The Electrical Conductance of Some Alkali- and Divalent Transition Metal TCNQ Salts

H. H. Afify, F. M. Abdel-Kerim, H. F. Aly * and A. A. Shabaka
National Research Centre, Physics Department and Atomic Energy Establishment*,
Cairo, Egypten

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The electrical resistivity of the tetracyanoquinodimethane salts of ten alkali and transition metal cations has been investigated at temperatures from 300 to 470 K. The measurements indicate a phase transition, the activation energy of conductance being smaller in the high temperature region. The nature of this phase transition is discussed.

Tetracyanoquinodimethane (TCNQ) is a well known strong electron acceptor which forms stable "simple" salts as well as "complex" salts containing both neutral TCNQ and the anion $TCNQ^-$. X-ray analysis [1] of TCNQ salts indicates face to face stacks. 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 ($\simeq 10^2\,\Omega^{-1}\,\text{cm}^{-1}$). For alkali metal salts [2], a phase transition has been reported in the temperature range from $-150°$ to 230 °C. So far, few investigations have been made on the electrical conduction of TCNQ salts with metal cations [3]. In the present work such measurements were carried out for four alkali metal and six $3d^n$ divalent transition metal-TCNQ salts.

Experimental

The salts were prepared as previously reported by Melby et al. [4]. The ten salts studied are: Li(TCNQ), Na(TCNQ), K(TCNQ), Cs(TCNQ)TCNQ $Mn(TCNQ)_2$, $Fe(TCNQ)_2$, $Co(TCNQ)_2$, $Ni(TCNQ)_2$ $Cu(TCNQ)_2$ and $Zn(TCNQ)_2$. The samples were in the form of discs having 5 mm diameter and 2–3 mm thickness, prepared under a pressure of $100\,\text{kg/cm}^2$. 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 previously [5]. The temperature was measured by a copper-constant an thermocouple placed close to the sample and the direct current was measured with a Multiflex galvanometer with a sensitivity of $4 \cdot 10^{-9}$ A.

Results and Discussion

The electrical resistivities (ϱ) of the investigated compounds at room temperature (20 ± 2 °C) are given in Table 1. They lie in the range of typical semiconductor resistivities [6]. The resistivity of TCNQ (order of $10^{10}\,\Omega$ cm) is low compared to that of ordinary organic materials such as naphthalene and anthrathene (order of $10^{19}\,\Omega$ cm). Infrared spectroscopic studies of TCNQ [7] indicate unsaturated C=C bonds in conjugation with C≡N bonds. This lowers the energy gap between the valence state and the next allowed energy state [6]. and could explain the relatively low resistivity of TCNQ.

According to Table 1 the resistivities of the TCNQ salts are by 3 to 6 orders of magnitude lower than that of neutral TCNQ. This can be interpreted as follows: IR and electron spectroscopic studies [8] show that the quinonoid structure of the TCNQ molecule changes into the benzenoid structure or salt formation. This will permit for a greater participation in the salts of the π-electrons in the process of conduction. X-ray analysis [9–11] of $M^{n+}(TCNQ)_n$ showed that the $TCNQ^-$ anions are stacked with interplaner distances of 3.2 and 3.5 Å. These values are remarkably smaller than the Van der Waals distances of the interplanar spacing between two aromatic-ring planes, which

Table 1. The electrical resistivity (ϱ) of TCNQ and its salts at room temperature (290 ± 2 K).

Substance	ϱ (Ωcm)	Substance	ϱ (Ωcm)
TCNQ	2.0×10^{10}	$Mn(TCNQ)_2$	3.4×10^5
Li-TCNQ	5.6×10^4	$Fe(TCNQ)_2$	3.4×10^5
Na-TCNQ	8.8×10^5	$Co(TCNQ)_2$	5.8×10^6
K-TCNQ	2.0×10^6	$Ni(TCNQ)_2$	3.5×10^6
Cs(TCNQ)	2.9×10^5	$Cu(TCNQ)_2$	5.2×10^5
TCNQ		$Zn(TCNQ)_2$	7.5×10^7

Reprint requests to Hassan H. Afify, Physics Department, National Research Centre, Dokki, Cairo, Ägypten.

are usually believed to be of the order 7.4 Å [10]. Therefore the antibonding π^* electron orbitals of the $TCNQ^-$ anions, which are perpendicular to the plane of the ring, will overlap and contribute to the electrical conductance. Ida [11] 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 observed resistivities of the simple alkali metal TCNQ salts follow the order $Li < Na < K$. This may be explained by a decrease in the interplanar spacing with decreasing cationic radius.

