

Incipient localization and the thermopower analog of the Mooij correlation

A. B. Kaiser

Max-Planck-Institut für Festkörperforschung, Postfach 800665, D-7000 Stuttgart 80,
Federal Republic of Germany

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Experimental data for a large number of amorphous metallic alloys are consistent with the thermopower analog of the Mooij correlation being an increase of thermopower magnitude $|S|$ as the square of resistivity, with S of either sign and showing only small deviations from linearity in temperature. We show that such behavior can arise from the reduction of conductivity by incipient localization.

Several years ago, Mooij¹ pointed out a remarkable correlation between the magnitude of metallic resistivity ρ and its temperature dependence: For $\rho > 150 \mu\Omega \text{ cm}$, the resistivity usually decreases as temperature T increases, in contrast to the normal metallic behavior seen for lower-resistivity systems. One widely quoted explanation² assumed the applicability of the Ziman-Faber diffraction model even to systems in which the mean free path is approaching the interatomic spacing, and ascribed the Mooij correlation to T dependence of the structure factor when scattering by phonons is ineffective. However, the resistivity decrease is often much stronger³⁻⁵ than that of the Debye-Waller factor for the main peak in the structure factor, which is very difficult to account for in the diffraction model. Indeed, structure-factor T dependence is more clearly responsible not for the Mooij correlation, but for its violation⁶ in low resistivity systems, such as Mg-Zn, that show negative temperature coefficients of resistivity. While inclusion of multiple scattering effects may influence the resistivity temperature dependence, there is now considerable theoretical and experimental evidence⁷⁻¹⁰ that incipient localization is likely to play a major role in causing the Mooij correlation.

In this paper, I derive the principal effects of quantum interference in backscattering (i.e., incipient localization) on thermopower, and suggest a new thermopower analog of the Mooij correlation. The previous suggestion of Nagel¹¹ was that thermopower tended to be positive for high-resistivity glassy metals ($\rho > 150 \mu\Omega \text{ cm}$) with a negative temperature coefficient of resistivity, which could be accounted for by the Ziman-Faber model. But the probable demise of the Ziman-Faber model as the cause of the resistivity Mooij correlation naturally calls this explanation into question.

The temperature dependence of the thermopower of most nonmagnetic amorphous metals is perhaps rather surprisingly well accounted for¹²⁻¹⁵ by a linear bare thermopower enhanced at low temperatures by the electron-phonon interaction.¹⁶ Thermopower in glassy metals is much simpler than that in crystals; because phonon drag is suppressed by the disorder scattering,¹⁷ there is little change with temperature in the balance of scattering (i.e., disorder scattering always dominates over phonon and impurity scattering), and any Neilsen-Taylor higher-order diagram contribution has the same T dependence as

electron-phonon enhancement.¹⁸

Figure 1 shows all thermopower-resistivity data pairs for nonmagnetic amorphous metals of which I am aware [except that the superseded data for MgZn (Ref. 19) are omitted, and where similar data have been obtained by more than one group only one data point is included]. The plotted data for Mg-Zn glasses are from Baibich, Muir, Altuvnian, and Tu,²⁰ with the resistivity ρ taken as the average of that given by the two different methods used. Data for Ca-Al, Cu-Zr, La-Ga, Pt-Ni-P, and Ti-Be-Zr are taken from the review by Naugle,²¹ and those for Cu-Sn, Mg-Cu, Ni-Nb, Pd-Ge, Pd-Si, and Pd-Si-Su from the review by Mizutani²² (these reviews should be consulted for the original data sources). I have also included more recent data for Ca-Al-Ga,²³ Cu-Hf,^{12,24} glassy Cu-Ti ribbons,¹³ amorphous Cu-Te films,³ Fe-Zr,^{25,26} La-Al,²⁷ Ni-P,²⁸ Ni-Zr,^{26,29} and Ta-Ir.⁴ Magnetic glassy metals, usually including Ni or Fe, tend to show negative thermopowers with resistivities typically in the range 100 to 170

