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Vacancy formation enthalpy at high pressures in tantalum

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Abstract

Using a mixed basis pseudopotential method, total energy calculations were performed to obtain the enthalpy of vacancy formation in Ta as a function of pressure, which is important for understanding the effects of pressure on mechanical properties. The vacancy formation enthalpy is found to increase from 2.95 eV at ambient pressures to 12.86 eV at 300 GPa, and the vacancy formation volume decreases from being $53 \pm 5\%$ of the bulk volume per atom at ambient pressure to $20 \pm 2\%$ at 300 GPa, for a 54-atom supercell. We also show that there is a strong correspondence between the vacancy formation enthalpy and the melting temperature in Ta.

The effects of compression on mechanical properties of transition metals are not easily addressed experimentally, yet are important in modelling dynamical behaviour of materials under compressive loads. This paper addresses for the first time the pressure dependence of the enthalpy of vacancy formation in tantalum. Ta remains stable in the simple body-centred cubic (bcc) structure over a wide pressure range [1] allowing study of the effects of compression on vacancy formation in a transition metal over a wide compression range without the complications of structural changes. High thermal, mechanical and chemical stability also makes Ta an important technological material [2].

The role of vacancies in controlling plasticity through the mobility of dislocations has not been fully explored. The vacancies allow the dislocations to overcome the interstitials and impurities by facilitating their climb to a plane normal to the glide plane by self-diffusion of atoms [3]. Moreover, dislocation glide depends upon double-kink formation [4], and though present calculations neglect vacancies in the calculation of double-kink formation energy [5], it is greatly modified by vacancies [6]. Computations of the vacancy formation enthalpy and its pressure dependence provide us with the vacancy concentration, which in turn determines the effects of vacancies on the dislocation motion. Small changes in the vacancy formation

enthalpy with pressure lead to large changes in vacancy concentration due to the exponential dependence of the vacancy concentration on the enthalpy.

The vacancy formation enthalpy [7], H_{vac} , is given by

$$H_{vac} = E_{vac}(P) + P\Omega_{vac}^f, \quad (1)$$

where E_{vac} is the vacancy formation energy and Ω_{vac}^f is the vacancy formation volume at pressure P . We find the vacancy formation energy by performing total energy calculations for supercells with one atom removed, and compare the energy of the N -atom supercell with the $(N - 1)$ -atom defective supercell. The atomic positions after the atom is removed are relaxed to minimize the total energy using analytic forces. Expressing E_{vac} and Ω_{vac}^f in terms of the system internal energy and volume one obtains

$$E_{vac}(P) = E(N - 1, P) - \frac{N - 1}{N}E(N, P) \quad (2)$$

and

$$\Omega_{vac}^f = V(N - 1, P) - \frac{N - 1}{N}V(N, P). \quad (3)$$

$E(N, P)$ and $V(N, P)$ are the internal energy and volume of an N -atom ideal system at pressure P , while $E(N - 1, P)$ and $V(N - 1, P)$ are the internal energy and volume of a system with $N - 1$ atoms and a vacancy at pressure P . Thus one needs the internal energy and volume of the ideal system and of the system with the vacancy, where the systems are at the *same* pressure, P .

We used the mixed basis pseudopotential method [8] within density functional theory to compute $E(N, V)$ and $E(N - 1, V)$. We used the local density approximation (LDA) [9], the Perdew–Wang [10] and PBE [11] generalized gradient approximations (GGA) for the treatment of the exchange–correlation potential. We found that the vacancy formation energy at a given volume varies little with the exchange–correlation potential chosen. We report the PBE GGA results below unless otherwise stated. Calculations have shown that computationally efficient mixed basis pseudopotential results are in close agreement to the all-electron, full potential linear-muffin-tin-orbital results for bcc transition elements at ambient pressure [12]. We generated a non-local, norm-conserving Troullier–Martins [13] semi-relativistic pseudopotential. The pseudopotential was generated from $5d^36s^26p^0$ atomic configurations with cut-off radii 1.46, 2.6 and 3.4 bohr for 5d, 6s and 6p potentials respectively, with non-linear core corrections. The basis set consists of pseudo-atomic orbitals and some low-energy plane waves with a cut-off of 60 eV. The cut-off for the plane waves used to expand the potential and charge density is 550 eV. The equation of state of Ta obtained from the pseudopotential method is in very good agreement with the LAPW calculations and the experiments [14]. The ambient pressure equilibrium volume obtained for Ta is 18.15 \AA^3 which is 1.5% higher than the experimental value and the bulk modulus is 199 GPa which is in very close agreement with the experimental value of 195 GPa [1]. A special k -point mesh [15] gives 35 k -points for the 16-atom supercell, and 10 k -points for the 54-atom supercell. Gaussian broadening with a width of 0.172 eV was used to optimize convergence with respect to the k -point sampling. Convergence of the vacancy formation energy of up to 0.001 eV was achieved with respect to k -point sampling.

