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CHARGE TRANSPORT IN CONDUCTING POLYMERS: POLYACETYLENE NANOFIBRES

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The preparation of individual polyacetylene nanofibres has allowed a more probing investigation of the properties of polyacetylene. A significant discovery is that at low temperatures, polyacetylene nanofibres show temperature-independent Zener-type tunnelling, that we suggest is tunnelling of the conjugated-bond pattern along single polyacetylene chains. At higher temperatures, the current shows a strong increase with temperature and the nonlinearity of the current-voltage characteristics decreases. We make a comparison with similar behaviour found in single-wall carbon nanotube networks, and show that the decrease in nonlinearity is consistent with our generic calculations for fluctuation-assisted tunnelling and thermal excitation. There is no evidence for superconductivity in resistance measurements on polyacetylene. The thermoelectric power of polyacetylene and other bulk organic conducting polymers indicates the absence of significant superconductivity arising from the conventional electron-phonon mechanism.

Keywords: current-voltage characteristics; nanofibres; polyacetylene; superconductivity

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1. INTRODUCTION

The conduction process in conducting polymers has some unusual features compared to that in conventional metals, as was evident from the earliest measurements [1–3]. One such feature is the mixture of metallic and non-metallic character seen even for highly conducting samples. A heterogenous conduction model is able to account for the change from non-metallic to metallic temperature dependence as temperature increases in highly conducting polymers, and also for the fact that thermopower remains metallic in character down to low temperatures [4,5]. The origin of this heterogeneity is the incomplete crystallinity of the polymers, which gives rise to disordered regions around the small crystallites [6]. Data for other aspects of conduction are also consistent with this model [7]. An analogous model involving metallic conduction interrupted by barriers accounts for the conduction behaviour observed in single-wall carbon nanotube networks [8].

Individual polyacetylene nanofibres of diameter 10–40 nm placed over electrodes separated by 100–200 nm provide a new way of probing for the intrinsic properties of polyacetylene that are not evident from bulk samples [9,10]. An advantage of the short length is that conduction at electric fields above 10^5 V/cm can be investigated by applying a potential difference of only a few volts across the electrodes. Using fields of this magnitude, measurements down to 2 K on lightly-doped polyacetylene nanofibres [11] revealed a remarkable change below 10–30 K to temperature-independent Zener-type current-voltage (*I-V*) characteristics. We have shown that this behaviour is consistent with tunnelling of the conjugated-bond pattern along a single polyacetylene chain, an intriguing new possibility for nanoscale conduction [12].

In this paper, we investigate the *I-V* characteristics of polyacetylene nanofibres at higher temperatures where an ohmic component becomes clearly visible and the nonlinearity is reduced. A comparison is made with the measured *I-V* characteristics of single-wall carbon nanotube (SWCNT) networks where similar behaviour is seen. We show that the evolution of the shape of these *I-V* characteristics is consistent with the generic behaviour of our numerical calculations for fluctuation-assisted tunnelling and thermal activation. Another aspect of current interest is the question of whether the incomplete crystallinity of bulk conducting polymers masks a possible presence of superconductivity. Superconductivity was reported in regioregular samples of poly(3-hexylthiophene), but this report has now been discounted [13]. Long ago polyacetylene was proposed as a candidate for high-temperature excitonic superconductivity [14]. We investigate the thermoelectric power of the highly conducting polymers, since it

is not so affected by the disorder as is resistivity, and metallic diffusion thermopower provides a probe of the electron-phonon interaction that causes conventional superconductivity.

