Thermoelectric power of magnetic and nonmagnetic amorphous metals

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The thermoelectric power of a number of magnetic and nonmagnetic amorphous metallic alloys has been measured as a function of temperature between 15 and 580 K. The temperature dependence of the thermopower for the magnetic alloys is qualitatively different from that for the nonmagnetic alloys. The data for the nonmagnetic alloys are consistent with the extended Ziman theory for transport in liquid and amorphous metals. It is argued that the data for the magnetic alloys are consistent with a model, based on the Kondo scattering of conduction electrons by spins situated in low internal fields, which was recently proposed to explain the resistivity minima observed in these materials.

Recent studies of electronic transport in metallic glasses have revealed two distinctly different types of anomalous resistivity behavior. Some of these glasses show a small but monotonic decrease of resistivity with increasing temperature, over as wide a range as 4 to 600 K in some cases.[1-5] The amorphous alloys Cu-Zr (Refs. 3 and 4) and Be-Ti-Zr (Ref. 5) are examples in this group, which consists of many glasses having no magnetic constituents. The other type of anomalous resistivity is found in amorphous alloys containing some ferromagnetic or antiferromagnetic elements, such as Fe-B, Fe-Ni-P-B, or Fe-Ni-Cr-P-B. In these, the resistivity shows a minimum in the temperature range 10 to 300 K and an approximate logarithmic increase of the resistivity with decreasing temperature below the minimum.[6,7] Such resistivity behavior could have been associated with the Kondo effect normally observed in crystalline alloys containing small amounts of magnetic atoms, except for the fact that these glasses are strongly ferromagnetic. As is well known, the large internal field experienced by the magnetic atoms in a ferromagnet precludes the possibility of their giving rise to Kondo scattering of the conduction electrons.

Several theories have been proposed to explain the negative temperature coefficient of resistivity, $\alpha \equiv (1/\rho)\, d\rho/dT$, observed in metallic glasses. One of these is the generalized Ziman theory of electronic transport in liquid metals.[1,8,9] It deals with the normal potential scattering contribution to the electrical resistivity as modified by the absence of periodic order in a glass, and can lead to a positive or negative value of α depending on the relative positions of $2k_F$ and k_p, where k_F is the Fermi wave vector of the conduction electrons and k_p denotes the position of the first peak in the x-ray structure factor of the glass. An alternative theory[6,10] proposes the existence of quantum-mechanical two-level tunneling states for some of the atoms in a disordered solid. The Hamiltonian for electrons scattering from the localized excitations arising from these tunneling states is assumed to be identical with the Kondo Hamiltonian, which can give rise to both a resistivity minimum and a negative value of α over a wide temperature range. However a recent calculation of this effect by Black *et al.*,[11] using parameters for the tunneling model deduced from ultrasonic experiments, indicates that this model would give a resistivity anomaly three orders of magnitude too small to fit the data.

A recent work[12] has resurrected the idea of a real Kondo effect in explaining the resistivity minima observed in the magnetic glasses. Instead of proposing a structural modification to the Kondo theory, it considers the spin-flip scattering of electrons from magnetic atoms sitting in regions of zero effective field.[13] That a small fraction of the magnetic atoms may actually exist in such field-free regions in a concentrated ferromagnet such as $Fe_{0.80}B_{0.20}$ has been demonstrated by Grest and Nagel[12] on the basis of Monte Carlo calculations of the effective-field distribution $P(H)$ in such materials, and follows essentially from the large disorder inherent in the glasses. This result therefore reconciles the coexistence of Kondo-type resistivity anomaly and ferromagnetism in these amorphous alloys and implicitly predicts a difference in the thermoelectric power behavior between magnetic and nonmagnetic glasses. Such a prediction would not, however, follow from the tunneling-level model which views both magnetic and nonmagnetic glasses identically as regards the effects of structure on their transport properties. Besides these three, other theories proposed to explain the negative α include the Mott s-d scattering model,[4] and those that study the interference between phonon and im-

purity scattering.[14]

