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The thermopower of amorphous Nb–Si near the metal–insulator transition

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Abstract. We present experimental thermopower data for amorphous $Nb_{100-x}Si_x$ ($55 \geqslant x \geqslant 91$) in the temperature range 4 K–280 K which extends through the metal/insulator transition. The higher Nb content samples clearly show metallic behaviour having a low temperature 'knee' attributed to electron–phonon mass enhancement. As the Nb concentration is reduced, deviations away from this behaviour are marked, the thermopower becoming largely independent of temperature. Further reduction of the Nb content causes the temperature dependence to return. At low temperatures, close to the metal/insulator transition, the thermopower appears to diverge and does not seem to conform to the universal behaviour described by Enderby and Barnes in 1990. This is probably because the density of states is still large at the Fermi energy and there is an appreciable hopping contribution to the conductivity.

1. Introduction

Thermoelectric effects in metals are very sensitive to the electronic structure; this dependence is quite complex and renders interpretation of experimental data difficult. However, some useful indications about the electronic structure near the Fermi energy can be obtained from the thermopower. The details of the behaviour of the thermopower near the metal/insulator transition have not been well studied (Mott 1987) and experimentally there have been relatively few attempts to follow the thermopower through the transition. Close to the metal/insulator transition we can expect the thermopower to behave in a number of ways. If there is a 'true' gap in the density of states the thermopower may have an activated temperature dependence diverging as $1/T$. On the other hand, in the variable range hopping (VRH) regime at low temperatures, the thermopower is predicted to go to zero as $\sqrt{T}$. If the conduction band is very narrow, or if the electrons are highly correlated, the Heikes formula predicts a temperature independent behaviour.

The magnitude of the thermopower in the metallic regime (high Nb concentration samples) is usually discussed in terms of the Mott formula (Ziman 1960):

$$S = (3\pi^2 k_B^2 T/eE_F)(\mathrm{d} \ln \sigma/\mathrm{d} \ln E)_{E=E_F}. \tag{1}$$

This expression is derived from the Kubo–Greenwood formula for a degenerate electron gas, and a slowly varying density of states or $\sigma(E)$. If the main conduction mechanism is d-band conduction, as we might expect with a high Nb concentration, then the conductivity is proportional to d density of states squared, $(N_d(E_F))^2$ (Weir *et al* 1983), and

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the thermopower is determined by $\mathrm{d}\ln N_d(E)/\mathrm{d}\ln E$. In an amorphous system the density of states is unlikely to have any sharp features and so the thermopower is expected to be only a few $\mu V\,K^{-1}$. Close to the metal/insulator transition, but on the metallic side and at low temperatures, equation (1) is still appropriate. Here we might expect $\sigma \propto (E - E_c)^{\nu}$, where E_c is the position of the mobility edge and ν is a characteristic exponent; the criterion for low temperatures is $k_B T \ll (E_F - E_c)$ so that the region around E_c is not sampled. In this case, $S \propto (E_F - E_c)^{-1}$:

$$S = 3\pi^2 \nu (k_B/e) k_B T/(E_F - E_c). \tag{2}$$

Therefore the low temperature behaviour of S/T would appear to diverge as the metal/insulator transition was approached. This kind of argument would also lead to a prediction of large thermoelectric figures of merit. The thermoelectric figure of merit is defined as $K = ST\sigma/\kappa$, thus close to the metal–insulator transition, $K \propto (E - E_c)^{\nu-2}$ and, since ν is typically between 0.5 and 1, K might diverge at the transition.

However, Enderby and Barnes (1990) considered an exact evaluation of the Kubo–Greenwood formula at all temperatures up to the Fermi temperature. The important point they make is that when there is a mobility edge, $\sigma(E)$ cannot be expanded in a Taylor series about E_F since it is not differentiable at the critical energy $E = E_c$ (the point at which the conductivity is zero at $T = 0$ K). Their main result is that at the mobility edge ($E_F = E_c$) the thermopower does not diverge but has a temperature independent universal value. The value is of the order of $100\,\mu V\,K^{-1}$ but depends only on the value of the conductivity exponent ν.

Therefore for samples close to the metal/insulator transition, we might expect to see a thermopower of the order of, or greater than, $100\,\mu V\,K^{-1}$. In fact we observe a surprisingly small thermopower for amorphous Nb–Si in the vicinity of the metal/insulator transition along with a very small temperature dependence. However, there is evidence that thermopower diverges at the lowest temperatures and closest to the transition. Because the thermopower does not change very much through the transition, the evidence for a metal–insulator transition, which in this series of samples is at 89% Si, comes from resistivity and magnetoresistance measurements carried out on samples produced under the same conditions (Pounder *et al* 1991).

