Article

Phase Stability, Elastic Modulus and Elastic Anisotropy of X Doped (X = Zn, Zr and Ag) Al₃Li: Insight from First-Principles Calculations

Jinzhong Tian ¹, Yuhong Zhao ^{1,*}, Shengjie Ma ¹ and Hua Hou ^{1,2}

¹ School of Materials Science and Engineering, North University of China, Taiyuan 030051, China; tianjinzhong@nuc.edu.cn (J.T.); s2003022@st.nuc.edu.cn (S.M.); houthua@nuc.edu.cn (H.H.)

² School of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030051, China

* Correspondence: zhaoyuhong@nuc.edu.cn

Abstract: In present work, the effects of alloying elements X (X = Zn, Zr and Ag) doping on the phase stability, elastic properties, anisotropy and Debye temperature of Al₃Li were studied by the first-principles method. Results showed that pure and doped Al₃Li can exist and be stable at 0 K. Zn and Ag elements preferentially occupy the Al sites and Zr elements tend to occupy the Li sites. All the C_{ij} obey the mechanical stability criteria, indicating the mechanical stability of these compounds. The overall anisotropy decreases in the following order: Al₂₃Li₈Ag > Al₃Li > Al₂₃Li₈Zn > Al₂₄Li₇Zr, which shows that the addition of Zn and Zr has a positive effect on reducing the anisotropy of Al₃Li. The shear anisotropic factors for Zn and Zr doped Al₃Li are very close to one, meaning that elastic moduli do not strongly depend on different shear planes. For pure and doped Al₃Li phase, the transverse sound velocities ν_{t1} and ν_{t2} among the three directions are smaller than the longitudinal sound velocity ν_l . Moreover, only the addition of Zn is beneficial to increasing the Θ_D of Al₃Li among the three elements.

Keywords: first-principles; anisotropy; elastic properties

Citation: Tian, J.; Zhao, Y.; Ma, S.; Hou, H. Phase Stability, Elastic Modulus and Elastic Anisotropy of X Doped (X = Zn, Zr and Ag) Al₃Li: Insight from First-Principles Calculations. *Crystals* **2022**, *12*, 7. <https://doi.org/10.3390/cryst12010007>

Academic Editors: Paolo Restuccia, James Ren and Sergio Brutti

Received: 15 November 2021

Accepted: 18 December 2021

Published: 21 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Al-Li alloys have gained widespread attention for their use as lightweight structural materials in the aerospace field due to their low density, high elastic modulus and specific stiffness compared with other alloys [1–4]. The mechanical behaviors of Al-Li alloys depend to a large extent on the structure and properties of precipitates [5,6]. Al₃Li (δ') phase plays a vital strengthening role in high lithium aluminum alloys, especially in binary Al-Li alloys [7,8]. However, Al-Li alloys invariably possess poor ductility due to the planar slip caused by the shear of δ' precipitates [8,9]. Given this situation, microalloying can improve the mechanical properties of Al-Li alloys.

The microalloying elements may affect the structure and properties of precipitate [10,11], which can be researched by different methods [12–14]. For example, the existence of Mg in Al-Li-Mg alloys increases the lattice parameters of the matrix and δ' , indicating that Mg has been incorporated into δ' [15]. Gault et al. have demonstrated that the Mg atoms are partitioned to Li sublattices in δ' precipitation [16,17]. Therefore, other alloying elements may also occupy the sublattice of either Al or Li in δ' precipitate. Hirose and Sato researched the atomistic behavior of various microalloying elements in Al-Li alloys at 273 K, which revealed that Ag, Pb and Pd are preferentially occupying Al sites and Mg, Zn and Cu tend to occupy the Li sites [18]. In addition, the influence of microalloying elements on the precipitation process of δ' phase has been systematically studied through experimental analysis [19,20]. Our previous work studied the influence of alloying elements on the elastic properties of δ' phase at higher doping concentrations [21]. However, there are few reports

concerning the influence of microalloying elements on the elastic anisotropy of doped δ' phase at the doping concentration of 3.125 at. %.

In the present study, the enthalpy of formation and transfer energy were employed to predict the relative stability of doped Al_3Li and the site preferences of alloying elements X (X = Zn, Zr and Ag), respectively. We adopted the first-principles method to reveal the effects of alloying elements X on the elastic modulus, anisotropy and Debye temperature of Al_3Li phase.

2. Computational Studies

Al_3Li phase is a cubic structure with $a = b = c = 4.010 \text{ \AA}$ and a $2 \times 2 \times 2$ supercell with 32 atoms which was employed to simulate the influence of doping elements, as shown in Figure 1. Only one alloying atom was selected to substitute either one Al atom or one Li atom, and the doping concentration of alloying element is 3.125 at. %. Hence the chemical formulas of doped Al_3Li phase can be labeled as $\text{Al}_{24}\text{Li}_7\text{X}$ and $\text{Al}_{23}\text{Li}_8\text{X}$ (X = Zn, Zr and Ag), respectively.

