The entropy of mixing of liquid Na–Cd alloys

B Karaoglu and W H Young

Department of Physics, College of Science, Sultan Qaboos University, PO Box 32486, Al-Khod, Oman

Abstract. The observed entropy of mixing of liquid Na–Cd alloys at 673 K can be explained using the binary hard sphere model provided diameter shrinkages are assumed to accompany the measured total volume contraction. No chemical short range order need be postulated. An implication of this result is that the system remains nearly free electron-like at all concentrations, notwithstanding the fact that, on the evidence of the concentration fluctuations, there is a pronounced tendency to compound formation in the Cd-rich region.

1. Introduction

In recent years, much attention has been given to the interpretation of the thermodynamic and electronic transport properties of liquid binary alloys of alkali metals with other simple metals (Tamaki 1987, Van der Lugt and Geertsma 1987, Tumidajski *et al* 1990). As a result, it would appear that valence difference Δz is an important indicator of general behaviour. Thus, when $\Delta z = 0$ (as in alkali–alkali alloys), it would seem that the fundamental nearly free electron (NFE) character is practically unaffected by the mixing. On the other hand, when $\Delta z = 3$ (as in alkali–lead alloys) there are large departures from NFE behaviour and indications of chemical complex formation or some similar phenomenon in the melt.

The situation is less clear for intermediate cases and the aim of the present work is to throw some light on the two systems Na–Cd ($\Delta z = 1$) and Na–Ga ($\Delta z = 2$). Each of these cases displays the interesting feature that the concentration fluctuations are large in one part of the composition diagram and small in another (Tamaki and Cusack 1979, Hoshino and Endo 1982, Iwase *et al* 1985, Harada *et al* 1988). In other words, each system has compositions at which there are respectively tendencies to phase separation and compound formation.

To achieve our objective, we consider the entropy of mixing of the alloys using the hard sphere model (Young 1977). This model, in simple form, views each alloy component, before mixing, as a collection of hard spheres of suitable diameter; then, on mixing, the hard spheres retain their integrity. It has long been known that the actual (non-ideal) volume of the alloy is a necessary part of the description and, furthermore, it is almost always assumed (although less compellingly) that the hard sphere diameters do not change when alloying takes place. This latter assumption is found to be unrealistic in the present applications but, nevertheless, it serves as a useful starting point from which to assess the measured entropies.

In the case of Na–Cd, a modified hard sphere system, in which the diameters are allowed to vary on alloying, is shown to provide a plausible description and, in this way, an NFE character is inferred. On the other hand, in Na–Ga, no such description is possible and we believe that this implies the occurrence of long-lived chemical complexes and accompanying NFE departures.

2. Binary hard sphere model

Consider an alloy modelled by a mixture of $c_1 N \equiv cN$ hard spheres of diameter σ_1 and $c_2 N \equiv (1-c)N$ hard spheres of diameter σ_2. The ionic masses are m_1, m_2, the valencies are z_1, z_2, the mean volume per atom is Ω and the temperature is T. Then (Umar *et al* 1974, 1976) the entropy per ion is

$$S = S_{gas} + S_c + S_\eta + S_\sigma + S_{elec} \tag{1}$$

where the first two terms correspond to ideal fluid mixing, the third depends on total packing only, the fourth on diameter mismatch and the last is a valence electron contribution. Explicitly

$$S_{gas}/k_B = \tfrac{5}{2} + \ln[\Omega(m_1^{c_1} m_2^{c_2} k_B T/2\pi\hbar^2)^{3/2}] \tag{2}$$

$$S_c/k_B = -(c_1 \ln c_1 + c_2 \ln c_2) \tag{3}$$

$$S_\eta/k_B = -(\zeta - 1)(\zeta + 3) \qquad \zeta = (1 - \eta)^{-1} \tag{4}$$

$$S_\sigma/k_B = A\, c_1 c_2 (\sigma_1 - \sigma_2)^2 \tag{5}$$

$$S_{elec}/k_B = \tfrac{1}{3}\pi^2 N(E_F) k_B T. \tag{6}$$

Here we have used expressions for S_η and S_σ which were derived by Umar *et al* (1976) from the Helmholtz free energy formula of Mansoori *et al* (1971), the latter work itself providing an accurate analytical fit to the computer simulation data.

