

## Transport properties of FeCl<sub>3</sub>-doped polypyrroles at different dopant concentrations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 10499

(<http://iopscience.iop.org/0953-8984/6/48/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 11:26

Please note that [terms and conditions apply](#).

## Transport properties of FeCl<sub>3</sub>-doped polypyrroles at different dopant concentrations

A Bhattacharya†, A De†§, S N Bhattacharya† and S Das‡

† Nuclear Chemistry Division, Saha Institute of Nuclear Physics, Sector 1, Block-AF, Bidhannagar, Calcutta-700 064, India

‡ Solid State and Molecular Physics Division, Saha Institute of Nuclear Physics, Sector 1, Block-AF, Bidhannagar, Calcutta-700 064, India

Received 2 June 1994, in final form 3 August 1994

**Abstract.** The electrical conductivities of FeCl<sub>3</sub>-doped polypyrrole samples with different dopant concentrations have been measured in the temperature range 25–300 K. Thermoelectric power measurements have been performed on two polypyrrole samples at low doping levels between 50 and 300 K. The variation in DC conductivity can be explained by Mott's variable-range hopping (VRH) model. Fitting with Mott's VRH theory, the conductivity data provide the values of the density  $N(\epsilon_F)$  of states at the Fermi level and the hopping distance  $R$ . The low value and the sublinear character of the thermoelectric power is consistent with the VRH theory.

### 1. Introduction

Recently the synthesis and characterization of conducting polymers [1] have received much attention from scientists because of the possibility of their wide application in solid state devices [2]. The conductivity of this intrinsically insulating material can be varied over a wide range by doping and is influenced by the dopant, the doping level, the synthesis processes and the temperature range of measurement [3–11]. Polypyrrole is a conjugated polymer based on an aromatic ring with a band of 2.5 eV. It has a conduction band of 3.8 eV created by the delocalized electrons of the unpaired  $2p_z$  orbitals of the carbon atoms in the chain and has non-degenerate ground states [12]. Doped polypyrrole has similarity with a three-dimensional disordered system in respect of the structure and morphology. Theoretical [13–15] and experimental [16–19] studies provide evidence for the creation of polaron and bipolaron defects in polypyrrole by doping. The polaron state having  $\frac{1}{2}$  spin is characterized by an ESR signal due to the enhancement of the spin concentration in *in-situ* ESR measurements [17] and by three optical absorption peaks [18] at 0.7, 1.4 and 2.1 eV within the band region. Two of the optical peaks appear from the transition between the valence band and the bonding and antibonding levels whereas the transition between the bonding and antibonding polaron levels gives rise to a third peak. The third optical peak is absent in the bipolaron state since the bonding level remains vacant. Moreover, the ESR signal will be absent because the spin of the bipolaron state is zero. Up to the intermediate doping level, polaron formation has recently been established [18] but, as the level of doping increases, both polarons and bipolarons may also be formed. A decisive conclusion about the transport mechanism in polypyrrole has not yet been drawn owing to the persistent structural disorder. It may be due to polarons or bipolarons in the polymer chain, to a

§ Author to whom correspondence should be addressed.

transition between chains, to hopping between localized states or to fluctuation-induced tunnelling, depending upon the temperature range or the existence of metallic regions. At present the highest room-temperature conductivity ( $\sigma_{RT}(\text{max}) > 10^5 \text{ S cm}^{-1}$ ) is obtained in the case of stretched oriented polyacetylene film doped with  $\text{FeCl}_3$  and iodine [20, 21]. Compared with  $\text{FeCl}_3$ -doped polyacetylene,  $\text{FeCl}_3$ -doped polypyrrole has not attracted much attention. Pron *et al* [22] have reported that polypyrrole can be prepared chemically using the  $\text{FeCl}_3$  method. They assigned the anion formed in the reaction as a high-spin  $\text{Fe(II)}$  species  $\text{FeCl}_4^-$  from the room-temperature Mössbauer spectroscopic studies. The isomer shift is identical and typical of  $\text{FeCl}_4^-$ . The motivation for this study is to investigate the temperature dependences of the conductivity and thermoelectric power (TEP) of polypyrrole doped with  $\text{FeCl}_3$  and to draw a correlation between the variation in conduction mechanism with the doping level.