Figure 1. Crystal structure of Al_3Li , $\text{Al}_{24}\text{Li}_7\text{X}$ and $\text{Al}_{23}\text{Li}_8\text{X}$ (X = Zn, Zr and Ag).

All the calculations in this work were carried out using the Cambridge Sequential Total Energy Package based on the density functional theory (DFT) [22]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function was employed [23]. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) was selected to optimize the structure of pure and doped Al_3Li , and the convergence thresholds for maximum displacement were set to $5.0 \times 10^{-4} \text{ \AA}$. For all calculations, the plane-wave cut-off energy was set to 500.0 eV, and a Monkhorst–Pack mesh with $26 \times 26 \times 26$ and $9 \times 9 \times 9$ k -points was chosen to sample the Brillouin zone of pure Al_3Li and alloying elements X doped Al_3Li , respectively.

3. Results and Discussion

3.1. Phase Stability and Site Preference

In this work, the enthalpy of formation (ΔH_f) is used to predict the relative stability of alloying elements X doped Al_3Li [24] and the ΔH_f can be calculated using the following formula [24]:

$$\Delta H_f = \frac{1}{(a + b + 1)} (E_{tot} - aE_{solid}^{Al} - bE_{solid}^{Li} - E_{solid}^X) \quad (1)$$

where a and b correspond to the number of Al and Li atoms, E_{tot} is the total energy of alloying elements X doped Al_3Li phase, and E_{solid}^{Al} , E_{solid}^{Li} and E_{solid}^X represent the energies per atom of Al, Li, X in solid states, respectively. As shown in Table 1, the enthalpies of formation for doped samples are negative, which implies that they can exist and be stable [25,26]. Moreover, a phase with lower ΔH_f is much easier to form than others. The ΔH_f of $\text{Al}_{24}\text{Li}_7\text{X}$ (X = Zn and Ag) are larger than those of $\text{Al}_{23}\text{Li}_8\text{X}$ (X = Zn and Ag), which indicates that $\text{Al}_{23}\text{Li}_8\text{X}$ (X = Zn and Ag) are easier to form. For Zr doped Al_3Li phase, the ΔH_f of $\text{Al}_{24}\text{Li}_7\text{Zr}$ is smaller than $\text{Al}_{23}\text{Li}_8\text{Zr}$, meaning that $\text{Al}_{23}\text{Li}_8\text{Zr}$ is harder to form.

$\text{Al}_{24}\text{Li}_7\text{Zr}$ phase has the smallest value of ΔH_f , suggesting that $\text{Al}_{24}\text{Li}_7\text{Zr}$ is more stable than other doped samples.

Table 1. Predicted enthalpy of formation ΔH_f (eV), normalized transfer energy $\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$ and site preference of doped Al_3Li at 0 GPa.

Element X.	ΔH_f		$\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$	Site Preference
	$\text{Al}_{24}\text{Li}_7\text{X}$	$\text{Al}_{23}\text{Li}_8\text{X}$		
Zn	−0.073	−0.097	−0.09	Al
Zr	−0.139	−0.096	3.15	Li
Ag	−0.080	−0.106	−2.27	Al

The site preference of a microalloying element in Al_3Li phase was investigated by normalized transfer energy ($\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$) and the formula of $\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$ is defined as follows [27,28]:

$$E_{\text{Al} \rightarrow \text{Li}}^{\text{X}} = E^{\text{X}}(\text{Al}) + E^{\text{Al}}(\text{Li}) - E^{\text{X}}(\text{Li}) - E_{\text{Al}_3\text{Li}} \quad (2)$$

$$E_{\text{Al} \rightarrow \text{Li}}^{\text{X}} = E^{\text{X}}(\text{Li}) + E^{\text{Li}}(\text{Al}) - E^{\text{X}}(\text{Al}) - E_{\text{Al}_3\text{Li}} \quad (3)$$

$$E_{\text{X}} = E_{\text{Al} \rightarrow \text{Li}}^{\text{X}} + E_{\text{Li} \rightarrow \text{Al}}^{\text{X}} \quad (4)$$

$$\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}} = E_{\text{Li} \rightarrow \text{Al}}^{\text{X}} / E_{\text{X}} \quad (5)$$

Here, $E_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$ and $E_{\text{Al} \rightarrow \text{Li}}^{\text{X}}$ represent the transfer energy of moving an alloying element X atom from a Li site to an Al site and from an Al site to a Li site, respectively. $E^{\text{X}}(\text{Al})$ and $E^{\text{X}}(\text{Li})$ stand for the energies of Al_3Li with an alloying element X atom in an Al site and a Li site, respectively. $E^{\text{Al}}(\text{Li})$ and $E^{\text{Li}}(\text{Al})$ represent the energies of an Al antisite and a Li antisite of Al_3Li . $E_{\text{Al}_3\text{Li}}$ stands for the total energy of Al_3Li . As listed in Table 1, the values of $\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$ for Zn and Ag doped Al_3Li are negative, which means that Zn and Ag show strong Al site preference [27,28]. The value of $\tilde{E}_{\text{Li} \rightarrow \text{Al}}^{\text{X}}$ for Zr doped Al_3Li is bigger than one, indicating that Zr elements tend to occupy the Li site. This result may be related to atomic radius difference between these elements. The atomic radius of Zn (1.39 Å) and Ag (1.44 Å) are closer to the atomic radius of Al (1.43 Å) and they tend to occupy the Al site. On the other hand, the atomic radius difference between Li (1.54 Å) and Zr (1.60 Å) is smaller than that of Al and Zr, which could be used to explain the site preference of Zr.