In (4), the packing fraction η is given by

$$\eta = \omega/\Omega \qquad \omega = c_1 \omega_1 + c_2 \omega_2 \qquad \omega_i = (\pi/6)\sigma_i^3 \tag{7}$$

where ω_i and σ_i are respectively the core volumes and diameters. Also, in (5),

$$A = [\zeta(\zeta - 1) - \ln \zeta](Y_1 + Y_2) + 3(\zeta - 1)Y_1 \tag{8}$$

where

$$Y_1 = \frac{\sigma_1 + \sigma_2}{c_1 \sigma_1^3 + c_2 \sigma_2^3} \qquad Y_2 = \frac{\sigma_1 \sigma_2 (c_1 \sigma_1^2 + c_2 \sigma_2^2)}{(c_1 \sigma_1^3 + c_2 \sigma_2^3)^2}. \tag{9}$$

In (6), $N(E_F)$ is the density of electronic states (two per orbital) at the Fermi level. This term is comparatively small and could be omitted; we include it here, however, in the Sommerfeld form

$$S_{elec}^{Som}/k_B = (\pi\Omega/3)^{2/3} z^{1/3} k_B T \qquad z = c_1 z_1 + c_2 z_2 \tag{10}$$

because, in the applications of this paper, we believe its role to be mildly beneficial.

For the corresponding pure liquid metals, we merely use $c_1 = 1$, $c_2 = 0$ and $c_2 = 1$, $c_1 = 0$ above. The formalism is much simplified and, in particular, $S_c = 0$ and $S_\sigma = 0$ in equation (1). From the known pure liquid entropies and volumes, we can infer from this

Table 1. Data for pure liquids Na and Ga at 843 K. Note that u is the atomic mass unit and a_0 is the Bohr radius. The measured entropies per atom, S, are taken from Hultgren *et al* (1973a) and the measured volumes per atom, Ω, are taken from Allen (1972). The output data are extracted from equation (1), with $c = 1$ (for Na) and $c = 0$ (for the second metal), using the input data shown. These output data from the pure metal analyses are then used as alloy calculation input.

	Input				Output		
	z	m/u	S/k_B	Ω/a_0^3	η	ω/a_0^3	σ/a_0
Na	1	22.99	10.745	316.0	0.293	92.7	5.61
Ga	3	69.74	10.497	135.6	0.385	52.2	4.64

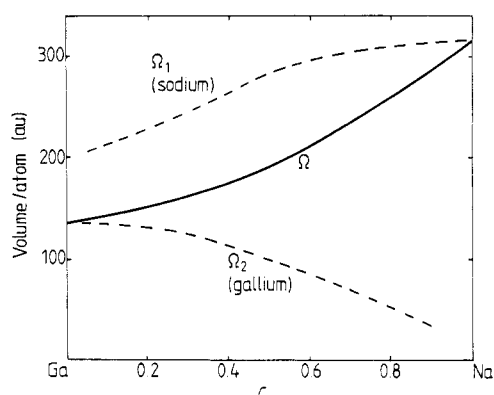**Figure 1.** Mean volume Ω per atom, for Na–Ga at 843 K, as measured by Hoshino and Endo (1982). The corresponding partial atomic volumes Ω_1 (for Na) and Ω_2 (for Ga) are also shown.

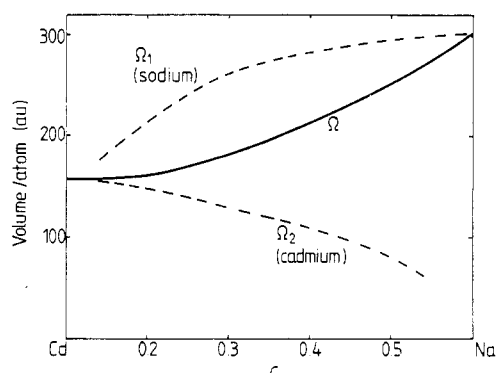**Figure 2.** Mean volume Ω per atom, for Na–Cd at 673 K, as measured by Hoshino and Endo (1982). The corresponding partial atomic volumes Ω_1 (for Na) and Ω_2 (for Cd) are also shown.

