

# BAND MODEL APPROACH TO CONDUCTION OF N-METHYL DERIVATIVES OF PYRIDINE WITH TETRACYANOQUINODIMETHANE (TCNQ)\*

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DC conductivity and thermoelectric power in the high temperature region are reported for polycrystalline samples N-methyl derivatives of pyridine (TCNQ)<sub>2</sub>. The data are interpreted in terms of band theory with neutral lattice scattering of carriers, resulting in temperature dependences of  $T^{1.5}$  and  $T^{-1.5}$  for the pre-exponential factor and charge mobility, respectively.

## 1. Introduction

During the last few years, interest in studies of complex TCNQ salts has increased. However, up to now little is known about the transport mechanisms in radical anion salts of TCNQ. In these salts, the Hall mobilities of the order of  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in many complexes [1-2] and the temperature-independent thermoelectric power [3] suggest that electrons are localized on specific TCNQ sites and movement is thermally activated. On the other hand, in other cases [4, 5], a mean free path of the same order as the inter-TCNQ spacing and negative temperature-dependence of mobility suggest that the band model is a more correct description.

Most of the TCNQ complexes salts exhibit large anisotropy of conductivity (quasi one-dimensional organic conductors) [6], but some have very low anisotropy in two different directions [5].

As was suggested by Chasseau [7], NMe<sub>2</sub>, 6MePy (TCNQ)<sub>2</sub> is two-dimensional organic system due to specific order in the TCNQ plane. With regard to the determination of the basic electrical parameters it is in this case reasonable to carry out the measurements on polycrystalline samples. In this paper, studies of electrical conductivity and ther-

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moelectric power in complex TCNQ salts with N-methyl pyridine and certain of their methyl derivatives are reported. The experimental results permit the calculation of the electron and hole mobilities. The data obtained can be interpreted in terms of band theory with neutral lattice scattering of charge carriers.

## 2. Sample preparation and experimental techniques

Synthesis of complex TCNQ salts with N-methyl pyridine and its methyl derivatives was carried out by the method of Melby [8]. Elemental analyses and electronic spectra showed the salts to have the 2 : 1 stoichiometry [9]. Measurements of conductivity were performed using the two-electrode technique already described [10]. A standard method was used to measure the thermoelectric e.m.f.: a thermal gradient of 1–2 deg was created between two silver blocks with a small supplementary heater. The d.c. conductivity and thermoelectric e.m.f. were measured in the high temperature region. The upper limit of temperature (350–360 K) is still below the temperature in which the sample becomes defected due to sublimation and mechanical processes. For this latter reason an increase in resistance was observed near 360 K presumably due to an increase in distance between individual particles of the sample.

## 3. Experimental results and discussion

The results for the d.c. electrical conductivity of the TCNQ salts studied are given in Table I, whereas Fig. 1 shows typical conductivity plots for the complex salts: NMe 3,5 MePy (TCNQ)<sub>2</sub>, NMe 2, 4, 6 MePy(TCNQ)<sub>2</sub>, and NMe 4 MePy (TCNQ)<sub>2</sub>. The conductiv-

TABLE I

Electrical properties of complex TCNQ salts

Salt	Conductivity $\sigma_{298}$ ( $\Omega^{-1}\text{cm}^{-1}$ )	Activation energy $E_a$ (eV)	Seebeck coefficient $S_{300}$ (mV/deg)	Carrier mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )		Mean free path of electron ( $\text{\AA}$ )
				$\mu_e$	$\mu_h$	
NMe Py (TCNQ) <sub>2</sub>	$8.85 \times 10^{-4}$	0.35	-0.16	88	68	63
NMe 4MePy (TCNQ) <sub>2</sub>	$4.59 \times 10^{-4}$	0.37	-0.06	129	118	93
NMe 2,6MePy (TCNQ) <sub>2</sub>	$5.40 \times 10^{-4}$	0.34	-0.40	50	26	36
NMe 3,5MePy (TCNQ) <sub>2</sub>	$1.18 \times 10^{-3}$	0.37	-0.11	274	237	197
NMe 2,4,6MePy (TCNQ) <sub>2</sub>	$9.60 \times 10^{-4}$	0.36	-0.13	179	147	129

ity data are somewhat different by comparison with those reported previously [10]. The results presented in this paper were obtained on samples not from the same process of synthesis. Nevertheless, the values of electrical measurements obtained on different samples of the same material are reproducible in the range of 3–5 percent.

