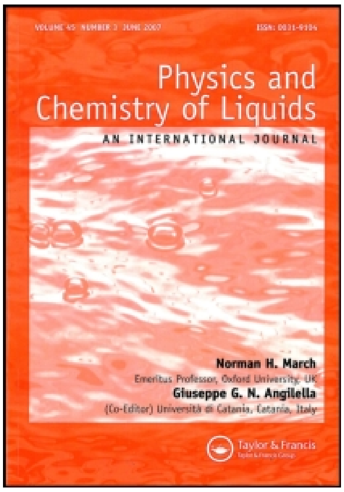

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VACANCY FORMATION ENERGIES IN CLOSE-PACKED CRYSTALS CORRELATED WITH MELTING TEMPERATURE VIA THERMODYNAMICS AND LIQUID STRUCTURE

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In earlier work, the vacancy formation energy E_v in close-packed crystals, in units of the thermal energy $k_B T_m$ at the melting temperature T_m, has been connected with compressibility and specific heats, plus terms dependent on the liquid structure at T_m.

Here, this connection has been examined quantitatively for (a) the insulating condensed rare gases Ne, Ar and Kr, and (b) a variety of close-packed metals. For case (a), $E_v/k_B T_m$ can be calculated directly from thermodynamic data to obtain agreement with experiment for Ar and Kr, though not for Ne. A "residual" contribution is estimated for Ar and Kr from diffraction and computer experiments on the density dependence of the liquid pair correlation function and is shown to be very small. Agreement is less impressive for case (b) for the eight close-packed metals for which all data required is known, the thermodynamic formula giving an average value $E_v/k_B T_m = 7.8 \pm 1.1$ whereas experiment yields 9.4 ± 1.8. However, for the body-centred cubic alkalis the thermodynamic average value of 4.5 ± 0.5 is much lower than the experimental value 11.5 ± 2.0 consistent with the known role of ionic relaxation round the vacancy in such open structures.

KEY WORDS: Vacancy formation energies, density-dependent structure, hot crystals.

I INTRODUCTION

For a density-independent pair potential theory which neglects atomic relaxation round a vacant lattice site, the vacancy formation energy E_v, in units of the thermal energy $k_B T_m$ at the melting temperature T_m, has been shown to be given by[1]

$$\frac{E_v}{k_B T_m} = \left\{\frac{(\gamma - 1)c_v/k_B}{\rho k_B T_m K_m}\right\}^{1/2} + \frac{\rho^2}{2k_B T_m}\int \frac{\partial g(r,\rho)}{\partial \rho}\phi(\mathbf{r})\,d\mathbf{r}\Bigg|_{T_m} \cdots \qquad (1.1)$$

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Here γ is the ratio of specific heats c_p/c_v, while K_m is the isothermal compressibility at the melting temperature.

The purpose of the present paper is two-fold:

i) To examine whether there is firm experimental evidence for connecting $E_v/k_B T_m$ with the thermodynamic quantities entering the first term on the right-hand side of Eq. (1.1), for both insulating condensed rare gases and metals.

ii) To attempt a numerical estimation of the term in Eq. (1.1) involving the density dependence of the liquid pair function at T_m.

In Section II, point (i) is fully considered for the condensed rare gases, the "correction" from density-dependent liquid structure for these same materials being dealt with in Section III. While the basis for writing Eq. (1.1) is firm for the condensed rare gases, it seemed also of interest to confront experimental data on $E_v/k_B T_m$ for the closed-packed metals with values of the first (thermodynamic) contribution on the right-hand side of Eq. (1.1). This is done in Section IV, where brief reference is also made to the very different situation obtaining in the open body-centred cubic alkali metals. Section V consists of a brief summary plus suggestions for further investigation.

II RELATION OF $E_v/k_B T_m$ TO SPECIFIC HEATS AND COMPRESSIBILITY FOR CONDENSED RARE GASES

Table 2.1 shows liquid specific heat data and the long wavelength limit of the liquid structure factor $S(0)$, all evaluated near to the melting temperature T_m for the condensed rare gases Ne, Ar and Kr. Also recorded is the measured vacancy formation energy E_v in units of $k_B T_m$. Following the liquid data, the final column shows also the first term of the right-hand side of Eq. (1.1), but now evaluated at the melting temperature T_m.

