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1990 J. Phys.: Condens. Matter 2 6755

(http://iopscience.iop.org/0953-8984/2/32/006)

J. Phys.: Condens. Matter 2 (1990) 6755–6762. Printed in the UK

Low-temperature enhancement of the thermopower of amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys

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Received 26 February 1990

Abstract. Enhancements of the low-temperature thermopower of amorphous melt-quenched $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys with $x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25 are shown to be in good agreement with the predictions for the electron–phonon enhancement. The results imply that the low-frequency part of the Eliashberg function $\alpha^2(\omega)F(\omega)$ is proportional to ω^n with $n > 1$ for these alloys. These alloys are weak-coupling superconductors, and the addition of Al reduces the electron–phonon coupling constant λ despite the tendency to strong coupling in simple amorphous metals.

1. Introduction

Over a limited temperature range the thermopower of most non-magnetic metallic glasses is linear in temperature, but at low temperatures, the magnitude of the slope is usually larger than at high temperatures, giving rise to a 'low-temperature knee'. Gallagher (1981) has interpreted this low-temperature enhancement in terms of the electron–phonon enhancement to the thermopower predicted by Opsal *et al* (1976). Large phonon-drag effects usually mask this effect in crystalline alloys; however, for amorphous metals the phonon scattering by electrons is much weaker than that arising from disorder so that the phonon-drag contribution to the thermopower of an amorphous metal is expected to be negligible (Jäckle 1980). Experimental evidence for a low-temperature knee in the thermopower for a large number of metallic glasses is now available: Cu–Zr (Gallagher 1981), Cu–Ti (Gallagher 1981, Fritsch *et al* 1984), Ni–Zr (Altounian *et al* 1983), $La_{0.76}Al_{0.24}$, $Ni_{0.5}Nb_{0.5}$, $Be_{0.4}Ti_{0.5}Zr_{0.1}$ (Gallagher 1981, Gallagher *et al* 1984), La–Ga (Armbrüster and Naugle 1981), Ca–Al and La–Al alloys (Naugle *et al* 1985) and for amorphous Cu–Ti films (Rathnayaka *et al* 1985). Calculations (Kaiser 1982) of the temperature dependence of the low-temperature thermopower produced by the electron–phonon mass enhancement using an experimental vibrational density of states and models of the electron–phonon coupling parameter $\alpha^2(\omega)$ for amorphous Cu–Zr and Cu–Ti alloys were in good agreement with the experiments by

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0953-8984/90/326755 + 08 $03.50

Gallagher (1981). Kaiser (1987) has shown that the thermopower for Chevrel compounds $Cu_{1.8}Mo_6S_{8-y}(Se, Te)_y$ also exhibits electron–phonon enhancement of the thermopower when the scattering is sufficiently large to suppress phonon drag.

Microscopic calculations (Nielsen and Taylor 1974, Hasegawa 1974, Lyo 1978, Vilenkin and Taylor 1978, Ono and Taylor 1980) indicate that there are a large number of effects related to the electron–phonon interaction which can affect the low-temperature thermopower. These include renormalisation of the electron energy, velocity and relaxation time plus higher-order terms involving virtual phonons. Many of the higher-order diagrams are not important for amorphous metals. Kaiser (1982, 1984) and Kaiser and Stedman (1985) have calculated the electron–phonon effects on thermopower for amorphous metals and shown that they can be broken into three terms: one due to energy renormalisation which is proportional to the bare thermopower S_b, another due to velocity and relaxation time renormalisation and a third due to higher-order terms. The temperature dependences of the three terms were found to be identical, but the latter two are not directly dependent on S_b. Kaiser and Stedman (1985) calculated the temperature dependence of the enhancement using a simple Debye phonon spectrum $F(\omega)$ and three models for the electron–phonon coupling in which the Eliashberg function $\alpha^2(\omega)F(\omega)$ varies as ω^n up to the Debye cut-off ω_D with $n = 1, 2$ or 3. The low-frequency part of $\alpha^2(\omega)F(\omega)$ plays the major role in determining the shape of the enhancement and also the superconducting transition temperature T_c of the metal. The soft-phonon coupling spectrum described by $n = 1$ gives a dramatically different temperature dependence for the low-temperature enhancement of the thermopower at temperatures below about $0.15\Theta_D$ than the harder spectra described by models with $n = 2$ or 3.

