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MONOVACANCY FORMATION ENERGY
and
DEBYE TEMPERATURE OF CLOSE-PACKED METALS

by

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MONOVACANCY FORMATION ENERGY AND DEBYE TEMPERATURE
OF CLOSE-PACKED METALS

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ABSTRACT

Energy of formation of monovacancies in close-packed metals has been calculated. It is shown that a simple Einstein model of the solid can be used to relate the formation energy and the Debye characteristic temperature. The predicted results from the above model agree quite well with the observed values. It appears that formation energies can be estimated from the proposed model with an uncertainty of not more than 5-10%. A justification for the observed correlation between the formation energy and the absolute melting temperature is given.

1. INTRODUCTION

Attempts have been made (Sosin and Brinkman 1959), Thompson 1960, Frenkel 1946) to correlate the energy of formation or motion of vacancies with other crystal properties such as the melting temperature and the heat of sublimation, etc. However these are mostly qualitative in nature. A few somewhat useful quantitative correlations have also been reported (Mukherjee 1964, Mukherjee 1964, Mehl et al. 1961). It will be shown in this paper that the formation energy of monovacancies in close-packed metals can be calculated from the corresponding Debye characteristic temperature of the metals.

The formation energy of a vacancy reflects the bond strength of the solid. Let us consider a phenomenological model of vacancy formation where a central atom is surrounded by Z number of nearest neighbors. Creation of a vacancy by removing this central atom will mean breaking Z number of bonds and then replacing the atom on a free surface thereby restoring on the average $Z/2$ bonds. Thus in the first approximation the formation energy of a vacancy is equal to $Z/2$ times the bond strength between a pair of atoms. Since the vibrational frequencies of the atoms in a solid are directly related to the bond strength, it seems logical to attempt a correlation between the vacancy formation energy and the characteristic frequency of the solid.

2. METHOD

Let us assume an Einstein model of the solid. In this model there are $3N$ independent oscillators, where N is the total number of atoms in the solid. Let the cohesive force $f(r)$ between atoms A and B in Fig. 1 be represented by

$$f(r) = C/r^n \quad \dots\dots\dots(1)$$

where C is a constant, r is the distance of separation between the two atoms at any instant of time, and n is an integer. In figure 1, r_0 is the equilibrium spacing between the atoms, so that the positions 1, 2, 3 etc. correspond to the minimum potential energy points. When the atoms occupy these positions then the attractive and the repulsive forces exactly balance each other. For a small displacement Δr of atom B (see Fig.1) from its equilibrium position, we can write from eqn. (1):

$$f(r) = C/(r_0 + \Delta r)^n \quad \dots\dots\dots (2)$$

Expanding the right hand side of eqn.(2) in a power series

$$f(r) = \left(C/r_0^n \right) \left[(1 - n \Delta r/r_0 + \dots) \right] \dots\dots (3)$$

Neglecting higher power terms in eqn.(3) (since $\Delta r/r_0$ is small) we get

$$f(r) = C/r_0^n - nC \Delta r/r_0^{n+1} \quad \dots\dots\dots (4)$$

Since the equilibrium separation between the two atoms does not change appreciably due to the small displacement Δr , we can,

in the first approximation, assume that the repulsive interaction force is still equal and opposite of C/r_0^n . Thus the net inward restoring force $f_R(\Delta r)$ is

$$f_R(\Delta r) = -nC \Delta r / r_0^{n+1} \dots\dots\dots (5)$$

Let W_k be the work required to remove atom B from site 2 to infinity, then

$$W_k = \int_{r_0}^{\infty} f(r) dr = C / (n-1) r_0^{n-1} \dots\dots\dots (6)$$

Combining eqns.(5) and (6)

$$f_R(\Delta r) = -n(n-1)W_k (\Delta r / r_0^2) \dots\dots (7)$$

Assuming simple harmonic motion of the oscillating atoms, the restoring force $f_R(\Delta r)$ can be written as

$$f_R(\Delta r) = -K \Delta r, \dots\dots\dots (8)$$

where K is a constant. Comparing eqns. (7) and (8)

$$K = n(n-1)W_k / r_0^2 \dots\dots\dots (9)$$

The classical vibration frequency ν of a particle whose mass is m, is given by

$$\nu = (1/2 \pi) (K/m)^{\frac{1}{2}} \dots\dots\dots (10)$$

Combining eqns.(9) and (10)

$$\nu = (1/2 \pi) \left[n(n-1)W_k / m r_0^2 \right]^{\frac{1}{2}} \dots\dots (11)$$

