

A SIMPLIFIED SEMI-EMPIRICAL POTENTIAL FOR SIMULATIONS OF Li, Na, AND K METALS AND BINARY ALLOYS

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Abstract. The techniques involved in designing a simple and transferable semi-empirical potential for numerical simulations of Li, Na, and K metals and alloys with a minimal fitting have been put forward. The embedded-atom method provides the most reliable and efficient semi-empirical atomic potentials used for various simulations. Here, this method is employed to study and theoretically reproduce some physical properties of materials, which are also gotten from the experiment and the *ab initio* calculations. To validate the suitability of this model, we optimally computed and reproduced the monovacancy formation energy and the elastic stiffness of these metals that comparably agree with the data from experiments. Additional properties like low index surface energies that were not used during fittings were computed. The obtained values reasonably agree with the data both from experiment and first principles. The little differences may be due to the inability to adequately determine the experimental values using Tyson's estimation. Lastly, the six possible binary alloys of these metals were studied. Only two experimental sets of data are available at the moment for $\text{Na}^{\text{H}}\text{K}^{\text{G}}$ and $\text{K}^{\text{H}}\text{Na}^{\text{G}}$, and our computed values are consistent with these data. Thus for a better and complete comparison, new experimental data are needed for other alloys.

Key words: monovacancy formation energy, elastic stiffness, low index surface energies, enthalpies of solution.

1. INTRODUCTION

Lithium is an excellent metal with high energy density useful in producing efficient lithium-ion batteries which are easily rechargeable. It also serves as a good material for aircraft companies. Sodium and potassium on the other hand, are wonderful materials for various technological applications. They easily conduct both heat and electricity. Their alloys are not only used as a heat-transfer medium but also found their applications in medicines.

In order to design and get the properties of interest of these metals, an adequate investigation and a detailed knowledge of the desired materials are germane. In recent times, there are major development and improvement in tools produced for experimental purposes such as the magnetic resonance imaging, the scanning

tunneling microscope, the high-resolution transmission electron microscope, the field ion microscope and so on, which are purposely used for studying at small scale the structures and defects in crystals. These tools are still inadequate to comprehensively study these structures [1]. Moreover, it is difficult to accurately obtain by experiment the atomic quantities like monovacancy formation energy, which are local environment dependent [2].

Over three decades, several interatomic potentials methods such as the embedded-atom method, Finnis and Sinclair method, glue model [3–5] and other techniques have been constructed and used to compute different properties of metals and alloys. These models are able to overcome several shortcomings found in using pair-potentials. As a result of its simplicity and computational efficiency, the embedded-atom method (EAM) has been widely employed in investigating many properties of interest. This model was originally derived by Daw and Baskes [3] and has been used by many researchers [6–11] to obtain many properties of metals and alloys, which include but not limited to the point defects, structural, energetic, thermal, mechanical, and phonon dispersion.

Unlike Finnis and Sinclair models [4], the EAM potentials are not commonly used for body-centered cubic (bcc) structures like Li, Na, and K metals and alloys. In putting the bonding's direction into consideration, an additional term was included to initial EAM potential [12] and it was tagged “modified embedded-atom method (MEAM)”. The new MEAM potential was employed by Zhang and coworkers [11] to study bcc transition metals. Similarly, Fang and coworkers [13] applied the MEAM to study the enthalpy of formation in binary immiscible alloys. In our previous studies [14–16], we employed both the EAM and MEAM to compute many properties of metals and alloys. Though, the modified version of the EAM add some complexities to the model but our computed results are still reasonably good when compared with data from experiment.

Presently, a simplified EAM has been extended to investigate the vacancies, elastic stiffness, and surface energies for low index crystal faces for in Li, Na and K metals. The enthalpies of solution of the binary alloys of these metals are considered. In Section 2 we present the computational procedures needed to have a complete EAM model for the study. In Section 3, our computed results with a simplified EAM model are presented and discussed, while the last Section briefly summarizes and concludes the work.

2. SIMULATION METHOD

In the current Section, we shall comprehensively analyze the computational method and simulation procedures for studying Li, Na, and K metals and alloys. The physics quantities that are useful in fitting the EAM curve so as to obtain the model parameters needed in the computation will be listed.