Bergmann (1971) has proposed a phase space argument which provides an explanation of the linear frequency ($n = 1$) dependence of $\alpha^2(\omega)F(\omega)$ observed at low frequencies in the tunnelling characteristics of most superconducting alloys containing only simple metals such as Ga, Bi, Pb or Sn. The low-frequency behaviour of $\alpha^2(\omega)F(\omega)$ with $n = 2$ corresponds to that predicted for high-resistivity metals by Meisel and Cote (1981) based on the Pippard–Ziman phonon ineffectiveness argument while the $n = 3$ model corresponds to predictions from the model of Poon (1980). Many simple amorphous metal alloys are very strong-coupling superconductors with electron-phonon coupling constants $\lambda \geqslant 2$ due to the low-frequency enhancement ($n = 1$) of $\alpha^2(\omega)F(\omega)$. Amorphous transition-metal alloys appear to be weak- to intermediate-coupling superconductors, however, with $\lambda = 0.7$–1.0 (Shull *et al* 1978). The limited tunnelling measurements of $\alpha^2(\omega)F(\omega)$ for amorphous transition metals (Nb and Mo) by Kimhi and Geballe (1980) indicate that $\alpha^2(\omega)F(\omega)$ is somewhat harder ($n = 2$ or 3) in agreement with the observation of weak- to intermediate-coupling behaviour. Analysis of the thermopower enhancement for amorphous La–Al and Ca–Al alloys (Naugle *et al* 1985) in terms of the Kaiser–Stedman predictions indicates that the Eliashberg function is best described by the harder spectra models, $n = 2$ or 3. We have recently studied the influence of the addition of a simple metal on superconductivity of amorphous Zr–Ni alloys (Agnolet *et al* 1990) and measured the electron transport properties of a series of amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys (Bhatnagar *et al* 1989). A low-temperature enhancement of the thermopower analogous to that attributed to electron–phonon enhancement was observed.

A detailed analysis of this thermopower enhancement, based on the predictions of Kaiser and Stedman (1985), is presented here for alloys with Al content $x = 0, 0.05, 0.10, 0.15, 0.20$ and 0.25. Although tunnelling measurements for $\alpha^2(\omega)F(\omega)$ for amorphous Al

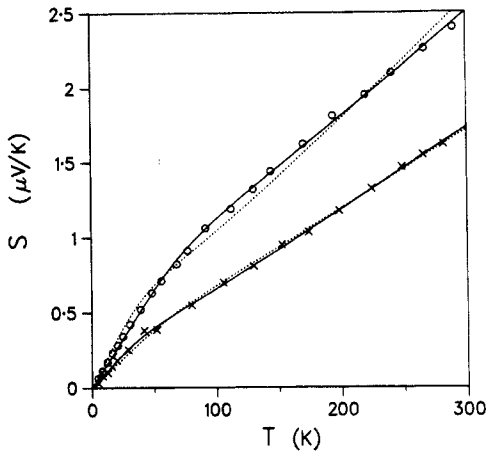

Figure 1. The measured thermopower as a function of temperature for two amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys with $x = 0$ (○) and $x = 0.25$ (×). Fits to a Debye Eliashberg function ($n = 2$) are shown, with adjustable effective Debye temperature T^* (——) and T^* equal to measured Debye temperature Θ_D (· · · ·).

are not available, one would expect it to show the softening at low energies typical of simple amorphous metals which produces the tendency to strong-coupling superconductivity. On the other hand, Zr–Ni alloys are relatively weak-coupling superconductors. Hence an interesting question regarding (Zr–Ni)–Al alloys is whether there is any sign of a softening of the Eliashberg function (i.e. a decrease in the exponent n) or an increase in T_c as the Al concentration is increased. Further investigation of the enhancement effect in thermopower also seems appropriate in view of the suggestion of an alternative explanation (Egorushkin and Melnikova 1987).

2. Experimental details

Master alloys of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ with $x = 0$, 0.05, 0.10, 0.15, 0.20 and 0.25 were prepared by melting 99.9% pure Ni, 99.6% pure Zr and 99.999% pure Al in an argon atmosphere with an arc furnace. Metallic glass ribbons were prepared from the homogenised master alloys in an argon atmosphere by induction melting the alloy in a quartz crucible and ejecting it onto a single-roller melt spinner. The surface wheel speed was approximately 27 m s^{-1}. The thermoelectric power of the glassy ribbons, 1–2 mm wide and 15–30 μm thick, was measured against a Pb reference foil using a standard differential technique. The absolute error is estimated at 5–8% over the temperature range from 4 to 280 K. The relative error is somewhat better. Further experimental details have been described elsewhere (Bhatnagar *et al* 1989).

