

Investigation of the Interaction of Electrons and Lattice Vibrations Using Glassy Metal Thermopower

A. B. Kaiser,^{A,B} A. L. Christie^A and B. L. Gallagher^C

^A Physics Department, Victoria University of Wellington,
Wellington, New Zealand.

^B Alexander von Humboldt Fellow,
Max-Planck-Institut für Festkörperforschung,
Postfach 80 06 65, D7000 Stuttgart 80, West Germany.

^C Department of Physics, University of Leeds, Leeds LS2 9JT, U.K.
Present address: Department of Physics, University of Nottingham,
Nottingham, NG7 2RD, U.K.

Abstract

We calculate the electron-phonon enhancement effect in thermopower using several different models for the Eliashberg function $\alpha^2 F(E)$ which describes the interaction of electrons and lattice vibrations. The behaviour of $\alpha^2 F(E)$ at low energies determines whether the predicted thermopower enhancement shows a peak at low temperatures, but the enhancement is rather insensitive to the detailed spectral shape of $\alpha^2 F(E)$ at higher energies. The calculations are able to give a good account of the thermopowers of several glassy metals measured by Gallagher and Hickey (1985), with slightly better agreement obtained for a smooth rather than a Debye-like $\alpha^2 F(E)$.

1. Introduction

It is well known that the interaction of electrons with lattice vibrations increases the effective mass of electrons in the vicinity of the Fermi surface by a factor of $1 + \lambda$, where λ ranges from 0.1 for non-superconductors to 1.5 for strong-coupling superconductors, leading to electron-phonon enhancement effects at low temperatures in for example the electronic specific heat (see e.g. Grimvall 1981). This interaction is significant only for electrons in a band at the Fermi level of width corresponding approximately to the Debye energy, i.e. the maximum phonon energy. Hence at temperatures above the Debye temperature T_D , the enhancement effect is expected to disappear. However, the temperature dependence of electron-phonon enhancement is usually masked by other larger effects (e.g. the lattice term in the specific heat or the phonon drag in crystalline thermopower). The thermopower of glassy metals, in which the strong disorder scattering suppresses phonon drag (Jäckle 1980), provides the first clear demonstration of the decay of electron-phonon enhancement with temperature (Gallagher 1981; Kaiser 1982).

Measurements on many glassy metals (see e.g. Gallagher and Hickey 1985; Naugle *et al.* 1985; Fritsch *et al.* 1985) and on amorphous films (Rathnayaka *et al.* 1985) have provided further evidence that electron-phonon enhancement is the dominant cause of nonlinear thermopowers in non-magnetic amorphous metals. Naugle *et al.* (1985) fitted their data on LaAl, CaAl and LaAlGa glassy metals to the calculated

thermopower shape (Kaiser and Stedman 1985) for a Debye-like Eliashberg function $\alpha^2 F(E)$.

In this paper we extend the theoretical calculations to other Eliashberg function shapes, and make fits to the detailed data of Gallagher and Hickey (1985) on many glassy metals. In seeking to test to what extent current theory accounts for the thermopower temperature dependence, it is of interest to look for possible systematic discrepancies that might be attributable to electron–electron correlations or to incipient localisation, which have recently been found (Imry 1980; R app *et al.* 1982; Howson 1984) to produce significant effects in the temperature dependence of the resistivity of glassy metals.

2. Theoretical Calculations

General Expressions

For many years it was believed that electron–phonon renormalisation of the electron mass did not affect d.c. transport properties (Prange and Kadanoff 1964). However, Opsal *et al.* (1976) pointed out that because thermopower involves the *derivative* of conductivity with respect to energy, and the energy scale is renormalised, it is enhanced by the factor $1+\lambda$ at low temperatures. Additional contributions are expected from velocity and relaxation time renormalisation (Lyo 1978; Vilenkin and Taylor 1978), as well as higher order diagrams (Ono and Taylor 1980), so that the low temperature thermopower enhancement is not simply $1+\lambda$. The size (and even sign) of these additional contributions in real systems remains uncertain.