2.1. THE EMBEDDED-ATOM METHOD

The total energy E_{tot} of EAM model [3] is presented as

$$E_{tot} = F(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}), \quad (1)$$

where $F(\rho_i)$ and $\phi(r_{ij})$ are the embedding function and the pair potential, respectively. For a complete and useable EAM model, $\phi(r)$, $f(r)$, and $F(\rho)$ must be defined.

The two-body potential is given as

$$\phi(r) = \phi_e \left[1 + \xi \left(\frac{r}{r_{1e}} - 1 \right) \right] \times \exp \left[-\gamma \left(\frac{r}{r_{1e}} - 1 \right) \right]. \quad (2)$$

The atomic electron density, $f(r)$ takes the form of [6]

$$f(r) = f_e \exp \left[-\beta \left(\frac{r}{r_{1e}} - 1 \right) \right]. \quad (3)$$

The embedding function $F(\rho)$ follows that of [17]

$$F(\rho) = -E_c \left[1 - \frac{\alpha}{\beta} \ln \left(\frac{\rho}{\rho_e} \right) \right] \left(\frac{\rho}{\rho_e} \right)^{\alpha/\beta} - 4\phi_e \left[1 - \frac{\xi}{\beta} \ln \left(\frac{\rho}{\rho_e} \right) \right] \left(\frac{\rho}{\rho_e} \right)^{\gamma/\beta} - 3\phi_e \left[1 - \frac{S\xi}{\beta} \ln \left(\frac{\rho}{\rho_e} \right) + \zeta(S-1) \right] \left(\frac{\rho}{\rho_e} \right)^{S\gamma/\beta} \times \exp[-\gamma(S-1)] \quad (4)$$

$$\rho(r) = \rho_e \exp \left[-\beta \left(\frac{r}{r_{1e}} - 1 \right) \right] \quad (5a)$$

$$\rho_e = 8f_e + 6f_e \exp[-\beta(S-1)] \quad (5b)$$

Here r_{1e} represents the first equilibrium nearest neighbour distance and $r_{2e} = Sr_{1e}$ and $S = \frac{2}{\sqrt{3}}$.

There are six undetermined parameters, f_e , α , β , ϕ_e , ξ , and γ that are to be evaluated. Although, β can be determined, it can also be treated as an adjustable parameter. For this work, β is set to be 6.

Here f_e is the atomic electron density evaluated at the equilibrium and is given as

$$f_e = \frac{SE_c}{\Omega} \quad (6)$$

$$\alpha = \sqrt{\frac{9\Omega B}{E_c}} \quad (7)$$

and $S = 1$, E_c , B , and Ω are the cohesive energy, bulk modulus, and the atomic volume, respectively.

To evaluate the remaining parameters, ϕ_e , ξ , and γ , the following three conditions must be satisfied

$$4r_{1e}\phi'(r_{1e}) + 3r_{2e}\phi'(r_{2e}) = 0 \quad (8)$$

$$4r_{1e}^2\phi''(r_{1e}) + 3r_{2e}^2\phi''(r_{2e}) = 15\Omega G \quad (9)$$

$$E_{1f} = 4\phi(r_{1e}) + 3\phi(r_{2e}) + \frac{1}{2}F''(\rho_e)[8f^2(r_{1e}) + 6f^2(r_{2e})] \quad (10)$$

Substituting the expressions for $\phi(r)$, $\phi'(r)$, $\phi''(r)$, $F''(\rho)$, and $f(r)$ we obtain

$$4(\gamma - \beta) + 3S[\gamma - \xi + \gamma\xi(S-1)] \times \exp[-\gamma(S-1)] = 0 \quad (11)$$

$$4\phi_e\gamma\{\gamma - 2\xi + [\gamma - 2\xi + \gamma\xi(S-1)] \times \exp[-\gamma(S-1)]\} = 15\Omega G \quad (12)$$

$$E_{1f} = \frac{8 + 6\exp[-2\beta(S-1)]}{2\beta^2\{8 + 6\exp[-2\beta(S-1)]\}^2} 4\phi_e + 3\phi_e[1 + \xi(S-1)] \times \exp[-\gamma(S-1)] + (9\Omega B - 15\Omega G) \quad (13)$$

With (11), (12), and (13) the parameters ϕ_e , ξ , and γ can be obtained. Also, the monovacancy formation energy for each metal considered in our present work can be computed using (13).

