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FIELD- AND FREQUENCY DEPENDENCE OF THE CONDUCTIVITY OF SOME SUBSTITUTED MORPHOLINIUM TCNQ$_2$ COMPOUNDS

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ABSTRACT

We present measurements on both the field and the frequency dependence of some substituted morpholinium TCNQ$_2$ compounds as well as on some salts with a 1:1 donor to acceptor ratio. The field dependence of all investigated 1:2 salts exhibit non-linear V-I characteristics. These anomalies are present only in the chain-direction. Furthermore, the shape of the conductivity vs. field curve is temperature independent and scales with the zero-field conductivity. This indicates that a single mechanism is responsible for the conductivity. The 1:1 salts do not exhibit these field-induced anomalies. First results are given for the frequency dependence of the conductivity. It is shown that both field and frequency dependence can be fitted to the same empirical formula.

INTRODUCTION

In this paper, new experimental results are presented on the conductivity of substituted (thio)morpholinum bis-tetracyanoquinodimethane (XY-(T)M TCNQ$_2$) compounds. Here the substitution (X,Y) of the morpholinium is with alkyl-groups CnH$_{2n+1}$ (n=0,1,2,..) *). This substitution and the substitution of the oxygen-

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*) The following abbreviations are used:
 (T)M = (thiomorpholinium; for the alkyl groups: H = hydrogen, M = methyl,
 E = ethyl, P = propyl, iP = isopropyl and B = buthyl.

atom of the morpholinium group by sulfur (thiomorpholinium) leads to a series of closely related compounds, enabling the study of the systematics of one-dimensional (semi)conductors.

For a large number of these compounds, the crystal structure has been determined, which allows one to calculate the band-structure parameters. This has been done by Van Smaalen and Kommandeur [1], who found that the intrachain transfer integral is typically 100 times larger than the interchain transfer integral. It was also found that the calculated band gap is very poorly related to the observed activation energies for the conductivity. In order to gain understanding of the conductivity mechanism in these compounds we have measured the field and frequency dependence of the conductivity for a large number of XY-(T)M TCNQ$_2$ compounds, which are presented below.

From the present study two classes of materials emerge. The first class of compounds is characterised by

(i) low room temperature conductivity ($\ll 1$ (Ω cm)$^{-1}$) and high activation energy (> 1 eV)

(ii) field and frequency independent conductivity,

while the second class, on which we will focus, has typically

(i) a room temperature conductivity of the order of 1 (Ω cm)$^{-1}$ and activation energies of order 0.01-0.1 eV.

(ii) a very strong dependence of the conductivity on both electric field and frequency.

The functional form of the field dependence of the conductivity scales with zero-field conductivity [2], indicating that a single process is responsible for the conductivity, unlike e.g. in CDW-systems, where one can split the conductivity into a single electron part and a cooperative part. In the concluding section of this paper we will discuss the implications of this point in more detail.

EXPERIMENTAL

All measurements were performed on single crystals obtained by slow cooling of an acetonitril solution of the constituents. The crystals and typical dimensions of 5×1×0.2 mm. In all measurements, silver paint was used to obtain electrical contact. Usually a two-probe configuration was employed, while checks were made on the contact linearity using a four-probe method. This confirmed that the contacts has a negligible resistance. In the measurements at high electric fields a pulsed voltage was set across the crystal, so as to minimize the Joule heating of the sample. The high-frequence measurements were made over the frequency range from 4-2600 MHz, using a Hewlett Packard 8754A network ana-

lyzer, with a 8502A reflection/transmission test set. In the experiment the reflection from a crystal mounted as the termination of a 50 Ohm coaxial lead is compared, both in magnitude and phase, with the incident signal. Due to the fragility of the crystals and their large thermal expansion coefficient, all high frequency measurements were confined to room temperature. Unless stated otherwise, the results refer to measurements at room temperature, with an electric field along the stacking axis of TCNQ.

