

Thermoelectric power of Fe-Zr and Co-Zr metallic glasses

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The thermopower of $\text{Fe}_{1-x}\text{Zr}_x$ ($0.57 < x < 0.76$ and $0.07 < x < 0.12$) and $\text{Co}_{1-x}\text{Zr}_x$ ($0.48 < x < 0.80$ and $0.07 < x < 0.12$) metallic glasses has been measured from 4 to 300 K. Compositions near the critical composition for ferromagnetism are found to have thermopowers which are very nonlinear in temperature. The nonlinearities are tied to the presence of spin fluctuations in these alloys. However, the form of the spin-fluctuation thermopower observed in Fe-Zr and Co-Zr glasses is significantly different from that previously observed in crystalline materials.

INTRODUCTION

Recent experimental measurements of the thermoelectric power of nonmagnetic glasses¹⁻⁴ have been discussed in terms of the Faber-Ziman theory for liquid-metal alloys. Qualitatively, this theory accounts quite well for the compositional behavior of the glassy alloys. It also predicts thermoelectric powers that are linear in temperature. The small nonlinearities observed in the temperature dependence of the nonmagnetic alloys have been explained either by the temperature dependence of the calculated structure factors⁵ or by electron mass enhancement due to phonons.⁶ The thermoelectric power of the magnetic alloys such as Fe-B exhibit strong composition and temperature dependences which cannot be explained within the framework of the Faber-Ziman model. Recent papers have shown that extrema in the temperature dependence of the thermoelectric power in these materials scale with their Curie temperatures.^{7,8} This strongly suggests that the dramatic compositional and temperature dependencies of the magnetic alloys are associated with their magnetism. In order to experimentally determine the effect of magnetism on the thermoelectric power, we have made measurements on a series of Fe-Zr (Ref. 9) and Co-Zr metal glasses. These alloys are nonmagnetic for high Zr concentration and magnetic for high Fe and Co concentrations. In addition, for Fe-Zr, the onset of magnetism occurs roughly at the composition $\text{Fe}_{37}\text{Zr}_{63}$, which is well within the continuous range of compositions over which glassy alloys can be made.¹⁰ The Fe-Zr system thus offers a unique opportunity to study the effect of magnetism on the thermoelectric power of metallic glasses.

EXPERIMENTAL METHODS

Amorphous samples of Fe-Zr were prepared by melt spinning in an inert atmosphere with Zr concentrations ranging from 57 to 76 at. % Zr and from 7 to 12 at. % Zr. All the alloys with Zr concentration less than 63 at. % are ferromagnetic. The Co-Zr system also has two composition windows in which amorphous samples can be prepared. The first, having Zr concentrations from 48 to 80 at. %, is paramagnetic and the second, with Zr concentrations from 7 to 12 at. %, is ferromagnetic. The sam-

ples were prepared by melt spinning on a copper wheel and were characterized by differential scanning calorimetry and x-ray diffraction. Details of the samples and their preparation are given in Ref. 10. The thermoelectric powers were measured against lead using a previously described integral method.¹

RESULTS AND DISCUSSION

The thermoelectric powers of Fe-Zr and Co-Zr are shown in Figs. 1 and 2, respectively. Uncertainty in the

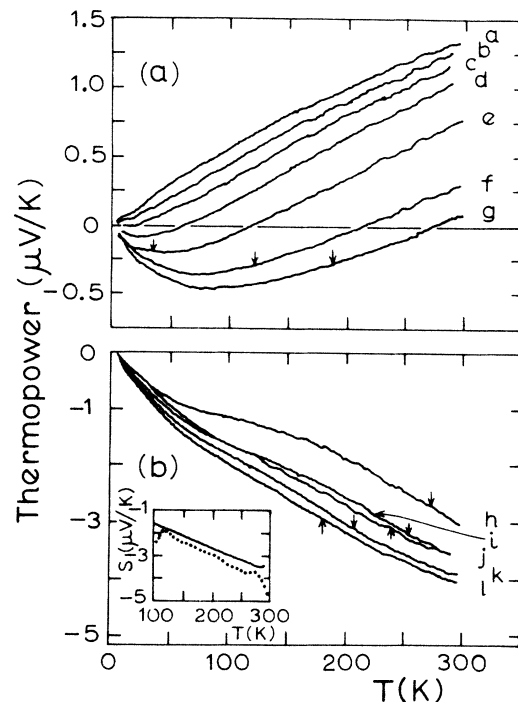


FIG. 1. Absolute thermoelectric power of Fe-Zr alloys. (a) Alloys with Zr atomic fraction from 0.57 to 0.76. (b) Alloys with Zr atomic fraction from 0.07 to 0.12. The arrows indicate the Curie temperatures of the magnetic alloys. The inset compares our data (solid line) with those of Bhatnagar *et al.* (dashed line) for $\text{Fe}_{90}\text{Zr}_{10}$. The letters correspond to the following atomic fraction of Zr: a, 0.76; b, 0.71; c, 0.67; d, 0.65; e, 0.63; f, 0.60; g, 0.57; h, 0.12; i, 0.11; j, 0.10; k, 0.08; and l, 0.07.

