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ON THE ELASTIC APPROXIMATION TO THE VACANCY
FORMATION ENERGY IN METALS

CASE FILE
COPY

by

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ABSTRACT

The isotropic elastic continuum model proposed by Friedel [1-3] to describe point defects in metals is suitably modified and used to calculate the energy and entropy of vacancy formation. The vacancy core is considered as a defect having elastic properties different from those of the surrounding lattice. Three criteria are set forth for the application of the model. Firstly, the boundary conditions are satisfied on the interface between the vacancy core and the lattice region so as to render the defect in the host lattice free of external stress, pressure or body force. Secondly, the ratio of vacancy volume to atomic volume is considered to be equal to the experimentally determined value. Thirdly, the Voigt [4] average of the single crystal elastic constants is employed in the calculations. Good agreement is obtained between theory and experiment for a variety of metals.

INTRODUCTION

There exists in the literature many models for estimating the energy of formation of vacancies in metals. Each of these models represents either one or the other of two basic approaches - the isotropic elastic continuum approximation [3,5-9] and the discrete atomic lattice model [5,10-18]. Hall [5] and Gibbs [8] made a qualitative comparison between the two models and showed how the discrete and elastic continuum models are basically related. The elastic model can represent the smoothing out of a discrete atomic displacement model without serious loss of quantitative stored energy value estimates.

To apply the isotropic elastic continuum model to the calculation of the energy of vacancy formation, three basic criteria must be satisfied. Firstly, the boundary conditions at the interface between the vacancy and the lattice region should be satisfied so as to render the defect free of external stresses [19]. Secondly, the ratio of the vacancy volume to atomic volume should be equal to the experimentally determined value which is found to be approximately 0.5 for metals with cubic symmetry [20-24]. Thirdly, a Voigt [4] average over the single crystal elastic constants should be used in order to maintain the isotropic concept. McLellan [9] applied the second criteria to the elastic continuum model described by Eshelby [7]. He found good agreement between calculated and experimental values for the energy and entropy of formation of vacancies. However, these calculations leave an internal pressure at

the vacancy core and the apparent use of the single crystal shear modulus C_{44} for the isotropic shear modulus seems unjustified.

Brooks [6] considers the vacancy as a vacant core region possessing a boundary surface energy and a surrounding distorted elastic region. By minimizing the total energy of the system, the displacement through which the surrounding lattice relaxes was found for copper. The resulting displacements are rather small and predict a vacancy to atomic ratio of 0.74. By using an uncommon method to average the elastic constants, Brooks obtained a value for the energy of vacancy formation which appears about twice that determined experimentally for copper.

The present work modifies the misfitting sphere model of Friedel [1-3], so that self-consistent elastic continuum relationships are obtained. In these calculations the three criteria for the model are satisfied. The thermodynamic parameters related to vacancy formation are developed and the calculated values are compared with known experimental results.

THE FRIEDEL MODEL

In the elastic model due to Friedel [1-3], a spherically symmetric isotropic material I is assumed having radius R , atomic radius a , and compressibility and shear modulus χ and μ respectively. A spherical cavity of volume $\left(\frac{4\pi a^3}{3}\right)$ is removed from the interior of the bulk and replaced by a material II with atomic radius a' , and compressibility and shear modulus χ' and μ' respectively. The two materials are then allowed to adjust under the influence of unbalanced surface stresses across their respective interfaces until the latter become one and the same interface. Continuity of the two media exists at a radius b . At this point, the surface traction on the two interfaces cancel to leave the resultant interface stress free. The displacements in material I and II have the respective functional forms

$$U_I(\vec{r}) = B\vec{r} + C \frac{\vec{r}}{|\vec{r}|^3} \quad (1)$$

$$U_{II}(\vec{r}) = A\vec{r} \quad (2)$$

where A , B and C are constants to be determined from the boundary conditions. Equations (1) and (2) can be suitably differentiated to yield the strains and, hence, the stresses in each material. Balancing the stresses in medium I and II at $r = b$ and imposing continuity of media yields:

$$A = -\eta \left\{ \frac{\chi'}{\chi\beta} \right\} \quad (3)$$

$$B = \frac{\eta b^3}{R^3} \left\{ \frac{1}{x\beta} \right\} \quad (4)$$

$$C = \eta b^3 \left\{ \frac{1}{\beta} \right\} \quad (5)$$

where $\eta = \frac{a' - a}{b}$, $x = \frac{3}{4\mu\chi}$, and $\beta = 1 + \frac{\chi'}{x\chi}$.

