

# The electrical behaviour and conduction mechanism of some mixed transition metal TCNQ salts

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The electrical behaviour of tetracyanoquinodimethane mixed transition metal salts (iron, cobalt, nickel and copper) has been investigated in the temperature range 290–533 K at constant pressure of 100 kbar  $\text{cm}^{-2}$ . The electrical resistivity measurements show a phase transition at nearly 380 and 390 K. The anomaly in the electrical resistivity is discussed. The activation energy of conductance has been calculated below and above the transition temperature. Further information concerning the electrical behaviour is obtained by considering the type and mechanism of the conduction process. This has been achieved by studying the effect of complex formation and temperature on the mobility and the number of charge carriers which take part in the conduction process.

## 1. Introduction

Fully conjugated cyano-compounds such as tetracyanoquinodimethane (TCNQ) are well known to play an important role as strong electron acceptors in the charge-transfer complexes [1]. TCNQ exhibits several exceptional properties of particular interest such as the ease with which this compound accepts one electron to form simple solid complexes. At room temperature TCNQ salts with metal cations generally show low to intermediate conductivities ( $10^{-5}$  to  $10^{-2} \Omega^{-1} \text{cm}^{-1}$ ) while its salts with cations of plane aromatic heterocyclic molecules show higher conductivities ( $\approx 10^2 \Omega^{-1} \text{cm}^{-1}$ ) [2].

Siemons *et al.* [3] reported the electronic properties of some organic and alkali metal TCNQ salts. Their results indicate that at the highest conductivity salts the electrons degenerate as in metals while for the less conductive salts the conduction takes place by means of an activated process. Nevertheless, it is not certain whether the carrier production or the carrier motion is activated. Leblanc [4] assumed that the conductivity states in the TCNQ salts arise from the motion of the odd electrons along face-to-face stacks of TCNQ molecules and a rearrangement of electrons to give two electrons as neighbours. Further, the energy required for this process is mainly due to Coulomb repulsion between adjacent unpaired electrons.

The major goal of this work is to study the electrical behaviour and the conduction mechanism of the mixed cation transition metal TCNQ salts.

## 2. Experimental details

The mixed cation TCNQ salts were prepared as previously reported by Melpy *et al.* [5]. The salts studied are Fe (TCNQ)<sub>2</sub>, FeCo(TCNQ), FeNi(TCNQ),

FeCu(TCNQ) as well as TCNQ. The samples were in the form of discs of 5 mm diameter and 2–3 mm thickness. They were prepared under a pressure of 100 kbar  $\text{cm}^{-2}$ . The front faces of the samples were covered with a thin graphite layer to achieve good contact. The cell used in the measurements has been described [6]. The temperature was measured by a copper–constantan thermocouple placed close to the sample and the temperature range was from 290 to 533 K. The direct current was measured by a Keithley Electrometer Type 610 B.

## 3. Results and discussion

The electrical resistivity ( $\rho$ ) of the investigated salts at room temperature ( $290 \pm 2$  K) is given in Table I. They lie in the range of typical semiconductor resistivity [7].

From Table I it is interesting to notice that the resistivity of TCNQ salts is lower by about  $10^4$  to  $10^6$  order of magnitude than that of neutral TCNQ. In previous work [8] the infrared and electronic spectroscopic studies of TCNQ salts show that the quinonoid structure of the TCNQ molecule changes into the benzenoid structure by salt formation. This will permit a great participation of the  $\pi$  electrons in the

TABLE I The electrical resistivity ( $\rho$ ) of TCNQ and its mixed transition metal salts at room temperature (290–2 K).

Substance	$\rho$ ( $\Omega \text{cm}$ )
TCNQ	$2.0 \times 10^{10}$
Fe(TCNQ) <sub>2</sub>	$4.4 \times 10^5$
FeCo(TCNQ)	$1.4 \times 10^6$
FeNi(TCNQ)	$1.2 \times 10^6$
FeCu(TCNQ)	$2.8 \times 10^4$