2. *I-V* CHARACTERISTICS

At very low temperatures (below 10–30 K), the *I-V* characteristics of lightly-doped polyacetylene nanofibres [11,12] follow the expression for Zener-type tunnelling [15]:

$$\sigma = \frac{j}{E} = \sigma_0 \exp\left(-\frac{E_0}{E}\right) \tag{1}$$

where j is the current density and σ the field-dependent conductivity at electric field E. For the case of tunnelling between the valence and conduction bands in a semiconductor [15], the fit constants σ_0 and E_0 can be expressed in terms of the semiconductor energy gap. Equation (1), however, has general application where the tunnelling distance is inversely proportional to the electric field, and is also the behaviour expected for tunnelling of charge-density waves as proposed by Maki [16] and Bardeen [17]. For the *trans*-polyacetylene chain, the lowest-energy charge excitations are solitons. We have therefore proposed [12] that tunnelling of a portion of the conjugated-bond system, with the creation of a positively-charged soliton at one end and a negatively-charged soliton at the other, is the mechanism of the Zener-type tunnelling conduction observed in polyacetylene nanofibres. The value of the measured field coefficient E_0 indicates that in this case, in contrast to the CDW case, tunnelling occurs along a single polyacetylene chain [12].

At higher temperatures, the *I-V* characteristic for polyacetylene nanofibres develops a strong temperature dependence, and the shape deviates from the Zener-type behaviour. In a more conducting nanofibre [10] such as that yielding the data in Figure 1, the nonlinearity of the *I-V* characteristic decreases as temperature increases, and an ohmic component is clearly seen at low fields. Near room temperature the ohmic component is dominant for these data. Obviously the conduction mechanism in this regime is very different from the field-driven Zener-type tunnelling seen at very low temperatures (for which the conductivity goes to zero in the low-field limit).

As illustrated in Figure 2, a remarkably similar set of *I-V* characteristics was measured by Kim *et al.* [18] in networks of SWCNTs. In this case fluctuation-induced tunnelling as proposed by Sheng [19] appeared to be consistent with the field dependence and the low-field conductivity temperature dependence.

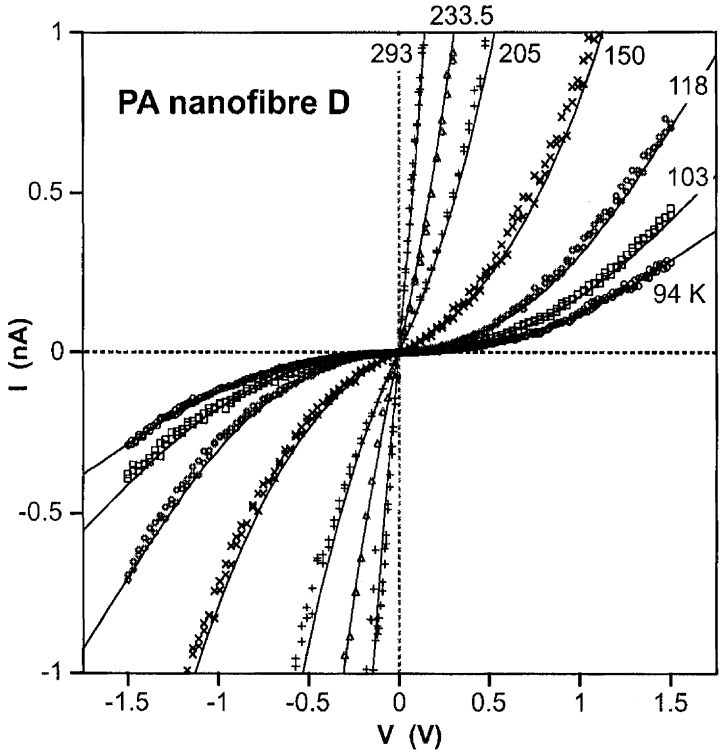


FIGURE 1 *I-V* characteristics for polyacetylene nanofibre D (of diameter approximately 20 nm) after doping with iodine [10]. The data are for temperatures of 293 K down to 94 K as indicated, and are for both increasing and decreasing voltage. The fits are to our generic expression Eq. (2) for fluctuation-assisted tunnelling and thermal activation.

We have made full numerical calculations for fluctuation-assisted tunnelling, extending the model of Sheng [19] to cases of higher conductivity where we include tunnelling up to the top of the barrier and thermal activation over the barrier. For a range of parameters, we obtain a generic shape for the field-dependent conductance G that is well described by the simple analytic expression

$$G = \frac{I}{V} = G_0 \frac{\exp(V/V_0)}{1 + h[\exp(V/V_0) - 1]}. \tag{2}$$

Here G_0 is the low-field conductance (the ohmic term). As field or applied voltage increase, the conductance increases exponentially on a scale determined by V_0. At higher field values, this exponential increase slows to an extent determined by the parameter h.