APPLICATION TO VACANCIES

1) The Elastic Model

To apply the Friedel model to vacancies, material II is assumed to be a compressible and perturbed Fermi electron gas originating from the local electron charge redistribution when a vacancy is formed and the local lattice relaxes. The effective electron gas pressure in the vacancy cavity is balanced with the negative pressure of the relaxing elastic material across the interface at $r = b$, so that

$$-\frac{4\mu\eta}{\beta} = \frac{3}{5\chi'} \quad (6)$$

The expression for the bulk modulus of an electron gas has been employed [25-26] in the above relation.

The elastic model described above defines the displacement at $r = b$ as radial and equal to $(b - a)$, so that the local vacancy dilatation is $\frac{3(b - a)}{a}$. We define the local vacancy dilatation as $(f - 1)\Omega$ where f is the experimentally evaluated relaxed atomic volume ratio. The local and atomic vacancy dilatations being assumed equal, it follows that:

$$\frac{3(b - a)}{a} = f - 1 \quad (7)$$

where the approximation $\frac{b-a}{a} \approx \left(\frac{b-a}{b}\right)$ has been made and an error of less than 10% introduced. The experimental values of f are accurate only to $\pm 5\%$ so that this assumption appears justified.

The continuity of media criterion of the elastic model shows:

$$b = \left\{ a' + \frac{1}{x} \frac{\chi'}{\chi} a \right\} \frac{1}{\beta} \quad (8)$$

Solution of equations 6, 7, and 8 shows that:

$$b = \frac{3}{4-f} a \quad (9)$$

$$a' = \frac{a}{4-f} \left[3 + (f-1) \frac{\chi'}{x\chi} \right] \quad (10)$$

and

$$\chi' = \frac{9}{20\mu(1-f)} \quad (11)$$

The elastic stored energy of the vacancy is found by evaluating the work done on the internal surface of medium I and the external surface of medium II, each surface undergoing determined displacements under known forces. Combining the two contributions to the total energy, one finds the elastic stored energy per vacancy to be:

$$E_o = \frac{8\pi\mu\eta^2 b^3}{1 + \frac{4\mu\chi'}{3}} \quad (12)$$

Use of equations 9, 10 and 11, reduces equation 12 to:

$$E_o = \frac{18(1-f)^2}{(4-f)^3} \left\{ 1 + \frac{3}{5(1-f)} \right\} \mu\Omega \quad (13)$$

2) Thermodynamics of the Model

The elastic stored energy E_0 is a Gibbs free energy associated with forming a vacancy. Following a development given by Friedel [1, 2], the total free energy change per vacancy in the crystal can be considered as the sum of two terms:

$$\Delta F = \Delta F_1 + \Delta F_2 \quad (14)$$

where ΔF_1 is the configurational free energy change associated with placing a vacancy in the crystal so that:

$$\Delta F_1 = kT \left\{ c_v \ln c_v + (1 - c_v) \ln(1 - c_v) \right\} \quad (15)$$

where c_v is the atomic concentration of vacancies and k and T have their usual meaning. ΔF_2 is the Gibbs free energy change per vacancy due to other contributing terms and may be written as

$$\Delta F_2 = \Delta U_2 - T\Delta S_2 \quad (16)$$

where ΔU_2 is the energy of formation of the defect and ΔS_2 is an entropy change due to the change in vibrational frequency of the atoms locally associated with the crystal defect. Knowing E_0 to be the Gibbs free energy change evaluated at low temperature (0°K in the present paper), one obtains the vacancy formation energy at any temperature T , as

$$\Delta U_2 = E_0 + \left(\frac{\partial E_0}{\partial T} \right)_P T \quad (17)$$

The total free energy change of the crystal is therefore

$$\Delta F = c_v \left[E_0 + T \left(\frac{\partial E_0}{\partial T} \right)_P - TS_2 \right] + kT \left[c_v \ln c_v + (1 - c_v) \ln(1 - c_v) \right] \quad (18)$$

The size effect refinement is neglected in this type of calculation [27] since the radius of the sample is assumed to be in the macroscopic size range of 1 cm. Upon minimizing ΔF with respect to c_v , one finds the equilibrium concentration of vacancies, c_v^0 , to be

$$c_v^0 = \exp \left[\frac{-E_0 - T \left(\frac{\partial E_0}{\partial T} \right)_P + T\Delta S_2}{kT} \right] \quad (19)$$

Differentiation of equation 12 with respect to T yields

$$\left(\frac{\partial E_0}{\partial T} \right)_P = E_0 \left[3\alpha + \frac{1}{\mu} \frac{d\mu}{dT} \right] \quad (20)$$

where α is the coefficient of linear expansion.