2. Experimental details

All specimens were produced by RF magnetron sputtering from targets which were of Specpure Nb and Si. Sample thickness was measured using a DEKTAK profiler and were all of the order of 0.6 μm. Sample size was 6 mm × 45 mm. Composition analysis was done using EDAX.

Thermopowers were measured in a purpose-built cryostat capable of taking measurements in the temperature range 1.2–280 K. A conventional integral technique was used, one end of the sample being held at a fixed temperature while the temperature of the other end is slowly increased. Typically the temperature was increased at a rate of 0.5 K min^{-1}. Temperature difference across the sample was measured using a Au[Fe(0.07%)]–chromel thermocouple and the thermopower of the sample was measured with reference to lead (Roberts scale).

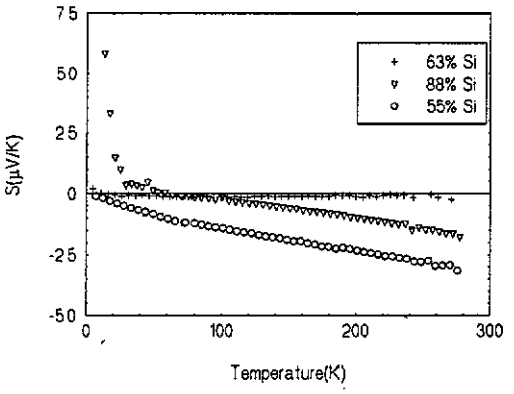

Figure 1. The thermopower versus temperature for $Nb_{100-x}Si_x$: (○) $x = 55$; (▽) $x = 63$; (+) $x = 88$.

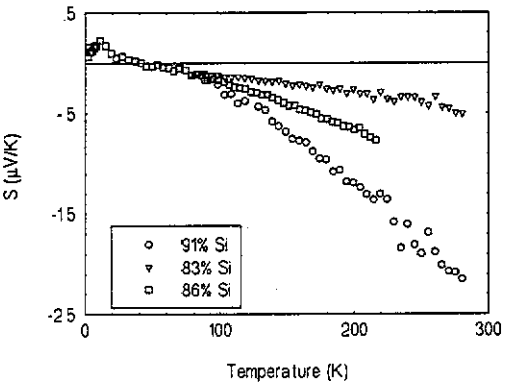

Figure 2. The thermopower versus temperature for $Nb_{100-x}Si_x$:(▽) $x = 83$; (□) $x = 86$; (○) $x = 91$.

3. Results and discussion

Generally, we find that all our thermopowers are small and negative as shown in figures 1 and 2. The sample $Nb_{45}Si_{55}$ is clearly a metal ($\rho \approx 200\ \mu\Omega$ cm) and exhibits electron–phonon mass enhancement with the low temperature 'knee' (Gallagher *et al* 1981). Although the diffusion thermopower, S_d, of a metal is proportional to temperature (1), at low temperatures the thermopower is also enhanced by electron–phonon mass enhancement, and the measured thermopower, S, is given by $S = (1 + \lambda(T))S_d$. The enhancement is largest at low temperatures, but $\lambda(T)$ approaches zero as the Debye temperature is reached. The phonon drag contribution to the thermopower, which normally dominates the low temperature thermopower, is not present in these amorphous systems because the phonon system is maintained in equilibrium by the disorder scattering (Gallagher *et al* 1981).

Figure 3 shows S/T for the $Nb_{44}Si_{55}$. The temperature dependence of S/T reflects the temperature dependence of $(1 + \lambda(T))$. The mass enhancement factor at low temperatures, $1 + \lambda(0)$ can be derived from the ratio of S/T at low temperatures to S/T at high temperatures, where $\lambda(T)$ is zero (Gallagher *et al* 1981). For the $Nb_{45}Si_{55}$ sample, the value of $\lambda(0)$ derived in this way is 0.46 ∓ 0.03. The Debye temperature can be roughly estimated from the thermopower since the value of S/T falls to half its low temperature value at approximately $\Theta_D/3$, in this case Θ_D is approximately 300 K. The

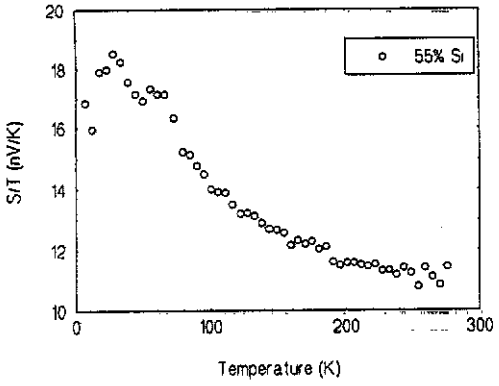

Figure 3. S/T versus temperature for $Nb_{45}Si_{55}$ showing the low temperature peak and the overall temperature dependence of $(1 + \lambda T))$.