It is clear that for Ar and Kr there is already quantitative agreement between the first thermodynamic contribution on the right of Eq. (1.1) and the observed value of $E_v/k_B T_m$. Indeed, it will be confirmed directly in Section III below that for these two materials the second term on the right of Eq. (1.1) is quite negligible. However, the situation is different for neon, and further investigation of this material is clearly called for.

III DENSITY DEPENDENCE OF PAIR CORRELATION FUNCTION FOR CONDENSED RARE GASES

With neglect of atomic relaxation round the vacancy site, formula (1.1) is complete for the condensed rare gases within a pair potential framework. In the light of Table 2.1 it is clearly of interest to show that the density-dependent term involving $\partial g(r, \rho)/\partial r$ is small for these materials.

We know of no suitable data for Ne, in which case Table 2.1 shows the discrepancy

Table 2.1 Thermodynamic contributions from Eq. (1.1) to vacancy formation energies in condensed rare gases.

Material	*Structure*	T_m (K)	$\frac{c_v}{k_B}$[2-4]	$\gamma = c_p/c_v$[2-4]	$S_{T_m}(0)$[3,5]	E_v[6] (eV)	$E_v/k_B T_m$	$\left\{\frac{(\gamma - 1)c_v}{S_{T_m}(0)k_B}\right\}^{1/2}$
Condensed Rare Gases								
Ne	fcc	24.5	2.23	1.97	0.052	0.021	9.95	6.45
Ar	fcc	84.0	2.36	2.20	0.050	0.055	7.60	7.53
Kr	fcc	117.0	2.60	2.10	0.049	0.077	7.64	7.64

(due perhaps to the $\partial g(r, \rho)/\partial r$ term) to be largest in this group. However, molecular dynamic data is available for Kr from the work of Bose *et al.*[7] for the Lennard-Jones 6-12 potential. In addition, we have attempted to estimate the $\partial g(r, \rho)/\partial \rho$ term for Ar from the measurements of Mikolaj and Pings.[8] However, the corresponding potential[9] is only known from the use of approximate structure theory, so these estimates should be regarded with more caution than the molecular dynamic results for Kr.

Starting with Kr, $\partial g(r, \rho)/\partial \rho$ has been calculated numerically from the pair functions given at various densities at 117 k by Bose *et al.*[7] Their potential was, of course, used consistently with the $\partial g(r, \rho)/\partial \rho$ described above in evaluating the final term in Eq. (1.1). Its numerical value is found to be 0.06, correcting the value 7.64 in the final column of Table 2.1 only in the second decimal place.

Similarly, using the measured state-dependent structural data of Mikolaj and Pings[8] for Ar, with the potential $\phi(r)$ which they extracted[9] from their data, the final term in Eq. (1.1) was estimated to be 0.07; again a very small correction to the thermodynamic contribution 7.53 recorded in Table 2.1.

IV MAGNITUDE OF THERMODYNAMIC TERM IN EQ. (1.1) FOR CLOSED-PACKED METALS

Though Eq. (1.1) rests on the assumption of density-independent pair potentials, which is certainly not true for the effective interactions in metals, depending as they do on the conduction electron density, it seemed nevertheless of interest to confront experimental data on $E_v/k_B T_m$ for, first, close-packed metals, with the thermodynamic term in Eq. (1.1).

Thus, in Table 4.1, the penultimate column records experimental values of $E_v/k_B T_m$, while the final column gives the values of the first term on the right-hand side of Eq. (1.1). In seven of the eight close-packed metals, it will be noted that, to within experimental error of the quantities recorded, $E_v/k_B T_m \geq$ first term in Eq. (1.1); the clear exception being Au. As to averages, one finds from Table 4.1 for the eight closed-packed metals that $E_v/k_B T_m|_{\text{average}} = 9.4 \pm 1.8$ while the thermodynamic term in the last column has average 7.8 ± 1.1. However, the departure, for example, for Mg is major and presently we do not know the origin of this, ionic relaxation, the $\partial g(r, \rho)/\partial \rho$ term in Eq. (1.1) and the density dependent part of the effective pair interaction all

Table 4.1 Calculated vacancy formation energies from thermodynamic data for various metals. For comparison the experimental values of formation energies are recorded.