Fortunately, the situation with respect to the temperature dependence of these thermopower contributions is much simpler: the calculation of the decay of the $1+\lambda$ thermopower enhancement (Kaiser 1982) is also applicable for the velocity and relaxation time effects (Kaiser 1984), and even for the higher order diagram contribution in glassy metals where elastic disorder scattering is large (Kaiser and Stedman 1985). The reason for this similarity is that in each case the temperature dependence is governed by virtual phonons.

The diffusion thermopower S can therefore be written as a function of temperature T as

$$S/T = X_b \{1 + a\lambda \bar{\lambda}_S(T)\}, \quad (1)$$

where X_b is the bare thermopower parameter S_b/T (S_b being the bare thermopower) in the absence of the electron–phonon interaction. For non-magnetic systems we expect S_b to be approximately linear in temperature, i.e. X_b constant, as given by the usual Mott formula (see e.g. Blatt *et al.* 1976). The effective enhancement factor at low temperatures is $1+a\lambda$, the constant a accounting for the additional contributions mentioned above and changing the effective enhancement from $1+\lambda$. We mention that the form of equation (1) is still valid in the presence of spin fluctuations provided the system is not too near the magnetic transition, the effect of the spin fluctuation enhancement λ_{sf} being to reduce the value of the constant a by the factor $1+\lambda_{sf}$ (Kaiser *et al.* 1984).

Finally, $\bar{\lambda}_S(T)$ gives the temperature dependence of the thermopower effects due to the electron–phonon interaction, normalised to unity at zero temperature, and is

expressed by (Kaiser 1984)

$$\bar{\lambda}_S(T) = \int_0^\infty dE \frac{\alpha^2 F(E)}{E} G_S(E/k_B T) / \int_0^\infty dE \frac{\alpha^2 F(E)}{E}, \quad (2)$$

where k_B is Boltzmann's constant, and $\alpha^2 F(E)$ is the Eliashberg function which depends on the lattice vibration density of states $F(E)$ at energy E modified by an electron-phonon coupling parameter α^2 . The universal function $G_S(y)$ is (Kaiser 1982)

$$G_S(y) = \frac{3}{\pi^2} \int_{-\infty}^{+\infty} dz \left(-\frac{\partial f}{\partial z} \right) z \int_{-\infty}^{+\infty} dt \frac{f(t)y^2}{(t-z)^2 - y^2}, \quad (3)$$

where $f(t)$ is the Fermi function.

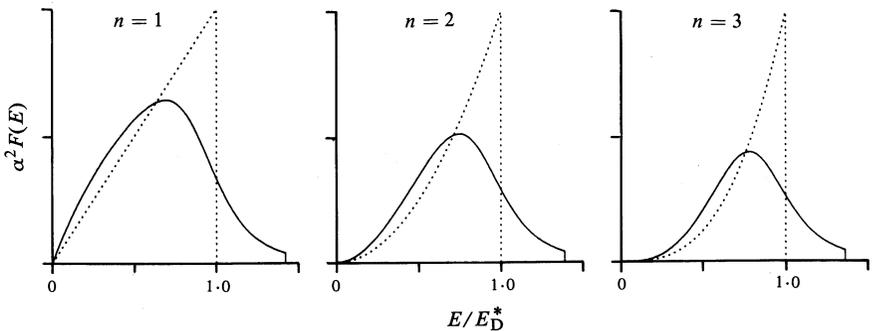


Fig. 1. Six models used for the Eliashberg function $\alpha^2 F(E)$, characterised by the power law index n of $\alpha^2 F(E)$ at low energies. The full curves show the smooth shapes defined by equations (4)–(7) with $m = 8$, and the dotted lines the corresponding Debye-like shapes. The vertical scale is arbitrary.

