Frequency-dependent transport in the pure and irradiation-disordered organic semiconductor N-methyl-(4-methyl) pyridinium (7,7,8,8-tetracyano-p-quinodimethanide)

Mariusz Przybylski* and Hans-Wilhelm Helberg

Third Physical Institute, University of Göttingen, D-3400 Göttingen, West Germany

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The introduction of controlled disorder in crystals of N-methyl-(4-methyl) pyridinium (7,7,8,8-tetracyano-p-quinodimethanide) by fast-electron irradiation provides information on the charge-transport properties. ac microwave conductivities at different frequencies (4.6, 9.3, and 23.5 GHz) of pure and irradiated samples are presented and discussed together with previously reported dc transport properties. The ac microwave conductivity measured along the long axis of the crystal increases with frequency and differs by a few orders of magnitude from σ_{dc}. This effect, present even in pure samples at low temperatures, develops gradually as the disorder is increased by irradiation. These results cannot be interpreted in terms of a simple Mott-Hubbard model with a strong on-site Coulomb interaction. A model involving the contribution of the localized-state transport is proposed to account for the frequency-dependent conductivity. We have shown that for high-disorder limit σ_{ac} varies as $A\omega^s$ with $s < 1$ and A proportional to T as predicted by the Mott-Davis model.

I. INTRODUCTION

N-methyl derivatives of pyridinium with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) are 1:2 charge-transfer salts. Up to now about six compounds of this homologous group have been extensively studied, especially in respect to transport, spectroscopic, magnetic, and structural properties.[1-6] It has been found that single crystals of these salts reveal low-dimensional semiconducting properties. The low-dimensional character of these solids is related to their molecular structures wherein TCNQ molecules are arranged in stacks. Moreover there is a strong dimerization[5] of the TCNQ molecules within the stacks, resulting in alternative charge-transfer integrals t, t' ($t' \ll t$) along the chain. The anisotropy characterized by the ratio (k) of the conductivity along the TCNQ chains $(\sigma_{\parallel})$ to the transverse conductivity in the highest conducting transverse direction $(\sigma_{\perp})$ is less than 10 for single crystals of these salts (the conductivity along the second transverse axis is about $10^1 - 10^2$ smaller than $\sigma_{\parallel}$). This is small compared with the anisotropy of $10^2 - 10^3$ observed in low-dimensional organic metals (e.g. tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), quinolinium ditetracyanoquinodimethanide [Qn (TCNQ)$_2$], etc.). Thus N-methyl derivatives of pyridinium with TCNQ are less one-dimensional than typical organic metals and that fact can be crucial in understanding the peculiarities of the electrical conductivity in these materials. From the very beginning, the main difficulty in the interpretation of experimental results has been understanding the charge transport together with the magnetic (or optical) properties of TCNQ metals and insulators.

Recently we have shown that the conductivity and the thermopower data of methyl derivatives of pyridinium with TCNQ can be interpreted in terms of a classical, partially compensated semiconductor model.[1,2] Consequently it was found that the low-temperature conduction along TCNQ stacks is governed by deep-level donor and acceptor impurities (of density $\sim 10^{16}/cm^3$). It was thought that the best method to verify the applicability of this model would be to introduce the defects (disorder) to these systems in a controlled way.

The previous studies on irradiation-induced disorder in crystals of pyridinium derivatives with TCNQ are contained in Refs. 7 and 8. Summarizing very briefly these results one can find that for a low-disorder limit the concept of electrically active dopants (donors or acceptors) is consistent with the experimental data of the dc conductivity σ_{dc} and the thermopower. Namely, for low defect concentrations the conductivity is increased to a value ten times larger and the activation energies of σ_{dc} agree very well with the slope of the Seebeck coefficient versus $1/T$. On the other hand in the high-disorder limit the transport is dominated by a strong localization process. While the conduction in these systems could be viewed in terms of single-electron extended states with the localized states introduced by irradiation (disorder) in the band tails near the band gap, the magnetism of these systems has a correlated character. The magnetic susceptibility was found to be typical of Heisenberg systems of localized spins interacting through exchange integrals of the order of 10 K.[9] Also the magnetism of defects themselves is inconsistent with the extended-state theory. In the light of the above facts Zuppiroli, Przybylski, and Pukacki[8] have proposed two alternative pictures, both involving strong Coulomb interactions. It has been suggested that N-methyl derivatives with TCNQ are Mott-Hubbard insulators or spinless-fermion Peierls insulators.[10,11] Regardless, the definite solution of the charge transport in this class of materials has still not been found.

