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Electrical resistivity and thermopower of the liquid alloy MgZn

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Abstract. We have measured the electrical resistivity, ρ, and the thermopower, S, for the liquid alloy MgZn across the entire concentration range. New data for ρ and S for pure liquid Zn are also reported. Data for the liquid alloy are shown to be consistent with the Faber–Ziman theory, provided the pseudopotential for Zn is assumed to be energy dependent. A comparison of the data for the liquid alloy with data previously reported for the solid amorphous alloy indicate that this energy dependence should also be considered in the solid.

1. Introduction

The last decade has seen considerable activity in the study of the electronic properties of both liquid binary alloy systems and amorphous solid metallic alloys. That studies of these systems should have followed similar paths is no surprise, since it is common to consider an amorphous metallic alloy to be similar to a random highly-viscous liquid. As a result, in many cases, the electronic properties of the amorphous alloys have been analysed using modifications of theories developed earlier for liquid metal systems. One of the most common theoretical formulations used to study either liquid alloys or solid amorphous alloys is that due to Faber and Ziman (1965). This formulation has been especially successful in describing the properties of weak-scattering liquid alloys.

Most amorphous binary solid alloys fall naturally into two classes: those alloys in which one component is a transition metal and the other is a simple metal; and those in which both components are simple metals. Many alloys in the former class have been studied, but, because of the presence of the transition metal component, the weak-scattering theory of Faber and Ziman is not appropriate for their analysis. Instead, the 'extended Faber–Ziman theory', developed by Evans and his co-workers (Evans *et al* 1971) for liquid transition metals and modified by others for amorphous alloys, has been applied (see Nagel 1978, Nagel *et al* 1978, Meisel and Cote 1978, Cote and Meisel 1979). Unfortunately, in spite of its wide application to transition metal systems, the validity of this approach is still open to some question. (In this formulation, for example, a well defined Fermi surface is assumed.) Moreover, in applications of this method to amorphous solid alloys, an averaged scattering potential and an averaged structure factor are often assumed, making the application just a bit more tenuous (see Cote and Meisel 1977). It would seem that solid amorphous alloys of the second class should provide a more direct test of the application of Faber–Ziman-type theories.

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Several amorphous binary solid alloys of the second class have been discovered recently. These include, among others, MgCu (Matsuda and Mizutani 1982b), AgCu (Mizutani and Yoshida 1982), and MgZn (Matsuda and Mizutani 1982a; Baibich *et al* 1982; and others). Of these, MgZn appears to form the most nearly ideal alloy and has been studied most extensively. Mizutani and Mizoguchi (1981) have measured the electronic specific heat of this solid and found it to be within 2% of its free-electron value; Mizoguchi *et al* (1980) found the Fermi wavevector, measured by positron annihilation techniques, to be within 3% of its free-electron value; and Baibich *et al* (1982) found that magnetic susceptibility measurements also confirm the free-electron nature of this solid amorphous alloy. Similarly, it is expected that liquid MgZn should be a well behaved nearly free-electron alloy. As a result, with no d contribution to the electronic properties, one expects that the Faber–Ziman theory in its weak-scattering form should be applicable to both the solid and the liquid systems. Baibich *et al* (1982) and Matsuda and Mizutani (1982a) have in fact measured the electrical resistivity, ρ, and the thermopower, S, of the amorphous solid alloy, a-MgZn, over the range of composition from about 20 to 35 at % Zn. Baibich and co-workers have analysed their results along the lines of the Faber–Ziman theory, finding that an approach akin to the full, non-averaged, theory may be needed. (They did, however, assume in their analysis that the energy dependence of the pseudopotentials for Mg and Zn could be ignored.) Matsuda and Mizutani (1982a) also employ the extended Ziman theory in their analysis of S.

We find that liquid MgZn should be an interesting alloy to study for several reasons. A study of the electronic properties of the liquid should shed light on the analysis of the results for the amorphous solid, since the full liquid alloy theory can be applied straightforwardly, employing the pseudopotentials of both alloy components as well as the measured or calculated (utilising the successful hard-sphere approximation) structure factors. Even though this alloy is divalent at all compositions, it is non-substitutional both structurally and electronically, forcing us to include in the analysis variations in Fermi energy with composition, as well as estimates of the three partial structure factors. It is also advantageous that the liquid alloy is expected to be homogeneous over the entire range of composition, making a much broader composition range available to us. In what follows, we report measurements of ρ and S for the liquid alloy MgZn, and compare our results with those calculated on the Faber–Ziman theory and with the results reported for the amorphous solid. We also consider the energy-dependence of the pseudopotentials in our analysis.