3.2. Elastic Properties

The elastic behavior, which when considered as a basic physical property, can be described by elastic constants (C_{ij}). Pure and Zr doped Al_3Li have three independent elastic constants, i.e., C_{11} , C_{12} and C_{44} . However, with the addition of alloying elements X (X = Zn and Ag), the lattice symmetry of Al_3Li decreases, thus, increasing the independent C_{ij} [29]. Hence, the $\text{Al}_{23}\text{Li}_8\text{X}$ (X = Zn and Ag) phases have a tetragonal structure, and the average elastic constants were not considered. As shown in Table 2, the predicted C_{ij} of Al_3Li are in good agreement with other reported values [30,31]. In addition, all the obtained C_{ij} obey the mechanical stability criteria [32,33], implying the mechanical stability of pure and doped Al_3Li .

Table 2. Computed elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa) and B/G ratio for pure and doped Al_3Li compounds.

Phase	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B	G	E	B/G
Al_3Li	125.3	125.3	40.8	40.8	31.7	31.7	62.9	43.1	105.2	1.46
$\text{Al}_{23}\text{Li}_8\text{Zn}$	127.7	125.7	45.6	47.6	31.1	30.7	62.9	47.0	112.9	1.34
$\text{Al}_{24}\text{Li}_7\text{Zr}$	127.9	127.9	43.1	43.1	38.1	38.1	68.0	43.8	108.2	1.55
$\text{Al}_{23}\text{Li}_8\text{Ag}$	128.8	127.6	40.7	44.2	32.3	31.2	63.9	44.3	108.0	1.44

The bulk modulus B , shear modulus G and Young's modulus E of pure and doped Al_3Li phase were calculated by adopting Voigt–Reuss–Hill approximation [34]. As displayed in Table 2, the value of B for $\text{Al}_{24}\text{Li}_7\text{Zr}$ is larger than that of other doped Al_3Li , indicating that $\text{Al}_{24}\text{Li}_7\text{Zr}$ has a stronger resistance to volume change. Moreover, Zr and Ag elements can improve the B of Al_3Li , while the value of B between pure and Zn doped is similar. The values of G can be sorted in the order of $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{24}\text{Li}_7\text{Zr} > \text{Al}_3\text{Li}$, which illustrate that the Zn, Ag and Zr can improve the shear deformation resistance. Compared to pure Al_3Li , the values of G for $\text{Al}_{23}\text{Li}_8\text{Zn}$, $\text{Al}_{23}\text{Li}_8\text{Ag}$ and $\text{Al}_{24}\text{Li}_7\text{Zr}$ increase by 9.1%, 2.9% and 1.6%, respectively. The values of E follow the order of $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{24}\text{Li}_7\text{Zr} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_3\text{Li}$, indicating that $\text{Al}_{23}\text{Li}_8\text{Zn}$ has the highest stiffness among these phases. Furthermore, the B/G ratios for all considered compounds are less than 1.75, implying that these compounds tend to exhibit brittle behavior based on the Pugh formulation [35]. The B/G ratios of Zr doped Al_3Li is larger than others, which suggests that Zr slightly decreases the brittleness of Al_3Li . As a whole, the Zn element plays a prominent role in enhancing the stiffness and shear deformation resistance compared with Ag and Zr elements. These three alloying elements have different effects on the elastic properties of Al_3Li , which may be due to the different strength of chemical bonds between different alloying elements and Al or Li.

3.3. Elastic Anisotropy

In order to comprehensively investigate the elastic anisotropy performance of Al_3Li with doping elements, a variety of different elastic anisotropy indices were selected. The universal anisotropy index A^U is applied to estimate the overall anisotropy of compounds and the calculation formula is as follows [36]:

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \quad (6)$$

where G_V (B_V) and G_R (B_R) represent the Voigt and the Reuss shear (bulk) modulus, respectively. When the value of A^U is zero, the crystal tends to be isotropic. Significant deviations from zero indicate high anisotropic characteristics. As displayed in Table 3, the A^U decreases in the following order: $\text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{24}\text{Li}_7\text{Zr}$. The obtained values of A^U are in the range of 0.002 to 0.030, indicating that pure and doped Al_3Li have relatively weak anisotropy. Consequently, $\text{Al}_{23}\text{Li}_8\text{Ag}$ has the strongest anisotropic behavior. In contrast, the existence of Zn and Zr has a positive effect on reducing the anisotropy of Al_3Li . Furthermore, the A^U for $\text{Al}_{24}\text{Li}_7\text{Zr}$ and $\text{Al}_{23}\text{Li}_8\text{Zn}$ is close to zero, implying that the elastic modulus of $\text{Al}_{24}\text{Li}_7\text{Zr}$ and $\text{Al}_{23}\text{Li}_8\text{Zn}$ shows similar elastic properties in all directions.

