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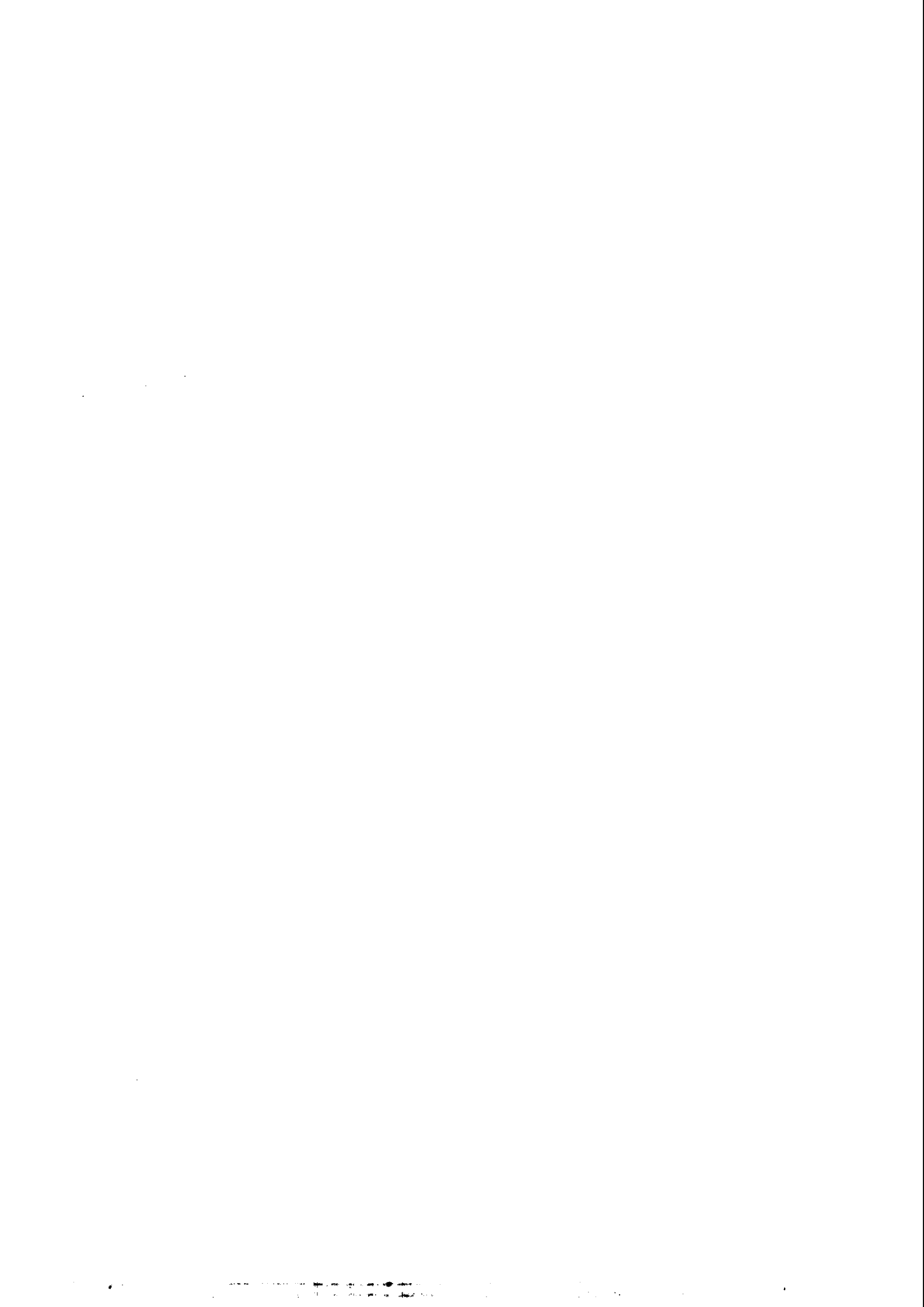


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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

**ELECTRICAL CONDUCTIVITY STUDY
ON POLYTHIOPHENES FILMS**

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ABSTRACT

The electrical conduction mechanism of two classes of polythiophenes: polythiophene (PT) and poly(3-methylthiophene) (PMT) films containing various levels of doping counterions was investigated. The temperature dependence of electrical conductivity obeys the Mott equation based on variable range hopping. The dimension of the variable range hopping is correlated with the structure of the conducting polymer. It seems for these polymers that carrier transport via mobile conjugational defects does not play a detectable role.

