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Vibrational properties of vacancy in transition metal Ta using modified embedded atom method Potential

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Abstract: *Vibrational behaviour of vacancy in bcc transition metal Ta is discussed using the modified embedded atom method (MEAM) potential. A second neighbours MEAM model is considered to obtain the force-constants of pure Ta and first and second neighbour atoms of vacancy. With the application of MEAM potential, the obtained force-constants are used to calculate the local vibrational density of states and mean square thermal displacements of first and second neighbours of vacancy using Green's function method and compared with that of the atoms in pure lattice. The value of vacancy formation entropy is also calculated and found to be in agreement with other available results.*

Keywords: *Modified embedded atom method; Phonon dispersions, Green's function; Vacancy formation energy: Force-constants; Vacancy; local density of states; Mean square displacement; formation entropy.*
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I. Introduction:

Hu et al [1] have employed the analytic MEAM model proposed by Ouyang and Zhang et al [2, 3] to calculate the phonon dispersions and some point defect properties including the vacancy formation energy and binding energy for bcc transition metals. In earlier studies of vibrational properties of vacancy Pohlong and Ram [4] have investigated the local density of states, vacancy formation entropy and mean square displacements in transition metals Fe, Mo and W using Johnson and Wilson (JW) potential. In recent studies, Gairola et al [5, 6] have employed the MEAM to investigate the vibrational properties of vacancy in some transition metals. The transition metal alloys have been studied for their unique properties such as high strength, toughness, soft magnetic properties, soft superconducting behaviour, corrosion resistance and catalytic activities. In view of the ability of analytic MEAM model [1] to reproduce the phonon dispersions of pure metals quite satisfactorily in most of the bcc transition metals, in the present work, we apply the MEAM potential to calculate the vibrational properties of vacancy in Ta including the local density of states, mean square displacements and vacancy formation entropy.

II. MEAM Model:

The MEAM potential consists of three parts: (i) the embedding function, which is the energy required to embed an atom in the field of other atoms, (ii) the pair potential, due to interaction of atomic cores and (iii) the modified term which takes in to account the non spherical distribution of electron density.
According to MEAM model [2] the total energy including a modifying term can be expressed as:

$$E = F(\rho) + \frac{1}{2}\sum_m \phi(r_m) + M(P), \quad (1)$$

where $F(\rho) = F(\rho_e)[1 - \gamma \ln(\frac{\rho}{\rho_e})](\frac{\rho}{\rho_e})^{\gamma}$ (2)

is the embedding function and

$$\phi(r) = \sum_{j=-1}^{4} k_j (\frac{r}{r_{1e}})^j \quad (3)$$

is the pair-potential function. (4)

The modified energy term is given as:

$$M(P) = \sigma\left(1 - \frac{P}{P_e}\right)^2 \exp[-(\frac{P}{P_e} - 1)^2]. \quad (5)$$

The force constants $\Phi_{ij}(l, m)$ required in the calculation can be obtained from the total energy as:

$$\Phi_{ij}(l, m) = \frac{\partial^2 E}{\partial r_i^l \, \partial r_j^m} \quad (6)$$

where l, m are the labels of the atoms and i, j are the Cartesian coordinates.
With the inclusion of embedding function and a modified term with the pair potential the vacancy formation energy is given by:

$$E_{1V}^F = 8F[\rho_e - f(r_{1e})] + 6F[\rho_e - f(r_{2e})] - \left[4\phi(r_{1e}) + 3\phi(r_{2e})\right] - 14F(\rho_e) + 8M[P_e - f^2(r_{1e})] + 6M[P_e - f^2(r_{2e})] - 14M(P_e). \quad (7)$$

II.1 Local density of states and mean square displacement:

The vibrational density of states of individual atom in the lattice is called as local density of states. The local density of states of an atom in pure lattice does not have any special significance as it is same for all atoms and in all directions is same as the frequency spectrum (density of states) of the crystal, but for a defect crystal, the situation is different: not only the local density of states of different atoms is different, but those of the same atoms in different directions may also be different. The total density of states is expressed as the sum of the density of states of all atoms in the crystal lattice. Local density of states can be expressed in terms of the imaginary part of Green's function of the defect lattice [7]. Assuming the presence of single impurity (vacancy), the Green's function $G(\omega)$ of imperfect lattice in terms of ideal lattice Green's function $G^0(\omega)$, may be written as:

$$G(\omega) = G^0(\omega)[I + V(\omega)G^0(\omega)]^{-1}, \quad (8)$$

where $V(\omega) = \Delta\phi\Phi + \mathrm{M}\omega^2 \quad and \quad \Delta\Phi = \Phi - \overset{0}{\Phi}$ is the perturbation matrix due to single vacancy, Φ is the force-constant in a lattice with vacancy and $\overset{0}{\Phi}$ that of the ideal lattice, and M is the mass of host atom. The imaginary part of 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:

$$Z_\alpha(l,\omega) = \frac{2\omega M}{\pi} ImG_{\alpha\alpha}(l,l;\omega) \quad (9)$$

