

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Vacancy Formation Energy in Close-packed Metals Connected with Liquid Thermodynamics at Melting

J. A. Alonso^{ab}, N. H. March^c

^a Departamento de Física Teórica, Universidad de Valladolid, Valladolid, Spain ^b School of Mathematics and Physics, University of East Anglia, Norwich, England ^c Theoretical Chemistry Department, University of Oxford, Oxford, England

To cite this Article Alonso, J. A. and March, N. H.(1989) 'Vacancy Formation Energy in Close-packed Metals Connected with Liquid Thermodynamics at Melting', *Physics and Chemistry of Liquids*, 20: 4, 235 – 240

To link to this Article: DOI: 10.1080/00319108908028454

URL: <http://dx.doi.org/10.1080/00319108908028454>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

VACANCY FORMATION ENERGY IN CLOSE-PACKED METALS CONNECTED WITH LIQUID THERMODYNAMICS AT MELTING

J. A. ALONSO

*Departamento de Física Teórica, Universidad de Valladolid, Valladolid, Spain**

and

*School of Mathematics and Physics, University of East Anglia,
Norwich NR47TJ, England*

and

N. H. MARCH

*Theoretical Chemistry Department, University of Oxford, 5 South Parks Road, Oxford
OX1 3UB, England.*

(Received 17 March 1989)

The vacancy formation energy in units of the melting temperature can be approximated for close-packed metals in terms of the difference in specific heats and the long wavelength limit of the liquid structure factor. Here, some results are first presented for *d*-electron metals to complement earlier data on *s-p* metals. Secondly, contact is made with the semiempirical treatment of Miedema.

KEY WORDS: Vacancies, hot crystals, Miedema's model.

1 INTRODUCTION

Doubtless for fully quantitative accuracy, the vacancy formation energy E_v will need to be calculated for individual metals, as done, for example, in the very recent work by Gillan on Al¹.

However, it remains of interest to elucidate further various known empirical correlations. In this area, of prime interest in the present work are (a) the correlation of E_v with the melting temperature T_m , and (b) the semi-empirical correlation of Miedema, relating E_v to atomic volume and boundary electron density n_b .

* Permanent address.

2 THERMODYNAMICS IN LIQUID AT T_m RELATED TO E_v

One of us² has proposed the approximate formula for the vacancy formation energy E_v in a close-packed crystal, where it is valid to neglect atomic relaxation round the vacant site:

$$\frac{E_v}{K_B T_m} \approx \left. \left\{ \frac{(\gamma - 1)C_v}{K_B S(0)} \right\}^{1/2} \right|_{T_m}, \quad (2.1)$$

where K_B is Boltzmann's constant, γ is the ratio C_p/C_v of the specific heats while $S(0)$ is the long wavelength limit of the liquid structure factor $S(k)$.

This formula has been evaluated using empirical data for some eight close-packed non-transition metals by Rashid and March³. The results may be summarized by quoting the average value of $E_v/K_B T_m$ from experiment as $E_v/K_B T_m = 9.4 \pm 1.8$ while the thermodynamic term (2.1) contributes an average of 8 ± 1 .

2.1 Thermodynamic Contribution for some Transition Metals

It is of some interest, first of all, to compare the above results with some transition metals for which the relevant data is available.

Table 2.1 therefore collects such data for Co, Ni and Pd. Here the average value of $E_v/K_B T_m$ is again $\sim 9.0 \pm 0.7$, but the average prediction from Eq. (2.1) is now 11.5 ± 0.6 . Thus, the "corrections" to the thermodynamic contribution (2.1) differ in sign from the s - p metals considered by Rashid and March³ (the one exception for the 8 close-packed s - p metals they considered being Au). In obtaining E_v from Eqn. (2.1) $S(0)$ and C_v were calculated from the thermodynamic relations⁴

$$S(0)|_{T_m} = \rho K_B T K|_{T_m}, \quad (2.2)$$

$$C_v = C_p - \frac{T\alpha^2 V}{K} \quad (2.3)$$

Table 2.1 Calculated vacancy formation energy from thermodynamic data. For comparison the experimental values, and the predictions of the Miedema formula Eq. (3.6) are recorded.

Metal	$T_m^{(a)}$ (K)	C_p/K_B	γ	$S(0)$	$E_v/K_B T_m$ (eV/at)		
					Eq. (2.1)	exp ^(b)	Miedema ^(c)
Ti	1812	3.95	1.15	0.0196	5.50	9.29	8.85
Co	1768	2.14	2.28	0.0184	12.20	8.16	7.61
Ni	1726	2.73	1.90	0.0194	11.25	9.41	7.25
Pd	1825	1.81	2.31	0.0197	10.97	9.56	8.04
La	1193	4.00	1.03	0.0181	2.57		10.69

^(a) From Ref. 5.

^(b) From Ref. 6.

^(c) From Eq. (3.6).

Table 2.2 Thermodynamic data for liquid metals at the melting point.

