

Vibrational Properties of Vacancy in Na and K Using MEAM Potential

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Abstract. The modified embedded atom method (MEAM) with the universal form of embedding function and a modified energy term along with the pair potential has been employed to determine the potentials for alkali metals: Na, K, by fitting to the Cauchy pressure $(C_{12} - C_{44})/2$, shear constants $G_v = (C_{11} - C_{12} + 3C_{44})/5$ and C_{44} , the cohesive energy and the vacancy formation energy. The obtained potentials are used to calculate the phonon dispersions of these metals. Using these calculated phonons we evaluate the local density of states of neighbours of vacancy using Green's function method. The local density of states of neighbours of vacancy has been used to calculate mean square displacements of these atoms and formation entropy of vacancy. The calculated mean square displacements of both 1st and 2nd neighbours of vacancy are found to be lower than that of host atom. The calculated phonon dispersions agree well with the experimental phonon dispersion curves and the calculated results of vacancy formation entropy compare well with the other available results.

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Key words: Embedded atom method (EAM), modified embedded atom method (MEAM), Green's function, force-constants, vacancy, phonon dispersion, local density of states, mean square displacement, formation entropy.

1 Introduction

Daw and Baskes [1,2] have derived so-called embedded atom method (EAM) on the basis of quasi atom concept and density functional theory, which has been widely used in computer simulation studies of various defects. Adams and Foiles [3] developed a model for bcc metal V (Vanadium) with the Morse form as pair potential between atoms; this

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model was successfully applied to calculate many-body potentials. Johnson and Oh [4] have presented an analytic EAM model for bcc metals in which electron density is taken as a decreasing function of the distance. The model has been found to be suitable for bcc alkali and transition metals except for Cr because of negative curvature required for embedding function. By introducing a few modifications in the Johnson and Oh model [4], Guellil and Adams [5] have applied the EAM Model in the study of alkali and transition metals and their alloys. These authors have studied the phonon dispersions along with the thermal and surface properties of these metals and alloys. An analytical embedded atom method for bcc transition metals including Cr was developed by Ouyang et al. [6]. In order to fit the negative Cauchy pressure an analytic modified term was introduced. The model has been successfully applied to study the dilute solution enthalpy and formation enthalpy of binary alloys of some transition metals.

Hu et al. [7] have employed the modified form of analytical EAM model proposed by Zhang et al. [8] by including the three contributions to the total energy term. The potential parameters were fitted to bulk properties such as cohesive energy, vacancy formation energy, elastic constants and lattice constants. This model is applied to investigate various properties of defects including interstitial formation energy and vacancy formation energy, surface energy and the obtained potentials were used to calculate phonon dispersion, which were agreed well with the experimental results.

The applications of the Analytic embedded atom method (AEAM) potentials in the alkali metals have been discussed by Hu & Masahiro [9] and the phonon dispersion, density of states, Debye temperature, heat capacity, surface energy and thermal expansion properties of these metals have been calculated. In addition, the properties of point defects; such as vacancy, divacancy, self-interstitials have also been calculated by these authors. Zhang et al. [10] have performed the calculation of the formation energy of mono vacancy of bcc metals including the alkali metals and both the binding and formation energies for di and tri-vacancy of these metals. In another study [11], these authors have calculated the phonon dispersions for five alkali metals: Li, Na, K, Rb and Cs using the modified embedded atom potentials and found their results in agreement with the experimental results. In all the above studies, various properties of bcc metals, their alloys and properties of point defects were investigated using embedded atom method (EAM) but none of the them have specifically investigated the vibrational and thermal properties of vacancies in metals including local density of states, formation entropy of vacancy and mean square thermal displacement. As regards the vibrational properties of crystal with point defects, a preliminary investigation of self-interstitials has been made by Pohlong and Ram [12]. The MEAM has widely been used to obtain the potentials for different metals and these potentials have been employed to calculate different properties of metals including static properties of point defect such as: formation energies of vacancy, interstitial and surface energy. However, the MEAM has hardly been used in the study of dynamics of point defects in metals. In view of the limited work in the study of the vibrational behaviour of point defects in bcc metals; in our present work we present the calculation of the vibrational properties of vacancies in Na and K using MEAM.