equation the one-component sphere volumes and diameters, which we will denote respectively by ω_i^0 and σ_i^0. Then if we assume

$$\omega_i = \omega_i^0 \qquad (i = 1, 2) \tag{11}$$

(i.e. that the core diameters and volumes are unchanged on alloying) and if we know the actual volume per atom of the alloy, we can use (1)–(10) to calculate the alloy entropy S and, thence, the excess entropy per atom,

$$\Delta S = S - c_1 S_1 - c_2 S_2. \tag{12}$$

In this way, we consider the two alloy systems Na–Ga and Na–Cd, tables 1 and 2 showing the pure liquid data and figures 1 and 2 the measured alloy volumes. The final results of the calculations are shown in figures 3 and 4.

In figure 3, the entropies thus calculated lie above the corresponding measured values. Such an eventuality is of common occurrence (e.g. as in alkali–Pb systems) and, in such cases, additional ionic ordering is postulated via valence electron action. Various possible ways of producing this order have been proposed (Bhatia and Hargrove 1973, 1974, Ruppersberg and Egger 1975, Van der Lugt and Geertsma 1987) but the matter

Table 2. Data for pure liquids Na and Cd at 673 K. The same comments apply as for table 1.

		Input				Output	
	z	m/u	S/k_B	Ω/a_0^3	η	ω/a_0^3	σ/a_0
Na	1	22.99	9.954	300.3	0.340	102.2	5.80
Cd	2	112.40	10.203	157.9	0.442	69.8	5.11
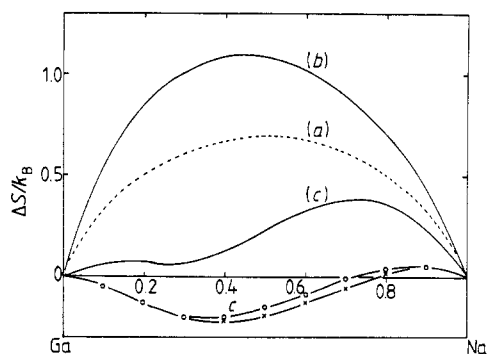
Figure 3. Excess entropy per atom for Na–Ga at 843 K in various approximations: (a) ideal mixing (given by S_c only); (b) zero excess volume ($\Delta\Omega = 0$) and rigid cores ($\Delta\omega_i = 0$); (c) observed excess volume (from figure 1) and rigid cores ($\Delta\omega_i = 0$); $-\circ-\circ-$, as measured (Hoshino and Endo 1982); $-\times-\times-$, as measured (Tamaki and Cusack 1979).
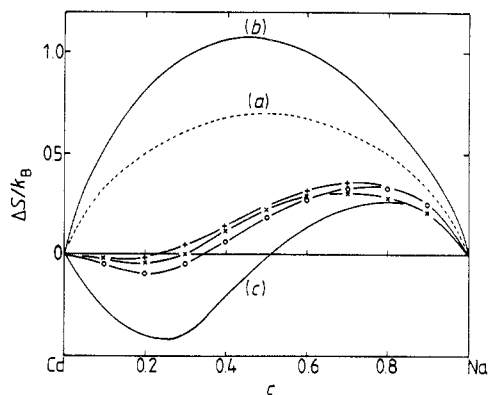
Figure 4. Excess entropy per atom for Na–Cd at 673 K in various approximations: (a) ideal mixing (given by S_c only); (b) zero excess volume ($\Delta\Omega = 0$) and rigid cores ($\Delta\omega_i = 0$); (c) observed excess volumes (from figure 2) and rigid cores ($\Delta\omega_i = 0$); $-\circ-\circ-$, as measured (Hoshino and Endo 1982); $-\times-\times-$, as measured (Harada *et al* 1988)—in essential agreement with Iwase *et al* (1985); $-+-+-$, as measured (Hultgren *et al* 1973b).

remains unresolved. Nevertheless, whatever the detail, it might be supposed that this is the principal mechanism for lowering the calculated entropy result in figure 3 to match the observed data. Accompanying this change, there will be departures from NFE behaviour.