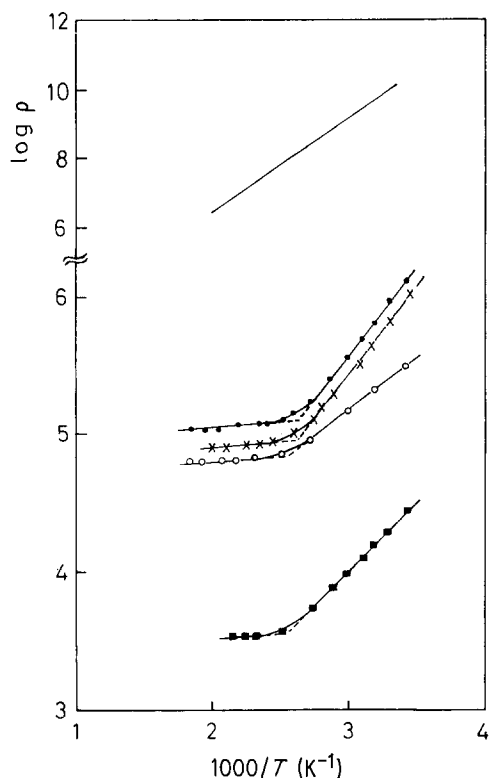


Figure 1 Relation between  $\log \rho$  and  $1000/T$  ( $K^{-1}$ ) for the studied mixed transition metal TCNQ salts. (— TCNQ, ● FeCo(TCNQ), × FeNi(TCNQ), ○ Fe(TCNQ)<sub>2</sub>, ■ FeCu(TCNQ)).

process of conduction in the case of the TCNQ salts. Jida [9] studied the electrical and optical properties of ten TCNQ salts including alkali metal cations. He concluded that an increase in the interplanar spacing decreases the overlap integrals of the unpaired-electron molecular orbits which decreases the electrical conductivity and vice versa.

The resistivity of the investigated mixed transition metal TCNQ salts at room temperature follow the order

$$\text{FeCo} > \text{FeNi} > \text{Fe} > \text{FeCu}$$

The temperature dependence of the electrical resistivity of the studied mixed salts is shown in Fig. 1 and that of TCNQ is plotted for comparison. The linear increase of  $\log \rho$  with  $1/T$  for the neutral TCNQ

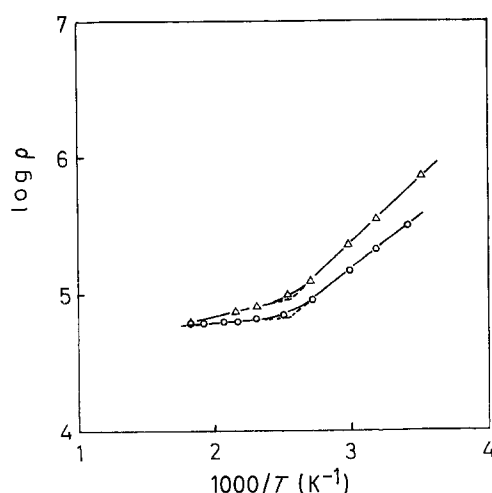


Figure 2 Relation between  $\log \rho$  against  $1000/T$  (K) on heating (○) and cooling (△) cycle for Fe(TCNQ)<sub>2</sub> salt.

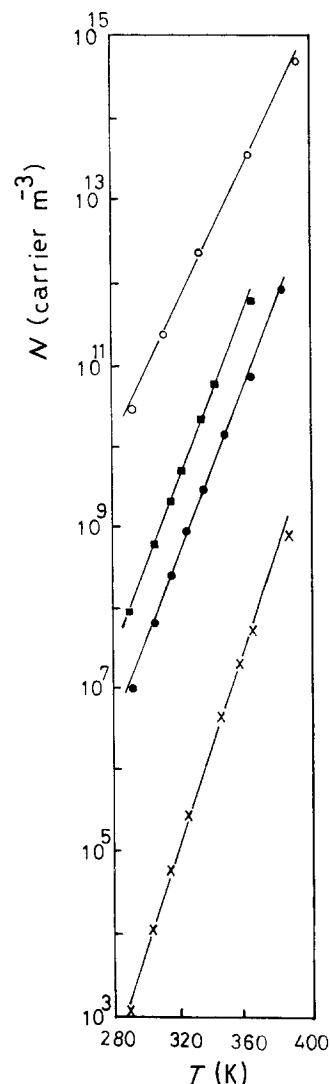


Figure 3 Effect of temperature on the number of carriers for the studied mixed transition metal TCNQ salts for  $T < T_1$ . (○ Fe(TCNQ)<sub>2</sub>, ■ FeCu(TCNQ), ● FeCo(TCNQ), × FeNi(TCNQ)).

indicates that it behaves like a typical intrinsic semiconductor material. On the other hand, the relation for the studied mixed transition salts consists of two linear regions connected with a curved region representing intermediate temperature region. This anomaly in the resistivity is observed at nearly 390 K for both Fe(TCNQ) and FeCu(TCNQ) salts and nearly 380 K for both FeCo(TCNQ) and FeNi(TCNQ) salts.

