spectrum.

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# Thermoelectric Power and Resistivity in a Metallic Glass

S. R. Nagel

*The James Franck Institute and The Department of Physics, The University of Chicago, Chicago, Illinois 60637*

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Several theories have attempted to explain the anomalous temperature dependence of the resistivity in metallic glasses including a generalized Ziman theory, a model based on Mott $s$-$d$ scattering, and a model based on a Kondo or tunneling mechanism. The thermoelectric power as well as the resistivity of a glass has been measured up to the crystallization temperature and was linear over the entire region. This behavior is only consistent with the Ziman theory.

Despite the considerable recent interest in metallic glasses, the nature of the transport properties in these materials has remained controversial. In a majority of nonmagnetic glasses the temperature dependence of the electrical resistivity, $\rho(T)$, is anomalous in that over a wide temperature range the resistivity decreases with increasing temperature.[1] This is to be contrasted to the normal behavior of ordered crystalline metals, where the temperature coefficient of resistivity, $\alpha = \rho^{-1} d\rho/dT$, is large and positive. Attempts to understand this behavior have led to a number of different models for the fundamental electronic scattering mechanism in the glass. These include (1) a generalized Ziman theory,[1-5] (2) a model based on the Kondo effect and on an analogy of a two-level tunneling system with the Kondo problem,[6,7] and (3) a model based on Mott $s$-$d$ scattering.[8,9] These models of course are all able to predict negative values for $\alpha$ and can all be fitted to the experimental data within some range of temperature. Therefore by a study of the resistivity alone it is impossible to distinguish persuasively between the various models and find the one that most accurately describes the transport in the glass. However, since the various models are all based on fundamentally different scattering processes, they will predict different behavior for other transport coefficients. In this paper I report the first study over an extended temperature range of the thermoelectric power of a glass and show how this can distinguish between the three transport models mentioned above. A study of the thermoelectric power is particularly valuable for this purpose since it is well known to be extremely sensitive to the nature of the electronic scattering,[10] and for metallic glasses it is particularly easy to interpret.

A theory for the resistivity of normal liquid metals was developed by Ziman[11] and subsequently extended by Evans, Greenwood, and Lloyd[12] to treat liquid transition metals. Since the glass and liquid have similar structures one may use this type of theory in the glass as well.[2] The

temperature dependence can be calculated assuming a Debye phonon spectrum[3-5] and over a wide temperature range was found to be

$$\rho(T) = \frac{30\pi^3\hbar^3}{me^2k_F^2E_F\Omega}\sin^2[\eta_2(E_F)] \times\{1+[S_0(2k_F)-1]e^{-2[W(t)-W(0)]}\}. \quad (1)$$

Here $k_F$ and $E_F$ are the Fermi wave vector and energy, respectively, and $\Omega$ is the atomic volume. $\eta_2(E_F)$ is the $d$-wave phase shift of the $t$ matrix describing the scattering of the electrons, of energy $E_F$, by the ion cores which each carry a muffin-tin potential. $S_0(2k_F)$ is the static structure factor at $T=0$ K and $e^{-2W(T)}$ is the Debye-Waller factor at temperature $T$. If $2k_F \cong k_p$ (where $k_p$ is the position of the first peak in the structure factor) then $\rho(T)$ will decrease with increasing temperature.

The Kondo effect can also lead to negative values of $\alpha$ if there are some magnetic impurities in an otherwise nonmagnetic host. An intriguing suggestion was made by Cochrane *et al.*[6] that there could be an analogy to a Kondo system if in the amorphous metal there existed some sites in which the ions were in a double potential well. Such a model was proposed by Anderson, Halperin, and Varma[13] and by Phillips,[13] for explaining the low-temperature linear term in the specific heat of insulating glasses. The two tunneling levels would provide the degree of freedom which was provided by the two spin orientations in the Kondo problem. The Hamiltonian describing the tunneling levels is claimed to be identical to the Kondo Hamiltonian so that there should be similar effects in the transport. This model proposed by Cochrane *et al.*[6] was originally intended to explain only the low-temperature resistance anomalies found in some amorphous metals. More recently, Tsuei[7] has used this model to explain the negative $\alpha$ found over a wide range of temperatures in many glasses. In his model the resistivity is $\rho(T) = \rho_0 - C\ln(T^2+\Delta^2)$ where $C$ is determined by the number of tunneling states in the sample and $\Delta$ is a temperature characteristic of the splitting of the two levels.