2. Theory

It is possible to cast the electrical resistivity, ρ, of a liquid binary alloy as (Faber and Ziman 1965):

$$\rho = \frac{3\pi\Omega}{e^2\hbar v_F^2}\langle F(K)\rangle \tag{1}$$

where Ω is the atomic volume, and v_F is the Fermi velocity. Here, too,

$$\langle F(K)\rangle \equiv 4\int_0^1 F(K)\left(\frac{K}{2k_F}\right)^3 \mathrm{d}\left(\frac{K}{2k_F}\right) \tag{2}$$

where k_F is the Fermi wavevector and K is the wavevector corresponding to momentum transfer. $F(K)$ for a binary alloy can be written as (Ashcroft and Langreth 1967b)

$$F(K) = c|U_2(K)|^2 A_{22}(K) + (1-c)|U_1(K)|^2 A_{11}(K) + 2[c(1-c)]^{1/2} U_1(K) U_2(K) A_{12}(K) \tag{3}$$

where $U_i(K)$ is the pseudopotential of the ith component, c is the atomic fraction of component '2', and $A_{ij}(K)$ is the partial structure factor as defined by Ashcroft and Langreth (1967a). This formulation should be appropriate for weak-scattering liquid alloys, and, with some modification, for weak-scattering amorphous solid alloys. The extended Ziman theory takes a similar form, but with the T-matrix replacing the pseudopotential in $F(K)$.

The partial structure factors, $A_{ij}(K)$, are available from neutron-scattering measurements (isotope enrichment techniques are used), or can be calculated on the basis of the hard-sphere approximation (Ashcroft and Langreth 1967a). In this calculation, one must choose a hard-sphere diameter, σ_2, and a ratio of hard-sphere diameters, $\alpha \equiv \sigma_1/\sigma_2$ for the two species. (The species '1' and '2' are chosen so that α is always $\leqslant 1$. The alloy packing fraction, η, must also be chosen. (For pure liquid metals, $\eta \simeq 0.456$ just above the melting temperature (Ashcroft and Lekner 1966).)

The pseudopotentials, $U_i(K)$, can be obtained from any of several model potentials presently available. In this work we will use the empty core model potential of Ashcroft (1968) as applied successfully to binary alloys (cf Tomlinson 1969):

$$U_i(x) = \frac{-\lambda^2 \cos(S_i x)}{x^2 + \lambda^2 f(x)} \left(\frac{Z_i}{Z}\right) \qquad i = 1, 2 \tag{4}$$

Here (in atomic units)

$$\lambda^2 = \frac{1}{\pi k_F} \qquad S_i = 2k_F R^i_{\text{core}}$$

$$x = K/2k_F \qquad Z = cZ_2 + (1-c)Z_1$$

and $f(x)$ is the Lindhard dielectric function. (The model potential is in units of $2E_F/3$.) R^i_{core} is the single adjustable parameter for the ith species, and can be obtained from fitting the calculated value of ρ to the measured value for each pure liquid metal at the melting point. In this calculation equations (1)–(3) are used, with $c = 0, 1$. A knowledge of $U_i(K)$ and $A_{ij}(K)$ then permits a calculation of $\rho(c)$ via equations (1)–(3).

The thermopower, S, of a binary liquid alloy can also be written in terms of $F(K)$ (cf Van Zytveld 1975):

$$S = \frac{-\pi^2 k_B^2 T}{3|e|E_F} x \tag{5}$$

where

$$x = 3 - 2q - r/2. \tag{6}$$

Here

$$q = F(2k_F)/\langle F(K)\rangle, \tag{7}$$

and

$$r = k_F\langle(\partial F(K,k)/\partial k)|_{k_F}\rangle/\langle F(K)\rangle. \tag{8}$$

If we may neglect the energy dependence of the pseudopotentials, the term 'r' in equation (6) will be zero. Then, utilising equation (1), we can write, for the binary alloy:

$$\frac{(3-x)}{\Omega}\rho = \frac{6\pi}{e^2 \hbar v_F^2} F(2k_F). \tag{9}$$

The advantage of this approach is that we do not have to specify $U_i(K)$ in order to calculate $x(c)$ from a knowledge of $\rho(c)$. We can apply the Faber–Ziman formalism independent of a choice of pseudopotential. In particular, at any concentration, c, we can find v_F, Ω, and the $A_{ij}(2k_F)$. Measurements of ρ and S for the *pure* constituents then permit 'experimental' estimates of the $U_i(2k_F)$ via equations (1), (3), (6), (7), making it possible to obtain $F(2k_F)$ for the alloy at any concentration (equation (3)). If we now have v_F, Ω, $F(2k_F)$ and $\rho(c)$ for the alloy at concentration c, we can calculate $x(c)$ via equation (9) and hence $S(c)$, to compare with our measured values.