## 2. Experimental details

### 2.1. Preparation of polypyrrole samples

Pyrrole (E Merck, Germany) employed as a monomer is distilled, purified and kept in an inert atmosphere prior to use. Polypyrrole samples having different dopant concentrations were prepared using different concentrations of  $\text{FeCl}_3$  (SD Fine Chemicals Ltd) solutions namely 0.75 M, 0.5 M, 0.25 M, 0.1 M and 0.04 M. The pyrrole concentration was always maintained at 0.05 M. To the 100 ml  $\text{FeCl}_3$  solutions in a beaker pyrrole was added dropwise with constant stirring. Polymerization took place almost instantly at room temperature. After about  $1\frac{1}{2}$  h the black precipitate of polypyrrole was separated from the solution. The precipitate was washed thoroughly with water until complete removal of the adhered  $\text{Fe}^{3+}$  and then dried under vacuum for 25 h.

### 2.2. Measurement technique of resistivity and thermoelectric power

The pellet of polymer was made by pressing in a Perkin–Elmer die. The pressed pellets were used to measure the electrical conductivity in the temperature range 25–300 K. The temperature-dependent resistivities of the samples were measured with the standard four-probe technique using silver paint contacts. A constant DC (about 1–3 mA) from a Lakeshore cryotronics model 120 constant-current source was passed through the sample and the voltage drop across the sample was measured with a Keithley model 181 nanovoltmeter. The current level was kept low to avoid heating of the electrical contact. The low-temperature measurement was performed using an Oxford model 22 closed-cycle helium refrigerator. The sample temperature was measured with a chromel–alumel thermocouple placed very near the sample. A calibrated Si diode was attached to the sample holder to act as the sensor. The temperature was controlled using a Lakeshore cryotronics model DTC500A temperature controller.

The TEP of polypyrrole samples was measured using a differential technique where a temperature gradient was created across the sample and the voltage  $\Delta E$  developed between the hot and cold ends of the thermocouple formed by the sample and Cu wires was measured. Two heaters were used (one at the top and the other at the bottom of the sample) so that either end of the sample may be heated with respect to the other. The temperature difference  $\Delta T$  between two ends of the sample was kept in the range  $\pm 0.5$  K throughout the measured temperature range (77–300 K). The temperature and temperature difference across the sample were measured with chromel–alumel thermocouples. Pressed pellets of

polypyrrole were mounted by pressure contact between the copper plates using silver paint and the whole system was placed in a glass Dewar. The sample temperature was controlled with a Si diode and a manganin heater. At each measurement the temperature of the sample was fixed using a temperature controller (Lakeshore cryotonic model DRC-93CA). At a particular temperature the values of  $\Delta E$  and  $\Delta T$  were recorded with the x-y recorder and the TEP  $S$  of the sample was calculated from the slope of the  $\Delta E$  versus  $\Delta T$  curve using the following relation:

$$\frac{\Delta E}{\Delta T} = \frac{S_{\text{Cu}} - S}{S_{\text{chromel}} - S_{\text{alumel}}}$$

### 3. Results and discussion

Mott [23] and Mott and Davis [24] (see also [25]) proposed a model for the phonon-activated variable-range hopping (VRH) between localized states irrespective of the presence and absence of polarons. Electrons interact very strongly with the dopant ions in the polymer crystal through an electrostatic interaction. Thus the polymer lattice itself will become deformed by the presence of the electrons. This results in the formation of polarons in localized states. Our data can be fitted much more reliably with the VRH model according to which the conductivity can be expressed as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/n}] \quad (1)$$

where the exponent  $n$  gives the dimensionality of the charge transport in the solid. The value of  $n$  is 3 for two-dimensional and 4 for three-dimensional transport.  $T_0$  is the characteristic temperature.

In the case of three-dimensional transport,  $T_0$  and  $\sigma_0$  are expressed as [26, 27]

$$T_0 = \frac{\lambda \alpha^3}{kN(\epsilon_F)} \quad (2)$$

and

$$\sigma_0 = e^2 R^2 \nu_0 N(\epsilon_F) \quad (3)$$

where  $R$  is the average hopping distance,  $\nu_0$  is the phonon frequency,  $k$  is the Boltzmann constant,  $\alpha$  is the inverse localization length and  $N(\epsilon_F)$  is the density of states at the Fermi level. Here  $\lambda$  represents a dimensionless constant (about 18.1) [26, 28–30].