Models for the Eliashberg Function

The above theory indicates that the temperature dependence of the electron-phonon thermopower effects, represented by $\bar{\lambda}_S(T)$, is determined once the Eliashberg function $\alpha^2 F(E)$ is known. In crystalline materials the electron-phonon coupling α^2 shows little variation with energy (see e.g. Grimvall 1981), so $\alpha^2 F(E)$ follows the phonon density of states by showing an E^2 variation at low energies. In amorphous materials, the situation is less clear. As a result of loss of wavevector conservation, a variation of α^2 with E^{-1} , and so of $\alpha^2 F(E)$ with E , has been predicted and observed at low energies in amorphous simple metals (Bergmann 1971; Poon and Geballe 1978). However, Kimhi and Geballe (1980) found that $\alpha^2 F(E)$ varies with E^2 at low energies in the amorphous transition metals Nb and Mo, and Meisel and Cote (1981) calculated this behaviour taking account of phonon ineffectiveness when the phonon wavelength exceeded the electron mean free path. Finally, Keck and Schmid (1976), Froböse and Jäckle (1981) and Poon (1980) calculated an E^3 variation of $\alpha^2 F(E)$ at low energies. Thus, we carried out calculations for $\alpha^2 F(E)$ varying with E^n , where $n = 1, 2$ and 3 , as indicated in Fig. 1. The dotted lines in Fig. 1 show the Debye-like approximation in which the energy dependence is taken as constant up to a sharp cut-off, corresponding to the Debye energy and temperature. The phonon density of states in amorphous metals, however, is smeared out to some extent, resembling a

gaussian shape (except at lowest energies) in CuZr and MgZn (Suck *et al.* 1980, 1981; Holden *et al.* 1981). We, therefore, also carried out calculations for smooth $\alpha^2 F(E)$ shapes such as those shown by the full curves in Fig. 1, and represented analytically by

$$\alpha^2 F(E) = c\{(1 + \bar{E}^{-n})(1 + \bar{E}^m)\}^{-1}, \quad (4)$$

where n gives the exponent of the power law at low energies ($n = 1, 2$ or 3), m determines the shape of the high energy tail (with $m = 8$ for the examples in Fig. 1), c is an arbitrary normalisation constant that does not affect $\bar{\lambda}_s(T)$, and

$$\bar{E} = E/E_0. \quad (5)$$

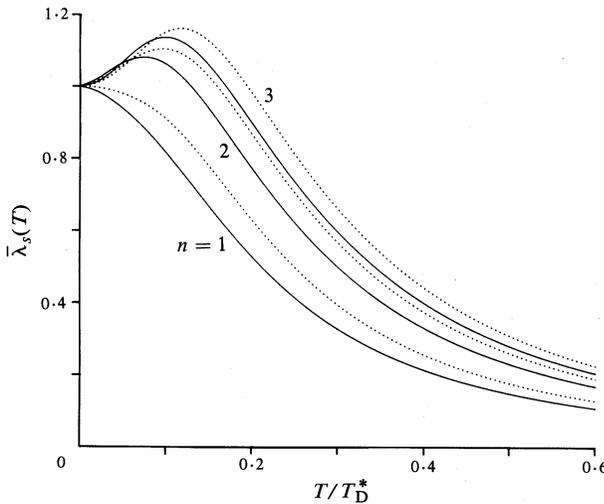


Fig. 2. Calculated temperature dependence of electron-phonon enhancement for the Eliashberg function models of Fig. 1 [full curves are for the smooth $\alpha^2 F(E)$ shapes and dotted curves for the Debye-like models]. For each set of three curves the value of n is indicated, while T_D^* is the effective Debye temperature defined by equation (6).

The effective Debye energy E_D^* and temperature T_D^* for our $\alpha^2 F(E)$ distributions are defined (Suck *et al.* 1981) as those for the Debye-like distributions having the same mean-square energy (indicated by the dotted lines in Fig. 1). In this case the energy scale parameter E_0 is given by

$$k_B T_D^* = E_D^* = E_0 \left(\frac{(n+3)I_2}{(n+1)I_0} \right)^{\frac{1}{2}}, \quad (6)$$

where

$$I_p = \int_0^{1.5} \bar{E}^p \{(1 + \bar{E}^{-n})(1 + \bar{E}^m)\}^{-1} d\bar{E} \quad (7)$$

[note that we have cut off the small high-energy tail of the $\alpha^2 F(E)$ distributions at $\bar{E} = 1.5$].

