Dynamic conductivity of TCNQ salts in the submillimeter band

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The submillimeter (8–32 cm^{-1}) spectra of the conductivity and of the dielectric constant of four organic one-dimensional salts based on TCNQ molecule TTF-TCNQ, MTPA$(TCNQ)_2$, MTPP$(TCNQ)_2$, MEM$(TCNQ)_2$ were measured. The TTF-TCNQ spectra in longitudinal polarization are determined at room temperature by the dynamics of the free electrons excited through the Peierls pseudogap $2\Delta \approx 0.06$ eV. At low temperatures the spectra reveal a strongly damped mode with natural frequency ≈ 40 cm^{-1}. A relaxation was observed in the spectra of MTPA$(TCNQ)_2$ in longitudinal polarization; its contribution varies with temperature in accordance with the activation law. These results are interpreted within the framework of interrupted-strand model. It is proposed that the submillimeter relaxation response in MTPA$(TCNQ)_2$ is determined by the dynamics of the free electrons contained in quasi-insulated tetramers of the TCNQ molecules.

We report here for the first time direct measurements, in the sub-millimeter (submm) band (8–32 cm^{-1}), of the conductivity spectra $\sigma(\nu)$ and of the dielectric constant $\varepsilon^1(\nu)$ of a number of organic one-dimensional conductors — salts based on the TCNQ (7, 7, 8,8-tetracyano-n-quinodimethane) molecule. Up to now there were practically no published data on the submillimeter electrodynamics of one-dimensional conductors, although the prevailing opinion is that these are the frequencies at which their spectra should exhibit singularities due to collective and single-particle relaxation conductivity.[1–4]

We have investigated the spectra of four compounds with substantially different properties: TTF-TCNQ (tetrathiofulvalene-TCNQ), MTPP $(TCNQ)_2$ (methyltriphenylphosphonium-$(TCNQ)_2$), MTPA$(TCNQ)_2$ (methyl-triphenylarsonium-$(TCNQ)_2$), and MEM $(TCNQ)_2$ (*n*-methyl-*n*-ethylmorpholinium-$(TCNQ)_2$).

1. TTF-TCNQ. This compound is at present the most investigated one-dimensional conductor. It consists structurally of parallel chains (stacks) of donor TTF molecules and acceptor TCNQ molecules. The charge transfer from the donor to the acceptor is incomplete at 0.59 (the average number of carriers per molecule).[5] The static conductivity along the stacks (the **b** axis) and the anisotropy of the conductivity at room temperature in TTF-TCNQ are respectively $\sigma_\parallel \approx 700$–$900$ $\Omega^{-1}\cdot cm^{-1}$ and $\sigma_\parallel/\sigma_\perp \approx 10^3$ (Ref. 5). As the temperature is lowered both these quantities increase and reach their maxima at $T \approx 58K$: $\sigma_\parallel(58)/\sigma_\parallel(300) \approx 10-100$, $(\sigma_\parallel/\sigma_\perp(58))/(\sigma_\parallel/\sigma_\perp(300)) \approx 6\cdot 10^3$ (Refs. 5–7). With further decrease of temperature, three phase transitions (PT) take place: of second order at 54 K and 49 K and of first order (with hysteresis ~ 1 K) at 38 K. The nature of the phase transition is associated with the appearance and dynamics of a charge-density wave (CDW) in the neighboring chains of the TTF and TCNQ molecules.

