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Evidence of small-polaron formation in polypyrrole

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Abstract. The DC conductivity of BF_4^--doped polypyrrole films has been measured in the temperature range 77–305 K and could be well represented by Mott's variable-range hopping mechanism. The conductivity data were used to extract the coupling constant γ, the effective polaron mass m_p, the effective dielectric constant ϵ_p, the Debye temperature Θ_D, the polaron radius r_p, the hopping distance R, the density of states at the Fermi level $N(E_F)$ and the hopping energy W, whose magnitudes confirm the formation of small polarons in polypyrrole.

1. Introduction

The electronic transport [1–12] in conjugated polymers based on the pyrrole ring has become an increasingly interesting area of research partly owing to its unique electronic properties [13] and partly because these materials possess a great potential for device applications [14]. The mechanism of conduction in polypyrrole (PPY) is difficult to establish because of persistent structural disorder [15] and also because the electrical properties of the polymer exhibit both semiconducting and metallic behaviours [2, 4, 5]. Because of these unusual features, several studies [10–13, 16–20] have been directed towards the understanding of the mechanism of conduction of conducting polymers which still remains a formidable task faced by physicists and engineers. The electrical conductivity [2], thermopower [2], Hall effect [2], infrared and visible spectroscopy [2, 5], photoelectron spectroscopy [21], NMR [5] and electron diffraction data together with the results of ESR experiments [22, 23] have been analysed [23] to conclude that the conventional metallic band transport theory would provide an inadequate description in PPY. The possibility of the metal-like mechanism can further be ruled out on the basis of the temperature dependence of DC conductivity [7, 12]. The electrical properties of conducting polymers are known to be influenced by conjugation [20] and the bond conjugation can be interrupted in systems such as *trans*-polyacetylene (*trans*-PA), giving rise to the topological defects designated as solitons [17, 18]. However, the absence of degenerate ground states excludes the stability of single-soliton excitations in PPY. Several independent theoretical models [17, 18] have been put forward to explain the observed spinless conduction in *trans*-PA but none of the existing models [17, 18] accounts for the conduction process satisfactorily [16, 19]. Recently we have used [10] the approach based on the polaronic hopping model [24, 25] to explain our data on AC conductivity over a wide range of frequencies and temperatures in lightly doped PPY. The mechanism of DC conduction [12] and the origin of dielectric relaxation [11, 26] in PPY have also been further

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investigated but the present understanding is insufficient to resolve many intricate issues.

The present paper is a report of our measurements of DC conductivity of BF_4^--doped PPY films in the temperature range 77–305 K. The analysis of the experimental results provides evidence of small-polaron formation in PPY.

2. Experimental details

PPY films doped with BF_4^- ions were prepared by electrochemical polymerization [1, 10] of pyrrole monomer (0.15 M) and tetraethylammonium tetrafluoroborate (0.10 M) and propylene carbonate as solvent in a single-compartment cell under isothermal conditions in an inert atmosphere. A polymerization current of about 1 mA cm^{-2} was passed for 70 min and self-supporting films of PPY (about 12 μm thickness) were obtained. The details of the preparation of the films have been described elsewhere [10]. The percentage of BF_4^- ions in PPY films was estimated [27] from the loss in weight of the polymer after dipping it in an aqueous solution of ammonia for different time intervals (from about 30 s to 30 min). No further weight loss was observed when these films were dipped for longer than 20 min. The measurement of DC conductivity was made on sufficiently lightly doped samples having a room-temperature conductivity of about $4.1 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and a doping level of $3.6 \pm 5\%$ of BF_4^- ions. Gold electrodes were vacuum deposited on both sides of these films, thus making an Au-PPY-Au structure. The DC conductivity was measured with a Keithley 610C electrometer in the temperature range 77–305 K. There was little spread (within $\pm 2\%$) in the conductivity values of different films of the same thickness (about 12 μm) and same doping level, confirming the good reproducibility of the fabrication process.