The deviation of the Cs-salt from the above sequence may be attributed to the presence of the neutral TCNQ molecule in the compound [8].

The resistivities at room temperature of the investigated transition metal TCNQ compounds follow the order

$$Mn < Fe < Cu < Ni < Co < Zn .$$

Here the trend depends not so much on the ionic radius of the cation than on it's ligand field strength. Increasing stability of the formed complexes will decrease the number of dislocated electrons and increase the resistivity. The data obtained in this work generally show that the electrical resistivity increases with the ligand field stabilization energy of the octahedral high spin configuration. Only the Ni-salt does not obey this rule.

The measured temperature dependences of the electrical resistivities are shown in Figs. 1–3 in the form of log ϱ vs. $1/T$-plots. Neutral TCNQ gives a linear relation (Fig. 3) which indicates that it behaves like a typical intrinsic semiconductor. On the other hand, the log ϱ vs. $1/T$-plots for the TCNQ salts consists of two linear sections, connected by a range of transition. The resistivity at the transition temperature is about 13 times lower than that at room temperature. From the slope of the linear parts in Figs. 1 and 2 the activation energies have been calculated as given in Table 2.

The investigated alkali metal cation TCNQ anion radical salts have activation energies from 0.43 to 0.16 eV below the transition temperature and from 0.057 to 0.023 eV above. The small activation energy of Li(TCNQ) compound may be attributed to the contribution of ionic conduction to its

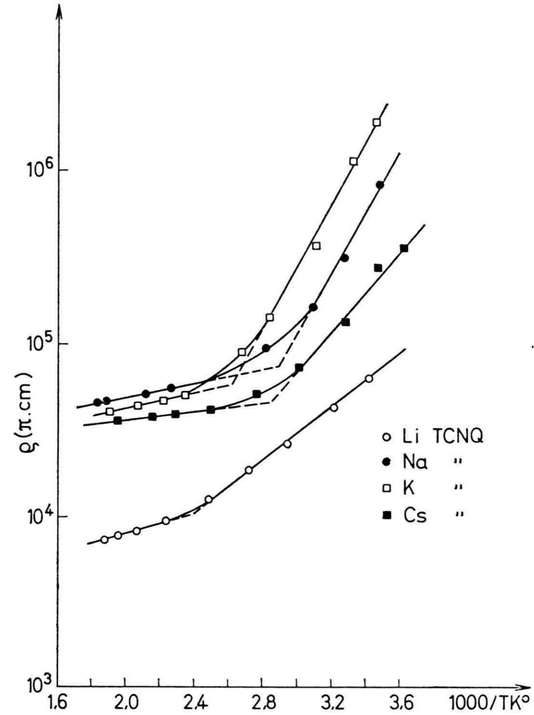

Fig. 1. Electrical resistivity (ϱ) against $1000/T$ (K) for the alkalimetal-TCNQ salts.

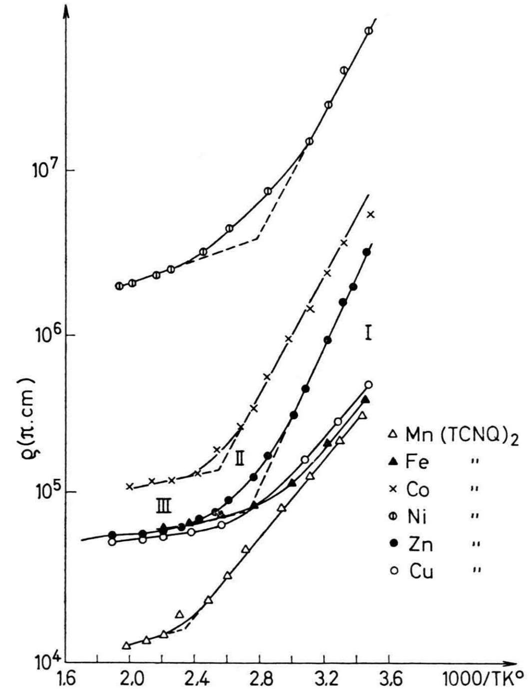

Fig. 2. Electrical resistivity (ϱ) against $1000/T$ (K) for the transition metal-TCNQ salts.