If a central atom has Z nearest neighbors, then creation

of a vacancy requires that Z bonds are broken and then the atom is replaced on a free surface thereby restoring Z/2 bonds. Thus if E_f is the energy of formation of a vacancy, then

$$E_f = (Z/2)(W_k) \dots\dots\dots (12)$$

Combining eqns.(11) and (12),

$$\nu = (1/2 \pi) \left[n(n-1)2E_f/Zmr_o^2 \right]^{1/2} \dots\dots\dots (13)$$

We now replace r_o by $(v)^{1/3}$, where v is the average atomic volume. In eqn.(13) we will write $Z = 12$ (for close-packed metals), and also in the first approximation we write $\nu = \nu_D$ where ν_D is the Debye characteristic frequency of the solid. Thus for the Debye characteristic temperature θ_D , we have

$$\theta_D = (h/2\pi k) \left[n(n-1)E_f/6mv^{2/3} \right]^{1/2}, \dots\dots\dots (14)$$

where h and k are the Plank's constant and the Boltzmann's constant respectively.

The type of cohesive force assumed in eqn.(1) is not new. This type of interaction was first assumed by Grüneisen (1908) and later applied by Lennard-Jones and Devonshire (1939), Fürth (1944) and many others. Although there is some doubt about the value of the exponent in eqn.(1), an average value of $n = 5$ can be taken from Fürth's (1944) results.

Thus by writing $n = 5$ and substituting the proper values of the constants and the conversion factor in eqn.(14), we have

$$\theta_D = 35.1 (E_f/MV^{2/3})^{1/2} \dots\dots\dots (15)$$

where E_f is in cal/gram-atom, M is the atomic weight in gram and V is the molar volume in cm^3 / gram-atom.

3. RESULTS AND DISCUSSION

Calculated values of the factor $(E_f/MV^{2/3})^{1/2}$ along with the observed Θ_D and E_f values are shown in table 1. The Θ_D values chosen are the experimental values at the liquid He temperature. These low temperature values are chosen for two reasons. First of all Θ_D is temperature dependent to some extent and most of the standard tables of Debye temperature of solids do not specify the temperature of measurement. Secondly at low enough temperature only the sound waves of very long wave-lengths are excited and thus the effect of the atomic structure is unimportant and Debye T^3 formula for the specific heat becomes exact.

In fig. 1, Θ_D versus $(E_f/MV^{2/3})^{1/2}$ values from table 1 are shown. The result is a linear plot and can be represented by

$$\Theta_D = 34.3 (E_f/MV^{2/3})^{1/2} \dots\dots\dots (16)$$

Considering the oversimplified model of the solid assumed in this work and the uncertainty in the value of the exponent n, the agreement between eqns.(15) and (16) is remarkable. Thus if the Debye temperature of the metal is known then E_f can be estimated from eqn.(16) with an uncertainty of not more than 5-10%.

From the foregoing a correlation between E_f and the absolute melting temperature T_m can be obtained immediately. Lindemann (1910) has shown a relation between Θ_D and T_m as follows:

$$\Theta_D = C_1 (T_m/MV^{2/3})^{1/2} \dots\dots\dots (17)$$

where the value of C_1 lies in the range of 130-160. If we write C_2 for the numerical constant in eqn.(16), then combining eqns.(16) and (17),

$$E_f = (C_1/C_2)^2 T_m \dots\dots\dots (18)$$

In table 2, calculated values of E_f from eqn.(18) are compared with the best experimental values. Again the agreement seems to be quite good. In using eqn.(18), C_1 must be calculated individually for each metal from eqn.(17).

The formation energy E_f for Ni, reported in this paper is not a directly measured value. Simmons and Balluffi (1963) have shown that for fcc metals $E_f = 0.55Q$, where Q is the activation energy of self-diffusion. The best experimental value of Q for Ni is 66.8 kcal/mole (Hoffman et al.1956), and this value is used to calculate E_f for Ni together with an estimated value by the present author elsewhere (Mukherjee 1964).

Thus it seems possible to estimate the formation energy of monovacancies in close-packed metals with a fair amount of certainty from either the Debye temperature or the melting temperature of the solid. The discussion in this paper is restricted to close-packed metals because not enough experimental values of E_f are available for open metals to test any proposed model. It is also interesting to note that eqn.(16) offers another method of calculating Debye temperature of close-packed metals if the monovacancy formation energy is known.

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Table 1. Debye temperature Θ_D , monovacancy formation energy E_f , and $(E_f/MV^{2/3})^{1/2}$ for some close-packed metals.

