FABE -TE 73- 0471

The Compressibility of Liquid Alloys

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Abstract

A theory of the compressibility of liquid metals is suggested, based upon the nearly-free electron model. When applied to binary alloys it leads to a simple formula for compressibility as a function of concentration. This formula fails to describe the data for liquid Na solutions reported recently by McAlister (1972), which implies that some of the assumptions of the NFE model are invalid for these systems.

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§ 1. Introduction

Measurements of the velocity of sound as a function of composition have now been made for a good many liquid binary alloy systems, and from the results, together with the results of density measurements, it is possible to deduce the adiabatic compressibility β_S; a good estimate can usually be made of the isothermal compressibility β_T, which is not very different. For many systems these quantities are almost linear functions of atomic concentration c, but significant departures from linearity are not unknown; one such has been reported recently by McAlister (1972), who has made measurements on several Na-based systems and on Na–Hg in particular.

The object of this paper is to suggest a simple way of predicting how the compressibility of liquid alloys *ought* to vary with concentration, if the assumptions that lie behind the conventional theory of their resistivity (Faber and Ziman 1965) are correct. These assumptions are: (*a*) that the NFE model is applicable; (*b*) that all the valence electrons of the solvent and solute ions (whose valencies are z_0 and z_1 respectively) are at large in the conduction band, so that the mean conduction electron density is given by

$$\bar{n} = N(c_0 z_0 + c_1 z_1)/\Omega, \quad \dots\dots\dots \quad (1)$$

where N is the number of atoms in volume Ω; and (*c*) that the two types of ion can be described by screened pseudo-potentials $u_0(q)$ and $u_1(q)$ which, because the screening is supposed to be linear, tend to $z_0\Omega/\mathcal{N}(E)_F$ and $z_1\Omega/\mathcal{N}(E)_F$ in the limit $q \to 0$. The theory is applied to liquid Na alloys, with disappointing results.

§ 2. Pure Metals

A theory of the compressibility of pure liquid metals has been developed in some detail elsewhere (Faber 1972). It leads to a result for the inverse of the compressibility, i.e. the bulk modulus K, which may be expressed in the form†

$$K_{\mathrm{int}} = \left(\frac{N}{\Omega}\right)^2 \left[w(0) + \frac{\Omega}{4\pi^2 N} \int_0^\infty \left(\frac{2}{15} q \frac{da}{dq} + \frac{3}{15} q^2 \frac{d^2 a}{dq^2} \right) w(q) q^2 \, dq \right], \quad . \quad (2)$$

where $a(q)$ is the usual interference function and $w(q)$ is the Fourier transform of the effective pair-potential between ions. This pair-potential is composed of a ' direct ' interaction

$$w''(q) = 4\pi (ze)^2 / q^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and an ' indirect ' one, involving the conduction electrons,

$$w'(q) = -q_{\mathrm{S}}{}^2 \epsilon' |u(q)|^2 / 4\pi e^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Near $q=0$ the two cancel rather effectively. It may be shown that if, for convenience, we describe the pseudo-potential in terms of the ' empty core ' model (Ashcroft 1966), which involves a single adjustable parameter R_{M}, then

$$w(0) = 4\pi (ze)^2 \left(\left(\frac{\epsilon'}{\epsilon q_{\mathrm{S}}{}^2} \right)_{q \to 0} + R_{\mathrm{M}}{}^2 \right). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For large q, however, where da/dq and d^2a/dq^2 are significant, w' is very small compared with w'', and the integral in (2) can be evaluated with considerable accuracy, i.e. to within about 3% in the case of liquid Na, by neglecting w' altogether. The answer is then

$$K_{\mathrm{int}} \cong 4\pi (ne)^2 \left[\left(\frac{\epsilon}{\epsilon q_{\mathrm{S}}{}^2} \right)_{q \to 0} + R_{\mathrm{M}}{}^2 - \frac{4}{45\pi} R_{\mathrm{A}}{}^3 \int_0^\infty (1-a) dq \right]. \quad . \quad . \quad (6)$$