In the present study we have followed the MEAM potential of Hu & Masahiro [9] proposed by Zhang et al. [10] and obtained the MEAM potential parameters for Na and K employing a 2nd neighbour model. The parameters are determined by fitting the Cauchy pressure, shear modulus G_v , C_{44} , cohesive energy and the vacancy formation energy. The obtained potential parameters are used to discuss the lattice dynamics: phonon dispersion of pure metals, local density of pure and nearest neighbours of vacancy up to 2nd neighbours. The total energy of perfect and defect crystal have been calculated using MEAM potentials and from the expression of total energy the force-constants in the perfect as well as crystal with vacancy and thereby force-constant changes around vacancy are obtained. The obtained force-constants in the perfect crystal have been used to obtain the phonons which are used for Green's function calculations. The force-constant changes are utilized to calculate the local density of states with the Green's function method and further local density of states is used to obtain the vacancy formation entropy and mean square displacements of nearest neighbour atoms of vacancy. The calculated results are found to be in agreement with the available experimental measurements for the Na, K.

2 Theory

2.1 MEAM model

In the MEAM model, a modifying term was introduced in the expression of total energy to resolve the problem of negative Cauchy pressure in Johnson's model [4]. This term describes the energy change due to the non-spherical distribution of the electron density ρ_i and deviation from the linear superposition of atomic electronic density. The modified energy term is a function of the argument P_i , which is represented as the sum of second-order of electron density to correct the assumption of the linear superposition of atomic electron density in the original EAM.

In the MEAM model [9] the contribution to the total energy of an atom at the site i is given by:

$$E_i = F(\rho_i) + \frac{1}{2} \sum_{j \neq i} j \phi(r_{ij}) + M(P_i). \quad (2.1)$$

The total energy of the system is represented as:

$$E_{tot} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{j \neq i} i, j \phi(r_{ij}) + \sum_i M(P_i), \quad (2.2)$$

where $\rho_i = \sum_{j(j \neq i)} f_j(r_{ij})$ and $P_i = \sum_{j(j \neq i)} f_j^2(r_{ij})$.

The embedding function $F(\rho)$ and the atomic density $f(r)$ are taken of the form [4] as:

$$F(\rho) = - \left[F_0 - \gamma \ln \left(\frac{\rho}{\rho_e} \right) \right] \left(\frac{\rho}{\rho_e} \right)^n \quad (2.3)$$

and

$$f(r) = f_e \left(\frac{r_1}{r} \right)^\beta, \quad (2.4)$$

where F_0 and γ are the model parameters, ρ_e is the equilibrium electron density and n is an adjustable parameter which can be determined by fitting the empirical energy-volume relationship of Rose et al. [13] and r_1 is the equilibrium first-nearest neighbour distance, β is equal to 6 and f_e is taken as unity [9].

The energy modification term is empirically taken as:

$$M(P) = \alpha \left(1 - \frac{P}{P_e} \right)^2 \exp \left[- \left(\frac{P}{P_e} - 1 \right)^2 \right]. \quad (2.5)$$

The pair-potential function [9] is of the form:

$$\phi(r) = \sum_{j=-1}^3 k_j \left(\frac{r}{r_1} \right)^j. \quad (2.6)$$

In this MEAM model, the atomic interactions up to the second-neighbours distances are considered and both $\phi(r)$ and $f(r)$ are truncated between the second and third-neighbour distances.

The elastic constants are calculated using the second derivative of total energy, i.e., the MEAM potential. The model parameters α and k_j ($j = -1, 0, 1, 2, 3$) are also obtained analytically by fitting to the experimental elastic constants, cohesive energy, formation energy of vacancy. In this calculation the cut-off distance is taken between 2nd and 3rd neighbours therefore, pair potential and embedded part including the modified term are calculated taking only up to the second neighbours of vacancy.