Notwithstanding the many investigations of the properties of TTF-TCNQ crystals, some crucial problems of their electrodynamics remain unsolved to this day. These include the temperature and dispersive behavior of the collective Fröhlich mode, and the ratio of the collective and single-particle contributions to the conductivity $\sigma_\parallel$ in the high-temperature phase at $T > T_c = 54$ K. According to one point of view,[8] the growth of the static and microwave conductivities with decrease of temperature at $T > T_c$ is due to the increase of the collective contribution due to the Fröhlich mode at zero frequency. On the other hand, a large positive dielectric constant of TTF-TCNQ at room temperature, $\varepsilon'_\parallel$ $(1\ cm^{-1}) \approx 2500$, is reported in Ref. 9, and can be explained only if intense excitation at a finite frequency is present. The large value of the low-temperature ($T < 20$ K) dielectric constant $\varepsilon'_\parallel$ (110 GHz = 3000–3500 (Refs. 8–10) is assumed to be due mainly to the contribution of the pinned Fröhlich mode. However, the estimates obtained for the pinning frequency ν_F in various papers differ greatly, ranging from $\nu_F \approx 1$–3 cm^{-1} (Refs. 11, 12) to $\nu_F \approx 80$ cm^{-1} in Ref. 13. Such differences between the experimental data are due mainly to the difficulty of measuring by traditional methods the IR spectra of substances having a reflection coefficient $R \approx 1$, such as conducting materials.

2. MTPA$(TCNQ)_2$, MTPP$(TCNQ)_2$, MEM$(TCNQ)_2$. These three salts have a similar structure, constituting a set of parallel chains of acceptor TCNQ molecules, with chains of donor molecules MTPA, MTPP, or MEM in the gaps between them.[14–16]. In the isomorphic salts MTPP and MTPA, the TCNQ molecules are grouped at all temperatures along the chains (the **b** axis) in tetramers of four each. Assuming total charge transfer, each acceptor tetramer has two electrons transferred to it by the donor molecules. A first-order phase transition takes place in MTPP $(TCNQ)_2$ at $T \approx 315$ K (Refs. 16, 17), accompanied by restructuring in the tetramer chain: in the high-temperature phase the distances between the TCNQ molecules increase within one tetramer and the distances between neighboring TCNQ molecules belonging to different tetramers. In both phases, MTPP $(TCNQ)_2$ and also MTPA$(TCNQ)_2$ are semiconductors with static conductivity $\sigma_\parallel(dc)$ $= 10^{-3} - 10^{-2}$ $\Omega^{-1}\cdot cm^{-1}$ (at room temperature) and with activation energy $E_a \approx 0.4$ eV.[17,18]

Two phase transitions take place in MEM$(TCNQ)_2$, of first order at $T = 338$ K,[19,20] and of second order at $T = 17$ K[21,22]. At $T > 338$ K the TCNQ molecules are distributed along a chain (**c** axis) uniformly. The static conductivity in

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this phase depends little on temperature and amounts to $\sigma_{\parallel}(\mathrm{dc}) \approx 30\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$ (Ref. 19). The phase transition into the intermediate semiconducting phase is accompanied by dimerization of the TCNQ molecules (Peierls transition) and by a decrease of the static conductivity by approximately three orders. In addition, partial ordering of the MEM ions takes place in the interval $280 < T < 320$ K and leads to anomaly in the $\sigma_{\parallel}(\mathrm{dc})$ temperature dependence.[23] The phase transition at $T = 17$ K (electronic Peierls transition) leads to tetramerization (dimerization of dimers) of the TCNQ molecules. The charge transfer from a donor to an acceptor in MEM $(TCNQ)_2$ is complete, i.e., one electron for every two TCNQ molecules.

EXPERIMENTAL PART

All the measurements were made with an "Epsilon" submilimeter spectrometer in which the radiation sources were frequency-tunable backward-wave oscillators.[24] The spectra of $\varepsilon'(\nu)$ and $\sigma(\nu)$ $(\varepsilon^*(\nu) = \varepsilon'(\nu) + i2\sigma(\nu)/\nu)$ were determined by direct calculation from the frequency dependences of the transmission coefficient and phase shift of the wave passing through a plane-parallel sample.

The TTF-TCNQ samples were mosaics with transverse dimensions 7×7 mm, in the form of assemblies of several single crystals, ground down to 10 μm thickness. The MTPA, MTPP, and MEM salt specimens were made of single crystals of relatively large size (up to 0.5 cm^2) and were $\approx 50\,\mu$m to ≈ 1 mm thick. The choice of specimen thickness was dictated by the spectrometer dynamic transmission-coefficient range $T > 10^{-5}$. To eliminate mechanical stresses in the TTF-TCNQ crystals, the specimens were not glued but clamped to a thin (1 μm) lavsan-film mount.

