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Thermoelectric power of Ni-Zr metal glasses

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We have measured the thermopower of Ni-Zr metallic glasses over the range of composition from $Ni_{70}Zr_{30}$ to $Ni_{25}Zr_{75}$. In contrast to the other simple nonmagnetic metallic glasses, Mg-Zn and Cu-Zr, the thermopower is a strong function of composition and changes sign at the Ni-rich end. The results are shown to be consistent with the Faber-Ziman model for liquid metals.

INTRODUCTION

The gross features of electron transport in amorphous- and liquid-metal alloys have much in common and for this reason the Ziman model,[1] originally developed for liquid metals, is often used to interpret results in amorphous metals. In liquid-metal *alloys,* where extensive experimental evidence has been accumulated, it has been found necessary to extend the original model to take account of the different way in which the various constituents contribute to the transport properties. Usually this is done through partial structure factors and individual t matrices or, in the case of weak scattering, pseudopotentials. This approach is often called the Faber-Ziman theory.[2]

In amorphous alloys, on the other hand, the available data are much more sketchy, especially with regard to composition dependence within one alloy system, and results, particularly on thermopower,[3] have been generally interpreted on the basis of the simpler Ziman model using an average structure factor and treating the conduction electrons as free. Some recent work, however, on Mg-Zn (Ref. 4) and Cu-Zr (Ref. 5), which presented both thermopower and resistivity over an extensive range of concentration, has shown this to be too simple an approach. Even in Mg-Zn, where one would suppose the conduction-electron wave functions at the Fermi-energy to have simple s-p symmetry, the thermopower could not be satisfactorily explained using the simple Ziman model. The Faber-Ziman theory gave, as one would expect, a much better description of the data, but neither Mg-Zn nor Cu-Zr provided a very strong test since the actual variation of both thermopower and resistivity with concentration was quite small. From this viewpoint Ni-Zr is a much better system to examine since, as we shall see, the thermopower changes sign as the Ni-rich end is approached. Thus a very strong concentration dependence of the thermopower occurs and it has been the purpose of the present study to see how this may be described first by the simple Ziman theory and then by the Faber-Ziman theory.

EXPERIMENTAL METHODS AND RESULTS

The alloys were prepared by melt spinning under helium atmosphere, as described previously.[6] Sam-

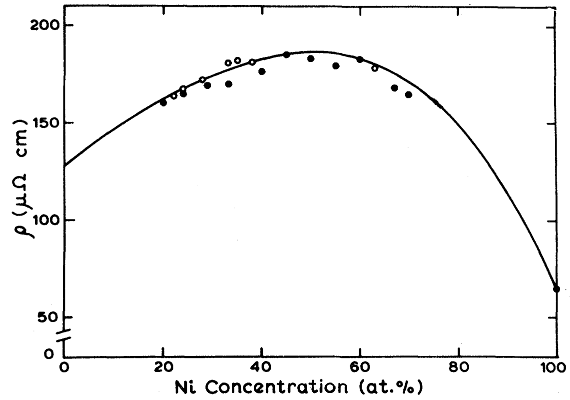

FIG. 1. Electrical resistivity of Ni-Zr metallic glasses at room temperature as a function of composition. The present work is given by solid circles.

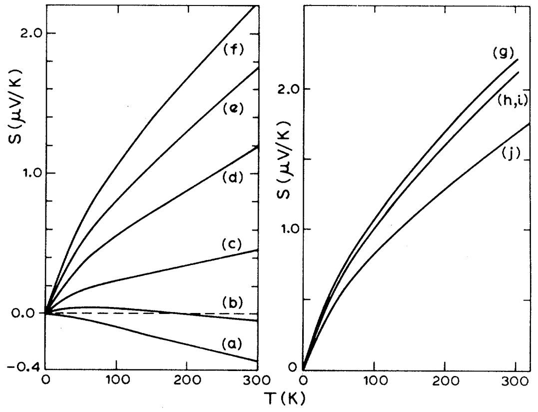

FIG. 2. Temperature dependence of the thermoelectric power of Ni-Zr metallic glasses. (a) $Ni_{70}Zr_{30}$; (b) $Ni_{68.7}Zr_{31.3}$; (c) $Ni_{65}Zr_{35}$; (d) $Ni_{63}Zr_{37}$: (e) $Ni_{60}Zr_{40}$: (f) $Ni_{50}Zr_{50}$; (g) $Ni_{40}Zr_{60}$; (h) $Ni_{33}Zr_{67}$; (i) $Ni_{29}Zr_{71}$; (j) $Ni_{25}Zr_{75}$.