The total (internal) energies of the ideal system and the system with the vacancy at constant pressure are obtained by fitting the volume dependence of the total energies for both systems to the Vinet equation of state [16]. Calculation of the internal energy of the system with the vacancy included structural relaxation, which allowed the ions to readjust their positions around the vacancy. Relaxation was considered complete when forces on the ions were less

Table 1. Comparison of available Ta vacancy formation energies (eV) at ambient pressure for the 16- and 54-atom supercells. The experimental value [17] is 3.1 eV.

References	16 atoms	54 atoms	54 atoms
	LDA	LDA	GGA
[12]		3.2	3.2
[18]	3.17	2.99	
Present work	3.23		2.95

Table 2. Total energy (GGA) in eV of the 54-atom supercell with and without a vacancy (ideal) for different system volumes (\AA^3). The total energy of the system with the vacancy includes the relaxation energy.

System volume	Energy for ideal system	Energy for system with a vacancy
953.547	-10 237.366	-10 045.202
868.987	-10 227.952	-10 037.075
789.579	-10 204.537	-10 015.561
715.163	-10 163.550	-9 977.176
645.576	-10 100.465	-9 917.673

than 0.001 (eV \AA^{-1}). The calculation of the vacancy formation volume, Ω_{vac}^f , is similar to that of the vacancy formation energy and was carried out by comparing the volumes of the N -atom supercell and the $(N - 1)$ -atom supercell with the vacancy at constant P .

Our ambient pressure vacancy formation energy is in good agreement with other computations (table 1). For the 54-atom supercell, the vacancy formation energies are within 3% of experimental values at zero pressure. Even for the 16-atom supercell the vacancy formation energy is within 5% of experimental values at zero pressure. The total energies of the 54-atom supercell with and without a vacancy for different system volumes are tabulated in table 2.

As pressure increases or system volume reduces, the system energy increases for both the ideal system and the system with the vacancy due to increasing repulsive interatomic interaction. The system energy increases at a lower rate in the presence of a vacancy compared to the ideal system. For the 54-atom supercell the vacancy formation energy increases from 2.95 eV at ambient pressure to 6.96 eV at 300 GPa. The vacancy formation energies of Ta are compared for the 16- and 54-atom supercells (figure 1). The maximum difference between the vacancy formation energies for the two supercell sizes is within 15% within the pressure range of 0–300 GPa, indicating that a 54-atom supercell is sufficient for the calculation.

At ambient pressure, Ω_{vac}^f is $53 \pm 5\%$ of the volume of a single atom in bulk Ta (figure 2). Our vacancy formation volume agrees well with other ambient pressure calculations for Ta [12, 18]. According to previous DFT–LDA calculations, amongst the bcc transition metals Ta has the highest vacancy formation volume after W [12]. As the pressure increases, the displacement of the atoms towards the vacancy increases, thus reducing the vacancy formation volume compared to that for a single atom at the same pressure. Figure 2 shows the decreasing trend of the vacancy formation volume with pressure. The displacement of the atoms towards the vacancy relaxes the system by reducing the total energy. The higher repulsive interatomic interaction at higher pressure results in larger atomic displacement towards the vacancy.

The vacancy formation enthalpy has a different pressure dependence to the vacancy formation energy. It increases with pressure similarly to the vacancy formation energy, but its rate of increase reduces with increasing pressure (figure 3). This behaviour occurs

