STATIC DIELECTRIC CONSTANT OF DISORDERED ORGANIC QUASI ONE-DIMENSIONAL CONDUCTORS:
LOCALIZATION BY DEFECTS

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We have measured the low temperature dielectric constant ε of two
similar quasi one-dimensional organic conductors, N-Me-iso Qn(TCNQ)$_2$
and Qn(TCNQ)$_2$. For N-Me-iso Qn(TCNQ)$_2$ below 10 K, ε is independent of
temperature and is frequency independent in the range 5×10^5 Hz to
9×10^9 Hz, within the 50% experimental uncertainty. Thus we believe
the low temperature microwave dielectric constant to be a good approxi-
mation of the static value in this salt. For Qn(TCNQ)$_2$ at low tempera-
tures, the relation $\varepsilon \propto (c+c_0)^{-2}$ holds, where c is the defect concen-
tration and c_0 is an effective defect concentration of the nominally
pure material. This relation is predicted by the model of interrupted
metallic strands with energy spacings larger than kT, and it indicates
that electrons are strongly localized by defects along the conducting
chains.

A variety of often contradicting models
has been proposed in the last decade to explain
the transport properties of quasi one-dimension-
al organic conductors with disordered cystal-
line structure, and the problem remains un-
settled today. Introduction of defects into
structurally ordered systems[1] smears the metal
insulator transition due to the three dimension-
al ordering of charge density waves. Similarly,
many disordered systems undergo a gradual metal
insulator transition with decreasing tempera-
ture[2] not accompanied by an ordering of charge
density waves.[3] These materials, although in-
sulating at low temperatures, exhibit an anoma-
lously large dielectric constant ($\varepsilon = 10^2 - 10^3$)
at microwave frequencies.[2]

High dielectric polarizability has been
suggested by Gorkov and Eliashberg for minute
metallic particles.[4] However, as pointed out by
Strassler et al.,[5] depolarization charges in-
duced in usual metal particle systems suppress
this effect. Rice and Bernasconi[6] have proposed
that the large polarization may be due to a
localization effect: electrons become localized
to metallic strands terminated by defects of the
conducting chains. The discrete energy level
structure of electrons confined to the strands
leads to an insulating and highly polarizable
material at temperatures $k_B T < \Delta E$, where ΔE is
the energy level spacing at the Fermi level.

Quasi one-dimensional organic conductors
are good candidates for interrupted metallic
strand behavior. The anisotropy of conductivi-
ty indicates a small interchain bandwidth. The
exponential decrease of conductivity with de-
fect concentration[7,8] shows that defects inter-
rupt the chains effectively, and overlap through
defects is small. Zuppiroli et al.[8] interpreted
the conductivity of irradiated highly conducting
quasi one-dimensional systems by assuming that
the electron energies increase with decreasing

segment length. Depolarization charges of a
single segment do not strongly screen the ap-
plied electric field. Neighboring segments do
give rise to local fields, but the randomness
of their spatial position will reduce the de-
polarization effect.

Rice and Bernasconi showed[6] (although the
details of their arguments were incorrect) that
the dielectric constant in the interrupted
metallic strand model is roughly

$$\varepsilon = q_o^2 \ell_o^2 \qquad (1)$$

where ℓ_0 is the mean distance between defects
and q_0 is the Thomas-Fermi wavevector of the
conduction electrons. Expression (1) is in
qualitative agreement with the observed micro-
wave dielectric constants of a number of quasi
one-dimensional conductors, if a defect concen-
tration of a few percent is maintained, and a
typical metallic value of q_0 is assumed.

The aim of this paper is twofold. First,
by measuring ε in a quasi one-dimensional
organic conductor over a frequency range of
5×10^5 Hz to 9×10^9 Hz, we show that at low
temperatures ε is independent of frequency.
Thus the microwave data, known for a large num-
ber of organic conductors, should agree with
the static values. At higher temperatures, as
shown by Alexander et al.,[9] this is not so.
Second, we present measurements of the low
temperature microwave dielectric constant of a
similar organic conductor irradiated with vari-
ous doses of neutrons. We show that ε in the
irradiated material depends on the inverse
square of the defect concentration c. This is
consistent with Eq. (1) if the strand length
$\ell_0 \sim 1/c$.

It is simple to show both in the free
electron and tight binding approximations that,
if screening is neglected, ε is proportional to

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$1/c^2$. From perturbation theory:

$\epsilon =$

$$1 + 4\pi e^2 \ N \sum_n \sum_{ij} \ p_c(n) \ \frac{|(\psi_{in}|x|\psi_{jn})|^2}{\epsilon_i - \epsilon_j} \ (f_i - f_j)$$

$$(2)$$

where $p_c(n) = c^2(1-c)^n$ is the concentration of strands with length na_0 (a_0 is the molecular spacing along the chain), N the density of molecules, and f_i is the occupation factor for site i. ψ_{in} in the free electron approximation is

$$\psi_{in} = (2/na_0)^{1/2} \ \sin\left[\frac{j\pi x}{na_0}\right] \quad \begin{array}{l} j = 1,2,\ldots \\ 0 \leq x \leq na_0 \end{array} \qquad (3)$$

The contributions to ϵ of nonvanishing transition moments in (2) are proportional to $(i-j)^{-3}$ and we thus neglect at zero temperature all terms except the one connecting the highest occupied and lowest unoccupied states. After summation over n we find:

$$\epsilon = 1 + K \ e^2 \ N \ a_0^2 \ A \ c^{-2}$$

$$A = ma_0/\hbar^2 k_F \qquad (4)$$

Within our approximation $K = 384/\pi^4$.