3. Results and discussion

The measured DC conductivity σ_{DC} of a PPY film as a function of reciprocal temperature is shown in figure 1. The general behaviour of the curve is similar to those reported earlier [8, 12]. It is evident from this figure that the conduction process has a temperature-dependent activation energy. The activation energies calculated at 300 K and 77 K are about 0.19 eV and about 0.05 eV, respectively, and are in good agreement with the values reported earlier [8, 12].

The DC conductivity σ_{DC} can be given by the following relation [25]:

$$\sigma_{DC} = \sigma_0 \exp(-W/kT) \tag{1}$$

where σ_0 is a constant pre-exponential factor, k is the Boltzmann constant and W is the activation energy which includes the hopping energy W_H and any energy difference W_D between the localized states due to disorder. Austin and Mott [28] have shown that

$$W = \begin{cases} W_H + \frac{1}{2}W_D & \text{for } T > \Theta_D/2 \quad (2) \\ W_D & \text{for } T < \Theta_D/4 \quad (3) \end{cases}$$

where $\Theta_D = \hbar\omega_0/k$ is the characteristic temperature of the phonon frequency ν_0 of the material. The lowest temperature activation energy (about 0.05 eV) can be taken

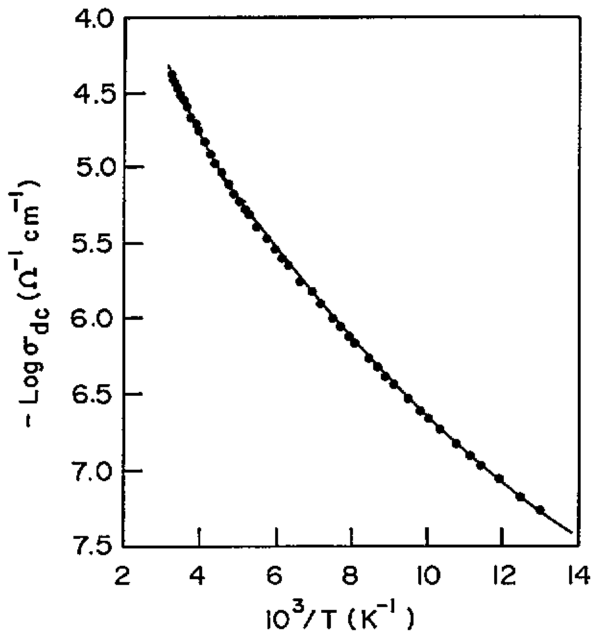

Figure 1. Variation in $\log \sigma_{DC}$ as a function of reciprocal temperature for a BF_4^--doped PPY film.

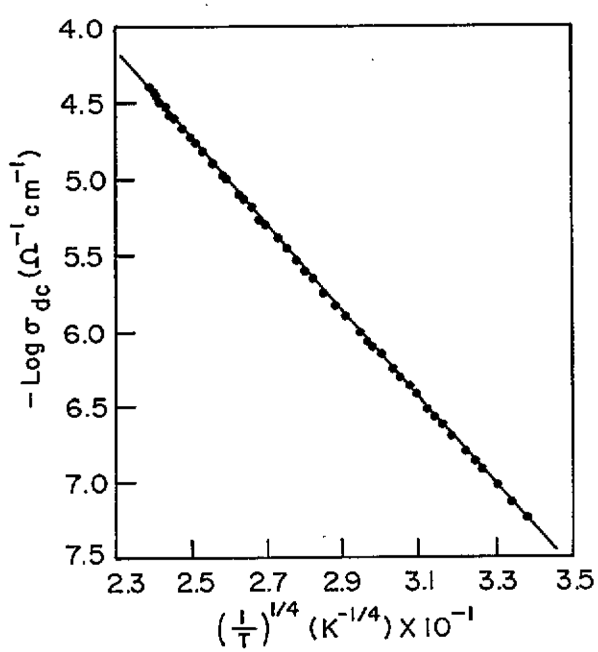

Figure 2. Plot of $\log \sigma_{DC}$ against $T^{-1/4}$.

as a measure of disorder energy W_D. An estimate of ω_0 can be made by taking the limiting value of $\hbar\omega_0 \simeq W_D/2$. A value of about 0.05 eV for W_D gives $\nu_0 \simeq 10^{13}$ Hz and $\Theta_D \simeq 290$ K.

