al > Al_3Hf > Al_3Ti > Al_3Mg > Al_3Zr > Al_3Li > Al_3Sc$.

The temperature-dependent isobaric heat capacity (C_p) curves of Al and $L1_2$ - Al_3M structures and the corresponding dependence in a narrower temperature range are shown in Figure 2. The C_p values of Al and Al_3M increase dramatically with temperature in the range of 0–300 K, and the rate increases gradually and the C_p value finally converges to 100 J/K/mol at about 700 K. Compared with Al, the C_p value of some Al_3M ($M = Yb, Lu, Er, \text{ and } Tm$) structures increases significantly, indicating a stronger thermal stability than for bulk Al. The Al_3Yb alloy firstly reaches a constant value of 100 J/K/mol at 0–500 K, confirming the beneficial effect of Yb atoms on the thermal stability of the Al alloys. However, Ti and Mg atoms do not show any positive effect on the thermal stability

of Al alloys. Lu, Er and Tm atoms have a positive and significant effect on the thermal stability of the Al alloys, especially in the temperature range of 0–600 K. The temperature-dependent relationship of the C_p of Al and its alloys is arranged in the following order: $\text{Al}_3\text{Yb} > \text{Al}_3\text{Lu} > \text{Al}_3\text{Er} > \text{Al}_3\text{Tm} > \text{Al}_4 > \text{Al}_3\text{Mg} > \text{Al}_3\text{Hf} > \text{Al}_3\text{Zr} > \text{Al}_3\text{Sc} > \text{Al}_3\text{Li} > \text{Al}_3\text{Ti}$.

Figure 1. The calculated temperature dependence of (a) the Gibbs free energy and (c) the entropy of pure Al and $\text{L}_{12}\text{-Al}_3\text{M}$ structures, where (b,d) represent this dependence, are limited to the specific temperature range of 0–400 K and 0–200 K, respectively.

Figure 2. (a) The isobaric heat capacity C_p –temperature curves of pure Al and $\text{L}_{12}\text{-Al}_3\text{M}$ structures; (b) C_p in a narrower temperature range of 0–400 K.

Remarkably, the descending order of Gibbs free energy is consistent with the ascending order of entropy and C_p , especially for Al_3Yb , Al_3Lu , Al_3Er , and Al_3Tm alloys. Considering that those structures have no enhancing effect on the thermodynamic properties of Al alloys, we focus on Al_3Yb , Al_3Lu , Al_3Er , and Al_3Tm structures.

In Figure 3a, we present the temperature-dependent coefficient of thermal expansion (α) of $L1_2$ structures calculated using Equation (6). The α value sharply increases with the temperature from 0 to 300 K and then gradually slows down. Above 600 K, the thermal expansion coefficient of the compound reaches a plateau, meaning that the material produces a linear thermal expansion. As described in thermal theory, the temperature dependence of $\alpha(T)$ is very similar to that of the isobaric heat capacity $C_p(T)$. In the temperature range from 0 to 125 K, the α value of Al_3Yb is the largest, but at 125 K, α - Al_3Mg reaches the highest α value, indicating that Al_3Mg is more prone to expansion at a certain temperature. This behavior is consistent with the trend of their Grüneisen parameters with the temperature increase. A high temperature increases the thermal effect on the lattice constant, raising the thermal expansion coefficient.

Figure 3. (a) Coefficient of thermal expansion α , and (b) Grüneisen parameter, γ for Al and $L1_2$ - Al_3M phases as a function of temperature.

The Grüneisen parameter (γ) is a key physical quantity for the thermoelasticity of materials [52–54]. At the same time, it is the basis for explaining phonon frequency variation with volume [55,56]. Figure 3b shows the temperature dependence curves of the Grüneisen parameter defined by Equation (10) for the $L1_2$ structures. The Al_3M phases exhibit the different temperature dependence of the Grüneisen parameter, γ , in the low-temperature region from 0 to 200 K. For Al_3Sc , Al_3Hf , and Al_3Zr , the γ value increases with the temperature, while for other compounds it decreases firstly in the low temperature range, and then increases. As we know, due to the quantum effect, the lattice and electron vibration of materials is more complex at low temperatures. For example, in the low-temperature limit, as the frequency of the excited lattice modes goes to zero, the volume dependences of the frequencies, are related to the volume dependences of the corresponding elastic constants [57,58]. This means that the variation law of the Grüneisen parameter at a low temperature is rather complicated, and the elastic-related properties remain to be calculated, which will not be discussed in this study. As expected, the γ values of all the alloys converge to a certain constant above 300 K. It can be found that in the temperature range of 100–1000 K, the Grüneisen parameter is sorted out as $\text{Al}_3\text{Yb} > \text{Al}_3\text{Lu} > \text{Al}_3\text{Er} > \text{Al}_3\text{Tm}$, which is in good agreement with the thermodynamic stability order discussed earlier.

In summary, Yb, Lu, Er, and Tm atoms with bigger atomic radii than the Al atom are beneficial for improving the thermal properties of Al Alloys, and the thermal stability of the L_{12} - Al_3M phases is arranged in the order of $Al_3Yb > Al_3Lu > Al_3Er > Al_3Tm > Al$. We would like to take the relationship between entropy and atomic radius at 1000K as an example to show the obvious relationship between the thermodynamic properties of the L_{12} - Al_3M structures and the atomic radius of alloying atoms M, and the result is illustrated in Figure 4. It is obvious that the structures are of L_{12} - Al_3M (M = Yb, Lu, Er, and Tm) with better thermal properties and a bigger radius in the M atom. The precise atomic radius values of Yb, Lu, Er, and Tm atoms are 1.940, 1.734, 1.757, and 1.746, respectively, which are more than 0.2 times larger than Al.