II.2 Mean Square thermal displacement and vacancy formation Entropy

The mean-square thermal displacement of atoms in pure lattice and in a lattice with vacancy is another important property to know about the vibrational behaviour of vacancy. The mean square thermal displacements can be computed by using the local density of states $Z_\propto(\omega)$ is given by the expression:

$$< U_\propto^2 >= \int \frac{\mathrm{Z}_\alpha(\mathrm{l},\omega)}{\mathrm{M}\omega^2} \epsilon(\omega, \mathrm{T}) \mathrm{d}\omega, \quad (10)$$

where $\epsilon(\omega, \mathrm{T}) = \frac{\hbar\omega}{2} \coth h\left(\frac{\hbar\omega}{2\mathrm{k_B T}}\right)$, then

$$< U_\propto^2 >= \int \frac{\hbar Z_\propto(\omega)}{2M\omega} \coth[\tfrac{\hbar\omega}{2k_B T}] d\omega. \quad (11)$$

The vacancy formation entropy can be given by the expression:

$$S_{1V}^F = k \int_0^\infty \sigma(\omega, T)\, \Delta Z \; d\omega \quad (12)$$

where, $\Delta\mathrm{Z}(\omega)$ is the change in frequency spectrum due to a single vacancy

III. Results and discussions:

We have used the potential parameters and input data for MEAM potential from [1]. Total energies of perfect crystal and crystal with vacancy as impurity have been calculated using MEAM potential parameters. From the expression of total energy (Eq. 1), corresponding force-constants are obtained. For the calculation of matrix elements of force constants Φ_{ij} in a relaxed lattice, the static displacements of first and second neighbours of the vacancy are taken from the molecular dynamics calculation of Taji et al. [8], which gives inward displacements of first neighbour and outward displacement of second neighbour from the vacant site along the coordinate axes. The mono vacancy formation energy is calculated by Eq. (7) and the obtained the value ($E_{1V}^F = 3.05\ eV$) which shows a very good agreement with the experimental and other results [9 -11] In the calculation of local density of states, the ideal lattice Green's functions are computed using phonon data from [12] derived on the basis of Born-Von-Karman fit to measured phonons in neutron scattering experiments. With new equilibrium positions of atoms in the defective crystal, using the MEAM potential, the force constants in the relaxed lattice are calculated. For the calculation of Green's functions, we have followed the modified Gilat-Raubenheimer method [13]. The calculated vibrational frequency spectrum (local density of states) of pure Ta (solid curve), first neighbour (dashed curves) and second neighbour atoms of vacancy (dotted curve) are shown in Fig. (1). The calculated local density of states of host Ta shows the similar behaviour of pure metal as obtained on the basis of Born-Von Karman fits to neutron scattering results [12]. The obtained results of local density of states of first neighbours of vacancy show a significant decrease mainly due to large relaxation in the presence of vacancy. For second neighbours of vacancy also, the local density of states decreases but it is closer to that of host atoms as a result of small change is second neighbour distance in the presence of vacancy.

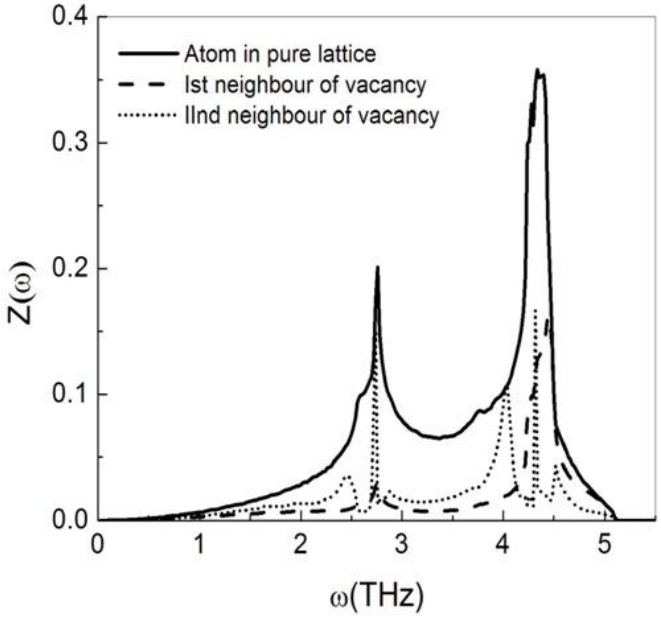

Fig. 1: Local density of states

The calculated local density of states of host Ta shows the similar behaviour of pure metal as obtained on the basis of Born-Von Karman fits to neutron scattering results [12]. The obtained results of local density of states of first neighbours of vacancy show a significant decrease mainly due to large relaxation in the presence of vacancy. For second neighbours of vacancy also, the local density of states decreases but it is closer to that of host atoms as a result of small change is second neighbour distance in the presence of vacancy.

