Vacancy Formation Energy at High Pressures in Tantalum

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Abstract

We have computed the variation of the vacancy formation energy with pressure for Ta. Total energy calculations were performed for 16 and 54 atom supercells using a mixed basis pseudopotential method which uses pseudo-atomic orbitals and low energy plane waves as the basis set, within density functional theory (LDA and GGA). The vacancy formation energy is found to increase from 2.95 eV at ambient pressures to 6.96 eV at 300 GPa, and the vacancy formation volume decreases from being 53.4% of the bulk volume per atom at ambient pressure to 19.6% at 300 GPa, for a 54 atom supercell. The structural relaxation energy is found to increase with pressure from 14% of the vacancy formation energy at ambient pressure to 16% at 300 GPa.

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I. INTRODUCTION

Vacancies control a number of mechanical and kinetic processes in metals, such as dislocation climb, self-diffusion etc. Mechanical properties of metals, are determined in part by finite temperature vacancy concentrations. Thus the material specific vacancy formation energy, which determines the finite temperature vacancy concentration, serves as an important parameter in understanding the mechanical behavior of the metal. Due to its high thermal, mechanical and chemical stability, Ta is an important technological material and also a good candidate for an internal pressure standard for high pressure experiments. We determine the vacancy formation energy and its pressure dependence for bcc Ta.

Direct experimental measurement of the pressure dependence of the vacancy formation energy would be extremely difficult, making ab-initio calculations particularly useful. Moreover, the ab-initio calculation results can be used to validate classical potentials which can then be used for large scale simulations required for understanding processes like dislocation motion, fractures etc, which occur at much larger length scales as compared to atomic length scales.

II. METHODOLOGY

The pseudopotential method within density functional theory (LDA and GGA) was used to compute the total energies of the 16 and 54 atom supercells with and without a vacancy. We generated a non-local, norm-conserving Troullier-Martins semi-relativistic pseudopotential. We have used a mixed-basis approach which uses pseudo-atomic orbitals and a few low-energy plane waves as the basis set with a cut-off of 60 eV. The cut-off for the plane waves used to expand the potential is 550 eV. A special k-point mesh was used, giving the number of k-points used in the irreducible wedge of the BZ for the cubic symmetry is 35(10) for N=16(54), where N is the number of atoms in the supercell. Convergence of the vacancy formation energy of up to 0.001 eV was achieved with respect
to k-point sampling. Structural relaxation was performed using analytic forces. Relaxation was considered complete when forces on the ions were less than 0.001 (eV/Å). The volume relaxed vacancy formation energy at a given pressure $P$, is obtained by comparing the total energy of a supercell with $N$ atoms $E_{\text{tot}}(N,P)$, with that of a supercell with $N-1$ atoms and a vacancy at the same pressure $P$, $E_{\text{tot}}(N-1,P)$,

$$E_{\text{vac}}(P) = E_{\text{tot}}(N-1,P) - (N-1/N)E_{\text{tot}}(N,P).$$

and similarly for the enthalpy $H = E + PV$. $E$, $P$, and $H$ are obtained by fitting the total energy results versus volume to the Vinet equation of state.\(^7\) In a bulk system, removal of one atom would not change the bulk pressure. However, for tractable supercell sizes creation of a vacancy in the supercell can change the pressure dramatically, especially at high pressure. Thus relaxation of the system with the vacancy is essential for obtaining sensible vacancy formation energies. This is evident from Fig.\(^1\) where the unrelaxed vacancy formation energy is plotted for the 16 and 54 atom supercells. Notice that at high pressure (smaller lattice constant), the vacancy formation energy becomes negative, which is unrealistic. Notice that the vacancy formation energy becomes negative at a lower pressure (larger lattice constant) for the 16 atom supercell compared to the 54 atom supercell. This can be understood as a supercell size effect. In a real crystal most of the atoms are not displaced from their positions with the introduction of a vacancy, most atoms are far from the vacancy, and the lattice constant of the system remains unchanged. As the supercell size decreases, more and more atoms undergo displacement because of the vacancy resulting in a change of lattice constant and volume relaxation.

III. RESULTS

Our ambient pressure vacancy formation energy is in good agreement with other computations (Table I). Also note that, for the 54 atom supercell the fully relaxed vacancy formation energies are within 3% of experiment at zero pressure. The total energy of the
54 atom supercell with and without a vacancy for different system volumes is tabulated in Table II.