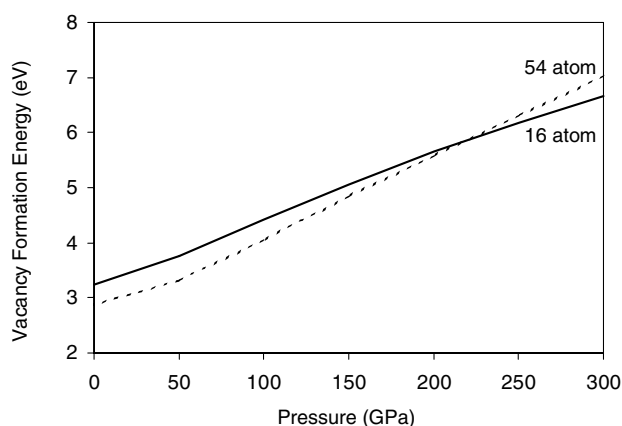


Figure 1. The dependence of the vacancy formation energy on the supercell size. The 16-atom (LDA) and the 54-atom (GGA) values are plotted. The maximum difference between the two supercell values is 15% for the pressure range of 0–300 GPa. Rough (without structural relaxation) estimates of 54-atom (LDA) values suggest that the supercell size effect will be much less than 15% if comparison is made between vacancy formation energy values with the same exchange and correlation.

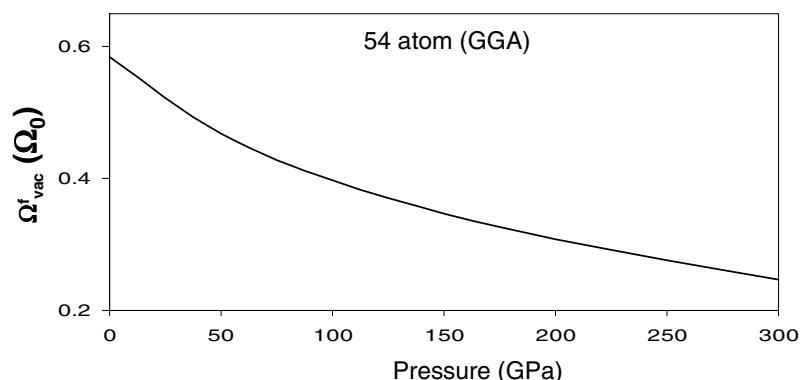


Figure 2. Vacancy formation volume, $\Omega_{vac}^f(P)$, versus pressure. The vacancy formation volume is expressed relative to the volume of a single atom, $(\Omega_0(P))$, in the ideal (without vacancy) Ta system.

because the vacancy formation energy does not increase sharply enough to compensate for the vacancy formation volume reducing with increasing pressures. The derivative of the vacancy formation enthalpy with respect to pressure at constant entropy (dH_{vac}/dP) is equal to the vacancy formation volume, $\frac{dH_{vac}}{dP} = \Omega_{vac}^f$. Thus one would expect the reduction in the vacancy formation volume at higher pressures to be echoed in a reduction of the pressure dependence of the vacancy formation enthalpy, which our calculations show. In order to test the convergence with respect to system size, we compare the vacancy formation enthalpy for the 16- and 54-atom supercells (figure 3). The maximum difference in vacancy formation enthalpy within the pressure range of 0–300 GPa is 12%. In the above plots, all the quantities are plotted with respect to pressure, P , as it is the natural variable for the experimentally verifiable quantity, enthalpy, H .

In bcc transition metals the atomic interactions are predominantly due to the strong directional d-state interactions [19], leading to higher (almost three times) vacancy formation

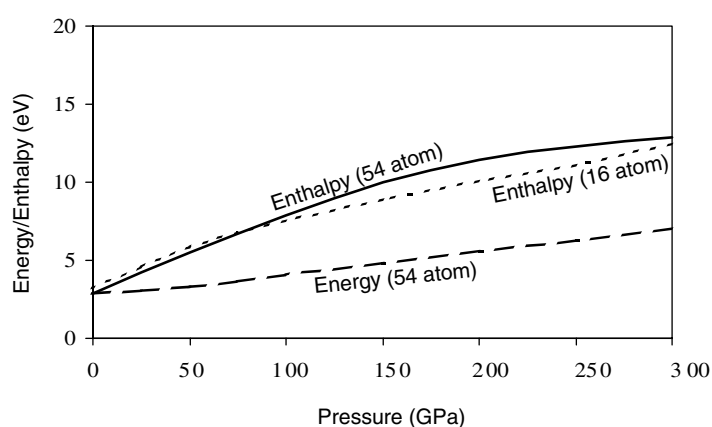


Figure 3. Comparison of vacancy formation enthalpies for 54- and 16-atom supercells. The vacancy formation enthalpy increases with pressure, but the rate of increase reduces with pressure, unlike the vacancy formation energy.

energies [12, 17], compared to those for typical metals like Al and Cu. The role of the d electrons in the directional atomic bonding and the consequent higher vacancy formation energy is also evident from the trend of decreasing vacancy formation energy as one goes across the row in the periodic table. The vacancy formation energy of Ta which is an early transition metal is three times that of Au which is a late transition metal, with filled d bands [17].