Therefore we have recently proposed detailed microwave studies of pure and irradiated crystals of N-methyl derivatives of pyridinium with TCNQ to gain a

deeper understanding of the problem of disorder (localization) in these systems. For this purpose we have chosen one salt of the pyridinium family, i.e., N-methyl-(4-methyl) pyridinium (7,7,8,8-tetracyano-p-quinodimethanide (N-Me4MePy(TCNQ)$_2$) (see Fig. 1). In this paper the experimental results of σ_{ac}, the dielectric constant ϵ' as a function of the temperature, the irradiation dose (disorder), and the frequency are discussed together with recent experimental data.

II. EXPERIMENTAL TECHNIQUES

Microwave measurements of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ were performed using the cavity perturbation technique already described in Refs. 12 and 13. The experiment on single crystals of N-Me4MePy(TCNQ)$_2$ was carried out at three different frequencies, 4.6, 9.3, and 23.5 GHz, in the temperature range between 80 and 300 K. Needle-shaped crystals were placed at the center of rectangular transmission TE$_{103}$ cavities of 9.3 and 23.5 GHz. For $f = 4.6$ GHz a coaxial line cavity excited in the fundamental mode was used. The cavities had at room temperature a unloaded quality factor Q of 4800,6400,4700 for $f = 4.6,9.3,23.5$ GHz, respectively, and the Q was found to increase as the temperature was decreased ($Q \simeq AT^{-0.5}$).

The complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ measured by the cavity perturbation technique is given by[12-14]

$$\epsilon - 1 = \frac{\Delta}{\alpha - N\Delta} , \qquad (1)$$

where $\Delta = (f_0 - f_s)/f_0 + i(1/Q_0 - 1/Q_s)/2$ is the normalized complex frequency shift, $\alpha = 2V_s/V_c$ the filling factor of a rectangular cavity, N the depolarization factor, V_s is the sample volume, and V_c the volume of the cavity (indexes 0 and s mean unloaded and loaded cavity respectively). The depolarization factor in the case of longitudinal samples ($a \gg b \gg c$) aligned along electric field can be calculated from the Osborn formula for ellipsoid probes:[13]

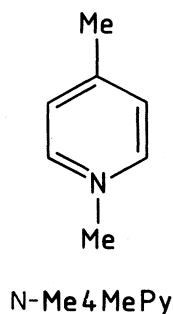$$N = \frac{bc}{a^2} \left[\ln \frac{4a}{b+c} - 1 \right] , \qquad (2)$$

FIG. 1. Donor molecule of the charge-transfer salt of N-Me4MePy(TCNQ)$_2$.

where a,b,c are dimensions of the sample. The change in quality ($Q_0 - Q_s$) and shift in resonance frequency ($f_0 - f_s$) are recorded and used to determine from Eqs. (1) and (2) the dielectric constant (ϵ') and ac microwave conductivity ($\epsilon'' = 4\pi\sigma_{ac}/\omega$). Due to the low dc conductivity of pure crystals of N-Me4MePy(TCNQ)$_2$ ($\sigma_{RT} \sim 5 \times 10^{-4} \, \Omega^{-1} \text{cm}^{-1}$) [RT = room temperature (300 K)], the relatively large sample $\sim 2 \times 0.5 \times 0.1$ mm^3 was chosen to obtain large frequency shift and cavity Q change. As was mentioned in the Introduction, the irradiation at small doses increases the conductivity of studied crystals and makes the microwave measurements not so critical in regards to the dimensions of the samples. However, for crystals irradiated with strong doses, the conductivity is significantly decreased (see Fig. 2), which did not permit us to carry out measurements on some small samples.

The irradiation of single crystals of N-Me4MePy(TCNQ)$_2$ was performed in the electron accelerator of Fontenay-aux-Roses. The samples were irradiated at 22 K with 2- or 2.5-MeV electrons at selected doses from 0 to 100 mC/cm^2. Perfect homogeneity of defects is provided by irradiation because the damage rate $-(1/\rho)(dE/x)$ by electrons of initial energy $E = 2$ MeV is constant over a range x of about 8 cm of crystal (ρ is the density).[8]

The previous studies provide an estimation of the defect concentration induced by a given amount of energy absorbed by the sample from the incident radiation. From the Curie-type tail in the magnetic susceptibility of N-Me4MePy(TCNQ)$_2$ it was found that the dose of 10 mC/cm^2 produces 8.3×10^{19} spins/cm^3 which corresponds to 2.8% of the TCNQ content. The linear dependence between the number of localized spins and the irradiation dose ϕ was observed up to doses of 50 mC/cm^2. The independent estimation from dc transport measurements leads to the value of the defect concentration (calculated as doping centers in a low-disorder limit) about one order of magnitude lower than the number of spins. Nevertheless recent optical studies on irradiated samples give a value of damaged TCNQ molecules only two times larger than the number of spins in the Curie-type tail.[15]