Another important properties to be considered are the three elastic stiffnesses (C_{11} , C_{12} , and C_{44}) of these metals. The following equations will be adopted:

$$\chi_x = \frac{a_0^2}{2\Omega_0} \left[\phi''(r_0) - \frac{1}{r_0} \phi'(r_0) \right] + \frac{a_0^2}{\Omega_0} F'(\rho_0) \left[f''(r_0) - \frac{1}{r_0} f'(r_0) \right] \quad (14)$$

$$\chi_y = \frac{8a_0^2}{\Omega_0} F''(\rho_0) [f'(r_0)]^2 \quad (15)$$

$$C_{11} = \chi_x + \chi_y \quad (16)$$

$$C_{12} = \frac{1}{2} \chi_x + \chi_y \quad (17)$$

$$C_{44} = \frac{1}{2} \chi_x \cdot \quad (18)$$

The bulk modulus of these metals can be evaluated:

$$B = \frac{2}{3} \chi_x + \chi_y \cdot \quad (19)$$

The surface energies for three low index crystal faces will also be calculated using the following equations:

$$\gamma_{100} = \frac{1}{a_0^2} (E_7 - E_8) \quad (20)$$

$$\gamma_{110} = \frac{\sqrt{2}}{a_0^2} (E_6 - E_8) \quad (21)$$

$$\gamma_{111} = \frac{1}{a_0^2 \sqrt{3}} (E_4 - E_8) \cdot \quad (22)$$

2.2. ENTHALPIES OF SOLUTION FOR ALLOYS

To compute the enthalpies of solution for possible combination of these metals' binary alloys, the extended alloy model of Johnson [7] will be employed with the first and second nearest neighbors taken into consideration.

The cross potentials using a mixing rule can be obtained as

$$\phi^{\text{HG}}(r_{1e}) = \frac{1}{2} \left[\frac{f_G(r_{1e})}{f_H(r_{1e})} \phi^{\text{HH}}(r_{1e}) + \frac{f_H(r_{1e})}{f_G(r_{1e})} \phi^{\text{GG}}(r_{1e}) \right] \quad (23)$$

and

$$\phi^{\text{HG}}(r_{2e}) = \frac{1}{2} \left[\frac{f_G(r_{2e})}{f_H(r_{2e})} \phi^{\text{HH}}(r_{2e}) + \frac{f_H(r_{2e})}{f_G(r_{2e})} \phi^{\text{GG}}(r_{2e}) \right], \quad (24)$$

where $\phi^{\text{HH}}(r)$ and $\phi^{\text{GG}}(r)$ are the monoatomic potentials in (2). Superscripts ‘‘H’’ and ‘‘G’’ indicate, respectively, the solvent (host) and the solute (guest) atoms. The important steps needed in calculating both the unrelaxed and relaxed enthalpies of solution were discussed in our previous work [16].

Some physical quantities that are important in fitting the potential curves were gotten from different works and are presented in Table 1.

Table 1

The physical quantities for Li, Na, and K metals. While the lattice constant was taken from [18], the cohesive energy was taken from [19]. The mono-vacancy energy and the elastic constants were taken from [20] and [21], respectively

Quantity	Li	Na	K
a_0 (Å)	3.5092	4.2906	5.3210
E_c (eV)	1.630	1.113	0.934
E_{1f} (eV)	0.48	0.340	0.340
C_{11} (eV/Å ³)	0.084	0.046	0.028
C_{12} (eV/Å ³)	0.071	0.039	0.023
C_{44} (eV/Å ³)	0.055	0.026	0.016

3. RESULTS AND DISCUSSION

The accuracy and consistency of any model is a function of its model parameters required in obtaining a desired and useful potential model. With the help of equations (6–13), we have obtained the six model parameters (f_e , α , β , ϕ_e , ζ , and γ). These parameters were determined using the input quantities shown in Table 2. The graph of the two-body potential against its relative distance and the embedding energy against its relative density are shown in Fig. 1 and Fig. 2, respectively. The minimum of the pair potentials that is close to the nearest-neighbour distance is clearly seen in Fig. 1.