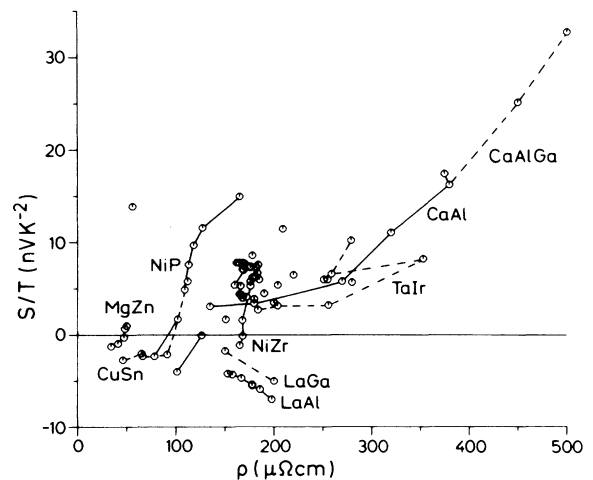


FIG. 1. Scatter diagram showing the correlation of thermopower parameter S/T for nonmagnetic amorphous metal alloys with resistivity ρ . Most data are for about room temperature (see text for data sources). Lines join data points for the same alloy series where these show a large variation, those mentioned in the text being specifically identified.

$\mu\Omega\text{ cm}$.²² However, the thermopower characteristically shows pronounced curvature³⁰ arising from specifically magnetic effects,³¹ so magnetic glasses form a special class and are not considered here. To characterize the size of thermopower, I have used the thermopower parameter S/T rather than S , since it is only weakly dependent on temperature for nonmagnetic systems. The temperature of the resistivity measurements is not too significant in the present context since it is also only weakly dependent on temperature. Most of the data in Fig. 1 were taken at room temperature, but the Cu-Sn film data are at 120 K.

The data, as illustrated by Naugle²¹ for selected systems, do indicate a correlation between S and ρ , although less clear than that¹ between the temperature coefficient of resistivity and ρ . There is some support for the hypothesis¹¹ that S becomes positive for $\rho > 150 \mu\Omega\text{ cm}$, although as recognized in previous works^{21,28} the La-based alloys are an exception. The correlation coefficient r of S/T and ρ is 0.64, which is highly significant statistically: For 79 data pairs a coefficient of 0.53 or higher between normally distributed random variables would arise only with a probability of 1 in 10^6 . However, the negative S data points also appear to show a trend toward becoming more negative as ρ increases. For this reason the correlation coefficient between $|S/T|$ and ρ is higher (0.71) than that between S/T and ρ . We also note that the correlation coefficient between $|S/T|$ and higher powers ρ^n is a little larger still ($r = 0.81 \pm 0.01$ for $n = 2$ to $n = 5$).

Having presented the experimental evidence for the existence of a correlation between $|S|$ and ρ independently of any theoretical model, we now investigate the effect of incipient localization. The Mooij correlation in resistivity can be understood in terms of incipient localization from the following expression^{9,32} for conductivity:

$$\sigma = \sigma_B - \Delta\sigma_{el} + \Delta\sigma_{in} , \quad (1)$$

where σ_B is the Boltzmann conductivity, $\Delta\sigma_{el}$ is the reduction at low T due to constructive quantum interference in backscattering:

$$\Delta\sigma_{el} = Ce^2/(3\pi^2\hbar l) , \quad (2)$$

and $\Delta\sigma_{in}$ represents the effect of the destruction of this interference³³ as inelastic scattering (by phonons) increases with temperature:

$$\Delta\sigma_{in} = Ce^2/(3\pi^2\hbar L_{in}) , \quad (3)$$

with

$$L_{in} = (\frac{1}{3} l l_{in})^{1/2} . \quad (4)$$

In these equations l is the elastic mean free path, l_{in} the inelastic mean free path ($l_{in} \gg l$ in glassy metals), e is electronic charge, and C is a constant of size 1 to 3 depending on choice of cutoff.^{9,32}

Sivan and Imry³⁴ have shown that metallic thermopower is given rather generally by the usual formula

$$S = \frac{1}{eT\sigma} \int dE \left[-\frac{\partial f}{\partial E} \right] E \sigma(E) , \quad (5)$$

where f is the Fermi function, and E electron energy measured from the Fermi level. The incipient localization

terms $\Delta\sigma_{el}$ and $\Delta\sigma_{in}$ in the conductivity will give rise to corresponding terms ΔS_{el} and ΔS_{in} in the thermopower:

$$S = S_B + \Delta S_{el} - \Delta S_{in} , \quad (6)$$

where S_B is the Boltzmann thermopower (including electron-phonon effects). These terms are evaluated as

$$\Delta S_{el} = (\Delta\sigma_{el}/\sigma)(S_B + A\partial \ln l/\partial \epsilon) , \quad (7)$$

