Article

Phase Stability, Elastic Modulus and Elastic Anisotropy of X Doped (X = Zn, Zr and Ag) Al\textsubscript{3}Li: Insight from First-Principles Calculations

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

\textsuperscript{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.); houhua@nuc.edu.cn (H.H.)
\textsuperscript{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 Al\textsubscript{3}Li were studied by the first-principles method. Results showed that pure and doped Al\textsubscript{3}Li 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\textsubscript{ij} obey the mechanical stability criteria, indicating the mechanical stability of these compounds. The overall anisotropy decreases in the following order: Al\textsubscript{3}Li\textsubscript{Ag} > Al\textsubscript{3}Li > Al\textsubscript{3}Li\textsubscript{Zn} > Al\textsubscript{3}Li\textsubscript{Zr}, which shows that the addition of Zn and Zr has a positive effect on reducing the anisotropy of Al\textsubscript{3}Li. The shear anisotropic factors for Zn and Zr doped Al\textsubscript{3}Li are very close to one, meaning that elastic moduli do not strongly depend on different shear planes. For pure and doped Al\textsubscript{3}Li phase, the transverse sound velocities \nu\textsubscript{t1} and \nu\textsubscript{t2} among the three directions are smaller than the longitudinal sound velocity \nu\textsubscript{l}. Moreover, only the addition of Zn is beneficial to increasing the \Theta\textsubscript{D} of Al\textsubscript{3}Li among the three elements.

Keywords: first-principles; anisotropy; elastic properties

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]. Al\textsubscript{3}Li (\delta') 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 \delta' 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 \delta', indicating that Mg has been incorporated into \delta' [15]. Gault et al. have demonstrated that the Mg atoms are partitioned to Li sublattices in \delta' precipitation [16,17]. Therefore, other alloying elements may also occupy the sublattice of either Al or Li in \delta' precipitate. Hirosawa 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 \delta' phase has been systematically studied through experimental analysis [19,20]. Our previous work studied the influence of alloying elements on the elastic properties of \delta' 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 Al3Li 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 Al3Li phase.

2. Computational Studies

Al3Li phase is a cubic structure with a = b = c = 4.010 Å and a 2 × 2 × 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 Al3Li phase can be labeled as Al24Li7X and Al23Li8X (X = Zn, Zr, and Ag), respectively.

![Figure 1. Crystal structure of Al3Li, Al23Li8X, Al24Li7X, Al23Li8X](image)

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 Al3Li, and the convergence thresholds for maximum displacement were set to 5.0 × 10−4 Å. For all calculations, the plane-wave cut-off energy was set to 500.0 eV, and a Monkhorst–Pack mesh with 26 × 26 × 26 and 9 × 9 × 9 k-points was chosen to sample the Brillouin zone of pure Al3Li and alloying elements X doped Al3Li, respectively.

3. Results and Discussion

3.1. Phase Stability and Site Preference

In this work, the enthalpy of formation (ΔHf) is used to predict the relative stability of alloying elements X doped Al3Li [24] and the ΔHf can be calculated using the following formula [24]:

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

(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 Al3Li 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 ΔHf is much easier to form than others. The ΔHf of Al23Li8X (X = Zn and Ag) are easier to form. For Zr doped Al3Li phase, the ΔHf of Al24Li7Zr is smaller than Al23Li8Zr, meaning that Al23Li8Zr is harder to form.
Al$_{23}$Li$_7$Zr phase has the smallest value of $\Delta H_f$, suggesting that Al$_{24}$Li$_7$Zr is more stable than other doped samples.

Table 1. Predicted enthalpy of formation $\Delta H_f$ (eV), normalized transfer energy $\tilde{E}^X_{\text{Li} \rightarrow \text{Al}}$ and site preference of doped Al$_3$Li at 0 GPa.