Table 2

The evaluated EAM model parameters for Li, Na, and K metals

Metal	f_e	ζ	ϕ_e	α	γ	β
Li	0.0754	3.4301	−0.070	2.9913	2.9101	6
Na	0.0282	4.0485	−0.048	3.6185	3.3027	6
K	0.0124	4.9741	−0.051	4.2598	03.8558	6

The parameters are dimensionless, except for ϕ_e , which is in eV

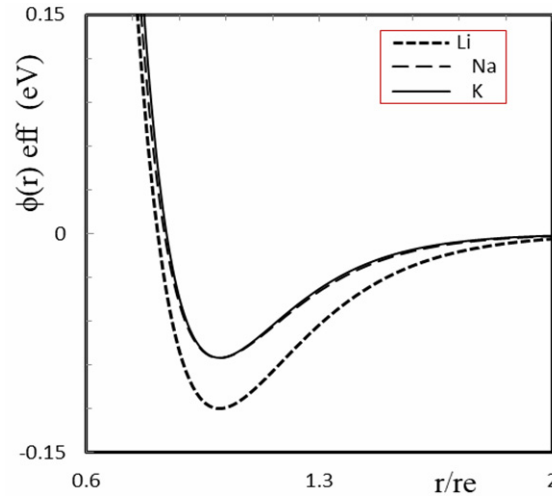


Fig. 1 – The graph of the two-body potential as a function of its relative distance.

To test the validity of this model, the monovacancy formation energy for each metal using (13) was reproduced. The strength of the bond in solids is determined by the formation energy of a vacancy. For comparison, the computed results alongside with the data from experiment and *ab initio* calculations are shown in Table 3. Although, Ho [22] applied the first principles to predict the monovacancy formation energy of these metals, which to some extent agree with our computed values except for Li metal, for which the value predicted is so low when compared with its corresponding experimental value. In general, our computed results are closer to data from experiment.

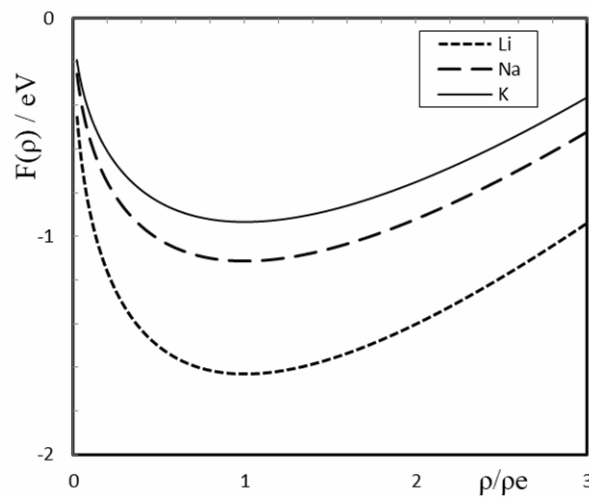


Fig. 2 – The graph of the embedding energy as a function of its relative density.

Table 3

The calculated and experimental values for the formation energy of monovacancy E_{Ij} in eV. The experimental and the first principle values were taken from [20] and [22], respectively

Metal	Present work	Exp. Data	First principle
Li	0.488	0.482	0.37
Na	0.338	0.342	0.39
K	0.359	0.348	0.36

Using (14–18), the three elastic stiffnesses C_{11} , C_{12} , and C_{44} were obtained. The results that were obtained are presented in Table 4 together with the corresponding data from experiment. As expected, experimentally $C_{11} > C_{12} > C_{44}$ for these metals (Li, Na, and K) and our computed values also follow this pattern. These elastic stiffnesses are plotted in Fig. 3, Fig. 4, and Fig. 5, for Li, Na, and K metals, respectively. As seen in these figures, the present model is able to comprehensively investigate the elastic properties of these metals since our computed values correlate with the results from experiment. Using the obtained elastic stiffness results, the bulk, young, and shear moduli can subsequently be obtained.