In order to identify the scattering mechanism which most accurately describes the transport in the glass it is necessary to study some transport property, other than the resistivity, whose predicted behavior in the various models will be substantially different. In a previous communication[5] a study of the resistivity α and the thermoelectric power Q in a Be-Ti-Zr glass over an extended range of temperature was reported. It was shown there that both the negative temperature coefficient of resistivity and the positive thermoelectric power varying linearly with temperature observed over the entire range from 10 to 600 K could be explained on the basis of the extended Ziman theory if the condition $2k_F \cong k_p$ was satisfied for the alloy. However, this behavior of Q was not consistent with the predictions of either the tunneling-level model or the *s-d* scattering model. In this paper we present a more extensive study of the thermoelectric power of both magnetic and nonmagnetic glasses.[15]

The samples were in the form of ribbons of width 1–2 mm and thickness 30–60 μm. The thermoelectric power of each sample was measured relative to that of a 99.999+% pure lead wire using the integral method.[5] The absolute thermopowers were calculated using the new standard scale for lead obtained by Roberts[16] for temperatures up to 350 K. At higher temperatures the standard values used were those of Cook, Laubitz, and Van der Meer,[17] which were adjusted to join smoothly with the scale of Roberts. The uncertainty in the data was estimated to be 0.1 μV/K.

Figure 1 shows the data for amorphous $Cu_{0.50}Zr_{0.50}$ together with that reported previously[5] on the metallic glass $Be_{0.40}Ti_{0.50}Zr_{0.10}$ (Metglas 2204; Metglas is a registered trademark of Allied Chemical Corp.). The thermopower of Cu-Zr is *positive* and *linear in T* over the *entire* temperature range 10 to 580 K, as it is for the Be-Ti-Zr glass. The magnitude of Q is small in both these samples and is more similar to that of a noble metal than of a transition metal. We have also measured the resistivities of both samples and found them to decrease monotonically with increasing temperature over the *entire* range 10 to 580 K. For Be-Ti-Zr and Cu-Zr, the decrease in resistivity over this temperature range is about 9% and 6%, respectively. Sinha[1] has measured the resistivity and thermoelectric power of $(Ni_xPt_{1-x})_{0.75}P_{0.25}$ glasses as a function of temperature, though over much more limited ranges than is reported here. His resistivity measurements showed that α was negative for the glasses for which $0.20 \leq x \leq 0.50$, and positive for the glass with $x = 0.60$. The thermoelectric power for all the samples was small (varying between 1 and 2.5 μV/K), positive and linear in T in the range 80 to 300 K.

The abovementioned results are incompatible with a Kondo-type theory[6,10] based on tunneling levels for transport in these glasses. For if such tunneling levels were truly an intrinsic feature of the glassy structure contributing to electronic transport then the anomaly associated with Kondo-like behavior should have appeared in the thermopower data. Within the detecting capacity of our experiment (0.1 μV/K in a total of 4.5 μV/K) no such structure has been observed. This is consistent with the work of Black *et al.*[11] who predict that the tunneling-level anomalies, if present, will be too small to be detected in an experiment of such a degree of sensitivity. The thermopower results are also incompatible with the predictions of the *s-d* scattering model.[4,13] According to the Mott formula $Q \propto [\partial \ln \rho(E)/\partial E]_{E=E_F}$, the thermopower of elements with less than half-filled *d* bands should be opposite in sign to the thermopower of elements having more than half-filled *d* bands. A recent photoemission experiment[18] on Cu-Zr glasses concludes that the electronic structure of Cu-Zr in the vicinity of the Fermi level is mainly determined by the Zr *d* band, which is less than half-filled. The electronic structure of the Be-Ti-Zr glass can also be expected to be similar to that of the Ti or Zr *d* band, whereas that for Ni-Pt-P should be close to the nearly full *d* band structure of Ni and Pt. The positive thermoelectric power observed in all three glasses then