The effective dielectric constant ϵ_p is calculated by using the following expression:

$$1/\epsilon_p = 1/\epsilon_\infty - 1/\epsilon_0 \tag{4}$$

where $\epsilon_0(= 250)$ and $\epsilon_\infty(= 10)$ are the static and infinite values of the dielectric constant [10], respectively. These values [10] of ϵ_0 at 300 K and ϵ_∞ have been used to calculate ϵ_p from equation (4), and ϵ_p was found to be equal to 10.416.

An estimate of the polaron radius r_p can be made by taking the polaron binding energy W_p as twice the activation energy at high temperatures [28] using the following expression:

$$W_p = \tfrac{1}{2}(e^2/\epsilon_p r_p) \tag{5}$$

and equals about 1.82 Å. The high-temperature activation energy (about 0.19 eV) leads to a value of 15 for the small-polaron coupling constant [28] $\gamma = W_p/\hbar\omega_0$ (taking $\nu_0 = 10^{13}$ Hz). This value of γ indicates that the strong-coupling requirement for the application of small-polaron theory to PPY is satisfied. This calculated value of coupling constant γ gives the effective polaron mass m_p as about 60 times the mass of the electron [29, 30].

Although the parameters derived from the above analysis are not unreasonable, the data in figure 1 can be interpreted much more convincingly in terms of the variable-range hopping model of Mott and Davis [25]. The variable-range hopping results in the following expression for conductivity at low temperatures:

$$\sigma_{DC} = \sigma_0 \exp[-(T_0/T)^{1/4}] \tag{6}$$

where T_0 and σ_0 are constants. A plot of $\log \sigma_{DC}$ versus $(1/T)^{1/4}$ should give a straight line. The experimental values of the conductivity of a PPY film (figure 1) have been plotted against $(1/T)^{1/4}$ in figure 2. It is evident from this figure that Mott's law is obeyed for the PPY film for the entire temperature range studied.

The constants T_0 and σ_0 in equation (6) are expressed functionally as [12, 31]

$$T_0 = \lambda\alpha^3/kN(E_F) \tag{7}$$

and

$$\sigma_0 = e^2R^2\nu_0N(E_F) \tag{8}$$

where e is the electronic charge, R is the hopping distance, ν_0 is a phonon frequency (about 10^{13} Hz) obtained from the Debye temperature Θ_D, and k is the Boltzmann constant. λ is a dimensionless constant [31] (equal to about 18.1), $\alpha(= 1/r_p)$ is the inverse rate of the fall in the wavefunction and $N(E_F)$ is the density of states at the Fermi level. The hopping distance R can be calculated from the following expression [12, 31]:

$$R = \left[\frac{9}{8\pi\alpha kTN(E_F)}\right]^{1/4}. \tag{9}$$

If we know R and $N(E_F)$, the average hopping energy W can be estimated from the following relation [12, 31]:

$$W = \frac{3}{4\pi R^3 N(E_F)}. \tag{10}$$

The value of T_0 has been estimated from figure 2 and is about 1.81×10^7 K. The calculated values of $N(E_F)$, R and W from the above equations are about 1.923×10^{21} cm^{-3} eV^{-1}, 10.71 Å and 0.10 eV, respectively, after taking the estimated value of $\alpha = 1/r_p$, where $r_p \simeq 1.82$ Å. This value of r_p confirms the formation of small polarons and yields the appropriate value of Mott's parameters R, W and $N(E_F)$ for PPY as has been observed for other amorphous systems [28, 30–32].

Further work is in progress to examine the applicability of this analysis to certain other conducting polymers which might resolve some intriguing issues pertaining to the mechanism of the conduction of conducting polymers.

4. Conclusions

The temperature dependence of the DC conductivity of BF_4^--doped PPY films gives evidence of formation of small polarons in PPY which can be explained well by using the variable-range hopping model of Mott and Davis. Mott's parameters for PPY, derived using the variable-range hopping model, turn out to have appropriate magnitudes.

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