The integral of $(1-a)$ has been evaluated using the recent results of Greenfield *et al.* (1971) for liquid Na and turns out to equal $2 \cdot 82 R_{\mathrm{A}}{}^{-1}$ at 200°C, where R_{A} is the atomic radius $(4\pi R_{\mathrm{A}}{}^3/3 = \Omega)$. The results of Waseda and Suzuki (1970) suggest that it is almost the same for liquid Hg at 80°C, and it is probably a fair approximation to replace the integral by $2 \cdot 82 R_{\mathrm{A}}{}^{-1}$ for all liquid metals at all temperatures. Finally, therefore, we have

$$K_{\mathrm{int}} \cong 4\pi (ne)^2 \left[\left(\frac{\epsilon'}{\epsilon q_{\mathrm{S}}{}^2} \right)_{q \to 0} + R_{\mathrm{M}}{}^2 - 0 \cdot 08 R_{\mathrm{A}}{}^2 \right]. \quad . \quad . \quad . \quad (7)$$

It should be explained that on a graph of K as a function of T at constant volume the quantity denoted here by K_{int} is an intercept on the $T=0$ axis, i.e.

$$K_{\mathrm{int}} = K - T(\partial K / \partial T)_{\Omega}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is only this intercept, which should be almost the same whether K_S or K_T is used, which can be calculated by this present method. Fortunately, $(T/K)(\partial K/\partial T)_{\Omega}$ is small; it seems to be almost zero for liquid Na (Endo 1963) and only about 0·14 for liquid Hg at normal densities (Davis and Gordon 1963).

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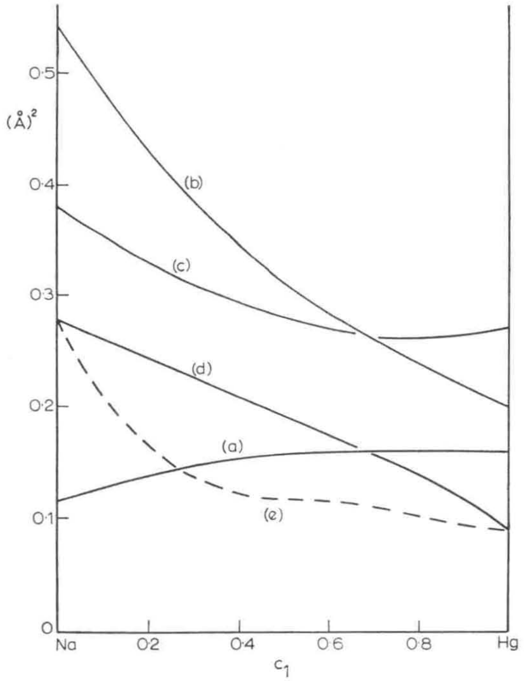
† Equation (2·84) in the reference quoted contains a regrettable error; the factor outside the integral appears incorrectly there as $\Omega / 2\pi^2 N$.

The dielectric constants ϵ' and ϵ and the screening parameter q_S are fully discussed by Faber (1972), who shows how the term $(\epsilon'/\epsilon q_S{}^2)$ in (7) may be calculated once n is known. This term by itself describes the bulk modulus of the equivalent jellium and includes corrections for correlation and exchange that are well known to be important in this context. The term $-0{\cdot}08 R_A{}^2$ may be thought of as an 'umklapp' correction; its evaluation presents no problems. As for $R_M{}^2$, which is a sort of core correction, we might as a first approximation evaluate this by using the values for R_M which have been quoted in various papers by Ashcroft and his colleagues. These are values adjusted, however, to explain properties such as the resistivity which depend upon the behaviour of $u(q)$ at large q; they do not necessarily describe at all accurately the curvature of $u(q)$ for small q, which is what matters here. The appropriate value of R_M for insertion into (7) may in principle be deduced from any pseudo-potential whose curvature for small q is known, whether or not it is based upon the empty core model, but the tabulated pseudo-potentials which are available in the literature give rather varied results. It therefore seems best to treat R_M as an adjustable parameter.