Results

Fig. 2 shows the calculated temperature dependence of electron-phonon enhancement corresponding to the six Eliashberg function models of Fig. 1. The following features are evident:

- (i) The curves scale with the Debye temperature T_D^* for a fixed shape of $\alpha^2 F(E)$.
- (ii) The behaviour of $\alpha^2 F(E)$ at low energies determines whether the predicted thermopower enhancement shows a peak at low temperatures, analogous to the peak in the electron-phonon mass enhancement at the Fermi level (Grimvall 1981). There is a peak for $n = 2$ or 3 but not for $n = 1$.
- (iii) The shape of the enhancement curves is less sensitive to variations in the high-energy shape of $\alpha^2 F(E)$, i.e. to the value of m or the presence of the Debye cut-off, the main effect being accounted for by a change in effective Debye temperature T_D^* . However, the peak in $\bar{\lambda}_S(T)$ is slightly smaller, and at lower temperatures relative to the decay in enhancement at higher temperatures, for a smooth $\alpha^2 F(E)$ than for a Debye-like $\alpha^2 F(E)$. For example, for $n = 2$, the temperature at which $\bar{\lambda}_S(T)$ has decayed to 0.5 is four times the temperature of the peak for the smooth $\alpha^2 F(E)$, but only 3.5 times for the Debye-like $\alpha^2 F(E)$.

3. Comparison with Experiment

Gallagher and Hickey (1985) have made accurate thermopower measurements on 14 non-magnetic glassy metals, so it is of interest to make a detailed comparison with our calculations. We have fitted each data set to the six enhancement curves in Fig. 2 to determine which value of n , and which shape, gives the best fit. The best of the three fits for each shape (smooth and Debye-like), with the corresponding value of n , are listed in Table 1, and best fits for the smooth $\alpha^2 F(E)$ shapes are compared with the data in Fig. 3. We can make the following observations:

- (i) Most of the alloys show a peak in S/T at low temperatures so, as concluded by Gallagher and Hickey (1985), the data suggest that in glassy metals $\alpha^2 F(E)$ varies as $n = 2$ or 3 rather than as $n = 1$ at low energies. Exceptions are the La-based alloys in which the thermopower is negative (see Fig. 3a).
- (ii) The fits using a smooth Eliashberg function are in general slightly better than those for a Debye-like shape, except for the $\text{Cu}_{90}\text{Hf}_{10}$ and $\text{Co}_{22}\text{Zr}_{78}$ glasses for which both fits are poor (see Fig. 3c).
- (iii) The fitted values of T_D^* are larger for the smooth $\alpha^2 F(E)$ shapes than for the Debye-like shapes (for the same value of n), as a result of the horizontal shift of the curves in Fig. 2 mentioned in Section 2. Since the effective Debye temperature T_D^* for thermopower enhancement applies to the $\alpha^2 F(E)$ distribution rather than the lattice vibration density of states $F(E)$, close agreement with values of T_D deduced from other properties such as the specific heat would not be expected. Nevertheless, it can be seen from Table 1 that there is in general reasonable agreement; for example, the lowest values of T_D^* are obtained for the La-rich glasses which have the lowest Debye temperatures.
- (iv) The fitted values of the low-temperature effective enhancement $a\lambda$ are similar to, but somewhat larger than, the usual mass enhancement (except for the poor fit for $\text{Co}_{22}\text{Zr}_{78}$ and the lower fitted value for $\text{Fe}_{24}\text{Zr}_{76}$), ranging from

Table 1. Best fits of the experimental thermopower measurements of Gallagher and Hickey (1985) to our theoretical expressions

Fits using Debye-like (D) and smooth (S) Eliashberg functions are shown on successive lines to aid comparison. The fitting parameters X_b , T_D and $a\lambda$ are defined in equations (1) and (6), with $n = 1, 2$ or 3 being the power of the energy dependence of $\alpha^2 F(E)$ at low energies, and σ^2 the residual variance of the fit. Also shown for comparison are the values of λ (estimated largely from superconducting transition temperatures) listed by Gallagher and Hickey (1985), and the Debye temperature T_D (from the specific heat), where available, from Mizutani (1983), Gallagher (1981) and Naugle *et al.* (1985).