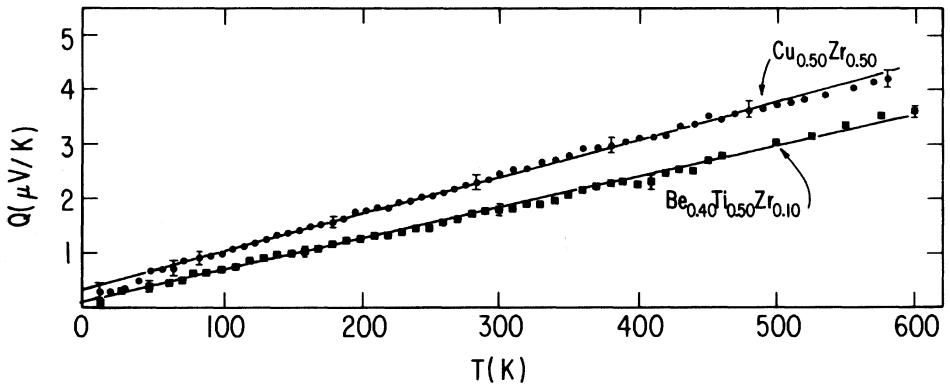

FIG. 1. Thermoelectric power of the nonmagnetic amorphous alloys $Be_{0.40}Ti_{0.50}Zr_{0.10}$ (Ref. 5) and $Cu_{0.50}Zr_{0.50}$.

directly contradicts the prediction of the *s-d* scattering model.

The generalized Ziman theory, on the other hand, is consistent with the temperature-dependent behavior of the transport coefficients reported above. The negative α of these glasses can be explained using the Ziman theory by assuming that the criterion $2k_F \cong k_p$ is satisfied for each alloy.[2,5,9] (Here k_p is not necessarily the first maximum of the total interference function but may be the maximum of one of the *partial* structure factors.) The same criterion also leads to a thermopower which is small, positive and linear in T, as was pointed out before.[5] The following expression for the thermoelectric power is obtained from the Ziman theory[19]:

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

where

$$q \equiv S(2k_F)|t(2k_F)|^2 \Big/ \int_0^{2k_F} |t(k)|^2 S(k) 4(2k_F)^{-4} k^3 \, dk \ ,$$

$S(k)$ denotes the structure factor, k_B is the Boltzmann constant, and r depends on the energy dependence of the t matrix, $t(k)$. From x-ray diffraction studies we find $k_p = 2.75$ Å^{-1} for Be-Ti-Zr (Ref. 5) and 2.73 Å^{-1} for Cu-Zr which, if $k_p \cong 2k_F$ (where we emphasize that a strict equality is not necessary and deviations of $\pm 15\%$ can be tolerated), give $E_F = 7.2$ and 7.1 eV, respectively. The measured slopes of the Q vs T curves for Be-Ti-Zr and Cu-Zr are 5.7×10^{-3} and 7×10^{-3} μV K^{-2}, respectively. Neglecting the term r in Eq. (1) above, these results imply $q = 2.3$ and 2.5 for the two glasses. These seem to be reasonable numbers if they are compared with a crude estimate of q from the definition in Eq. (1) with again $2k_F$ taken to be close to k_p.