ples were stored under liquid nitrogen immediately after manufacture. Electrical resistance was measured on long (up to 1 m) sections of ribbons using a simple two-terminal technique and a digital voltmeter. Using measured length and density, resistance was converted to resistivity to within an estimated 1% accuracy. Thermopower was measured using the method described in Ref. 4. Experimental results are shown in Figs. 1—3. The resistivity data in Fig. 1 include data obtained from the results of other investigators for the purpose of comparison.[7] Figure 2 shows the temperature dependence of the thermopower, separated into two parts for clarity. Uncertainty in the data varies from approximately the thickness in the line at 4.2 K to about ±0.05 μV/K at room temperature. The characteristic feature of the thermopower is a linear variation at high temperature with a "knee" at about 50 K. Figure 3 shows the room-temperature thermopower as a function of composition, together with the temperature coefficient of resistivity $\alpha = d(\ln\rho)/dT$. Thermopower data of other investigators is included for comparison.[8] Our values of α are almost always more negative than those previously reported.[7] Since values for α in the *crystalline* phase are positive and of much larger magnitude, quenched-in crystallites amounting to only ~2% of the sample are sufficient to account for the discrepancy. In fact the measured α is, in principle, only an upper bound.

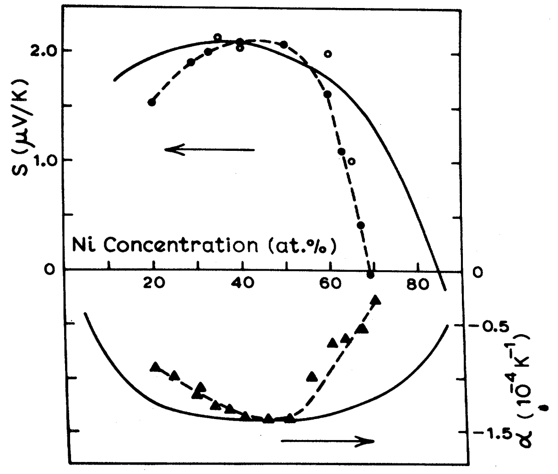

FIG. 3. Room-temperature thermopower S and the temperature coefficient of resistivity $\alpha = (1/\rho)(d\rho/dT)$ as a function of composition in Ni-Zr metallic glasses. The present data are given by the solid circles and triangles, respectively.

DISCUSSION

In its most general form for liquid or amorphous alloys the Faber-Ziman theory can be shown[2] to give a resistivity of the form

$$\rho = \frac{1}{4k_F^4}\frac{3\pi\Omega_0}{\hbar e^2 V_F^2}\{c_1\langle |t_1|^2 a_{11}\rangle + c_2\langle |t_2|^2 a_{22}\rangle + c_1 c_2[\langle |t_1|^2(1-a_{11})\rangle + \langle |t_2|^2(1-a_{22})\rangle + \langle (t_1 t_2^* + t_1^* t_2)(a_{12}-1)\rangle]\}\ , \quad (1)$$

where Ω_0 is the average atomic volume, t_i is the single-site matrix for elastic scattering off atom type i, and the a's are the various partial structure factors. c_1 and c_2 are the concentrations of the two constituents and the other parameters take their usual meaning. The average $\langle f(K)\rangle$ means

$$\langle f(K)\rangle = \int_0^{2k_F} f(K)K^3\,dK\ . \quad (2)$$

The thermopower S may now be found from (1) using the well-known Mott expression

$$S(T) = \frac{\pi^2 k_B^2 T}{3|e|}\left.\frac{\partial \ln\rho}{\partial E}\right|_{E_F} = \frac{-\pi^2 k_B^2 T}{3|e|E_F}\xi\ . \quad (3)$$

