

Article

# The Effect of Alloying Elements on the Structural Stability, Mechanical Properties, and Debye Temperature of Al<sub>3</sub>Li: A First-Principles Study

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**Abstract:** The structural stability, mechanical properties, and Debye temperature of alloying elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) doped Al<sub>3</sub>Li were systematically investigated by first-principles methods. A negative enthalpy of formation  $\Delta H_f$  is predicted for all Al<sub>3</sub>Li doped species which has consequences for its structural stability. The Sc, Ti, Zr, Nb, and Mo are preferentially occupying the Li sites in Al<sub>3</sub>Li while the Co, Cu, and Zn prefer to occupy the Al sites. The Al–Li–X systems are mechanically stable at 0 K as elastic constants  $C_{ij}$  has satisfied the stability criteria. The values of bulk modulus  $B$  for Al–Li–X (X = Sc, Ti, Co, Cu, Zr, Nb, and Mo) alloys (excluding Al–Li–Zn) increase with the increase of doping concentration and are larger than that for pure Al<sub>3</sub>Li. The Al<sub>6</sub>LiSc has the highest shear modulus  $G$  and Young's modulus  $E$  which indicates that it has stronger shear deformation resistance and stiffness. The predicted universal anisotropy index  $A^U$  for pure and doped Al<sub>3</sub>Li is higher than 0, implying the anisotropy of Al–Li–X alloy. The Debye temperature  $\Theta_D$  of Al<sub>12</sub>Li<sub>3</sub>Ti is highest among the Al–Li–X system which predicts the existence of strong covalent bonds and thermal conductivity compared to that of other systems.

**Keywords:** first-principles; doping concentration; alloying elements; mechanical properties; Debye temperature; lightweight structural materials; Al<sub>3</sub>Li

## 1. Introduction

Lightweight structural materials such as the Al–Li based alloys have excellent comprehensive performance, such as low density, good corrosion resistance, and high elastic modulus [1,2], and it is the basic reason why Al–Li based alloys are so widely used in aviation and aerospace field. The metastable Al<sub>3</sub>Li ( $\delta'$ ) precipitates has an important influence on the mechanical properties of Al–Li based alloys [3,4]. The  $\delta'$  phase is highly ordered with an L1<sub>2</sub> structure and forms as spheres possessing a cube–cube orientation relationship with matrix [5]. The lattice constant of  $\delta'$  phase (4.02 Å) and dilute Al–Li solid solutions (4.04 Å) are almost equal, and the corresponding precipitate-to-matrix misfit results in an interfacial strain of approximately  $0.08 \pm 0.02\%$  [6]. Due to the small lattice misfit, strong orientational habit and low interfacial strains, the  $\delta'$  phase remain crystallographically coherent with the parent solid-solution matrix and the crystallographic orientation relationship is  $(111)_{\text{Al}_3\text{Li}} // (111)_{\text{Al}}$  [7,8]. The  $\delta'$  precipitates are considered the most important strengthening phases of Al–Li alloys [9].

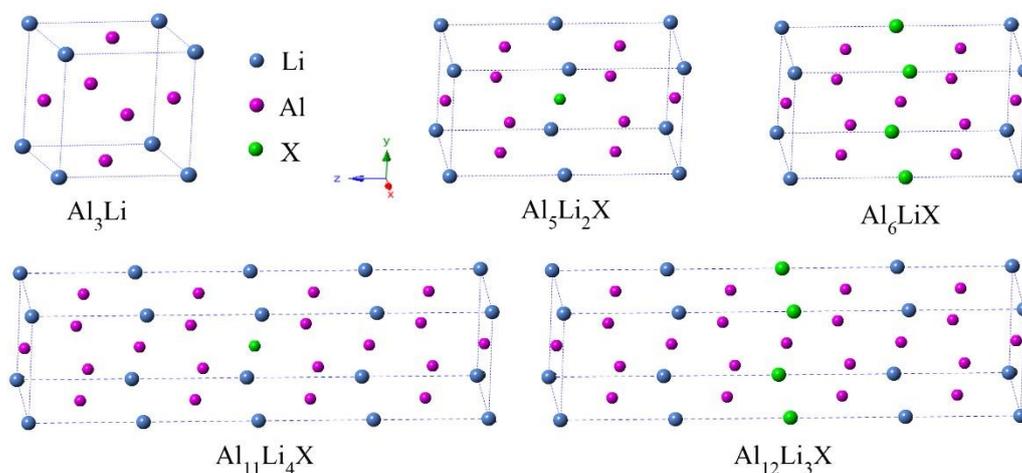
As far as the importance of  $\delta'$  precipitates is concerned, its structure and electronic properties, mechanical properties, nucleation and growth mechanism, and coarsening behavior have been widely studied both experimentally and theoretically [10–13]. The solubility and stability of  $\delta'$  phase in Al–Li alloy have been reported by Mao et al. [14], which suggest that vibrational entropy