Material	*Valency*	*Structure*	T_m (K)	$\frac{c_v}{k_B}$ [10,11]	$\gamma = \frac{c_p}{c_v}$ [10,11]	$S_{T_m}(0)$ [5,10]	E_v [12] (eV)	$E_v/k_B T_m$	$\left\{\frac{(\gamma - 1)c_v}{S_{T_m}(0)k_B}\right\}^{1/2}$
Close-packed Metals									
Cu	1	fcc	1356.0	2.99	1.45	0.021	1.31	11.22	8.00
Ag	1	fcc	1234.0	3.00	1.45	0.019	1.11	10.44	8.43
Au	1	fcc	1336.2	2.99	1.32	0.012	0.94	8.17	8.93
Mg	2	hcp	923.0	2.96	1.38	0.025	0.89	11.19	6.71
Zn	2	hcp	692.7	3.10	1.25	0.014	0.54	9.05	7.44
Cd	2	hcp	594.2	3.10	1.23	0.012	0.39	7.62	7.71
Al	3	fcc	933.2	3.11	1.25	0.017	0.66	8.21	6.76
Pb	4	fcc	600.6	2.90	1.20	0.009	0.50	9.66	8.03
Other Metals									
Li	1	bcc	454.0	3.40	1.20	0.031	0.34	8.69	4.68
Na	1	bcc	370.8	3.40	1.12	0.024	0.42	13.15	4.12
K	1	bcc	336.6	3.50	1.11	0.023	0.39	13.45	4.09
Rb	1	bcc	311.8	3.40	1.15	0.022	0.31	11.54	4.81
Cs	1	bcc	301.8	3.20	1.18	0.024	0.28	10.77	4.90
Ga	3	orthorhombic	302.8	3.20	1.08	0.005	0.50	19.17	7.16
In	3	bct	429.8	3.16	1.12	0.007	0.45	12.15	7.36
Semiconductors									
Si	4	diamond	1683.0			0.046	4.00	27.59	
Ge	4	diamond	1210.4			0.024	2.40	23.02	

being possible contributors to the difference between the last two columns in Table 4.1 in this metal. Apart from the exceptional case of Mg (here $S_{T_m}(0)$ is large, making the entry in the final column small), it is tempting to argue from Table 4.1 that the thermodynamic term exhibited on the right-hand side of Eq. (1.1) is, though less decisively than for Ar and Kr, still the main contribution to $E_v/k_B T_m$.

Some further evidence relating to ionic relaxation can be obtained by examining data on the open body-centred alkalis, which is recorded in the lower part of Table 4.1. There are now major differences between the last two columns in the table, the average of $E_v/k_B T_m$ for the alkali metals being 11.5 ± 2.0 while the average of the thermodynamic term recorded in the final column is 4.5 ± 0.5. This finding is in accord with the conclusions of Flores and March[13] on Na and K. There they found that the ionic relaxation round the vacancy site contributes a major part of the formation energy.

One necessary condition, it would appear, for arguments which relate the vacancy formation energy E_v to the temperature at the freezing transition and liquid state quantities, is that the force fields should have the same character in the liquid as in the crystal. Though the data is presently incomplete, we thought it of interest to record finally in Table 4.1 data for Si and Ge. These covalently bonded semiconductors in the crystalline phase are liquid metals with four conduction electrons per atom above T_m. The penultimate column shows that the $E_v/k_B T_m$ are large compared with the other cases in Table 4.1. We have not been able to find liquid state data to convert c_p into c_v for Si and Ge. However, we expect γ to resemble Al and Pb, and hence the final column to be much less than $E_v/k_B T_m$ in these two cases.

V SUMMARY AND DIRECTIONS FOR FURTHER WORK

As Table 2.1 makes quite clear, for Ar and Kr, $E_v/k_B T_m$ is almost completely determined by the first, thermodynamic, term on the right-hand side of Eq. (1.1). The term involving the density dependence of the pair function $g(r, \rho)$ has been estimated at 0.07 and 0.06 for Ar and Kr, respectively, and therefore plays a negligible role. Further work, however, is clearly called for in the case of neon, to understand the origin of the difference between the last two columns in Table 2.1.