III. RESULTS

The effect of electron irradiation on the long-axis room-temperature conductivity is shown in Fig. 2. We have plotted the data of σ_{ac} (23.5 GHz) and σ_{dc} (taken from Ref. 8) to show the defect sensitivity of both experiments. There is no important effect of temperature on these curves in the range 80–300 K for σ_{dc} (see Refs. 7 and 8) and σ_{ac} as well. At first sight there is no significant difference between the curves of $\sigma_{dc}(\phi)$ and $\sigma_{ac}(\phi)$. The ac microwave conductivity reproduces all the features of $\sigma_{dc}(\phi)$, i.e., there is a broad maximum which corresponds to a value of about ten times larger than in pure samples. But for higher doses (> 20 mC/cm^2) after σ_{max} there is an essential discrepancy between the values of σ_{dc} and σ_{ac}. Namely, the σ_{ac} values are, for all irradiation doses, higher than those of pure samples (even for the highest ϕ), while σ_{dc} decreases appreciably with ϕ (for
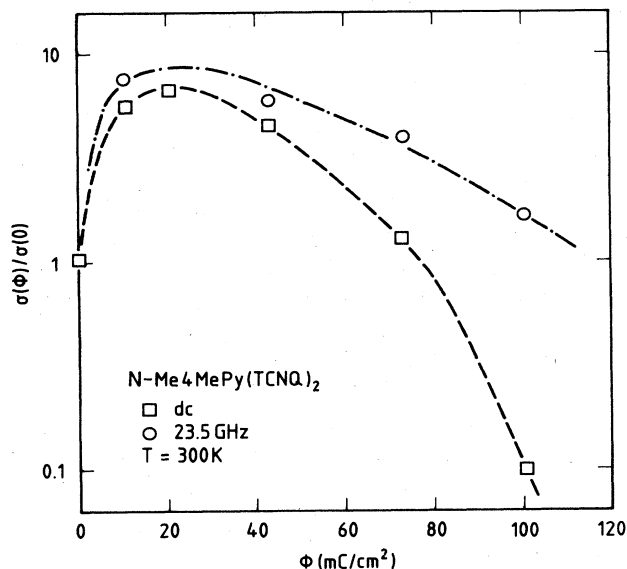
FIG. 2. Logarithm of the ac microwave (23.5 GHz) and dc conductivity (Ref. 8) plotted as a function of the irradiation dose ϕ.

$\phi > 20$ mC/cm^2), reaching values ten times smaller (at $\phi = 100$ mC/cm^2). Figures 3–7 show the temperature behaviors of σ_{dc} and the ac microwave conductivity measured at different irradiation doses, i.e., 0, 10, 43, 74, and 100 mC/cm^2. The characteristic feature of all these plots is that for all cases a low-temperature frequency-dependent conductivity is observed (i.e., conductivity increases with increasing frequency). For pure and low-dose-irradiated samples (see Figs. 3 and 4) the dispersion of the conductivity is not so large and appears in the low-temperature region only. There is practically no difference within experimental accuracy between the value of σ_{dc} and the microwave conductivity at room temperature. Up to 200 K, σ_{dc} and σ_{ac} have almost the same activated character. However, in the high-disorder limit the difference between σ_{ac} and σ_{dc} increases with the irradiation dose ϕ. For $\phi \geq 43$ mC/cm^2 the ac microwave conductivity in the low-temperature region depends very weakly on T (for a given frequency) and differs from σ_{ac} values by a few orders of magnitude. Furthermore, at $\phi = 74$ mC/cm^2 very large dispersion of the conductivity is also observed at room temperature. In the extreme case, i.e., for crystals irradiated at $\phi = 100$ mC/cm^2, there are no similarities between the temperature dependences of σ_{dc} and the ac microwave conductivity in a whole temperature region. In this case the microwave conductivity depends very weakly on temperature, decreasing to $\frac{1}{5}$ its room temperature value at 80 K while σ_{dc} decreases exponentially with the activation energy $\Delta E = 0.26$ eV. Our remarks on the dispersion of the conductivity are summarized in Fig. 8 where the ratio σ_{ac}/σ_{dc} is plotted versus the dose for two distinct temperatures 300 and 166 K. It is apparent that the dispersion of the conductivity appears gradually as the irradiation dose increases or the tempera-
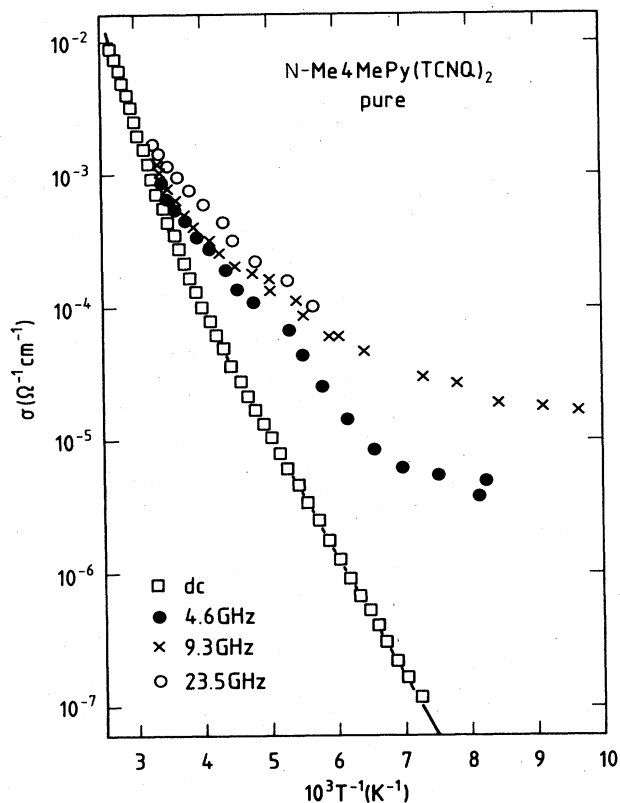

