Thermopower and resistivity in amorphous $Cu_{1-x}Zr_x$ alloys

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The thermopower and resistivity of a series of $Cu_{1-x}Zr_x$ alloys have been measured between 2 and 300 K for $0.3 < x < 0.7$. The composition dependence of the results cannot be explained on the basis of the simple Ziman liquid-metal model. Inclusion of partial structure factors in the Faber-Ziman sense considerably improves the agreement with experiment. This improvement is almost entirely due to the "cross" term containing the Cu-Zr partial structure factor and indicates the crucial role played by this term in calculating the thermopower.

INTRODUCTION

Historically the thermopower of amorphous metals has been interpreted for the most part on the basis of the simple Ziman liquid-metal model[1-10] which treats the conduction electrons as free and assumes that average structure factors are sufficient to describe the alloys. In a recent paper[11] we have measured the thermopower of amorphous Mg-Zn alloys as a function of composition. These alloys are almost perfect free-electron materials having both k_F and electronic specific heats within a few percent of the free-electron value.[12,13] Neither Mg nor Zn has a large "d"-like component in the wave functions describing the electrons at the Fermi surface in the crystalline material and we therefore expected that the simple Ziman model would explain the thermopower of amorphous Mg-Zn alloys. To our surprise we found that the simple Ziman model did not fit the thermopower results and concluded that even these very simple materials had to be treated as alloys in the Faber-Ziman[14] sense. Unfortunately a complete Faber-Ziman treatment requires a knowledge of the partial structure factors for the individual constituents of the alloy and these have not yet been reported for Mg-Zn. We developed a simple two-component model which can be considered as an extreme simplification of the Faber-Ziman model and showed that a satisfactory fit to the experimental results could be obtained. In order to more fully explore the applicability of the Faber-Ziman model to amorphous-metal alloys we have made measurements on the Cu-Zr system where three sets of partial structure factors have been reported. Two sets were obtained from x-ray measurements[15,16] while the third was obtained from neutron diffraction experiments.[17] In this paper we will compare the measured thermopower of amorphous $Cu_{1-x}Zr_x$ alloys with the thermopower calculated from the simple Ziman theory and with that calculated by the Faber-Ziman theory for all the sets of partial structure factors. We will also show that our simple two-component model correlates the resistivity and thermopower in the composition range where it is expected to apply.

EXPERIMENTS

The thermopower and resistivity were measured using apparatus and techniques previously described.[11,18] The alloys were prepared by melt-spinning in an inert atmosphere. After preparation x-ray diffraction showed no crystalline component present in the alloys. As a further precaution all samples were kept in liquid nitrogen until used. Details of the sample preparation, structure, and stability have been published elsewhere.[19]

The results of the thermopower measurements are shown in Fig. 1 and the relative resistance of these samples is shown in Fig. 2. The composition dependence of the resistivity ρ, its temperature derivative $\partial\rho/\partial T$, and the thermopower S all measured at 300 K are shown in Fig. 3. The thermopower data were obtained from a linear regression performed on the results shown in Fig. 1 for values of T greater than 80 K. The resistivity values were calculated from the measured resistance, length, density, and mass. The densities were measured by Archimedes's method with the use of toluene.
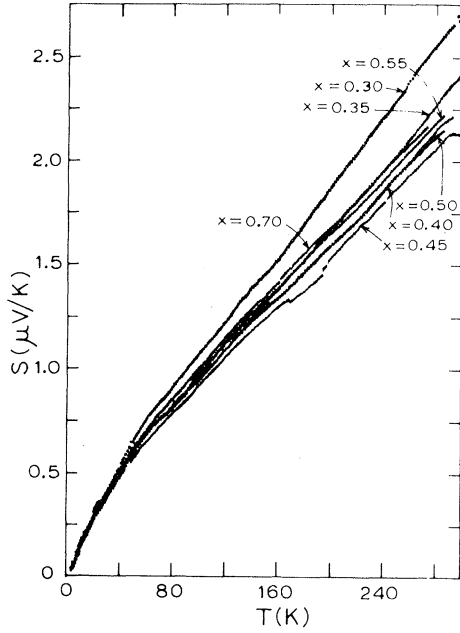
FIG. 1. Thermopower of $Cu_{1-x}Zr_x$ alloys as a function of temperature.