In the tight binding approximation a similar expression is found but here

$$A = [2|t| \ \sin(k_F a_0)]^{-1} \qquad (5)$$

where $D = 4|t|$ is the bandwidth. In deriving (5) the contribution of transition moments connecting electrons on different sites are neglected. In the limit of strong electron-electron correlations and in the case of quarter-filled bands, equations (4) and (5) are approximately valid if k_F is replaced by $2k_F$.

A theory by Bush[10] of weak random potentials localizing electronic states on a one-dimensional metal leads to a dielectric constant proportional to L^2 where L is the localization length at the Fermi surface. If the plausible assumption is made that L is inversely proportional to the density of defects, the same c^{-2} dependence of ϵ is found. In contrast to the interrupted chain model in this case the density of localized states is finite at the Fermi level and a frequency (ω) dependent conductivity is expected proportional to ω^2 even at zero temperature.

If the electric field is screened from the segments then the dielectric constant varies as c^{-1} since in this case the interruptions may be viewed as capacitances in series.[9]

Our dielectric constant experiments reported here were performed on two closely related organic conductors, N-Me-iso Qn(TCNQ)$_2$ and Qn(TCNQ)$_2$. These materials have identical structures and similar physical properties.[11] The respective room temperatures conductivities are 100 Ω^{-1} cm^{-1} and 70 Ω^{-1} cm^{-1}, and both show smooth transitions to insulating states which are well established below 200 K. This behavior is typical of disordered organic conductors.[2]

Experiments performed on N-Me-iso Qn(TCNQ)$_2$ involved only nominally pure crystals, while experiments investigating the effects of randomly distributed defects were performed on

neutron-irradiated Qn(TCNQ)$_2$ crystals. The neutron flux used in the irradiation process was 3×10^{12} neutrons/cm^2 sec for energies over 1 MeV, and irradiation times ranged from 2 to 90 hours. Details of the irradiation are described elsewhere.[12] A rough estimate of the defects induced is 0.2% disintegrated molecules per 1 hour of irradiation. The dielectric constant was measured between 5×10^5 Hz and 1×10^8 Hz using an r.f. capacitance bridge with a two contact configuration. At 9.1×10^9 Hz a contactless cavity perturbation method[2] was used. For the two-contact measurements, we verified, using different sample geometrics, that contact capacitances at low temperatures are negligible. The absolute values of ϵ were determined from the measured capacitances and the crystal dimensions.

Figure 1 displays the measured dielectric constant versus frequency for N-Me-iso Qn(TCNQ)$_2$ at 10 K. Measurements on a given sample show no variation from 5×10^5 Hz to 10^8 Hz within the experimental error of $\pm 20\%$. Scatter is somewhat larger from sample to sample due to uncertainties in the sample dimensions. The difference between microwave and low frequency values is also within the uncertainties in sample dimensions and calibration. We conclude that within the frequency range of four orders of magnitude, the variation of ϵ, if any, is less than a factor of two. Thus the dielectric constant measured at microwave frequency is probably a good approximation to the static value. Figure 2 shows ϵ vs. temperature for N-Me-iso Qn(TCNQ)$_2$ at two selected frequencies.
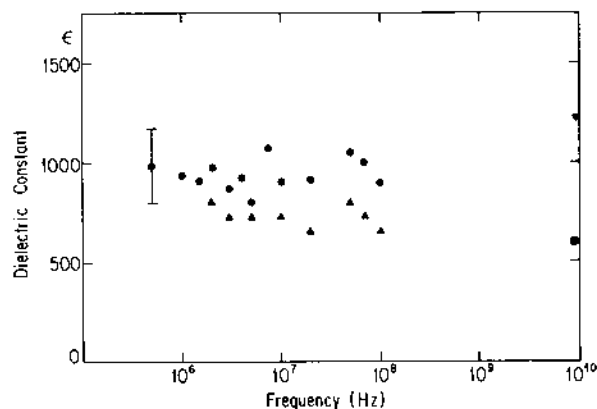

Fig. 1. Low temperature (T ≈ 10 K) dielectric constant of N-Me-iso Qn(TCNQ)$_2$ as a function of frequency. Different symbols denote different samples.

Below approximately 12 K, ϵ is independent of the temperature.