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Since the first preparation by both Kaneto et al [1] and Tourillon et al [2] of a flexible film from thiophene by electrochemical oxydation, a lot of attention has been paid to polythiophenes. The polythiophenes films are an interesting conducting polymer material not only because of their high electrical conductivity [3] and their good environmental stability but also because of the possible application on solar energy [4-6] and electrochromic display devices [7].

The conduction mechanism of electrically conducting polymer has been widely investigated [8-11,14,15]. With polyheterocycles, such as polypyrrole (PP), polythiophene (PT), poly(3-methylthiophene) (PMT) a spinless model involving bipolarons has been proposed as a charge carrier [11]. The bipolarons are mobile along the conjugated system of a polymer chain. In actual films, however, the carrier must hop not only across the defects in the conjugated system but also across the interchain and interfibrill gaps. In this respect the analysis of the temperature dependence of electrical conductivity gives us useful information. Also, most of authors interpret there conductivity data in terms of variable range hopping (VRH) of carriers among atomic sites in the three dimensions [8-10]. However, very little work has been carried out on the quantitative analysis relating to the conduction mechanism.

In order to study the transport properties of polythiophenes films containing different amounts of counter-ions and thereby having different room temperature, we have prepared electrochemically a group of PT and PMT films. Details of the preparation method were already reported [12]. The d.c. conductivity ($\sigma_{d.c}$) was measured by using the classical four point method. The contacts on the samples are made by gold wires with electrodag 502 or silver paste. The temperature (T) range lies between the liquid nitrogen temperature and 300 K.

In Fig. 1, the variation of $\sigma_{d.c}$ with temperature, $10^3/T$, is shown for PF_6^- doped PMT and PT samples. The conductivity of both polymers behaves very similarly. The T-dependence of $\sigma_{d.c}$ becomes weaker with the increase of the doping level. For all concentrations the decrease of $\sigma_{d.c}$ is more pronounced in the PT films than in the PMT films. The measured $\sigma_{d.c}(y, T)$ are quite general and not limited to the PF_6^- doped samples. Similar data were obtained with other dopants. In these plots, the lines are continuously curved and, hence, the T-dependence of $\sigma_{d.c}$ does not follow an Arrhenius type behaviour. To obtain a better fit, we analyzed the dependence of d.c. conductivity according to the framework of Mott's model [13] :

$$\sigma_{d.c} = \sigma_0 T^{-1/2} \exp[-(T_0/T)^{1/4}] \quad (1)$$

$$T_0 = 24\alpha^3 / \pi k_B N(E_F) \quad (2)$$

$$\sigma_0 = \frac{9}{8} \sqrt{\frac{3}{2\pi}} e^2 \nu_0 \left(\frac{N(E_F)}{k_B \alpha} \right)^{1/2} \quad (3)$$

The d.c. conductivity data for PMT obeys very well the $T^{-1/4}$ relationship (Fig. 2) suggesting that electrical conduction is dominated mainly by the mechanism based on variable range hopping. As a reasonable guess we fix the wave function decay $\alpha^{-1} = 5\text{\AA}$. Inserting this parameter and the adjusted Mott parameters (σ_0, T_0), we obtained realistic values of the density of localized states $N(E_F)$ at the Fermi level summarized on table 1. The fitting, however poses some problems. The values of T_0 ranged from $10^4 - 10^6$. Ehinger and Roth have reported that the variable range hopping is applicable under the requirement of $(T_0/T)^{1/4} > 10$ [14]. The data were out of range as have been

observed in the PP fitting [8]. Mott and Davis have pointed out that VRH occurs in the system in which the wave function is confined in a small space [13]. The small $(T_0/T)^{1/4}$ obtained here, i.e. 3 - 10 could be due to the fact that the wave function is highly delocalized as has been reported by Brédas et al [11]. On the other hand, we could not derive any reasonable values of $N(E_F)$ and α^{-1} by using the prefactor (σ_0) and optical phonon frequency ($\nu_{ph} \sim 6.10^{13} s^{-1}$ [8]), the former value of α^{-1} is far smaller than the realistic one and the $N(E_F)$ value far bigger. As can be seen in table 1 the values of the attempt frequency ν_0 appear to exceed the optical phonon frequency, and the ratio ν_0/ν_{ph} is quite smaller (2 - 27), except for the less doped sample with a ratio of 350. Notwithstanding these problems, the data of σ_0 and T_0 obtained here gave valuable information. The slope T_0 , decreases when increasing doping level. As can be seen from equation (2) this implies the decrease of $\alpha^3/N(E_F)$ ratio. The density of states shows a minimum near the Fermi level subsequently filled up with increasing dopant concentration [14]. Although the contribution of short decay length, on the higher T_0 values observed in the film containing small level doping cannot be ruled out.