FIG. 3. Thermopower S, resistivity ρ, and the temperature derivative of the resistivity $\partial\rho/\partial T$ all at 300 K as a function of composition x. ∇ are the data of Ref. 9, $\triangle$ is data of Ref. 8.

DISCUSSION

The pronounced break which occurs in the temperature dependence of the thermopower at ~ 50 K is characteristic of many nonmagnetic amorphous alloys and as yet has not been satisfactorily explained although some interesting speculations have been put forward.[9,20] We are reserving a discussion of this temperature dependence to a future paper and for the present will limit ourselves to consideration of the composition dependence of the thermopower of $Cu_{1-x}Zr_x$ alloys.

The most striking aspect of the experimental results is the almost composition-independent value of

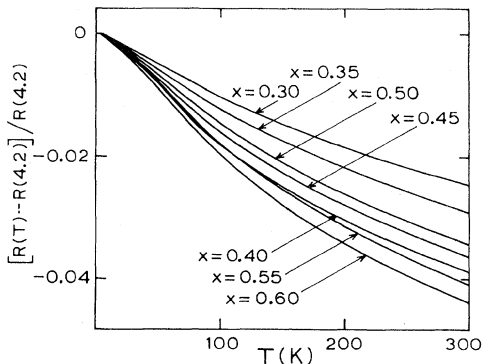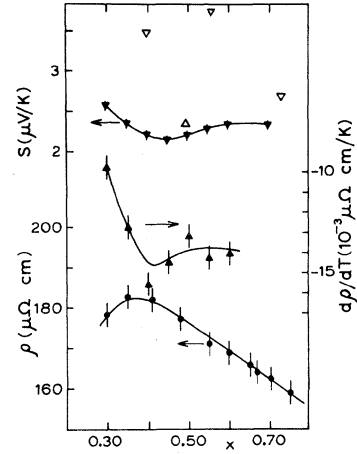the thermopower in these alloys. The value changes by less than 10% for Zr concentration ranging between 35 and 70 at. %. This is at least in part a consequence of the fact that the Fermi energy E_F is essentially independent of composition varying by no more than 2% over the entire measured range of alloy compositions. Before undertaking a complete Faber-Ziman analysis of the data we will calculate the thermopower on the basis of the simple Ziman model. In this case the thermopower S is given by[21]

$$S = -\frac{\pi^2 k^2 T}{3|e|E_F}(3 - 2q - \tfrac{1}{2}r) , \qquad (1)$$

where k is Boltzman's constant, T is the absolute temperature, and e is the electronic charge. The quantities q and r are given by

$$q = \frac{|U(2k_F)|^2 a(2k_F)}{\langle |U(K)|^2 a(K)\rangle} \qquad (2)$$

and

$$r = \frac{k_F\langle[\partial|U(K)|_v/\partial k]a(K)\rangle}{\langle|U(K)|^2 a(K)\rangle} , \qquad (3)$$

where $U(K)$ is an appropriate pseudopotential and $a(K)$ is the average structure factor of the material. The angle brackets indicate an average of the form

$$\langle f(q)\rangle = \int_0^1 d\left[\frac{q}{2k_F}\right]4f(q)\left[\frac{q}{2k_F}\right]^3 .$$

The same model gives the resistivity as

$$\rho = \frac{3\pi\Omega_0}{he^2 V_F^2}\langle|U(K)|^2 a(K)|\rangle , \qquad (4)$$

FIG. 2. Relative resistance as a function of temperature for the alloys of Fig. 1.

where V_F is the Fermi velocity and

$$\Omega_0 = \frac{(1-x)M_{Cu} + xM_{Zr}}{0.602d} \quad (5)$$

is the atomic volume in A^3. The quantities M_{Cu} and M_{Zr} are the atomic weights of Cu and Zr and d is the density of the alloy in g/cm^3. The Fermi energy $E_F = h^2 k_F^2/2m$ is determined from the Fermi wave vector k_F which is given by

$$k_F = \left[\frac{3\pi^2 Z}{\Omega_0} \right]^{1/2} \quad \text{with } Z = (1-x)Z_{Cu} + xZ_{Zr} , \quad (6)$$

where Z_{Cu} and Z_{Zr} are the valences of Cu and Zr, respectively. The value of q can be determined using Eq. (2). The denominator is obtained from the measured resistivity using Eq. (4) while the numerator is obtained from the measured structure factor $a(2K_F)$ and a suitable pseudopotential $U(2k_F)$.