With the inclusion of embedding function and a modified term with the pair potential the vacancy formation energy is given by:

$$E_{1V}^F = 8F[\rho_e - f(r_{1e})] + 6F[\rho_e - f(r_{2e})] - 14F(\rho_e) \\ + 8M[P_e - f^2(r_{1e})] + 6M[P_e - f^2(r_{2e})] - 14M(P_e). \quad (2.7)$$

As an application of these potentials, we have calculated phonons in metals: Na & K. The phonon spectra were calculated as usual by diagonalizing the dynamical matrix obtained from the Fourier transform of the force-constant tensor $\phi_{ij}(l, m)$, and the force-constants are derived from the energy expression Eq. (2.1) in a straightforward manner as:

$$\phi_{ij}(l, m) = \frac{\partial^2 E_{tot}}{\partial r_l^i \partial r_m^j}, \quad (2.8)$$

where l, m are the labels of the atoms. The force-constant corresponding to the total en-

ergy given by Eq. (2.2) and Eq. (2.8), with $l \neq m$,

$$\begin{aligned} \frac{\partial^2 E_{tot}}{\partial r_l^i \partial r_m^j} = & - \left[\phi''(r_{lm}) - \frac{\phi'(r_{lm})}{r_{lm}} \right] \frac{r_{lm}^i r_{lm}^j}{r_{lm}^2} - \delta_{ij} \frac{\phi'(r_{lm})}{r_{lm}} + \sum_{n \neq l, m} F''(\rho_n) f'(r_{ln}) f'(r_{mn}) \frac{r_{ln}^i r_{mn}^j}{r_{ln} r_{mn}} \\ & + 4 \sum_{n \neq l, m} M''(P_n) f'(r_{ln}) f(r_{ln}) f'(r_{mn}) f(r_{mn}) \frac{r_{ln}^i r_{mn}^j}{r_{ln} r_{mn}}, \end{aligned} \quad (2.9)$$

where i, j are Cartesian components and ϕ' , ϕ'' are first and second derivatives of the pair-potential.

2.2 Local density of states

For the calculation of the local density of states of the neighbours of a vacancy we have used the Green's function method of Ram [14]. The local density of states can be expressed in terms of the Green's function of the defect lattice. The vacancy is taken at the origin and its interaction with its neighbours is modelled by missing springs to these atoms which are then relaxed to new positions. This results in the change in the force-constants between neighbouring atoms. The remaining atoms of the host crystal beyond 2nd neighbours are assumed to be unperturbed.

The Green's function G for the defect lattice in terms of the ideal lattice Green's function G^0 as is given by:

$$G(\omega) = G^0(\omega) [1 + V(\omega)G^0(\omega)]^{-1}, \quad (2.10)$$

where

$$V(\omega) = \Delta\phi + M^0\omega^2 \quad \text{and} \quad \Delta\phi = \phi - \phi^0. \quad (2.11)$$

ϕ is the force-constant in a relaxed lattice and ϕ^0 that of the ideal lattice, and M^0 is the mass of the host atom. The Green's function $G(\omega)$ is used to obtain the local density of states of an atom l in the α direction in the defect lattice as:

$$Z_\alpha(l, \omega) = \frac{2\omega M}{\pi} \text{Im} G_{\alpha\alpha}(l, l; \omega). \quad (2.12)$$

The local density of states provides an elegant way to discuss those properties of the solids which do not depend on the atom-atom correlation in the lattice. All the thermodynamic properties of the crystal can be expressed in terms of the local spectra of the atoms. The local density of states is particularly useful in those situations where a defect mode, resonant or localized mode, is dominated by the vibration of the defect only: Since, then, such modes are easily identified as resonant-type peaks in the local spectrum of the defect.

2.3 Formation entropy and mean square thermal displacement

The production of a vacancy increases the entropy of the crystal and this increase in entropy is known as the vacancy-formation entropy. The vacancy formation entropy is closely related to the local density of states of neighbours of the vacancy. The formation entropy of the vacancy may be calculated in terms of the change in the frequency spectrum in the presence of the vacancy. The vibrational contribution to the entropy is given by [14]:

$$S = k \int_0^{\infty} \sigma(\omega, T) Z(\omega) d\omega, \quad (2.13)$$

where $Z(\omega)$ is the total frequency spectrum. Whereas the formation entropy is given by:

$$S_{1V}^F = k \int_0^{\infty} \sigma(\omega, T) \Delta Z(\omega) d\omega, \quad (2.14)$$

where $\Delta Z(\omega)$ is the change in frequency spectrum due to a single vacancy.