The hopping distance  $R$  may be expressed as

$$R = \left( \frac{9}{8\pi \alpha k T N(\epsilon_F)} \right)^{1/4} \quad (4)$$

Considering the VRH model, Epstein *et al* [31] gave an expression relating  $\sigma$  and  $T$  in three dimensions as

$$\sigma = K_0 T^{-1/2} \exp[-T_0/T]^{1/4} \quad (5)$$

where

$$T_0 = 16\alpha^3/kN(\epsilon_F) \quad (6)$$

and

$$K_0 = 0.39[N(\epsilon_F)/\alpha k]^{1/2}v_0e^2. \quad (7)$$

We have studied five samples prepared with different concentrations of  $\text{FeCl}_3$ , namely  $x = 0.04$  M, 0.1 M, 0.25 M, 0.5 M and 0.75 M, which are referred to hereafter as samples  $A_1$ ,  $A_2$ ,  $A_3$ ,  $A_4$  and  $A_5$ , respectively. The temperature-dependent behaviour of the resistivity was studied in the temperature range 25–300 K and the TEPs of samples  $A_1$  and  $A_2$  were measured in the temperature range  $50 \text{ K} < T < 300 \text{ K}$ . In the case of our polycrystalline samples we obtain a conductivity much less than that obtained by others for polypyrrole films. The properties of polycrystalline material are different from those of single crystals. This property variation is generally attributed to the grain boundaries, i.e. to the localized defects which separate the grains of different orientations, rather than to the differences in the orientations themselves [32–34]. The comparatively large value of resistivity obtained for our samples may arise from the random orientation of microcrystals and their weak coupling through the grain boundary. The influence of the grain boundaries may also have a marked effect on our TEP measurements. Considering equation (1) for  $\sigma(T)$  in Mott's VRH theory the activation energy may be expressed as

$$E = -\frac{d(\ln \sigma)}{d(1/kT)} = -k\frac{1}{n}T_0^{1/n}T^{-(1/n-1)}. \quad (8)$$

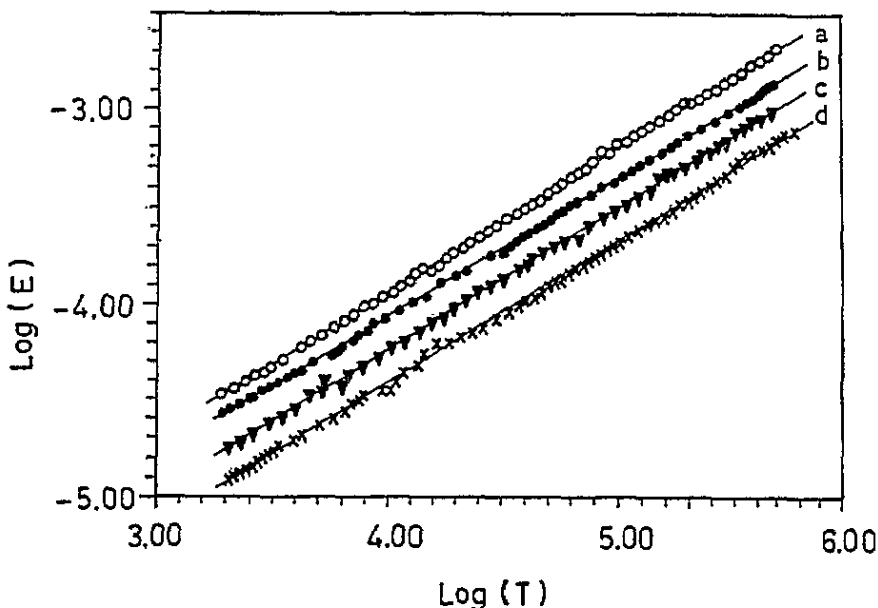


Figure 1. Hill plot showing the change in  $\ln E$  ( $E$  is the activation energy) as a function of  $\ln T$ .

