The calculated vacancy formation energies of Al, Ni, Cu, Pd, Ag, and Pt.

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A molecular dynamics simulation that made use of the Sutton-Chen many-body potential calculated the bulk vacancy formation energies (E_v) for Al, Ni, Cu, Pd, Ag, and Pt single crystals. The E_v values for single crystals with the surface orientations of (111), (100) and (110) were calculated at temperatures ranging from 0 K to 1000 K. In the case of Cu and Al which showed premelting below 1000 K, E_v values were calculated up to below their respective premelting temperatures. The values obtained for vacancy formation energies at 0 K exhibited surface orientation dependence and compared well to values obtained from literature. The (111) surface had the closest packed surface, with few atoms bonding to a surface adatom, and had the highest bulk vacancy formation energy. The (100) surface had average E_v values that compare well with surface-independent literature values. The (110) surface had deep surface binding sites with the largest number of surface atoms able to bond to an adatom and had the lowest bulk vacancy formation energy. For an increase in temperature a slight decreasing trend in E_v values was observed, which is associated with atoms in the bulk that bond less strongly as a result of the crystal expansion at higher temperatures. Disordering was observed at temperatures well below the melting points of Al, Cu, Ag and Ni. At these temperatures where surface disordering occurred in (110), surface instability interfered with deep binding sites on the surface, reflected in a slight increase in E_v values. Disordering occurring in (111) and (100) surface orientations at high temperatures conversely allowed deeper binding sites in the tightly packed surfaces and resulted in a slight drop in E_v values.

1. Introduction

The vacancy formation energy is an important factor in atomic transport, and is of fundamental importance in diffusion kinetics. The vacancy formation energy, (E_v) has been shown to be dependent on surface orientation in both Al and Cu. [1,2] What has not yet been extensively studied is the effect of temperature on these vacancy formation energies, but with the use of density functional theory (DFT) it has been shown for Pt, Pd and Mo that the vacancy formation energy increases with temperature. [3]

The Sutton-Chen potential (Ui) is an embedded atom potential with a many-body term that uses particle densities in FCC metals. The total energy of a simulated crystal (U) can be calculated by using

$$U = \sum_i U_i = \varepsilon \sum_i \left[\tfrac{1}{2} \sum_{i \neq j} \tfrac{1}{2} V\left(r_{ij}\right) - c\sqrt{\rho_i} \right] \tag{1}$$

Where ε is an energy parameter and c is a dimensionless scaling parameter. V is the pairwise repulsive potential and ρ_i is a density like term;

$$V\left(r_{ij}\right) = \left(\frac{a}{r_{ij}}\right)^n \tag{2}$$

$$\rho_i = \sum_{i \neq j} \phi\left(r_{ij}\right) = \sum_{i \neq j} \left(\frac{a}{r_{ij}}\right)^m \tag{3}$$

with r_{ij} the distance between atoms i and j, a is the lattice constant, n a positive integer that determines the repulsive potential and m is a positive integer that determines the range of the repulsive potential such that $n > m$. The parameters that were are those published by Sutton and Chen, which are listed in Table 1.

Perfect crystals of Al, Ni, Cu, Pd, Ag, and Pt were simulated with the use of an embedded atom potential developed by Sutton and Chen. [4] Using the Sutton-Chen potential, the cohesive energy of the different metals were determined and compared to literature values. The crystals were simulated with surface orientations of

(100), (110) and (111), (see Fig. 1) at a range of temperatures and the vacancy formation energy was calculated. The calculations were repeated for both 0 K and at progressively higher temperatures in steps of 50 K.