Table 4

The elastic stiffness in $\text{eV}/\text{\AA}^3$ for Li, Na, and K metals

Metal	Elastic constant	Present work	Exp. data
Li	C_{11}	0.0851	0.0838
	C_{12}	0.0721	0.0706
	C_{44}	0.0584	0.0600
Na	C_{11}	0.0461	0.0474
	C_{12}	0.0372	0.0396
	C_{44}	0.0284	0.0269
K	C_{11}	0.0251	0.0232
	C_{12}	0.0177	0.0197
	C_{44}	0.0132	0.0118

The experimental values were taken from [23]

To further validate the suitability of this model, additional properties of these metals that were not used during the potential fittings were computed. We have obtained the surface energies for low index crystal faces using (20–22). The computed values, data from experiment, and values from first principle calculations are shown in Table 5. The values from experiment were extrapolated at 0 K for the polycrystalline solids. As seen in Table 5, the present model is able to describe the surface energy of three low index crystal faces γ_{100} , γ_{110} , and γ_{111} of these metals due to the suitable $F(\rho)$ used in the model. It is somehow difficult to completely compare our calculated values with data from experiment because the experiment did not present the values for different crystal planes. Nevertheless, with the help of population density factor of Tyson's model [24], one can obtain from average, the surface energies of any particular face. The values of these energies as predicted by Johnson and Oh [9] and

FS models [4] are reported to be 80% of the results gotten from Tyson's model [24]. Although our computed results are reasonably good with the data from both the experiment [24] and the first principle calculations [25], the little differences in the results may be due to the inability to adequately obtain the experiment values using Tyson's estimation. The ratio $\frac{\gamma_{111}}{\gamma_{100}}$ should be about 0.87. For Li and Na, this ratio is approximately 0.862, but for K it is 0.81. Generally, the computed average value of each metal with the present model is less than the corresponding experimental value.

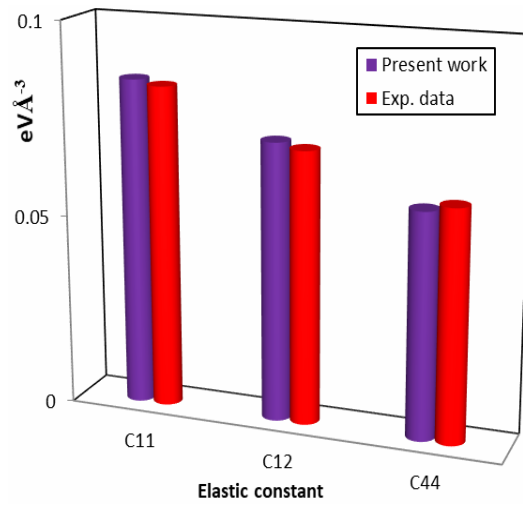


Fig. 3 – The comparison of elastic stiffness for Li metal.

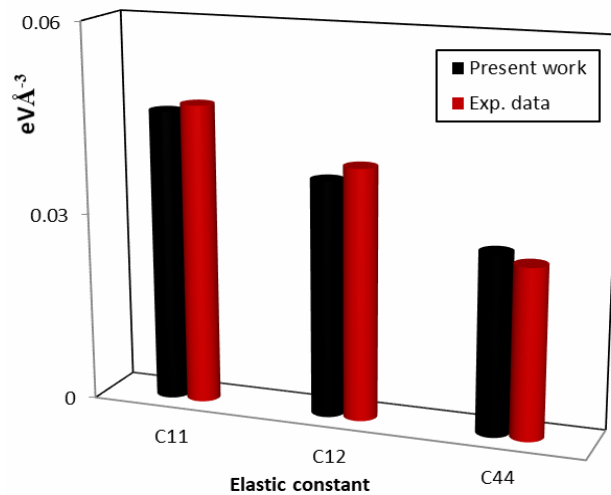


Fig. 4 – The comparison of elastic stiffness for Na metal.

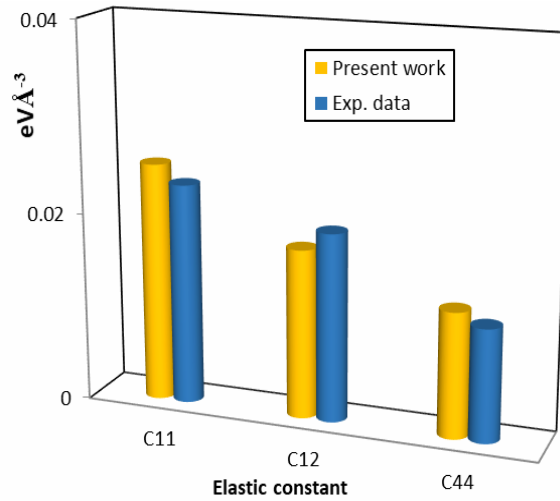


Fig. 5 – The comparison of elastic stiffness for K metal.