3. Sample materials and experimental methods

The pure metals used in forming the alloys in this study were obtained from two sources: Mg, of nominal purity 99.99%, was obtained from the Atomergic Chemetals Co., and Zn, purchased from Johnson–Matthey (Aesar) Co., was nominally 99.9999% pure.

While measurements were being made, the liquid alloys were held in high-density high-purity Al_2O_3 tubes. Electrical contact to the samples was made via holes drilled through the sides of these tubes; electrical leads were then attached over thin Mo foils (0.1 mm thick) which were drawn tightly over the holes to prevent leakage of the liquid. Prior to making measurements, each sample was stirred with a Mo stirring wire to ensure the homogeneity of the alloy and to eliminate any bubbles that might have formed. Chromel–alumel thermocouples were used to measure the temperature at various points on the sample; pure Cu wire provided the counter electrode material for thermopower measurements. (We have used the results of Roberts (1981) for S(Cu).) The sample tubes were calibrated at room temperature with double-distilled Hg to provide the dimensional constant needed to extract the sample resistivity from the measured resistance, and the thermal expansion coefficient of Al_2O_3 was utilised in extracting $\rho(T)$ at higher temperatures.

Resistivity measurements were made via a standard four-probe DC technique. Thermopower measurements were made by holding one junction at constant temperature and by obtaining the thermal voltage of the Cu–sample–Cu couple as a function of the temperature of the warmer junction.

4. Experimental results

The measured resistivity, $\rho(c)$, of liquid MgZn is shown in figure 1 as a function of the atomic fraction, c, of Zn. All data displayed are for the 700 °C isotherm. The results for $\rho(c)$ fall on a smooth, nearly parabolic curve, and show no evidence of the double-peaked feature reported by Steeb *et al* (1970). The estimated uncertainties in the measured values of ρ are smaller than the points displayed in the figure, and therefore are not explicitly shown. We have also measured ρ for pure liquid Zn in the temperature range spanning 700 °C; our result, 35.5 $\mu\Omega$ cm at 700 °C, agrees well with the value of 35.65 $\mu\Omega$ cm given in the Lyon (1952), but falls substantially below the value of 36.4 $\mu\Omega$ cm given by Roll and Motz (1957). (Roll and Motz used a contactless rotating magnetic field measurement technique, as did Steeb *et al* (1970). The latter estimate the uncertainty in their measurements of ρ to be ±6%.)

Measured values of $\mathrm{d}\rho/\mathrm{d}T$ (c) are also shown in figure 1. Over much of the concentration range ($c > 0.3$), $\mathrm{d}\rho/\mathrm{d}T < 0$, consistent with Faber–Ziman theory for $Z \simeq 2$.

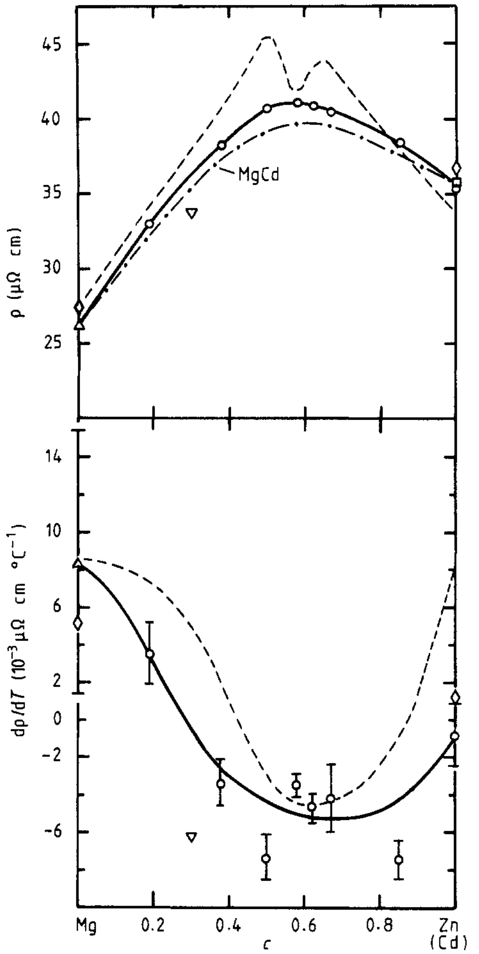

Figure 1. Electrical resistivity, ρ, and $\mathrm{d}\rho/\mathrm{d}T$ for the liquid alloy MgZn as a function c, the atomic fraction of Zn. Data displayed are on the 700 °C isotherm. (○), present results; (△), Van Zytveld *et al* (1972); (□) Lyon (1952); (▽) Hafner *et al* (1980), quoting Oberle *et al*; (◇), Roll and Motz (1957); ----- Steeb *et al* (1970); (–·–·–) ρ for liquid MgCd displayed for comparison (see text), measured by Enderby *et al* (1968), but not previously published.