$$\Delta S_{in} = (\Delta\sigma_{in}/\sigma)[S_B + \frac{1}{2} A(\partial \ln l/\partial \epsilon + \partial \ln l_{in}/\partial \epsilon)] , \quad (8)$$

$$S_B = [1 + \lambda_s^{ph}(T)]S_{Bb} + \lambda_s^{ph}(T)\zeta T , \quad (9)$$

$$S_{Bb} = (\pi^2 k_B^2 T/3e)(\partial \ln \sigma_B/\partial \epsilon) , \quad (10)$$

$$A = [1 + \lambda_s^{ph}(T)](\pi^2 k_B^2 T/3e) , \quad (11)$$

where $\lambda_s^{ph}(T)$ is the electron-phonon enhancement of thermopower due to energy renormalization,¹⁶ and the term involving the constant ζ in Eq. (9) gives the effect of velocity and relaxation-time renormalization, and Neilsen-Taylor higher-order diagrams.^{16,18} The experimental data¹⁵ indicate that ζT is usually smaller than S_{Bb} .

The physical meaning of these expressions is as follows. S_{Bb} is the bare Boltzmann thermopower in the absence of the electron-phonon interaction, while S_B includes the electron-phonon interaction effects that give rise to the characteristic low-temperature knee in glassy-metal thermopower, but are small at high temperatures. These effects have been discussed previously.^{16,18} The main effect of incipient localization arises from the term ΔS_{el} given by Eq. (7), since $\Delta\sigma_{el}$ is much larger than $\Delta\sigma_{in}$ for $l \ll l_{in}$. First, the Boltzmann thermopower S_B (whichever its sign) is amplified because conductivity is reduced. Second, there is an additional term involving $\partial l/\partial \epsilon$ because the effect of incipient localization may vary across the Fermi level (being largest where the mean free path is smallest), and so altering the energy dependence of conductivity. These two effects are more likely to add than cancel since $\partial \sigma_B/\partial \epsilon$ is partly determined by $\partial l/\partial \epsilon$. The predicted temperature dependence of thermopower is still essentially that of S_B , i.e., linear except for the electron-phonon enhancement effect.

Incipient localization will, however, produce a small additional nonlinearity in thermopower via the second correction term ΔS_{in} arising from the destruction of the backscattering interference by inelastic scattering, since $\Delta\sigma_{in}$ is T dependent. First, ΔS_{in} reduces slightly the enhancement of Boltzmann thermopower S_B in Eq. (7) as T increases. Second, there is another term involving $\partial L_{in}/\partial \epsilon$ that depends on whether the destruction of backscattering interference is greatest above or below the Fermi level. It can be seen that the form of the T dependence in the thermopower parameter S/T will be approximately the same as that in the resistivity ρ , and would most often be a reduction in the thermopower amplification due to incipient localization. This nonlinearity in S is, in fact, the closest analog of the Mooij correlation, since both are produced by the inelastic scattering term $\Delta\sigma_{in}$. But a change in slope of a similar relative size to the change in ρ (i.e., typically a few percent or less) is not easy to see when the usual electron-phonon enhancement effect produces an increase in slope of up to 100% as T decreases.¹⁵ However,

Naugle *et al.*¹⁴ found a decrease in S/T at high temperatures larger than that expected from electron-phonon enhancement in the Ca-Al and Ca-Al-Ga alloys of highest resistivity, which raises the possibility of a contribution to nonlinearity from incipient localization.

We can deduce the dependence of S on ρ as follows. $\Delta\sigma_{el}$ depends on l^{-1} , and so is approximately proportional to resistivity ρ , at least when disorder scattering represented by the Boltzmann resistivity ρ_B is dominant. Thus our prediction from Eq. (7) for the initial resistivity dependence of the thermopower correction due to incipient localization is

$$|\Delta S_{el}| \sim \rho^2 \quad (12)$$

for constant $\partial\sigma_B/\partial\varepsilon$ and $\partial l/\partial\varepsilon$. Sivan and Imry³⁴ have already investigated the critical behavior near the metal-insulator transition by substituting in Eq. (5) the conductivity given by scaling theory. They find for their model (that omits inelastic scattering) that S remains linear in T until the mobility edge is of order $k_B T$ from the Fermi level, its magnitude diverging like ρ as the transition is approached. For their case, where the mobility edge was below the Fermi level, S takes large negative values, but if the nearest mobility edge were above the Fermi level, S would diverge to large positive values. Thus we expect the increase of $|S|$ as ρ increases to be a rather general and ultimately very large effect, going initially as ρ^2 and later near the metal-insulator transition as ρ .