Metal	Θ_D Observed	E_f cal/gram-atom Observed #	$(E_f/MV^{2/3})^{1/2}$	$\Theta_D/(E_f/MV^{2/3})^{1/2}$
Au	165 ^a	21667 \pm 2074	4.83 \pm 0.2	34.2 \pm 2
Ag	225 ^{a,b}	25124 \pm 2305	7.02 \pm 0.3	32.0 \pm 2
Cu	345 ^{a,c,d}	26968 \pm 2305	10.72 \pm 0.3	32.3 \pm 2
Al	418 ^e	17748 \pm 1613	11.89 \pm 0.5	32.8 \pm 2
Pb	94.5 ^{e,f}	\approx 12216	2.90 \pm 0.3	32.7 \pm 2
Pt	229 ^e	32270 \pm 2305	6.16 \pm 0.2	37.2 \pm 2
Mg	406 ^{e,g}	20514 \pm 1613	12.02 \pm 0.4	33.8 \pm 2
Ni	441 ^h	34575 \pm 2305	12.50 \pm 0.5	33.1 \pm 2

Only chosen values are shown, for reference see table 2.

- a. Corak et al. (1955).
- b. Keesom and Pearlman (1955).
- c. Giauque and Medas (1941).
- d. Leighton (1948).
- e. Keesom and Pearlman (1954).
- f. Eisenstein (1954).
- g. Smith (1955).
- h. Rayne (1956).

Table 2. Correlation between the monovacancy formation energy and the absolute melting temperature of some close-packed metals.

Metal	$(C_1/C_2)^2$	$E_f = (C_1/C_2)^2 T_m$		E_f eV. Experimental
		cal/gram-atom	eV	
Au	16.06	21456	0.93	0.94 ± 0.09^a 0.95 ± 0.10^b
Ag	17.77	21912	0.95	1.09 ± 0.10^c 1.10 ± 0.04^d
Cu	17.51	23743	1.03	1.17 ± 0.10^e 1.0^f
Al	20.03	18682	0.81	0.75 ± 0.07^g 0.76 ± 0.04^h 0.79 ± 0.04
Pt	18.55	37953	1.64	1.40 ± 0.10^j 1.30 ± 0.10^k 1.4^l
Pb	18.17	10909	0.47	0.53^m
Ni	19.90	34387	1.49	$1.50 \pm 0.10^*$
Mg	21.41	19783	0.86	0.89 ± 0.06^n

* Please see the discussion.

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|---------------------------------|-----------------------------------|
| a. Simmons and Balluffi (1962). | h. Bradshaw and Pearson (1957). |
| b. Bradshaw and Pearson (1957). | i. DeSorbo and Turnbull (1959). |
| c. Simmons and Balluffi (1960). | j. Bradshaw and Pearson (1956). |
| d. Doyama and Koehler (1962). | k. Bacchella et al. (1959). |
| e. Simmons and Balluffi (1963). | l. Gertsriken and Novikow (1960). |
| f. Airoidi et al. (1959). | m. Feder and Nowick (1958). |
| g. Simmons and Balluffi (1960). | n. Beevers (1963). |

FIGURE CAPTIONS

Fig. 1. Model of a linear chain of vibrating atoms. Positions 1,2,3 etc. are the equilibrium positions and r_0 is the mean equilibrium distance between any two atoms.

Fig. 2. Debye characteristic temperature θ_D versus $(E_f/MV^{2/3})^{1/2}$ for close-packed metals. E_f is in cal/gram-atom and M and V are the mass and volume respectively of a gram-atom.