Figures 2 and 3 show the absolute thermopower of five ferromagnetic Metglas alloys as a function of temperature between 15 and 580 K. In the low-temperature range up to 300 K our thermopower results for the Metglas alloys 2826, 2826A, and 2605A agree very well with those of Baibich *et al.*,[20] who have recently published data up to 300 K from measurements carried out independently in three different laboratories on three separately obtained batches of Metglas alloys. For the Metglas 2605 alloy our data agree well with that of Elzinga and Schroeder in that work,[20] but differs from the data of the other two measurements by almost 1 μV/k at 300 K. Between 300 and 580 K our results for the same alloy differ by the same amount from that of Teoh *et al.*,[21] whose high-temperature data on Metglas 2605 alloy join smoothly with the low-temperature data of Baibich and Muir (from Ref. 20) at 300 K. It is at once seen that the behavior of Q for these samples is *qualitatively different* from that for the nonmagnetic glasses shown in Fig. 1. For all magnetic samples the thermopower is negative, and has a negative slope at low temperatures, i.e., below 100 K. Most importantly, Q is *not linear* in T over any large range of temperature and shows structure similar to that observed in crystalline Kondo systems, i.e., nonmagnetic hosts containing dilute amounts of magnetic impurities. The resistivities of all these alloys also show minima similar to that observed in crystalline Kondo systems. However, the glasses all contain large concentrations of magnetic elements and it is not immediately clear why they should exhibit a Kondo-like behavior. Table I shows the compositions and some characteristics of the transport properties of the samples studied here.

The transport behavior of the magnetic samples cannot obviously be explained by the use of the Ziman theory. The tunneling-level model may lead to Kondo-like anomalies in the transport properties of the magnetic glasses, but it fails to explain why simi-

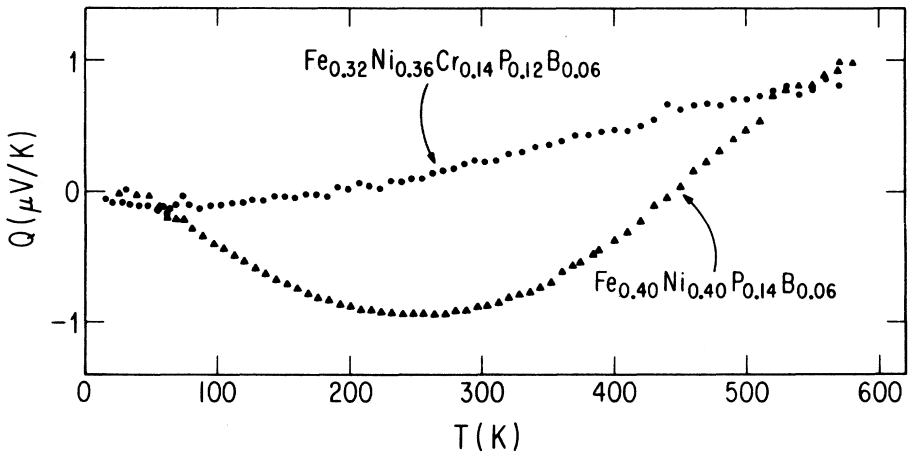

FIG. 2. Thermoelectric power of the amorphous magnetic alloys $Fe_{0.40}Ni_{0.40}P_{0.14}B_{0.06}$ and $Fe_{0.32}Ni_{0.36}Cr_{0.14}P_{0.12}B_{0.06}$.