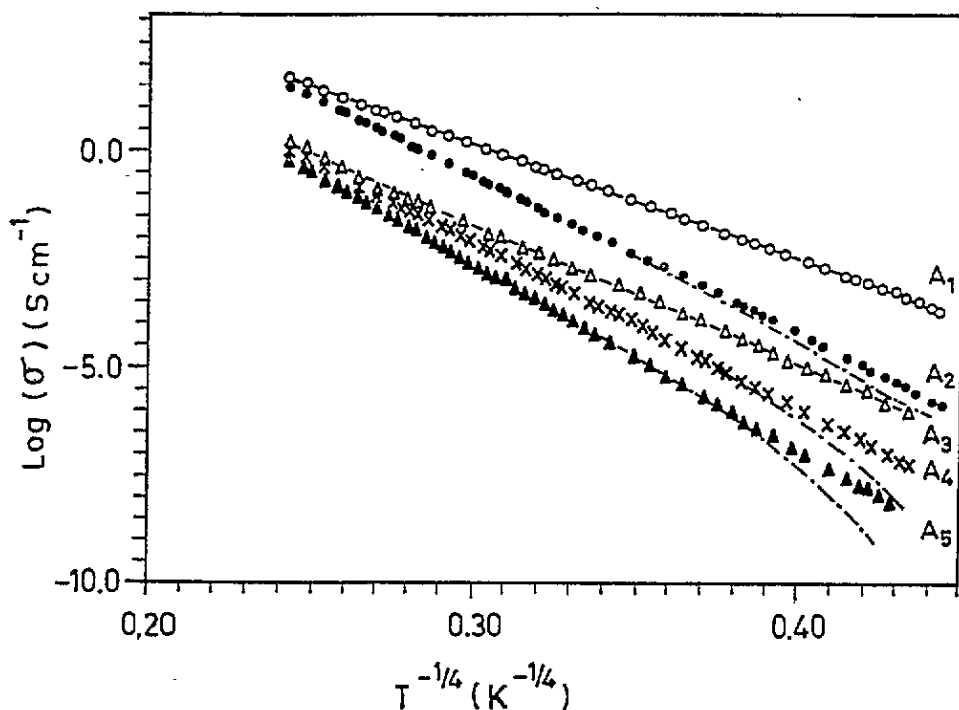


Figure 2. Variation in  $\ln \sigma$  as a function of  $T^{-1/4}$  for different samples.

A Hill [35] plot ( $\ln E$  versus  $\ln T$  curve) is shown in figure 1 which is a straight line of gradient  $-(1/n - 1)$ . This plot actually presents the effect of the different levels of doping on the conductivity. The value of  $n$  may change from  $n = 4$  for various reasons such as variation in dimensionality, spatial inhomogeneities or variation in the density of states with energy. From the gradient of the straight line the value of  $n$  is determined. It is found that for all the samples the value of  $n$  is 4. So the Hill plot indicates that the three-dimensional VRH mechanism plays an important role in the conduction process in our samples. We analysed our conductivity data in the light of the VRH theory with  $n = 4$ . In figure 2 we plotted  $\ln \sigma$  versus  $T^{-1/4}$  together with the theoretical fit curve. It is observed that the curve is linear for all the samples although the range of temperatures for linearity varies. To avoid unrealistic parameters we used guessed values of  $T_0$  and  $\sigma_0$  for fitting from the slope and intercept, respectively, of the experimental conductivity curves presented in figure 2. Table 1 represents the different parameters obtained by fitting with Mott's VRH theory. Here we have assumed that the localization length  $\alpha^{-1}$  of localized electrons is about four pyrrole rings [15]. From the calculation of the energetics of polaron and bipolaron formation on polypyrrole chains, Bredas *et al* [15] showed that the formation of a bipolaron is favoured over that of two polarons by 0.45 eV and the bipolaron length extends to about four pyrrole rings. According to Ehring and Roth [37] the VRH theory becomes valid when at low temperatures the condition  $(T_0/T)^{1/4} \gg 10$  is fulfilled. Mott and Davis derived the VRH theory on the assumption that the wavefunction becomes localized in a small area of the system. The values of  $(T_0/T)^{1/4}$  obtained here are 6–10. The small values obtained in this case indicates delocalization of the wavefunction in polypyrrole as seen by Bredas *et al* [15]. We also fitted the data with Epstein's model, but the fit is not so good as for

Mott's VRH model. Figure 3 presents the  $\ln(T^2\sigma)$  versus  $T^{-1/4}$  plot. The slope  $T_0^{1/4}$  and hence  $T_0$  obtained by fitting with equation (1) are plotted in figure 4. The plot shows a systematic increase in  $T_0$  with increasing dopant concentration. From equation (2) it is seen that the value of  $T_0$  depends largely on the localization length and the density of states at the Fermi level. The variation in these two parameters in the system with different dopant concentrations may induce change in the value of  $T_0$ . The value of  $N(\epsilon_F)$  found here is in agreement with the other experimental values obtained by different experimental techniques [38]. It is found that the values of  $N(\epsilon_F)$  and  $R_0$  change with the dopant concentration. This may be due to the arbitrary choice of the localization length  $\alpha^{-1} = 10 \text{ \AA}$  for the samples. From equation (3) the value of the hopping frequency  $\nu_0$  is calculated and found to be about  $10^{13} \text{ s}^{-1}$ .