The effect of defect concentration on the dielectric constant of Qn(TCNQ)$_2$ is shown in Fig. 3, where we have plotted $\epsilon^{-1/2}$ as a function of irradiation time (i.e., defect concentration). In this plot we find a linear variation and a good fit can be made to

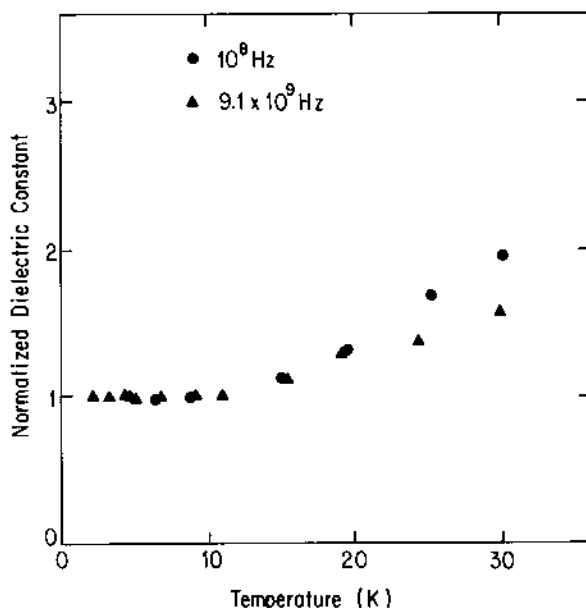$$\epsilon = B(c_0 + c)^{-2} \qquad (6)$$

Fig. 2.   Dielectric constant (normalized to the lowest temperature value) as a function of temperature of N-Me-iso Qn(TCNQ)$_2$. •: 10^8 Hz. ▲: 9.1×10^9 Hz.
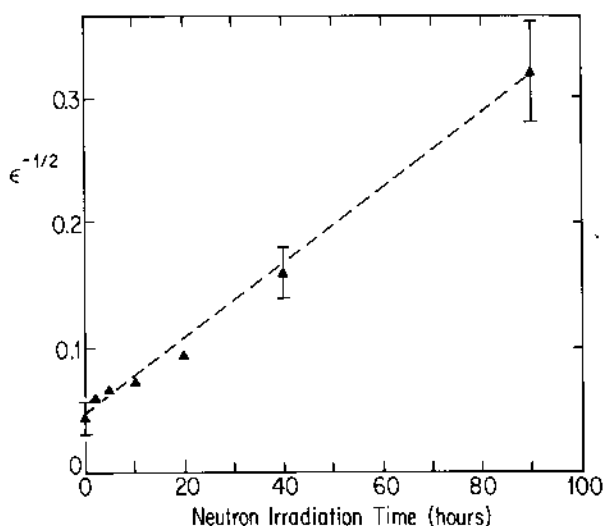

Fig. 3. $\epsilon^{-1/2}$ as a function of neutron irradiation time in Qn(TCNQ)$_2$. A rough scale is 0.2% of molecules damaged by 1 hour neutron irradiation. The dotted line is a fit to expression (5).

where c_0 is the effective defect concentration of the nominally pure material. Our fit yields $c_0 = 3\%$ thus an average strand length of about 30 a_0. This could be a result of the localization due to the disordered orientation of donor

dipoles,[13] or simply the concentration of defected TCNQ molecules along the chains. Cooper et al.[14] obtained a similar value for c_0 from the analysis of the low temperature susceptibility of a series of neutron irradiated Qn(TCNQ)$_2$ samples.

From the fit B = 0.45 is found for Qn(TCNQ)$_2$. This should be compared to the free electron value $B_F = 1.5$ or the tight binding one (with a bandwidth D = 0.5 eV) $B_{TB} = 5.2$. The agreement is not particularly good, but in view of the numerous approximations made, a better agreement is hardly to be expected. On the other hand the screened metallic particle model does not fit the data at all.

Do defects lead to a strong or a weak localization of states? In the former case the electronic energy structure consists of discrete energy levels with separations determined by the segment length. In the latter case no segments can be defined and a continous band of localized states exists. The bandwidth in conducting organic charge transfer salts is generally believed to be about D = 0.5 eV, thus the condition of the energy spacing $\Delta E > kT$ below 20 K is fulfilled for most segments even in the nominally pure material. It is difficult, however, to estimate the energy spreading due to the random potential of defects on other segments. There are indications that this is less than the energy separation. The exponential decrease with defect concentration of the dc conductivity found in a number of quasi one-dimensional systems was attributed by Zuppiroli et al.[8] to an increase of energy differences between states of neighboring segments. At microwave frequencies ($\hbar\omega \ll \Delta E$) we found that the conductivity of N-Me-iso Qn(TCNQ)$_2$ steadily decreased with temperature with an activation energy of about 15 K between 2 K and 10 K. The appearance of vibrational modes in the far infrared spectrum of heavily doped[15] Qn(TCNQ)$_2$ also points to the existence of a dip in the density of states at the Fermi level.

In conclusion, we have shown that the anomalously large low temperature dielectric constant of disordered quasi one-dimensional organic charge transfer salts is frequency independent from 5×10^5 to at least 9×10^9 Hz. It decreases as the square of defect concentration induced by neutron irradiation, and this supports the idea that these materials may be viewed at low temperatures as a collection of one dimensional strands with discrete energy level spacings.

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