Our results here agree reasonable well with those of Steeb *et al* (1970), as can also be seen in the figure. The value we have used for $\mathrm{d}\rho/\mathrm{d}T$ for pure Mg is from the data of Van Zytveld *et al* (1972), but the data have been reanalysed with a resulting reduction in the estimated uncertainty. This new estimate of uncertainty is also displayed in the figure.

Measured thermopowers, $S(c)$, of the liquid MgZn alloys, also on the 700 °C isotherm, are shown in figure 2. $S(c)$ is seen to be weakly parabolic. We have also measured S for pure liquid Zn from 650 to 725 °C, and find $S\,(\mu\mathrm{V}\,{}^{\circ}\mathrm{C}^{-1}) = 1.70 + 3.2 \times 10^{-3}\,(T - 700\,{}^{\circ}\mathrm{C})$; this value compares well with that reported by Marwaha and Cusack (1965) over the temperature range $420\,{}^{\circ}\mathrm{C} \leqslant T \leqslant 725\,{}^{\circ}\mathrm{C}$: $S\,(\mu\mathrm{V}\,{}^{\circ}\mathrm{C}^{-1}) = 1.63 + 4.3 \times 10^{-3}\,(T - 700\,{}^{\circ}\mathrm{C})$. (Here we have adjusted Marwaha and Cusack's results to Roberts' new values for S(Cu).)

Because of the anticipated similarity between the liquid and amorphous alloy systems, we compare our measurements of $\rho(c)$ and $S(c)$ for liquid MgZn with similar

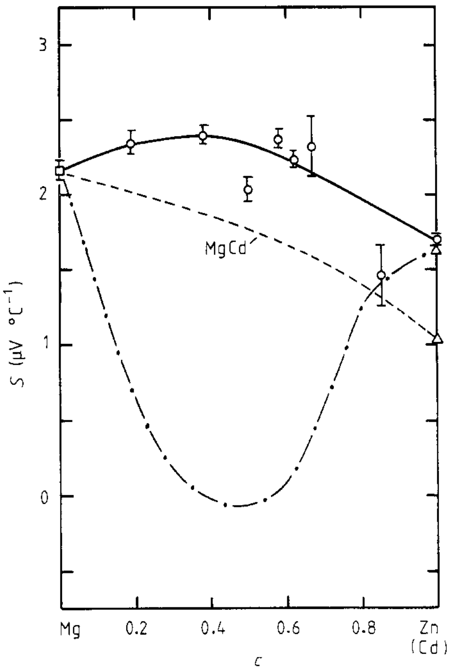

Figure 2. Thermopower, S, for liquid MgZn as a function of c, the atomic fraction of Zn. The data are for the 700 °C isotherm. (○), present results; (□), Van Zytveld *et al* (1973); (△), Marwaha and Cusack (1965). (Both of these have been adjusted to accommodate the new data of Roberts (1981) for S(Cu)); (–·–·–) calculated on Faber–Ziman theory (see text); (-----) $S(c)$ for liquid MgCd displayed for comparison (see text), Enderby *et al* (1968).

measurements by Baibich *et al* (1982) and Matsuda and Mizutani (1982a) for the amorphous alloy. We show these in figure 3, where our results for the liquid are extrapolated to 23 °C for comparison with the amorphous alloy at that temperature. For both ρ and S the comparison with Baibich *et al* (1982) is remarkably good. The data for S agree to well within the experimental uncertainty; the data for ρ are not quite so consistent: ρ for the amorphous alloys increases linearly for $c > 0.2$, whereas the data for the liquid curve downward and go through a maximum. The data for the liquid do not agree quite so well with the data of Matsuda and Mizutani (1982a). We do note, however, that Baibich and co-workers saw that the measured thermopower of one of their alloys was depressed by about 1 μV °C^{-1} when that sample was partially crystallised. It is possible that some degree of crystallisation may also have occurred in the samples of Matsuda and Mizutani. In terms of magnitudes and concentration dependence, however, the general agreement between the liquid and amorphous solid data must be considered good, and provides experimental justification for the suggested similarity between these solid and liquid systems.