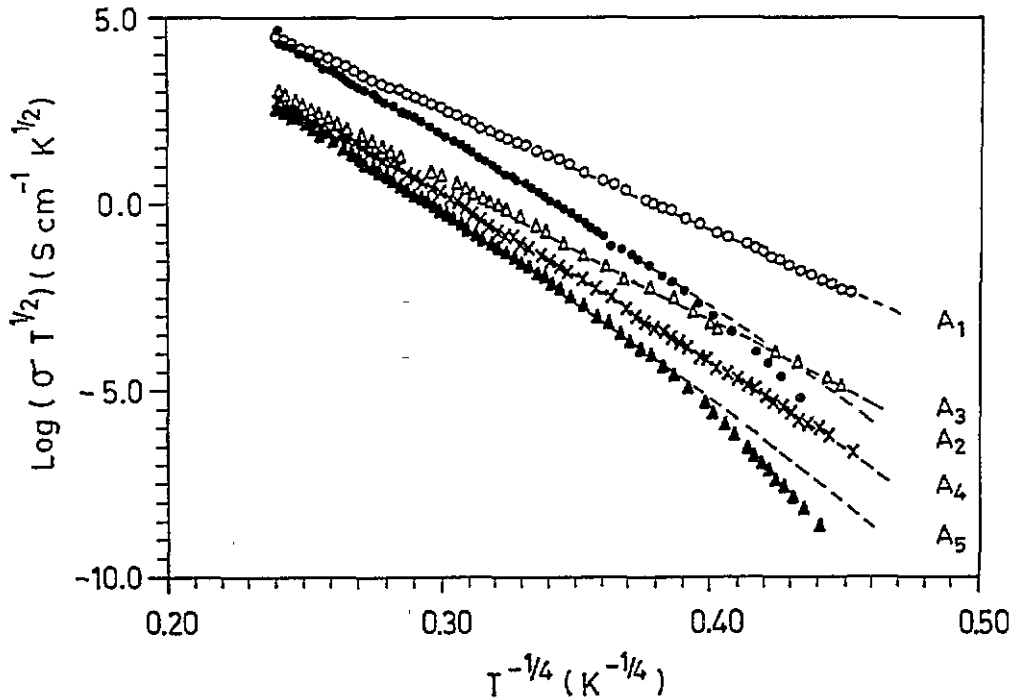


Figure 3. Plot of  $\ln(\sigma T^{1/2})$  versus  $T^{-1/4}$ : ---, theoretical curve fitting with Epstein's formula.

Table I. Variable-range hopping parameters for three-dimensional hopping in  $\text{FeCl}_3$ -doped polypyrrole.

Sample	Characteristic temperature $T_0$ (K)	Density of states $N(\epsilon_F)$ ( $\alpha^{-1} = 10 \text{ \AA}$ ) ( $\text{eV}^{-1} \text{ cm}^{-3}$ )	Hopping distance $R_{300}$ ( $\alpha^{-1} = 10 \text{ \AA}$ ) $\text{\AA}$
A <sub>1</sub>	169985	$1.236 \times 10^{21}$	32.54
A <sub>2</sub>	460050	$4.566 \times 10^{20}$	23.47
A <sub>3</sub>	989474	$2.123 \times 10^{20}$	28.43
A <sub>4</sub>	2216717	$9.476 \times 10^{19}$	19.56
A <sub>5</sub>	3477484	$6.044 \times 10^{19}$	38.92

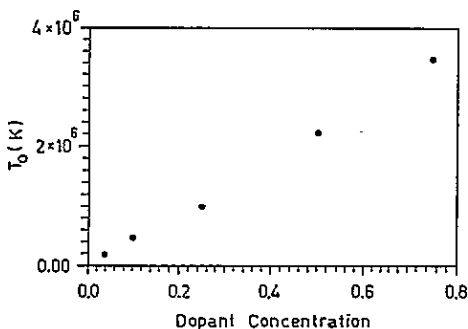


Figure 4. Characteristic temperature  $T_0$  versus doping concentration.