<i>Metal</i>	$C_p/K_B^{(a)}$	$\alpha (\times 10^5)^{(b)}$	$V^{(c)}$ (cm^3/mole)	$K_T^{(d)}$ ($10^{-12} \text{dyn}^{-1} \text{cm}^{-2}$)
Ti	4.53	5.5	11.52	1.40
Co	4.87	12.3	7.70	0.96
Ni	5.18	12.6	7.41	1.03
Pd	4.18	11.8	10.19	1.32
La	4.13	4.0	23.48	4.29

^(a) From Ref. 7.^(b) From Ref. 8.^(c) From Ref. 5.^(d) From Ref. 9.

respectively. Here ρ is the number density, K is the isothermal compressibility, α is the volume expansion coefficient and V is the volume. The intermediate data used in the computation of $S(0)$ and C_v from the above equations is given in Table 2.2.

Two other metals, Ti and La, have been included in Table 2.1. Here the agreement with the thermodynamic formula is poor (Miedema's prediction from Eq. (3.6) below can be used as a reasonable estimate of E_v for La, since the experimental result is unknown to us). Our interpretation is that, because these metals have high temperature bcc phases, one cannot use the present type of theory, since underlying it is the assumption that one can characterize the structure of the hot solid by the liquid pair function. This assumption is inappropriate if the coordination number in the relevant (hcp) crystalline phase is appreciably different from that in the liquid at the melting point. This seems to be the case for Ti and La.

After this discussion, let us turn to consider the connection between the thermodynamic formula (2.1) and the semiempirical approach of Miedema.

3 CONNECTION WITH SEMI-EMPIRICAL TREATMENT OF MIEDEMA

The simplest form of the Miedema⁵ treatment is to write

$$E_v = Q\Omega^{2/3}n_b, \quad (3.1)$$

where Ω is the atomic volume, n_b is the electron density at the boundary of the Wigner-Seitz cell in the pure metals, and Q is an empirical constant.

It is noteworthy, in contrast to Eq. (2.1), that Eq. (3.1) is, essentially, a "ground state" formula, involving the microscopic boundary electron density n_b . To make contact with Eq. (2.1), which is our present aim, it seems therefore most natural to first attempt to eliminate n_b from Eq. (3.1). To achieve this, we next invoke the empirical relation^{10,11} between the compressibility K and n_b at melting, namely

$$K_{T_m} \equiv K_m = a(\Omega N n_b^2)^{-1} \quad (3.2)$$

where N is Avogadro's number and a an empirical constant. Substituting Eq. (3.2) into (3.1) then yields

$$E_v = Q\Omega^{1/6} \left(\frac{a}{NK_m} \right)^{1/2}. \quad (3.3)$$

If we now measure E_v in units of $K_B T_m$, the result from Eq. (3.3) is

$$\frac{E_v}{K_B T_m} = \frac{Q\Omega^{1/6}}{K_B T_m} \left(\frac{a}{K_m N} \right)^{1/2}. \quad (3.4)$$

Utilizing the well-known result of fluctuation theory⁴ at T_m , given in Eq. (2.2), Eq. (3.4) becomes

$$\frac{E_v}{K_B T_m} = \frac{Q}{\Omega^{1/3}} \left(\frac{a}{NK_B T_m} \right)^{1/2} \frac{1}{S(0)^{1/2}}. \quad (3.5)$$

This form has been reached by eliminating the isothermal compressibility K_m using Eq. (2.2).

It is to be noted that $S(0)^{-1/2}$ appears now in both Eqs. (2.1) and (3.5). This is the point to note, however, that Miedema's formula (3.1) correlates only roughly with experiment for a single value of the "constant" Q . A better correlation is obtained through the formula

$$E_v = Q \left(\frac{Z_{\text{eff}}}{Z} \right)^{3/5} \Omega^{2/3} n_b, \quad (3.6)$$

where now Q takes one value for non-transition metals and another for transition metals, while Z is the total number of valence ($s + d$) electrons and Z_{eff} is an effective valence (equal to the product Ωn_b). The latter quantity has been discussed by a number of workers, a recent discussion being that of Flores, Gabbay and March¹², with earlier references quoted there.

One obvious difference between the thermodynamic formula (2.1) and Miedema's treatment is that the latter does not need to distinguish between close-packed and open structures. Since Eq. (2.1) is not valid for open bcc metals, one can only make a comparison with Miedema's work for the case of close-packed crystals. Carrying out the calculation of $E_v/K_B T_m$ using Miedema's work in the form (3.6), the values obtained are recorded in the final column of Table 2.1. The average value (for Co, Ni and Pd) is then 7.6 ± 0.4 , i.e. lower than the experimental average 9.0, in contrast to the predictions of the thermodynamic formula (2.1). For completeness, Table 3.1 records results for the eight s - p metals considered in Ref. 3. The experimental result quoted for Mg in Ref. 6 is more consistent with the theoretical predictions (the last two columns of the Table) than the value quoted in Ref. 3. Again, adoption of the experimental values quoted in Ref. 6 leads to improved agreement with the thermodynamic prediction in the case of noble metals. Vacancy formation energies for noble metals cannot be calculated from Eq. (3.6) because of the uncertainty in choosing Z_{eff} for those metals.