The final theory which we will consider is Mott $s$-$d$ scattering. If the carriers at the Fermi surface can be separated into two distinct groups with different mobilities then a two-carrier model can be used. The $s$ or $p$ electrons, which carry the current, can be scattered into $d$ holes at the Fermi surface so that the resistivity is proportional to $N_d(E_F)$, the density of $d$ states at the Fermi level.[8] As the temperature is raised, because of the shift of $E_F$ and the thermal broadening, one obtains a temperature dependence of $\rho$. Assuming for simplicity that $N_d(E) = C(E_0 - E)^{1/2}$ near $E_F$, one obtains

$$\rho(T) = \rho_0[1 - \tfrac{1}{6}\pi^2(kT)^2(E_0 - E_F)^{-2}]. \quad (2)$$

For a nearly filled $d$ band the resistivity should decrease with increasing temperature.

Each of these theories predicts different behavior for the thermoelectric power, $Q$. It is well known[10,14] that the Kondo effect gives rise to giant thermoelectric anomalies. The values of $Q$ reach a maximum near the Knodo temperature and are about an order of magnitude larger than is observed in simple metals (as large as 40 $\mu$V/K). This would be true for the tunneling-level model as well if the analogy to the Kondo system is valid. For Mott $s$-$d$ scattering one expects to have a thermoelectric power comparable to those found in the transition metals. For a nearly filled $d$ band, which is necessary for $\alpha$ to be negative, the sign of the thermoelectric power should be negative. In the Ziman theory one expects a much more normal behavior for $Q$ which can be solved for explicitly[15]:

$$Q = -\frac{\pi^2k^2T}{3|e|E_F}[3 - 2q - \tfrac{1}{2}r], \quad (3)$$

where

$$q = \frac{S(2k_F)|t(2k_F)|^2}{\int_0^1|t|(k)|^2S(k)4(k/2k_F)^3d(k/2k_F)},$$

and $r$ depends on the energy dependence of the $t$ matrix, $t(k)$, which is small unless $E_F$ lies near the $d$-band resonance. In the present case we believe that $E_F$ is substantially below the resonance which should occur when the $d$ bands are approximately half-full. In this theory the thermoelectric power should be a linear function of temperature with a small slope. The sign will depend on the magnitudes of $q$ and $r$. The parameter $q$ will be large if $2k_F \sim k_p$. The thermoelectric power will then be positive. The condition $2k_F \sim k_p$ is just what was needed to have a negative $\alpha$.

The system we have chosen to study is $Be_{40}Ti_{50}Zr_{10}$ (Metglas No. 2204 of Allied Chemical). This system is particularly interesting because the temperature coefficient of resistivity is negative and large. The normalized resistivity for this material is shown as a function of temperature in Fig. 1. The absolute magnitude of $\rho$ is $280 \pm 20$ $\mu\Omega$ cm. There is a 10% change in the resistivity as the temperature is varied from

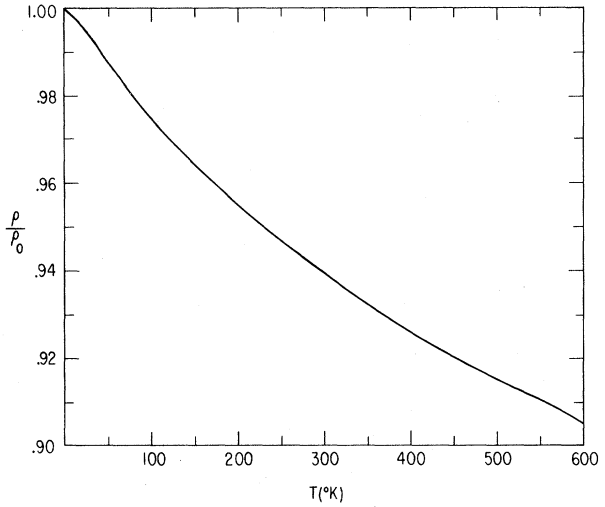


FIG. 1. Normalized resistivity of $Be_{40}Ti_{50}Zr_{10}$ glass showing large negative temperature coefficient of resistivity from 4°K to the crystallization temperature near 600°K.

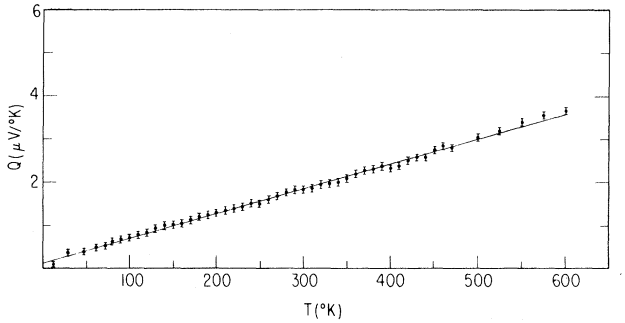


FIG. 2. Thermoelectric power of $Be_{40}Ti_{50}Zr_{10}$ glass showing linear behavior over entire temperature range from 4°K to 600°K.