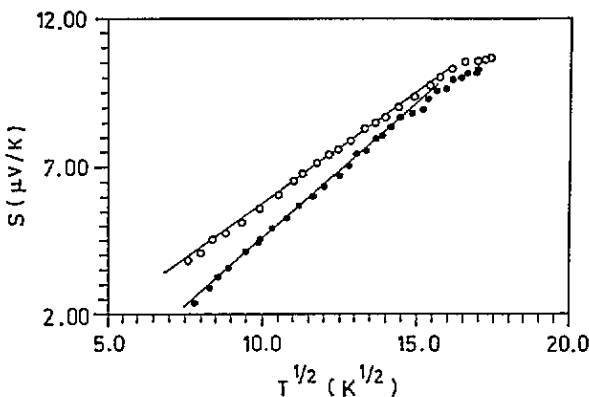


Figure 5. Variation in thermopower  $S$  with square root ( $T^{1/2}$ ) of temperature.

The TEP measurement is an extremely useful probe for investigating the intrinsic electronic conduction mechanism of the system. The contribution of the hopping mechanism is also suggested by the measurement of the TEP. According to Mott's VRH theory the TEP can be expressed as [24, 39]

$$S(T) = (k^2/2e)(T_0T)^{1/2} d(\ln N)/d\epsilon_{\epsilon=\epsilon_F} \quad (9)$$

i.e. the TEP is approximately proportional to  $(T)^{1/2}$ . Here  $T_0$  is the parameter appearing in the Mott's VRH law for the conductivity. The TEP at room temperature is  $10.20 \mu\text{V K}^{-1}$  for sample A<sub>1</sub> and  $9.17 \mu\text{V K}^{-1}$  for sample A<sub>2</sub>. The observation of low TEP values is consistent with the VRH theory. The TEP presents a non-linear behaviour with the variation in temperature and in both the cases the TEP decreases with decrease in temperature. In figure 5 we have plotted the TEP against  $T^{1/2}$  which gives a linear curve, indicating that the VRH model is applicable here. To bring the two TEP curves into the same figure we have added 0.5 to all the TEP values for sample A<sub>2</sub>. From the slope of the curve the value of  $d(\ln N)/d\epsilon$  is determined to be  $2.8 \text{ eV}^{-1}$  for sample A<sub>1</sub> and  $1.5 \text{ eV}^{-1}$  for sample A<sub>2</sub>. In our samples the contribution from hopping becomes predominant and a linear metal-like component is absent. The magnitude of the TEP is largely consistent with the values for semiconductive polymers. It is found that the nature of the TEP does not change with the dopant concentration.



#### 4. Conclusion

We have measured the DC conductivity of FeCl<sub>3</sub>-doped polypyrrole in the temperature range 25 K < T < 300 K and TEP between 50 and 300 K. The temperature dependence can be explained well using the VRH developed by Mott and Davis where the polaronic hopping plays the dominant role in the transport process. The parameters obtained from the VRH model are in good agreement with those obtained by other experimental techniques. The contribution of the hopping mechanism is also suggested by the measurement of the TEP. The TEP decreases with decrease in temperature. This observation is in good agreement with that in the case of the interchain conduction by hopping carrier. So Mott's VRH mechanism plays an important role in the conduction mechanism for doped polypyrrole in the insulating regime, and both sets of results presented here appear to be consistent with the model of an amorphous semiconductor.

#### Acknowledgments

The authors are grateful to Professor B Ghose and other colleagues of the Low Temperature Physics Section of the Saha Institute for rendering help in the resistivity and TEP measurement.