Volume relaxed Ta vacancy formation energies increase with pressure for the 16 and 54 atom supercells (Fig. 2a). The value of the vacancy formation energy is lower for the 16 atom supercell than the 54 atom supercell at all pressures. The difference in the vacancy formation energy for the 16 and 54 atom supercells increases with pressure from 10% at ambient pressures to 15% at 300 GPa.

The volume relaxed vacancy formation energy is lower for GGA compared to LDA at all pressures (Fig. 2b). The difference between LDA and GGA increases slightly with pressure, (from 6% at ambient pressures to 9% at 300 GPa). We also find that the vacancy formation energy using PBE GGA is essentially the same as that obtained by using PW91 GGA.

The fully relaxed (volume and structural relaxation) and the volume relaxed vacancy formation energies of Ta are compared for the 16 and 54 atom supercells (Figs. 2c and 2d). For the 54 atom supercell the fully(only volume) relaxed vacancy formation energy increases from 2.95(3.26) eV at ambient pressure to 6.96(8.16) eV at 300 GPa. The structural relaxation energy which is the difference between the fully relaxed and the volume relaxed vacancy formation energies is sensitive to the supercell size. It increases with the size of the supercell. At ambient pressure the structural relaxation energy for the 54 atom supercell is 14% of the vacancy formation energy compared to 1% for the 16 atom supercell. The high relaxation energy of 14% for the 54 atom supercell at ambient pressures has been obtained in previous calculations. The pressure dependence of the relaxation energy reduces with supercell size. The structural relaxation energy increases from 1% to 10% for the 16 atom supercell compared to 14% to 16% for the 54 atom supercell with increase in pressure from ambient to 300 GPa. It is important to check the convergence of the vacancy formation energy with respect to the supercell size. For small supercells introduction of a vacancy in the system leads to an unreasonably high vacancy concentration which can lead to drastic change in the elastic properties of the system. Moreover, inter-vacancy interactions in the smaller supercell may alter the vacancy formation energy. In order to test the convergence with
respect to system size, we compare our results with those of molecular dynamics simulations with a periodic cell of 1458 Ta atoms. The potential used in the simulations was fitted to our zero pressure vacancy formation energies in the same sized supercell. Our fully relaxed vacancy formation energy for the 54 atom supercell is within 5% of the molecular dynamics results for zero pressure. The convergence indicates that in the 54 atom supercell vacancy-vacancy interactions are reduced to a negligible level, thus allowing us to calculate vacancy formation energies for an isolated vacancy. The difference between our results and the molecular dynamics results increases with pressure to 20% at 300 GPa. This difference can be attributed to the difference in the atomic relaxations obtained from the interatomic potential used in the molecular dynamics simulations which are smaller compared to our calculations.

The vacancy formation enthalpy is the important quantity at non-zero pressures. The vacancy formation enthalpy increases with pressure similar to the vacancy formation energy, but its rate of increase is slower and it saturates at high pressure (Fig. 3). This saturation behavior is due to decreasing vacancy volume and increasing vacancy formation energy with increasing pressure.

Volume relaxation results in displacement of all atoms towards the vacancy with a consequent reduction in the volume of the supercell. Structural relaxation results in oscillatory displacement of atoms around the vacancy with the nearest neighbor moving towards the vacancy and the successive neighbors moving alternately away (negative displacement) and towards (positive displacement), the vacancy. The oscillatory atomic displacement around the vacancy due to structural relaxation has also been observed in Mo at ambient pressures. In the context of a real crystal, the partitioning of the atomic displacement due to volume and structural relaxation is rather artificial; probably a more relevant quantity would be the total atomic displacement due to both volume and structural relaxation. The total atomic displacement retains the oscillatory nature in Ta, but all the atomic displacements are towards the vacancy (positive) (Fig. 4a). The atomic displacement due to volume relaxation enhances the positive displacement due to structural relaxation and reduces the negative
displacement. Even the furthest neighbor of the vacancy has non-zero displacement as it includes the effects of both volume and structural relaxations. With increasing pressure, all the atomic displacements become increasingly positive, i.e., towards the vacancy. The pressure dependence of the displacements for the first and second nearest neighbor of the vacancy is shown in Fig. 4b. One can see that the pressure dependence of the first nearest neighbor displacement is negligible beyond 100 GPa. In contrast, the displacement of the second nearest neighbor towards the vacancy increases continuously with increasing pressure.