4°K to 600°K. This is one of the largest values of $\alpha$ known in a metallic glass and this should therefore be an excellent system in which to check the scattering mechanism responsible for the negative temperature coefficient. The resistivity was measured using a standard four-probe technique. The thermoelectric power was measured relative to that of a 99.999+% pure lead wire standard. The values of the lead absolute thermoelectric power were taken from the new scale obtained by Roberts.[16] At higher temperatures the standard values used were those of Cook, Laubitz, and Van der Meer,[17] which were adjusted to fit smoothly onto the scale of Roberts. One end of the sample was held at a fixed temperature while the temperature of the other end was varied. The derivative of the voltage with respect to temperature gave the values of the relative thermoelectric power.

The absolute thermoelectric power of the metallic glass $Be_{40}Ti_{50}Zr_{10}$ is shown in Fig. 2. It is linear and positive over the *entire* range from 4 K up to the crystallization temperature near 600 K with a slope of $5.7\times10^{-3}$ $\mu V/K^2$. The absolute value of $Q$ is small and is more similar to a noble metal than to a transition metal. There are no phonon-drag effects since the mean free path for phonons scattering from the lattice is extremely short.

If we compare these results of the thermoelectric power with the various theories outlined above we find that is is incompatible with a Kondo or tunneling (or localized spin fluctuation) model. Even if one expects *an order of magnitude* smaller thermoelectric anomaly for the tunneling model than in a true Kondo system, one would still expect to see structure in the curve which is of order 4 $\mu V/K$. Our data show no such structure outside our estimated error which was 0.1 $\mu V/K$. If the tunneling levels do contribute to the temperature dependence of the resistivity they would contribute to $Q$ also as specified by the Nordheim-Gorter rule[15] (i.e., their contribution to the thermoelectric power would be weighted by the proportion that they contribute to the resistivity). We therefore estimate that they would be responsible for considerably less than 2% of the total scattering. The data are also inconsistent with a model based on $s$-$d$ scattering. As we mentioned above, this model would predict a large negative thermoelectric power whereas experimentally we find a small positive one.

The extended Ziman theory, however, is consistent with both the resistivity and thermoelectric power data if $2k_F \sim k_p$. From an x-ray diffraction study[18] we find that $k_p = 2.75$ Å$^{-1}$ which, if $2k_F = k_p$, would imply that $E_F = 7.3$ eV. This low value of $E_F$ implies that there are somewhat less than 2 electrons per atom in the valence band. This should be compared with the value $E_F = 8.2$ eV found by Hasegawa and Tanner[19] in their study of superconductivity in binary Be:Zr alloys. Using our value for $E_F$, we find $q = 2.3$ which is not unreasonable if $2k_F = k_p$. The glass we are studying is an alloy with a high concentration of Be which is a very light element. This suggests that the Debye-Waller factor may be quite large leading to a large negative temperature coefficient of resistivity[3] as observed in Fig. 1. Also the fact that $2k_F \sim k_p$ is consistent with a

recent suggestion[20] that an alloy will be able to form a glass more easily when $2k_F \sim k_p$.

The picture of the electronic structure which emerges is that, because the mean free path of all the electrons is so short, it is no longer possible to separate the electrons into two distinct groups with different scattering times. Therefore a model[8] based on Mott $s$-$d$ scattering is no longer applicable. In addition the data reported here are of comparable magnitude and have the same sign as the value of $Q$ calculated at room temperature[21] for a $Ni_{75}P_{25}$ glass and that found for ternary $(Ni_xPt_{1-x})_{75}P_{25}$ glasses.[2] In the $Be_{40}Ti_{50}Zr_{10}$ glass, one would expect that the resonant Ti and Zr levels lie above the Fermi level while in these other glasses one would expect that the resonant Ni and Pt level lie below $E_F$. The energy derivative of the potential, the parameter $r$ in Eq. (3), is of opposite sign for these two cases and therefore must be small in order for the thermoelectric power in all these systems to be so similar. This implies that $E_F$ is reasonably far from the resonance in all these cases. Clearly this measurement cannot distinguish very well between various theories that predict a linear thermoelectric power (other disorder models for a negative $\alpha$ may well give the same results as the Ziman analysis for $Q$), nor can it rule out a theory based upon two or more scattering mechanisms, each with a large linear thermoelectric power, which cancel to yield a total linear thermoelectric power with a small slope. However this measurement is able to differentiate between the three theories most often proposed to explain the transport in these glasses since these theories predict very different thermoelectric behavior. The fact that the measured thermoelectric power is linear over the *entire* range of temperature, from 4 K up to 600 K, is essential for this to be a convincing test of the theories. Although the material used in this study was chosen because it had one of the largest negative temperature coefficients of resistance known in a metallic glass, it is clear that further studies over an extended temperature range of the thermoelectric power in other glasses is necessary to corroborate these conclusions. Finally a recent calculation by Black[22] has indicated that the analogy between the two-level tunneling model and the Kondo problem may not be complete. What we have shown is that even if the tunneling levels exist, they do not play a significant role in the scattering of electrons.

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