For metals, the present work makes it clear that any approach starting from Eq. (1.1) is inappropriate for open structures such as the body-centred cubic alkali metals. There can be no doubt in these metals that ionic relaxation round the vacant site makes a major contribution[13] to $E_v/k_B T_m$, which is not embraced by writing Eq. (1.1). Even though this equation (1.1) does not have the same fundamental status for metals as for the condensed rare gases, because metal effective potentials are inevitably density-dependent, nevertheless Table 4.1 makes clear that for close-packed metals, the first, thermodynamic, contribution on the right of Eq. (1.1) can still be usefully viewed as a major contribution to $E_v/k_B T_m$.

Returning to the matter of ionic relaxation, we think, in the future, that it will be of considerable interest to build vacancy formation volumes into the above treatment. Here, however, presently, there is a need for further work, both theory and experiment.

A final, cautionary note is called for relating to the calculation of E_v in a polyvalent metal-like Al. As was emphasized in the calculations of Stott *et al.*[14] based on electron theory, E_v comes out as a small quantity ($\sim \frac{1}{2}$ eV) which arises from a cancellation between large numbers. Recently, Gillan[15] has carried out numerical computations of E_v within a pseudopotential framework, which lead to an effective interaction of the form reported by Duesbery and Taylor.[16] While Gillan finds only a small contribution of ionic relaxation round the vacancy to E_v for face-centred cubic Al, his most important conclusion in the present context is that, with a Duesbery-Taylor-like form for the effective pair interaction, three- (and perhaps higher-) body forces make an important contribution to E_v. This, we feel, makes it the more important to develop further an approach like the one advocated here, in which $E_v/k_B T_m$ is represented, at least as a major contribution, by a thermodynamic part such as displayed in Eq. (1.1).

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References

1. N. H. March, *Phys. Chem. Liquids*, **16**, 209 (1987).
2. D. G. Naugle, *J. Chem. Phys.*, **56**, 5730 (1972).
3. J. S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths, London, 1969).
4. W. B. Street and L. A. K. Staveley, *J. Chem. Phys.*, **55**, 2495 (1971).
5. J. A. Alonso and M. Silbert, *Phys. Chem. Liquids*, **17**, 209 (1987) and references therein; J. A. Alonso and N. H. March, *Sur Sci.*, **160**, 509 (1985); R. Evans and W. Schirmacher, *J. Phys.*, **C11**, 2437 (1978) and references therein.
6. A. B. Lidiard, in *Defects and Their Structure in Nonmetallic Solids*, Eds. B. Henderson and A. E. Hughes (Plenum Press, 1975); P. Varotsos and K. Alexopoulos, *Phys. Rev.*, **B15**, 4111 (1977) and references therein.
7. T. K. Bose, W. Brostow and J. S. Sochanski, *Phys. Chem. Liquids*, **11**, 65 (1981).
8. P. W. Schmidt and C. W. Thompson, in *Simple Dense Fluids*, Eds. H. L. Frisch and Z. W. Salsburg (Academic Press, New York), 31–118 (1968); P. G. Mikolaj and C. J. Pings, *J. Chem. Phys.*, **46**, 1401 (1967).
9. P. G. Mikolai and C. J. Pings, *J. Chem. Phys.*, **46**, 1412 (1967).
10. M. Shimoji, *Liquid Metals* (Academic Press, London, 1977); T. E. Faber, *Introduction to the Theory of Liquid Metals* (Cambridge University Press, 1972).
11. I. Ohkoshi, I. Yokoyama, Y. Waseda, B. P. Alblas and W. Van Der Lugt, *Physica*, **113B**, 195 (1982); I. Yokoyama, I. Ohkoshi and W. H. Young, *Phys. Chem. Liquids*, **10**, 273 (1981); *Metals Reference Book*, Ed. C. J. Smithells (Butterworths, London, 1978).
12. J. M. Bernasconi, N. H. March and M. P. Tosi, *Phys. Chem. Liquids*, **16**, 39 (1986); A. D. Franklin, in *Point Defects in Solids*, Eds. J. H. Crawford Jr. and L. M. Slifkin, Vol. 1 (Plenum Press, 1980); N. H. March, *J. Phys.*, **F3**, 233 (1973).
13. F. Flores and N. H. March, *J. Phys. Chem. Solids*, **42**, 439 (1981).
14. M. J. Stott, S. Baranovsky and N. H. March, *Proc. Roy. Soc. London*, **A316**, 201 (1970).
15. M. J. Gillan, Private communication to N. H. March.
16. M. S. Duesbery and R. Taylor, *Phys. Rev.*, **B7**, 2870 (1973).