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Thermopower and resistivity in amorphous $Mg_{1-x}Zn_x$ alloys

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Thermopower and resistivity have been measured on a series of $Mg_{1-x}Zn_x$ amorphous alloys ($0.2 < x < 0.35$) over the temperature range 4–300 K. The thermopower data cannot be explained on the basis of the simple Ziman model. Using a two-component model, which can be considered as an extreme simplification of the Faber-Ziman theory of liquid-metal alloys, we were able to fit the experimental data over the entire range of compositions. The success of this model strongly implies that the usual simplification of average properties involved in the simple Ziman model is inappropriate to amorphous metal alloys.

INTRODUCTION

Thermopower and electrical resistivity measurements as a function of composition and temperature give information about the electron scattering mechanisms and their energy derivatives, respectively, in the alloy system studied. Previous thermopower measurements on amorphous materials have been few in number in comparison to the large body of literature on the resistivity of these materials.[1] Of these few, most have presented measurements on one or two members of one alloy system or else a heterogeneous collection of measurements on different alloys.[2–11] In this paper, we present a systematic study of the composition and temperature dependence of the thermopower and resistivity of the Mg-Zn amorphous alloy system over the greatest possible composition range.[12] For certain nonmagnetic amorphous alloys the simple Ziman liquid-metal theory has been used as a framework for correlating the resistivity with the thermopower.[13] This theory[14] was developed assuming free-electron behavior for liquid metals, and its extension to amorphous metals by Sinha[2] and others[4] retained this feature. Recently, Mizutani and Mizoguchi[15] have measured the electronic specific heat of an amorphous $Mg_{70}Zn_{30}$ alloy and found it to be within 2% of the free-electron value. Mizoguchi *et al.*[16] have measured $2k_F$ using positron annihilation and found a value of 2.92 $Å^{-1}$ which is very close to the free-electron value of 2.83 $Å^{-1}$. Recent magnetic susceptibility measurements in this laboratory confirm the free-electron nature of these alloys. Amorphous Mg-Zn alloys would appear to be excellent materials for examining the applicability of the simple Ziman model to amorphous metal alloys.

RESULTS

The alloys were prepared by melt-spinning in a helium atmosphere. The samples were all checked by x-ray diffraction and no sharp lines could be detected. After manufacture the samples were stored in liquid nitrogen until measured. The thermopower measurements were made against lead using the integral technique. After subtracting the integrated thermopower of lead[17] the results were differentiated to obtain the thermopower S of the samples. The thermoelectric potentials were measured using a circuit similar to that developed by Edwards but having the superconducting chopper replaced by a mechanical contact modulator.[18] The results for the thermopower of five amorphous Mg-Zn alloys are shown in Fig. 1 along with the results for a crystallized sample of composition $X = 0.30$. Our previous result of $\sim -1\ \mu V/K$ for the thermopower of an amorphous $Mg_{70}Zn_{30}$ sample is almost certainly wrong due to partial crystallization of that sample at the time of measurement.[11] The resistivity was measured using a four-wire ac technique previously described[20] and the results are shown in Fig. 2 where we have plotted $[R(T)-R(4.2)]/R(4.2)$ as a function of temperature. Carini *et al.*[9] have proposed a relation between the temperature coefficient resistivity $\alpha = (1/\rho)(d\rho/dT)$ and the thermopower which appears to be obeyed by the present alloys as shown in the inset of Fig. 2. The nonlinearity of the temperature dependence of the thermopower of these alloys is small and has been ignored in the following analysis; however, it can be accounted for by the temperature dependence of the structure factor.[19] The resistivity as a function of concentration at 300 K is shown in Fig. 3(b). Our results

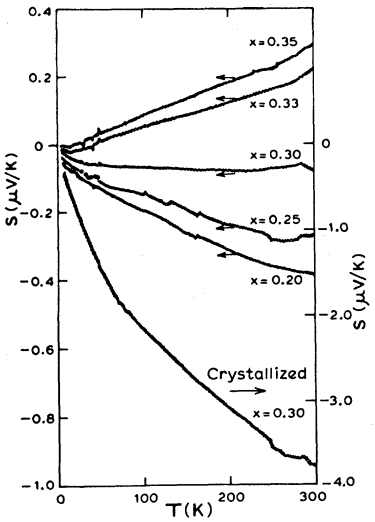

FIG. 1. Thermopower of $Mg_{1-x}Zn_x$. Also shown are the results for a crystallized sample of composition $x=0.30$.

for the temperature dependence of the resistance of $Mg_{70}Zn_{30}$ are similar to those reported elsewhere.[21] However, our value for the resistivity of $Mg_{70}Zn_{30}$ is somewhat lower and compares favorably to that found in the liquid alloy.[22].

