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 Cij obey the mechanical stability criteria, indicating the mechanical stability of these compounds. The overall anisotropy decreases in the following order: Al₃Li₄Ag > Al₃Li > Al₃Li₄Zn > Al₃Li₇Zr, 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 v₁ and v₂ among the three directions are smaller than the longitudinal sound velocity v₃. Moreover, only the addition of Zn is beneficial to increasing the ΘD of Al₃Li 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]. 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. Hirosawa and Sato researched the atomistic behavior of various microalloying elements in Al-Li alloys at 273 K, which revealed that Ag, Pb, and Pb 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 $\delta'$ 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$_3$Li 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$_3$Li phase.

2. Computational Studies

Al$_3$Li phase is a cubic structure with $a = b = c = 4.010$ Å 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$_3$Li phase can be labeled as Al$_{24}$Li$_7$X and Al$_{23}$Li$_8$X (X = Zn, Zr and Ag), respectively.

![Crystal structure of Al$_3$Li, Al$_{24}$Li$_7$X and Al$_{23}$Li$_8$X (X = Zn, Zr and Ag).](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 Al$_3$Li, and the convergence thresholds for maximum displacement were set to $5.0 \times 10^{-4}$ Å. For all calculations, the plane-wave cut-off energy was set to 500.0 eV, and a Monkhorst–Pack mesh with $26 \times 26 \times 26$ and $9 \times 9 \times 9$ $k$-points was chosen to sample the Brillouin zone of pure Al$_3$Li and alloying elements X doped Al$_3$Li, respectively.

3. Results and Discussion

3.1. Phase Stability and Site Preference

In this work, the enthalpy of formation ($\Delta H_f$) is used to predict the relative stability of alloying elements X doped Al$_3$Li [24] and the $\Delta H_f$ can be calculated using the following formula [24]:

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

(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$_3$Li 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 $\Delta H_f$ is much easier to form than others. The $\Delta H_f$ of Al$_{23}$Li$_8$X (X = Zn and Ag) are larger than those of Al$_{23}$Li$_8$X (X = Zn and Ag), which indicates that Al$_{23}$Li$_8$X (X = Zn and Ag) are easier to form. For Zr doped Al$_3$Li phase, the $\Delta H_f$ of Al$_{24}$Li$_7$Zr is smaller than Al$_{23}$Li$_9$Zr, meaning that Al$_{23}$Li$_9$Zr 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 \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) and site preference of doped Al_{3}Li at 0 GPa.

| Element X. | \( \Delta H_f \) | \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) | Site Preference |
|------------|-----------------|---------------------------------|-----------------|
| Zn         | -0.073          | -0.097                          | -0.09           |
| Zr         | -0.139          | -0.096                          | 3.15            |
| Ag         | -0.080          | -0.106                          | -2.27           |

The site preference of a microalloying element in Al_{3}Li phase was investigated by normalized transfer energy \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) and the formula of \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) is defined as follows [27,28]:

\[
\begin{align*}
\tilde{\varepsilon}^X_{Li\rightarrow Al} &= E^X_{Li\rightarrow Al} - E^X_{Li} - E^X_{Al} + E^X_{AL} \\
E^X_{Li\rightarrow Al} &= E^X_{Li} + E^X_{Al} - E^X_{AL}
\end{align*}
\]

Here, \( E^X_{Li\rightarrow Al} \) and \( E^X_{Li\rightarrow Al} \) 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. \( E^X_{Li} \) and \( E^X_{Al} \) stand for the energies of Al_{3}Li with an alloying element X atom in an Al site and a Li site, respectively. \( E^X_{Li} \) and \( E^X_{Al} \) represent the energies of an Al antisite and a Li antisite of Al_{3}Li. \( E^X_{AL} \) stands for the total energy of Al_{3}Li. As listed in Table 1, the values of \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) for Zn and Ag doped Al_{3}Li are negative, which means that Zn and Ag show strong Al site preference [27,28]. The value of \( \tilde{\varepsilon}^X_{Li\rightarrow Al} \) for Zr doped Al_{3}Li 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_{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.