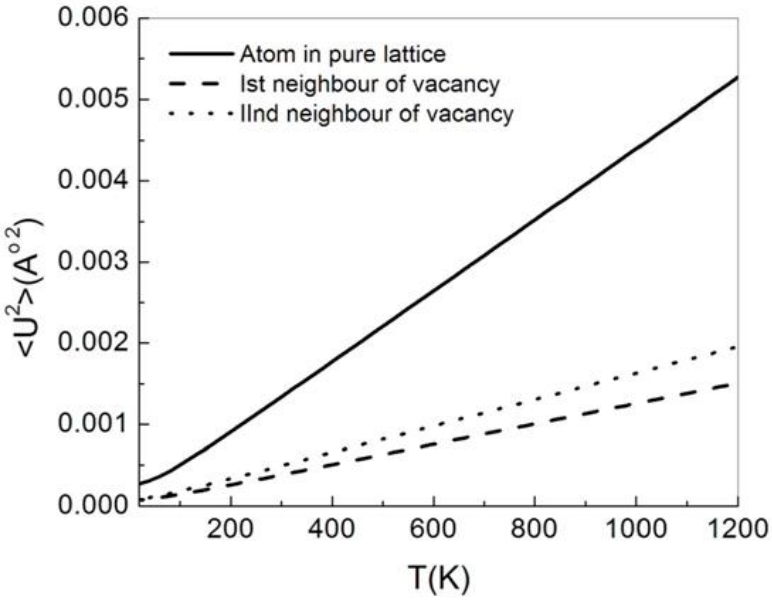

Fig. 2: Mean Square displacement

The calculated local density of states is used to determine the formation entropy S_{1V}^{F} of the vacancy. As there are no reliable experimental results of formation entropy of vacancies available in Ta, we compare our result ($S_{1V}^{F} = 2.8\ k_B$) of formation entropy of with the results of transition metals of other workers available in literature [4, 5, 14-15]. Burton [14] has reported the values (2.2 - 2.6 k_B) for all bcc metals, these results were based on the first neighbour model taking only the pair potential. Schober et al [15] have also mentioned a value of 1.8 k_B for all bcc metals. On comparing with other calculations the obtained value (2.8 k_B) of formation entropy S_{1V}^{F} is found to be very close to the value obtained in the earlier paper of Vandana et al [5] for W metal and falls within the range of values calculated by Pohlong and Ram [4] using JW potential. The obtained

density of states has been further used to calculate the mean square displacements of first and second neighbour atoms of vacancy. The mean square displacement of first neighbours and second neighbours is smaller than that of the atoms in perfect crystal as shown in Fig. 2. The overall decrease in the mean square displacement is due to the decrease in the frequency spectrum.

IV. Conclusions:

A theoretical study of vibrational properties of vacancy in Ta transition metal using second neighbour MEAM potential has been presented. Using second neighbour MEAM model the force-constants are obtained for pure Ta and relaxed lattice in the presence of vacancy. The obtained force constants are used to calculate vibrational local density of states, mean square displacement of pure Ta and first and second neighbour of vacancy and formation entropy are calculated. The decrease in the local density of states and mean square thermal displacements is largely due to strong relaxation of lattice in the presence of vacancy. The obtained values of vacancy formation energy and vacancy formation entropy are found to consistent with available experimental and other calculated values.

References:

[1]. W. Hu, X. Shu, and B Zhang, *Comput. Mater. Sci.* **23,** 175 (2002).
[2]. Y. Ouyang, B. Zhang, L Shuzhi and Z. Jin, *Z. Phys. B* **101,** 161 (1996).
[3]. B. Zhang, Y. Ouyang, L. Shuzhi and Z .Jin, *Physica B* **262,** 218 (1999).
[4]. S S Pohlong and P N Ram, Journal of physics: Condensed matter **10**, 10901 (1998).
[5]. V. Gairola, P. D. Semalty and P. N. Ram, *Pramana- journal of physics* **80,** 1041 (2013).
[6]. V. Gairola, P. D. Semalty and P. N. Ram, *Indian J. Phys.* **88,** 171(2014).
[7]. P. N. Ram, Radiation *Effects and Defects in Solids* **118,** 1 (1991).
[8]. Y. Taji, T. Iwata, and M. Fuse, *Phys. Rev. B* **39** 6381 (1989).
[9]. R. A. Johnson and D. J. Oh, J. *Mater. Res.* **4,** 1195 (1989).
[10]. W. Hu, X. Shu, and B. Zhang, *Computational Material Science* **23,** 175 (2002).
[11]. P. J. Feibelman, *Phys. Rev. B,* **53** 13740 (1996).
[12]. A. D. B. Woods Phy. Rev. **136**, A781 (1964).
[13]. G .Gilat and L. J. Raubenheimer, *Phys. Rev.* **144,** 390 (1966).
[14]. J. J. Burtan, *Phys. Rev. B* **5** 2948 (1972).
[15]. H. R. Schober, W. Petry and J Tramtenau, *J. Phys.: Condens. Matter* **4,** 9321 (1992).