According to McAlister the isothermal bulk moduli of pure Na and pure Hg at 300°C are $4{\cdot}3 \times 10^{10}$ and 18×10^{10} dyne cm^{-2} respectively; the corresponding values for K_{int} should be about $4{\cdot}3 \times 10^{10}$ and 15×10^{10}. To fit these values with the aid of (7) we require R_M to be 0·73Å and 0·45Å for Na and Hg respectively, which appear to be consistent with the pseudo-potentials in current use. The relative magnitude of the three terms in (7) is shown in the figure.



Concentration-dependence in liquid Na–Hg at 300°C of (*a*) $(\epsilon'/\epsilon q_S{}^2)_{q\to 0}$; (*b*) $R_M{}^2$; (*c*) $0{\cdot}08\ R_M{}^2$; (*d*) $((\epsilon'/\epsilon q_S{}^2)_{q\to 0}+\overline{R_M{}^2}-0{\cdot}08\ \overline{R_A{}^2}))$; (*e*) $K_{\text{int}}/4\pi(\bar{n}e)^2$.

§ 3. EXTENSION TO ALLOYS

Equation (7) should still be valid for a binary alloy, granted the assumptions listed in § 1 above, provided that $\bar{n}$, $\overline{R_{\mathrm{M}}^2}$ and $\overline{R_{\mathrm{A}}^2}$ are replaced by appropriate mean values, $\bar{n}$, $\overline{R_{\mathrm{M}}^2}$ and $\overline{R_{\mathrm{A}}^2}$. It is not difficult to show (see, for example, the discussion of $w_{\alpha\beta}$ on p. 434 of Faber (1972)) that

$$\overline{R_{\mathrm{M}}^2} = \frac{(c_0 z_0 R_{\mathrm{M}}{}^2{}_{,0} + c_1 z_1 R_{\mathrm{M}}{}^2{}_{,1})}{c_0 z_0 + c_1 z_1}\,, \quad \ldots \ldots \quad (9)$$

where $R_{\mathrm{M},0}$ and $R_{\mathrm{M},1}$ are the core radii for solvent and solute ions respectively, which we may take to be independent of concentration. The umklapp term involves the partial interference functions $a_{00}(q)$, $a_{11}(q)$ and $a_{01}(q)$. For many alloy systems the behaviour of these three functions near their main peaks is likely to be similar to the behaviour of $a(q)$ for a pure liquid. In that case the most plausible interpolation formula for $R_{\mathrm{A}}{}^2$ turns out to be

$$\overline{R_{\mathrm{A}}^2} = \frac{3\Omega}{4\pi}\left[\frac{c_0{}^2 z_0{}^2 R_{\mathrm{A},0}{}^{-1} + 2c_0c_1z_0z_1(\tfrac{1}{2}(R_{\mathrm{A},0}+R_{\mathrm{A},1}))^{-1} + c_1{}^2 z_1{}^2 R_{\mathrm{A},1}{}^{-1}}{(c_0z_0+c_1z_1)^2}\right]. \quad (10)$$

Equations (9) and (10) have been used to calculate the concentration-dependence of $R_{\mathrm{M}}{}^2$ and $-0{\cdot}08R_{\mathrm{A}}{}^2$ in liquid Na–Hg and the results are plotted in the figure. A third curve shows the expected variation of $(\epsilon'/\epsilon q_{\mathrm{S}}{}^2)_{q\to 0}$ and a fourth one shows the sum of these three quantities.