is essential for the simulation of solubility. Phase-field method is applied for the investigation of coarsening kinetics of  $\delta'$  precipitates in the binary Al–Li alloys [15]. The formation enthalpy, electronic structures, and vibrational and thermodynamic properties of the  $\delta'$  phase were systematically reported by employing the first-principles methods [16–21]. Yao et al. have reported that point defects play an important role in determining the physical properties of off-stoichiometric  $\delta'$  phase [22]. The  $\delta'$  phase in binary Al–Li alloys provide limited room temperature strength due to their inability to form in high volume fractions unlike precipitates in Al–Cu or Al–Zn–Mg alloys [23]. In this regard, it is important to improve the mechanical properties of  $\delta'$  phase. For strengthening phases, doping with the additional alloying elements is an effective way to improve their specific properties [24–26]. The alloying elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) are often adopted to improve the specific properties of alloys. However, no one has reported the influences of alloying elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) on the mechanical properties of  $\delta'$  phase.

In this paper, first-principles methods were employed to study the effect of alloying elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) and doping concentration on the structural stability, elastic properties, hardness, elastic anisotropy, and Debye temperature of  $\text{Al}_3\text{Li}$  phase.

## 2. Computational Studies

The  $\text{Al}_3\text{Li}$  phase has a cubic structure with a space group of pm-3m (No. 221), which contains 3 Al atoms and 1 Li atom (see Figure 1). The Al and Li atom occupy 3c (0 0.5 0.5) and 1a (0 0 0) Wyckoff position, respectively. Based on the  $\text{Al}_3\text{Li}$  phase, the supercells of  $1 \times 1 \times 4$  and  $1 \times 1 \times 2$  were constructed to study the doping effects at various alloying concentrations of 6.25 and 12.5%, respectively. In the supercells, Al or Li sites can be substituted by single alloying element X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo), while the chemical formulas of doped species can be represented as  $\text{Al}_3\text{Li}$ ,  $\text{Al}_6\text{LiX}$ ,  $\text{Al}_5\text{Li}_2\text{X}$ ,  $\text{Al}_{12}\text{Li}_3\text{X}$ , and  $\text{Al}_{11}\text{Li}_4\text{X}$ , respectively.



**Figure 1.** Crystalline structures of  $\text{Al}_3\text{Li}$  doped with alloying element X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) at different alloying concentrations of 6.25 and 12.5%.

All the first-principles calculations were carried out with CASTEP package [27] based on the density functional theory (DFT) [28]. The ultrasoft pseudopotential [29] in reciprocal space was performed to describe the ion–electron interactions. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function [30] was applied to describe the exchange–correlation potential. Al  $3s^23p^1$ , Li  $1s^22s^1$ , Sc  $3s^23p^63d^14s^2$ , Ti  $3s^23p^63d^24s^2$ , Co  $3d^74s^2$ , Cu  $3d^{10}4s^1$ , Zn  $3d^{10}4s^2$ , Zr  $4s^24p^64d^25s^2$ , Nb  $4s^24p^64d^45s^1$ , and Mo  $4s^24p^64d^55s^1$  were treated as valence electrons. The plane-wave energy cutoff of 500 eV was selected for all calculations. The  $21 \times 21 \times 21$  k-points mesh was set for  $\text{Al}_3\text{Li}$ , and  $21 \times 21 \times 11$  and  $21 \times 21 \times 5$  k-points meshes were adopted for

sampling the  $1 \times 1 \times 4$  and  $1 \times 1 \times 2$  supercells of  $\text{Al}_3\text{Li}$ , respectively. The convergence threshold of  $5.0 \times 10^{-6}$  eV/atom was chosen for maximum energy change.

### 3. Results and Discussion

#### 3.1. Site Preference and Phase Stability

The predicted lattice constants, volume, mass density, and formation enthalpy of pure  $\text{Al}_3\text{Li}$  phase are listed in Table 1. The DFT is one of the calculation methods to simplify the solution of the Schrodinger equation [31]. Thus, the discrepancies between the calculated and experimental values are inevitable. In Table 1, the obtained lattice constant and mass density is consistent with the experimental values, illustrating the reliability of the present computational model.