| Phase      | \( C_{11} \) | \( C_{33} \) | \( C_{44} \) | \( C_{66} \) | \( C_{12} \) | \( C_{13} \) | \( B \)   | \( G \)   | \( E \)   | \( B/G \) |
|------------|--------------|--------------|--------------|--------------|--------------|--------------|---------|---------|---------|---------|
| Al_{3}Li   | 125.3        | 125.3        | 40.8         | 40.8         | 31.7         | 31.7         | 62.9    | 43.1    | 105.2   | 1.46    |
| Al_{23}Li_{8}Zn | 127.7        | 125.7        | 45.6         | 47.6         | 31.1         | 30.7         | 62.9    | 47.0    | 112.9   | 1.34    |
| Al_{23}Li_{7}Zr | 127.9        | 127.9        | 43.1         | 43.1         | 38.1         | 38.1         | 68.0    | 43.8    | 108.2   | 1.55    |
| Al_{23}Li_{8}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$_3$Li phase were calculated by adopting Voigt–Reuss–Hill approximation [34]. As displayed in Table 2, the value of $B$ for Al$_{23}$Li$_7$Zr is larger than that of other doped Al$_3$Li, indicating that Al$_{23}$Li$_7$Zr has a stronger resistance to volume change. Moreover, Zr and Ag elements can improve the $B$ of Al$_3$Li, while the value of $B$ between pure and Zn doped is similar. The values of $G$ can be sorted in the order of Al$_{23}$Li$_8$Zn > Al$_{23}$Li$_8$Ag > Al$_{23}$Li$_7$Zr > Al$_3$Li, which illustrate that the Zn, Ag and Zr can improve the shear deformation resistance. Compared to pure Al$_3$Li, the values of $G$ for Al$_{23}$Li$_8$Zn, Al$_{23}$Li$_8$Ag and Al$_{23}$Li$_7$Zr increase by 9.1%, 2.9% and 1.6%, respectively. The values of $E$ follow the order of Al$_{23}$Li$_8$Zn > Al$_{24}$Li$_7$Zr > Al$_{23}$Li$_8$Ag > Al$_3$Li, indicating that Al$_{25}$Li$_6$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$_3$Li is larger than others, which suggests that Zr slightly decreases the brittleness of Al$_3$Li. 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$_3$Li, 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$_3$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]:

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

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: Al$_{23}$Li$_8$Ag > Al$_3$Li > Al$_{23}$Li$_8$Zn > Al$_{24}$Li$_7$Zr. The obtained values of $A^U$ are in the range of 0.002 to 0.030, indicating that pure and doped Al$_3$Li have relatively weak anisotropy. Consequently, Al$_{23}$Li$_8$Ag has the strongest anisotropic behavior. In contrast, the existence of Zn and Zr has a positive effect on reducing the anisotropy of Al$_3$Li. Furthermore, the $A^U$ for Al$_{23}$Li$_7$Zr and Al$_{23}$Li$_8$Zn is close to zero, implying that the elastic modulus of Al$_{24}$Li$_7$Zr and Al$_{23}$Li$_8$Zn shows similar elastic properties in all directions.

| Phase        | $A_1$ | $A_2$ | $A_3$ | $A^U$ |
|--------------|-------|-------|-------|-------|
| Al$_3$Li     | 0.871 | 0.871 | 0.871 | 0.023 |
| Al$_{23}$Li$_8$Zn | 0.951 | 0.954 | 0.986 | 0.003 |
| Al$_{23}$Li$_7$Zr | 0.959 | 0.959 | 0.959 | 0.002 |
| Al$_{23}$Li$_8$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:

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

\[
A_2 = \frac{C_{44}(C_L + 2C_{13} + C_{33})}{C_LC_{33} - C_{13}^2} \text{ for the (110) plane}
\]

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

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

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 their elastic moduli do not strongly depend on the (010), (100), (001) and (110) planes.

