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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.

§ 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

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

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 $q \rightarrow 0$. 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[†]

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

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,

$$w'(q) = -q_S^2\epsilon'|u(q)|^2/4\pi e^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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

$$w(0) = 4\pi(ze)^2\left(\left(\frac{\epsilon'}{\epsilon q_S^2}\right)_{q\to 0} + R_M^2\right). \quad . \quad . \quad . \quad . \quad (5)$$

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

$$K_{int} \simeq 4\pi(ne)^2\left[\left(\frac{\epsilon'}{\epsilon q_S^2}\right)_{q\to 0} + R_M^2 - \frac{4}{45\pi}R_A^3\int_0^\infty (1-a)dq\right]. \quad . \quad . \quad (6)$$

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 $2 \cdot 82R_A^{-1}$ at 200°C, where R_A is the atomic radius $(4\pi R_A^3/3 = \Omega)$. 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 $2 \cdot 82R_A^{-1}$ for all liquid metals at all temperatures. Finally, therefore, we have

$$K_{int} \simeq 4\pi(ne)^2\left[\left(\frac{\epsilon'}{\epsilon q_S^2}\right)_{q\to 0} + R_M^2 - 0 \cdot 08R_A^2\right]. \quad . \quad . \quad (7)$$

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.

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

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 $0 \cdot 14$ for liquid Hg at normal densities (Davis and Gordon 1963).

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