**Table 1.** Simulated lattice constant  $a$  (Å), volume  $V$  (Å<sup>3</sup>), mass density (Kg/m<sup>3</sup>), and formation enthalpy  $H_{form}$  (eV) of pure  $\text{Al}_3\text{Li}$  phase at 0 K.

Species	$a$	$V$	Mass Density	$H_{form}$
Present	4.034	65.65	2.223	−0.097
Cal. [17]	4.030	65.45	2.221	-
Cal. [14]	4.029	65.40	-	−0.100
Exp. [32]	4.01	64.48	2.260	-

The structural stability of doped  $\text{Al}_3\text{Li}$  phase can be predicted by the simulated value of enthalpy of formation ( $\Delta H_f$ ). The  $\Delta H_f$  can be calculated with the help of Formula (1) [33].

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

where  $E_{tot}$  represents the total energy of doped  $\text{Al}_3\text{Li}$  phase,  $E_{solid}^{Al}$ ,  $E_{solid}^{Li}$ , and  $E_{solid}^X$  denote the energies per atom of Al, Li, and X in solid states,  $n$  stands for the total number of atoms in the Al–Li–X system while  $a$  and  $b$  are the number of Al and Li atoms. The predicted  $\Delta H_f$  and site occupancy behaviors of doping elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) in  $\text{Al}_3\text{Li}$  are listed in Table 2. A negative  $\Delta H_f$  is predicted for all doped  $\text{Al}_3\text{Li}$ , indicating its structural stability. Generally, a higher negative value of the  $\Delta H_f$  means the material is more stable. Thus, the Sc, Ti, Zr, Nb, and Mo are preferentially occupying the Li sites in  $\text{Al}_3\text{Li}$  while the Co, Cu, and Zn prefer to occupy the Al sites. Moreover, the  $\Delta H_f$  of  $\text{Al}_6\text{LiZr}$  phase is smaller than other systems, which led us to predict that the occupancy of alloying elements Zr in Li site can substantially improve the stability of alloy.

**Table 2.** Simulated enthalpy of formation  $\Delta H_f$  (eV) and site occupancy behaviors of doping elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) in  $\text{Al}_3\text{Li}$  at 0 K.

Element X	$\Delta H_f$		Site Preference	Element X	$\Delta H_f$		Site Preference
	$\text{Al}_6\text{LiX}$	$\text{Al}_5\text{Li}_2\text{X}$			$\text{Al}_{12}\text{Li}_3\text{X}$	$\text{Al}_{11}\text{Li}_4\text{X}$	
Sc	−0.267	−0.154	Li	Sc	−0.180	−0.127	Li
Ti	−0.232	−0.127	Li	Ti	−0.169	−0.108	Li
Co	−0.185	−0.202	Al	Co	−0.140	−0.152	Al
Cu	−0.057	−0.128	Al	Cu	−0.075	−0.111	Al
Zn	−0.017	−0.099	Al	Zn	−0.057	−0.098	Al
Zr	−0.276	−0.148	Li	Zr	−0.191	−0.118	Li
Nb	−0.188	−0.098	Li	Nb	−0.150	−0.094	Li
Mo	−0.100	−0.059	Li	Mo	−0.107	−0.075	Li

#### 3.2. Mechanical Properties

Elastic constants ( $C_{ij}$ ) is an important parameter which can be used to predict the physical properties and mechanical stability of materials [34,35]. In this paper, the  $C_{ij}$  is obtained by employing

the strain–stress method, based on the general Hooke’s law [36,37]. The pure cubic crystal of Al<sub>3</sub>Li has three independent elastic constants, i.e.,  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ . As shown in Figure 1, the doped Al<sub>3</sub>Li has tetragonal structure, which is slightly distorted from the pure Al<sub>3</sub>Li crystal [24,38]. Hence, there are six independent elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ ,  $C_{44}$ , and  $C_{66}$ ) for doped Al<sub>3</sub>Li. Moreover,  $C_{ij}$  can be used as an important criterion to judge the mechanical stability of pure and doped Al<sub>3</sub>Li. For the cubic crystals this criterion can be used as:

$$C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0, C_{11} + 2C_{12} > 0$$