Table 1. The Sutton–Chen parameters for Al, Ni, Cu, Pd, Ag, and Pt. [4]

Element	ε (eV)	*a* (Å)	c	n	m
Al	$3.3147\ 10^{-2}$	4.05	16.399	7	6
Ni	$1.5707\ 10^{-2}$	3.52	39.432	9	6
Cu	$1.2382\ 10^{-2}$	3.61	39.432	9	6
Pd	$4.1790\ 10^{-3}$	3.89	108.27	12	7
Ag	$2.5415\ 10^{-3}$	4.09	144.41	12	6
Pt	$1.9833\ 10^{-2}$	3.92	34.408	10	8

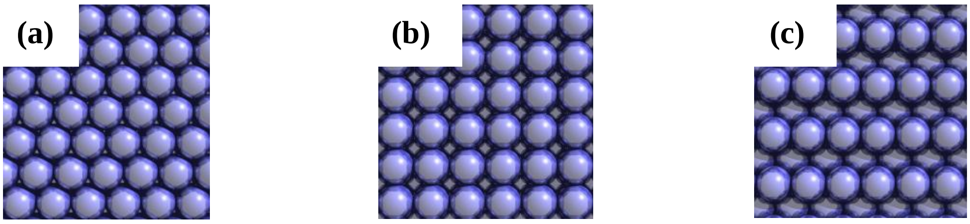

Figure 1. Schematics of the three different surface orientations of the bulk crystals: (111) in 1(a), (100) in 1(b) and (110) in 1(c).

Although controlling the shape of nanoparticles is difficult, transition metal nanocubes have been synthesized by solution phase methods. [5] Nanocubes of Pt as small as 8 nm have been synthesized by Zhang et al.[6] Cu nanocubes in a range of sizes have also been successfully synthesized. [7]

The cohesive energy was also calculated for Cu nanocubes of 56 nm, such as the one shown in Fig. 2, and the vacancy formation energy at 0 K was also calculated for the nanocube with the lowest cohesive energy.

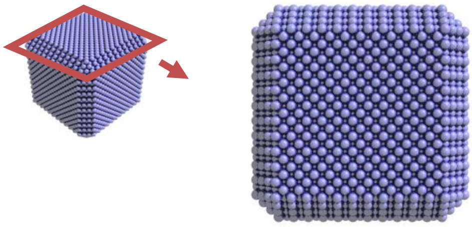

Figure 2. a Cu nanocube with sides of (100) orientation, edges of (110) orientation and corners of (111) orientation.

2. Calculations

Using the Sutton-Chen (SC) potential, the potential energy from atomic interactions could be evaluated. This potential energy evaluated for perfect crystals ($U_{perfect}^{total}$) was used to calculate the cohesive energy as follows: [8]

$$E_{coh} = (U_{r=\infty}^{total} - U_{perfect}^{total}) / n \tag{4}$$

where $U_{perfect}^{total}$ is the total potential energy of the perfect crystal and $U_{r=\infty}^{total}$ is the total potential energy of the system where the n number of atoms are infinitely far removed from each other, in ground state and at 0 K. When using the SC potential to evaluate system energies, it is important to note that the potential energies are entirely due to atom interactions, and that the total system energy with all atoms infinitely far removed is 0 eV. Thus equation 4 can be simplified to:

$$E_{coh} = U_{perfect}^{total} / n. \tag{5}$$

The calculation of the vacancy formation energy (E_v) for the Schottky defect has previously been simplified to the energy difference between the energy needed to extract an atom from inside the crystal bulk and the energy obtained from adding an atom to the crystal surface [1-2,9]. Figure 3 shows a schematic of a Schottky vacancy formation and a simplification. The vacancy formation energy can be calculated with:

$$E_v = E_{extract}^{(\text{bulk})} - E_{adatom}^{(\text{surface})}. \tag{6}$$

$E_{extract}^{(\text{bulk})}$ is the energy needed for an atom to be removed from the bulk of a crystal to a position infinitely far away, and $E_{adatom}^{(\text{surface})}$ is the energy gained for adding the extracted atom (adatom) on the surface. For simplification these energies will be defined as the extraction energy $E_{extract}^{(\text{bulk})}$ and the adatom energy $E_{adatom}^{(\text{surface})}$.