5. Discussion

We have calculated $\rho(c)$ for the liquid alloy utilising equations (1)–(3) with a variety of methods. In 'method a', we have used the binary liquid alloy hard-sphere approximation (Ashcroft and Langreth 1967a) to calculate the $A_{ij}(K)$, assuming that the packing fraction $\eta_i = 0.456$ for each pure constituent, i, (at 700 °C), and $\eta = 0.456$ for the alloy

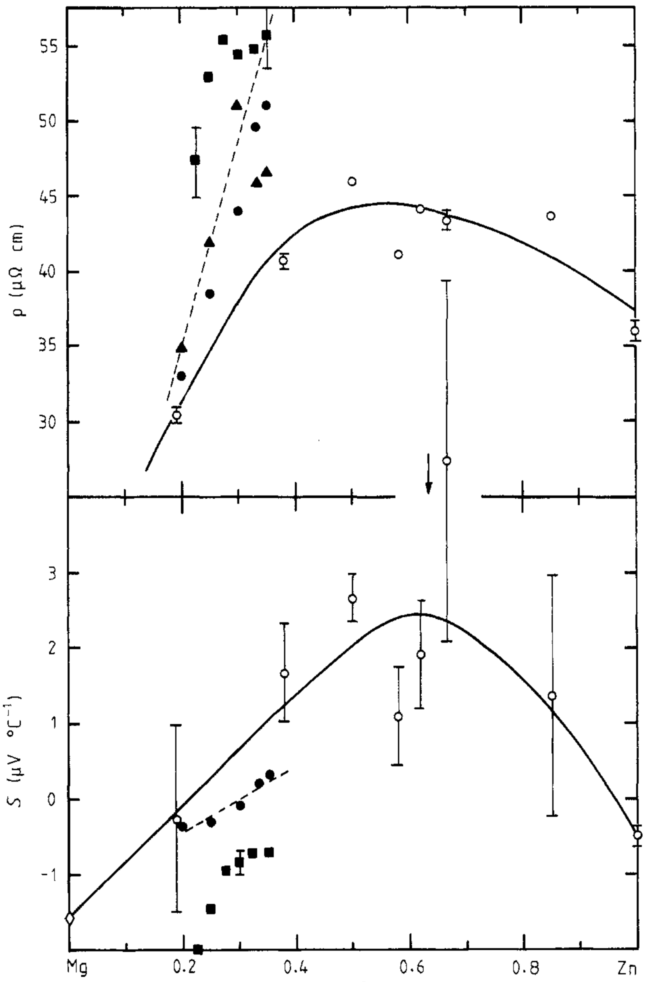

Figure 3. ρ and S for MgZn as a liquid alloy and as an amorphous solid alloy, both as functions of the atomic fraction, c, of Zn. (●, ▲), data for a-MgZn at 23 °C from Baibich *et al* (1982); (■), data for a-MgZn at 23 °C from Matsuda and Mizutani (1982a); (○), present data for the liquid, extrapolated to 23 °C.

also. This should be a good assumption for both Mg and Zn, since the isotherm in question (700 °C) is close to the melting temperature for Mg (T_{mp} = 650 °C), and $A(K)$ (and hence, η) for Zn is seen to be nearly independent of temperature in neutron diffraction experiments (Wingfield and Enderby 1968). We have also used the Ashcroft empty-core model potential, $U(K)$, for each constituent (equation (4)). ρ, as calculated via equations (1)–(4) for *pure* liquid metals, is often found to be a double-valued function of R^i_{core}; hence there are often two values of R^i_{core} that will make the calculated ρ fit the measured value for a pure liquid metal. We find this to be true for both Mg and Zn. In this way we find, for pure liquid Mg, that R_{core} (Mg) = 0.6006 Å or 0.7305 Å; for pure liquid Zn, we obtain R_{core}(Zn) = 0.4660 or 0.6682 Å. Using all combinations of these R^i_{core}, and taking $\alpha \equiv \sigma(\mathrm{Zn})/\sigma(\mathrm{Mg})$ as the only adjustable parameter, we find a very good fit of the calculated $\rho(c)$ to the measured curve for α = 0.731, with R_{core}(Zn) = 0.4660 Å and R_{core}(Mg) = 0.6006 Å (see table 1, method 'a'). (All other combinations

Table 1. Parameters used in calculating $\rho(c)$ for liquid MgZn.