For tetragonal crystals:

$$C_{11} > |C_{12}|, C_{44} > 0, C_{66} > 0, C_{33}(C_{11} + C_{12}) > 2C_{13}^2$$

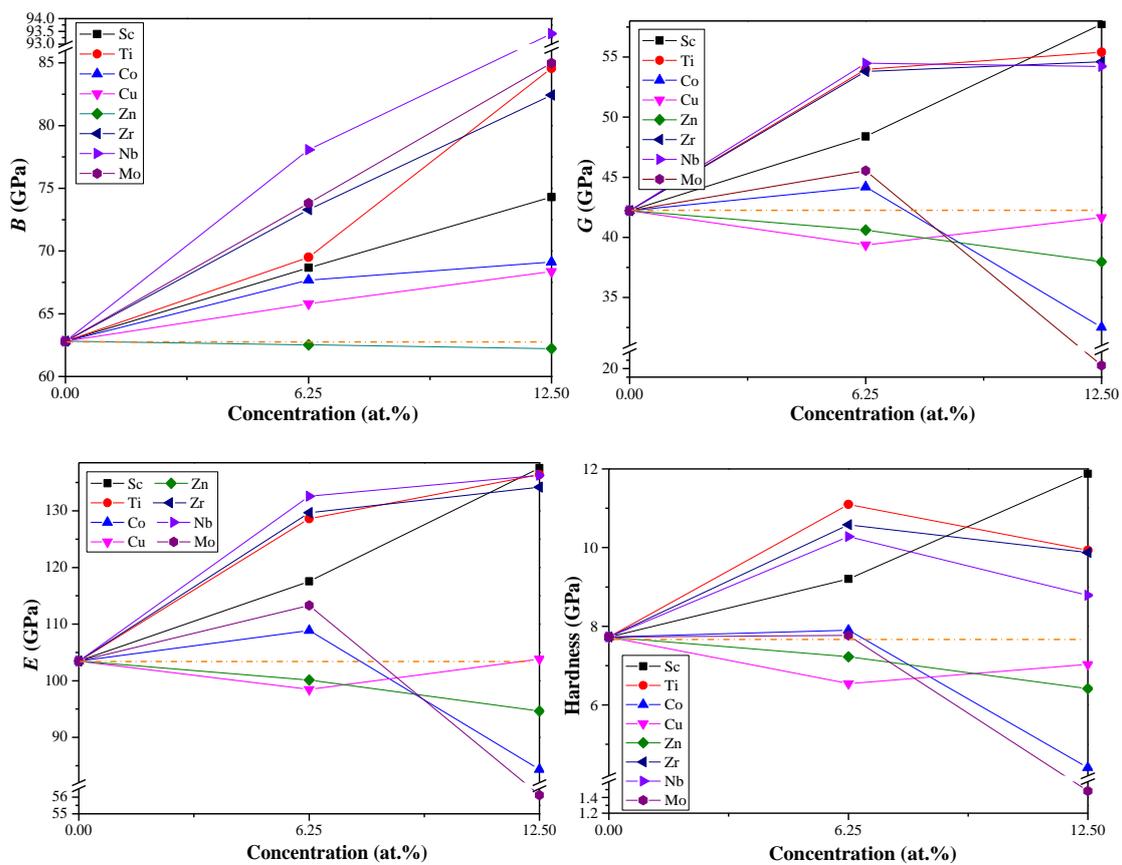
The predicted  $C_{ij}$  for pure and doped Al<sub>3</sub>Li at 0 K are summarized in Table 3. The simulated  $C_{ij}$  of pure Al<sub>3</sub>Li has a strong correlation with the already reported experimental and calculated results [17,39], implying the accuracy of our simulations. As shown in Table 3, all the predicted  $C_{ij}$  satisfied the stability criteria, indicating that the pure and doped Al<sub>3</sub>Li are mechanically stable at 0 K. All the  $C_{ij}$  of Al–Li–X (X = Sc, Ti, Zr, and Nb) systems are higher than those of pure Al<sub>3</sub>Li, which indicate that the doping elements X (X = Sc, Ti, Zr, and Nb) can effectively improve the  $C_{ij}$  of pure Al<sub>3</sub>Li. At high concentration (12.5 at %), the compression for Al<sub>6</sub>LiX (X = Sc, Zr, and Nb) and Al<sub>5</sub>Li<sub>2</sub>X (X = Co, Cu, and Zn) systems in the direction of the x-axis was more difficult than other axis owing the largest  $C_{11}$ , and the deformation resistance for Al–Li–X (X = Ti and Mo) systems along z-axis are higher than others due to higher  $C_{33}$ . When the doping concentration drops to 6.25 at %, the  $C_{33}$  for Al<sub>12</sub>Li<sub>3</sub>X (X = Ti, Zr, Nb, and Mo) systems are higher than other  $C_{ij}$  demonstrating that z-axis exhibits incompressibility.

**Table 3.** Simulated elastic constants  $C_{ij}$  (GPa), elastic moduli  $B$ ,  $G$ , and  $E$  (GPa), hardness  $H$  and universal anisotropy index  $A^U$  for pure and doped Al<sub>3</sub>Li at 0 K and 0 GPa.