3. Results

Examples of the thermopower for these alloys are plotted as a function of temperature in figure 1. The sign of the thermopower in all the alloys is positive. At higher temperatures, S is approximately linear in temperature but, as the temperature decreases, a 'low-temperature knee' is observed. This 'knee' corresponds to the rapid increase in

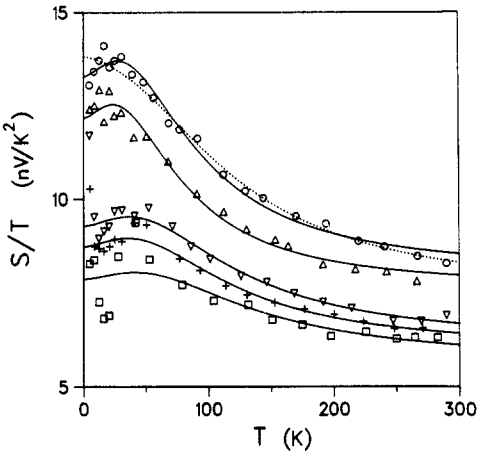

Figure 2. The thermopower divided by the temperature as a function of temperature for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys with (from the top) x = 0, 0.05, 0.10, 0.15 and 0.20: ——, fits to equation (4) with an $n = 2$ smooth function for $\alpha^2(\omega)F(\omega)$ with T^* as an adjustable parameter (fitted parameters are listed in table 1); · · · ·, predicted behaviour for $n = 1$.

S/T as the temperature decreases (figure 2) seen for all these alloys. The high-temperature value of S/T decreases as the Al concentration is increased. This decrease in S with x is discussed in relation to the behaviour of the other transport coefficients (Hall coefficient and resistivity) by Bhatnagar *et al* (1989) and Rhie *et al* (1990). The onset temperature for the enhancement does not appear to vary appreciably as a function of concentration. At the lowest temperatures, S/T appears to show a decrease for all concentrations of Al.

4. Analysis of data

Kaiser (1984) and Kaiser and Stedman (1985) showed that the thermopower of a metallic glass can be expressed as

$$X(T) = S/T = X_b[1 + \lambda\bar{\lambda}_{ph}(T)] + \alpha'\lambda\bar{\lambda}_{ph}(T) \tag{1}$$

where $X_b = S_b/T$ is the bare thermopower parameter (taken as a constant according to the usual Mott formula) and $\lambda\bar{\lambda}_{ph}$ is the temperature-dependent enhancement of the thermopower with

$$\bar{\lambda}_{ph} = \int_0^\infty d\omega\, \omega^{-1}\alpha^2(\omega)F(\omega)G_s\left(\frac{\hbar\omega}{k_B T}\right) \Big/ \int_0^\infty d\omega\, \omega^{-1}\alpha^2(\omega)F(\omega) \tag{2}$$

with the universal function $G_s(y)$ defined by

$$G_s(y) = \frac{3}{\pi^2}\int dz\left(-\frac{\partial f}{\partial z}\right)z \int dt \frac{f(t)y^2}{(t-z)^2 - y^2}. \tag{3}$$

Here f is the Fermi function, $F(\omega)$ is the phonon density of states, $\alpha^2(\omega)$ is the frequency-dependent electron–phonon coupling constant and λ is the parameter describing the mass enhancement of the specific heat and the electron–phonon coupling in the theory of superconductivity. The first correction is proportional to the bare thermopower S_b and arises from energy renormalisation. The second term arises from velocity and relaxation time renormalisation and higher-order scattering diagrams. The effect of

spin-fluctuation enhancement λ_{sf} can be included by replacing the term $1 + \lambda\bar{\lambda}_{ph}$ with $1 + \lambda\bar{\lambda}_{ph} + \lambda_{sf}$ (Kaiser *et al* 1984). We have fitted the thermopower to the relation