But what are we to make of figure 4 for Na–Cd? Less ordering, rather than more, is indicated here and an obvious mechanism suggests itself—core shrinkage on alloying. We now turn to a detailed consideration of such an effect.

3. Thermal pressure coefficients of pure liquids

As a prelude, and for reasons that become apparent later, we study, in this section, the thermal pressure coefficients of the pure liquid constituents of the alloys under consideration. The method of analysis is due to Harder *et al* (1979).

Table 3. Data for pure liquids Na, Cd, Ga at the melting temperatures. Entropies are taken from Hultgren *et al* (1974a), densities from Allen (1972) and thermal pressure coefficients from Shimoji (1977). The results for Na were first calculated by Harder *et al* (1979).

		Input					Output	
	T/K	z	m/u	S/k_B	Ω/a_0^3	$\Omega\gamma/k_B$	η	ω/a^3	$(\partial \ln \omega/\partial \ln \Omega)_T$
Na	371	1	22.99	7.893	278.0	3.88	0.425	118.0	0.594
Cd	594	2	112.40	9.700	157.3	7.56	0.459	72.1	0.269
Ga	303	3	69.72	7.181	128.1	7.91	0.485	62.1	0.361

Quite generally, the thermal pressure coefficient is

$$\gamma \equiv (\partial P/\partial T)_\Omega = (\partial S/\partial \Omega)_T \tag{13}$$

the second relationship being a Maxwell identity. This quantity is measured by invoking the relationship

$$\gamma \equiv (\partial P/\partial T)_\Omega = \Omega(\partial P/\partial \Omega)_T (1/\Omega)(\partial \Omega/\partial T)_P = B_T \alpha_P \tag{14}$$

where B_T and α_P are respectively the isothermal bulk modulus and the thermal expansion coefficient.

But also, by the final part of equation (13), γ is conveniently accessible to theory. On using equation (1), we have

$$\frac{\Omega\gamma}{k_B} = 1 + \frac{\eta S'_\eta}{k_B}\left(\frac{\partial \ln \eta}{\partial \ln \Omega}\right)_T + \frac{\Omega}{k_B}\left(\frac{\partial S_\sigma}{\partial \Omega}\right)_T + \frac{\Omega}{k_B}\gamma_{elec} \tag{15}$$

where, by (4), $\eta S'_\eta/k_B = -2\eta(2-\eta)/(1-\eta)^3$ and, if we use (10), $\Omega\gamma_{elec} = \frac{2}{3}S_{elec}^{som}$. Furthermore, if we confine our attention to pure liquids, the third S_σ term is zero. In this way, by using experimentally determined thermal pressure coefficients and such data as are given in tables 1 and 2, we can extract

$$\lambda \equiv (\partial \ln \omega/\partial \ln \Omega)_T = 1 + (\partial \ln \eta/\partial \ln \Omega)_T. \tag{16}$$

The thermal pressure coefficients are available only at the melting points so we can analyse only for such temperatures. Results for the three metals under consideration are shown in table 3. By this measure, the Na ion shrinks strongly as the total volume diminishes, whereas the Cd ion responds less. The Ga ion is intermediate.

4. Hard sphere volume variation on alloying

We think it appropriate to imagine alloying, at any given composition, to take place in two stages:

(i) before mixing, the pressure is used to make the specific volume of each pure liquid component equal to the partial volume as observed in the alloy;

(ii) mixing then takes place and electronic adjustment induces further changes.

For brevity, we refer to the consequences of (i) and (ii) as, respectively, the physical and chemical effects.