The change in the frequency spectrum can be expressed in terms of difference between local frequency spectra of atoms in a defective and ideal lattice:

$$S_{1V}^F = k \int_0^{\infty} \sigma(\omega, T) \sigma_l [Z(l, \omega) - Z^0(l, \omega)] d\omega. \quad (2.15)$$

For a weakly perturbing defect like the vacancy we expect the local frequency spectra of only a few neighbouring atoms to be significantly different from that of the host spectrum.

The mean square thermal displacement of the atom can be calculated by using the frequency spectrum $Z(\omega)$:

$$\langle U^2 \rangle = \int \frac{Z(\omega)}{2M\omega} \coth \left[\frac{\hbar\omega}{2kT} \right] d\omega. \quad (2.16)$$

3 Results and discussions

3.1 Determination of potential parameters, effective pair potential and embedding functions

In order to determine the MEAM potential, the input parameters are listed in Table 1, the parameters are determined by fitting the Cauchy pressure, shear modulus $G(V)$ and C_{44} , the cohesive energy and the vacancy formation energy. The best fit to C_{44} and E_{1V}^F ultimately determines the final choice of these parameters, which are then utilized to calculate C_{11} and C_{12} .

The fitted elastic constants and formation energy are presented in Table 1. The model parameters F_0, γ, α and k_j ($j = -1, 0, 1, 2, 3$) are obtained analytically by fitting to the experimental elastic constants, cohesive energy, formation energy of vacancy. The

Table 1: Input (experimental) data: Lattice constant $a(\text{\AA})$, cohesive energy E_c (eV), vacancy formation energy E_v (eV) and elastic constants 10^{12} dyn/cm^2 .

	Na	K
a	4.225 [9]	5.225 [9]
E_c	1.113 [9]	0.934 [9]
C_{11}	0.116	0.0432
C_{11}	0.0736 [15]	0.0448 [15]
C_{12}	0.061	0.0341
C_{12}	0.0624 [15]	0.0368 [15]
C_{44}	0.041	0.0198
C_{44}	0.0416 [15]	0.0256 [15]
E_v	0.345	0.33
E_v	0.34 [16]	0.34 [17]

Table 2: The MEAM model parameters for metals: Na & K.

	Na	K
$\alpha(eV) \times 10^{-6}$	7.6648	0.9637
$\gamma(eV)$	0.577	0.454
$F_0(eV)$	0.332	0.237
$K_1(eV)$	7.90187	8.92967
$K_2(eV)$	-3.74485	-4.14300
$K_3(eV)$	0.63419	0.69202
$K_{-1}(eV)$	1.9348	2.4436
$K_0(eV)$	-6.86288	-8.04281
n	0.1302	0.154

model parameters calculated from the input parameters and the adjustable parameters are listed in Table 2. The experimental values of elastic constants for Na and K are taken from [15], the values of cohesive energy and lattice parameter are taken from [9], vacancy formation energy for Na is from Fader et al. [16] and for K it is from Mc Donald et al. [17]. The electron density parameter β is taken as 6 for both metals. The calculated values of C_{11} , C_{12} , C_{44} and E_{1V}^F along with the experimental values are presented in Table 1. The effective two-body pair potentials for Na and K with MEAM model are presented in Fig. 1. The embedding functions for these metals are shown in Fig. 2. The modified energy functions for Na and K are shown in Fig. 3.

3.2 Phonon dispersion curves

To test the ability of the potential parameters obtained from MEAM model, we have calculated the phonon dispersion by obtaining the force constants for both perfect and

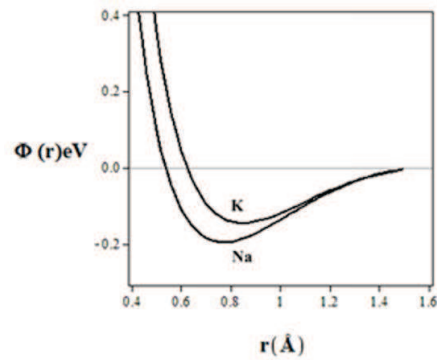


Figure 1: Effective pair-potential for Na and K.