<table>
<thead>
<tr>
<th>Element X.</th>
<th>$\Delta H_f$</th>
<th>$\tilde{E}^X_{\text{Li} \rightarrow \text{Al}}$</th>
<th>Site Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-0.073</td>
<td>-0.097</td>
<td>Al</td>
</tr>
<tr>
<td>Zr</td>
<td>-0.139</td>
<td>-0.096</td>
<td>Li</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.080</td>
<td>-0.106</td>
<td>Al</td>
</tr>
</tbody>
</table>

The site preference of a microalloying element in Al$_3$Li phase was investigated by normalized transfer energy ($\tilde{E}^X_{\text{Li} \rightarrow \text{Al}}$) and the formula of $\tilde{E}^X_{\text{Li} \rightarrow \text{Al}}$ is defined as follows [27,28]:

\[
\tilde{E}^X_{\text{Li} \rightarrow \text{Al}} = E^X_{\text{AL}} - E^X_{\text{Li}}
\]

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$_3$Li 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$_3$Li decreases, thus, increasing the independent $C_{ij}$ [29]. Hence, the Al$_{23}$Li$_8$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$_3$Li 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$_3$Li.

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$_3$Li compounds.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_{11}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$B/G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_3$Li</td>
<td>125.3</td>
<td>125.3</td>
<td>40.8</td>
<td>40.8</td>
<td>31.7</td>
<td>31.7</td>
<td>62.9</td>
<td>43.1</td>
<td>105.2</td>
<td>1.46</td>
</tr>
<tr>
<td>Al$_{23}$Li$_8$Zn</td>
<td>127.7</td>
<td>127.7</td>
<td>45.6</td>
<td>47.6</td>
<td>31.1</td>
<td>30.7</td>
<td>62.9</td>
<td>47.0</td>
<td>112.9</td>
<td>1.34</td>
</tr>
<tr>
<td>Al$_{23}$Li$_8$Zr</td>
<td>127.9</td>
<td>127.9</td>
<td>43.1</td>
<td>43.1</td>
<td>38.1</td>
<td>38.1</td>
<td>68.0</td>
<td>43.8</td>
<td>108.2</td>
<td>1.55</td>
</tr>
<tr>
<td>Al$_{23}$Li$_8$Ag</td>
<td>128.8</td>
<td>127.6</td>
<td>40.7</td>
<td>44.2</td>
<td>32.3</td>
<td>31.2</td>
<td>63.9</td>
<td>44.3</td>
<td>108.0</td>
<td>1.44</td>
</tr>
</tbody>
</table>
The bulk modulus $B$, shear modulus $G$ and Young’s modulus $E$ of pure and doped $\text{Al}_3\text{Li}$ phase were calculated by adopting Voigt–Reuss–Hill approximation [34]. As displayed in Table 2, the value of $B$ for $\text{Al}_{23}\text{Li}_8\text{Zr}$ is larger than that of other doped $\text{Al}_3\text{Li}$, indicating that $\text{Al}_{23}\text{Li}_8\text{Zr}$ has a stronger resistance to volume change. Moreover, $\text{Zr}$ and $\text{Ag}$ elements can improve the $B$ of $\text{Al}_3\text{Li}$, while the value of $B$ between pure and $\text{Zn}$ doped is similar. The values of $G$ can be sorted in the order of $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{23}\text{Li}_7\text{Zr} > \text{Al}_3\text{Li}$, which illustrate that the $\text{Zn}$, $\text{Ag}$ and $\text{Zr}$ can improve the shear deformation resistance. Compared to pure $\text{Al}_3\text{Li}$, the values of $G$ for $\text{Al}_{23}\text{Li}_8\text{Zn}$, $\text{Al}_{23}\text{Li}_8\text{Ag}$ and $\text{Al}_{23}\text{Li}_7\text{Zr}$ increase by 9.1%, 2.9% and 1.6%, respectively. The values of $E$ follow the order of $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{23}\text{Li}_7\text{Zr} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_3\text{Li}$, 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 $\text{Zr}$ doped $\text{Al}_3\text{Li}$ is larger than others, which suggests that $\text{Zr}$ slightly decreases the brittleness of $\text{Al}_3\text{Li}$. As a whole, the $\text{Zn}$ element plays a prominent role in enhancing the stiffness and shear deformation resistance compared with $\text{Ag}$ and $\text{Zr}$ elements. These three alloying elements have different effects on the elastic properties of $\text{Al}_3\text{Li}$, which may be due to the different strength of chemical bonds between different alloying elements and $\text{Al}$ or $\text{Li}$.