FIG. 3. Temperature dependence of the ac microwave ($f = 4.6, 9.3, 23.5$ GHz) and dc conductivities of pure samples.
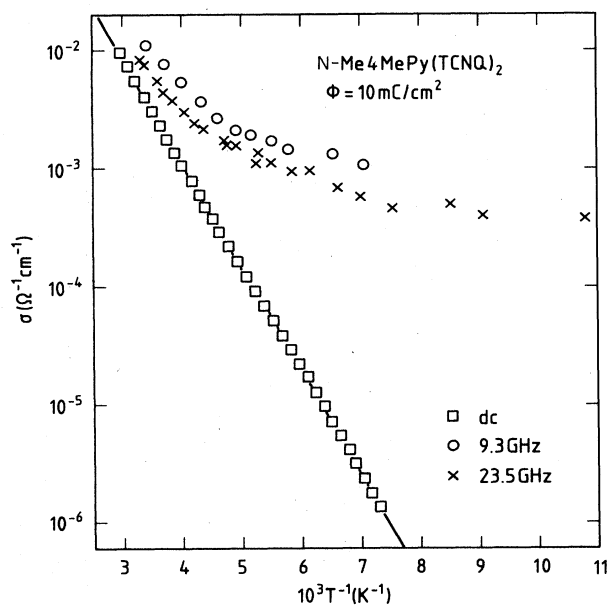

FIG. 4. Temperature dependence of the ac microwave (9.3, 23.5 GHz) and dc conductivities of samples irradiated at $\phi = 10$ mC/cm^2 (low-disorder limit).
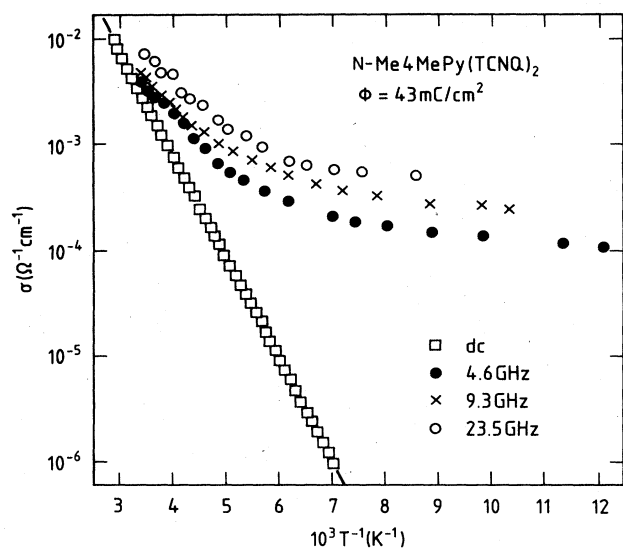
FIG. 5. Temperature dependence of microwave (4.6,9.3,23.5 GHz) and dc conductivities of samples irradiated at $\phi = 43$ mC/cm².

ture is lowered. For example, the crystals irradiated at $\phi = 100$ mC/cm² have the ac microwave conductivity 4 orders of magnitude higher than σ_{dc}, measured at 166 K. On the other hand in a low-disorder limit the ratio σ_{ac}/σ_{dc} tends to 1 at high temperatures.

