Divacancy Binding Energy, Formation Energy and Surface Energy of bcc Alkali Metals Using MEAM Potential

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Abstract

The Modified Embedded Atom Method (MEAM) potential parameters have been employed to calculate the unrelaxed divacancy formation energy, binding energy, and surface energies for low-index planes in body-centered cubic (bcc) alkali metals. The calculated divacancy binding energies and vacancy formation energies show good agreement with experimental data and other available computational results.

Keywords: Modified embedded atom method; Phonon dispersions; Formation energy; Divacancy binding energy; Surface energy.
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Introduction

Johnson and Oh [1] presented an analytical EAM model for bcc metals in which the electron density is treated as a decreasing function of distance. The model has been found suitable for bcc alkali and transition metals, except for Cr, due to the negative curvature required for the embedding function. By introducing a few modifications to the Johnson and Oh model [1], Guellil and Adams [2] applied the EAM model to study phonon dispersions, as well as the thermal and surface properties of bcc alkali and transition metals and their alloys. W. Hu *et al.* [3] employed a modified form of the analytical EAM model to investigate various defect-related properties, including interstitial and vacancy formation energies, surface energies, and phonon dispersions. Zhang *et al.* [4] calculated the formation energy of mono-vacancies in bcc metals, along with the binding and formation energies for di- and tri-vacancies.

Cui et al. [5] applied the MEAM model to study the thermal and surface properties of the alkali metal lithium (Li). Yuan *et al.* [6] also conducted a detailed study on bcc Li using the same MEAM model, performing surface energy calculations. In earlier calculations by W. Hu *et al.* [3] on unrelaxed surface and divacancy binding energies, a molecular dynamics approach was used. Most earlier studies on binding and surface energies involved significant computational effort. In recent studies, the MEAM potentials developed by W. Hu *et al.* [3] have been used by Vandana et al. [7, 8] to investigate the vibrational properties of vacancies in bcc transition metals such as Nb, Fe, Mo, and W. Vandana and Semalty [9] further extended this investigation to bcc alkali metals Na and K. Ram P. N. *et al.* [10] also explored the vibrational properties of vacancies in bcc metals.

The aim of the present work is to calculate the unrelaxed divacancy formation, binding, and surface energies of bcc alkali metals using a simplified approach with a minimal set of MEAM potential parameters obtained by Zhang *et al.* [11]. The calculated results show reasonable agreement with some of the earlier reported values.

Method

MEAM Model

In the MEAM model, the total energy is given by:

$$E_t = \sum_i [F(\rho_i) + \frac{1}{2}\sum_{j\neq i} \phi(\mathrm{r_{ij}}) + M(P_i)], \qquad (1)$$

The embedding function $F(\rho)$ and the atomic density $f(r)$are given as:

$$F(\rho) = -F_0[1 - n\ln(\frac{\rho}{\rho_e})](\frac{\rho}{\rho_e})^n , \qquad (2)$$

and

$$f(r) = f_e(\frac{r_1}{r})^\beta \qquad (3)$$

where$F_0 = E_c - E_V$,ρ_e is the equilibrium electron density and$n$is a parameter which can be determine by fitting the empirical energy-volume relationship of Rose *et al.* [12] and β is taken equal to 6.

$$\phi(r) = k_0 + k_1\left(\frac{r}{r_{1e}}\right)^2 + k_2\left(\frac{r}{r_{1e}}\right)^4 + k_3\left(\frac{r}{r_{1e}}\right)^{12} \qquad (4)$$

is the pair potential used for the bcc alkali metals.

The energy modification term is taken as:

$$M(P_i) = \alpha\left(1 - \frac{P}{P_e}\right)^2 \exp[-(\frac{P}{P_e} - 1)^2], \qquad (5)$$

Where α is another adjustable parameter and M(P_i) is the modified embedding function.

In the calculation of Unrelaxed Vacancy formation energy, Binding formation energy and Surface energies, we have considered a MEAM model up to the second neighbors of vacancy. The model parameters α and k_j ($j = 0, 1, 2, 3$) are obtained analytically by fitting to the experimental elastic constants, cohesive energy, formation energy of vacancy.

Unrelaxed Vacancy formation energy

In simple terms, the energy required to create a vacancy in an otherwise perfect lattice is known as the vacancy formation energy. When a vacancy is formed, the atom that would have occupied the vacant site no longer contributes to the charge density at various atomic sites within the lattice.