The vacancy formation volume \((\Omega_{\text{vac}}^f)\), is given by,

\[
\Omega_{\text{vac}}^f(P) = \Omega_0(P) - (\Omega_N(P) - \Omega_{N-1}(P)),
\]

where, \(\Omega_N = N\Omega_0\). \(\Omega_N\) is the volume of \(N\) atom supercell and \(\Omega_{N-1}\) is the volume of the relaxed \(N-1\) atom supercell with a vacancy. At ambient pressure \(\Omega_{\text{vac}}^f\) is 53.4\% of the volume of a single atom in bulk Ta. Our vacancy formation volume agrees well with other ambient pressure calculations for Ta.\(^{12,13}\) Amongst the bcc transition metals Ta has the highest vacancy formation volume after W.\(^{13}\) Note that with relaxation \(\Omega_{N-1}\) decreases thus reducing the vacancy formation volume compared to the volume of a single atom \(\Omega_0\). The vacancy formation volume is smaller than the volume of a single atom at the same pressure (Fig. 5). As the pressure increases the displacement of the atoms towards the vacancy increases, thus reducing the vacancy formation volume compared to a single atom at the same pressure. Fig. 5 shows the decreasing trend of the vacancy formation volume with pressure. Note that the vacancy formation volume reduction rate appears to approach saturation at higher pressures. The difference in the vacancy formation volume due to structural relaxation increases with pressure from being 23.6\% at ambient pressure to 49.5\% at 300 GPa for the 54 atom cell.

**IV. DISCUSSION**

Transition metals tend to have the highest vacancy formation energies compared to other elemental metals because of the presence of strong angular forces arising from d-state
interactions. Amongst the transition metals, Ta has the second-highest vacancy formation energy at ambient pressure; W having the highest vacancy formation energy\textsuperscript{13} The Ta vacancy formation energy is almost three times as that of a typical elemental metal like Cu.

Vacancies play an important role in controlling the rheology of the material. Plastic deformation under an applied stress is due to dislocation motion in the system. The strain rate $d\epsilon/dt$ in the quasi-steady-state regime can be expressed as:

$$d\epsilon/dt = \rho bv,$$

where $\rho$ is the density of mobile dislocations, $b$ is the Burgers vector and $v$ is the average velocity of the dislocations.\textsuperscript{14} A dislocation usually glides until its motion is obstructed by impurities, interstitials or is entangled by other dislocations. After overcoming these obstacles the dislocation again glides till it encounters the next obstacle. So the average dislocation velocity $v$ can be expressed as:

$$v = \delta L/(t_g + t_o),$$

where $\delta L$ is the distance traveled by the dislocation, $t_g$ is the time for which it glides and $t_o$ is the time taken to overcome the obstacle. Dislocations can overcome the obstacle by climbing to a plane normal to its glide plane. The dislocation climb occurs by self-diffusion of atoms with the aid of vacancies.\textsuperscript{13} Vacancies also aid in the unentanglement of dislocations. Thus $t_o$ in the above equation is determined by the vacancy concentration. The high vacancy formation energy in Ta will translate to low probability of dislocation climb and unentanglement of dislocations. This would result in lower dislocation velocity in Ta and consequently lower plastic flow and higher yield strength\textsuperscript{14} compared to a typical metal like Cu, especially at high pressure. Vacancies also cause plastic flow at high temperatures and low stress by diffusion creep. In diffusion creep in the presence of non-hydrostatic stress there arises a stress field in the crystal. This in turn results in a flux of vacancies in the crystal causing shear deformation.\textsuperscript{13} The high vacancy formation energy in Ta would reduce the probability of diffusion creep even at high temperatures.
In the bcc transition elemental metals, at ambient pressure, there is a strong correspondence between the vacancy formation energy $E_v$, and the melting temperature $T_m$, (see Fig. 6). The straight line shows that for all these elements the dimensionless quantity, $E_v/k_B T_m$, is similar and is given by the slope of the straight line; $k_B$ being the Boltzmann constant. The number of vacancies ($n$), in a crystal with $N$ atoms, at a finite temperature ($T$), is determined by the vacancy formation energy ($E_v$):

$$n/N = e^{-E_v/k_B T}.$$  \hspace{1cm} \text{(5)}

Thus, similar values of $e^{-E_v/k_B T_m}$ indicate that all these metals have similar vacancy concentration close to their melting temperatures or that the vacancy formation energy and the melting temperature scale similarly with the atomic interaction strength. This indicates that vacancies might play an important role in the melting of the elemental metals.