RESULTS AND DISCUSSION

The field- and frequency dependence of the conductivity discussed below is a one dimensional feature. For some samples the field-dependence was measured perpendicular to the TCNQ stacking axis. In these directions the anomalies were at least a factor 100 smaller than along the stacking axis (cf. figure 1). For several samples showing non-linear behaviour, the temperature dependence was measured. Apart from the structural phase transitions occurring in some of the compounds, a thermally activated behaviour was found, in accordance with previously reported results [3]. An important feature is the above-mentioned scaling of the field dependence of the conductivity, i.e., the function $\sigma(E,T)/\sigma(0,T)$ is independent of temperature. From this one is led to conclude that a single mechanism determines the conductivity. The results can be fitted to the empirical formula [2]

$$\sigma(E)/\sigma(0) = 1 + A \, \exp\left[-\left(\varepsilon_m/E\right)^\alpha\right] \qquad (1)$$

where α is a parameter, which can be related to the amount of disorder present in the system (note that for $\alpha = 1$, one has the familiar Zener tunneling formula used in connection with CDW-systems [4]). However, even for systems without any known degree of disorder, specifically METM-TCNQ$_2$, α is markedly different from unity. As discussed in [2] a value of $\alpha < 1$ can be explained by assuming a distribution of depinning fields ε_m.
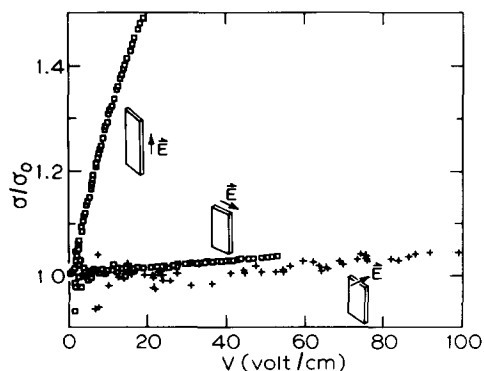

Fig. 1 Field dependence of the conductivity of METM TCNQ$_2$ along three principal axes at room temperature. The conductivity is scaled to the zero field values: $10(\Omega \text{ cm})^{-1}$ for E ‖ c and 100 to 1000 times less for E ⊥ c.

A similar situation is encountered with the frequency dependence of the conductivity. Although there is in general no precise mapping of the field- and frequency dependence, the real part of the conductivity $\sigma'(\omega)$ obeys, when scaled to $\sigma(0)$, eq.(1) with the electric field replaced by the frequency. Fig.2 shows both the frequency and electric field dependences of the conductivity of several of the investigated compounds.

In anticipation of the discussion of the results, we notice that no anomalies in the field dependence of the conductivity have been found in any 1:1 morpholinium TCNQ salts.
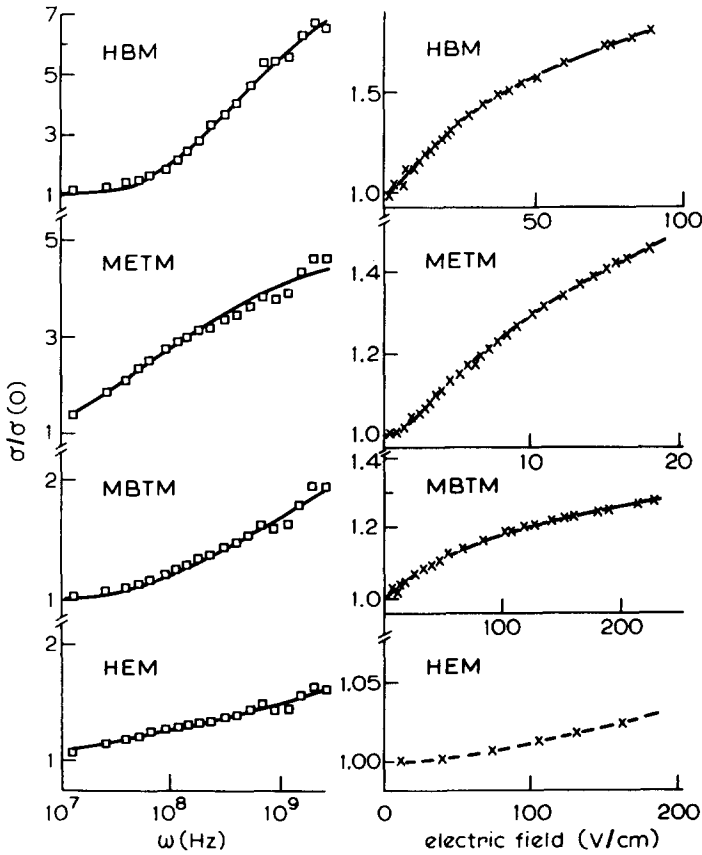
Fig. 2. Dependence of the conductivity of some XY(T)M TCNQ$_2$ compounds on frequency (left) and electric field (right). The drawn lines are fits to eq.(1).