By including the embedding function and a modification term alongside the pair potential, the monovacancy formation energy can be calculated using the following expression:

$$E_{1V}^F = 8F[\rho_e - f(r_{1e})] + 6F[\rho_e - f(r_{2e})] - [4\phi(r_{1e}) + 3\phi(r_{2e})] - 14F(\rho_e) + 8M[P_e - f^2(r_{1e})] + 6M[P_e - f^2(r_{2e})] - 14M(P_e). \qquad (6)$$

After the formation of a divacancy, 14 atoms lose one of their first nearest neighbors, and 12 atoms lose one of their second nearest neighbors. In total, 26 atoms are affected in the second-neighbor model.

The divacancy formation energy E_{2V}^F at the first-neighbor distance is calculated using the following expression:

$$E_{2V}^F = 14F[\rho_e - f(r_{1e})] + 12F[\rho_e - f(r_{2e})] - 26F(\rho_e) - [8\phi(r_{1e}) + 6\phi(r_{1e})] + \phi(r_{1e}) + 14M[P_e - f^2(r_{1e})] + 12M[P_e - f^2(r_{2e})] - 26M(P_e) \qquad (7)$$

In the case of a divacancy at the second-neighbor distance, the formation of the divacancy results in 8 atoms losing one of their first nearest neighbors, 4 atoms losing two of their second nearest neighbors, and 10 atoms losing one of their second nearest neighbors. Thus, a total of 22 atoms are affected.

Therefore, the divacancy formation energy E_{2V}^F, including the contributions from the embedding and modified embedding energy terms at the second-neighbour distance, is calculated using the following expression:

$$E_{2V}^F = 8F[\rho_e - f(r_{1e})] + 4F[\rho_e - 2f(r_{2e})] + 10F[\rho_e - f(r_{2e})] - 22F(\rho_e) - [8\phi(r_{1e}) + 6\phi(r_{1e})] + \phi(r_{1e}) + 8M[P_e - f^2(r_{1e})] + 4M[P_e - 2f^2(r_{2e})] + 10M[P_e - f^2(r_{2e})] - 22M(P_e) \qquad (8)$$

where r_{1e} and r_{2e} are first neighbour and second neighbour equilibrium distances.
One way to test the suitability of MEAM potentials is to use them for calculating properties that were not included in the fitting process. Accordingly, we have employed the MEAM potential parameters to calculate the unrelaxed binding energy E_{2V}^B of seven transition metals. The unrelaxed binding energy of a divacancy is given by:

$$E_{2V}^B = 2E_{1V}^F - E_{2V}^F \qquad (9)$$

where, E_{1V}^F andE_{2V}^F are the formation energy of monovacancy and divacancy.

The unrelaxed binding energy of divacancy at first neighbour distance is given by:

$$E_{2V}^B = 2F[\rho_e - f(r_{1e})] - 2F(\rho_e) - \phi(r_{1e}) + 2M[P_e - f^2(r_{1e})] - 2M(P_e) \qquad (10)$$

The unrelaxed binding energy of divacancy at second neighbour distance is given by:

$$E_{2V}^B = 8F[\rho_e - f(r_{1e})] - 4F[\rho_e - 2f(r_{2e})] + 2F[\rho_e - f(r_{2e})] - 6F(\rho_e) - \phi(r_{1e}) + 8M[P_e - f^2(r_{1e})] - 4F[\rho_e - 2f(r_{2e})] + 2M[\rho_e - f(r_{2e})] - 6M(P_e) \qquad (11)$$

Unrelaxed Surface Energy

In solid-state physics, surfaces are intrinsically less energetically favorable than the bulk of a material. This is because atoms or molecules at the surface experience fewer bonding interactions, resulting in higher energy compared to those in the bulk. If surface atoms were more stable than bulk atoms, there would be a natural driving force for surfaces to form spontaneously, ultimately leading to the disappearance of the bulk material.