Fig. 2 shows the electrical resistivity on the cooling and the heating cycle for Fe(TCNQ)<sub>2</sub>. A slightly higher resistivity value is obtained during the cooling cycle than that during initial heating. At room temperature the resistivity in the second thermal cycle is a little higher than the initial value. However the agreement of the transition temperature  $T_1$  in heating and cooling

TABLE II The activation energies of the TCNQ salts

Substance	$E_1$ (eV)	$E_2$ (eV)
TCNQ	0.560	—
Fe(TCNQ) <sub>2</sub>	0.867	0.06
FeCo(TCNQ)	1.059	0.05
FeNi(TCNQ)	1.283	0.10
FeCu(TCNQ)	1.000	0.10

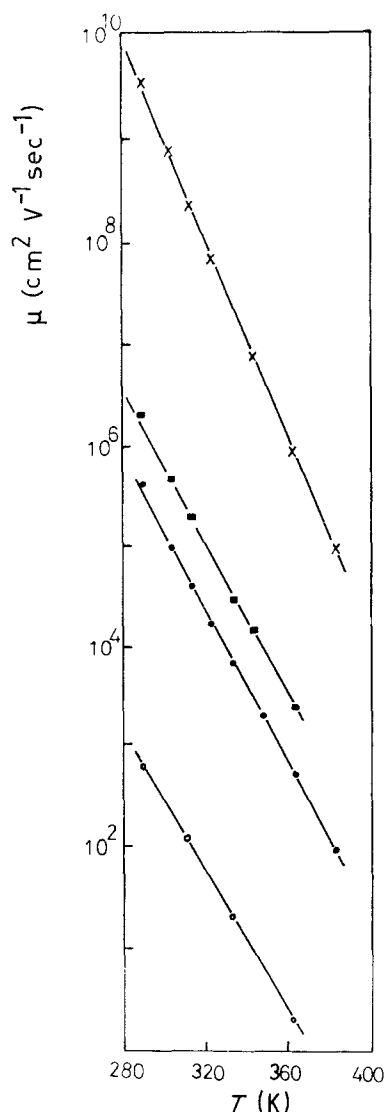


Figure 4 Effect of temperature on the carrier mobility for the studied mixed transition metal TCNQ salts for  $T < T_1$  (x FeNi(TCNQ), ■ FeCu(TCNQ), ● FeCo(TCNQ), ○ Fe(TCNQ)<sub>2</sub>).

processes is obvious. This indicates that the anomaly in the electrical resistivity is not a decomposition process.

Since TCNQ and its metal salts are composed of units stacked in a plane to plane manner with some periodicity in the column, the anomaly may be principally the result of change in the manner of packing between the metal ions and the TCNQ column together with a change in the periodicity of the TCNQ column at the transition temperature.

The activation energies have been calculated from the slope of the linear parts of Fig. 1 and are given in Table II.

$E_1$  and  $E_2$  are the activation energies for  $T \geq T_1$ . They are in the range from 1.283 to 0.867 eV for  $T < T_1$  and from 0.10 to 0.06 eV for  $T > T_1$ . The activation energy in the low temperature range is greater than that in the high temperature range. This can be explained by considering the effect of temperature on the stacking in the column and the intramolecular forces. As the temperature increases the interplanar distance will be increased. Therefore, the stacking becomes loosely packed and the charges pass freely through the potential barrier leading to a decrease in the energy required for activation.

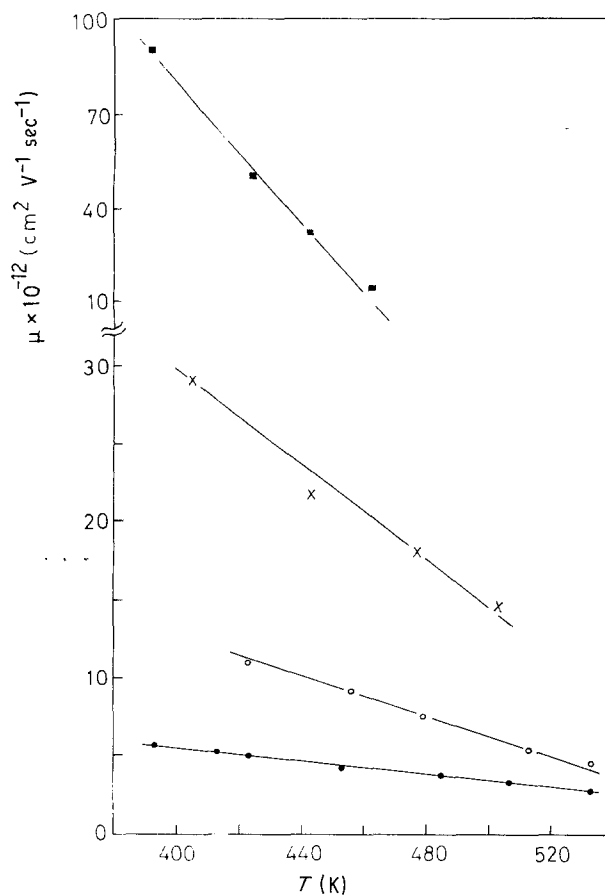


Figure 5 Effect of temperature on the carrier mobility for the studied mixed transition metal TCNQ salts for  $T > T_1$  (■ FeCu(TCNQ), x FeNi(TCNQ), ○ Fe(TCNQ)<sub>2</sub>, ● FeCo(TCNQ)).