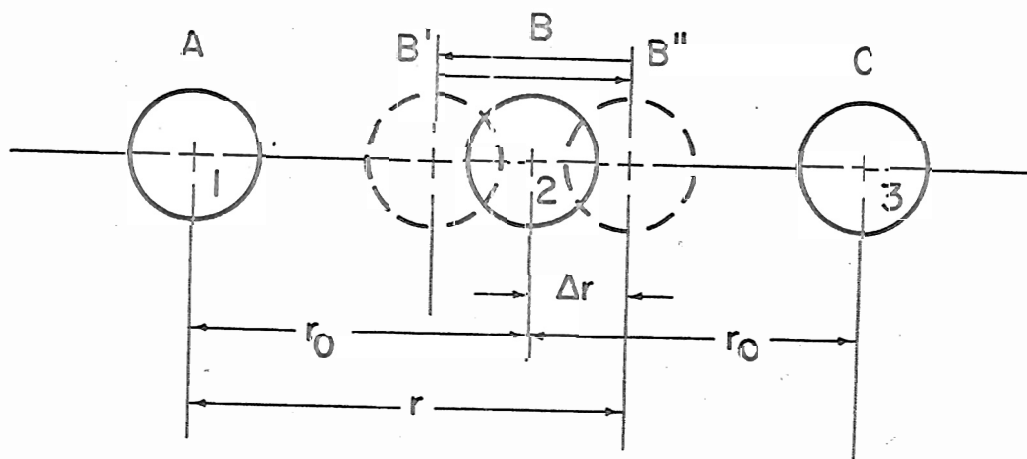


fig. I

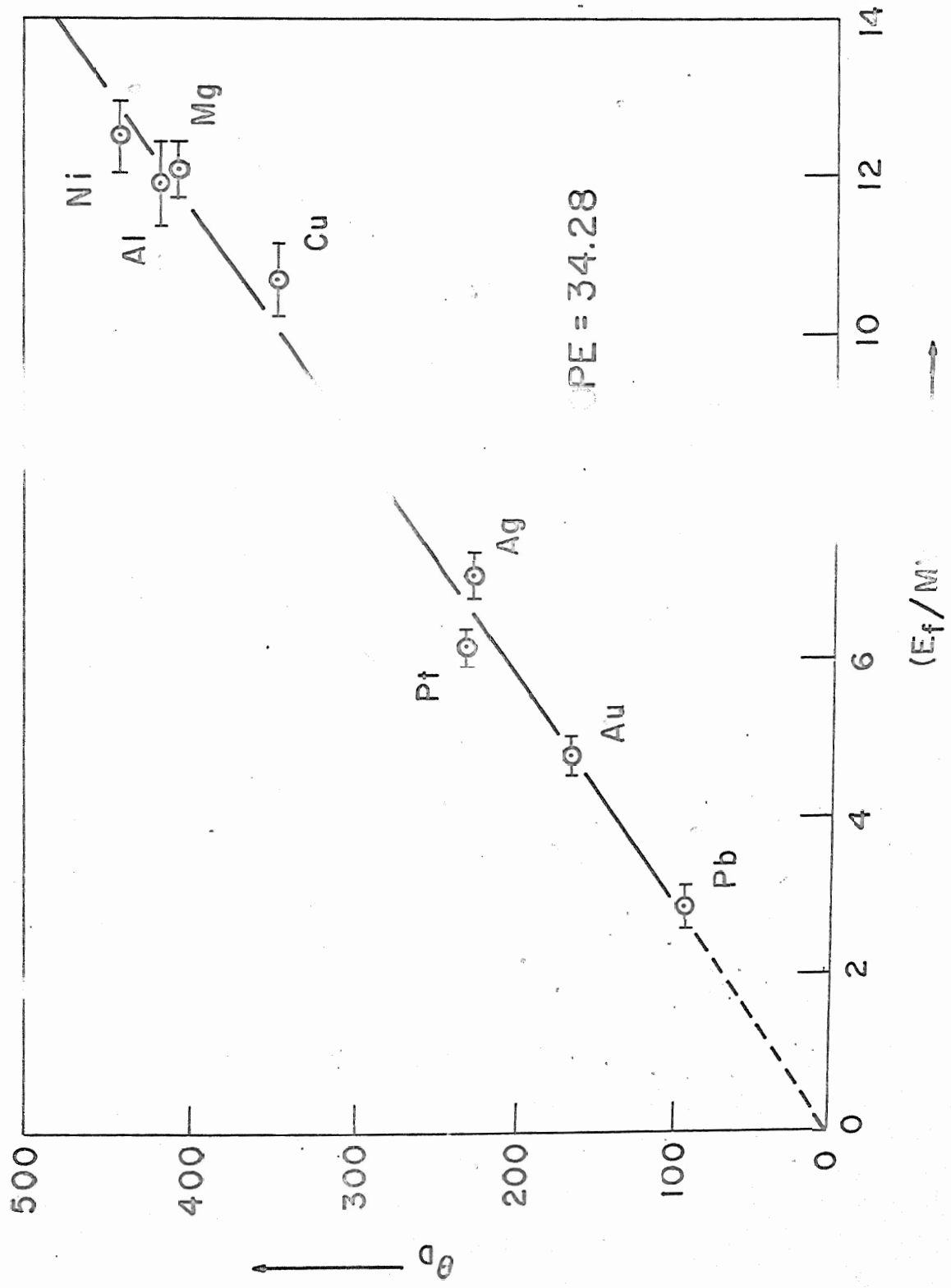


Fig. 2