A straightforward application of this method to Cu-Zr alloys presents some difficulties because it is known from heat capacity,[22] thermal conductivity,[23] and magnetic susceptibility measurements[19] that these alloys depart considerably from the free-electron model. Photoemission studies[24] show that the "d" band of Zr dominates the density of states at E_F in these alloys and this large density of states undoubtedly accounts for the composition independence of E_F in Cu-Zr. Since the valence state of Zr is $4d^2, 5s^2$ and as a general rule "d" electrons are not very mobile we assume that Zr contributes two electrons and Cu one electron to the conduction band of amorphous Cu-Zr.

The thermopower may now be calculated as outlined using Eqs. (1) to (6), the measured structure factors[15] and suitable pseudopotentials. While a pseudopotential for Cu is available in the literature[25] one for Zr with valence 2 is not. We therefore use the phase shifts derived by Waseda and Chen[16] for amorphous Cu-Zr alloys, where Zr was assumed by them to have valence 2. We then use the formalism of Dreirach et al.[26] to calculate the t-matrix equivalent of the required pseudopotential. For Cu we find $U_{Cu} = |t_{Cu}| = |2.62 - i0.319| = 2.64$ eV which compares favorably with the value of ~ 2.6 eV found in the literature.[25] For Zr we find $U_{Zr} = |t_{Zr}| = |-3.32 - i2.00| = 3.87$ eV. The thermopower calculated using the simple Ziman model, assuming r in Eq. (1) is negligible, is shown in Fig. 4 for the three compositions for which the
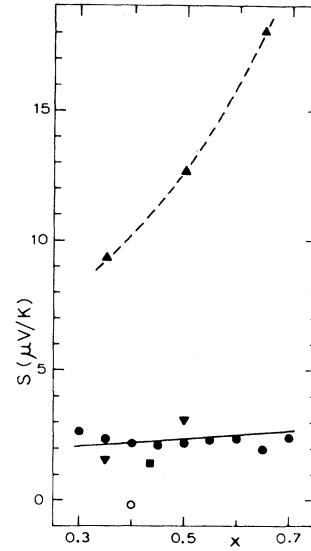

FIG. 4. Calculated and measured thermopower S as a function of composition x. ● Measured thermopower; ▲ thermopower calculated using the simple Ziman model and the total structure factors of Ref. 15; ▼ thermopower calculated using the Faber-Ziman theory and the x-ray partial structure factors of Ref. 15; ○ thermopower calculated using the Faber-Ziman theory and the neutron partial structure factors of Ref. 17; ■ thermopower calculated using the Faber-Ziman theory and the x-ray partial structure factors of Ref. 16; —— thermopower calculated using the two-component model as discussed in the text.

structure factor has been measured.[15] For comparison the measured thermopower is also shown. The best that can be said is that the simple Ziman model predicts the correct sign for the thermopower of amorphous Cu-Zr alloys. On the basis of the simple Ziman model Carini[8] et al. have proposed that the thermopower should be proportional to the temperature coefficient of resistivity $\alpha = (1/\rho)(\partial\rho/\partial T)$. Figure 5 shows a plot of S against α. We see that the proposed relation is not obeyed.