The phase transition may be attributed to a change in the type of packing and a volume change. This change in the lattice would be expected to cause a change in the singlet-triplet separation energy. Therefore, the relatively small value of the activation energy obtained above the transition temperature may be attributed to a change in the singlet-triplet separation energy.

Further information concerning the electrical behaviour was obtained by considering the type and mechanism of the conduction process. This can be achieved by studying the effect of temperature on the mobility  $\mu$  and the number of current carriers  $N$  which take part in the conduction process. The number of charge carriers can be obtained by calculating the Fermi distribution function and the density of state function [10, 11]. The product of the two functions gives the actual number of carriers per cubic metre  $N$ . The mobilities of the charge carriers  $\mu$  ( $\text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$ ) are also calculated using the single model relation [12]

$$\sigma = Ne\mu$$

where  $\sigma$  is the electrical conductivity in  $\Omega^{-1} \text{cm}^{-1}$  and  $e$  is the electronic charge.

The effect of temperature on the number of carriers and its mobilities for the studied mixed salts are shown in Figs 3 and 4 for  $T < T_1$ . Inspection of Figs 3 and 4 show that the mobility of the carriers for all the studied compounds decreases with increasing temperature while the density of the carriers increases in

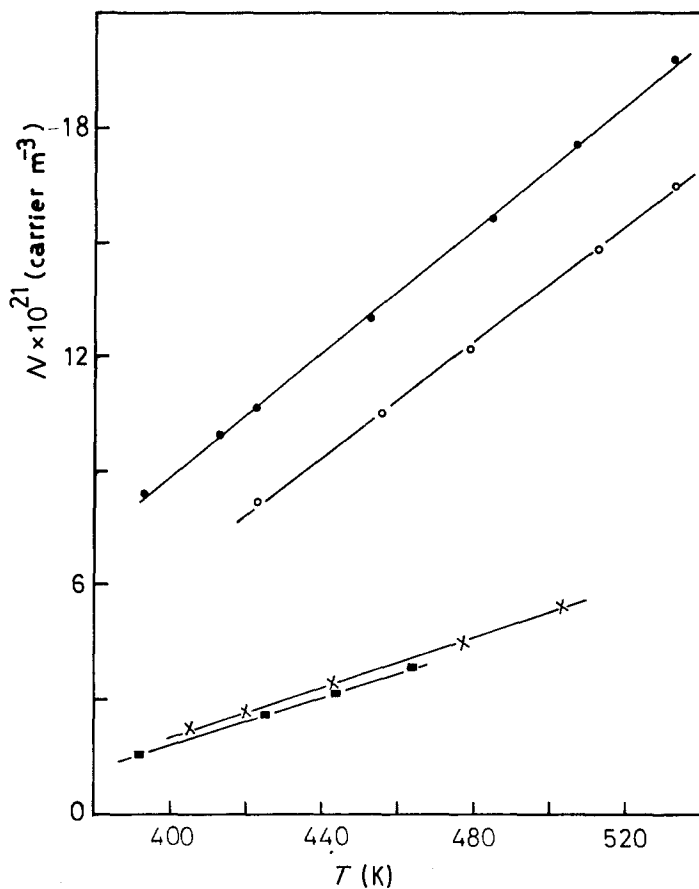


Figure 6 Effect of temperature on the number of carriers for the studied mixed transition metal TCNQ salts for  $T > T_1$  (● FeCo(TCNQ), ○ Fe(TCNQ)<sub>2</sub>, × FeNi(TCNQ), ■ FeCu(TCNQ)).

the region  $T < T_1$ . This indicates that the activation process is due to the electron transfer from the valence band to the conduction band by the thermal activation and the decrease in the electrical resistivity of the mixed transition metal complexes may be due to the production of carriers in the conduction band.

For  $T > T_1$  the mobility increases with increasing temperature for the studied salts while the carrier number increases with increasing temperature, Figs 5 and 6. This indicates that the conduction process is a contribution from the increased drift velocity of the carriers as well as their concentration.

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