4.1. The physical effect

To implement our programme, we introduce the partial volumes Ω_i defined, in the usual way, by

$$\Omega = c\Omega_1 + (1 - c)\Omega_2 \tag{17a}$$

$$d\Omega/dc = \Omega_1 - \Omega_2 \tag{17b}$$

or, inversely and explicitly, by

$$\Omega_1 = \Omega + (1 - c)\,d\Omega/dc \tag{18a}$$

$$\Omega_2 = \Omega - c\,d\Omega/dc. \tag{18b}$$

We infer from equations (17) that Ω_i is the volume to be associated with a particle of type i and we calculate these Ω_i, for the systems under consideration, from the observed Ω data and equations (18). The results are shown in figures 1 and 2.

We now image our pure liquid samples compressed to the appropriate specific volumes, Ω_i. Then, as we saw in section 3, the core volumes will be different too. In fact, if we denote these volumes, pertaining to the pressure prepared pure phases, by ω_i^p, then we take

$$\omega_i^p = \omega_i^0[1 + \lambda_i(\Omega_i - \Omega_i^0)/\Omega_i^0] \tag{19}$$

where the λ_i are those of equation (16) and table 3. The ω_i^0 are, as explained earlier, the pure metal core volumes and are given numerically by the ωs of tables 1 and 2. Likewise, the Ω_i^0 are the pure liquid volumes, described by $\Omega(c_i = 1)$ in the earlier notation and given numerically by the Ωs of tables 1 and 2.

The definition (19) coincides with (16) only, of course, in the limit of small volume changes. Moreover, the λs of table 3 are strictly applicable only at the melting temperatures. Nevertheless, in the absence of any further experimental information, we proceed, of necessity, as indicated.

4.2. The chemical effect

We now mix the prepared fluids. In principle, electronic rearrangement at this stage could give rise to significant ionic ordering but we will assume that the only effect is to change the sphere volumes. Accordingly, we write the final values as

$$\omega_1 = \omega_1^p + \omega_{12}c_2 \qquad \omega_2 = \omega_2^p + \omega_{21}c_1. \tag{20}$$

These equations acknowledge that $\omega_1 = \omega_1^p$ when $c_2 = 0$ and $\omega_2 = \omega_2^p$ when $c_1 = 0$, but linearity of the ω_i (i.e. constancy of ω_{12}, ω_{21}) with respect to concentration is also assumed, *faute de mieux*. Under such circumstances, ω_{12} is the increase in ω_1^p when one atom of liquid 1 is immersed in liquid 2, and there is a similar description for ω_{21}.

Unfortunately, we have no independent means of obtaining reliable estimates of ω_{12} and ω_{21}, so we must now regard these, in principle, as the two fitting parameters of the analysis. The ω_i^p are found unequivocally from (19) and then, on choosing ω_{12} and ω_{21}, equation (20) gives us core volumes and diameters for use in the formalism of section 2.
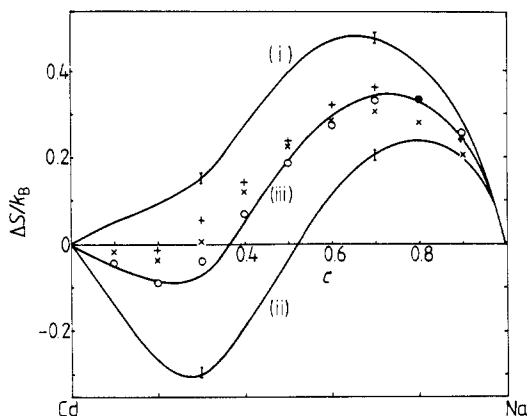
Figure 5. Excess entropy per atom for Na–Cd at 673 K in various non-rigid sphere approximations, the sphere volumes being calculated using equation (20). In the descriptions below, remember that $\bar{\omega} \equiv \frac{1}{2}(\omega_{12} + \omega_{21})$.

(i) $\bar{\omega} = 0$. The curve shown corresponds to $\omega_{12} = 0$, $\omega_{21} = 0$, thus ignoring the chemical effect (see text). If we write (in atomic units) $\omega_{12} = \pm 10$ and $\omega_{21} = \mp 10$, so that $\bar{\omega}$ continues to be zero, we obtain curves separated from curve (i) by amounts indicated by the vertical bars. The stability of the results indicates that the single effective assumption is $\bar{\omega} = 0$.