Calculation Method†		Density ($\mathrm{g\,cm^{-3}}$)	R_{core} (Å)	δ_0	δ_1	α
a	Mg	1.58	0.6006	—	—	0.731
	Zn	6.92	0.466	—	—	
b	Mg	1.58	0.6006	—	—	0.055
	Zn	6.92	0.686	—	—	
c	Mg	1.58	0.7305	—	—	0.682
	Zn	6.92	—	2.89	0.08	
d	Mg	1.58	0.6006	—	—	0.804
	Zn	6.92	—	2.89	0.08	

† See the text.

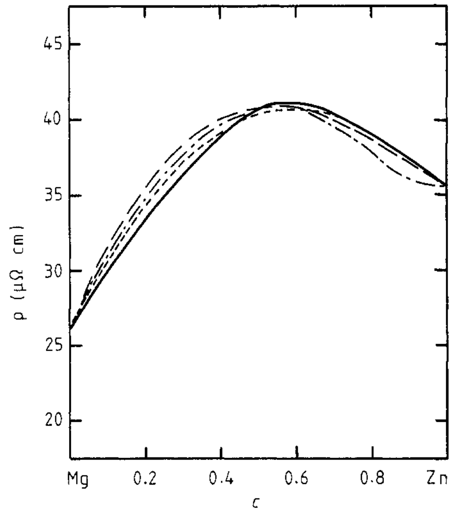

Figure 4. Calculated and experimental values of $\rho(c)$ for liquid MgZn. (——), experimental $\rho(c)$; calculated $\rho(c)$ via: (-----), method 'a'; (———), method 'c'; (———), method 'd'. (See table 1, and the text.)

of values of R^i_{core} result in clearly inferior fits for all values of α.) This calculated $\rho(c)$ is shown in figure 4. The value $\alpha = 0.731$ is quite reasonable, being moderately close to the value of 0.85 that one obtains from calculating the σ_i for each constituent separately, via a knowledge of the atomic density and packing fraction of each pure liquid. These values of R^i_{core}, however, are smaller than those used in other studies: Ashcroft and Langreth (1967b) used a value of $R_{\mathrm{core}}(\mathrm{Zn})$ (=0.673 Å), essentially the same as our larger value, in calculating $\rho(c)$ for liquid HgZn. (η for Hg may have been unrealistically low, however, in this study.) Van Zytveld (1975) used $R_{\mathrm{core}}(\mathrm{Mg}) = 0.744$ Å in his study of the liquid alloy LiMg; this is also virtually the same as our larger value for Mg. In both cases, the smaller values of R^i_{core} result in $U_i(K)$ that do not have any zeros for $K < 2k_{\mathrm{F}}$. This may be reasonable for Zn, but is not likely to be a good description of $U(K)$ for Mg (see, for example, Animalu and Heine (1965)).

We also note that in this calculation we have used $A_{ij}(K)$ calculated on the hard-sphere approximation. The hard-sphere structure factor, $A_{\mathrm{HS}}(K)$, for pure liquid Mg