#### References

- [1] Bredas J L 1986 *Handbook of Conducting Polymers* vol 2, ed T A Skotheim (New York: Dekker) p 859
- [2] Scoch K F Jr 1986 *IEEE Electron. Insul. Magn.* 2 20
- [3] Travers J P, Audebert P and Bidan G 1985 *Mol. Cryst. Liq. Cryst.* 118 B-149
- [4] Bukhs E and Hodges I M 1985 *J. Chem. Phys.* 83 5976
- [5] Satoh M, Imanishi K, Yashuda Y, Tsushima R, Akoi S and Yoshino K 1988 *J. Phys. D: Appl. Phys.* 21 1782
- [6] Sato K, Yamaura M, Hagiwara T, Murata K and Tokumoto M 1991 *Synth. Met.* 44 35
- [7] Singh R, Tandon R P, Panwar V S and Chandra S 1991 *J. Appl. Phys.* 69 2504
- [8] Singh R, Tandon R P and Chandra S 1993 *J. Phys.: Condens. Matter* 5 1313
- [9] Roy R, Sen S K, Digar M and Bhattacharya S N 1991 *J. Phys.: Condens. Matter* 3 7849
- [10] Watanabe A, Tanaka M and Tanaka J 1981 *Bull. Chem. Soc. Japan* 43 2271
- [11] Castillo-Ortega M M, Inoue M B and Inoue M 1989 *Synth. Met.* 28 C65
- [12] Street G B 1986 *Handbook of Conducting Polymers* vol 1, ed T A Skotheim (New York: Dekker) p 265
- [13] Bredas J L, Themans B, Fripiat J G, Andre J M and Chance R R 1984 *Phys. Rev. B* 29 6761
- [14] Brazovskii S H and Kirova N N 1981 *JETP Lett.* 33 5
- [15] Bredas J L, Scott J C, Yakushi K and Street G B 1984 *Phys. Rev. B* 30 1023
- [16] Ford W K, Duke C B and Salocneck W R 1982 *J. Chem. Phys.* 77 5030
- [17] Genoud F, Gugliemi M, Nechtschein M, Genies E and Salmon M 1985 *Phys. Rev. Lett.* 55 118
- [18] Zotti G and Schiavon G 1989 *Synth. Met.* 30 151
- [19] Nechtschien M, Devreax F, Genoud F, Vieil E, Pernaut J M and Genies E 1986 *Synth. Met.* 15 59
- [20] Naarmann H and Theophilon N 1985 *Synth. Met.* 22 1
- [21] Tsukamoto J, Takahashi A and Kawasaki K 1990 *Japan. J. Appl. Phys.* 29 125
- [22] Pron A, Kucharski Z, Budrowski C, Zagorska M, Krichene S, Suwalski J, Dehe G and Lefrant S 1985 *J. Chem. Phys.* 83 5923
- [23] Mott N F 1967 *Adv. Phys.* 16 49; 1969 *Phil. Mag.* 19 835
- [24] Mott N F and Davis E A 1979 *Electronic Processes in Noncrystalline Materials* (Oxford: Clarendon) pp 32-4
- [25] Chien J C W 1984 *Polyacetylene* (Orlando, FL: Academic) p 485
- [26] Paul D K and Mitra S S 1973 *Phys. Rev. Lett.* 31 1000
- [27] Nair K and Mitra S S 1977 *J. Non-Cryst. Solids* 24 1
- [28] Ambegaokar V, Halperin B I and Langer J S 1971 *Phys. Rev. B* 4 2612
- [29] Fritzsche H 1974 *Amorphous Semiconductors* ed J Tauc (New York: Plenum) p 233

- [30] Broadsky M H and Gambino R J 1972 *Proc. 4th Int. Conf. on Amorphous and Liquid Semiconductors (Ann Arbor, MI, 1971)* ed M H Cohen and G Lukovsky (Amsterdam: North-Holland) p 742
- [31] Epstein A J, Rommelmann H, Egelow R, Gibson H W, Hoffman D and Tanner D B 1983 *Phys. Rev. Lett.* **50** 1866
- [32] Amilinckx S and Dekeyser W 1959 *Solid State Physics* vol 8, ed F Seitz and D Turnbull (New York: Academic) p 325
- [33] Lormand G 1982 *J. Physique Coll.* **43** C6 283
- [34] Rossiter P L 1987 *The Electrical Resistivity of Metals and Alloys (Cambridge Solid State Science Series)* ed R W Cahn, E A Davis and I M Ward (Cambridge: Cambridge University Press) p 185
- [35] Hill R M 1976 *Phys. Status Solidi* **34** 601
- [36] Bottger H and Bryskin V V 1985 *Hopping Conduction in Solids* (Weinheim: VCH) p 155
- [37] Ehring K and Roth S 1986 *Phil. Mag.* **B 53** 301
- [38] Pfluger P, Gubler U M and Street G B 1984 *Solid State Commun.* **49** 911
- [39] Kaiser A B 1989 *Springer Series in Solid State Sciences* vol 91, ed H Kuzmany, M Mehring and S Roth (Berlin: Springer) p 29