The extraction energy was evaluated by determining the potential energy of a perfect crystal ($U_{perfect}^{total}$), finding the potential energy for the crystal once a vacancy had been formed in the middle by extracting an atom ($U_{vacancy}^{total}$) and finding the difference:

$$E_{extract}^{(\text{bulk})} = U_{perfect}^{total} - U_{vacancy}^{total}. \tag{7}$$

To find the binding energy for the adatom $E_{adatom}^{(\text{surface})}$, the system energy was evaluated for the crystal with a vacancy in the centre, as an adatom was moved closer to the surface from infinity (see Fig. 3). This was done for all possible positions on surface to find the most preferred binding positions. Preferred binding sites were chosen as the points where the potential energy of the system from adding the adatom to the surface was a minimum. Using likely bonding sites, the average surface-adatom binding energy ($U_{adA-surf}^{total}$) for each crystal was determined and used to calculate the adatom energy:

$$E_{adatom}^{(\text{surface})} = U_{adA-surf}^{total} - U_{vacancy}^{total} \tag{8}$$

Finally the vacancy formation energy was calculated using equation 6.

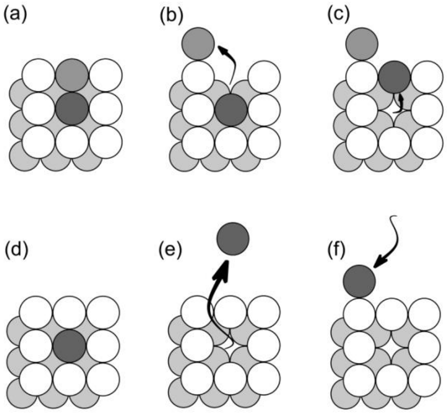

Figure 3. The Schottky mechanism for vacancy formation. (a) and (d) shows a simplified perfect FCC crystal containing only a surface defect at the top. The Schottky mechanism involves atoms moving into open defect positions, such as the surface (b) or existing vacancies (c). A simplified version of the vacancy-adatom pair formation which only represents the initial (d) and final (f) crystal states approximates the process and allows effective calculations of the vacancy formation energy. Thus in (e) the atom is extracted straight from the middle of the crystal and deposited on the surface in (f).

3. Results And Discussions

Bulk

Using equation 5, the cohesive energy for each element was evaluated and compared to literature values (Table 2). All the values calculated for cohesive energy compare well with established literature values reported by

Kittel (2005). [10] This shows that the SC potential accurately models the atomic binding energies in the crystals simulated.

Table 2. Cohesion energy as calculated for Al, Ni, Cu, Pd, Ag, and Pt and compared to values form literature. [10]

Element	Calculated (eV/atom)	Literature (eV/atom)
Al	3.23	3.39
Ni	4.24	4.44
Cu	3.34	3.49
Pd	3.81	3.89
Ag	2.82	2.95
Pt	5.75	5.84

Crystals with the (111), (100) and (110) surface orientations for Al, Ni, Cu, Pd, Ag, and Pt were simulated at 0 K. The extraction energy was determined from equation 7. Each crystal simulated in order to calculate the extraction energy also had its surface characterized using equation 8. Finally from the extraction energy and the adatom energy, the vacancy formation energy was calculated using equation 6. The vacancy formation energy was evaluated for Al, Ni, Cu, Pd, Ag, and Pt at 0 K, and are tabulated in Table 3. The values calculated experimentally compare well to values form literature.

Table 3. The results for each metal are detailed below. Results for these metals from previous studies are also detailed; bulk values with surface orientation dependent values are noted below results calculated in this article, in the relevant surface orientation column. Bulk values without a surface orientation component are noted in a separate column.