To evaluate ΔS_2 , it is assumed that each atom can be approximated as a simple harmonic oscillator vibrating with a frequency ν . Applying a high temperature approximation to a quantum statistical average vibrational energy, the free energy per oscillator per degree of freedom is found to be $kT \ln \left(\frac{h\nu}{kT} \right)$ [28]. Differentiating this expression with respect to temperature; one finds the change in atomic vibrational entropy to be

$$\Delta S_2 = -k \ln \left(\frac{\nu'}{\nu} \right) \quad (21)$$

where ν' is a reduced vibrational frequency per atom associated with the relaxed lattice neighboring the vacancy. Because ν' is very close to ν , $\ln \frac{\nu'}{\nu}$ can be expanded in a Taylor series around ν . Multiplying and dividing by the local lattice dilatation, $\frac{\Delta V}{\Omega}$, it is found per Z nearest

neighbor oscillators per degree of freedom that:

$$\frac{\Delta S_2}{\Delta V} = - Z \frac{k}{\Omega} \frac{d(\ln \nu)}{d(\ln V)}$$

The negative of the differential is the Grüneisen's constant, γ , which is relatively independent of the temperature and the Einstein frequency. Since the local atomic dilatation per oscillator surrounding the vacancy is given by $\frac{(1-f)}{Z}$ and we assume as did Cottrell [29] for the atoms near the core of a dislocation, that only one degree of freedom has its frequency perturbed, equation (22) becomes:

$$\Delta S_2 = k\gamma(1-f) \quad (23)$$

Applying relations (20) and (23) to (19), one obtains:

$$c_v^0 = \exp \left[\frac{-E_0}{kT} \right] \exp \left[\frac{-E_0(3\alpha + \frac{1}{\mu} \frac{d\mu}{dT}) + k\gamma(1-f)}{k} \right] \quad (24)$$

3) Application of the Model to Experiment

The concentration of vacancies is determined experimentally either by resistivity measurements on the bulk sample [30, 31] or by the simultaneous measurement of length and lattice parameter change [32]. When $\ln c_v^0$ or some property proportional to c_v^0 is plotted vs $1/kT$, the slope of the resultant straight line is designated E_v^f and the intercept at $\frac{1}{T} \rightarrow 0$ is designated S_v^f . From equation (24) then it appears:

$$E_0 = E_v^f \quad (25)$$

and

$$S_V^f = k\gamma(1 - f) - E_o \left(3\alpha + \frac{1}{\mu} \frac{d\mu}{dT} \right) \quad (26)$$

4) Prediction and Results of the Model

The present model has been solved, i.e., equations (13) and (26) evaluated for a variety of metals with cubic symmetry using the experimentally determined value of 0.5 for f . Low temperature values (near 0°K) of the elastic constants published by Simmons [33] were used in the calculations. All the investigators cited in Simmons and the value of the elastic constants which each investigator determined for a particular metal were carefully compared to ensure a choice of values which warrant most confidence. The Voigt elastic constants μ_V and χ_V were evaluated as described by Hirth and Lothe [34] and $\frac{1}{\mu} \frac{d\mu}{dT}$ was calculated at room temperature from the selected single crystal data published by Simmons. Values of Ω and α were taken from the Metals Handbook [35], and values of γ were taken from Mott & Jones [28]. Table I lists the values of the actual physical constants employed. The temperature for which the elastic constants were determined was 0°K unless stated otherwise.

A wide range of experimental values of E_V^f and S_V^f were found to exist in the literature. Friedel's [2] published values, being averages of many experimental observations, were in turn averaged with more recent experimental results to yield the experimental values cited in Tables II and III.

Table II suggests that the present model with the value of 0.5 for f yields good agreement with the experimentally determined values of vacancy formation energy for the cubic metals other than the alkalis Li and K. Agreement was also found in the case of the almost ideally packed h.c.p. Mg ($c/a = 1.623$) and f.c.c. Co. This agreement can be expected since the value of $f = 0.5$ used in calculating E_f is that determined experimentally on gold and copper. However, using the same value of f in the case of b.c.t. Sn and h.c.p. Zn and Cd ($c/a = 1.856$, 1.886 respectively), the agreement was poor. Knowing the experimentally determined values of vacancy formation energy for these metals, f was adjusted in equation (13) until agreement was obtained. For Cd and Zn a value of $f = 0.78$ and for Sn a value of $f = 0.75$ was obtained. These f values are in fair agreement with the value of 0.67 for f assumed by Wallmark and Gilder [36] in their work on Zn. Higher values of f than 0.5 suggest that there is less lattice relaxation in the non-cubic lattices than the fcc lattices.