PT films show a departure from this behaviour and the best fit to the measured T-dependence of the d.c conductivity is given by the following analytical expression (Fig. 3):

$$\sigma_{d.c} = \sigma'_0 \exp[-(T_a/T)^{1/3}] \quad (4)$$

Still several possible charge transport mechanisms give the same type of exponential dependence: two dimensional VRH [13], tunnelling of carriers [14], or interchain conductivity [15]. Using the conductivity data alone, one cannot distinguish between these three models. However only the two first mechanisms indicate that the slope T_a of the curves becomes progressively smaller when the dopant concentration increases. This is observed in our case. We rather believe that the observed conductivity is due to a complicated superposition of various transport mechanisms. A quantitative explanation of the difference in conductivity in the two materials is not simple. But one can try to associate this difference with the structure of the two polymers (difference in their chain arrangements, the conjugation length of the chain and the position of the counter-ions with respect to the chain). With its helicoidal structure, dopants in PMT may cause less disturbance in the polymer chains, in particular, it is possible for the dopant to infiltrate the polymer as an intercalant [16]. In the case of PT, several structural defects occur in the polymeric chain, like cross link, β linkage of heterocycle, inhibiting π electron delocalisation. The reticulation of the polymer chain, as observed in PT, leads to the trapping of dopants and thus the impossibility of controlling the undoping process [17]. Doping again the polymer may follow already established pathways to the dopant sites, thus causing inhomogeneous doping. So carriers tunnelling among more extending conducting regions reflecting inhomogeneities in the dopant determines the transport properties. The interchain transfer may be important in reducing the dimensionality of the electrical conductivity.

This study indicates that observed properties of polythiophenes films are consistent with the VRH model and tunnelling-hopping. The nature of polymer structure determines the importance of mechanism conduction. Quantitative models can be fitted to experimental data and reasonable parameters are obtained.

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Figures and table caption :

Table 1 : Parameters for three dimensional VRH deduced from d.c conductivity and assuming $\alpha^{-1} = 5\text{\AA}$.

Figure 1: d.c conductivity versus $10^3/T$ of a)poly(3-methylthiophene) and b)polythiophene.

Figure 2 : $\ln(\sigma_{d.c}T^{1/2})$ versus $T^{-1/4}$ of poly(3-methylthiophene) ; solid lines correspond to the fitting curves.

Figure 3 : $\ln(\sigma_{d.c}T^{2/3})$ versus $T^{-1/3}$ of polythiophene ; solid lines correspond to the fitting curves.

Table 1

y (%)	T_0 (K)	σ_0 ($S.cm^{-1}.K^{1/2}$)	$N(E_F)$ ($eV^{-1}.cm^{-3}$)	ν_0 (s^{-1})	ν_0/ν_{ph}
0.5	4.610^6	7.810^5	1.510^{20}	2.110^{16}	350
4	2.610^5	1.810^5	2.710^{21}	1.610^{15}	27
11	8.610^4	1.310^5	8.210^{21}	4.810^{14}	8
19	4.010^4	1.210^5	1.810^{22}	3.010^{14}	5