Returning now to the experimental data, we note that since the magnitude and sign of S_B depend sensitively on electronic structure, a wide range of thermopower values is expected for different systems. The scatter of the data in Fig. 1 amply fulfil this expectation. For example, the thermopower of Ni-Zr and Ni-P alloys decreases strongly with little variation in ρ (although this behavior may be associated with the appearance of magnetism and its characteristic negative thermopower at higher Ni concentrations). Nevertheless, my prediction that the increase $|\Delta S_{el}|$ in $|S|$ goes as ρ^2 does find support from the data, as indicated by the correlation coefficients quoted above. A correlation between $|\Delta S_{el}|$ and ρ^2 would cause $|S| \approx |\Delta S_{el} + S_B|$ also to show a correlation with ρ^2 , but with more statistical scatter as S_B varies. The observed correlation between $|S|$ and ρ^2 is therefore evidence in favor of my prediction. This is illustrated more clearly in Fig. 2, which shows the trends of S and ρ^2 with concentration for the three alloy systems in which the resistivity reaches the highest values (in which incipient localization effects should be largest): These trends are remarkably similar. (Again we use S rather than ΔS_{el} , but clearly trends in ΔS_{el} will be reflected in S provided S_B does not show larger variations.)

We now consider very briefly other effects on thermopower. The Ziman model mechanism of Nagel¹¹ may still operate to produce a tendency for positive thermopowers, particularly for the low-resistivity glasses [although current calculations for Mg-Zn (Ref. 35) give the wrong

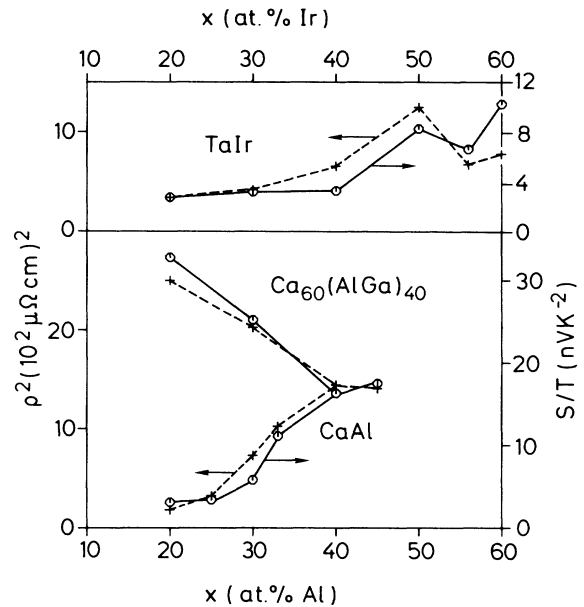


FIG. 2. Correlation between trends in thermopower parameter S/T and squared resistivity ρ^2 (at about 300 K) for the amorphous alloy series with highest resistivities: $\text{Ca}_{1-x}\text{Al}_x$ (from Naugle, Ref. 21), $\text{Ca}_{60}\text{Al}_x\text{Ga}_{40-x}$ (from Naugle *et al.*, Ref. 23), and $\text{Ta}_{1-x}\text{Ir}_x$ (from Rathnayaka, Trodahl, and Kaiser, Ref. 4).

trend as a function of concentration]. Another mechanism possibly affecting S is the Ioffe-Regel criterion³⁶ $l \geq \lambda/2$ relating an electron's minimum free path to its wave length λ : For the nearly free-electron case the criterion allows shorter free paths above the Fermi level and so produces a positive contribution to thermopower as l approaches its minimum value. I have not considered electron-electron interaction effects that are likely to affect thermopower, like resistivity, principally at the lowest temperature.¹⁵

In summary, it has been shown that the effect of incipient localization is to increase thermopower magnitude $|S|$ initially as ρ^2 . The analog of the decrease in resistivity with T for high-resistivity glassy metals is a small change in thermopower slope of a similar relative order of magnitude (that is masked to some extent in practice by the usual electron-phonon enhancement effect). I have presented all the available data for nonmagnetic amorphous metals and shown that they are consistent with these predictions: The correlation coefficient between $|S|$ and ρ^2 is 0.8, and there is a marked similarity in the concentration dependences shown in Fig. 2.

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