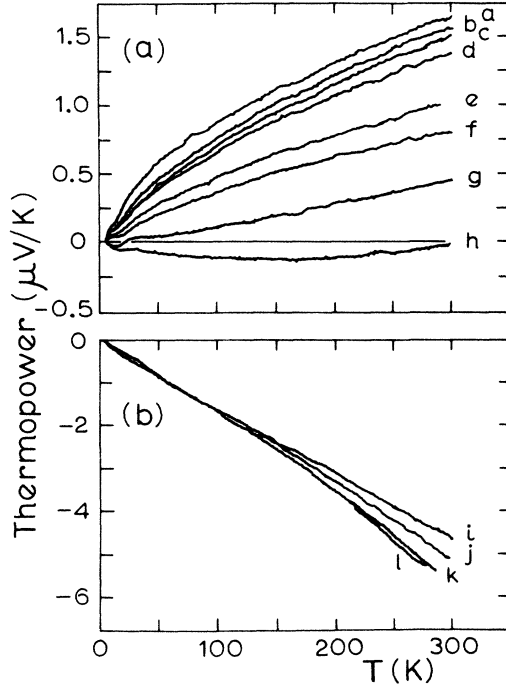


FIG. 2. Absolute thermoelectric power of Co-Zr alloys. (a) Nonmagnetic alloys with Zr atomic fraction from 0.48 to 0.80. (b) Magnetic alloys with Zr atomic fraction from 0.07 to 0.12. The Curie temperatures all lie above 300 K. The letters correspond to the following atomic fraction of Zr: a, 0.75; b, 0.67; c, 0.80; d, 0.60; e, 0.55; f, 0.53; g, 0.50; h, 0.50; i, 0.12; j, 0.10; k, 0.08; and l, 0.07.

measurements range from the thickness of the lines at 4.2 K to not more than $\pm 0.05 \mu\text{V/K}$ at 300 K. The inset in Fig. 1(b) compares our data for $\text{Fe}_{90}\text{Zr}_{10}$ with those of Bhatnagar *et al.*,¹¹ who used the copper thermoelectric power data of Cusack and Kendall¹² to obtain their value of the absolute thermoelectric power of $\text{Fe}_{90}\text{Zr}_{10}$. According to Roberts,¹³ this copper thermoelectric power is as much as $0.3 \mu\text{V/K}$ too negative. After making this correction our data and those of Bhatnagar are in good agreement from 120 to 300 K. We cannot explain the difference in the results below 120 K.

The Curie temperature¹⁰ for the ferromagnetic Fe-Zr alloys fall within the range of our thermoelectric power measurements and are shown by small arrows in Fig. 1. The Curie temperatures for the Co-Zr system lie above the crystallization temperature for the alloys.¹⁴ Conspicuously absent from the Fe-Zr thermoelectric power data, and from other thermoelectric power data on amorphous alloys,^{7,8,15} are the sharp changes of slope at $T = T_C$ which are seen in crystalline ferromagnets¹⁶ and usually attributed to the onset of spin disorder scattering. This is probably not very surprising for the following reason. The total thermoelectric power S can be written approximately in terms of the characteristic thermoelectric power S_i associated with the i th scattering mechanism as

$$S = \sum_i (\rho_i / \rho_T) S_i,$$

where ρ_i is the resistivity associated with the i th scatter-

ing mechanism and ρ_T is the total resistivity.¹⁷ In particular,

$$\frac{dS}{dT} = \frac{S_C}{\rho_T} \frac{d\rho_C}{dT} + \frac{\rho_C}{\rho_T} \frac{dS_C}{dT} + \frac{S_0}{\rho_T} \frac{d\rho_0}{dT} + \frac{\rho_0}{\rho_T} \frac{dS_0}{dT},$$

where ρ_C and S_C are the resistivity and thermoelectric powers associated with disordering as the temperature passes through the critical point at the Curie temperature. ρ_0 and S_0 are the resistivity and thermoelectric power associated with all other scattering mechanisms and are assumed to vary slowly if at all with temperature in the vicinity of the Curie temperature. The change in slope of the thermoelectric power at the Curie temperature is then

$$\frac{dS}{dT} = S_C \frac{1}{\rho_T} \frac{\partial \rho_C}{\partial T} + \frac{\rho_C}{\rho_T} \frac{\partial S_C}{\partial T}.$$