The shear anisotropy of Al\(_{23}\)Li\(_8\)Ag along the (010), (100) and (110) 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 (110) 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 (110) 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:

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

For tetragonal symmetry:

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

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\(_{23}\)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]:

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

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

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

\[
v_l = \sqrt{\frac{3B + 4G}{3\rho}}
\]
The sound velocities, density and Debye temperature of pure and doped Al\textsubscript{3}Li phase are summarized in Table 4. The obtained Θ\textsubscript{D} of Al\textsubscript{3}Li is 570.9 K, which is consistent with the reported value in the literature [40]. The value of Θ\textsubscript{D} from high to low is as follows: Al\textsubscript{23}Li\textsubscript{8}Zn > Al\textsubscript{3}Li > Al\textsubscript{23}Li\textsubscript{8}Ag > Al\textsubscript{24}Li\textsubscript{7}Zr, which indicates that the Θ\textsubscript{D} of Al\textsubscript{24}Li\textsubscript{7}Zr is smaller than that of the others. Among the three elements, only the addition of Zn is beneficial to increase the Θ\textsubscript{D} of Al\textsubscript{3}Li at the doping concentration of 3.125 at. %.

Table 4. The density ρ, transverse sound velocity v\textsubscript{t}, longitudinal sound velocity v\textsubscript{l}, mean sound velocity v\textsubscript{m} and Debye temperature Θ\textsubscript{D} of pure and doped Al\textsubscript{3}Li phase.

| Phase          | ρ (g/cm\textsuperscript{3}) | v\textsubscript{t} (m/s) | v\textsubscript{l} (m/s) | v\textsubscript{m} (m/s) | Θ\textsubscript{D} (K) |
|----------------|-----------------------------|--------------------------|--------------------------|--------------------------|------------------------|
| Al\textsubscript{3}Li | 2.22                        | 4403.2                   | 7358.2                   | 4872.2                   | 570.9                  |
| Al\textsubscript{23}Li\textsubscript{8}Zn | 2.36                        | 4466.8                   | 7301.2                   | 4931.8                   | 578.8                  |
| Al\textsubscript{23}Li\textsubscript{8}Ag | 2.47                        | 4213.4                   | 7159.1                   | 4669.6                   | 545.5                  |
| Al\textsubscript{23}Li\textsubscript{8}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\textsubscript{3}Li phases were systemically studied and the formulas are as follows [41]:

For tetragonal crystals:

\[ [100] : [100] \ v_t = [010] \ v_t = \sqrt{\frac{C_{11}}{\rho}} ; [001] \ v_{l1} = \sqrt{\frac{C_{44}}{\rho}} ; [010] \ v_{l2} = \sqrt{\frac{C_{66}}{\rho}} \]  \hspace{1cm} (18)

\[ [001] : [001] \ v_t = \sqrt{\frac{C_{33}}{\rho}} ; [100] \ v_{l1} = [010] \ v_{l2} = \sqrt{\frac{C_{66}}{\rho}} \]  \hspace{1cm} (19)
\[
\begin{align*}
[110] : [110] v_l &= \sqrt{\frac{(C_{11} + C_{12} + 2C_{66})}{2\rho}}; [001] v_{l1} &= \sqrt{\frac{C_{44}}{\rho}}; [1\overline{1}0] v_{l2} = \sqrt{\frac{(C_{11} - C_{12})}{2\rho}} \\
\end{align*}
\]

For cubic crystals:

\[
\begin{align*}
[100] : [100] v_l &= \sqrt{\frac{C_{11}}{\rho}}; [010] v_{l1} = [001] v_{l2} = \sqrt{\frac{C_{44}}{\rho}} \\
[110] : [110] v_l &= \sqrt{\frac{(C_{11} + C_{12} + 2C_{44})}{2\rho}}; [1\overline{1}0] v_{l1} = \sqrt{\frac{(C_{11} - C_{12})}{\rho}}; [001] v_{l2} = \sqrt{\frac{C_{44}}{\rho}} \\
[111] : [111] v_l &= \sqrt{\frac{(C_{11} + 2C_{12} + 4C_{44})}{3\rho}}; [11\overline{2}] v_{l1} = v_{l2} = \sqrt{\frac{(C_{11} - C_{12} + 4C_{44})}{3\rho}}
\end{align*}
\]