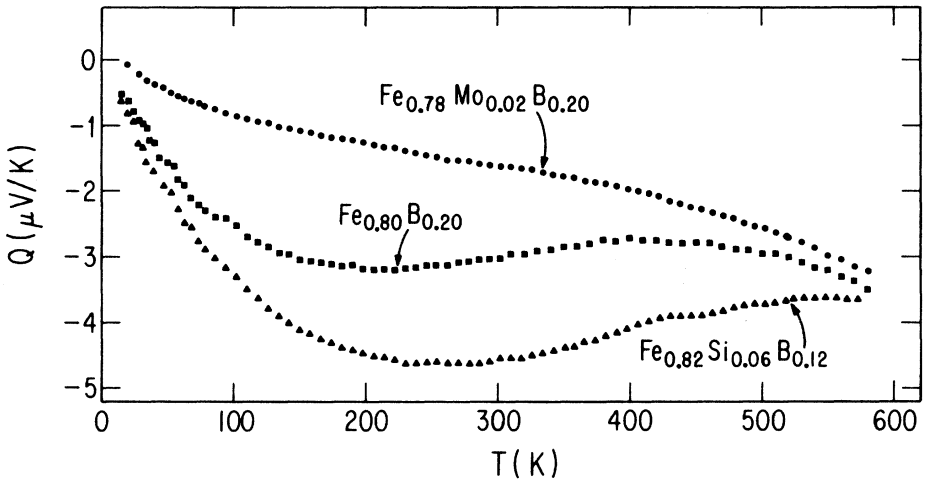

FIG. 3. Thermoelectric power of the amorphous magnetic alloys $Fe_{0.80}B_{0.20}$, $Fe_{0.78}Mo_{0.02}B_{0.20}$, and $Fe_{0.82}Si_{0.06}B_{0.12}$.

lar anomalies are not observed in the thermopower of the nonmagnetic glasses as well. However, the work of Grest and Nagel leads naturally to such anomalous transport behavior in magnetic glasses only and not in the nonmagnetic ones, whose positive and linear thermopower result therefore does not conflict with the central idea of this model.

In crystalline alloys the Kondo effect gives rise to anomalously large structures in the Q vs T curves, the magnitude of which can be ten times as much as that observed in the present case. It is argued in the following that this relative lack of structure in the thermopower does not rule out the possibility of a Kondo effect in the glasses. One reason for this is to be found in the Nordheim-Gorter rule,[19] according to which the thermopower contribution from a given electron scattering mechanism will be weighted by the relative contribution to the resistivity arising from that process. This relative contribution is given by ρ_K/ρ_T, where ρ_K is the Kondo contribution to the total resistivity, ρ_T. For the magnetic glasses Baibich *et al.*[20] have estimated this ratio to be $\sim 10^{-3}$ from the depth of the low-temperature minima observed in their ρ vs T curves. This means that even the unusually large Kondo contribution of 100 μV/K will produce a structure in the thermopower only on the order of 0.1 μV/K. Since this is below the detecting capacity of the present experiments, they conclude that the thermopower data do not exhibit any effect of the Kondo scattering. However, for reasons presented below, we believe that the above estimate of the size of ρ_K/ρ_T is incorrect since ρ_K is much larger than that suggested by the apparent low-temperature anomaly in the resistivity of these alloys. This can be understood in the light of the work of Grest and Nagel,[12] whose calculations yield an effective-field distribution $P(H)$ in such glasses that has a long tail extending through zero field to negative values of H. The Kondo contribution to a transport coefficient $J(J \equiv \rho$ or $Q)$ arising from this distri-

TABLE I. Transport data for amorphous alloys.

Metglas alloy	Composition	$\rho_{300\text{ K}}$ ($\mu\Omega$ cm)	$\rho_{4.2\text{ K}}/\rho_{300\text{ K}}$[a]	T_{min}[a] (K)	$Q_{300\text{ K}}$ μV/K	Ferromagnetic T_c[a]
2826	$Fe_{0.40}Ni_{0.40}P_{0.14}B_{0.06}$	145 ± 15	0.962	26	−0.90	537
2826A	$Fe_{0.32}Ni_{0.36}Cr_{0.14}P_{0.12}B_{0.06}$	155 ± 15	1.020	270	+0.25	250
2605	$Fe_{0.80}B_{0.20}$	130 ± 15	0.960	14	−3.00	647
2605A	$Fe_{0.78}Mo_{0.02}B_{0.20}$	120 ± 15	0.992	7 & 80	−1.60	595
2605S	$Fe_{0.82}Si_{0.06}B_{0.12}$	140 ± 15	0.966	16	−4.60	
2204	$Be_{0.40}Ti_{0.50}Zr_{0.10}$	300 ± 30	1.060	None	+1.85	Nonmagnetic
	$Cu_{0.50}Zr_{0.50}$	210 ± 20	1.043	None	+2.45	Nonmagnetic