Surface energy can thus be defined as the excess energy at the surface of a material relative to the bulk. The unrelaxed surface energy for three low-index planes is given by:

$$S_{100} = \frac{1}{a^2}[\Delta E_{1}^{100} + \Delta E_{2}^{100}] \qquad (12)$$

$$S_{110} = \frac{\sqrt{2}}{a^2}[\Delta E_{1}^{110} + \Delta E_{2}^{110}] \qquad (13)$$

$$S_{111} = \frac{1}{\sqrt{3}a^2}[\Delta E_{1}^{111} + \Delta E_{2}^{111}] \qquad (14)$$

where ΔE_{1} is contribution due the change in embedded and modified embedded energy term and ΔE_{2} is the contribution due to change in pair potential part and are given as under:

$$\Delta E_{1}^{100} = F[\rho_e - 4f(r_{1e}) - f(r_{2e})] + F[\rho_e - f(r_{2e})] - 2F[\rho_e] + M[P_e - 4f^2(r_{1e}) - f(r_{2e})]$$
$$+M[P_e - f^2(r_{2e})] - 2M[P_e] \qquad (15)$$

$$\Delta E_{2}^{100} = -2\phi(r_{1e}) - \phi(r_{2e}). \qquad (16)$$

$$\Delta E_{1}^{110} = F[\rho_e - f(r_{1e}) - 2f(r_{2e})] - F[\rho_e] + M[P_e - f^2(r_{1e}) - 2f^2(r_{2e})] - M[P_e], \qquad (17)$$

$$\Delta E_{2}^{110} = -\phi(r_{1e}) - \phi(r_{2e}), \qquad (18)$$

and

$$\Delta E_{1}^{111} = F[\rho_e - 4f(r_{1e}) - 3f(r_{2e})] - F[\rho_e] + M[P_e - 4f^2(r_{1e}) - 3f^2(r_{2e})] - M[P_e], \qquad (19)$$

and

$$\Delta E_{2}^{111} = -2\phi(r_{1e}) - \frac{3}{2}\phi(r_{2e}). \qquad (20)$$

Results and Discussions

For the calculation of unrelaxed vacancy formation, binding, and surface energies, the necessary MEAM potential parameters for all bcc alkali metals (Li, Na, K, Rb, and Cs) are adopted from Zhang *et al.* [11]. The monovacancy and divacancy formation energies are computed using Eqs. (6) and (7), while the unrelaxed divacancy binding energies for both first-neighbor and second-neighbor configurations are calculated using Eqs. (6-11).

As an additional application of the MEAM parameters, the unrelaxed surface energies for three low-index surfaces (100), (110), and (111) are evaluated using the expressions provided in Equations (12-14).

For the bcc alkali metals, the calculated values of unrelaxed divacancy binding energies, monovacancy and divacancy formation energies, and surface energies for the (100), (110), and (111) planes are presented in Table 1 and Table 2, along with available experimental data and other theoretical results.

Unrelaxed Vacancy formation energy and Divacancy binding energy in bcc alkali Metals

Table 1: Calculated values (underlined) of unrelaxedmono vacancy formation energy$\boldsymbol{E_{1V}^{F}}$, first and second neighbor divacancy formation energy$\boldsymbol{E_{2V}^{F}}$, first and second neighbour divacancy binding energy$\boldsymbol{E_{2V}^{B}}$for bcc alkali metals along with other results.

	Li	**Na**	**K**	**Rb**	**Cs**
Cal $E_{1V}^{F}(eV)$ **Exp**	0.3446 0.48^{a} 0.34^{b} 0.34^{e}	0.3324 0.3408^{a} 0.42^{b} 0.34^{e}	0.3440 0.3413^{a} 0.42^{b} 0.34^{e}	0.3406 0.3420^{a} ------- 0.341^{e}	0.3184 0.3249^{a} ------- 0.322^{e}
at r_{1e} $E_{2V}^{F}(eV)$ **at r_{2e}**	0.638 0.761^{c} 0.89^{d} 0.893^{a}	0.615 0.665^{c} 0.631^{d} 0.6333^{a}	0.637 0.665^{c} 0.63^{d} 0.6342^{a}	0.631 0.628^{c} 0.632^{d} 0.6354^{a}	0.589 0.592^{c} 0.598^{d} 0.6037^{a}
	0.645 0.77^{c} 0.89^{d} 0.8931^{a}	0.622 0.673^{c} 0.632^{d} 0.6333^{a}	0.644 0.673^{c} 0.633^{d} 0.6344^{a}	0.637 0.636^{c} 0.634^{d} 0.6355^{a}	0.594 0.599^{c} 0.599^{d} 0.6038^{a}
at r_{1e} $E_{2V}^{B}(eV)$ **at r_{2e}**	0.0514 0.067^{c} 0.069^{d} 0.0684^{a}	0.0494 0.049^{d} 0.04837 0.055^{c}	0.0515 0.055^{c} 0.049^{d} 0.0484^{a}	0.0504 0.052^{d} 0.0486^{a} 0.052^{c}	0.048 0.048^{c} 0.047^{d} 0.0461^{a}
	0.045 0.057^{c} 0.068^{d} 0.0683^{a}	0.043 0.047^{c} 0.048^{d} 0.0483^{a}	0.044 0.047^{d} 0.047^{d} 0.0482^{a}	0.044 0.044^{c} 0.047^{d} 0.0485^{a}	0.043 0.041^{c} 0.045^{d} 0.0460^{a}

Superscripts ^{a,b,c,d} and ^{e} used with data in Table (1) are ref. [4], [2], [13], [14] and [11] respectively.