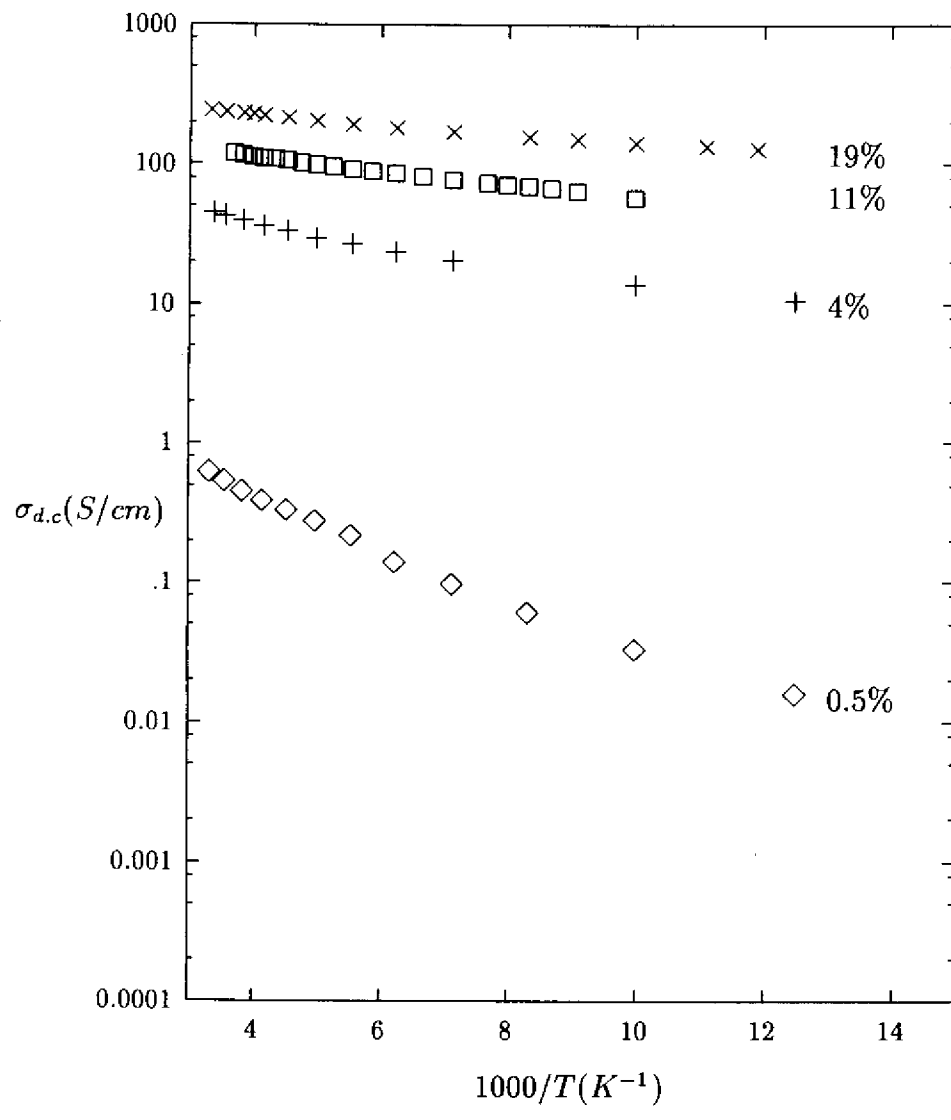


Fig. 1a