The strong directional d bonds that give rise to high vacancy formation energies also give rise to high melting temperatures in transition metals as reflected in the correspondence between the vacancy formation energy and the melting temperature T_m (figure 4). We found that for Ta this correspondence holds even at high pressures (figure 4). Although this correspondence has been shown before for ambient pressure, the fact that the correspondence holds even at higher pressures strongly reinforces the idea that the vacancy formation enthalpy and the melting temperature scale similarly with the atomic interaction strength. Note that the Ta melting temperature at high pressures obtained from the above correspondence is in good agreement with experiments [20, 21].

Recent experimental investigation of the pressure dependence of the melting temperature for elemental metals has provided further evidence of the sensitivity of the melting temperature to the atomic interactions and its pressure dependence. Besides the marked difference in the ambient pressure melting temperature, the rate of increase of the melting temperature with pressure is markedly different for transition metals as compared to elemental metals such as Al and Cu [21]. Now that the experimental values are available [21], it will be interesting to calculate the pressure dependence of the vacancy formation enthalpy for these metals and verify their correspondence with the melting temperatures at non-ambient pressure. If the correspondence is validated, it will be a useful tool for studying the pressure dependence of the atomic interaction and melting temperatures on the basis of the vacancy formation enthalpy. This would be especially useful in the context of the difficulty involved in the high-pressure experiments [1].

This correspondence between the vacancy formation enthalpy and the melting temperatures over the wide pressure range considered here bolsters the expectation of applicability of homologous temperature scaling. Instead of explicitly calculating the pressure dependence of these parameters over the entire pressure range of interest, one can extract the impact of pressure from calculations done for a limited pressure range in conjunction

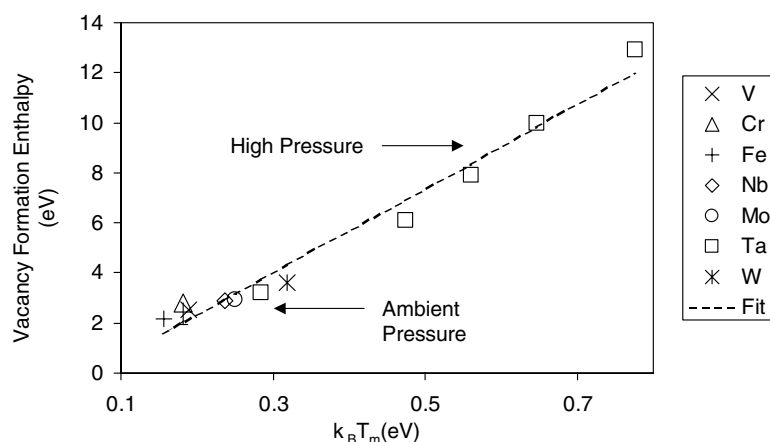


Figure 4. The vacancy formation enthalpy is plotted with respect to the melting temperatures [22] T_m , for the elemental bcc transition metals. The size of the symbols for all elements except Cr is larger than the uncertainty in the experimental values [12, 17]. The theoretical values are also within the symbol size [23]. For Ta, our vacancy formation enthalpy at pressures higher than the ambient pressure is included in the figure. The melting temperatures for Ta at higher pressures were obtained from molecular dynamics simulations which are in good agreement with experiments [20]. The dashed line is obtained by a linear fit to the data. The correlation coefficient of the fitted line is 0.971.

with homologous temperature scaling [24]. According to the scaling, once the melting curve (the pressure dependence of the melting temperature) is known, as is the case with Ta, the parameters can be expressed as a function of the pressure-dependent melting temperature and the system temperature. The scaling serves as a powerful tool in high-pressure studies and was explicitly verified for the scaling of the diffusion constant with pressure for MgO [24]. This scaling should be very useful in extracting the pressure and temperature dependences of parameters describing plasticity.

In conclusion, we have calculated the vacancy formation enthalpy for Ta from first principles using a mixed basis pseudopotential method. Our ambient pressure vacancy formation energy is in good agreement with experiment and previous theoretical calculations. Furthermore, correspondence between the vacancy formation enthalpy and the melting temperature is demonstrated.

Acknowledgments

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