Element	110 (eV)	100 (eV)	111 (eV)	Surface orientation independent (eV)
Al	0.59±0.05	0.64±0.02	0.78±0.01	0.69±0.03 [18], 0.68 [11]
Ni	1.38±0.02	1.68±0.01	1.91±0.01	1.67, 1.78 [12]
Cu	1.08±0.02	1.33±0.01	1.51±0.01	1.29±0.02 [13]
Pd	1.49±0.01	1.80±0.01	2.09±0.01	1.71, 1.70 [3]
Ag	1.20±0.01	1.47±0.01	1.65±0.01	1.31 [14]
Pt	1.41±0.07	1.59±0.03	1.96±0.02	1.68 [15]

Next the process was repeated for the same perfect crystals at progressively higher temperatures. Some premelting was found in Cu and Al crystals.

Previous work in literature with an embedded atom model simulating a Cu(110) surface also showed the formation of an adlayer at 900 K through a generation of vacancies, and surface premelting at 80 K below the simulated bulk melting point. [16] Another study used a semi-empirical potential based on the tight-binding method to study the thermal behaviour of low index copper surfaces [17] and it was found in Cu(110) that above 700 K an adlayer formed due to adatom/vacancy formation, which lead to roughening and premelting of the Cu(110) surface. The results for Cu bulk crystals are shown in Fig. 4. Figure 4(a) shows the extraction energy, figure 4(b) shows the adatom energy and the final E_v for Cu is shown in Fig. 4(c). A slight linear trend can be observed in Fig. 4.

The Sutton-Chen potential used to simulate the Al crystals showed melting of the surface at very low temperatures. Although the melting temperature of Al is found at 660 K, melting was found to occur at temperatures as low as 400 K. This underestimation of the melting temperature in Al has also been observed before in thermodynamic studies of Al clusters and bulk simulations. [18-22] The Al surface was further found to premelt at temperatures below its melting temperature. [23]

As with Cu, a trend of decreasing E_v was observed for all the metals and are summarised in Table 4. It was found that for all the FCC metals studied $E_v^{(111)} > E_v^{(100)} > E_v^{(110)}$. Further the slope of the change of $E_v^{(111)}$ was generally the greatest. This is most probably due to disordering of the surface, where surface roughening is observed but the surface has not become amorphous.

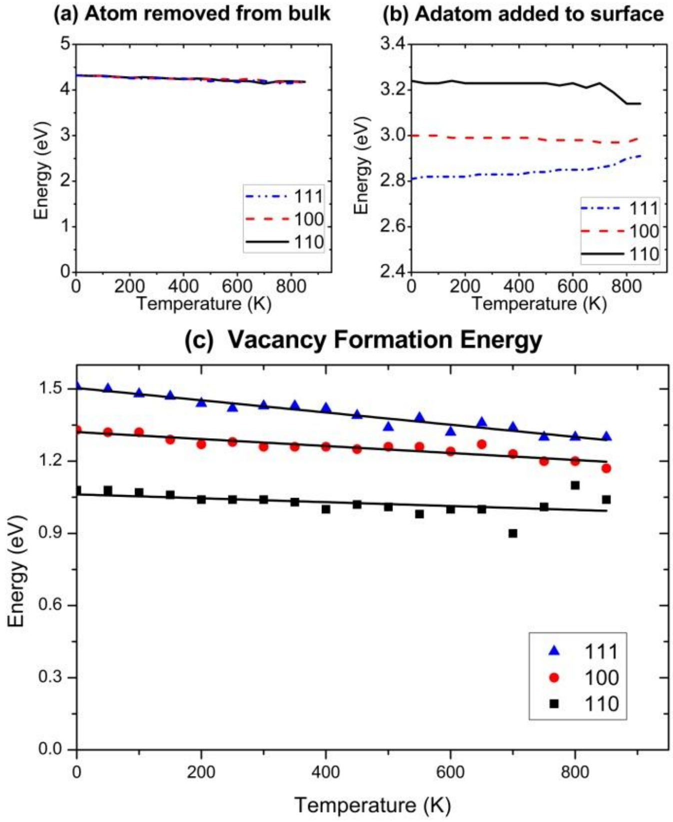

Figure 4. (a) The extraction energy for copper, which is the same for all three orientations. (b) shows the surface-adatom binding energy which is different for the (110), (100) and (111) surface orientations. As a result the vacancy formation energy in (c) is different for the different surface orientations.