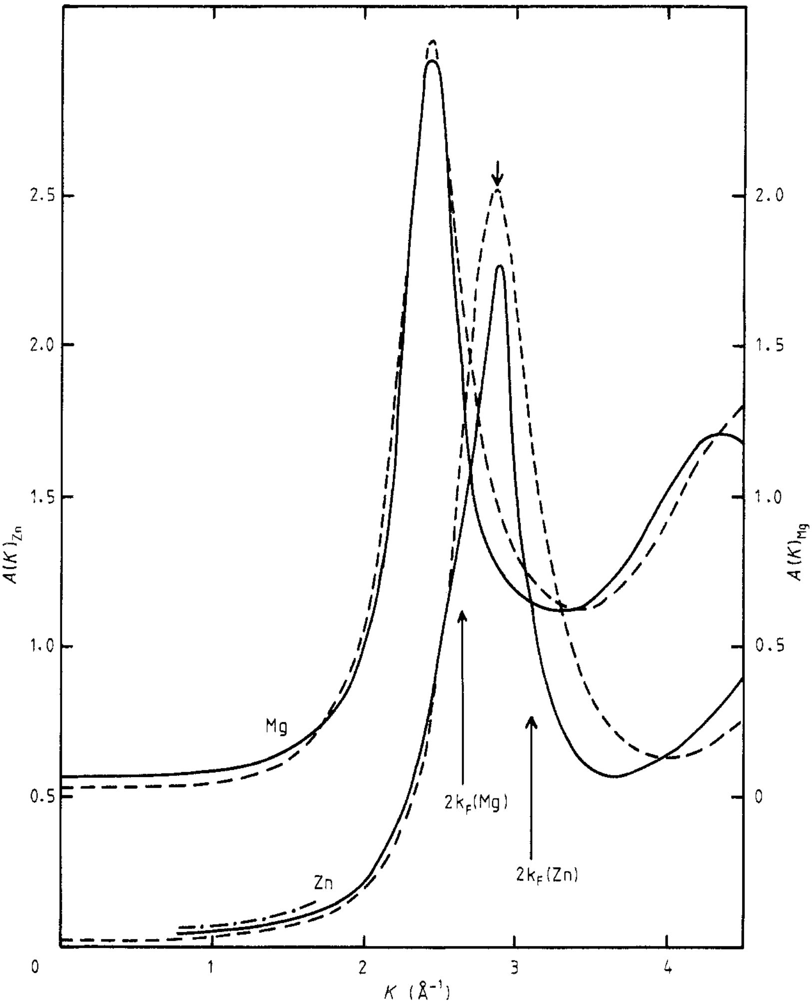

Figure 5. Structure factors, $A(K)$, for the pure liquids Mg and Zn just above their respective melting temperatures. (- - - - -), $A(K)$ calculated on the hard-sphere approximation, Ashcroft and Lekner (1966); (——) (for Mg) Woerner *et al* (1965), measured by x-ray diffraction: —— (for Zn) North *et al* (1968), measured by neutron diffraction; (-·······-) Egelstaff *et al* (1966), measured by neutron diffraction; arrow-peak position for Zn, Gamertsfelder (1941), measured by x-ray diffraction.

follows that measured by x-ray diffraction methods very well for $K < 2k_F$, but the agreement is not nearly so good for liquid Zn (see figure 5). In particular, the first peak in the measured $A(K)$ for Zn is displaced slightly to larger values of K, but more noticeable is the fact that the height of this peak for the measured $A(K)$ is well below that for $A_{HS}(K)$. The shape of the first peak in the measured $A(K)$ for Zn is also non-ideal, rising more slowly on the low-K side and falling more rapidly for high K. It is reasonable to expect that, if we were to use an experimental $A(K)$ for liquid Zn, we would improve our calculated $\rho(c)$, bringing it even closer to the measured curve.

To test this, we have therefore also taken the measured $A(K)$ for pure liquid Zn (North *et al* 1968) renormalised for use with the Ashcroft formalism for $F(K)$ for the alloy (equation (3)), together with the calculated hard-sphere $A(K)$ for Mg and for the cross-term, $A_{ij}(K)$ with $i \neq j$, and from this have calculated $\rho(c)$. The $R_{\text{core}}(\text{Zn}) = 0.686$ Å which reproduces $\rho(\text{Zn})$ is quite reasonable, but the value of $\alpha = 0.055$ needed to obtain the experimental value of $\rho(c = 0.5)$ appears to be non-physical. (These parameters are shown in table 1 under method 'b'.) Thus the use of an experimental $A(K)$ for Zn does not appear to result in an improvement in the calculated $\rho(c)$.

We also note that Meisel and Cote (1983) have been fairly successful in studying a-MgZn using a standard model potential for Mg and a phase-shift expansion of $U(K)$ for Zn, calculated along the lines of the T-matrix method of Evans (see Evans *et al* 1971). Cast in this form

$$U(K) = \frac{2\pi\hbar^3}{m(2mE_{\text{F}})^{1/2}}\,\Omega \sum_l (2l+1)\sin[\delta_l(E_{\text{F}})]\,e^{i\delta_l(E_{\text{F}})}P_l(\cos\theta) \qquad (10)$$

where E_{F} is the Fermi energy, δ_l is the phase shift associated with the lth partial wave, and $P_l(\cos\theta)$ is the lth Legendre polynomial. Meisel and Cote assume that for Zn only the s- and p-phase shifts are non-zero, and that the Friedel sum rule holds. In this way δ_0 can be obtained as the only adjustable parameter in fitting the measured and calculated values of ρ for pure liquid Zn. We find $\delta_0 = 2.89$ and $\delta_1 = 0.08$, close to the values of 2.87 and 0.09 reported by Meisel and Cote. (Here we have again calculated $A_{ij}(K)$ via the method of Ashcroft and Langreth (1967a) for all three partial structure factors). We find fairly good agreement for $\rho(c)$ with reasonable values of α for both values of $R_{\text{core}}(\text{Mg})$ (see table 1, methods 'c' and 'd', and figure 4). These calculated curves, $\rho(c)$ are slightly inferior to that obtained by method 'a'. It appears that a phase-shift expansion for $U_{\text{Zn}}(K)$ *is* reasonable.