3.3. Elastic Anisotropy

In order to comprehensively investigate the elastic anisotropy performance of $\text{Al}_3\text{Li}$ 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]:

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6$$  \hspace{1cm} (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: $\text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_{23}\text{Li}_7\text{Zr}$. The obtained values of $A^U$ are in the range of 0.002 to 0.030, indicating that pure and doped $\text{Al}_3\text{Li}$ have relatively weak anisotropy. Consequently, $\text{Al}_{23}\text{Li}_8\text{Ag}$ has the strongest anisotropic behavior. In contrast, the existence of $\text{Zn}$ and $\text{Zr}$ has a positive effect on reducing the anisotropy of $\text{Al}_3\text{Li}$. Furthermore, the $A^U$ for $\text{Al}_{23}\text{Li}_7\text{Zr}$ and $\text{Al}_{23}\text{Li}_8\text{Zn}$ is close to zero, implying that the elastic modulus of $\text{Al}_{23}\text{Li}_7\text{Zr}$ 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 $\text{Al}_3\text{Li}$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A^U$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_3\text{Li}$</td>
<td>0.871</td>
<td>0.871</td>
<td>0.871</td>
<td>0.023</td>
</tr>
<tr>
<td>$\text{Al}_{23}\text{Li}_8\text{Zn}$</td>
<td>0.951</td>
<td>0.954</td>
<td>0.986</td>
<td>0.003</td>
</tr>
<tr>
<td>$\text{Al}_{23}\text{Li}_7\text{Zr}$</td>
<td>0.959</td>
<td>0.959</td>
<td>0.959</td>
<td>0.002</td>
</tr>
<tr>
<td>$\text{Al}_{23}\text{Li}_8\text{Ag}$</td>
<td>0.839</td>
<td>0.857</td>
<td>0.915</td>
<td>0.030</td>
</tr>
</tbody>
</table>

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:**

$$A_1 = A_2 = A_3 = \frac{2C_{44}}{C_{11} - C_{12}}$$  \hspace{1cm} for the $\{100\}$ plane  \hspace{1cm} (7)
For tetragonal symmetry:

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

(8)

\[
A_2 = \frac{C_{44}(C_L + 2C_{13} + C_{33})}{C_LC_{33} - C_{13}^2} \text{ for the (1\overline{1}0) plane}
\]

(9)

\[
C_L = C_{44} + \frac{(C_{11} + C_{12})}{2}
\]

(10)

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

(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 Al\(_{23}\)Li\(_8\)Ag along the (010), (100) and (1\overline{1}0) plane is much higher than others, while the degree of anisotropy of Al\(_{23}\)Li\(_8\)Zn is the smallest in the (001) plane. Compared with the other two microalloying elements, Ag slightly increased the shear anisotropy of Al\(_3\)Li in the (010), (100) and (1\overline{1}0) plane. In addition, the shear anisotropic factors for Zn and Zr doped Al\(_3\)Li are close to one, meaning that their elastic moduli do not strongly depend on the (010), (100), (001) and (1\overline{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:

\[
\frac{1}{E} = S_{11} - 2\left(S_{11} - S_{12} - \frac{S_{44}}{2}\right)\left(l_1^4l_2^4 + l_2^4l_3^4 + l_1^4l_3^4\right)
\]

(12)

For tetragonal symmetry:

\[
\frac{1}{E} = S_{11}\left(l_1^4 + l_2^4\right) + (2S_{13} + S_{44})\left(l_1^2l_2^2 + l_2^2l_3^2 + l_3^2l_1^2\right) + S_{33}l_1^4 + (2S_{12} + S_{66})l_2^2l_3^2
\]

(13)

where, \(S_{ij}\) represents the elastic compliance coefficients of pure and doped Al\(_3\)Li, 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\(_3\)Li deviate from the sphere, which match well with the results of \(A_U\). The 3D surface diagram of Al\(_{24}\)Li\(_7\)Zr and Al\(_{23}\)Li\(_8\)Zn are close to the sphere, especially Al\(_{24}\)Li\(_7\)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 (\(\Theta_D\)). The \(\Theta_D\) can be calculated by the following expression [39]:

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

(14)

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

(15)

\[
v_l = \sqrt{\frac{G}{\rho}}
\]

(16)

\[
v_l = \sqrt{\frac{3B + 4G}{3\rho}}
\]

(17)
Here, $\hbar$, $k_B$, $n$, $N_A$, $\rho$, $M$ 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$_3$Li phase are summarized in Table 4. The obtained $\Theta_D$ of Al$_3$Li is 570.9 K, which is consistent with the reported value in the literature [40]. The value of $\Theta_D$ from high to low is as follows: Al$_{23}$Li$_8$Zn > Al$_3$Li > Al$_{23}$Li$_8$Ag > Al$_{24}$Li$_7$Zr, which indicates that the $\Theta_D$ of Al$_{24}$Li$_7$Zr is smaller than that of the others. Among the three elements, only the addition of Zn is beneficial to increase the $\Theta_D$ of Al$_3$Li at the doping concentration of 3.125 at. %.