Table 1 lists the fitting parameters to eq.(1) for the anomalous behaviour of some compounds. Some general remarks can be made:

(i)   The anomalies tend to be larger for semi-conductors with low activation energies.

(ii)   The frequency-induced increase in the conductivity is always larger than the increase resulting from high electrical fields (cf. also fig.2).

(iii) The value of α in eq.(1) is roughly the same for both the field and frequency dependences.

(iv)   For the series $(1-2-M)_x(1-2-TM)_{1-x}$, it was concluded [2] that α is related to the amount of disorder on the donor chain.

(v)   The ratio between the characteristic fields and frequencies (last column) is of the same order for all compounds (0.1-1 V/cm MHz).

From the fact that the above conclusions are made for a whole range of compounds, one may conclude that one is confronted with the same conduction mechanism in all compounds, featuring analogous non-linear behaviour.

TABLE 1

Donor group	E_a	Frequency		Electric field		E/ω *)
		A_ω	α_ω	A_E	α_E	
MEM	0.23	no anomaly		no anomaly		---
MEM 350 K	0.0	?		4.8	0.28	?
(MEM)0.84						
(METM)0.16	0.1	> 20	0.11	> 5	0.15	0.15
METM	0.07	3.9	0.49	1.7	0.50	0.5
HEM	0.37	1.3	0.22	small effect at high field		---
HiPM	0.22	5.0	0.71	small effect at high field		---
HBM	0.13	8.0	0.48	2.4	0.45	0.3
MBTM	?	1.5	0.41	1.1	0.33	0.85
PiPM	?	no anomaly		no anomaly		---
EiPM	0.56	no anomaly		no anomaly		---

*) At moderate fields and frequencies, the conductivity increases linearly with field (frequency). E/ω is ratio between field-slope and frequency-slope.

Previously [2], we have argued that none of the commonly used models is capable of accounting for the observed features. We briefly summarize the objections:

- models involving tunneling through random barriers fail to explain the effects seen in systems without any known disorder

- solitons (suggested recently [5]) can not be formed since the ground-state is not degenerate with respect to different alternations of the transfer integral

- macroscopic CDW-like charge transport is not possible in systems where the charge density wave is commensurate with the unit cell.

To account for the above presented observations, the authors have considered the $M-TCNQ_2$ system with two different order parameters: one which accounts for alternation of the transfer integral; the other accounts for potential alternation within the unit cell [6]. In doing so, one finds that cooperative charge transport is possible by varying both order parameters in a coherent fashion. This eventually leads to a description in terms of coupled optical phonons. From the model one finds temperature activated conductivity with an activation energy which is related to optical phonon energies rather than to the gap in the single particle spectrum. This may clarify the absence of a clear relation between the one electron gap and the activation energy for morpholinium $TCNQ_2$ compounds as found by the authors of ref. 1.

In conclusion we can say that the set of data collected on a large group of $TCNQ_2$ compounds is suggestive of a single, new type of conduction for which the optical phonon mediated process [1] is a likely candidate.

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