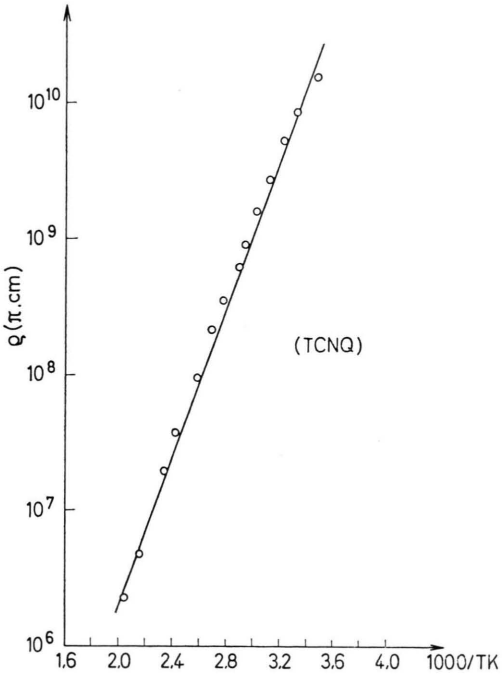

Fig. 3. Relation between the electrical resistivity (ϱ) and $1000/T$(K) for tetracyanoquinodimethane (TCNQ).

Table 2. Activation energies of TCNQ and its salts.

Substance	E_1 (e. v)	E_2 (e. v)	E_1/E_2
TCNQ	0.56	—	—
Li-TCNQ	0.16	.057	2.80
Na-TCNQ	0.34	.041	8.29
K-TCNQ	0.43	.047	9.15
Cs(TCNQ) TCNQ	0.25	.023	8.69
$Mn(TCNQ)_2$	0.23	.097	2.37
$Fe(TCNQ)_2$	0.24	.033	7.27
$Co(TCNQ)_2$	0.39	.052	7.50
$Ni(TCNQ)_2$	0.46	.050	9.20
$Cu(TCNQ)_2$	0.25	.031	8.06
$Zn(TCNQ)_2$	0.37	.155	2.39

E_1 = Activation energy for the low temperature range.
E_2 = Activation energy for the high temperature range.

electrical conductivity [12]. On the other hand, the transition metal TCNQ compounds have activation energies from 0.45 to 0.22 eV below the transition temperature and from 0.15 to 0.03 eV above. The activation energies of the transition metal TCNQ compounds are formed to be larger in general than those of alkali metal TCNQ compounds. This could be attributed to the interactions between the electrons in the d orbitals of the metal cations and the anti bonding π orbitals of the ligand TCNQ. This interaction will localize the π electronic charge on the ligand, i.e. the energy required for excitation of the localized π electron will increase. The activation energy in the low temperature range is greater than in the high temperature range by a factor ranging from 2.4 to 9. This factor is mainly related to the metal cation. In case of the alkali metal TCNQ compounds, it is found that this factor depends to a great extent on the metal cation ionic radius, i.e. its value increases with increasing ionic radius. On the other hand, for the Mn and Zn TCNQ compounds the value of this factor is the same while its value increases from the Fe- to the Ni-salt. This can be explained by the fact that, as the temperature increases, the interplanar distance increases.

The phase transition phenomenon was observed in all investigated compounds. The transition temperatures are 420 and 347–373 K for the Li-, Na-, K-, and Cs-salts and range from 340 to 370 K for the transition metal salts. These phase transitions 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 activation energy value obtained above the transition temperature may be attributed to a change in the singlet-triplet separation energy.

This phenomenon was also observed by measurements of the absolute paramagnetic susceptibility and the electrical conductivity [2, 11]: the transition temperatures formed were in the range of 338–391 K [13], or 348–395 K [2] for Na(TCNQ), K(TCNQ) and Rb(TCNQ) [1].

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