(ii) $\bar{\omega} = 10$. The curve shown corresponds to $\omega_{12} = \omega_{21} = 10$ and the bars indicate the modified results for $\omega_{12} = 10 \pm 10$ and $\omega_{21} = 10 \mp 10$. Curve stability implies that the only effective assumption is $\bar{\omega} = 10$.

(iii) $\bar{\omega} = 5$. The curve shown arises from equating ω_{12} and ω_{21} but this is practically devoid of significance because comments similar to those on curves (i) and (ii) again apply. We regard this curve (iii) as a satisfactory fit to the data.

Measured data are given by points; for details, see figure 4 (caption).

In practice, however, in the Na–Cd system at least, we have only one parameter to fit the data. This follows from the fact, to be demonstrated later, that S_σ (recall equation (1)) is negligible in relation to the experimental uncertainty. This means that only the packing, as given by equation (7), is significant. But, by equation (20), the mean core volume per atom is

$$\omega = \omega^P + 2\bar{\omega}c_1 c_2 \tag{21}$$

where $\omega^P = c_1 \omega_1^P + c_2 \omega_2^P$ and $\bar{\omega} = \frac{1}{2}(\omega_{12} + \omega_{21})$. Thus, $\bar{\omega}$ is the only effective parameter.

4.3. Calculations

We show, in figure 5, our results for $\bar{\omega} = 0$, 5 and 10 au and the consequences of a variety of individual choices of ω_{12} and ω_{21}, within these constraints, are indicated. It will be noted that, given the experimental spread, it is impossible to fix the parameters separately. Nevertheless, $\bar{\omega}$ is reasonably well located in the region of 5 au, a parameter that happens to fit the data of Hoshino and Endo rather well (curve (iii)).

Figure 6 shows the finally selected ω (based on $\bar{\omega} = 5$) and figure 7 the corresponding packing fraction η. Also shown on these diagrams are the rigid sphere results (corresponding to figure 4, curve (c)), denoted by ω^0 and η_0 respectively, and the data (superscript p) for the case when the pressure prepared pure phases are mixed without
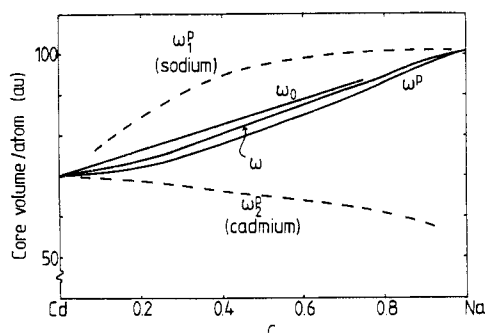
Figure 6. Core volumes for Na–Cd at 673 K using equations (19) and (20). The ω_i^p are given by equation (19) (i.e. by the physical effect) and $\omega^p = c_1\omega_1^p + c_2\omega_2^p$ is the corresponding mean core volume per atom. The curve indicated by ω underlies the satisfactory fit (iii) of figure 5 and corresponds to $\bar{\omega} = 5$ au in equation (21). The rigid core result is given by the straight line $\omega^0 = c_1\omega_1^0 + c_2\omega_2^0$.
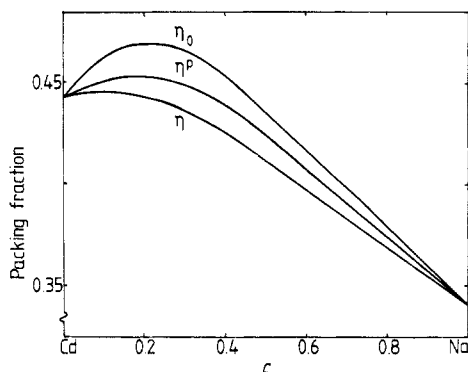
Figure 7. Na–Cd at 673 K; the packed fractions $\eta = \omega/\Omega$, $\eta^p = \omega^p/\Omega$ and $\eta_0 = \omega_0/\Omega$. The ωs are shown in figure 6 and Ω is as in figure 2.

subsequent change in the core sizes (zero chemical effect). Evidently core shrinkage is an essential part of the description with both the physical and chemical effects playing significant roles.