Table 3. Predicted universal anisotropy index (A^U) and shear anisotropic factors (A_1 , A_2 and A_3) of pure and doped Al_3Li .

Phase	A_1	A_2	A_3	A^U
Al_3Li	0.871	0.871	0.871	0.023
$\text{Al}_{23}\text{Li}_8\text{Zn}$	0.951	0.954	0.986	0.003
$\text{Al}_{24}\text{Li}_7\text{Zr}$	0.959	0.959	0.959	0.002
$\text{Al}_{23}\text{Li}_8\text{Ag}$	0.839	0.857	0.915	0.030

The shear anisotropic factors (A_1 , A_2 and A_3) can be used to describe the shear anisotropies of crystal and are defined as follows [37]:

For cubic symmetry:

$$A_1 = A_2 = A_3 = \frac{2C_{44}}{C_{11} - C_{12}} \text{ for the } \{100\} \text{ plane} \quad (7)$$

For tetragonal symmetry:

$$A_1 = \frac{C_{44}(C_{11} + 2C_{13} + C_{33})}{C_{11}C_{33} - C_{13}^2} \text{ for the (010) or (100) plane} \quad (8)$$

$$A_2 = \frac{C_{44}(C_L + 2C_{13} + C_{33})}{C_L C_{33} - C_{13}^2} \text{ for the } (1\bar{1}0) \text{ plane} \quad (9)$$

$$C_L = C_{44} + \frac{(C_{11} + C_{12})}{2} \quad (10)$$

$$A_3 = \frac{2C_{66}}{C_{11} - C_{12}} \text{ for the (001) plane} \quad (11)$$

For an isotropic crystal, the values of A_1 , A_2 and A_3 are equal to one, otherwise, the crystal presented anisotropy. As listed in Table 3, the predicted A_1 , A_2 and A_3 are less than one, which reveals that they show anisotropic characteristics in different shear planes. The shear anisotropy of $\text{Al}_{23}\text{Li}_8\text{Ag}$ along the (010), (100) and $(1\bar{1}0)$ plane is much higher than others, while the degree of anisotropy of $\text{Al}_{23}\text{Li}_8\text{Zn}$ is the smallest in the (001) plane. Compared with the other two microalloying elements, Ag slightly increased the shear anisotropy of Al_3Li in the (010), (100) and $(1\bar{1}0)$ plane. In addition, the shear anisotropic factors for Zn and Zr doped Al_3Li are close to one, meaning that their elastic moduli do not strongly depend on the (010), (100), (001) and $(1\bar{1}0)$ planes.

The three-dimensional (3D) surface construction of Young's modulus has become an effective method to display the elastic anisotropy of compounds visually and can be determined by the following expressions [38]:

For cubic symmetry:

$$\frac{1}{E} = S_{11} - 2\left(S_{11} - S_{12} - \frac{S_{44}}{2}\right)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_1^2 l_3^2) \quad (12)$$

For tetragonal symmetry:

$$\frac{1}{E} = S_{11}(l_1^4 + l_2^4) + (2S_{13} + S_{44})(l_1^2 l_3^2 + l_2^2 l_3^2) + S_{33}l_3^4 + (2S_{12} + S_{66})l_1^2 l_2^2 \quad (13)$$

where, S_{ij} represents the elastic compliance coefficients of pure and doped Al_3Li , and l_1 , l_2 and l_3 stand for the directional cosines corresponding to the x, y and z axes. If the 3D surface diagram is spherical, it indicates that the phase shows isotropic behavior. Otherwise, the phase exhibits anisotropic behavior. As plotted in Figure 2, the 3D surface diagrams of pure and doped Al_3Li deviate from the sphere, which match well with the results of A^U . The 3D surface diagram of $\text{Al}_{24}\text{Li}_7\text{Zr}$ and $\text{Al}_{23}\text{Li}_8\text{Zn}$ are close to the sphere, especially $\text{Al}_{24}\text{Li}_7\text{Zr}$.

3.4. Debye Temperature and Anisotropic Sound Velocities

The thermodynamic properties of crystals, such as specific heat and melting point, can be described by Debye temperature (Θ_D). The Θ_D can be calculated by the following expression [39]:

$$\Theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (14)$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (15)$$

$$v_t = \sqrt{\frac{G}{\rho}} \quad (16)$$

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}} \quad (17)$$

Figure 2. The 3D Young's modulus E visualization surfaces of pure and doped Al_3Li phases.

Here, h , k_B , n , N_A , ρ , M and v_m represent Planck's constant, Boltzmann's constant, total number of atoms, Avogadro's number, density, molecular weight and average wave velocity, respectively. v_t and v_l are the transverse and longitudinal sound velocities of materials, respectively.