Using the data in Ref. 18 for Fe-Zr, we estimate $(1/\rho_T)(\partial \rho_C / \partial T) \sim 10^{-6} \text{ K}^{-1}$ and $\rho_C / \rho_T = 10^{-4}$. From the present data a change in $|dS/dT| = 10^{-3} \mu\text{V/K}^2$ at T_C would be just observable as would a change in $|S|$ of $0.02 \mu\text{V/K}$. If this change in S were attributed to a change in S_C , then the minimum change in $|\partial S_C / \partial T|$, which would just produce an observable change in the slope of the thermoelectric power at T_C , is estimated to be $\sim 10 \mu\text{V/K}^2$. This is 2–3 orders of magnitude greater than the observed change in slope for crystalline materials.¹⁶ The dominance of the structural disorder scattering prevents the observation of any additional scattering effects that might occur at the Curie temperature.

Recent resistivity measurements have shown that spin fluctuations play an important role in the resistivity of glassy Fe-Zr alloys.¹⁸ Accordingly, we have analyzed the thermoelectric power data for evidence of spin fluctuations. Since different sources of thermoelectric power are additive,¹⁹ the total thermoelectric power S of a material with spin fluctuations is

$$S = S_n + S_f,$$

where S_f is the component of the thermoelectric power due to spin fluctuations and S_n is the thermoelectric power the material would have in the absence of spin fluctuations. We assume that spin fluctuations are unimportant in materials with high Zr concentrations and consider that the $\text{Fe}_{24}\text{Zr}_{76}$ alloy will show little if any effects due to spin fluctuations.¹⁸ If we assume that S_n is simply the thermoelectric power of $\text{Fe}_{24}\text{Zr}_{76}$, then the difference between the measured thermoelectric powers and the thermoelectric power of $\text{Fe}_{24}\text{Zr}_{76}$ should be the spin-fluctuation term. This difference is plotted in Fig. 3(a). Figure 3(b) shows the results of a similar analysis for Co-Zr, assuming spin fluctuations are negligible in $\text{Co}_{20}\text{Zr}_{80}$. Figure 4 shows the thermoelectric power of Ni-Zr, Fe-Zr, and Co-Zr at 300 K as a function of Zr concentration. The influence of spin fluctuations on Ni-Zr is thought to be small,¹⁰ and if the thermoelectric power of Ni-Zr is representative of S_n in the other alloys, then we might expect S_n in both Fe-Zr and Co-Zr to have strong composition dependences, especially at low Zr concentrations. However, for Zr concentrations greater than 60 to 65 at.%, the approximation of S_n by the thermoelectric

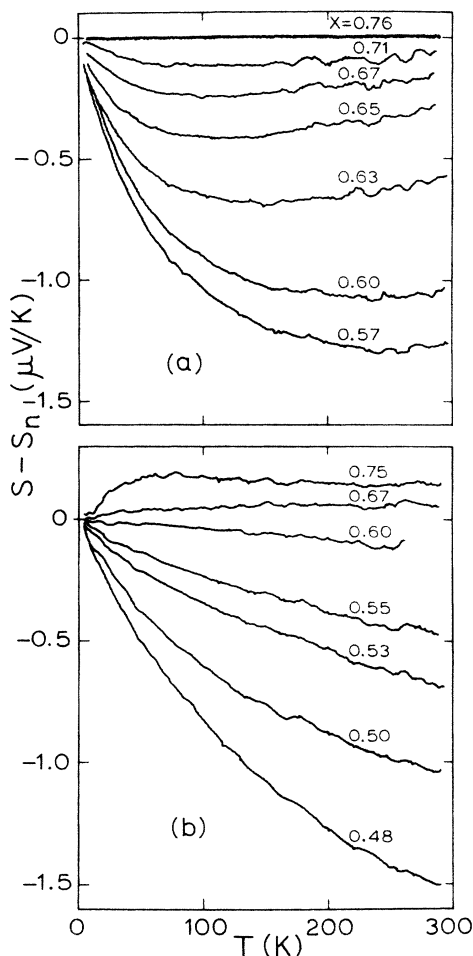


FIG. 3. Spin-fluctuation thermoelectric power for (a) Fe-Zr and (b) Co-Zr alloys. x is the atomic fraction of Zr. The small positive deviation in $Co_{25}Zr_{75}$ is probably due to the compositional dependence of Sn (see text).

power of $Fe_{24}Zr_{76}$ and $Co_{20}Zr_{80}$ is probably reasonable.