DISCUSSION

Mizoguchi *et al.*[16] have measured the interference function $S(Q)$ for amorphous $Mg_{70}Zn_{30}$. This measurement along with the experimental value of $2k_F=2.92$ Å^{-1}, the free-electron nature of the alloys,[15,16] and the known values of orthogonalized-plane-wave (OPW) form factors for Mg and Zn[23] provide sufficient information to estimate the thermopower of the amorphous Mg-Zn alloys using the simplified Ziman theory. The thermopower is given by

$$S=-\frac{\pi^2k^2T}{3\,|e|\,E_F}\xi\,, \tag{1}$$

where k is Boltzmann's constant, T is the temperature in kelvin, $|e|$ is the electronic charge, $E_F=h^2k_F^2/2m$ is the Fermi energy, and ξ is the thermoelectric parameter which in the free-electron case is given by

$$\xi=3-2q-\tfrac{1}{2}r\,, \tag{2}$$

where, using Harrison's notation,[24]

$$q=\frac{4N\,|S(k)|^2\,|\langle k+K\,|\,\omega(k)\,|\,k\rangle|^2_{k=2k_F}}{\int_0^2 N\,|S(K)|^2\,|\langle k+K\,|\,\omega(k)\,|\,k\rangle|^2x^3dx}\,, \tag{3}$$

$x=k/k_F$ and k_F is the Fermi wave vector. The quantity r accounts for possible variation of the OPW form factors with energy and is usually assumed to be small.[2,4] The same model gives the electrical resistivity ρ as

$$\rho=C\int_0^2 N\,|S(k)|^2\,|\langle k+K\,|\,\omega(k)\,|\,k\rangle|^2x^3dx\,, \tag{4}$$

where $N\,|S(k)|^2$ is the experimentally determined interference function $S(Q)$ and

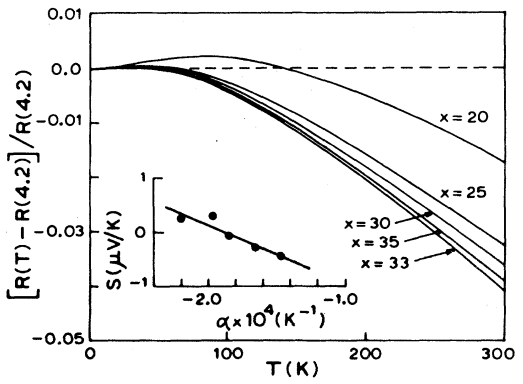

FIG. 2. Relative resistance $[R(T)-R(4.2)]/R(4.2)$ as a function temperature. The inset shows $\alpha=(1/\rho)(d\rho/dT)_{300}$ as a function of S.

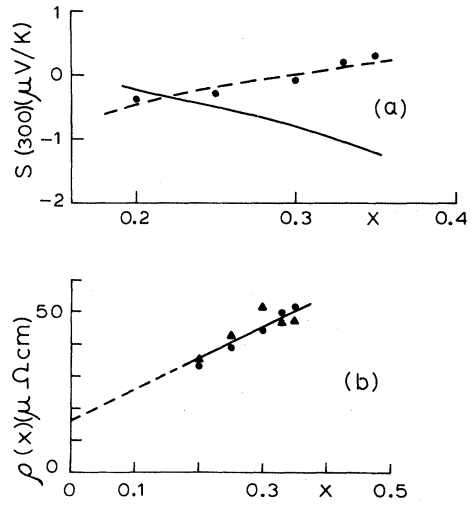

FIG. 3. (a) Thermopower at 300 K: ● measured results; — calculated using the simple Ziman model, - - - calculated using the two-component model. (b) Resistivity at 300 K as a function of composition x; ● calculated from the caliper dimensions, ▲ calculated from density measurements.

$$C=\frac{3\pi m\Omega_0}{8\hbar e^2E_F}\ , \tag{5}$$

where m is the electron mass and Ω_0 is the atomic volume. The denominator in Eq. (3) is given by ρ/C and the value of the OPW form factor $\langle k+K\,|\,\omega(k)\,|\,k\rangle$ at $k=2k_F$ is given as 0.06 for Mg and 0.07 for Zn.[23] The thermopower was calculated using Eqs. (1)–(5) and an average value of the OPW form factor weighted in proportion to the concentration of Mg and Zn in the alloy. For compositions other than $x=0.3$ the value of k_F was scaled in proportion to $\Omega_0^{1/3}$ where Ω_0 is the average atomic volume derived from density measurements. For $x=0.3$ the experimental value $k_F=1.46$ Å^{-1} given in Refs. 15 and 16 was used. The results of the calculation along with the experimental results are shown in Fig. 3(a). The agreement between the simple Ziman model and the measured thermopower is, at best, tenuous even for this most free-electron amorphous metal alloy.