The sound velocities, density and Debye temperature of pure and doped Al_3Li phase are summarized in Table 4. The obtained Θ_D of Al_3Li is 570.9 K, which is consistent with the reported value in the literature [40]. The value of Θ_D from high to low is as follows: $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{24}\text{Li}_7\text{Zr}$, which indicates that the Θ_D of $\text{Al}_{24}\text{Li}_7\text{Zr}$ is smaller than that of the others. Among the three elements, only the addition of Zn is beneficial to increase the Θ_D of Al_3Li at the doping concentration of 3.125 at. %.

Table 4. The density ρ , transverse sound velocity v_t , longitudinal sound velocity v_l , mean sound velocity v_m and Debye temperature Θ_D of pure and doped Al_3Li phase.

Phase	ρ (g/cm ³)	v_t (m/s)	v_l (m/s)	v_m (m/s)	Θ_D (K)
Al_3Li	2.22	4403.2	7358.2	4872.2	570.9
$\text{Al}_{23}\text{Li}_8\text{Zn}$	2.36	4466.8	7301.2	4931.8	578.8
$\text{Al}_{24}\text{Li}_7\text{Zr}$	2.47	4213.4	7159.1	4669.6	545.5
$\text{Al}_{23}\text{Li}_8\text{Ag}$	2.48	4225.0	7036.3	4673.6	548.0

According to the Debye model, the sound velocity is one of the critical parameters for obtaining Debye temperature, which is closely related to the elastic properties of crystals. Longitudinal sound waves are related to the compressibility and density of crystals. The transverse sound velocity is considered to be the origin of shear deformation, which can be obtained by shear modulus and density [41]. In addition, the direction of sound propagation has an impact on the sound velocity of crystal. Thus, the sound velocity anisotropy of doped Al_3Li phases were systematically studied and the formulas are as follows [41]:

For tetragonal crystals:

$$[100] : [100] \ v_t = [010] \ v_l = \sqrt{\frac{C_{11}}{\rho}}; [001] \ v_{t1} = \sqrt{\frac{C_{44}}{\rho}}; [010] \ v_{t2} = \sqrt{\frac{C_{66}}{\rho}} \quad (18)$$

$$[001] : [001] \ v_l = \sqrt{\frac{C_{33}}{\rho}}; [100] \ v_{t1} = [010] \ v_{t2} = \sqrt{\frac{C_{66}}{\rho}} \quad (19)$$

$$[110] : [110] \nu_l = \sqrt{\frac{(C_{11} + C_{12} + 2C_{66})}{2\rho}}; [001] \nu_{t1} = \sqrt{\frac{C_{44}}{\rho}}; [1\bar{1}0] \nu_{t2} = \sqrt{\frac{(C_{11} - C_{12})}{2\rho}} \quad (20)$$

For cubic crystals:

$$[100] : [100] \nu_l = \sqrt{\frac{C_{11}}{\rho}}; [010] \nu_{t1} = [001] \nu_{t2} = \sqrt{\frac{C_{44}}{\rho}} \quad (21)$$

$$[110] : [110] \nu_l = \sqrt{\frac{(C_{11} + C_{12} + 2C_{44})}{2\rho}}; [1\bar{1}0] \nu_{t1} = \sqrt{\frac{(C_{11} - C_{12})}{\rho}}; [001] \nu_{t2} = \sqrt{\frac{C_{44}}{\rho}} \quad (22)$$

$$[111] : [111] \nu_l = \sqrt{\frac{(C_{11} + 2C_{12} + 4C_{44})}{3\rho}}; [11\bar{2}] \nu_{t1} = \nu_{t2} = \sqrt{\frac{(C_{11} - C_{12} + C_{44})}{3\rho}} \quad (23)$$

where ν_{t1} and ν_{t2} stand for the first and second mode transverse sound velocity. The directional sound velocities for pure and doped Al_3Li phases are listed in Table 5. The values of sound velocities are different in different directions, indicating the anisotropy of sound velocity. The ν_{t1} and ν_{t2} for pure and Zr doped Al_3Li are equal in the $[100]$ and $[111]$ directions, while the ν_{t1} and ν_{t2} of $\text{Al}_{23}\text{Li}_8\text{X}$ ($\text{X} = \text{Zn}, \text{Ag}$) have the same value along the $[001]$ directions. However, the values between ν_{t1} and ν_{t2} are different for Al_3Li and $\text{Al}_{23}\text{Li}_8\text{Zr}$ in the $[110]$ direction. For Al_3Li , the longitudinal sound velocity decreases in the $[100]$ direction after element doping. The transverse sound velocities ν_{t1} and ν_{t2} among the three directions are smaller than the longitudinal sound velocity ν_l . For Al_3Li , $\text{Al}_{23}\text{Li}_8\text{Zn}$ and $\text{Al}_{24}\text{Li}_7\text{Zr}$, the value of ν_l in the $[100]$ direction is the largest, while $\text{Al}_{23}\text{Li}_8\text{Ag}$ has the largest ν_l along the $[001]$ direction.