The dielectric constant ϵ' was found to be frequency independent in both pure and irradiated samples. The room temperature ϵ' value was found to be 3.4±0.2 for pure
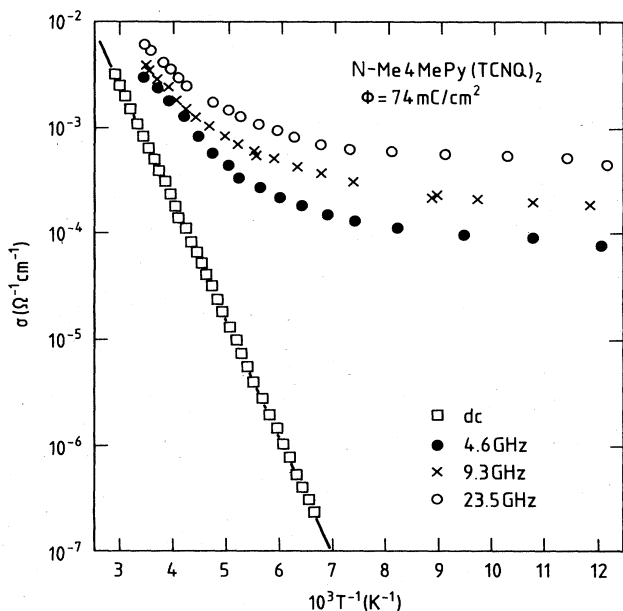

FIG. 6. Temperature dependence of microwave (4.6,9.3,23.5 GHz) and dc conductivities of samples irradiated at $\phi = 74$ mC/cm² (high-disorder limit).
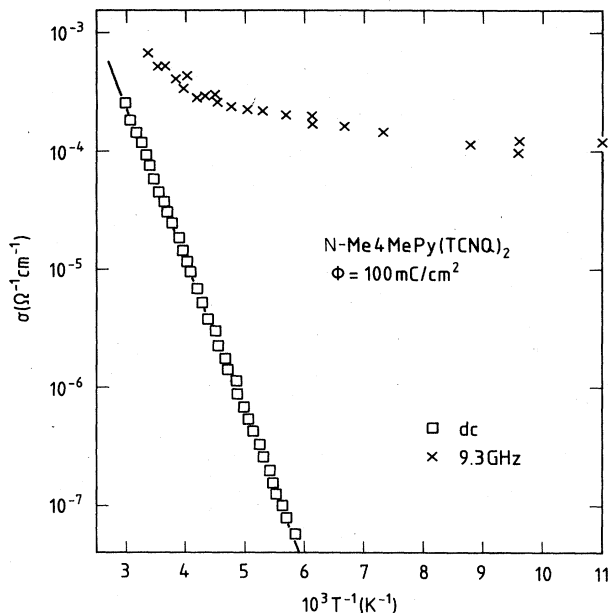

FIG. 7. Temperature dependence of microwave (9.3 GHz) and dc conductivities of samples irradiated at $\phi = 100$ mC/cm² (high-disorder limit).

crystals and was in good agreement with preliminary results obtained on the other N-methyl derivatives of pyridinium with TCNQ.[16,17] We have found that the dielectric constant of pure and all irradiated species was temperature independent within the accuracy of the measurements. The effect of the irradiation is also very small. Up to doses of 74 mC/cm² no change of the ϵ' value was observed. We have detected only for some samples irradiated at $\phi = 100$ mC/cm² a small increase in the dielectric constant of about 10%. Generally we have to point out that the dielectric constant is not affected by strong radiation defects in studied systems.
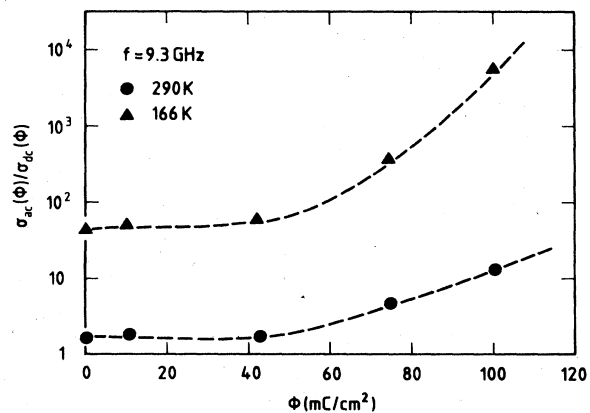

FIG. 8. Ratio of the microwave conductivity to the dc conductivity $\sigma_{ac}(\phi)/\sigma_{dc}(\phi)$ as a function of the irradiation dose at two different temperatures.

IV. DISCUSSION

The results of ac microwave conductivity measurements have evidently proved the frequency dependence of charge transport in crystals of N-Me4MePy(TCNQ)$_2$. Moreover, the dispersion effect of the conductivity increases as the disorder is increased.