Table 3.1 Values of $E_v/K_B T_m$ calculated from the thermodynamic equation (2.1), compared with experimental data and with predictions of Miedema's theory based on Eq. (3.6).

<i>Metal</i>	<i>exp</i> ^(a)	<i>Eq. (2.1)</i> ^(b)	<i>Miedema</i> ^(c)
Cu	12.22(8.87)	8.00	
Ag	10.44(9.26)	8.43	
Au	8.17(8.10)	8.93	
Mg	11.19(7.30)	6.71	6.78
Zn	9.05(8.68)	7.44	9.38
Cd	7.62(8.30*)	7.71	12.55
Al	8.21(8.12*)	6.76	7.73
Pb	9.66(9.61*)	8.03	8.81

^(a) The first set of values is from Ref. 3. Values in brackets are from Ref. 6. Asterisks mark the most reliable ones.

^(b) From Ref. 3.

^(c) From Ref. 6.

4 DISCUSSION AND SUMMARY

In discussing the above results it is worth briefly noting the assumptions underlying the presently available derivation of the thermodynamic formula. These are:

- i) Density-independent pair potentials.
- ii) Absence of significant relaxation round the vacant site.
- iii) Neglect of the density dependence of the pair correlation function $g(r)$ at the melting temperature.

From screened-ion pseudopotential theories of the simple metals, pair potentials emerge at second-order perturbation theory but these are density dependent and thus a final theory of the vacancy in metals will have to relax assumption (i). Assumption (ii) is quite useful for close-packed metals, but is responsible for the failure of the thermodynamic formula for open structures like bcc Na. As to assumption (iii), this has only been shown, to date, to be quantitatively accurate for the non-metallic close-packed solids Ar and Kr, for which assumptions (i) and (ii) are also valid.

In spite of these reservations, it is still true that the thermodynamic contribution (2.1) is accounting for the major part of $E_v/K_B T_m$ in both close-packed s - p and d -electron metals. However, it must be added that the signs of "correction" terms are grossly different for s - p metals on the one hand and d metals on the other.

As to the connection with Miedema, common elements with the thermodynamic formula have been exposed, in particular the presence of the factor $S(0)^{-1/2}$ in both treatments.

The need for different values of the constant Q for s - p metals and for d -metals established by Miedema⁶ in connection with Eq. (3.6) has been mentioned in Section 3 above. The values of Q differ by about a factor 2, the value for transition metals being the larger one. We suspect that this empirical fact could be related to the quantitatively different values of $(\gamma - 1) C_v$ in those two groups of metals. Restricting again our

discussion of metals to which Eq. (2.1) provides a valid approximation, we find that the average value of $[(\gamma - 1)C_v/K_B]^{1/2}$ for the group of transition metals formed by Co, Ni and Pd is 1.57. On the other hand, the corresponding average for the group of non-transition metals (Mg, Zn, Cd, Al, Pb) is 0.88. The factor 2 between these two averages is very suggestive but further work is evidently needed to fully justify our interpretation.

The thermodynamic formula (2.1) leads to a large value of $E_v/K_B T_m$ because of the factor $S(0)^{-1/2}$, the long wavelength limit of the structure factor being typically in the range 0.01–0.025, though the difference in the specific heats clearly also affects the quantitative values. As Eq. (3.5) shows, the same factor $S(0)^{-1/2}$ also determines the order of magnitude of $E_v/K_B T_m$ in the Miedema scheme.

Acknowledgements

The contribution of J.A.A has been supported by DGICYT (Programa de Movilidad del Personal Investigator and Grant P886-0654-CO2). The same author acknowledges the hospitality of the University of East Anglia.

References

1. M. J. Gillan, *J. Phys: Condensed Matter*, **1**, 689 (1989).
2. N. H. March, *Phys. Chem. Liquids*, **16**, 209 (1987).
3. R. I. M. A. Rashid and N. H. March, *Phys. Chem. Liquids*, **19**, 41 (1989).
4. M. Shimoji, *Liquid Metals*, (Academic Press, London, 1977).
5. A. R. Miedema and R. Boom, *Zeit. Metallk.*, **69**, 183 (1978).
6. A. R. Miedema, *Zeit. Metallk.*, **70**, 345 (1979).
7. R. Hultgren, P. Desay, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, Selected Values of the Thermodynamic Properties of the Elements. American Society for Metals, Metals Parks, Ohio (1973).
8. A. F. Crawley, *Internat. Metallurg. Rev.*, **19**, 32 (1974).
9. Y. Waseda and S. Ueno, *Sci. Rep. Inst. Tohoku Univ.*, **34A**, 1 (1987).
10. J. A. Alonso and N. H. March, *Surf. Sci.*, **160**, 509 (1985).
11. J. A. Alonso and M. Silbert, *Phys. Chem. Liquids.*, **17**, 209 (1987).
12. F. Flores, I. Gabbay and N. H. March, *Chem. Phys.*, **63**, 391 (1981).