Table 4. The density $\rho$, transverse sound velocity $v_t$, longitudinal sound velocity $v_l$, mean sound velocity $v_m$ and Debye temperature $\Theta_D$ of pure and doped Al$_3$Li phase.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$v_t$ (m/s)</th>
<th>$v_l$ (m/s)</th>
<th>$v_m$ (m/s)</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_3$Li</td>
<td>2.22</td>
<td>4403.2</td>
<td>7358.2</td>
<td>4872.2</td>
<td>570.9</td>
</tr>
<tr>
<td>Al$_{23}$Li$_8$Zn</td>
<td>2.36</td>
<td>4466.8</td>
<td>7301.2</td>
<td>4931.8</td>
<td>578.8</td>
</tr>
<tr>
<td>Al$_{23}$Li$_8$Ag</td>
<td>2.47</td>
<td>4213.4</td>
<td>7159.1</td>
<td>4669.6</td>
<td>545.5</td>
</tr>
<tr>
<td>Al$_{24}$Li$_7$Zr</td>
<td>2.48</td>
<td>4225.0</td>
<td>7036.2</td>
<td>4673.6</td>
<td>545.8</td>
</tr>
</tbody>
</table>

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$_3$Li phases were systemically studied and the formulas are as follows [41]:

For tetragonal crystals:

\[
[100] : [100] \ v_l = \sqrt{\frac{C_{11}}{\rho}} ; [001] \ v_l = \sqrt{\frac{C_{44}}{\rho}} ; [010] \ v_l = \sqrt{\frac{C_{66}}{\rho}} \quad \text{(18)}
\]

\[
[001] : [001] \ v_l = \sqrt{\frac{C_{33}}{\rho}} ; [100] \ v_l = [010] \ v_l = \sqrt{\frac{C_{66}}{\rho}} \quad \text{(19)}
\]
The addition of Zr and Ag elements can improve the B phase. The following conclusions are reached:

(1) The enthalpies of formation for doped samples are negative, indicating that they are mechanically stable and tend to exhibit brittle behavior. Pure and doped Al\textsubscript{3}Li\textsubscript{7}Zr, the value of \(v_1\) in the [100] direction is the largest, while Al\textsubscript{2}Li\textsubscript{3}Ag has the largest \(v_1\) along the [001] direction.

(2) Pure and doped Al\textsubscript{3}Li are equal in the [100] and [110] directions, while the \(v_1\) and \(v_2\) of Al\textsubscript{2}Li\textsubscript{8}X (X = Zn, Ag) have the same value along the [001] directions. However, the values between \(v_1\) and \(v_2\) are different for Al\textsubscript{3}Li and Al\textsubscript{2}Li\textsubscript{3}Zr in the [110] direction. For Al\textsubscript{3}Li, the longitudinal sound velocity decreases in the [100] direction after element doping. The transverse sound velocities \(v_1\) and \(v_2\) among the three directions are smaller than the longitudinal sound velocity \(v_3\) for pure and Zr doped Al\textsubscript{3}Li phases are listed in Table 5. The values of sound velocities are different in different directions, indicating the anisotropy of sound velocity. The \(v_1\) and \(v_2\) for pure and Zr doped Al\textsubscript{3}Li are equal in the [100] and [111] directions, while the \(v_1\) and \(v_2\) of Al\textsubscript{2}Li\textsubscript{8}X (X = Zn, Ag) have the same value along the [001] directions. However, the values between \(v_1\) and \(v_2\) are different for Al\textsubscript{3}Li and Al\textsubscript{2}Li\textsubscript{3}Zr in the [110] direction. For Al\textsubscript{3}Li, the longitudinal sound velocity decreases in the [100] direction after element doping. The transverse sound velocities \(v_1\) and \(v_2\) among the three directions are smaller than the longitudinal sound velocity \(v_3\). For Al\textsubscript{3}Li, Al\textsubscript{2}Li\textsubscript{8}Zn and Al\textsubscript{2}Li\textsubscript{3}Zr, the value of \(v_1\) in the [100] direction is the largest, while Al\textsubscript{2}Li\textsubscript{8}Ag has the largest \(v_1\) along the [001] direction.