5. Discussion

The hard sphere mixture, in which the spheres are unaltered in size from those in the corresponding pure liquid metals, is a useful reference system from which to assess the entropies of alloys. Consider cases in which there is a substantial volume contraction on mixing. Then, if the actual entropy is lower than the reference one, we can expect that something like complex formation has occurred; on the other hand, if it is substantially higher, it seems most likely that the cores retain their integrity but shrink in response to the total volume contraction. Two such cases are discussed in the present paper and we conclude that some additional short range chemical ordering, with an accompanying modification of the NFE structure, takes place in Na–Ga, but no such radical changes occur in Na–Cd.

We also think (recall section 4) that the hard sphere mixture, in which the spheres have the sizes of those of the pressure prepared pure liquids (the physical effect) is another useful reference system. Because it ignores electronic rearrangement and the consequent ordering, this system should always provide an upper bound to the entropy (as it does for Na–Cd with curve (i), figure 5). This should always be an appropriate point from which to consider the electronic effect.

Finally, this work would appear to have implications for the quantitative thermodynamic analysis of systems with strong NFE departures, for example of those to which the charged sphere model of Waisman (1973) might be applicable (Copestake and Evans 1982, Hafner *et al* 1984). It would seem that a volume dependent diameter choice should

be built into the model, a conclusion that Ruppersberg and Saar (1989) have also recently suggested as a possibility.

Acknowledgments

References

Allen B C 1972 *Liquid Metals, Chemistry and Physics* ed S Z Beer (New York: Marcel Dekker) p 186
Bhatia A B 1977 and Hargrove W H 1973 *Lett. Nuovo Cimento* **8** 1025; 1974 *Phys. Rev.* B **10** 3186
Copestake A P and Evans R 1982 *J. Phys. C: Solid State Phys.* **15** 4961
Hafner J, Pasturel A and Hicter P 1984 *J. Phys. F: Met. Phys.* **14** 1137, 2279
Harada S, Takahashi S, Takeda S, Tamaki S, Gray P and Cusack N E 1988 *J. Phys. F: Met. Phys.* **18** 2559
Harder J M, Silbert M, Yokoyama I and Young W H 1979 *J. Phys. F: Met. Phys.* **9** 1005
Hoshino H and Endo H 1982 *Phys. Chem. Liq.* **11** 327
Hultgren R, Desai P D, Hawkins D T, Gleiser M, Kelley K K and Wagman D D 1973a *Selected Values of the Thermodynamic Properties of the Elements* (Metals Parks, OH, American Society of Metals)
Hultgren R, Desai P D, Hawkins D T, Gleiser M and Kelley K K 1973b *Selected Values of the Thermodynamic Properties of Binary Alloys* (Metals Parks, OH: American Society of Metals)
Iwase M, Sugino S, Ichise E and Waseda Y 1985 *J. Chem. Thermodyn.* **17** 601
Mansoori G A, Carnahan N F, Starling K E and Leland T W 1971 *J. Chem. Phys.* **54** 1523
Ruppersberg H and Eyger H 1975 *J. Chem. Phys.* **63** 4095
Ruppersberg H and Saar J 1989 *Liquids* **1** 9729
Shimoji M 1977 *Liquid Metals* (London: Academic)
Tamaki S 1987 *Can. J. Phys.* **65** 286
Tamaki S and Cusack N E 1979 *J. Phys. F: Met. Phys.* **9** 403
Tumidajski P J, Petric A, Takenaka T, Saboungi M-L and Pelton A D 1990 *Liquids* **2** 209
Umar I H, Watabe M and Young W H 1974 *Phil. Mag.* **30** 957
Umar I H, Yokoyama I and Young W H 1976 *Phil. Mag.* **34** 535
Van der Lugt W and Geertsma W 1987 *Can. J. Phys.* **65** 326
Waisman E 1973 *J. Chem. Phys.* **59** 495
Young W H 1977 *Liquid Metals 1976* (*Inst. Phys. Conf. Ser. 30*) (Bristol: Institute of Physics) p 1