We have also calculated $\rho(c)$ using an Ashcroft model potential for Mg, the phase shift expansion of $U(K)$ for Zn, an experimental $A(K)$ for Zn, and a hard-sphere $A(K)$ for both Mg and for the cross term: $A_{ij}(K)$, $i \neq j$. $\rho(c)$ calculated on this method differs substantially from the measured curve, and we do not display the result. It appears that we can calculate $\rho(c)$ rather well with any of several methods, all within the basic Faber–Ziman formalism; we are somewhat surprised, however, that use of an experimental $A(K)$ is not more successful. It is not clear why this is the case.

It is possible, however, to minimise some of the difficulties associated with these calculations of $\rho(c)$ (i.e., obtaining a realistic model-potential and obtaining a good estimate of the three $A_{ij}(K)$) by looking instead at an analysis of $S(c)$. In particular, if we can ignore the energy dependence of the model-potential (as was also done by Baibich *et al* (1982)), we can write a single relation which couples $x(c)$, $\rho(c)$ and the parameters $U_i(K)$ and $A_{ij}(K)$, but with these last two evaluated only at $2k_{\text{F}}$ for the alloy (see equation (9), and the discussion following). We assume in applying this procedure, that the $U_i(2k_{\text{F}})$ so obtained are independent of c between the limits of $2k_{\text{F}}(\text{Mg})$ and $2k_{\text{F}}(\text{Zn})$. This should be a reasonably good assumption. Moreover, because the A_{ij} in the function $F(2k_{\text{F}})$ must now only be evaluated at $2k_{\text{F}}$, we can use $A_{\text{HS}}(K)$ and rather readily estimate the errors that might be introduced by this approximation. Using the experimental $\rho(c)$ and the hard-sphere $A_{ij}(K)$, and proceeding as outlined to obtain $F(2k_{\text{F}})$, we find the $x(c)$ and hence the $S(c)$ as shown in figure 2. It is clear that this curve compares poorly with the measured $S(c)$. Moreover, attempts to incorporate measured values of $A_{ij}(2k_{\text{F}})$ into an estimate of $S(c)$ do not improve the agreement with the measured thermopowers.

We are reminded, however, of the considerable similarity between $\rho(c)$ and $S(c)$ measured for liquid MgZn and these same parameters reported earlier for liquid MgCd (see figures 1 and 2). The liquid alloy MgCd is simpler, in that it is a substitutional alloy:

both k_F and the mean atomic volume, Ω, are nearly independent of c. This is *not* the case fo MgZn, in which k_F and Ω vary by about 16% and 48% respectively. In spite of this, the similarity in $\rho(c)$ and $S(c)$ is striking. We are further reminded that the analysis of the results for liquid MgCd implied strongly that the energy dependence of the model-potentials could not be ignored. (Enderby *et al* 1968). We are led to propose that the energy dependence of $U(K)$, at least for Zn, must be included here as well (see also Wingfield and Enderby (1968)).

Looking initially at pure liquid Zn, we see that S is measured to be about 1.7 μV °C^{-1} (see figure 1). This implies via equation (5) that x is about -0.66. Using any of several model pseudopotentials, we find that q should fall into the range of 0.1 to 1.1, implying that r should be in the range of 2.9 to 6.9. This value of r is considerably larger than q, and clearly should not be ignored in a study of pure liquid Zn. We also anticipate that this energy dependence of $U(K)$ for Zn must also be considered in an analysis of $S(c)$ for the MgZn alloy.

In order to make progress in estimating the effect of this for the alloy, we assume that we can ignore the energy dependence of $U(K)$ for Mg but not for Zn, and we further assume that $U(K, k)$ (Zn) is linear in k. We can then formally evaluate $r(c)$, equation (8), using $F(K, c)$, equation (3). Proceeding in this way we find that $r(c)$ for the alloy varies from 0 to about 4, with a mean value of about 2.5. We also estimate $q(c)$ to have a mean value of about 1. We see, therefore, that r for the alloy is, if anything, a bit larger than q, and also that r and q are of about the magnitude needed to explain the measured $S(c)$.

We conclude, therefore that Faber–Ziman theory can be applied meaningfully to liquid MgZn, and, we propose, to a-MgZn as well. Unfortunately, it appears that the energy dependence of the pseudopotentials cannot be ignored in the calculation of $S(c)$ for the liquid alloy; it is anticipated that ignoring the r term in the analysis of $S(c)$ for the amorphous solid is also unwise, and the analysis of Baibich *et al* (1982) should be altered to reflect this. This also weakens the argument made by Baibich and co-workers against the averaging approximations often made in analysing ρ and S for amorphous alloys.

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