Comment on "Vacancy formation energy of small particles"

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Recently, Qi *et al*. have developed a general method to account for vacancy formation energy of small particles [1]. In this method, they obtained a very simple linear relation between the cohesive energy and the vacancy formation energy of small particles by extending Tiwari's model which is used to predict corresponding bulks [2] (Equations 1 and 4 of Ref. [1]). We comment on this prediction.

In Tiwari's model, the equation $E_V = (Kmn/Z)E_0$ is available for any metals, but all the Ref. [2] and references therein cannot give the physical significance of K, m, and n, and furthermore, for different metals they give different values of m and n, which seems to lack enough physical background.

It is known that vacancy formation energy E_V is defined as the energy to take out an interior atom from a normal lattice site and replace on the surface of crystal [3], then we can write the E_V as the composing of three parts of energy [4], first one E_1 is the increasing energy when breaking the bonds of the interior atom to its surroundings with Z_B dangling bonds of surrounding atoms created, second one E_2 is the decreasing energy when putting the missing atom to the surface of crystal with Z_S dangling bonds of surface atoms combined, and the last one E_3 is the decreasing energy caused by the relaxation of surrounding atoms with the birth of vacancy, where Z_S is the coordination number of surface atom and Z_B the corresponding bulk one. It is known that the total cohesive energy equals the energy that can divide crystal into whole isolated atoms by destroying all bonds [5, 6], then we can regard E_1 as E_0 and E_2 as $-(Z_S/Z_B)E_0$ [4]. According to Brooks' consideration [7], the surface tension of the vacancy will tend to contract the size of the hole by distorting the rest of the crystal elastically, then E_3 equals the minimum of the total of the changed surface energy of vacancy caused by distortion and the additional deformation energy. Based on the discussion above, E_V can be described as follows [4]:

$$E_V = E_1 + E_2 + E_3 = \left(1 - \frac{Z_S}{Z_B}\right)E_0 - \frac{\pi d^2\gamma^2}{\gamma + Gd} \quad (1)$$

where d denotes atomic diameter, G and γ are the shear modulus and the surface energy per unit area surrounding the vacancy.

For different structures A1, A2, A3, and A4 metals, $(1\text{-}Z_S/Z_B)$ is calculated as 13/36, 1/2, 29/72, and 1/4, respectively based on the broken-bond theory [4, 8]. In order to prove the quantitative effectiveness of our method, the prediction results of our model, Tiwari's model [2] and experimental values are shown in Table I.

It is apparent that the predictions of our model are more consistent with the experimental values than Tiwari's model, for the prediction results of Tiwari's model are all much smaller than experimental values.

Note that the contraction of vacancy calculated in E_3 is fairly small and elastic, the shear module of the particle can be regarded as unchanged when the size decreases, also the surface energy of the particle can be regarded as size independent for the surface of the particle is free of reconstruction after small contraction [18]. Therefore, according to the discussion of Ref. [1], using E_P to replace E_0, we get

$$E_{VP} = \left(1 - \frac{Z_S}{Z_B}\right)E_P - \frac{\pi d^2\gamma^2}{\gamma + Gd} \quad (2)$$

TABLE I Comparison on the prediction results of our model, Tiwari's model and experimental values (R is in Å, G and γ_0 are in $10^{10} \times$ J/N^2 and J/m^2, E_0 and E_V are in eV)

Metal (structure)	R [13]	G [14]	γ [8, 15, 16]	E_0 [17]	E_V (our model)	E_V (experiment)	E_V (Tiwari's model)
Be (A3)	1.12	15.6	2.64[8]	3.32	1.16	1.11[9]	0.87
Ca (A1)	1.97	2.40	0.49[8]	1.84	0.59		0.48
Cr (A2)	1.26	11.53	2.40[16]	4.10	1.82	2.00 [10]	1.53
Mn (A1)	1.27	7.95	1.60[16]	2.92	1.03		0.93
Fe (A2)	1.23	8.16	2.55[16]	4.28	1.80	1.79 [11]	1.29
Co (A3)	1.25	8.20	2.69[8]	4.39	1.39	1.35 [9]	0.88
Rb (A2)	2.43	0.09	0.12[16]	0.85	0.31	0.31[12]	0.11
Sr (A1)	2.15	0.60	0.38[8]	1.72	0.44		0.44
Cs (A2)	2.62	0.07	0.09[15]	0.80	0.30	0.28 [12], 0.35 [12]	0.10

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Let Equation 2 minus Equation 1, and inserting Equation 3 of Ref. [1], we have

$$E_{VP} = E_V\left(1 - 3 \cdot \frac{d}{D} \cdot k\right) \quad (3)$$

Where $k = [1 - (Z_S/Z_B)]E_0/E_V$. The above equation is the basic relationship to calculate the size dependence on the E_V of small particles. Apparently, the cohesive energy and the vacancy formation energy is not a simple linear relation, and Equation 3 of this paper is more precise than Equation 5 of Ref. [1] when used to predict the E_V of small particles.

Acknowledgment

Helpful discussions with Dr. W. H. Qi are gratefully appreciated.

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Received 13 October
and accepted 10 December 2004