Table 4. The percentage decrease in vacancy formation energy with increased temperature over the temperature range studied for the different surface orientations of the Al, Ni, Cu, Pd, Ag, and Pt crystals.

Element	110 (%)	100 (%)	111 (%)
Al	8.5	4	6
Ni	9	9	15
Cu	4	12	15
Pd	10	9	12
Ag	4.5	13	17
Pt	10	7.5	12

Nanocube

The cohesive energy per atom was calculated for Cu nanocubes where the edges and corners were systematically cut away, show in Fig. 5. The lowest cohesive energy was for a cube of 15 atoms to a row, column or line (15^3 packing), about 56 nm across, where edge atoms have been cut away to reveal a (110) orientated surface 3 binding positions wide. The vacancy formation energy was calculated for this nanocube and is given in Table 5, as 1.30 eV. This value compares well to the surface orientation independent bulk vacancy formation energy.

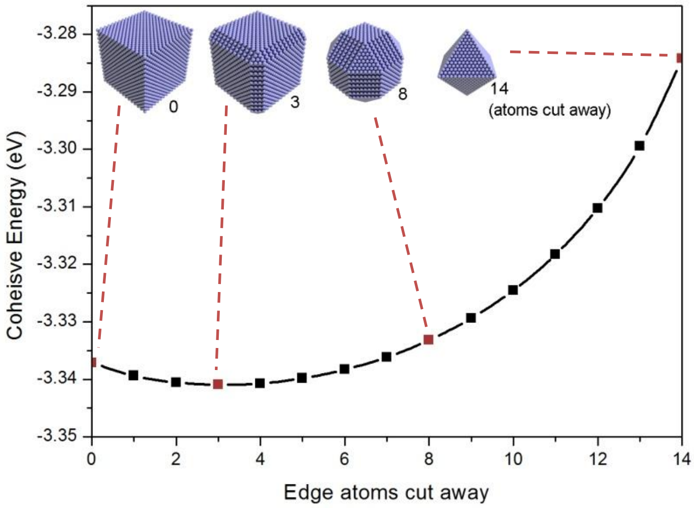

Figure 5. The cohesive energy for copper nanocubes with sides of (100) orientation, edges of (110) orientation and corners of (111) orientation. More and more atoms are cut from the edges until only (111) orientated "corners" remain.

Table 5. Energy values calculated for a nanocube with atoms cutaway at the edges and corners to reveal edges 3 atoms wide.

Ecoh	3.34 eV
Ebulk	4.31 eV
Esurface	3.01 eV
Evac	1.30 eV

4. Conclusion

The Sutton Chen potential was used to simulate Al, Ni, Cu, Pd, Ag, and Pt FCC crystals with (110), (100) and (111) surface orientations at a range of temperatures. To establish the accuracy of the model, cohesive energies were calculated at 0 K for all the crystals. The calculated cohesive energies compared very well with values from literature. The vacancy formation energy for Schottky defects was calculated. It was found that the surface orientation of a crystal influences the vacancy formation energy of the underlying bulk crystal, in that $E_v^{(111)} > E_v^{(100)} > E_v^{(110)}$. This is evident in all six FCC metals studied. Some premelting was seen in Al and Cu. A decrease in vacancy formation energy resulting from crystal expansion at higher temperatures was observed for all the vacancy formation energies calculated. The vacancy formation energy was also caluclated for a Cu nanocube of 15^3 with (110) edges 3 atoms wide, the result $E_v = 1.30$ eV.

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