$$X(T) = X'_b[1 + a\lambda\bar{\lambda}_{ph}(T)] \tag{4}$$

for several different models of $\alpha^2(\omega)F(\omega)$. The parameters in the fit are X'_b, $a\lambda$ and the effective Debye temperature T^* for the particular model $\alpha^2(\omega)F(\omega)$ distribution. The models for $\alpha^2(\omega)F(\omega)$ include a Debye-like approximation with $\alpha^2(\omega)F(\omega)$ proportional to ω^n ($n = 1, 2, 3$) up to the sharp cut-off frequency corresponding to T^* and smoothed spectra (Kaiser *et al* 1986) for $\alpha^2(\omega)F(\omega)$ with the same ω^n low-frequency dependence. When $n = 2, 3$ the electron–phonon enhancement produces a peak in S/T at T/T^* near 0.1 which is absent for $n = 1$ (as illustrated in figure 2). In the absence of spin-fluctuation enhancement, X'_b is the bare diffusion thermopower parameter, $X_b = S_b/T$ and $a\lambda$ is $(1 + \alpha' X_b^{-1})\lambda$, which is usually only slightly larger than the electron–phonon coupling λ. When spin fluctuations are important and the characteristic spin-fluctuation temperature is larger than T^*, X_b is $X'_b(1 + \lambda_{sf})^{-1}$ and $a\lambda$ is $(1 + \alpha' X_b^{-1})\lambda(1 + \lambda_{sf})^{-1}$.

We show in figure 1 fits of the thermopower to equation (4) using a Debye model ($n = 2$) for the Eliashberg function $\alpha(\omega)F(\omega)$. The fits are carried out with the effective Debye temperature T^* as an adjustable parameter (full curves) or held constant with the value $T^* = \theta_D$ (dotted curves) determined from heat capacity measurements (Yamada *et al* 1987). The largest difference between the two fits is for the $x = 0$ sample, while the difference for the other samples (e.g. for the $x = 0.25$ sample illustrated) is smaller.

The low-temperature behaviour of $\alpha^2(\omega)F(\omega)$ is shown more clearly in the plots of the ratio S/T in figure 2 (the data for $x = 0.25$ are omitted for clarity). Also shown in the figure are fits to the smooth Eliashberg function for $n = 2$ with T^* adjustable, which give a better overall fit to the data than the Debye-like function, as might be expected on physical grounds (the improvement, however, is very small, as found previously (Kaiser *et al* 1986)). Table 1 lists values of the fitting parameters for these fits, and also for fits to Debye functions ($n = 2$) for T^* adjustable and $T^* = \Theta_D$. We also include in figure 2 an example of the smooth $\alpha^2(\omega)F(\omega)$ function for the $n = 1$ case (dotted curve), which does not fit the data quite as well since it shows no peak in S/T at low temperatures. The $n = 3$ curves are rather similar to those for $n = 2$, with a slightly larger peak, and also fit the data well.

It can be seen from table 1 that there is some variation in the values of T^*, $a\lambda$ and X_b depending on the model assumed for the Eliashberg function. Values of T^* when it is adjustable are generally larger than the values Θ_D of the Debye temperature deduced from the specific heat, although close agreement is not expected since Θ_D is not derived for the Eliashberg function. There is no significant difference between $a\lambda$ for the Debye-like or smooth Eliashberg functions (with T^* adjustable). Values of $a\lambda$ for the $n = 1$ models are higher than those for $n = 2$, while those for $n = 3$ are slightly smaller. The decrease in X'_b as x increases reflects the decrease in S/T at high temperatures and indicates a reduced overall energy dependence of the electronic properties affecting conductivity near the Fermi level.

For comparison, values of the electron-phonon coupling can be estimated from the McMillan (1968) formula for the superconducting transition temperature

$$T_c = (\langle\omega\rangle/1.2)\exp[-1.04(1 + \lambda)/(\lambda - \mu^* - 0.62\mu^*\lambda)] \tag{5}$$

where

$$\langle\omega\rangle = \int_0^\infty d\omega\, \alpha^2(\omega)F(\omega) \Big/ \int_0^\infty d\omega\, \omega^{-1}\alpha^2(\omega)F(\omega). \tag{6}$$

This expression was obtained by linearisation of the Eliashberg equations and use of a

Table 1. Summary of results from fitting $X = S/T$ to the theory of the electron–phonon enhancement for $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ amorphous alloys. The fitted parameters are X'_b and $a\lambda$. For each concentration the first line gives results using a Debye function ($n = 2$) for $\alpha^2(\omega)F(\omega)$. The first values (second and third columns) listed are obtained with the effective Debye temperature T^* as a fitting parameter while, for the second set of values (fifth and sixth columns), T^* was set equal to measured values of the Debye temperature Θ_D. The fitted values given on the second line for each concentration (second, third and fourth columns) are those determined for a smooth $\alpha^2(\omega)F(\omega)$, again with $n = 2$. The electron–phonon enhancement λ_m is estimated from the McMillan formula with $\mu^* = 0.13$.