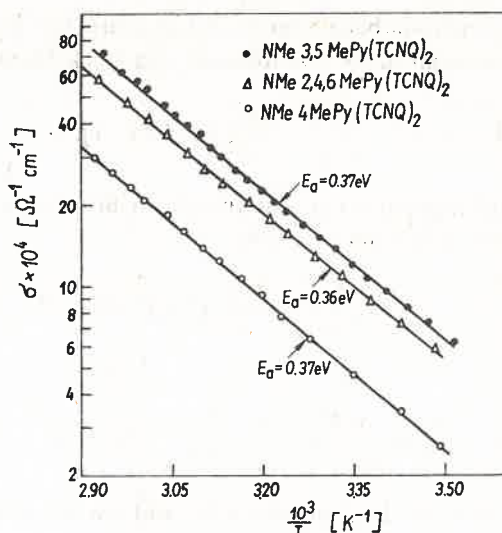


Fig. 1. Plots of log conductivity against reciprocal temperature for TCNQ complex salts

The band theory gives the following formula for the temperature-dependence of conductivity

$$\sigma = \frac{2(2\pi m^* kT)^{1.5}}{h^3} e(\mu_e + \mu_h) \exp(-E_a/kT) = \sigma_0 \exp(-E_a/kT)$$

with  $m^*$  effective mass, and  $\mu_e$  and  $\mu_h$  electron and hole mobilities. Since, as shown in Fig. 1, the log  $\sigma$  versus  $10^3/T$  plot is linear,  $\sigma_0$  is constant with temperature, and the mobilities have to depend on temperature as  $T^{-1.5}$ . From band theory, this dependence of mobility corresponds to neutral lattice scattering of carriers. The results for the temperature-dependences of the Seebeck coefficient are shown in Fig. 2. The thermoelectric power of our complexes exhibits a weak temperature-dependence. The magnitude of the Seebeck coefficient (from  $-60$  to  $-400 \mu\text{V/K}$  for different salts) and its temperature dependence

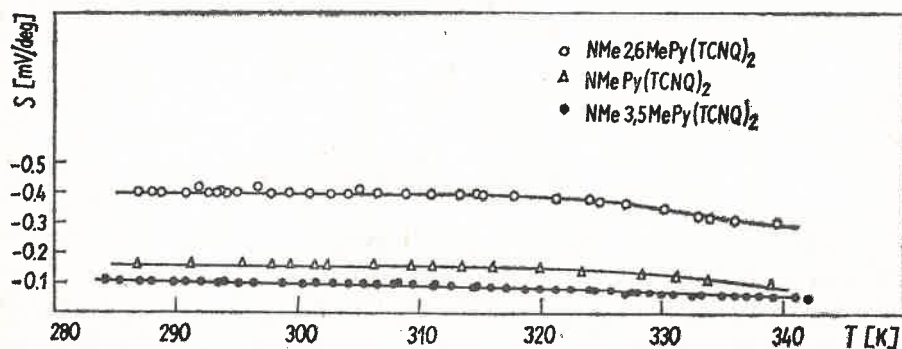


Fig. 2. Temperature dependence of thermoelectric power

is strongly suggestive of intrinsic behaviour in our systems. For intrinsic semiconductors, the thermoelectric power is given by the Johnson and Lark-Horovitz formula [11]:

$$S = - \frac{k}{e} \left[ \frac{\mu_e - \mu_h}{\mu_e + \mu_h} \right] [E_a/kT + A],$$

where  $A$  is the scattering parameter. For scattering by neutral lattice  $A = 2$  and the mobilities can be expressed by following relations:

$$\mu_e = \frac{\sigma}{2ne} \left[ 1 - \frac{Se}{k} (E_a/kT + 2)^{-1} \right]$$

and

$$\mu_h = \frac{\sigma}{2ne} \left[ 1 + \frac{Se}{k} (E_a/kT + 2)^{-1} \right].$$

By having recourse to the observed conductivity and carrier density calculated from

$$n = \frac{2(2\pi m^* kT)^{1.5}}{h^3} \exp(-E_a/kT)$$

and assuming equality between the free electron mass and effective mass (such a relationship has been found in similar complex salts [12]) the electron and hole mobilities can be calculated.

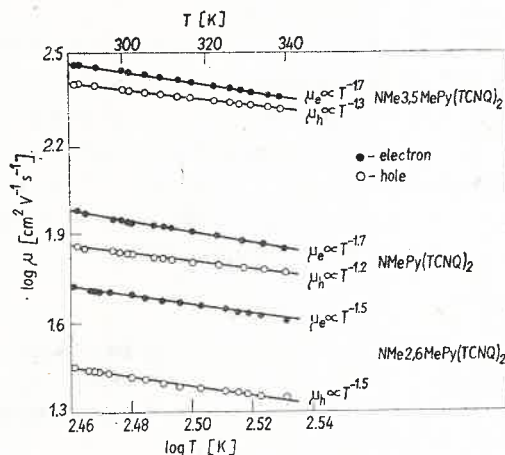


Fig. 3. Temperature dependence of mobility

The mobilities of the carriers as functions of temperature is shown in Fig. 3. Generally, temperature-dependences near  $T^{-1.5}$  were obtained for all derivatives of N-methyl pyridine (TCNQ)<sub>2</sub>. The good agreement between the mobility temperature-dependences determined from the conductivity data and those from Seebeck effect strongly suggests that the band model with phonon scattering of electrons and holes is the correct transport

mechanism. The values of mobilities were in the range from 30 to 270  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Such mobilities correspond to a mean free path (Table I) which is greater than the inter TCNQ spacing (about 3.2–3.5 Å). The negative temperature-dependence of mobility and the mean free path of the same order as the lattice spacing exclude hopping as the predominant transport process. The band model approach to conduction with neutral lattice scattering of charge carriers is proposed as an appropriate description for our complexes in the temperature range investigated.

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