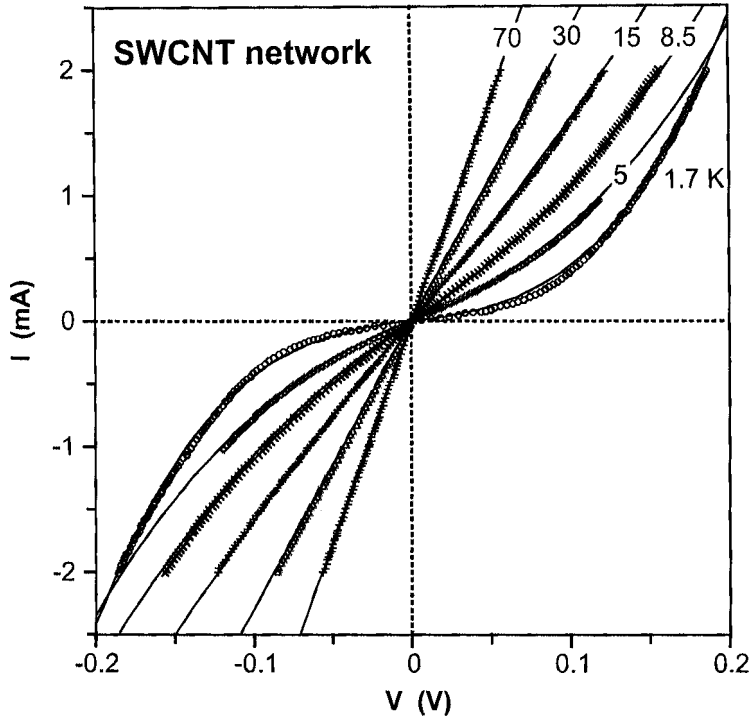


FIGURE 2 Measured *I-V* characteristics for a network of single-wall carbon nanotubes (Kim *et al.* [18]) at temperatures from 1.7 K up to 70 K, fitted to our calculated behaviour Eq. (2) for fluctuation-assisted tunnelling and thermal activation.

It can be seen from the fits in Figure 2 that this model can give a good account of the changing shape of the *I-V* characteristics of the SWCNT network as temperature increases. Physically, the nonlinear characteristics at the lowest temperatures correspond to tunnelling through barriers with thermal fluctuations considerably smaller than the barrier height. The conductivity increases as the temperature and thermal fluctuations increase, and as the fluctuations become comparable to the barrier height the nonlinearity of the *I-V* characteristic diminishes. At 70 K, the thermal energy is comparable to the barrier heights and the ohmic term becomes dominant.

The same generic form of field dependence also gives an excellent description of the behaviour of the polyacetylene nanofibre, as shown in Figure 1, although the change occurs at higher temperatures corresponding to a higher "barrier" energy. Another difference from the SWCNT case in that the measured low-field conductance G_0 for the polyacetylene nanofibre shows activated behaviour (Figure 3), suggesting thermal