The discrepancy could be explained if r, in Eq. (2), is not negligible. In this case r would have to vary from 0 to ~ -3 as x goes from 0.2 to 0.35, while q only changes from 0.84 to 1.5 over the same composition range. This strong composition variation of r seems unlikely since as yet we have not taken into account that these materials are alloys and should be treated in the manner suggested by Faber and Ziman for liquid-metal alloys.[25] To estimate the thermopower using this theory we require a knowledge of the experimental partial structure factors of the Mg-Zn amorphous alloy system which are not presently available.

A suggestive calculation may, however, be made in which we assume two independent scattering mechanisms which lead in the simplest case, to diffusion thermopowers of the form $S_1=aT$ and $S_2=bT$, where subscripts 1 and 2 refer to the scattering mechanisms. The Nordheim Gorter relation (Ref. 14) gives the measured thermopower of the alloy as

$$S=\frac{\rho_1}{\rho_1+\rho_2}aT+\frac{\rho_2}{\rho_1+\rho_2}bT\ , \tag{6}$$

where ρ_1 and ρ_2 are the resistivities associated with the respective scattering mechanisms. If we further suppose that ρ_1 and ρ_2 vary linearly with the concentration of the Mg and Zn in the alloy, then ρ_1 and ρ_2 can be written as $\rho_1=(1-x)\rho_a$ and $\rho_2=x\rho_b$. The resistivity as a function of composition $\rho(x)$ is then

$$\rho(x)=\rho_1+\rho_2=\rho_a+x(\rho_b-\rho_a)\ . \tag{7}$$

Figure 3(b) shows that the measured resistivity is indeed a linear function of composition in the limited concentration range of the measurements. Results for liquid Mg-Zn alloys[22] also show a linear variation of resistivity with composition for $0<x<0.4$.

The thermopower, Eq. (3), can now be expressed as

$$\frac{S(x)}{T}=\frac{1-x}{\rho(x)}\rho_a(a-b)+b\ . \tag{8}$$

A straight-line fit to a plot of $S(x)/T$ against $(1-x)\rho(x)$ gives values of $a=10.3\times10^{-3}$ μV/K^2 and $b=3.5\times10^{-3}$ μV/K^2. In evaluating a we used $\rho_a=16$ $\mu\Omega$ cm, obtained by extrapolating to $\rho(x)$ to $x=0$ in Fig. 3(b). From the values of a and b the characteristic thermopowers at 300 K are $S_1=-3.1$ μV/K and $S_2=+1.05$ μV/K. Using the above values of a, b, ρ_a, and Eq. (8) the thermopower at 300 K has been calculated as a function of composition and is shown as the dashed line in Fig. 3(a). A remarkably good fit to the data has been obtained with this simple two-component model. The values of the characteristic thermopowers, -3.1 and $+1.05$ μV/K, are not inconsistent with the measured thermopowers of amorphous metal alloys which range between approximately -2 and $+2$ μV/K at 300 K.[6]

The success of the two-component model suggests that the Ziman liquid-metal model as extended by Faber and Ziman[25] to alloys may indeed be applicable to amorphous metal alloys. We are at present completing measurements on a series of amorphous Cu-Zr alloys where the partial structure factors are known and a more detailed calculation of the thermopower can be made.

CONCLUSIONS

We have measured the thermopower and resistivities of a series of amorphous Mg-Zn alloys. The thermopower of these free-electron alloys was calculated using the simple Ziman model as proposed by Sinha.[2] No agreement with the experimental results was obtained. By using a two-component model, which can be considered as an extreme simplification of the Faber-Ziman[25] model for liquid-metal alloys, we were able to obtain an excellent fit to the experimental data over the entire range of available compositions. The success of this model strongly indicates that amorphous metals must be considered as the alloys they are when analyzing their electron transport properties, and that the usual simplification, where average properties only are considered, is an inappropriate oversimplification of the problem.

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