Phase	Species	$C_{11}$	$C_{33}$	$C_{44}$	$C_{66}$	$C_{12}$	$C_{13}$	$B$	$G$	$E$	$H$	$A^U$
Al <sub>3</sub> Li	Present	129.7	-	37.7	-	29.4	-	62.8	42.2	103.5	7.73	0.099
	Cal. [17]	128	-	39	-	30	-	63.3	42.8	116.8	-	-
	Exp. [39]	123.6	-	42.8	-	37.2	-	66	43	105.9	-	-
Al <sub>12</sub> Li <sub>3</sub> Sc	Present	136.2	130.4	46.1	51.7	31.0	38.3	68.7	48.4	117.6	9.20	0.019
Al <sub>12</sub> Li <sub>3</sub> Ti	Present	141.3	147.7	52.4	54.4	35.2	31.2	69.5	54.0	128.6	11.10	0.007
Al <sub>11</sub> Li <sub>4</sub> Co	Present	138.0	118.9	39.4	48.1	29.0	39.2	67.7	44.2	108.9	7.90	0.085
Al <sub>11</sub> Li <sub>4</sub> Cu	Present	126.7	116.2	37.0	37.5	37.7	37.0	65.8	39.4	98.5	6.55	0.032
Al <sub>11</sub> Li <sub>4</sub> Zn	Present	124.3	121.8	36.9	38.9	33.8	31.2	62.5	40.6	100.1	7.23	0.049
Al <sub>12</sub> Li <sub>3</sub> Zr	Present	143.4	147.5	53.1	55.9	42.2	35.2	73.3	53.8	129.7	10.58	0.008
Al <sub>12</sub> Li <sub>3</sub> Nb	Present	147.8	163.5	53.1	54.9	50.8	35.5	78.1	54.5	132.6	10.28	0.041
Al <sub>12</sub> Li <sub>3</sub> Mo	Present	118.7	147.0	52.0	51.5	66.9	36.6	73.8	45.4	113.3	7.77	0.426
Al <sub>6</sub> LiSc	Present	146.6	136.8	61.3	62.0	35.2	41.3	74.3	57.7	137.6	11.88	0.040
Al <sub>6</sub> LiTi	Present	153.7	157.5	55.0	62.0	51.8	48.2	84.6	55.4	136.4	9.93	0.020
Al <sub>5</sub> Li <sub>2</sub> Co	Present	144.9	76.5	35.9	34.0	15.6	58.2	69.1	32.5	84.3	4.41	1.534
Al <sub>5</sub> Li <sub>2</sub> Cu	Present	134.6	122.0	37.3	41.8	39.3	36.6	68.4	41.6	103.8	7.03	0.055
Al <sub>5</sub> Li <sub>2</sub> Zn	Present	123.2	116.4	33.5	36.4	37.0	30.9	62.2	38.0	94.7	6.42	0.082
Al <sub>6</sub> LiZr	Present	153.9	143.0	55.7	60.5	51.6	47.2	82.4	54.6	134.2	9.88	0.026
Al <sub>6</sub> LiNb	Present	162.0	156.2	54.2	64.0	56.4	61.9	93.4	54.2	136.3	8.88	0.047
Al <sub>6</sub> LiMo	Present	90.3	146.3	39.6	50.9	86.8	67.9	85.0	20.2	56.1	1.48	17.33

The elastic moduli (bulk modulus  $B$ , shear modulus  $G$ , and Young’s modulus  $E$ ) of pure and doped Al<sub>3</sub>Li were estimated by Voigt–Reuss–Hill method [40,41]. Generally,  $B$  describes the resistance to volume change. As shown in Table 3 and Figure 2, the values of  $B$  for Al–Li–X (X = Sc, Ti, Co, Cu, Zr, Nb, and Mo) alloys increase with the increase of doping concentration which is higher than that of pure Al<sub>3</sub>Li. The greater  $B$  is, the better the ability to resist to volume change is. When the

doping concentration is constant, the values of  $B$  for Al–Li–Nb are greater than other counterpart species, indicating that Al–Li–Nb has the stronger resistance to volume change. Thus, we inferred that the addition of Nb can effectively improve the resistance to volume change in Al–Li–X. The  $G$  and  $E$  measure the resistance to shape change and stiffness of Al–Li–X system, respectively. At low concentration (6.25 at %), the addition of Cu and Zn elements can reduce the  $G$  and  $E$  of  $\text{Al}_3\text{Li}$ . On the other hand, the  $\text{Al}_{12}\text{Li}_3\text{Nb}$  has higher values of  $G$  and  $E$ . when the doping concentration up to 12.5 at %, the Sc, Ti, Zr, and Nb elements can play an important role in enhancing the  $G$  and  $E$  of  $\text{Al}_3\text{Li}$ . The  $\text{Al}_6\text{LiSc}$  has higher  $G$  and  $E$  which consequently gives stronger shear deformation resistance and stiffness. Comparative analysis of these parameters led us to conclude that the values of  $E$  ( $G$ ) decrease with the higher concentration (from 6.25 to 12.5%) of Co, Zn, and Mo (Co, Zn, Nb, and Mo). In short, this high doping concentration may decrease the overall performance of the material.