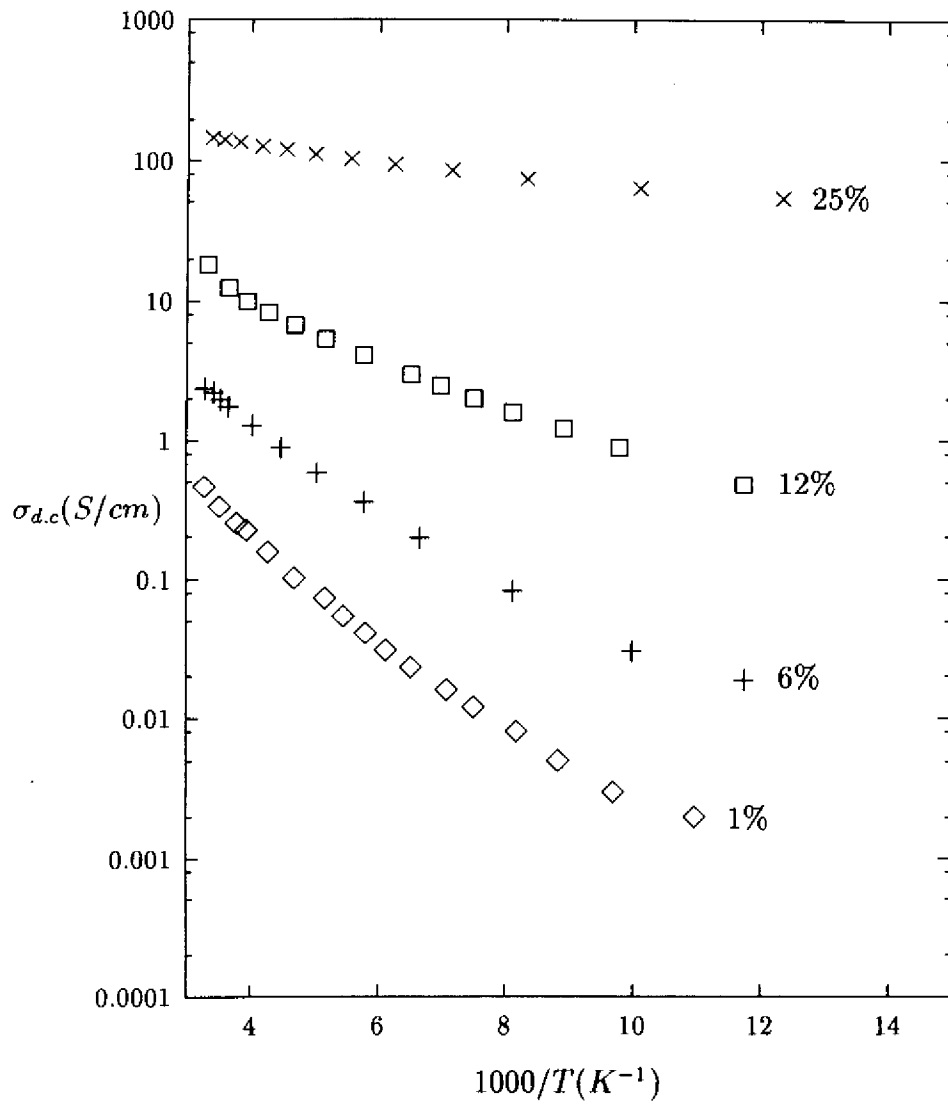


Fig. 1b

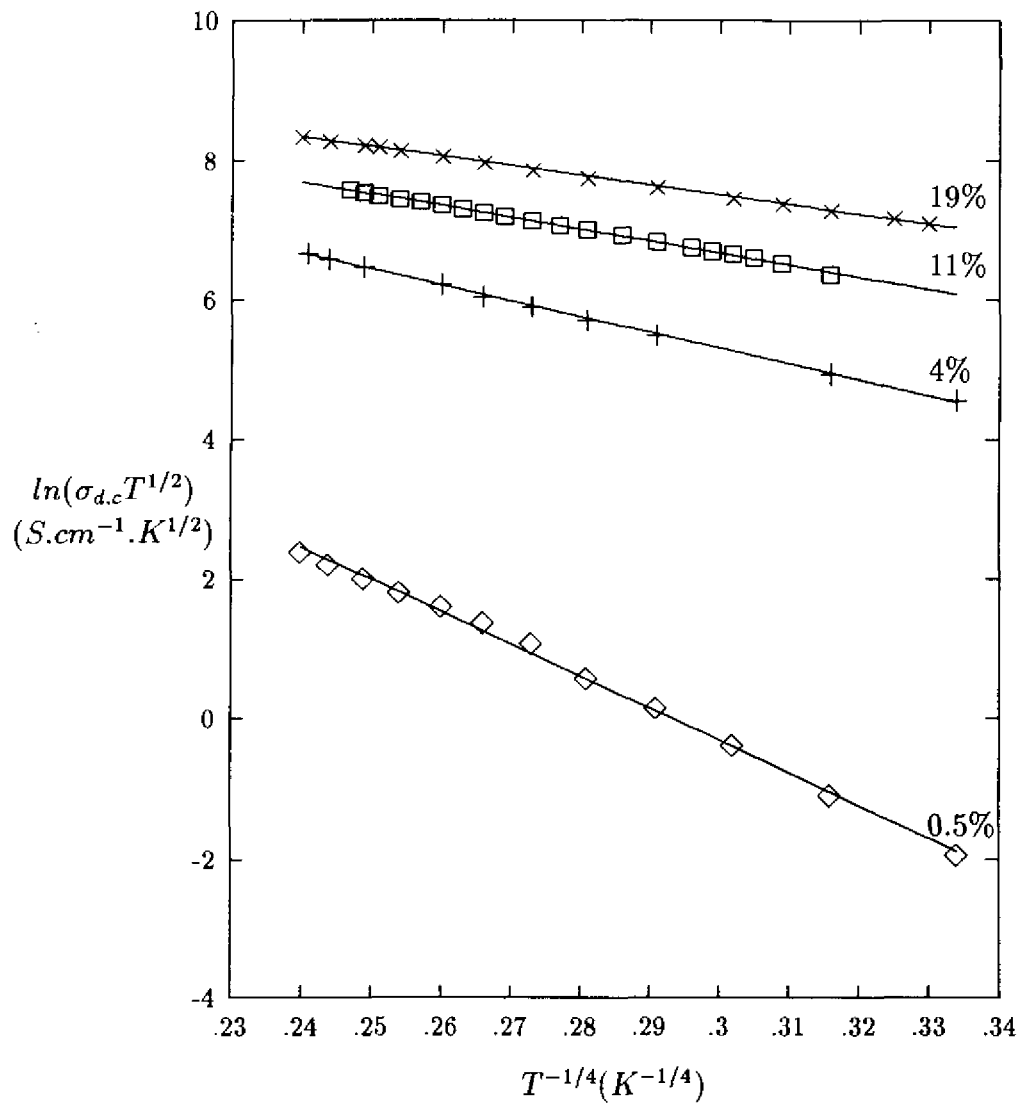