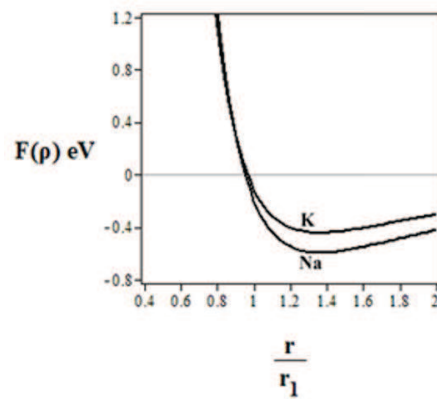


Figure 2: Embedding function for Na and K.

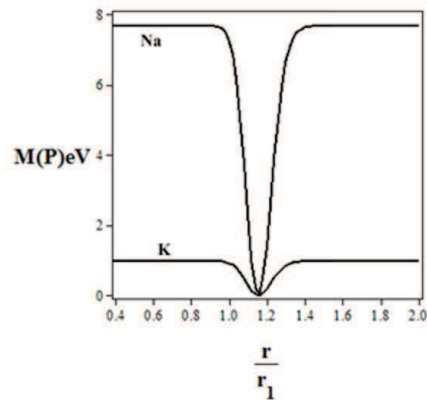


Figure 3: Modified energy function for Na and K.

defect crystals using this model. The dispersion curves for both of the metals: Na, K have been calculated using MEAM potential and compared our results with experimental phonons [18, 19] fitted to the Born-Von Karman force model. The calculated phonon

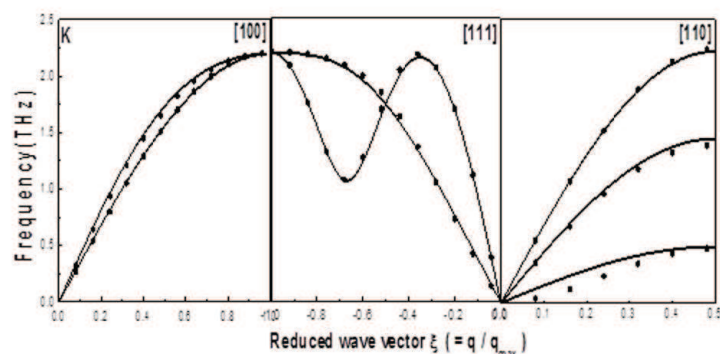


Figure 4: Phonon dispersion curves for K. The solid curve: calculated results with MEAM potential and the points are the experimental data.

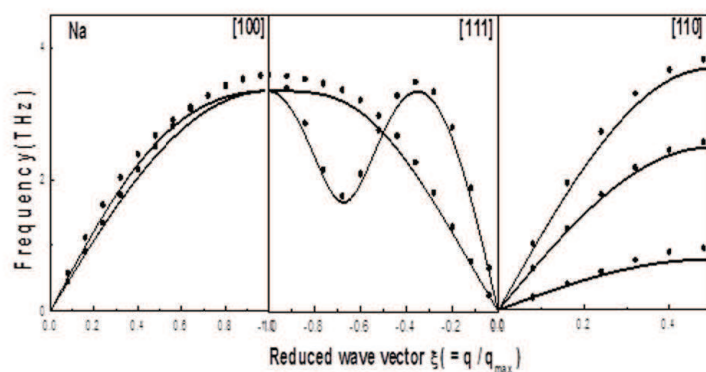


Figure 5: Phonon dispersion curves for Na. The solid curve: calculated results with MEAM potential and the points are the experimental data.

dispersions for Na, K using MEAM potentials in the (100), (110), (111) directions are presented in Figs. 4-5 along with the experimental phonons, the agreement with the experimental phonons is excellent in the case of K, whereas it is reasonably good for Na as compared with the results of Hu [9].