where \(v_{l1}\) and \(v_{l2}\) stand for the first and second mode transverse sound velocity. The directional sound velocities for pure and doped Al\(_3\)Li phases are listed in Table 5. The values of sound velocities are different in different directions, indicating the anisotropy of sound velocity. The \(v_{l1}\) and \(v_{l2}\) for pure and Zr doped Al\(_3\)Li are equal in the [100] and [111] directions, while the \(v_{l1}\) and \(v_{l2}\) of Al\(_{23}\)Li\(_8\)X (X = Zn, Ag) have the same value along the [001] directions. However, the values between \(v_{l1}\) and \(v_{l2}\) are different for Al\(_3\)Li and Al\(_{23}\)Li\(_8\)Zr in the [110] direction. For Al\(_3\)Li, the longitudinal sound velocity decreases in the [100] direction after element doping. The transverse sound velocities \(v_{l1}\) and \(v_{l2}\) among the three directions are smaller than the longitudinal sound velocity \(v_l\). For Al\(_3\)Li, Al\(_{23}\)Li\(_8\)Zn and Al\(_{23}\)Li\(_8\)Zr, the value of \(v_l\) in the [100] direction is the largest, while Al\(_{23}\)Li\(_8\)Ag has the largest \(v_l\) along the [001] direction.

Table 5. The calculated anisotropic sound velocities (m/s) of pure and doped Al\(_3\)Li phase.

| Cubic Crystals | [100] | [110] | [111] |
|----------------|-------|-------|-------|
| Al\(_3\)Li     | \(v_{l1}\) | \(v_{l2}\) | \(v_{l1}\) | \(v_{l2}\) | \(v_{l1}\) | \(v_{l2}\) |
|                | 7596.8 | 4411.3 | 7429.4 | 6629.3 | 4411.3 | 7372.8 | 4597.3 | 4597.3 |
| Al\(_{23}\)Li\(_7\)Zr | 7201.2 | 4178.1 | 7148.9 | 6034.3 | 4178.1 | 7085.2 | 4237.5 | 4237.5 |

| Tetragonal Crystals | [100] | [110] |
|---------------------|-------|-------|
| Al\(_{23}\)Li\(_8\)Zn | \(v_{l1}\) | \(v_{l2}\) |
|                      | 7363.3 | 4401.4 |
| Al\(_{23}\)Li\(_8\)Ag | 7201.1 | 4047.6 |

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\(_3\)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\(_3\)Li are mechanically stable and tend to exhibit brittle behavior. The addition of Zr and Ag elements can improve the 8. Moreover, the Zn element plays an obvious role in enhancing the stiffness and shear deformation resistance.

(3) The \(A^L_i\) decreases in the following order: Al\(_{23}\)Li\(_8\)Ag > Al\(_3\)Li > Al\(_{23}\)Li\(_8\)Zn > Al\(_{23}\)Li\(_7\)Zr, implying that Zn and Zr can reduce the anisotropy of Al\(_3\)Li. Pure and doped Al\(_3\)Li show anisotropy in different shear planes. The addition of Ag slightly increased the anisotropy of Al\(_3\)Li in the (010), (100) and (110) plane. The longitudinal sound velocity of Al\(_3\)Li decreased in the [110] direction after element doping. In addition, the transverse sound velocities \(v_{l1}\) and \(v_{l2}\) among the three directions are smaller than the longitudinal sound velocity \(v_l\).
(4) The value of $\Theta_D$ from high to low is as follows: $\text{Al}_{23}\text{Li}_8\text{Zn} > \text{Al}_3\text{Li} > \text{Al}_{23}\text{Li}_8\text{Ag} > \text{Al}_{24}\text{Li}_9\text{Zr}$, which shows that the addition of Zn is beneficial for increasing the $\Theta_D$.

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