System	$\alpha^2 F(E)$ model	n	X_b (nV K ⁻²)	$a\lambda$	T_D (K)	σ^2 (nV K ⁻²) ²	λ	T_D (K)
La ₇₈ Ga ₂₂	D	1	-5.31	0.95	115	0.043		
	S	1	-5.27	1.01	132	0.027	0.8	109
La ₇₆ Al ₂₄	D	1	-4.73	1.09	110	0.016		
	S	1	-4.70	1.17	123	0.012	0.8	125
Ni ₆₀ Nb ₄₀	D	2	1.57	0.66	127	0.006		
	S	2	1.56	0.69	141	0.006	0.6	240
Ni ₆₄ Zr ₃₆	D	2	2.50	0.97	213	0.010		
	S	3	2.50	0.96	207	0.009	0.4	
Ni ₃₆ Zr ₆₄	D	2	8.13	0.71	233	0.077		
	S	2	7.99	0.74	266	0.069	0.6	235
Cu ₅₀ Ti ₅₀	D	2	4.25	0.55	196	0.011		
	S	3	4.25	0.54	191	0.011	0.3	297
Fe ₂₄ Zr ₇₆	D	2	5.38	0.31	197	0.025		
	S	3	5.38	0.31	191	0.025	0.7	
Ti ₅₀ Be ₄₀ Zr ₁₀	D	2	6.47	0.49	224	0.067		
	S	2	6.41	0.51	253	0.062	0.3	190
Cu ₃₀ Zr ₇₀	D	2	8.42	0.62	216	0.047		
	S	2	8.34	0.64	242	0.034	0.6	184
Cu ₅₀ Zr ₅₀	D	2	8.69	0.59	200	0.043		
	S	3	8.69	0.58	192	0.039	0.4	231
Cu ₇₀ Zr ₃₀	D	2	9.65	0.51	192	0.042		
	S	3	9.65	0.50	186	0.039	0.3	230
Cu ₅₀ Hf ₅₀	D	3	11.36	0.52	142	0.033		
	S	3	11.30	0.53	156	0.028	0.4	
Cu ₉₀ Hf ₁₀	D	3	13.28	0.23	181	0.129		
	S	3	13.26	0.23	198	0.138	0.1	
Co ₂₂ Zr ₇₈	D	3	5.88	2.07	293	19.048		
	S	3	6.14	1.94	311	19.125	0.6	

about 1.1 for the La-rich glasses to 0.2 for Cu₉₀Hf₁₀. [Our fitted values for $a\lambda$ are slightly larger than those estimated from the high and low temperature S/T values by Gallagher and Hickey (1985) as a result of the slow decay of $\bar{\lambda}_S(T)$ at high temperatures and the stronger than expected decrease of the data often seen at the lowest temperatures.] Although there is evidence that other virtual phonon effects, at least in NiZr, increase the value of $a\lambda$ above λ when S is positive (Kaiser 1984; Kaiser and Stedman 1985), the reasonable agreement of the fitted $a\lambda$ values with λ suggests that energy-renormalisation enhancement has the dominant effect on the thermopower.