**Figure 2.** The predicted elastic moduli  $B$ ,  $G$ , and  $E$  (GPa) and hardness  $H$  of  $\text{Al}_3\text{Li}$  doped with alloying element  $X$  ( $X = \text{Sc}, \text{Ti}, \text{Co}, \text{Cu}, \text{Zn}, \text{Zr}, \text{Nb}$ , and  $\text{Mo}$ ).

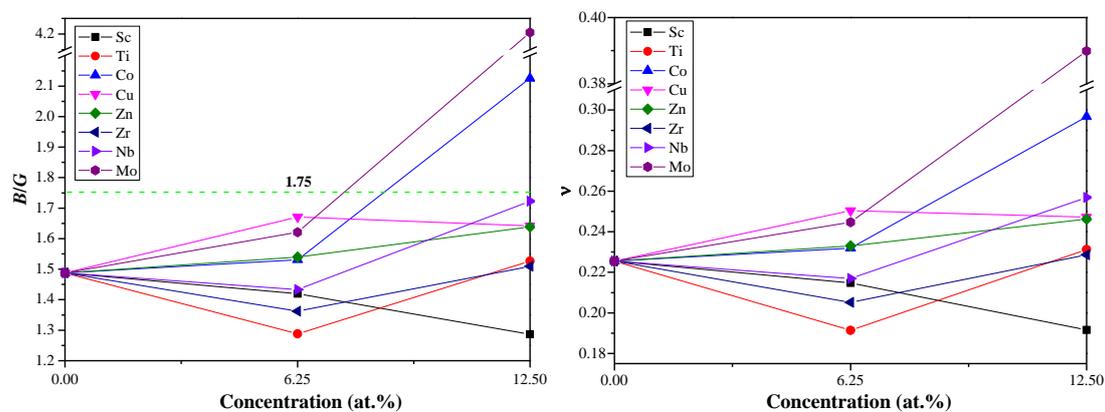
Hardness ( $H$ ) is an important parameter of materials which can be estimated by the ability to resist localized deformation [42]. The defects (i.e., dislocations) and grain sizes of materials have great influence on the hardness [43] and it is very difficult to get the exact value of  $H$  through empirical method. In this paper, the  $H$  was roughly predicted by the following semi-empirical formulas [44]:

$$H = \frac{(1 - 2\nu)}{6(1 + \nu)} E \quad (2)$$

As described in Figure 2, the  $H$  of Al–Li–Zn follow a descending trend with the increase of doping concentration, but it increases in case of Al–Li–Sc. For Al–Li– $X$  ( $X = \text{Ti}, \text{Co}, \text{Zr}, \text{Nb}$ , and  $\text{Mo}$ ), the  $H$  reached to the maximum when 6.25% doping concentration is considered. Besides, the  $\text{Al}_6\text{LiSc}$  and  $\text{Al}_6\text{LiMo}$  have maximum and minimum values of  $H$ , respectively. However, the difference between

the hardness of  $\text{Al}_6\text{LiSc}$  and  $\text{Al}_{12}\text{Li}_3\text{Ti}$  is small (about 0.78 GPa). Hence, considering high cost of Sc, the addition of Ti may be the best choice to improve the hardness of pure  $\text{Al}_3\text{Li}$ .

The brittle or ductile behavior of Al–Li–X system can be roughly evaluated from the ratio of  $B/G$ . Hence, the materials tend to brittle (ductile) if the ratios of  $B/G$  is smaller (larger) than 1.75 [45]. As shown in Figure 3, all the Al–Li–X systems present brittle behavior with a doping concentration of 0 to 6.25 at.%. The Al–Li–X ( $X = \text{Co}$  and  $\text{Mo}$ ) systems tend to be ductile due to the higher  $B/G$  ratios while other Al–Li–X systems still possess brittle behavior at high concentration (12.5 at.%). Comparative analysis of this behavior led us to suggest that the existence of Co and Mo can transform the intrinsic brittleness of  $\text{Al}_3\text{Li}$  into ductility. Moreover, the  $B/G$  ratios for the Al–Li–Sc system decrease with the increase of Sc concentration (from 0 to 12.5%), while an increasing trend of  $B/G$  ratios is found in the Al–Li–X ( $X = \text{Co}$ , Zn, and Mo) systems. In short, it is necessary to choose an appropriate doping element and its concentration for the desired ductility or brittleness of materials.