From our calculations, we find that among the bcc alkali metals, lithium (Li) exhibits the highest monovacancy formation energy, whereas Caesium (Cs) shows the lowest. In general, there is a clear correlation between vacancy formation energy and atomic number: the formation energy tends to decrease with increasing atomic number of the alkali metals, with the exception of potassium (K), which deviates from this trend.

When comparing our calculated results with other available theoretical data, we observe that our unrelaxed vacancy formation energies are in good agreement with those reported by Zhang *et al.* [4], except for Li. In contrast, our results for Li show very good agreement with those obtained by Guellil and Adams [2], compared to the other alkali metals. The experimental values of vacancy formation energy cited by Zhang *et al.* [11] are also found to align closely with our calculated values.

The calculated values of unrelaxed divacancy binding and formation energies, along with earlier reported results, are presented in Table 1. Upon comparison, we find that our values for divacancy formation and binding energies are generally in good agreement with those reported by Hu *et al.* [13], Zhang *et al.* [4], and Ouyang *et al.* [14], except for Li. For lithium, our calculated values are lower than those reported in these studies. However, our results are higher than the earlier pseudopotential calculations of Takai and Doyama [15].

The MEAM model predicts that divacancies are more strongly bound and more stable at the first-neighbor distance compared to the second-neighbor configuration. In the present work, we have neglected relaxation effects in the calculation of divacancy formation and binding energies, primarily due to the significant computational resources required to include these effects. Nonetheless, previous work by Hu and Masahiro [13] indicates that the relaxation effect is relatively small for second-neighbor configurations compared to first-neighbor ones.

The determination of lattice relaxation at a metal surface is influenced by the degree of electron screening of the ionic cores. Therefore, we expect that surface energy calculations are sensitive to the exact form of the three-dimensional electron density profile. A similar consideration applies to the determination of the phonon contribution to the temperature dependence of surface energy.

Unrelaxed Surface energy of bcc alkali metals

The calculated unrelaxed surface energies for the three low-index planes are presented in Table 2. Our calculated results of unrelaxed surface energies are seen to be in an increasing order: S_{111}, S_{110}, S_{100}, i.e., highest for S_{100} and lowest for S_{111}. A similar variation in surface energies was also reported by Rose and Dobson [18], as expected from bond-breaking arguments, which suggest that the denser crystal face possesses lower surface energy.

It is also observed that our calculated surface energies are generally lower than those obtained from other theoretical studies [2,11,13] and experimentally measured values [16, 17]. The discrepancy between calculated and experimental results can be attributed to the fact that experimental values often represent averaged measurements over multiple crystal orientations in bulk samples. Additionally, experimental values, typically extrapolated to 0 K, do not always account for surface orientation-specific energies.

Table 2: Calculated values (underlined) of unrelaxed surface energies S_{100}, S_{110} and $S_{111}$for bcc alkali metals along with other results.

	Li	**Na**	**K**	**Rb**	**Cs**
S_{100} (erg/cm^2)	199 269^e 215^f 282^g	133 133^e 138^f 154^g	86 83^e 92^f 97^g	74 73^e 77^f -------	58 59^e 63^f -------
S_{110} (erg/cm^2)	182 252^e 203^f 231^g	122 124^e 127^f 138^g	79 78^e 83^f 88^g	68 68^e 69^f -------	54 56^e 56^f -------
S_{111} (erg/cm^2)	133 310^e 264^f	89 153^e 162^f	58 96^e 106^f	50 83^e 88^f	39 68^e 72^f
S_{avg} (erg/cm^2)	472^h 525^i	234^h 260^i	129^h 130^i	104^h 110^i	84^h 95^i

Superscripts $^{e,\,f,\,g,\,h}$ and ^{i} used with data in Table (2) are ref. [11], [13], [2], [16] and [17] respectively.