First let us discuss the present results in relation to the correlated-electron picture proposed by Zuppiroli, Przybylski, and Pukacki.[8] The authors of this work have postulated that substantial Coulomb interactions are needed to explain the insulating character of these compounds. The inclusion of the electron-electron interactions leads to two alternative models for N-methyl derivatives with TCNQ: (i) Mott-Hubbard insulator, $4t \gg U \gg 4t'$ (consistent with the magnetism of these compounds); (ii) spinless-fermion half-filled-band Peierls insulator, $U \gg 4t \gg 4t'$ (solitons with charge $\pm e/2$). It is difficult to discuss the microwave properties in terms of the latter model since in the basic works of Hubbard,[10] and Rice and Mele,[11] σ versus frequency was not a subject of studies. Regardless, the magnetic susceptibility in this model is Curie-type, while the two-dimensional Heisenberg model was found to account for the magnetic properties of N-Me4MePy(TCNQ)$_2$ and related compounds.[3,9] Furthermore, Cohen and Heeger[18] have found out that in TTF-TCNQ and tetraselenafulvalene-tetracyanoquinodimethane (TSeF-TCNQ) the activation energy of conduction is a function of applied field and the onset of non-Ohmic conductivity at fields of a few V/cm appears gradually as the temperature is lowered. The authors have suggested that these results can be interpreted in terms of a nonlinear kink soliton excitation of the pinned charge-density-wave (CDW) system. Lately we have carried out

the field-dependent transport experiment on pure and irradiated single crystals of some N-methyl derivative of pyridinium with TCNQ.[19] By using the standard four-probe-pulse technique, the deviation from Ohmic law was observed up to an electric field of 200 V/cm both for pure and low-irradiated samples. Also any influence of temperature on the appearance of nonlinearity of σ was detected as well.

Gunning and Heeger[20] have interpreted the low-temperature conductivity of TTF-TCNQ in terms of soliton transport. But in this case the ac microwave conductivity was insensitive to the defect concentration. Smaalen[21] has calculated the interdimer and intradimer transfer integrals for N-methyl-(2,4-methyl)pyridinium (7,7,8,8-tetracyano-p-quinodimethane) [N-Me2,4MePy(TCNQ)$_2$]. He has obtained the intradimer value $t = 0.177$ eV and the interdimer transfer integral $t' = 0.063$ eV. This gives for the gap Δ in the spinless-fermion Peierls-insulator model [$\Delta = 4(t - t')$] the value of 0.46 eV, which is somewhat smaller than 0.66 eV determined from dc transport.[4] Thus this model seems to be not adequate to describe the physical properties of pyridinium-derivative—TCNQ salts.

On the other hand, the problem of the applicability of the classical Mott-Hubbard model to quasi-one-dimensional systems is not new. It has been intensively studied by several theorists in the early 1970s.[22–28] There is experimental evidence of the existence of a strong Coulomb interaction in alkali-TCNQ salts.[29,30] Holczer[27] has calculated the conductivity of a quarter-filled narrow-band Hubbard chain (similar to that in 1:2 TCNQ salts) with an interaction U_1 between nearest neighbors ($U_1 \gg b$) and a strong on-site Coulomb interaction U_0 ($U_0 \to \infty$) with electron-lattice coupling (polaronic effects). Then $\sigma(\omega)$ is given by

$$\sigma(\omega) = \frac{e^2 b^2 a^2 \tanh(\frac{1}{2}\beta\omega)}{L\omega(1 + e^{\beta U_1/2})^3} \frac{\pi}{2\Gamma} \left\{ 4 e^{\beta U_1} e^{\omega^2/2\Gamma} + (e^{\beta U_1/2} + e^{-(3\beta U_1/2)}) \left[\exp\left[\frac{-(\omega - U_1)^2}{2\Gamma} \right] + \exp\left[\frac{-(\omega + U_1)^2}{2\Gamma} \right] \right] \right\},$$

(3)

where b is the transfer integral, a is lattice constant, L the volume of conducting chain, $\beta = (kT)^{-1}$, and Γ is the function expressed by

$$\Gamma = \frac{1}{2}g^2 \coth(\frac{1}{2}\beta\Omega) ,$$

(4)

where Ω is the frequency of the Einstein oscillators, and g is the electron—intramolecular-vibration coupling constant. The following set of parameters has been taken to simulate the σ-versus-ω dependence in Eq. (3), i.e., $U_1 = 0.09$ eV, $b = 0.06$ eV, $\Omega = g = 0.017$ eV, which are rather reasonable for TCNQ salts.[22,27] Nevertheless, the conductivity $\sigma(\omega)$ was found to be frequency independent in the range of about 100 kHz to 30 GHz (even changing significantly the above values of the parameters). Also the model of Bari[24] calculated for a half-filled-band Hubbard model gives a similar $\sigma(\omega)$ dependence. Thus simple Hubbard models cannot explain the strong frequency-dependent conductivity of these salts. In other words the electron-electron and electron-phonon interactions are not

sufficient to account for conduction in these materials. We need significant disorder (localization) leading to band tailing or localized states in a gap to have a strong dispersion of the conductivity. Therefore we recall Mott and Davis[31] ideas about the electrical conductivity of disordered solids. Then, for the disorder-induced localization, the conductivity can be expressed by