3.3 Calculation of local-density of states

We have calculated the local density of states of the neighbours of the vacancies in metals: Na, K with the Green's function method. To calculate the local density of states of atoms near a vacancy we have evaluated the force-constants in the vicinity of the vacant site and for ideal lattice. In the present work the ideal lattice Green's function G^0 for metals: Na, K, have been calculated using force-constants based on the MEAM potential. For the calculation of matrix elements of force constants ϕ in a relaxed lattice, the static displacements of first and second neighbours of the vacancy for Na, K are taken from the molecular dynamics calculation of Flocken and Hardy [20], which gives inward displace-

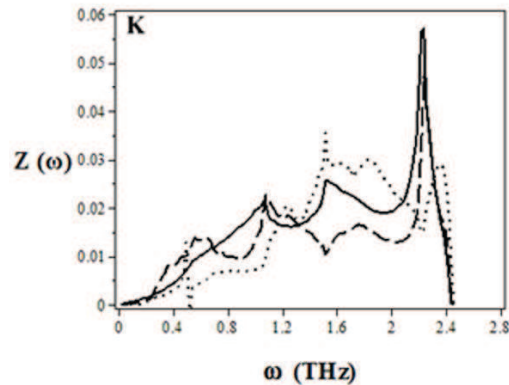


Figure 6: Local density of 1st neighbours (...), 2nd neighbours (---) of vacancy and solid curve of host K atom.

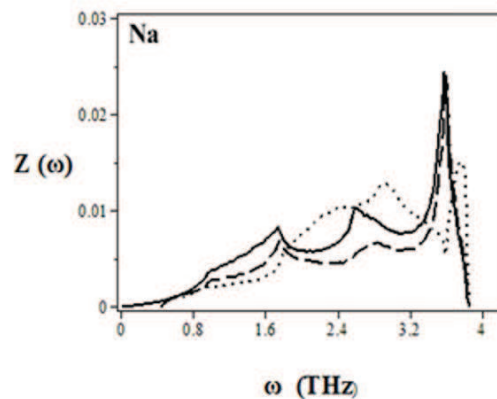


Figure 7: Local density of 1st neighbours (...), 2nd neighbours (---) of vacancy and solid curve of host Na atom.

ments of first neighbour and outward displacement of second neighbour away from the vacant site along the coordinate axes. The atoms falling in the cluster of first and second neighbours of the vacant site take-up the new equilibrium positions and other atoms beyond the second neighbours are considered to be in their perfect lattice positions. With new equilibrium positions of atoms in the defect space, we have new distances between the atoms. Using the MEAM potential, the force constants are calculated at the new equilibrium interatomic distances.

The local density of states of the neighbours of the vacancy in Na, K has been calculated using Eq. (2.12) for relaxed lattice using MEAM potential along with the local density of host atoms (atoms in pure crystal) using experimental phonons. In the relaxed lattice a significant change in the local density of states of the nearest neighbours of the vacancy as compared to that of the host lattice is expected. As shown in Figs. 6-7, for the 1st and 2nd neighbours of vacancy in the defective lattice of Na and K, there is an overall decrease in the frequency spectrum. In the case of K there is a small increase in the local

density of states in the mid region of frequency and shift towards higher frequency for 1st neighbours of vacancy and for the 2nd neighbours, there is a decrease towards higher frequency and a shift towards the lower frequency. For Na, there is a slight increase in the frequency spectrum in the mid region for the 1st neighbours of vacancy and for 2nd neighbours there is a small decrease in frequency spectrum but not much different from that of host atoms. This behaviour can be explained by the loss of coupling between the vacancy and the neighbouring atoms and as a result of relaxations of 1st and 2nd neighbours of vacancy in opposite directions.