It may be seen that the fourth curve is almost a straight line, and it looks as though it would turn out that way for many other systems besides Na–Hg. In that case the theory implies that

$$K_{\mathrm{int}} \cong \bar{n}^2\left[\frac{c_0 K_{\mathrm{int},0}}{n_0{}^2} + \frac{c_2 K_{\mathrm{int},1}}{n_1{}^2}\right], \quad \ldots \ldots \quad (11)$$

and hence that for dilute alloys

$$\left(\frac{1}{K_{\mathrm{int}}}\frac{dK_{\mathrm{int}}}{dc_1}\right)_{c_1\to 0} \cong 2\left(\frac{z_1-z_0}{z_0}\right) - 2\left(\frac{1}{\Omega}\frac{d\Omega}{dc_1}\right)_{c_1\to 0} + \left(\frac{\Omega_1{}^2 z_0{}^2 K_{\mathrm{int},1}}{\Omega_0{}^2 z_1{}^2 K_{\mathrm{int},0}} - 1\right). \quad (12)$$

To improve upon these simple predictions would require more information about partial structure factors than is yet available.

§ 4. DISCUSSION

A broken curve in the figure shows how $(K_{\mathrm{int}}/4\pi(\bar{n}e)^2)$ varies with concentration for liquid Na–Hg at 300°C according to McAlister. (In deriving $\mathrm{K}_{\mathrm{int}}$ from McAlister's curve for K_T it has been assumed that $(T/K_T)(\partial K_T/\partial T)_\Omega$ varies with concentration in a linear fashion between the values quoted above for the pure constituents.) The agreement with experiment is far from satisfactory.

The Na–Hg system is not a particularly straightforward one, of course; it is possible that the compound $\mathrm{NaHg_2}$ survives in the liquid phase, and this could affect the compressibility. The disagreement between theory and experiment is just as serious, however, for the other Na-based systems studied by McAlister. His results for $(\Omega^{-1}d\Omega/dc_1)$ and $(K_S{}^{-1}dK_S/dc_1)$ in very dilute solutions, together with some results for Na–K reported by Abowitz and Gordon (1962), are listed in columns (4) and (7) of the table. The figures in column (5) are rough estimates for $(\Omega_1{}^2z_0{}^2K_1/\Omega_0{}^2z_1{}^2K_0)$, derived, except in the case of Na–K and Na–Hg, by using for Ω_1 and K_1 the molar volume and isothermal bulk modulus of the pure solute just above its melting point. The figures in column (6), derived from eqn. (12), are in very poor agreement with the experimental results in (7), except perhaps in the case of Na–K. The experimental values for $(K^{-1}dK/dc_1)$ are much less than expected and curiously insensitive to the valency of the solute.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solute	T°C	$\left(\dfrac{z_1-z_0}{z_0}\right)$	$\left(\dfrac{1}{\Omega}\dfrac{d\Omega}{dc_1}\right)_{c_1\to 0}$	$\left(\dfrac{\Omega_1{}^2z_0{}^2K_1}{\Omega_0{}^2z_1{}^2K_0}\right)$	$\left(\dfrac{1}{K}\dfrac{dK}{dc_1}\right)_{c_1\to 0}$	
					Eqn. (12)	Expt.
K	100	0	0·84	1·77	−0·9	−1·3
Au	300	0	−1·40	(2·1)	(3·9)	1·26
Cd	300	1	−0·96	0·52	3·5	1·24
Hg	300	1	−1·06	0·31	3·4	1·36
In	300	2	−1·00	0·33	5·3	1·22
Sn	300	3	−1·31	0·23	7·8	1·41
Pb	300	3	−1·50	0·26	8·3	1·36

The weakest link in the theoretical argument is probably the assumption of linear screening; a polyvalent ion transplanted into a matrix of pure Na may well represent too strong a perturbation, so far as the conduction electrons are concerned, for the screening to be even approximately linear. In an extreme case it might retain some of its valence electrons in localized states around itself, and hence behave as though its valency were less than z_1. Quite good agreement between theory and experiment could be achieved if one were prepared, in the context of the table, to replace z_1 by unity for all the solute elements listed. In most metallic alloy systems, however, the assumption of localized states is usually thought to be inconsistent with the observed behaviour of transport properties such as the Hall coefficient.

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