x	X'_b (nV K^{-2})	$a\lambda$	T^* (K)	X'_b (nV K^{-2})	$a\lambda$	Θ_D (K)	T_c (K)	λ_m
0	8.2	0.61	320	9.0	0.51	220[a]	2.54[c]	0.58
	8.0	0.65	360					
0.05	7.8	0.56	280	8.1	0.51	228[a]	1.98[b]	0.54
	7.6	0.60	320				2.05[c]	
0.10	6.4	0.48	380	6.9	0.39	276[a]	1.52[b]	0.49
	6.2	0.50	490				1.62[c]	
0.15	6.2	0.44	390	6.8	0.32	240[a]	1.06[b]	0.47
	6.0	0.46	480					
0.20	5.8	0.36	460	6.4	0.24	260[a]	0.86[b]	0.45
	5.7	0.39	550					
0.25	5.6	0.47	260	5.3	0.54	357[a]		
	5.5	0.49	290					

[a] From Yamada *et al* (1987) for amorphous $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$ alloys.
[b] Agnolet *et al* (1990).
[c] Bhatnagar *et al* (1989).

model density $F(\omega)$ of phonon states representative of niobium. For the niobium density of phonon states, $\langle\omega\rangle/1.2$ can be replaced by $\theta_D/1.45$, but this approximation leads to much poorer agreement between the predicted value of T_c and the measured value than that for T_c predicted from (5) and (6) with tunnelling-derived values of $\alpha^2(\omega)F(\omega)$ (Dynes 1972). However, since no tunnelling data for these alloys are available, we have estimated the electron–phonon enhancement λ_m from measured values of T_c and θ_D from (5) with $\langle\omega\rangle/1.2$ replaced by $\theta_D/1.45$. Values of λ_m for comparison with $a\lambda$ are listed in table 1.

5. Conclusion

The fact that the data suggest a value of $n = 2$ or 3 for the energy dependence of the Eliashberg function at low energies agrees with the theoretical calculations of Poon (1980) and Meisel and Cote (1981), which give a reduced electron–phonon coupling $\alpha^2(\omega)$ at low energies owing to the more localised nature of d electrons and the ineffectiveness of coupling between electrons and phonons when the phonon wavelength exceeds the electron mean free path. There is no observable softening in $\alpha^2(\omega)F(\omega)$ at low energies as seen in simple metal alloys (Bergmann 1971) up to an Al content $x = 0.25$ (unfortunately, we have not been able to make amorphous alloys beyond this concentration). This apparent higher-power behaviour of $\alpha^2(\omega)F(\omega)$ is also consistent with the fact that there is no enhancement of T_c as Al concentration is increased. In fact, T_c falls with increasing x (table 1), in such a way that the λ_m deduced from the McMillan

formula parallels the values of $a\lambda$ deduced from the thermopower fits which show a similar decrease. (Since we do not expect $k_B\Theta_D$ to be the same as the root mean square energy for $\alpha^2(\omega)F(\omega)$, and since allowing T^* to vary gives a better description of the data, we take the values of $a\lambda$ from thermopower to be those given by either of the fits in table 1 with T^* varied.) This agreement of $a\lambda$ and λ_m suggests that the decrease in T_c is associated with a decrease in λ, which in turn could be caused by the decrease in the density $N(0)$ of states at the Fermi level (Agnolet *et al* 1990). The increase in resistivity as the Al concentration increases is also consistent with a reduction in $N(0)$, although increasing structural disorder would also increase resistance by decreasing the electronic mean free path.

Finally, the agreement that we find in magnitude, and change with Al concentration, between $a\lambda$ and λ_m also provides evidence that the enhancement is in fact associated with the electron–phonon interaction, provided of course that the additional terms that could change the parameter a from the value unity are not large. In the model of Egorushkin and Melnikova (1987), in which a similar thermopower shape arises from the interference of electron–electron interactions and elastic scattering from concentration fluctuations, no obvious connection between λ_m and thermopower enhancement would be expected, and no correlated decrease in enhancement size and T_c. Further, electron–electron ineraction effects normally increase as resistivity increases (Cochrane and Strom-Olsen 1984), whereas the enhancement in our data shows the opposite behaviour. We conclude that our analysis produces additional evidence in favour of the electron–phonon interaction as the cause of the thermopower knee.

Acknowledgments

This research was supported in part by grants from the National Science Foundation (DMR-87-15433), the Robert A Welch Foundation (Houston, TX) and the Texas Advanced Technology Program (3606). We also acknowledge support in establishing the facilities for these experiments from the Texas A&M Board of Regents Materials Research Initiative. One of us (AKB) would like to thank the Physics Department of Texas A&M University for their support and hospitality during his stay. We thank Mr G Mountjoy for assistance in the data analysis.

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