The ratio $E_{\text{core}}/E_{\text{total}}$, the fraction of core energy to total energy of vacancy formation, is found from the theory to be

$$E_{\text{core}}/E_{\text{total}} = 3/[5(1 - f) + 3].$$
 Table II shows this ratio varies from 0.55 for cubic crystals to 0.72 for the h.c.p., indicating that the largest portion of the total defect formation energy is contributed by the core region. One minus this ratio clearly yields the fraction of the total energy of formation stored as elastic energy in the lattice surrounding the vacancy, i.e., medium I.

In addition to the results reported in Table II, the energy of vacancy formation was calculated using the arithmetic average [37] of the Voigt and Reuss [34] appropriate elastic constants for each element. The energies thus evaluated were found to be consistently smaller in value by 30% than those shown in Table II.

Table I
Physical Constants Used in the Calculations
of the Energy and Entropy of Vacancy Formation

Element	μ_{Voigt} x10 ⁻¹² dynes/cm ²	Ω x10 ²⁴ cm ³	α x10 ⁶ (°K) ⁻¹	γ	$-\left(\frac{1}{\mu} \frac{d\mu}{dT}\right)$ x10 ³ (°K) ⁻¹
Cu	0.593	11.77	16.5	1.96	0.266
Ag	0.375	17.07	19.7	2.4	0.373
Au	0.337	16.94	14.2	3.03	0.24
Pt ⁽¹⁾	0.665	15.11	8.9	2.54	0.13
Na ⁽²⁾	0.044	39.85	71	1.25	1.2
Li ⁽³⁾	0.071	21.5	56	1.17	0.412
K ⁽⁴⁾	0.017	75.3	83	1.34	--
Ni	1.011	10.94	13.3	1.88	0.329
Al	0.29	16.59	23.9	2.17	0.536
W ⁽⁵⁾	1.753	15.82	4.3	1.62	0.099
Pb	0.137	30.34	29.3	2.73	0.735
Co ⁽⁶⁾	0.8	11.13	12.4	1.87	0.24
Mg	0.194	23.23	25.0	1.51	0.40
Sn	0.26	27.3	23.0	2.14	1.21
Cd	0.319	21.6	29.8	2.19	1.09
Zn	0.51	15.24	39.7	2.01	0.42

(1) Extrapolated to 0°K from 300°k

(2) " " 0°K from 90°K

(3) " " 0°K from 78°K

(4) Value at 83°K

(5) Extrapolated to 0°K from 77°K

(6) " " 0°K from 300°K

Table II

Theoretical Predictions of the Model and the Experimentally
Determined Values of the Energy of Vacancy Formation

Element	χ' $\times 10^{12}$	$\frac{E_{\text{core}}}{E_{\text{tot}}}$	E_Y^f calc	E_V^f exp	Reference
	$\left[\text{dynes/cm}^2 \right]^{-1}$		e.v.	e.v.	
Cu	1.52	0.55	1.00	1.02	2,38,39
Ag	2.4	0.55	0.92	0.96	2,40
Au	2.67	0.55	0.82	0.84	2,41,42
Pt	1.41	0.55	1.44	1.4	2,42-44
Na	22.5	0.55	0.25	0.28	2,45
Li	13.0	0.55	0.22	0.31	9
K	53.0	0.55	0.18	0.4	2
Ni	0.895	0.55	1.59	1.4	46,47
Al	3.13	0.55	0.69	0.69	2,48-50
W	0.55	0.55	3.9	3.3	51
Pb	6.56	0.55	0.60	0.59	2,52
Co	1.1	0.55	1.28	1.25	56
Mg	4.64	0.55	0.65	0.58	56
Sn	6.95	0.71	0.5	0.5	2,53
Cd	6.42	0.72	0.42	0.4	54
Zn	4.0	0.72	0.47	0.5	36

Table III
Theoretical and Experimental Values of the
Entropy of Vacancy Formation