Table 5. The calculated anisotropic sound velocities (m/s) of pure and doped Al_3Li phase.

Cubic Crystals	[100]			[110]			[111]		
	[100]	[010] ν_{t1}	[001] ν_{t2}	[110] ν_l	[1 $\bar{1}$ 0] ν_{t1}	[001] ν_{t2}	[111] ν_l	[11 $\bar{2}$] ν_{t1}	[11 $\bar{2}$] ν_{t2}
Al_3Li	7596.8	4411.3	4411.3	7429.4	6629.3	4411.3	7372.8	4597.3	4597.3
$\text{Al}_{24}\text{Li}_7\text{Zr}$	7201.2	4178.1	4178.1	7148.9	6034.3	4178.1	7131.4	4237.5	4237.5
Tetragonal Crystals	[100]			[001]			[110]		
	[100] ν_l	[001] ν_{t1}	[010] ν_{t2}	[001] ν_l	[100] ν_{t1}	[010] ν_{t2}	[110] ν_l	[001] ν_{t1}	[1 $\bar{1}$ 0] ν_{t2}
$\text{Al}_{23}\text{Li}_8\text{Zn}$	7363.3	4401.4	4495.6	6993.0	3951.6	3951.6	7343.2	4401.4	4528.5
$\text{Al}_{23}\text{Li}_8\text{Ag}$	7201.1	4047.6	4216.1	7367.0	4534.9	4534.9	7085.2	4047.6	4408.0

4. Conclusions

We investigated the effects of alloying elements X ($\text{X} = \text{Zn}, \text{Zr}$ and Ag) on the phase stability, elastic properties, anisotropy and Debye temperature of pure and doped Al_3Li phase. The following conclusions are reached:

(1) The enthalpies of formation for doped samples are negative, indicating that they can exist and be stable at 0 K. The Zn and Ag elements preferentially occupy the Al sites and Zr elements tend to occupy the Li sites.

(2) Pure and doped Al_3Li are mechanically stable and tend to exhibit brittle behavior. The addition of Zr and Ag elements can improve the B . Moreover, the Zn element plays an obvious role in enhancing the stiffness and shear deformation resistance.

(3) The A^U decreases in the following order: $\text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{24}\text{Li}_7\text{Zr}$, implying that Zn and Zr can reduce the anisotropy of Al_3Li . Pure and doped Al_3Li show anisotropy in different shear planes. The addition of Ag slightly increased the anisotropy of Al_3Li in the (010), (100) and (1 $\bar{1}$ 0) plane. The longitudinal sound velocity of Al_3Li decreased in the $[100]$ direction after element doping. In addition, the transverse sound velocities ν_{t1} and ν_{t2} among the three directions are smaller than the longitudinal sound velocity ν_l .

(4) The value of Θ_D from high to low is as follows: $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{24}\text{Li}_7\text{Zr}$, which shows that the addition of Zn is beneficial for increasing the Θ_D .