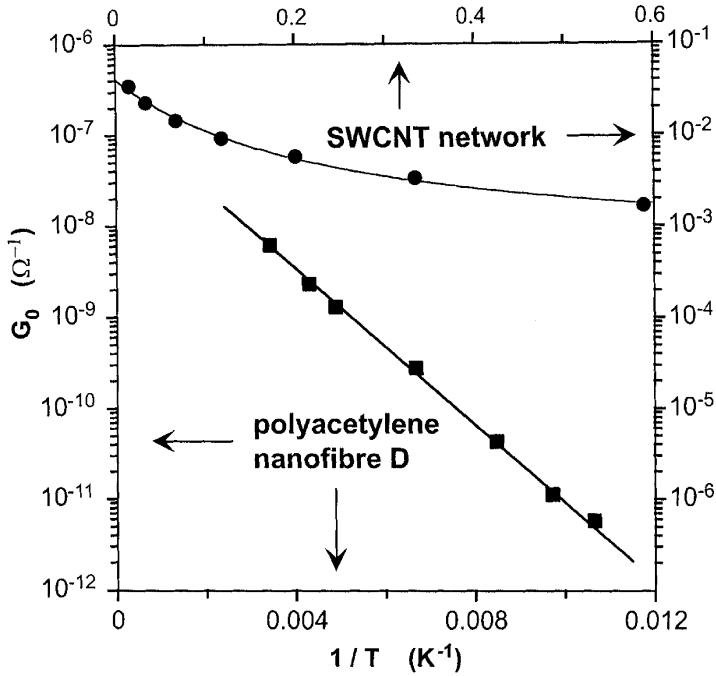
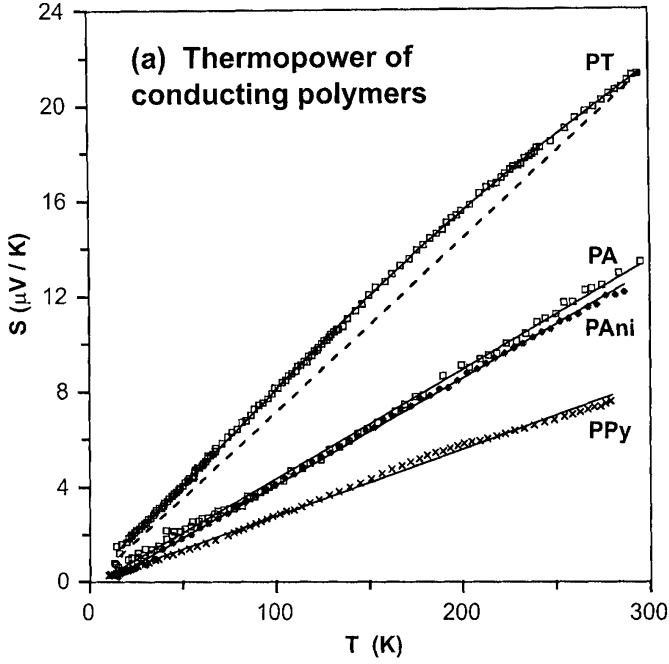


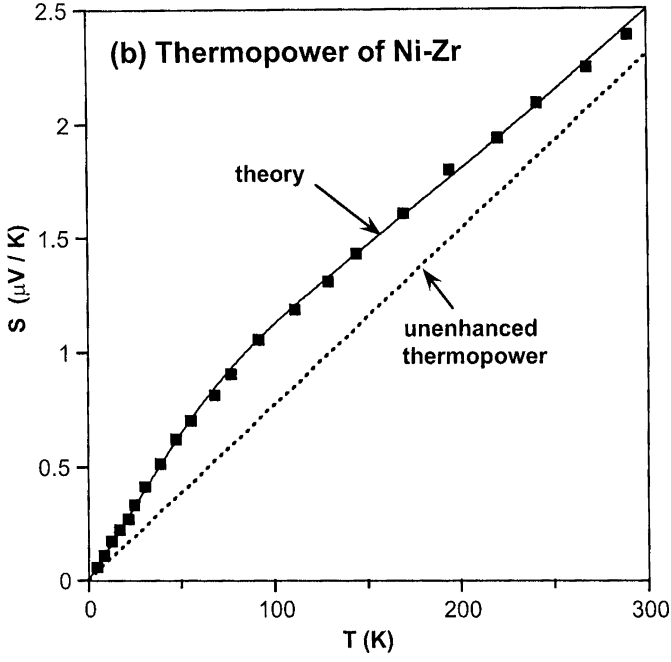
FIGURE 3 Conductance G_0 for the ohmic portion of the *I-V* characteristic measured at low fields for polyacetylene nanofibre D (data from Park *et al.* [10]) and for the network of single-wall carbon nanotubes (Kim *et al.* [18]). Note the different temperature and conductance scales for each data set.

excitation across a gap, whereas the SWCNT behaviour (in a lower temperature range) has the form expected for fluctuation-induced tunnelling [18]. We note that the value of the apparent energy gap for the activation behaviour for the polyacetylene nanofibre is approximately 0.17 eV, much less than the soliton pair creation energy of 0.8 eV or the band gap of 1.4 eV in polyacetylene, suggesting that the conduction mechanism is not pure activation.