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s ,$$

(5)

where $s \leq 1$ and A is a constant with little dependence on the temperature. In fact (as follows from Figs. 5—7), in the low-temperature region where an activated term of σ_{dc} can be neglected, it is possible to fit the data of $\sigma(\omega)$ to the ω^s law (in the microwave frequency range). For example, for samples irradiated at $\phi = 74$ mC/cm^2 and temperatures lower than 160 K, s was found to be temperature independent and equal to 0.76. Generally it resulted that s increases with the irradiation dose (disorder) reaching a value of about 0.9 for samples irradiated with the

highest electron flux. It is noteworthy that for temperatures > 200 K, the exponent s begins to decrease as the temperature is raised. This fact is not astonishing because for high T the large σ_{dc} term can mask the ω^s dependence connected with disorder (see Figs. 3—7).

It is very tempting at this point to analyze more precisely the temperature variation of the disorder contribution to the ac conductivity. The exact formula for the hopping transport by electrons with energies near the Fermi level E_F is given by[31]

$$\sigma(\omega) = \tfrac{1}{3}\pi e^2 kT[N(E_F)]\alpha^{-5}\omega\left[\ln\left[\frac{\nu_{ph}}{\omega}\right]\right]^4, \qquad (6)$$

for the frequencies $\omega \ll \nu_{ph}$ (phonon frequency). In Eq. (6), $N(E_F)$ is the density of states at the Fermi level, α^{-1} is the falloff of the electronic wave function with distance from the defect center. The last term in Eq. (6), $\omega[\ln(\nu_{ph}/\omega)]^4$, can be written as ω^s, where s is a weak function of frequency if $\omega \ll \nu_{ph}$. In Fig. 9, σ at 9.3 GHz versus temperature is plotted in the range 100—250 K for the sample irradiated at $\phi = 100$ mC/cm^2. The experimental data have been perfectly fitted to Eq. (6) with $\alpha^{-1} = 3.2$ Å (average inter-TCNQ spacing in the chain), $\omega/2\pi = 9.3$ GHz, $s = 0.9$, and $N(E_F) = 7 \times 10^{21}$ eV^{-1} cm^{-3}. Assuming a bandwidth of 0.25 eV, the last value corresponds to $\sim 1.7 \times 10^{21}$ cm^{-3} of localized centers (defects), close to the *ESR* evaluation of unpaired spins in the Curie tail.[8] The results of dc transport are consistent with this model as well. Namely, the thermopower measurements[7,8] have shown that the slope of the Seebeck coefficient (S) versus T^{-1} tends to a very small value as the defect concentration is increased. That means that the band gap disappears with an increase of disorder favoring the transport near E_F. Regardless, according to Halpern[32] Eq. (5), attributed generally to the hopping of carriers between the localized states, can be extended for systems in which the conductivity can be regarded as a classical activated process with a distribution of activation energies (for example, motion of electrons over a barrier, etc.). However, this does not change our general conclusion that disorder (leading to electron localization) is responsible for the frequency-dependent electrical conductivity in N-Me4MePy(TCNQ)$_2$. The type of localization in N-Me4MePy(TCNQ)$_2$ is essentially different from that observed in low-dimensional organic metals such as Qn(TCNQ)$_2$, TTF-TCNQ, tetramethyltetraselenafulvalene-dimethyltetracyanoquinodimethane (TMTSF-DMTCNQ), etc. The extensive transport and magnetic studies of irradiated organic conductors performed by the Fontenay-aux-Roses group[33—36] have shown that the interrupted-strand model with transverse hopping is applicable for systems which have an anisotropy of conductivity $\sigma_{\parallel}/\sigma_{\perp}$ more than 10^2. The authors have postulated that each defect interrupts the conducting chain (segmentation of the conducting chain) and the electrons are forced to jump to a neighboring chain. This leads to an exponential decrease of the conductivity with increasing defect concentration. That model (weakly interacting segments) also has other physical consequences like the defect-concentration-dependent dielectric constant, $\epsilon \sim c^{-2}$, e.g., in Qn(TCNQ)$_2$,[37] an exponential decrease of the ESR linewidth,[38] a frequency- and field-dependent transport. However, this is valid as long as the system has one-dimensional character, i.e., for a sufficiently high anisotropy of conductivity. When the anisotropy factor $k = \sigma_{\parallel}/\sigma_{\perp}$ is smaller than 10 the system becomes more quasi-two-dimensional than quasi-one-dimensional, which is what takes place in N-Me4MePy(TCNQ)$_2$ $(k \simeq 5)$. It is obviously easier for charges to go around large random potentials in two dimensions (2D) than in one dimension. In a 2D system the conductivity is not expected to decrease exponentially with the defect concentration as was demonstrated for one of the methyl derivatives of pyridinium with TCNQ: N-methyl-(2,6-methyl)pyridinium (7,7,8,8-tetracyano-p-quinodimethane) [N-Me2,6MePy(TCNQ)$_2$]. In this case the anisotropy factor $k = \sigma_{\parallel}/\sigma_{\perp} \simeq 1$ and only a very weak decrease of the conductivity was observed for doses higher than 80 mC/cm^2.[8] The other transport properties are very similar to those of N-Me4MePy(TCNQ)$_2$. Looking carefully at Fig. 2 one can find that $\sigma(\phi)$ is also not exponentially dependent on the defect concentration. Thus the dimensionality effect on the type of localization is of great importance and accounts for differences in transport properties of strongly irradiation-disordered organic metals [e.g., Qn(TCNQ)$_2$] and systems such as N-Me4MePy(TCNQ)$_2$.