Figure 4. The relationship between entropy and solute atomic (M) radius of Al_3M at 1000 K.

3.2. Electronic Structure

The microstructure of materials is closely correlated to their electron structures [59,60]. When alloying atoms join in an Al matrix, they inevitably cause the electron charge redistribution. Hence, the underlying mechanisms of the change in thermal properties can be analyzed and understood in terms of charge density redistribution. Differential charge density can clearly give information about inter-atomic interactions, such as charge transfer and bonding types between atoms. Bonding charge density (BCD) is defined as a difference in the self-consistent charge density, ρ , of the compound from the first-principle calculations and the reference charge density constructed from the simple superposition of the non-interacting atomic charge density at the crystal sites. The differential charge density, $\Delta\rho$, is defined as $\Delta\rho = \rho(Al_3M) - \rho(Al \text{ atoms}) - \rho(M \text{ atoms})$.

Figure 5 displays a 3D plot of the differential charge density of the $L1_2$ - Al_3M compounds. The color of the electron cloud indicates the degree of charge enrichment, with red and green indicating the charge gain and reduction, respectively. Most of the electron clouds are localized between two adjacent atoms of Al and M, showing covalent bonding properties, but the bonding strength varies between the different atom types. At the same time, the electron cloud of Al_3Er , Al_3Lu , and Al_3Tm alloys are mainly localized at the tetrahedral sites. In contrast, the charge density is significantly reduced at the octahedral sites, mainly due to the hybridization of d or f orbitals of M atoms with their nearest neighbors. Conclusively, these $L1_2$ - Al_3M structures have good thermal stability due to the strong covalent bonding between Al-M atoms.

Figure 5. 3D map of the differential charge density of $L1_2$ - Al_3M ($M = Yb, Lu, Er, \text{ and } Tm$) compounds.

Figures 6 and 7 describe the charge density distribution of bonding on the $\{100\}$ and $\{111\}$ surfaces of the $L1_2$ - Al_3M phases, respectively. The color shades reflect the strength of the bonding energy: red indicates an increase in the charge accumulation after bonding (i.e., the increase in electron density); blue represents a decrease in the charge density. Electrons are localized between the Al and M atoms, showing strong covalent bonding. From Figure 6 it can be seen that the doping with M elements forms strong Al-M bonds ($M = Er, Tm, Yb, \text{ and } Lu$). Figure 7 shows that the charge decreases around the Al and M atoms, while there is a strong tendency of charge accumulation between them, which corroborates well the results shown in Figure 5.

Figure 6. Charge density distribution of the $L1_2$ - Al_3M phases in (100) plane: (a) Al_3Yb , (b) Al_3Lu , (c) Al_3Er , and (d) Al_3Tm . All the contour plots are on the same scale, and the interval between the contour lines is $0.001e/bohr^3$.

At the same time, we performed a Bader charge analysis on these structures to quantify the amount of charge transfer, which is the most intuitive and simplest way to obtain the charge transfer number between atoms. Table 2 summarizes the Bader charge analysis of several doped elements of the $L1_2$ - Al_3M structure. A large amount of charge migrates from the doping element M to Al atoms, resulting in strong Al-M bonds, which provide a strong intrinsic basis for the stability of the $L1_2$ - Al_3M structures.

Table 2. The calculated charge transfer numbers caused by solute atoms in the $L1_2$ - Al_3M structures.

Solutes/Solvent	Yb	Lu	Er	Tm
	−0.7329	−1.0468	−0.9388	−0.9579
Al1	0.3314	0.2593	0.2770	0.4411
Al2	0.2131	0.3892	0.3889	0.2740
Al3	0.1885	0.3983	0.2729	0.2429

Figure 7. Charge density distribution of the $L1_2$ - Al_3M phase in (111) plane: (a) Al_3Yb , (b) Al_3Lu , (c) Al_3Er , and (d) Al_3Tm . All the contour plots have the same scale, and the interval between the contour lines is $0.001e/\text{bohr}^3$.

4. Conclusions

We systematically analysed the thermodynamic properties of $L1_2$ - Al_3M ($M = Er, Hf, Lu, Sc, Si, Ti, Tm, Yb, Li, Mg, Zr$) compounds using density functional theory. The small enthalpies and lattice mismatches indicate that the $L1_2$ - Al_3X ($M = Er, Hf, Lu, Sc, Ti, Tm, Yb, Li, Mg, Zr$) structural compounds could exist stably in an Al matrix. Furthermore, the thermodynamic data (including the Gibbs free energy F , entropy S , isobaric heat capacity C_p , thermal expansion coefficient α and Grüneisen parameter γ) implied that the addition of Yb, Lu, Er, and Tm atoms with an atomic radius 0.2 times larger than Al has a positive effect on the thermal stability of the Al alloys. The thermal stability of these structures is ranked in the following order: $Al_3Yb > Al_3Lu > Al_3Er > Al_3Tm > Al$. The internal cause of this thermal stability was investigated from the microscopic point of view of electron bonding through the analysis of charge density. A differential charge density map and Bader charge analysis show that covalent bonds are easily formed between M ($M = Er, Lu, Tm, Yb$) and Al. The charge density is mainly distributed in the $\langle 111 \rangle$ direction at the tetrahedral sites, while the charge density is significantly reduced at the octahedral sites. The strong bonding of the Al-M bonds provides a strong intrinsic basis for the stability of the Al_3M structures.

It is found that the elements Er, Lu, Tm, and Yb are suitable replacements of Sc, which would reduce the cost and improve the thermodynamic properties of aluminum alloys at the same time.

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