McMillan formula can also be used to determine λ using this estimate of Θ_D, the measured value of T_c (2.9 K) and an estimated μ^* of 0.13. This estimate of λ is 0.48 ∓ 0.02 which compares well with the value obtained directly from the mass enhancement of the thermopower, showing that the low temperature knee observed in this sample is consistent with electron–phonon mass enhancement. A low temperature peak in the S/T is also observed at around 15 K. This indicates that the Eliashberg function $\alpha^2F(\omega)$ is proportional to ω^n, where $n > 2.5$ (Howson and Gallagher 1988).

The rest of the samples we have investigated do not have the expected linear thermopower with a low temperature knee. On increasing the silicon content further in this system to sample $Nb_{37}Si_{63}$ the observed thermopower becomes almost independent of temperature over a wide temperature range with a constant thermopower of approximately 0.1 $\mu V K^{-1}$. As the silicon content is increased still further to $Nb_{17}Si_{83}$, the temperature dependence begins to increase again but is never as large as the clearly metallic behaviour observed in the $Nb_{44}Si_{55}$ sample and no electron–phonon mass enhancement is observed. This is despite the fact that these samples are still well within the metallic regime. Since the magnitude of the thermopower is related to the logarithmic derivative of the conductivity and through the conductivity to the density of states, such small thermopowers imply a rapid drop in the slope of the density of states at the Fermi energy as though the Fermi energy were in the region of a minimum in the density of states, this minimum being relatively insensitive to the Nb concentration once the concentration is below ≈40%. Such a minimum might be evidence for splitting of the Nb d band at around this concentration and there is some evidence for this from recent XPS (Soldner *et al* 1989). The other possibility is that we have contributions to the thermopower from two separate bands, the contributions being of opposite sign and cancellation leading to a small thermopower.

It is possible to get a small temperature independent thermopower if the electron gas is highly correlated as in the case of a strong Hubbard U on-site repulsion between the Nb d electrons. This is unlikely at such a high Nb concentration but might be important closer to the transition where the Nb concentration is low and there is little overlap between neighbouring Nb sites.

$Nb_{14}Si_{86}$ is the first sample to exhibit signs of an impending metal–insulator transition, although the thermopower is still surprisingly small over most of the temperature range. The thermopower changes sign at approximately 30 K, becoming positive at low temperatures and increasing rapidly before peaking at around 15 K. Sample $Nb_{12}Si_{88}$,

which is just on the metallic side of the transition—determined from resistivity measurement reported elsewhere (Pounder and Howson 1991)—follows a similar trend to $Nb_{14}Si_{86}$ but changes sign at approximately 55 K and diverges to large positive values with no apparent peak. However, the sample is still metallic so the thermopower must be zero at $T = 0$ K and a peak must exist at lower temperatures. This large peak may be evidence of the Fermi energy being within k_BT of the mobility edge. For temperatures such that $k_BT \ll E_F - E_c$ equation (2) is appropriate. The onset of the peak at a few tens of Kelvin implies $E_F - E_c$ is of the order of 0.002 eV. This would lead to a thermopower of about 50 mV K^{-1} at around 1 K (2).

Sample Nb_9Si_{91} had an extremely high resistance even at room temperature and it proved impossible to measure the thermopower, using our integral method, below 100 K. This sample is clearly on the insulating side of the transition and the rising thermopower at 300 K is probably the onset of activated behaviour at higher temperatures. However, below 300 K this sample again has a surprisingly small thermopower which has similar features to the thermopower measured on the metallic side. It appears that the thermopower may change sign at low temperatures although unfortunately we were unable to measure S at a low enough temperature to confirm this. The resistivity measurements on this sample (Pounder and Howson 1991) show variable-range hopping behaviour below 300 K and this is probably why the thermopower is so small in this temperature range. At higher temperatures we might expect to see activated behaviour.

4. Conclusion

We have measured the thermopower of a series of Nb–Si amorphous films. The high Nb content samples behave as expected exhibiting a metallic-like thermopower with evidence of electron–phonon mass enhancement. For samples with lower Nb content, the thermopower drops to very small values. This may be evidence for a quite dramatic change in the electronic structure of Nb–Si around 40% Nb. The thermopowers of the samples close to the metal–insulator transition continue to be surprisingly small, although there is evidence for a diverging thermopower at low temperatures which we have argued is related to the proximity of the mobility edge.

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