3.4 Calculation of vacancy formation entropy and mean square thermal displacement

The obtained results of change in the local density of states between relaxed and ideal lattice are used to calculate the vacancy formation entropy S_{1V}^F using Eq. (2.15) in both the metals. There have been few calculations on the vacancy formation entropy of bcc metals giving different results. It seems that, the effect of relaxation of lattice in the presence of vacancy very much depends on the choice of potential. Burton [21] has reported values of S_{1V}^F ($2.2-2.6k_B$) for all bcc metals based on the empirical relation between formation entropy and lattice relaxation due to vacancy using Morse potential. Schober et al. [22] have predicted the value vacancy formation entropy $S_{1V}^F \sim 1.8k_B$ for all bcc metals. Our calculated vacancy formation entropy S_{1V}^F ($3.05k_B$) for K is somewhat higher than ($2.53k_B$) obtained by Burton [21] whereas for Na our value ($2.27k_B$) agrees very well with that of value of Burton ($2.25k_B$). Pohlong and Ram [14] in their study of vibrational density of states of neighbours of vacancy in bcc transition metals have observed that the effect of relaxation in the presence of vacancy is different for different metals. In our calculation also, we have found that the behaviour of local density of states at lower frequencies and the calculated values of vacancy formation entropy varies differently for K and Na. The change in the formation entropy closely related to the local density of states Eqs. (2.14)-(2.15). As shown in Fig. 6, the shift of the spectrum of 2nd neighbours of vacancy towards the lower frequency can be considered as a possible cause of the increase in the vacancy formation entropy in K.

The local frequency spectrum of Na, K using MEAM model has been used to calculate the mean square displacements of neighbours of vacancy using Eq. (2.16) and the results are presented in Figs. 8-9, along with mean square displacement of host atoms obtained by using the experimental frequency spectrum. As expected the mean square displacement varies linearly at high temperatures. In both the cases the mean square displacements for both 1st and 2nd neighbours of vacancies are lower than that of the atoms in perfect crystal. Beyond 2nd neighbours of vacancy, the mean square displacements for these metals is assumed to be almost same as that of the host atom which is obvious as the atoms far away from the vacant site will be least affected. The decrease in the mean square displacements of 1st and 2nd neighbours of the vacancy in both the metals resulted due to the general decrease in the local frequency spectrum.

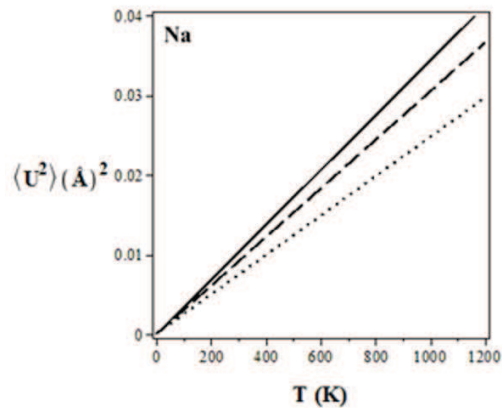


Figure 8: Mean square displacement of 1st neighbours (...), 2nd neighbours (---) of vacancy and solid line for host Na atom.

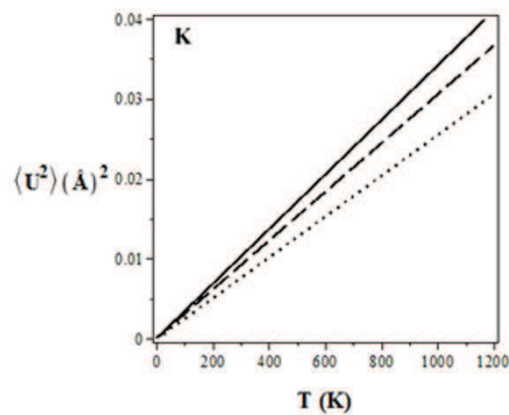


Figure 9: Mean square displacement of 1st neighbours (...), 2nd neighbours (---) of vacancy and solid line for host K atom.

To conclude, a detailed study of the dynamics of metals: Na, K and vibrational properties of vacancy in these metals have been carried out using MEAM potentials. The calculated phonon dispersions by using MEAM the obtained potential parameters agree well with the phonons obtained from neutron scattering experiments. The local density states of these metals have been calculated with Green's function method and there is a general shift of frequency spectrum towards the higher frequency of 1st neighbour of vacancy and an overall decrease for 2nd neighbours of vacancy. This behaviour of local density of states can be explained as the relaxations of 1st and 2nd neighbour atoms of vacancy are in opposite directions. The use of local density of states has been made in the calculation of mean square displacements and formation entropy of vacancy and the obtained results agrees well with available results in the literature. On the basis of our calculation in these metals, it has been found that the vibrations of the first and second neighbours of vacancy are significantly changed compared to those of a host atom.

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