However, using Tyson's simple model of the "*population density factor*," Tyson and Miller [16] demonstrated that it is possible to estimate the surface energy of a specific crystallographic face from a generalized "average" surface energy. This reinforces the idea that our face-specific MEAM-based calculations provide valuable insight despite the apparent differences with bulk-averaged experimental data.

Conclusions

In this study, the unrelaxed vacancy formation energy, divacancy formation and binding energies, and low-index surface energies for bcc alkali metals have been calculated using MEAM potential parameters.

Our results for unrelaxed monovacancy formation energy show excellent agreement with available experimental data for alkali metals. Additionally, the calculated mono- and divacancy formation energies are in good agreement with previously reported theoretical studies. A clear correlation is observed between vacancy formation energy and the atomic number of the alkali metals: the energy generally decreases with increasing atomic number, except for potassium (K), which deviates from the trend. This correlation also parallels the variation in cohesive energy Ec across the series.

We have also evaluated the divacancy binding energies for bcc alkali metals and found that our results are consistent with both experimental observations and earlier theoretical work. The calculated binding energies suggest that divacancies are more stable in the first-neighbor configuration compared to the second-neighbor configuration.

Overall, our findings are consistent with expected trends and show good agreement with experimental and other theoretical studies, further validating the applicability of MEAM potentials for defect and surface property calculations in bcc alkali metals.

References

1. Johnson R.A., Oh D.J. (1989). *Analytic embedded atom method model for bcc metals*. J. Mater. Res.**4**, 1195–1201.
2. Guellil A.M., Adams J.B. (1992). *The application of the analytic embedded atom method to bcc metals and alloys*. J. Mater. Res.**7**(3), 639–652.
3. Hu W., Shu X., Zhang B. (2002). *Point-defect properties in body-centered cubic transition metals with analytic EAM interatomic potentials*. Comput. Mater. Sci.**23**, 175–189.
4. Zhang J.M., Wen Y.N., Xu K.W. (2006). *Atomic simulation of the vacancies in BCC metals with MAEAM*. Central European Journal of Physics**4**, 481–493.
5. Cui Z., Gao F., Cui Z., Qu J. (2012). *Developing a second nearest-neighbor modified embedded atom method interatomic potential for lithium*. Modelling Simul. Mater. Sci. Eng.**20**(1), 015014.
6. Yuan X., Takahashi K., Yin Y., Onzawa T. (2003). *Development of modified embedded atom method for a bcc metal: lithium. Modelling Simul. Mater*. Sci. Eng.**11**, 447–456.
7. Gairola V., Semalty P.D., Ram P.N. (2013). *Vibrational properties of vacancy in bcc transition metals using embedded atom method potentials*. Pramana – J. Phys.**80**, 1041–1050.
8. Gairola V., Semalty P.D., Ram P.N. (2014). *Vibrational properties of vacancy in bcc Nb using embedded atom method*. Indian J. Phys.**88**, 171–176.
9. Gairola V., Semalty P.D. (2014). *Vibrational Properties of Vacancy in Na and K Using MEAM Potential. Commun*. Comput. Phys.**15**, 556–568.
10. Ram P.N., Gairola V., Semalty P.D. (2016). *Vibrational properties of vacancy in Au using modified embedded atom method potentials*. J. Phys. Chem. Solids**94**, 41–46.
11. Zhang J.M., Wen Y.N., Xu K.W. (2008). *MAEAM Investigation of Phonons for Alkali Metals*. J. Low Temp. Phys.**150**, 730–738.
12. Rose J.H., Smith J.R., Guinea F., Ferrante J. (1984). *Universal features of the equation of state of metals*. Phys. Rev. B**29**, 2963–2969.
13. Hu W., Masahiro F. (2002). *The application of the analytic embedded atom potentials to alkali metals*. Modelling Simul. Mater. Sci. Eng.**10**(6), 707–718.
14. Ouyang Y., Zhang B., Liao S. (1994). *Vacancies in metals*. Sci. China A**24**, 834–839.
15. Takai O., Doyama M. (1987). *Interactions between point defects and migration energies of trivacancies in metals*. Mater. Sci. Forum**15–18**, 161–168.
16. Tyson W.R., Miller W.A. (1977). *Surface free energies of solid metals: Estimation from liquid surface tension measurements.*Surf. Sci.**62**(1), 267–276.
17. De Boer F.R. (1988). *Cohesion in Metals: Transition Metal Alloys*. North-Holland, Amsterdam.
18. Rose J.H., Dobson J.F. (1981). *Face dependent surface energies of simple metals*. Solid State Commun.**37**(2), 91–96.