[a]The entries in the columns $\rho_{4.2\text{ K}}/\rho_{300\text{ K}}$, T_{min}, and T_c are from Ref. 7 except for Fe-Si-B and Cu-Zr, for which the data are from the present work. The data for 2204 are from Ref. 5.

bution should approximately be of the form

$$J(T) = \int_{-\Delta}^{\Delta} J(T,H) P(H)\, dH \ , \qquad (2)$$

where $J(T,H)$ is the transport contribution due to Kondo scattering from a single spin in field H. The cutoff, Δ, in this integral is not known, but should not extend to such high fields that the concept of Kondo scattering from independent spins breaks down. The temperature dependence of the resistivity due to Kondo scattering from spins in low fields may be approximated by the Hamann formula[22] with T replaced by $(T^2+H^2)^{1/2}$. Thus the divergent term $\ln T$ in the resistivity is replaced by $\ln(T^2+H^2)$. In convoluting over $P(H)$ in Eq. (2) this H-dependent term smears out the low-T divergence, which might be the reason why the observed anomaly in the resistivity of the magnetic glasses is small compared to that in crystalline alloys. However the behavior of the thermoelectric power does not change drastically due to a small applied magnetic field.[23] Therefore, unlike in the resistivity, the convolution over $P(H)$ does not smear out the structure in the thermoelectric power. What may happen, in large applied fields, is that the peak in $Q(T)$ will shift to higher temperatures.[23] This would account for why the peaks we observe in $Q(T)$ seem to be at somewhat higher temperatures than is usually observed in crystalline materials. Although it is still important to use the Nordheim-Gorter rule, it is difficult to estimate the size of ρ_K/ρ_T since ρ_K may be much larger than simply the apparent divergence seen in the low-temperature resistivity of these alloys.

It is possible to make some qualitative remarks about the effects of Cr and Mo on the thermopower anomalies observed. It is known that in crystalline Kondo systems Cr produces a very small anomaly in Q, unlike the large negative anomalies produced by Fe, Co, etc. It appears from the data of Fig. 2 that even the small structure in Q observed in the Fe-Ni-P-B glass is substantially washed out by the addition of Cr, as is observed for the Fe-Ni-Cr-P-B glass. This could be the result of an algebraic addition of the Kondo anomalies separately produced by the magnetic species in these samples. Similarly the addition of Mo, which has a d-band structure resembling that of Cr, is seen to reduce the structure in Q of the Fe-B glass, as shown in Fig. 3. By contrast, the addition of Si is seen to further depress the thermopower curves for Fe-B and Fe-Ni-P-B,[20] although such behavior is not readily explained by the position of Si in the Periodic Table. However, since the presence of even minute amounts of magnetic impurities may produce substantial effects on the thermopower in crystalline materials, there remains a fair degree of uncertainty in the predictions of thermopower behavior based only on the nominal compositions of these glasses. For example, an analysis of the Metglas alloys 2605 and 2605S showed that the former contained ~ 150 ppm Cr and ~ 1000 ppm Mn, while the latter had ~ 750 ppm Cr and ~ 200 ppm Mn in it. Such magnetic impurities might have made significant contributions to the thermopower data.

In conclusion, our experiments appear to point out a qualitative difference in the transport behaviors of magnetic and nonmagnetic glasses. In the former the resistivity shows a minimum and the thermopower a Kondo-like structure, both of which are expected results from the work of Grest and Nagel. In the nonmagnetic glasses, the resistivity decreases with increasing temperature and the thermoelectric power is positive and linear in T over the entire temperature range studied. Both these observations can be explained by the extended Ziman theory with suitable assumptions about the relationship between the Fermi wave vector and the partial structure factors. These assumptions are also consistent with a model[24] for the stability of these glasses. The tunneling-level model and the s-d scattering model appear to be incompatible with these two groups of thermopower data.

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