The thermoelectric power parameter ξ is often written in the form

$$\xi=(3-2q-\tfrac{1}{2}r)\ , \qquad (4)$$

where q reflects the values of the integrands in Eq. (1) at $K=2k_F$ and r their derivatives with energy. Direct application of (1)–(4) is very difficult in most cases since neither the t matrices nor the partial structure factors are generally available with sufficient accuracy to allow meaningful calculations to be made. One way around this difficulty is to reduce the expression (1) back to the original Ziman form by writing

$$\rho=\frac{3\pi\Omega_0}{\hbar e^2V_F^2}\,\frac{1}{4k_F^4}\langle\,|t|^2a\rangle \qquad (5)$$

so that q and r become

$$q=\frac{|t(2k_F,E_F)|^2a(2k_F)}{\langle\,|t|^2a\rangle}\ ,$$
$$r=\left\langle a\left|k_F\frac{\partial}{\partial k}|t|^2\right|\right\rangle\Big/\langle\,|t|^2a\rangle\ . \qquad (6)$$

t and a are suitably averaged over composition and are, of course, composition dependent. If one ignores the r term, then (4) and (5) have been argued[9] to give a simple qualitative correlation between S and the temperature coefficient of resistivity $\alpha=d\ln\rho/dT$. The argument runs as follows: The largest positive value of S occurs for the largest value of q which in turn should occur when $2k_F$ lies around the peak K_p of $a(K)$. This condition also produces the greatest negative value of α. Reference to Fig. 3 shows that this simple prediction is remarkably well obeyed, even to the detail of S and α approaching a sign change at much the same composition. Under closer examination however the correlation is less impressive. Structure factor data[10] suggest that the condition $2k_F=K_p$ cannot be satisfied.[11] Also the t matrices for Ni (Ref. 12) and Zr (Ref. 13) are believed to be very different, giving a concentration dependence to the average t matrix, in addition to the concentration dependence of the average structure factor. Finally one would expect r for Ni-Zr, with its open d bands, to be large and again strongly concentration dependent. We can illustrate how important r is by calculating q starting with the full expression (1), using the partial structure factors given by Waseda and Chen[10] for $Ni_{30}Zr_{70}$ and the t matrices for Zr (Ref. 13) and Ni (Ref. 12). The result gives a contribution to the thermopower at 300 K of 7.1 μV/K. Since the actual thermopower is only 2.0 μV/K this calculation suggests that r is at least as large as q and so cannot be ignored. Perhaps the real challenge with the correlation in Fig. 3 is to explain why it works so well.

An alternate way around the problems of applying Eqs. (1)–(4) is to limit oneself to reproducing only the concentration dependence of ρ, α, and S. Equation (1) may be written as

$$\rho=c_1\rho_1+c_2\rho_2+c_1c_2\rho_3 \qquad (7)$$

which allows us to cast S in the form

$$S=\frac{\pi^2k_B^2T}{3|e|}\left[\sum_{i=1}^{3}c_i\frac{\partial\rho_i}{\partial E}\bigg|_{E_F}\Big/\sum_{i=1}^{3}c_i\rho_i\right]\ , \qquad (8)$$

with c_3 being written for c_1c_2. Equation (8) may in fact be thought of as a generalization of the Nordheim-Gorter relation. In spite of their apparent simplicity, (7) and (8) still prove difficult to apply since, in general, both k_F and E_F change with composition and in consequence the range over which the averages are taken changes also. Thus no single set of values can be taken for ρ_i and $(\partial\rho_i/\partial E)\,|_{E_F}$, which must be left as fitting parameters at each composition. However, in Ni-Zr the ratio Z/Ω_0 is almost the same for both constituents so that k_F and E_F should be essentially constant over the concentration range. Thus, as all averages are now taken over the same range of k, ρ_i changes only with Ω_0 and the variation of ρ is basically quadratic with composition with a small modification caused by the concentration dependence of Ω_0. In practice, as we shall see, this leads to large changes in S near the pure constituent extremes with small changes between. To actually fit Eq. (7) to the data we used the following procedure: ρ_1 was taken from liquid-Ni data[14] by extrapolating the measured ρ to 300 K using the measured α. Unfortunately the same procedure cannot be applied to ρ_2 since no data is available for liquid Zr. Consequently, ρ_2 and ρ_3 were determined by fitting the data at two points. All ρ_i's were scaled by the appropriate atomic volume. The solid line in Fig. 1 shows the resultant variation for ρ, which is in good agreement with the data. The value predicted for the resistivity of amorphous Zr is 120 $\mu\Omega$ cm which compares with a value of 235 $\mu\Omega$ cm predicted theoretically for liquid Zr.[15] However such theoretical predictions are typically only within a factor 2 of experimental results, so we consider our value for ρ_2 to be quite satisfactory.