Large amplitude atomic vibration and thermal creation of vacancies have been known to destabilize the crystal and induce melting. The vacancy concentration for these metals as estimated from the slope of the straight line is $6.21 \times 10^{-4}$. The close packed elemental metals also exhibit similar correspondence between their vacancy formation energies and their melting temperatures.

To summarize, our computations show that the mixed basis pseudopotential method has the potential of giving correct vacancy formation energies. We find that the volume relaxation energies become increasingly important with pressure but their importance reduces with increasing supercell size. On the other hand structural relaxation energies increase with the supercell size. We find that the difference between LDA and GGA results do not change appreciably with pressure. The vacancy formation energies were found not to depend on the kind of GGA exchange correlation used, PBE or PW91. The dependence on pressure of the vacancy formation enthalpy was found to be different compared to the vacancy formation energy. After an initial increase the enthalpy saturates with pressure whereas the vacancy formation energy increases with pressure without saturation.
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FIG. 1. Plot of unrelaxed vacancy formation energy with respect to pressure for the 16 and 54 atom supercells. As pressure increases the unrelaxed vacancy formation energy becomes negative indicating the importance of relaxation at high pressures.
FIG. 2. Dependence of the vacancy formation energy $E_{\text{vac}}$ on supercell size, exchange correlation and structural relaxations. (a) Plot of the volume relaxed vacancy formation energies with respect to pressure for the 16 and 54 atom supercells. As pressure increases the difference in $E_{\text{vac}}$ for the two supercell sizes increases. (b) Plot of volume relaxed vacancy formation energies with respect to pressure for the 54 atom supercell for LDA and GGA. (c) Comparison of volume relaxed and fully relaxed vacancy formation energies for the 54 atom supercell. (d) Comparison of volume relaxed and fully relaxed vacancy formation energy for the 16 atom supercell.

FIG. 3. Comparison of volume relaxed vacancy formation enthalpy and vacancy formation energy for a 54 atom supercell for GGA. The vacancy formation enthalpy saturates at high pressure.
FIG. 4. (a) Atomic displacement around a vacancy of the neighbor atoms for the 54 atom supercell during full (volume and structural) relaxation. (b) First and second nearest neighbor displacements versus pressure for the 54 atom supercell during full (volume and structural) relaxation.

FIG. 5. Vacancy formation volume, $\Omega_{\text{vac}}^f(P)$, versus pressure. The vacancy formation volume is expressed relative to the volume of a single atom in the ideal (without vacancy) Ta system, ($\Omega_0(P)$).

FIG. 6. Theoretical values of the vacancy formation energies $E_v$ are plotted with respect to the melting temperatures $T_m$, for the elemental bcc transition metals. The dashed line is obtained by a linear fit to the data. The correlation coefficient of the fitted line is 0.886.
TABLES

TABLE I. Comparison of available Ta vacancy formation energies (eV) at ambient pressure. The volume relaxed (vol rel) and fully relaxed (full rel) values for the 16 and 54 atom supercells are tabulated. The experimental value is 3.1 eV.

|        | 16 atom | 54 atom | 54 atom |
|--------|---------|---------|---------|
|        | LDA     | LDA     | GGA     |
|        | volume  | fully   | volume  | fully   | volume  | fully   |
|        | relaxed | relaxed | relaxed | relaxed | relaxed | relaxed |
| Ref. 12| 3.29    | 3.17    | 3.51    | 2.99    |         |         |
| Ref. 13|         | 3.6     | 3.2     | 3.2     |         |         |
| Present Work | 3.26   | 3.23    | 3.6     | 3.25    | 2.95    |         |

TABLE II. Total energy (GGA) in eV of the 54 atom supercell with and without vacancy (ideal) for different system volumes (Å)³.

| System Volume | Energy for Ideal System | Energy for System with a vacancy |
|---------------|-------------------------|---------------------------------|
| 953.547       | -10237.366              | -10044.717                      |
| 868.987       | -10227.952              | -10036.252                      |
| 789.579       | -10204.537              | -10014.345                      |
| 715.163       | -10163.550              | -9975.546                       |
| 645.576       | -10100.465              | -9915.540                       |