<table>
<thead>
<tr>
<th>Cubic Crystals</th>
<th>[001] (v_1)</th>
<th>[010] (v_{12})</th>
<th>[100] (v_{12})</th>
<th>[110] (v_1)</th>
<th>[110] (v_{12})</th>
<th>[111] (v_1)</th>
<th>[111] (v_{12})</th>
<th>[112] (v_1)</th>
<th>[112] (v_{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{3}Li</td>
<td>796.8</td>
<td>4411.3</td>
<td>2490.4</td>
<td>6629.3</td>
<td>4411.3</td>
<td>7372.8</td>
<td>4597.3</td>
<td>4597.3</td>
<td>4597.3</td>
</tr>
<tr>
<td>Al\textsubscript{2}Li\textsubscript{7}Zr</td>
<td>7201.2</td>
<td>4178.1</td>
<td>7448.9</td>
<td>6034.3</td>
<td>4178.1</td>
<td>7131.4</td>
<td>4237.5</td>
<td>4237.5</td>
<td>4237.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tetragonal Crystals</th>
<th>[001] (v_1)</th>
<th>[010] (v_{12})</th>
<th>[100] (v_{12})</th>
<th>[101] (v_1)</th>
<th>[101] (v_{12})</th>
<th>[110] (v_1)</th>
<th>[110] (v_{12})</th>
<th>[112] (v_1)</th>
<th>[112] (v_{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}Li\textsubscript{8}Zn</td>
<td>7363.3</td>
<td>4401.4</td>
<td>4495.6</td>
<td>6993.0</td>
<td>3951.6</td>
<td>7343.2</td>
<td>4401.4</td>
<td>4528.5</td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}Li\textsubscript{8}Ag</td>
<td>7201.1</td>
<td>4047.6</td>
<td>4216.1</td>
<td>7367.0</td>
<td>4534.9</td>
<td>7085.2</td>
<td>4047.6</td>
<td>4408.0</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusions

We investigated the effects of alloying elements X (X = Zn, Zr and Ag) on the phase stability, elastic properties, anisotropy and Debye temperature of pure and doped Al\textsubscript{3}Li 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\textsubscript{3}Li are mechanically stable and tend to exhibit brittle behavior. The addition of Zr and Ag elements can improve the B phase. Moreover, the Zn element plays an obvious role in enhancing the stiffness and shear deformation resistance.

(3) The \(A_{ii}\) decreases in the following order: Al\textsubscript{2}Li\textsubscript{8}Ag > Al\textsubscript{3}Li > Al\textsubscript{2}Li\textsubscript{8}Zn > Al\textsubscript{2}Li\textsubscript{7}Zr, implying that Zn and Zr can reduce the anisotropy of Al\textsubscript{3}Li. Pure and doped Al\textsubscript{3}Li show anisotropy in different shear planes. The addition of Ag slightly increased the anisotropy of Al\textsubscript{3}Li in the (010), (100) and (101) plane. The longitudinal sound velocity of Al\textsubscript{3}Li decreased in the [100] direction after element doping. In addition, the transverse sound velocities \(v_{12}\) among the three directions are smaller than the longitudinal sound velocity \(v_1\).
(4) The value of $\Theta_D$ from high to low is as follows: $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{24}\text{Li}_2\text{Zr}$, which shows that the addition of Zn is beneficial for increasing the $\Theta_D$.

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. XJ201909); 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


10. Bai, G.; Tian, J.; Guo, Q.; Li, Z.; Zhao, Y. First Principle Study on Mg$_2$X (X = Si, Ge, Sn) Intermetallics by Bi Micro-Alloying. Crystals 2021, 11, 142. [CrossRef]


29. Yao, X.; Mao, Y.; Guo, Y.-F. First-principles study of the alloying effects on the structural stability and mechanical properties of L1$_2$-Pt$_3$Hf. *J. Alloys Compd.* **2022**, *911*, 161982. [CrossRef]