With the failure of the simple Ziman model to describe the thermopower of amorphous CuZr we have calculated the thermopower on the basis of the Faber-Ziman model[14] for the available partial structure factors.[15-17] This is easily done[26] by replacing $|U(K)|^2 a(K)$ by $\overline{T}$ in Eqs. (2) and (4), where

$$\overline{T} = |t_{Cu}|^2 [x(1-x) + (1-x)^2 a_{CuCu}(k)] + |t_{Zr}|^2 [x(1-x) + x^2 a_{ZrZr}(K)]$$

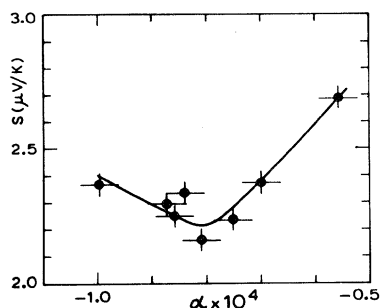$$+ x(1-x)(t_{Cu}^* t_{Zr} + t_{Cu} t_{Zr}^*)(a_{CuZr}(K) - 1) \quad (7)$$

FIG. 5. Thermopower S at 300 K as a function of $\alpha=(1/\rho)\partial\rho/\partial T$ at 300 K illustrating the breakdown of the relation suggested in Ref. 8.

and $a_{CuCu}(K)a_{ZrZr}(K)$ and $a_{CuZr}(K)$ are the measured partial structure factors.[15-17] The results of this calculation, where again we neglect r, are also shown in Fig. 5. While the agreement is not outstanding the improvement over the simple Ziman model is indisputable. In particular we note that the term containing the Cu-Zr partial structure factor is negative and plays an important role in improving the agreement between the calculated and measured thermopowers. The large scatter present in the calculated thermopowers using the Faber-Ziman theory prevents us from making any detailed comments on the r term in Eq. (1) which accounts for the possible energy dependence of the pseudopotentials. We note, however, that r values ranging between -1.85 and 4.62 are sufficient to ensure agreement between theory and experiment in all cases. These values are similar to those found for liquid-metal alloys.

In our paper[11] on amorphous Mg-Zn alloys we developed a simple two-component model based on the Nordheim Gorter relation, for correlating the thermopower and resistivity when the resistivity is a linear function of composition. This model predicts that the composition dependence of the thermopower $S(x)$ is

$$S(x)=(1-x)\frac{\rho_a}{\rho(x)}(a-b)T+bT , \qquad (8)$$

where

$$\rho(x)=\rho_a+x(\rho_b-\rho_a) \qquad (9)$$

and ρ_a and ρ_b are the values of the resistivity obtained by extrapolating the linear region to $x=0$ and $x=1$, respectively. The quantities a and b related to the characteristic diffusion thermopowers

$S_a=aT$ and $S_b=bT$ corresponding to ρ_a and ρ_b. The results of fitting Eq. (8) to the thermopower data are shown in Fig. 4. The values obtained in the fitting procedure are $S_a=1.72$ μV/K and $S_b=2.61$ μV/K at 300 K.

CONCLUSIONS

We have measured the thermopower and resistivity of a series of $Cu_{1-x}Zr_x$ amorphous alloys over the composition range $0.3<x<0.7$. We find that the simple Ziman model is totally inadequate to describe the thermopower of these alloys. Considerable improvement between calculation and experiment, is obtained when the Faber-Ziman model is used to calculate the thermopower of the alloys. An important contribution to this improvement comes from the term containing the Cu-Zr partial structure factor. This term can be and is negative for Cu-Zr and thus plays a crucial role in calculating the thermopower. Unfortunately the discrepancy between the various published partial structure factors does not allow us to draw any conclusions about the importance of the energy dependence of the pseudopotential [r term in Eq. (1)] in calculating the thermopower. We note that the model we developed in Ref. 2 which correlates the resistivity and the thermopower, when the resistivity is a linear function of x, works for Cu-Zr alloys. Finally we suggest that further progress in the understanding and correlation of the thermopower and resistivity in amorphous alloys can be made either by a complete and detailed partial structure factor analysis of the alloys in which thermopower and resistivity are measured or by a suitable extension of our simple model to include the important cross term which arises in the Faber-Ziman analysis. A severe test of such a model would be an alloy system in which the thermopower changes sign as a function of composition. We speculate that Ni-Zr alloys might be suitable since the thermopower of liquid Zr is positive and that of liquid Ni is negative. Accordingly, measurements on amorphous Ni-Zr alloys have been undertaken.

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