We now compare our results for the spin-fluctuation component of the thermoelectric power in the glassy alloys to the results in the classic Pd-Ni spin-fluctuation system.^{20,21} The spin-fluctuation thermoelectric power in Pd-Ni is negative with a peak of $\sim 10 \mu V/K$ at the spin-fluctuation temperature. The size of the peak increases with Ni concentration until the onset of magnetic ordering, at which point it rapidly decreases. Glassy Fe-Zr and Co-Zr have a negative spin-fluctuation thermoelectric power of order $1 \mu V/K$, with no well-defined peak. The size of the effect increases with increasing Fe concentration well beyond the onset of magnetic ordering; however, the rate of increase appears to diminish with the onset of magnetic ordering at about 35 at. % Fe in Fe-Zr. This lack of similarity would at first glance indicate that the effects in Fe-Zr are not due to spin fluctuations. Before drawing this conclusion we should examine in detail the nature of the spin-fluctuation effects in Pd-Ni alloys. The thermoelectric power may be written

$$S - S_h = (S_{di} - S_{dh}) \frac{\rho_i}{\rho_T} + \Delta S_g + \Delta S_f,$$

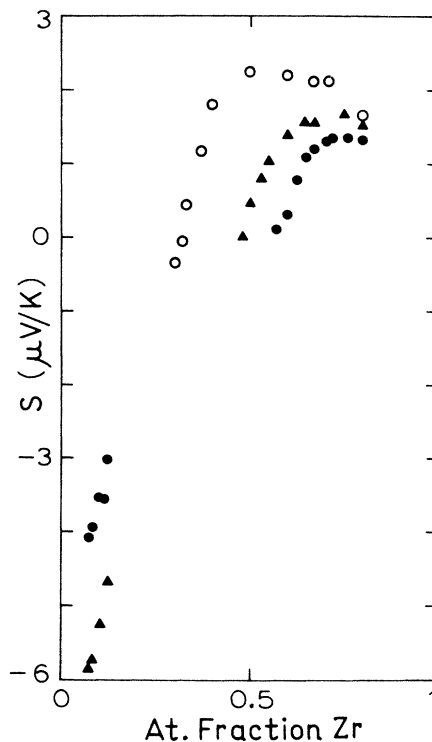


FIG. 4. Composition dependence of the absolute thermoelectric powers of Ni-Zr (Ref. 4); \circ , Fe-Zr, \bullet ; and Co-Zr, \triangle .

where S and S_h are the observed thermoelectric powers of the alloy and the host, respectively. S_{di} and S_{dh} are the characteristic diffusion thermoelectric powers of the impurity (Ni) and the host (Pd), respectively, and ρ_i is the component of the total resistivity ρ_T due to impurities. ΔS_g and ΔS_f are the differences in the phonon drag and spin-fluctuation drag terms between the host and the alloy. For Pd-Ni alloys it has been shown that ΔS_g and ΔS_f are small and thus that the spin-fluctuation term in the thermoelectric power is due to the diffusion term, which is weighted by ρ_i/ρ_T .²² In crystalline alloys at low temperatures $\rho_i/\rho_T \sim 1$; however, as we have mentioned earlier the dominance of the structural term in the resistivity of glassy metals makes ρ_i/ρ_T essentially zero in these materials. The mechanism producing the spin-fluctuation thermoelectric power in glassy metal alloys must therefore be essentially different from that operating in dilute crystalline alloys and perhaps it is not surprising that the observed effects are also different.

The nature of the spin-fluctuation term in glassy metals is not clear. We can speculate that spin-fluctuation mass-enhancement effects similar to the phonon mass-enhancement effects proposed to explain the temperature variation of the thermoelectric power in Cu-Zr, Ni-Zr, and related alloys might provide a mechanism. It seems clear that whatever the actual mechanism is that correctly describes the thermoelectric power in glassy magnetic materials, it cannot be an additional scattering mechanism of the type so widely invoked to explain "anomalous" thermoelectric powers observed in crystalline alloys.

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