**Figure 3.** Simulated  $B/G$  and  $\nu$  of  $\text{Al}_3\text{Li}$  doped with alloying element  $X$  ( $X = \text{Sc}$ ,  $\text{Ti}$ ,  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Zr}$ ,  $\text{Nb}$ , and  $\text{Mo}$ ) as a function of doping concentration.

The Poisson's ratio  $\nu$  is defined as  $\nu = (3B - 2G)/(6B + 2G)$  and adopted to reveal the stability of the crystal against shear stress. As shown in Figure 3, the values of  $\nu$  for  $\text{Al}_6\text{LiMo}$  and  $\text{Al}_5\text{Li}_2\text{Co}$  are bigger than those of other Al–Li–X alloys, indicating that  $\text{Al}_6\text{LiMo}$  and  $\text{Al}_5\text{Li}_2\text{Co}$  have a higher structural plasticity [46,47]. Besides, the typical values of  $\nu$  for ionic and metallic materials are 0.25 and 0.33, respectively [48,49]. The predicted  $\nu$  for Al–Li–X systems (excluding  $\text{Al}_5\text{Li}_2\text{Co}$  and  $\text{Al}_6\text{LiMo}$ ) are close to 0.25, which shows that main chemical bonding is ionic bonding. The calculated  $\nu$  for  $\text{Al}_6\text{LiMo}$  (0.39) and  $\text{Al}_5\text{Li}_2\text{Co}$  (0.30) are closer to 0.33 than 0.25, implying that the metallic bonding plays the dominant position. Thus, the main chemical bonds of  $\text{Al}_6\text{LiMo}$  and  $\text{Al}_5\text{Li}_2\text{Co}$  are different from that of other Al–Li–X alloys, and this may be the reason why  $\text{Al}_6\text{LiMo}$  and  $\text{Al}_5\text{Li}_2\text{Co}$  tend to be ductile.

Furthermore, the elastic anisotropy plays a vital role in the mechanical/physical processes such as crack behavior and phase transformations [50]. The elastic anisotropy of pure and doped  $\text{Al}_3\text{Li}$  can be predicted from the universal anisotropy index ( $A^U$ ) and its formula is defined as follows [51]:

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \quad (3)$$

where  $G_V$  and  $G_R$  represent the Voigt and Reuss shear modulus,  $B_V$  and  $B_R$  are the Voigt and Reuss bulk modulus, respectively.

As listed in Table 3, the predicted  $A^U$  for pure and doped  $\text{Al}_3\text{Li}$  is higher than 0, implying the anisotropy of the Al–Li–X alloy. In case of Al–Li–X alloy, the  $A^U$  shows an upward trend with the increase of doping concentration (6.25 to 12.5%). The  $A^U$  for most of the Al–Li–X (except  $\text{Al}_5\text{Li}_2\text{Co}$ ,  $\text{Al}_6\text{LiMo}$ , and  $\text{Al}_{12}\text{Li}_3\text{Mo}$ ) systems are near zero and smaller than that for pure  $\text{Al}_3\text{Li}$ , which indicates that most doping elements can reduce the anisotropy of materials. The  $A^U$  of  $\text{Al}_6\text{LiMo}$  is much larger

than other species. The reason behind this is that a large difference between  $C_{44}$  ( $C_{11}$ ) and  $C_{66}$  ( $C_{33}$ ) in  $\text{Al}_6\text{LiMo}$  alloy [52].

### 3.3. Debye Temperature

The Debye temperature  $\Theta_D$  is an important parameter of a solid and it is associated with thermodynamic properties of materials, such as entropy, thermal expansion, and vibrational internal energy. One of the standard methods of calculating the Debye temperature is from elastic constant data. Thus, the  $\Theta_D$  was predicted from averaged sound velocity by employing the following formula [53]:

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

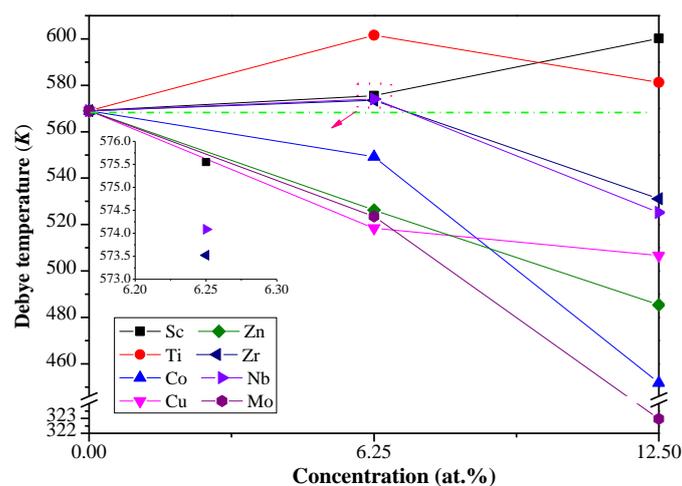
$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (5)$$

$$v_s = \sqrt{\frac{G}{\rho}} \quad (6)$$

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}} \quad (7)$$

where  $h$ ,  $k_B$ ,  $n$ ,  $N_A$ ,  $\rho$ ,  $M$ , and  $v_m$  stand for Planck's constant, Boltzmann's constant, total number of atoms, Avogadro's number, density, molecular weight, and average wave velocity, respectively.  $v_s$  and  $v_l$  represent the shear and longitudinal sound velocities of materials, respectively.

As depicted in Figure 4, the predicted value of  $\Theta_D$  for pure  $\text{Al}_3\text{Li}$  is 568.9 K at 0 K, which is in consistent with the already reported data (573 K) [19]. The  $\Theta_D$  decreases (increases) with the increase of Co, Cu, Zn, and Mo (Sc) concentration in the Al–Li–X systems. In general, a higher  $\Theta_D$  implies that the materials have higher thermal conductivity and stronger covalent bonds. The  $\Theta_D$  of  $\text{Al}_{12}\text{Li}_3\text{Ti}$  is higher among the Al–Li–X systems, which illustrates that the strength of covalent bonds and thermal conductivity of  $\text{Al}_{12}\text{Li}_3\text{Ti}$  are better than others. Furthermore, the predicted density of  $\text{Al}_{12}\text{Li}_3\text{Ti}$  (2.5 g/cm<sup>3</sup>) is close to the density of  $\text{Al}_3\text{Li}$  (2.2 g/cm<sup>3</sup>), which demonstrates that  $\text{Al}_{12}\text{Li}_3\text{Ti}$  may be a better reinforcement phase in aerospace materials.



**Figure 4.** The calculated  $\Theta_D$  for  $\text{Al}_3\text{Li}$  doped with alloying element X (X= Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) with different doping concentration.

#### 4. Conclusions

The effect of alloying elements X (X = Sc, Ti, Co, Cu, Zn, Zr, Nb, and Mo) and doping concentration on the structural stability, mechanical properties, and Debye temperature of Al<sub>3</sub>Li were systematically investigated through density functional theory. The main contents of this work can be summarized as follows:

(1) All doped Al<sub>3</sub>Li systems are structural stability. The Sc, Ti, Zr, Nb, and Mo preferentially occupied the Li sites in Al<sub>3</sub>Li while the Co, Cu, and Zn prefer to occupy the Al sites rather than Li sites.

(2) All the C<sub>ij</sub> of Al–Li–X (X = Sc, Ti, Zr, and Nb) systems are higher than those of pure Al<sub>3</sub>Li, which indicate that the doping elements X (X = Sc, Ti, Zr, and Nb) can effectively improve the C<sub>ij</sub> of pure Al<sub>3</sub>Li. The values of B for Al–Li–X (X = Sc, Ti, Co, Cu, Zr, Nb, and Mo) alloys (excluding Al–Li–Zn) increase with the increase of doping concentration and are higher than that for pure Al<sub>3</sub>Li. The Al<sub>6</sub>LiSc has higher G and E, which consequences stronger shear deformation resistance and stiffness.

(3) All the Al–Li–X systems present brittle behavior with the increase in doping concentration (from 0 to 6.25 at %). The Al–Li–X (X = Co and Mo) systems tend to ductile while other Al–Li–X systems still possess brittle behavior at high concentration (12.5 at %), which suggests that the existence of Co and Mo can transform the intrinsic brittleness of Al<sub>3</sub>Li into ductility. Moreover, the Al<sub>6</sub>LiSc and Al<sub>6</sub>LiMo have maximum values of H and A<sup>U</sup>, respectively.

(4) A higher  $\Theta_D$  is observed for Al<sub>12</sub>Li<sub>3</sub>Ti, responsible for strong covalent bonds and higher thermal conductivity, compared to other Al–Li–X systems.

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