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Evaluation of the Relative Volume of a Vacancy

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An understanding of many processes in solids, especially at high temperatures, requires the knowledge of not only the vacancy formation energy, but also the vacancy volume. In addition to theoretical [1] and experimental [2] evaluations, this quantity is often estimated from semiempirical correlations [3] between various thermodynamic and thermal properties.

The vacancy formation energy and volume are also important for describing the properties of condensed islands deposited in vacuum and of small particles prepared by various methods (examples of such properties are the diffusivity, the lattice parameter, and so on). Analysis of expressions for the vacancy formation energy in small particles [4, 5] shows that they can be used for estimating the vacancy volume. In particular, the vacancy volume can be evaluated from the decrease in melting temperature of small particles as their size is reduced. Analysis of such a possibility is the subject of this communication.

As a starting point, we assume that the vacancy formation energy E_v is proportional to the melting temperature T_s:

$$E_v = \gamma T_s, \tag{1}$$

where γ is a constant dependent on the type of crystal structure. If the melting temperature is changed by ΔT (e.g., when we consider small particles instead of bulk samples), the vacancy formation energy also changes as

$$\Delta E_v = \gamma \Delta T. \tag{2}$$

On the other hand, it was shown earlier [5] that the transition from bulk samples to small particles, which is accompanied by a decrease in the melting temperature $\Delta T = T_r - T_s$, can be described in terms of application of an effective pressure ΔP, such that

$$\Delta E_v = \Delta P V_v, \tag{3}$$

where V_v is the vacancy volume. The effective pressure can be readily found, because ΔT and ΔP are related by a simple equation

$$\Delta P = \frac{dP}{dT}\Delta T \tag{4}$$

Taking into account the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\lambda}{T_s \Delta V} \tag{5}$$

relation (4) can be rewritten as

$$\Delta P = \frac{T_r - T_s}{T_s}\frac{\lambda}{\Delta V} \tag{6}$$

Here λ is the heat of fusion and ΔV is the change in volume upon melting. Correspondingly,

$$\Delta E_v = \frac{T_r - T_s}{T_s}\frac{\lambda}{\Delta V} V_v \tag{7}$$

Making use of the fact that $\Delta V = \Omega\delta$ (δ is the relative change in volume upon melting and Ω is the atomic volume), we can show that

$$\Delta E_v = \frac{T_r - T_s}{T_s}\frac{\lambda}{\Omega\,\delta} V_v \tag{8}$$

Equating expressions (2) and (8) for ΔE_v and taking into account relation (1), we obtain the following equation for the relative vacancy volume

$$\frac{V_v}{\Omega} = \frac{E_v}{\lambda}\delta \tag{9}$$

This expression contains quantities (the vacancy formation energy, heat effusion, and relative change in volume upon melting) that are well known for most substances. Thus, the vacancy volume near the melting point can be evaluated from expression (9).

Using relation (9), we calculated the ratio V_v/Ω for some metals, in particular, for those whose vacancy volumes are known from experiments or were calculated in [1] using the microscopic and thermodynamic parameters. The table shows that there is a certain correlation between the calculated and published data on the vacancy volumes. This indicates that relation (9) can, indeed, be used' for evaluating the vacancy volumes.

Comparison of calculated and published data on vacancy volumes

Element	E_v, eV[l]	λ, kJ/mol [8]	δ, % [8]	V_v/Ω, from (9)	V_v/Ω, published data	
					calculated [1]	experiment [2]
Ag	0.92 1.09 [7]	11.3 [9]	3.8	0.299 0.350	0.370	0.78 [13]
Au	1.08 0.94 [7]	12.37 [9]	5.1	0.429 0.374	0.315	0.52-0.85 [13]
Pt	1.58 1.7 [14]	19.7	6.6 [10]	0.529 0.549	0.274	0.5
Al	0.77 [7]	10.47	6.5	0.461	0.414	0.5
Cu	1.11 [7]	13.02	4.2	0.346		
Ni	1.4 [14]	17.71	4.5 5.4 [10]	0.343 0.412		
Pb	0.49	4.98	3.5	0.332	0.273	0.5
Zn	0.54	7.2	4.7	0.34	0.335	0.5
Cd	0.41	6.41	4.0	0.247	0.262	
In	0.53	3.27	2.0	0.313	0.26	0.39 [11]
P-Sn	0.52	7.08	2.3	0.163	0.235	
|3-Na	0.42	2.64	2.5	0.383	0.508	0.4 [12]
K	0.25	2.34	2.55	0.263	0.304	0.25
Rb	0.22	2.198	2.5	0.241	0.252	0.25
Cs	0.21	2.09	2.6	0.252	0.252	0.25

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