Fig. 2

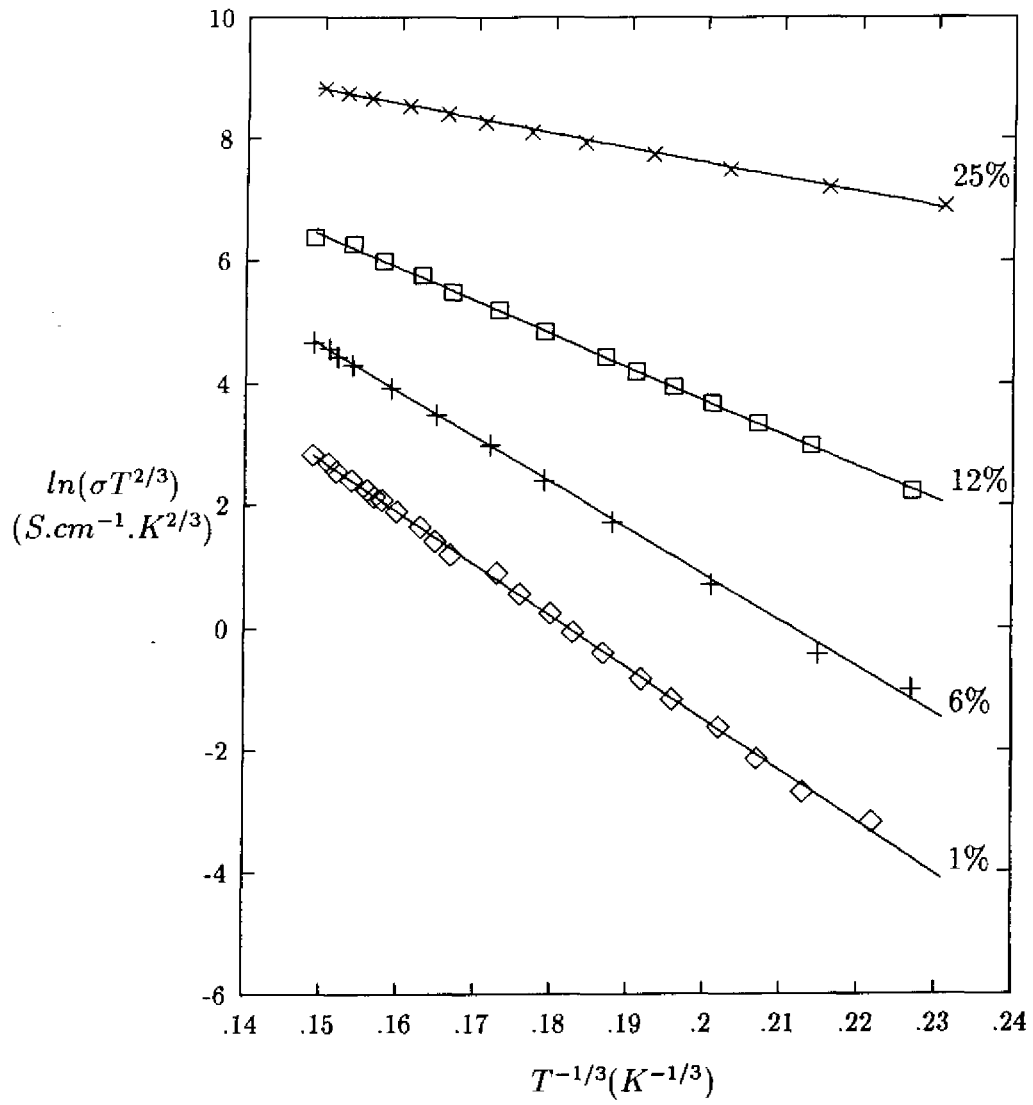


Fig.3