Although the fit for ρ is good, the significance of this is restricted by the fact that the data only cover the insensitive region of concentration. A much better test is provided by S, which changes sign. Equation (8) is used to fit S in exactly the same way as Eq. (7) was used to fit ρ. The values of ρ_i are now known, of course, which leaves only the three parameters $(\partial\rho_i/\partial E)\,|_{E_F}$ or their equivalents,

$$\xi_i=-\frac{\partial\ln\rho_i}{\partial\ln E}\bigg|_{E_F}\ ,$$

to be determined, ξ_1 comes from liquid Ni (Ref. 14) scaled to 300 K and ξ_2, ξ_3 are chosen for best fit. The result is shown in Fig. 3, where the solid line used the parameters $\xi_1=6.5$, $\xi_2=1.4$, and $\xi_3=5.0$. For convenience of scale we have left off the scaled liquid Ni end point of -7.0 μV/K. Inclusion of that datum would place deviations between experiment and theory in proper perspective and would emphasize that the Faber-Ziman theory reproduces the observed maximum in thermopower and the sharp decrease at the Ni-rich end. This behavior derives from a change in the balance between competing contributions to the thermopower and is not associated with the position of $2k_F$ with respect to the average structure factor. So far as the values of the ξ_i are concerned, all are well within the ranges observed for liquid metals. The lack of data for pure Zr once again prevents any conclusion being drawn from ξ_2; we simply note that our fitted value of the thermopower has the same sign as that calculated by Hirata *et al.*[15] Also shown in Fig. 3 is our fit to α, made once again in the same way using Ni as a fixed point. As with S, the fit reproduces the essential features of the data.

One final point concerns the temperature dependence of S. The knee at 50 K *could* be caused by temperature dependences in q and r. An alternative suggestion by Gallagher[16] relates the change of slope to the electron-phonon coupling parameter λ which appears in the McMillan equation for superconductivity. We intend to return to this point in a later study, and will simply comment here that we have not so far been able to obtain quantitative agreement with this idea.

In conclusion, we find that the Faber-Ziman model gives a good account of the resistivity, its temperature dependence, and the thermopower in glassy Ni-Zr. We believe that the discrepancies are not significant and are well within the errors introduced by the simplifying assumptions made in applying the model.

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[11] Frequently correlations are given between the position $K_p=(4\pi\sin\theta/\lambda)$ of the principal peak in the x-ray diffraction intensity pattern $I(K)$ and the position of $2k_F$. The proper way to determine K_p is from the position of the peak in the structure sensitive part $a(K)$ which is obtained from the experimental $I(K)$ by well established procedures [B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, New York, 1969)]. For $Ni_{30}Zr_{70}$, one obtains a value of 2.56 Å^{-1} for K_p from $I(K)$, whereas $a(K)$ gives a value of 2.88 Å^{-1} (Ref. 10). The subsequent partial structure factor analysis showed that the peaks of the three partial structure factors were located at 2.61, 2.88 Å^{-1}, and 2.98 Å^{-1} for the Zr-Zr, Ni-Zr, and Ni-Ni pairs, respectively. It appears that, based on the data of Ref. 10, when measuring K_p directly from $I(K)$ one obtains K_p for $a_{\text{Zr-Zr}}(K)$. Thus, published data on correlations between K_p and $2k_F$ for Ni-Zr [K.H.J. Buschow and N. M. Beekmans, Phys. Rev. B 19, 3843 (1979); Y. D. Dong, G. Gregan, and N. G. Scott, J. Non-Cryst. Solids 43, 403 (1981)] are in fact between K_p(Zr-Zr) and $2k_F$ and, therefore, not very significant.

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