Author Contributions: Investigation, J.T.; software, Y.Z. and H.H.; writing—original draft preparation, J.T. and S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science and Technology Major Project of Shanxi Province (Nos. 20181101014, 20191102008, 20191102007); National Natural Science Foundation of China (Nos. 52074246, 22008224, 51774254, 51774253, 51804279, 51801189); Scientific Research Fund Project of North University of China (No. XJJ201909); Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (No. 2020L0280); Platform and Talent Project of Shanxi Province (No. 201805D211036); Applied Basic Research Foundation of Shanxi Province (No. 20210302124632).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. El-Aty, A.A.; Xu, Y.; Guo, X.; Zhang, S.; Ma, Y.; Chen, D. Strengthening mechanisms, deformation behavior, and anisotropic mechanical properties of Al-Li alloys: A review. *J. Adv. Res.* **2018**, *10*, 49–67. [\[CrossRef\]](#)
2. Rioja, R.J.; Liu, J. The evolution of Al-Li base products for aerospace and space applications. *Metall. Mater. Trans. A* **2012**, *43*, 3325–3337. [\[CrossRef\]](#)
3. Chen, L.; Zhao, Y.; Li, M.; Li, L.; Hou, L.; Hou, H. Reinforced AZ91D magnesium alloy with thixomolding process facilitated dispersion of graphene nanoplatelets and enhanced interfacial interactions. *Mater. Sci. Eng. A-Struct.* **2021**, *804*, 140793. [\[CrossRef\]](#)
4. Zhao, Y.-H.; Ying, J.-H.; Chen, L.-W.; Xu, F.; Hou, H. Current Research Status of Interface of Ceramic-Metal Laminated Composite Material for Armor Protection. *Acta Metall. Sin.* **2021**, *57*, 1107–1125.
5. Ovri, H.; Lilleodden, E.T. New insights into plastic instability in precipitation strengthened Al-Li alloys. *Acta Mater.* **2015**, *89*, 88–97. [\[CrossRef\]](#)
6. Decreus, B.; Deschamps, A.; De Geuser, F.; Donnadiou, P.; Sigli, C.; Weyland, M. The influence of Cu/Li ratio on precipitation in Al-Cu-Li-x alloys. *Acta Mater.* **2013**, *61*, 2207–2218. [\[CrossRef\]](#)
7. Wang, Y.; Zhang, S.; Wu, R.; Turakhodjaev, N.; Hou, L.; Zhang, J.; Betsofen, S. Coarsening kinetics and strengthening mechanisms of core-shell nanoscale precipitates in Al-Li-Yb-Er-Sc-Zr alloy. *J. Mater. Sci. Technol.* **2021**, *61*, 197–203. [\[CrossRef\]](#)
8. Wu, L.; Wang, Q.; Shu, S.; Li, Y.; Li, X.; Wang, H.J. Interactions between cadmium and Al_3Li precipitates: A new mechanism of accelerating dissolution and transformation of phases in Al-Li-Cu alloy. *Mater. Sci. Eng. A-Struct.* **2021**, *806*, 140607. [\[CrossRef\]](#)
9. Pletcher, B.; Wang, K.; Glicksman, M. Experimental, computational and theoretical studies of δ' phase coarsening in Al-Li alloys. *Acta Mater.* **2012**, *60*, 5803–5817. [\[CrossRef\]](#)
10. Bai, G.; Tian, J.; Guo, Q.; Li, Z.; Zhao, Y. First Principle Study on Mg_2X (X = Si, Ge, Sn) Intermetallics by Bi Micro-Alloying. *Crystals* **2021**, *11*, 142. [\[CrossRef\]](#)
11. Jiang, C.J. First-principles study of site occupancy of dilute 3d, 4d and 5d transition metal solutes in L_{10} TiAl. *Acta Mater.* **2008**, *56*, 6224–6231. [\[CrossRef\]](#)
12. Zhao, Y.; Zhang, B.; Hou, H.; Chen, W.; Wang, M. Phase-field simulation for the evolution of solid/liquid interface front in directional solidification process. *J. Mater. Sci. Technol.* **2019**, *35*, 1044–1052. [\[CrossRef\]](#)
13. Hou, H.; Zhao, Y.; Zhao, Y. Simulation of the precipitation process of ordered intermetallic compounds in binary and ternary Ni-Al-based alloys by the phase-field model. *Mater. Sci. Eng. A-Struct.* **2009**, *499*, 204–207. [\[CrossRef\]](#)
14. Zhang, J.; Wang, H.; Kuang, W.; Zhang, Y.; Li, S.; Zhao, Y.; Herlach, D. Rapid solidification of non-stoichiometric intermetallic compounds: Modeling and experimental verification. *Acta Mater.* **2018**, *148*, 86–99. [\[CrossRef\]](#)
15. Gregson, P.; Flower, H. δ' precipitation in Al-Li-Mg-Cu-Zr alloys. *J. Mater. Sci. Lett.* **1984**, *3*, 829–834. [\[CrossRef\]](#)
16. Gault, B.; Cui, X.Y.; Moody, M.P.; De Geuser, F.; Sigli, C.; Ringer, S.P.; Deschamps, A. Atom probe microscopy investigation of Mg site occupancy within δ' precipitates in an Al-Mg-Li alloy. *Scr. Mater.* **2012**, *66*, 903–906. [\[CrossRef\]](#)
17. Deschamps, A.; Sigli, C.; Mourey, T.; De Geuser, F.; Lefebvre, W.; Davo, B. Experimental and modelling assessment of precipitation kinetics in an Al-Li-Mg alloy. *Acta Mater.* **2012**, *60*, 1917–1928. [\[CrossRef\]](#)
18. Hirose, S.; Sato, T. Monte Carlo computer simulation of the atomistic behaviour of microalloying elements in Al-Li alloys. *Model. Simul. Mater. Scr.* **2001**, *9*, 129. [\[CrossRef\]](#)
19. Joh, C.-H.; Yamada, K.; Miura, Y. Effect of Sc-Addition on the Coarsening Behavior of Al_3Li Precipitates in Al-Li Alloys. *Mater. Trans.* **1999**, *40*, 439–442. [\[CrossRef\]](#)