Table 5

The low index surface energy for Li, Na and K metals. For comparison, the experimental and the first principle values were taken from [24] and [25], respectively

Metal	Surface Energy	Present work	Exp. Data	First Principle
Li	γ_{100}	0.485	0.520	0.522
	γ_{110}	0.291		0.556
	γ_{111}	0.418		0.590
Na	γ_{100}	0.254	0.260	0.264
	γ_{110}	0.201		0.253
	γ_{111}	0.219		0.287
K	γ_{100}	0.165	0.145	0.142
	γ_{110}	0.115		0.135
	γ_{111}	0.135		0.152

Table 6

The computed enthalpies of solution for alloys of Li, Na, and K. The host atom (solvent) and the guest atom (solute) are respectively denoted as H and G

Alloy	$\Delta H[\text{eV}]$		Exp. data	Others
	Unrelaxed	Relaxed		
$\text{Li}^{\text{H}}\text{Na}^{\text{G}}$	0.262	0.232	–	0.176 [28]
$\text{Li}^{\text{H}}\text{K}^{\text{G}}$	0.238	0.229	0.28 [26]	0.117 [29]
$\text{Na}^{\text{H}}\text{Li}^{\text{G}}$	1.803	1.751	–	–
$\text{Na}^{\text{H}}\text{K}^{\text{G}}$	0.066	0.059	–	0.124 [28]
$\text{K}^{\text{H}}\text{Li}^{\text{G}}$	–0.100	–0.121	–	–
$\text{K}^{\text{H}}\text{Na}^{\text{G}}$	0.052	0.044	0.033 [27]	0.319 [29]

Lastly, to validate again the flexibility and transferability of this model, the cross potentials needed for alloy systems of these metals were considered. The procedures

for evaluating the binary alloys of metals were previously discussed by our team [16] for face-centered cubic alloys. The only difference is that the second nearest neighbour distance is highly put into consideration in this work. The computed results of the enthalpies of solution for the possible binary alloys are shown in Table 6. The values for the unrelaxed enthalpies of solution were firstly determined and thereafter, the relaxed enthalpies of solution were considered. It is practically impossible to completely compare our computed values due to limited available data from both the experiment and other authors. Out of six possible alloys, only two experimental values $\text{Na}^{\text{H}}\text{K}^{\text{G}}$ and $\text{K}^{\text{H}}\text{Na}^{\text{G}}$ are available. Our computed result for $\text{Na}^{\text{H}}\text{K}^{\text{G}}$ reasonably agrees with value from experiment likewise the value for $\text{K}^{\text{H}}\text{Na}^{\text{G}}$. The computed values for both $\text{Li}^{\text{H}}\text{Na}^{\text{G}}$ and $\text{Na}^{\text{H}}\text{Li}^{\text{G}}$ agree with the calculated results from Hultgren and coworkers [29]. We cannot compare the results for possible alloys of $\text{Li}^{\text{H}}\text{K}^{\text{G}}$ and $\text{K}^{\text{H}}\text{Li}^{\text{G}}$ because there are no data from both the experiment and other authors. Experimental data are highly needed for a better comparison for these alloys.

4. CONCLUSIONS

We have simulated Li, Na, and K metals and alloys with a simplified semi-empirical model called the embedded-atom method (EAM). Fittings to the model potential required some physical quantities that are shown in Table 1. The six model parameters required in obtaining a meaningful and efficient EAM model were determined. Some quantities used in the fitting were optimally reproduced. Other properties of the metals and alloys that were not used in fitting of the model potential were computed. The present model is able to describe the surface energy of three low index crystal faces γ_{100} , γ_{110} , and γ_{111} of these metals due to the suitable $F(\rho)$ used in the model. It is somehow difficult to completely compare our calculated values with data from experiment because the experiment did not present the values for different crystal planes. The computed enthalpies of solution for $\text{Li}^{\text{H}}\text{Na}^{\text{G}}$ and $\text{Na}^{\text{H}}\text{Li}^{\text{G}}$ agree with the calculated results from Hultgren and coworkers [29]. We cannot compare the results for possible alloys of $\text{Li}^{\text{H}}\text{K}^{\text{G}}$ and $\text{K}^{\text{H}}\text{Li}^{\text{G}}$ because there are no data from both the experiment and other authors. In general, our computed results are closer to available data from experiment.

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