In the light of these facts, the small and temperature-independent values of the dielectric constant $(\epsilon' \simeq 3.4)$ of pure and irradiated N-Me4MePy(TCNQ)$_2$ are also not surprising. For example in an insulating TCNQ system such as potassium tetracyanoquinodimethane, K-TCNQ, ϵ' was found also to be temperature independent and equal to 5.8.[39] The high values of ϵ' $(\sim 10^3)$ observed in some quasi-one-dimensional conductors [e.g., TTF-TCNQ (Ref. 40)] are related to the formation of a metallic state and collective transport like charge-density waves (CDW). In
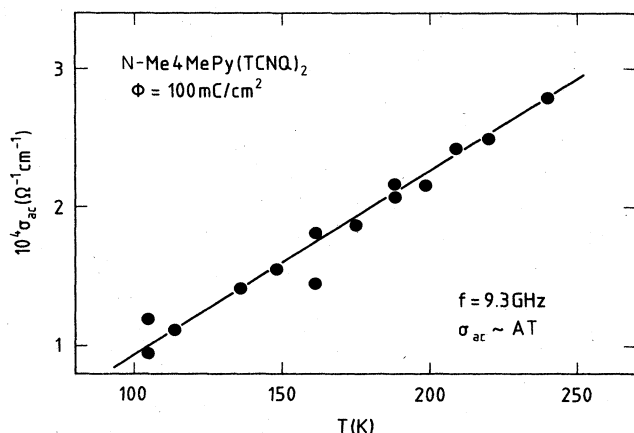

FIG. 9. Low-temperature variation of the microwave conductivity plotted as a function of temperature for the sample irradiated with $\phi = 100$ mC/cm^2. The line plotted is the best fit to Eq. (6) with $\alpha^{-1} = 3.2$ Å, $\omega/2\pi = 9.3$ GHz, $s = 0.9$, $N(E_F) = 7 \times 10^{21}$ eV^{-1} cm^{-3}.

these systems due to one-dimensionality the disorder can result in a frequency- and temperature-dependent dielectric constant[41] (as well as conductivity) as has been observed in $Qn(TCNQ)_2$. These experimental facts have also been accounted for by the simple random-barrier, classical hopping model (with the metallic strands between the barriers) of Alexander et al.[35] In another low-dimensional conductor, $NbSe_3$, similar properties were interpreted by depinning of the CDW (bounded to defects) at high frequency (this effect is also observed at large electric field).[42]

V. CONCLUSION

We have shown in this paper that the charge transport of the organic semiconductor N-Me4MePy$(TCNQ)_2$ is strongly affected by disorder. By increasing disorder in a controlled way, the significant localization process has been monitored in microwave properties of crystals of N-Me4MePy$(TCNQ)_2$. The discussion on some transport mechanisms has led us to the conclusion that the simple Mott-Hubbard model cannot account for the whole set of results. The strong frequency-dependent conductivity can be only understood in terms of disorder-induced localization in low-dimensional structures of these materials. It was found that ac conductivity varies as $A\omega^s$ (for $T = $ const and $s \leq 1$), and A depends linearly on T, exactly as predicted by Mott and Davis.[31] The present results and discussion have revealed that the question of the charge transport in these low-dimensional insulating TCNQ salts is very complicated. Our studies have proved in addition to the electron-electron and electron-phonon interactions, the disorder resulting in localized states of the Mott-Davis type is needed to understand the electrical conductivity in N-methyl derivatives of pyridinium with TCNQ.

*On leave from Institute of Molecular Physics of Polish Academy of Sciences, 60-179 Poznań, Poland.

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