20. Gu, B.; Liedl, G.; Sanders, T., Jr.; Welpmann, K. The influence of zirconium on the coarsening of σ' (Al_3Li) in an Al-2.8 wt.% Li-0.14 wt.% Zr alloy. *Mater. Sci. Eng.* **1985**, *76*, 147–157. [\[CrossRef\]](#)
21. Tian, J.; Zhao, Y.; Hou, H.; Wang, B. The effect of alloying elements on the structural stability, mechanical properties, and debye temperature of Al_3Li : A first-principles study. *Materials* **2018**, *11*, 1471. [\[CrossRef\]](#)
22. Segall, M.; Lindan, P.J.; Probert, M.A.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. First-principles simulation: Ideas, illustrations and the CASTEP code. *J. Phys. Condens. Matter* **2002**, *14*, 2717–2744. [\[CrossRef\]](#)
23. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [\[CrossRef\]](#)
24. Liu, S.; Zhan, Y.; Wu, J.; Chen, X.; Ye, H. Site preference of the alloying additions on mechanical and electronic properties of B2 ZrRu-based compounds. *Comput. Mater. Sci.* **2016**, *117*, 1–6. [\[CrossRef\]](#)
25. Ma, Z.-N.; Wang, X.; Yan, T.-T.; Li, Q.; Xu, Q.-C.; Tian, J.-L.; Wang, L. First-principles study on thermodynamic stability and electronic characteristics of long-period stacking ordered phases in Mg–Zn–Y alloys. *J. Alloys Compd.* **2017**, *708*, 29–33. [\[CrossRef\]](#)
26. Xin, T.; Zhao, Y.; Mahjoub, R.; Jiang, J.; Yadav, A.; Nomoto, K.; Niu, R.; Tang, S.; Ji, F.; Quadir, Z.; et al. Ultrahigh specific strength in a magnesium alloy strengthened by spinodal decomposition. *Sci. Adv.* **2021**, *7*, eabf3039. [\[CrossRef\]](#)
27. Ruban, A.V.; Skriver, H.L. Calculated site substitution in ternary γ' - Ni_3Al : Temperature and composition effects. *Phys. Rev. B* **1997**, *55*, 856. [\[CrossRef\]](#)
28. Ruban, A.V.; Popov, V.A.; Portnoi, V.K.; Bogdanov, V.I. First-principles study of point defects in Ni_3Al . *Philos. Mag.* **2014**, *94*, 20–34. [\[CrossRef\]](#)
29. Yao, X.; Mao, Y.; Guo, Y.-F. First-principles study of the alloying effects on the structural stability and mechanical properties of L_{12} - Pt_3Hf . *J. Alloys Compd.* **2022**, *891*, 161982. [\[CrossRef\]](#)
30. Yu, H.; Duan, X.; Ma, Y.; Zeng, M. First Principles Study of Al-Li Intermetallic Compounds. *Chin. J. Chem. Phys.* **2012**, *25*, 659–665. [\[CrossRef\]](#)
31. Mao, Z.; Chen, W.; Seidman, D.N.; Wolverton, C. First-principles study of the nucleation and stability of ordered precipitates in ternary Al–Sc–Li alloys. *Acta Mater.* **2011**, *59*, 3012–3023. [\[CrossRef\]](#)
32. Zhao, Y.; Qi, L.; Jin, Y.; Wang, K.; Tian, J.; Han, P. The structural, elastic, electronic properties and Debye temperature of D_{022} - Ni_3V under pressure from first-principles. *J. Alloys Compd.* **2015**, *647*, 1104–1110. [\[CrossRef\]](#)
33. Tian, J.; Zhao, Y.; Wang, B.; Hou, H.; Zhang, Y. The structural, mechanical and thermodynamic properties of Ti-B compounds under the influence of temperature and pressure: First-principles study. *Mater. Chem. Phys.* **2018**, *209*, 200–207. [\[CrossRef\]](#)
34. Hill, R. The elastic behaviour of a crystalline aggregate. *Proc. Phys. Soc.* **1952**, *65*, 349–354. [\[CrossRef\]](#)
35. Zhao, Y.; Deng, S.; Liu, H.; Zhang, J.; Guo, Z.; Hou, H. First-principle investigation of pressure and temperature influence on structural, mechanical and thermodynamic properties of Ti_3AC_2 (A = Al and Si). *Comp. Mater. Sci.* **2018**, *154*, 365–370. [\[CrossRef\]](#)
36. Ranganathan, S.I.; Ostoja-Starzewski, M. Universal elastic anisotropy index. *Phys. Rev. Lett.* **2008**, *10*, 055504. [\[CrossRef\]](#)
37. Lau, K.; McCurdy, A.K. Elastic anisotropy factors for orthorhombic, tetragonal, and hexagonal crystals. *Phys. Rev. B* **1998**, *58*, 8980. [\[CrossRef\]](#)
38. Nye, J.F. *Physical Properties of Crystals: Their Representation by Tensors and Matrices*; Oxford University Press: New York, NY, USA, 1985; p. 145.
39. Anderson, O.L. A simplified method for calculating the Debye temperature from elastic constants. *J. Phys. Chem. Solids* **1963**, *24*, 909–917. [\[CrossRef\]](#)
40. Hu, W.C.; Liu, Y.; Li, D.J.; Zeng, X.Q.; Xu, C.S. Mechanical and thermodynamic properties of Al_3Sc and Al_3Li precipitates in Al–Li–Sc alloys from first-principles calculations. *Physica B* **2013**, *427*, 85–90. [\[CrossRef\]](#)
41. Khanzadeh, M.; Alahyarizadeh, G. A DFT study on pressure dependency of TiC and ZrC properties: Interconnecting elastic constants, thermodynamic, and mechanical properties. *Ceram. Int.* **2021**, *47*, 9990–10005. [\[CrossRef\]](#)