Element	$\frac{-E_0 \left[\frac{1}{\mu_v} \frac{d\mu}{dT} + 3\alpha \right]}{k}$	$\gamma(1 - f)$	$\frac{S_v^f}{k}$ calc	$\frac{S_v^f}{k}$ exper	Reference
Cu	2.5	0.98	3.48	1.5	2,38,39
Ag	3.35	1.2	4.55	1.5	2,40
Au	1.9	1.51	3.41	1.2	2,41,42
Pt	1.6	1.27	2.87	1.4	2,42-44
Na	2.68	0.62	3.3	2.0	2,45
Li	1.0	0.58	1.58	1.8	9
K	--	0.67	--	--	2
Ni	5.34	0.94	6.28	--	46-7
Al	3.7	1.08	4.78	2.4	2,48-50
W	3.7	0.81	4.51	1.4	51
Pb	4.8	1.36	6.16	2.6	2,52
Co	3.1	0.93	4.0	--	--
Mg	2.4	0.75	3.15	0.3	56
Sn	7.0	0.53	7.53	1.4	2,53
Cd	5.08	0.48	5.56	0.7	54
Zn	1.74	0.44	2.18	2.3	36

DISCUSSION

Table II shows that the present model predicts rather well the energy of vacancy formation in many metals with the exception of two of the b.c.c. alkalis. This agreement is rather surprising when one considers the weaknesses of the present model which must alter the true representation of the displacement field. The linear anisotropic elastic solution to this problem for crystals of cubic symmetry has been recently published by Masumura and Sines [55]. These authors normalized the anisotropic radial displacement to the isotropic case. The present authors find this normalizing constant to be the same as that used in the current calculations, i.e., C in equation (1). Therefore, it is expected that the displacement strengths in the current study are comparable to those of the anisotropic solution even though the direction and senses are somewhat different. Energy calculations are not sensitive to the anisotropy of the displacements but depend strongly on their magnitude. There also exists non-elastic continuum and quantum mechanical effects at the vacancy site which are impossible to consider in the light of a linear elastic continuum approach.

There are, however, distinct advantages to the current type of calculation. The local ion core rearrangement due to their mutual repulsion [5], and the electron charge density redistribution at the vacancy site have, in fact, been qualitatively considered through the estimated core distortion as a medium of different compressibility and

shear modulus from the host lattice. Secondly, the maximum strain around the vacant site has been estimated as 14%, which is not so large as to be considered unreasonable for a linear model. In fact, this value is in accord with the results of previous investigators [10-15]. Thirdly, the model predicts more than one half of the energy of vacancy formation to be local core energy and the remaining amount to originate from the elastic distortion of the surrounding medium. This result is in good agreement with the work of Hall [5], who also quantitatively compared the core to surrounding lattice stored energy. In the latter work, the comparison is made from a discrete lattice type calculation and the average value of the ratio of core energy to the total energy of vacancy formation was 0.5 for cubic crystals. Fourthly, this method produces a continuous stress and strain field associated with the vacancy everywhere in the body. Therefore, the model should be able to be extended to predict the interaction effects of vacancies with either interstitials or substitutional impurities in metals.

Table II shows that the predicted formation energies are lower than the experimental values for the b.c.c. alkali metals Li and K. Adjusting the f value to give agreement between experiment and theory shows $f = 0.27$ for Li and 0 for K. It seems difficult to justify such a large local vacancy formation volume. It is possible vacancy formation in the b.c.c. alkali metals may be accompanied by atomic rearrangements in the $\langle 111 \rangle$ direction such that the configuration appears more like two

split half vacancies. In this case, our model would not be applicable and agreement between theory and experiment not expected.

Table III shows the order of magnitude agreement between the experimental values of entropy of vacancy formation and those predicted by the current model. Analytically, the calculated values of the entropy of vacancy formation are quite sensitive to the values of $\frac{1}{\mu_v} \frac{d\mu}{dT}$ employed. This coefficient can vary considerably with temperature and in the present work was evaluated at room temperature from the elastic constant data [33]. These data are sparse and exhibit scatter appreciably between differing experimenters studying the same metal.

The data points taken for vacancy concentrations representative of high temperatures near the melting point are extrapolated several orders of magnitude to infinite temperature ($\frac{1}{T} \rightarrow 0$) in order to find the intercept of the $\ln c_v$ vs $\frac{1}{T}$ curve. This intercept is related to the experimental value of S_v^f and due to the above extrapolation procedure, is very sensitive to the accuracy of the data points. For these reasons, the agreement we find between experiment and theory for S_v^f is considered satisfactory.

In summary, it appears the advantages enumerated above for the current model favor a reliable calculation of the energy and entropy of monovacancy formation in metals. This agreement results even though the actual displacement field surrounding the defect may in some cases be quite different from that predicted by the model.

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