3. THERMOPOWER AND IMPLICATIONS FOR SUPERCONDUCTIVITY

The long-standing interest in the possibility of superconductivity in polyacetylene, and more recently in other conducting polymers, has not yet led to any reproducible success in finding signs of superconductivity. One obvious problem is the inability to measure the intrinsic resistivity of the





crystalline regions of conducting polymers owing to the dominance of the resistance of the disordered barrier regions. This is especially true at low temperatures where the metallic sign of the temperature dependence is suppressed and the resistance decreases as temperature increases. The disordered regions, however, provide less of a barrier to thermal conduction, and so typically thermopower shows metallic temperature dependence to lower temperatures than resistivity [5].

In fact, as shown in Figure 4(a), the most highly conducting polymers [20–23] show surprisingly good metallic diffusion thermopower behaviour (linear in temperature) over a wide temperature range. There is little evidence for the nonlinearities due to phonon drag effects seen in good crystalline metals. Even if phonon drag is suppressed by disorder scattering, conventional disordered metals show a change in slope of thermopower at roughly one quarter of the Debye temperature owing to the loss of electron-phonon mass enhancement as temperature increases [24]. This effect is particularly evident in conventional superconductors, since these have a large electron-phonon interaction, as illustrated in Figure 4(b) for the superconductor $Ni_{0.64}Zr_{0.36}$ [25]. From the value of the superconducting transition temperature ($T_c = 2.54\,\mathrm{K}$), the electron-phonon enhancement parameter is calculated from the McMillan formula as $\lambda \approx 0.58$. The low-temperature slope of thermopower, which in the simplest model is enhanced by the factor $(1 + \lambda)$, yields a value $\lambda \sim 0.61$. A larger effect is seen in Chevrel superconductors that are sufficiently disordered for phonon drag to be suppressed [24].

Examining the linearity of the thermopower of the highly conducting polymers, we conclude that the electron-phonon interaction does not appear sufficient to give rise to significant superconductivity. In polythiophene, there is evidence for a small nonlinearity, but even if that is ascribed to the electron-phonon effect ($\lambda \approx 0.29$ in the fit shown) it is still appears too small to produce superconductivity above around 1 K.

4. CONCLUSION

Polyacetylene nanofibres have been found to show a temperature-independent highly nonlinear Zener-type behaviour at low temperatures, but

FIGURE 4 Thermopower of conducting polymers polyacetylene (PA) [20], polyaniline (PAni) [21], polypyrrole (PPy) [22] and polythiophene (PT) [23] (a) compared to the thermopower of the superconductor $Ni_{0.64}Zr_{0.36}$ [25] ($T_c = 2.54\,\mathrm{K}$) (b). The fits are to the electron-phonon thermopower enhancement theory [24] for $Ni_{0.64}Zr_{0.36}$ and PT, while linear fits are shown for the other polymers. The dashed line is included to show the deviation from linearity of the PT data.

at higher temperatures there is a strong increase of conduction, and the extent of nonlinearity in the *I-V* characteristics decreases. This behaviour is very similar to that observed in SWCNT networks. In both materials, the evolution of the shape of the *I-V* characteristics is described very well by the expression Eq. (2) suggested by our full numerical calculations of fluctuation-assisted tunnelling and thermal activation.

There is no evidence for thermopower nonlinearities in highly conducting polymers that might indicate an electron-phonon interaction for charge carriers sufficient to lead to significant superconductivity. That does not, of course, rule out superconductivity arising from another mechanism. We note that the thermopower of carbon nanotube samples typically does show strong similarities, so the same conclusion does not hold for that case.

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