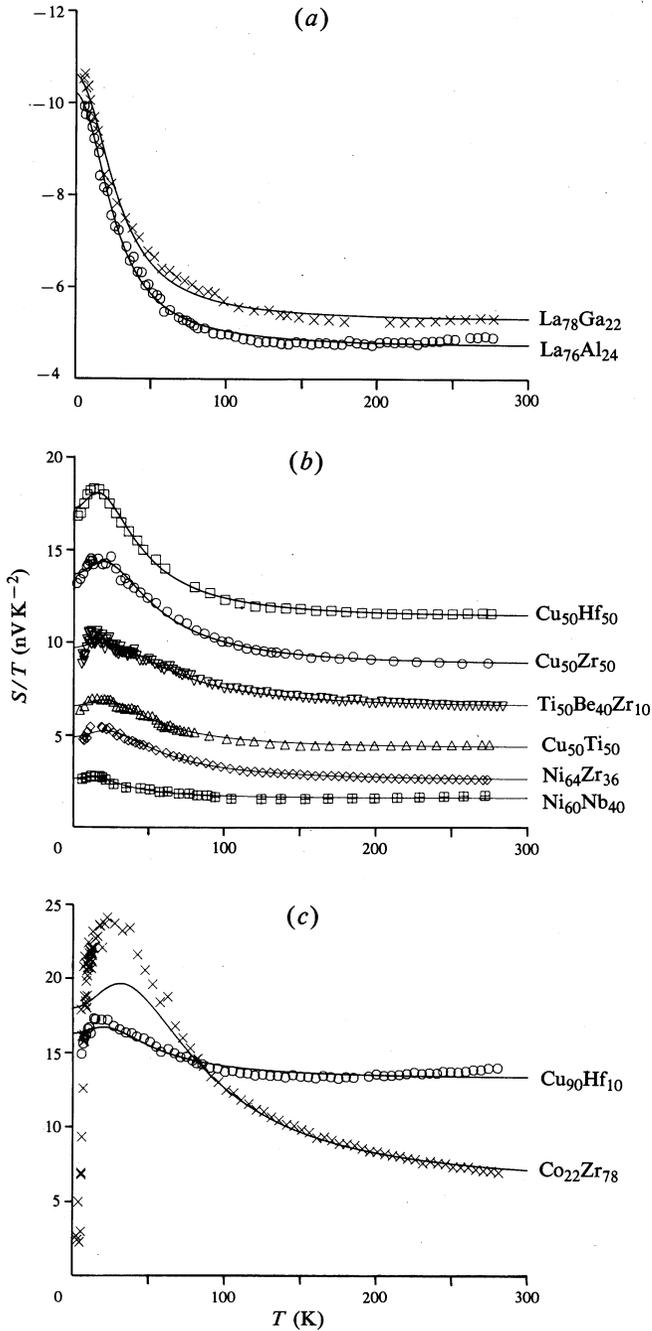


Fig. 3. Fits of the present calculations for the smooth Eliashberg model to the data of Gallagher and Hickey (1985) for: (a) two La-based glasses which best fit the $n = 1$ models (parameter values for the fits are given in Table 1); (b) six alloys with positive thermopower (some fits listed in Table 1 that overlap those shown are omitted); and (c) the last two alloys of Table 1 for which the fits are worst.

4. Conclusions

Our calculations are clearly able to explain the main features of the data with reasonable values of the effective Debye temperature T_D^* and zero-temperature effective enhancement $a\lambda$, providing further evidence that the characteristic curvature of glassy metal thermopower at low temperatures is largely due to electron-phonon enhancement. For all cases except the La-based glasses, a better fit is obtained for the Eliashberg function varying with E^2 or E^3 at low energies, rather than linearly, since a peak is seen in the low temperature thermopower. Naugle *et al.* (1985) found slightly better agreement for the E^2 dependence even for their La-based glassy metals and amorphous films. There is little difference in the quality of fits for the E^2 and E^3 variations, so we cannot make a choice between these possibilities. The data do give a slightly better fit for an Eliashberg function with a smooth rather than a sharp Debye-like peak, although we have shown that the calculated enhancement is not too sensitive to the shape of $\alpha^2 F(E)$ at higher energies.

The main discrepancy between theory and experiment is that the S/T data decrease more sharply than predicted as the temperature decreases below the peak, the discrepancy being the largest for $\text{Co}_{22}\text{Zr}_{78}$. The disagreement cannot be removed by allowing the peak size to increase by increasing the value of n , since as mentioned above, this pushes the peak to higher relative temperatures in conflict with the data. Obviously, it is difficult to measure the ratio S/T accurately in the low temperature limit, since both quantities go to zero, but there is a possibility that correlation effects that cause an increase in resistivity below about 15 K could also affect thermopower in this temperature range. Apart from this possible anomaly at very low temperatures, there is no obvious evidence for correlation or localisation effects in the temperature dependence of thermopower. In particular, the approximately linear thermopower S at higher temperature suggests that if incipient localisation has any effect it is largely to change the size of the linear slope (i.e. the parameter X_b).

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