The measurements were made for two polarizations: longitudinal, with the vecotr **E** of the electromagnetic field parallel to the maximum-conductivity axis (**E**$\parallel$**b** in TTF-TCNQ and MTPA$(TCNQ)_2$, and **E**$\perp$**c** in MEM$(TCNQ)_2$), and transverse with the vecotr **E** perpendicular to this axis. The operating frequency and temperature ranges were $\nu = 8$–30 cm^{-1}, $T = 5$–300 K (TTF-TCNQ); $\nu = 8$–18 cm^{-1}, $T = 153$–335 K (MTPP$(TCNQ)_2$); $\nu = 8$–32 cm^{-1}, $T = 85$–348 K (MTPA$(TCNQ)_2$); $\nu = 8$–18 cm^{-1}, $T = 5$–350 K (MEM$(TCNQ)_2$).

EXPERIMENTAL RESULTS

1. TTF-TCNQ. Figure 1 shows the obtained submillimeter conductivities $\sigma_{\parallel}$ (10 cm^{-1}) of TTF-TCNQ at **E**$\parallel$**b**, together with the results of the statistical $\sigma_{\parallel}$ (dc) and microwave $\sigma_{\parallel}$ (9.1 GHz) measurements (data of Ref. 4). Attention is called to the qualitatively different temperature dependence of the submillimeter conductivity in the region $T > T_c$ compared with the microwave and static conductivity, namely, the decrease of the former starting directly with $T = 300$ K. This effect cannot be attributed to any faults produced in the specimen. Special measurements have shown that in the interval from $T = 300$ K to $T = 290$ K, where a continuous decrease of $\sigma_{\parallel}(T)$ with decrease of T is observed, thermal cycling of the specimens did not affect the submillimeter conductivity.

At room temperature, $\varepsilon'_{\parallel}$ and $\sigma_{\parallel}$ (Fig. 2a) are practically independent of the frequency of the submillimeter radiation. The low-temperature spectra of $\varepsilon'_{\parallel}(\nu)$ and $\sigma_{\parallel}(\nu)$

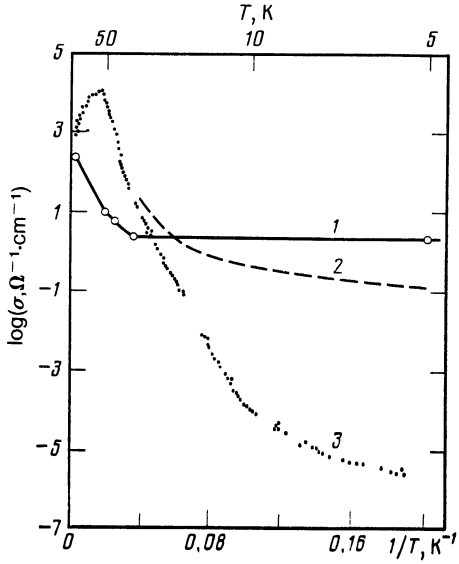

FIG. 1. Temperature dependence of the submillimeter ($\nu = 10$ cm^{-1}) conducitivity of TTF-TCNQ (1) for longitudinal polarization **E**$\parallel$**b**. The plots for the microwave (2) ($\nu = 9.1$ GHz) and static (3) conductivities are taken from Ref. 9.

(Fig. 2b) point to the presence of strongly damped excitation at the frequency $\nu_0 > 30$ cm^{-1}. Data reduction by least square (solid line in Fig. 2b) using the classical-oscillator equation

$$\varepsilon^*(\nu) = \varepsilon^\infty + S(\nu_0^2 - \nu^2 + i\nu\Gamma_0)^{-1} \qquad (1)$$

yields for the oscillator strength, natural frequency, and damping the respective values $S = 1.6\cdot10^5$ cm^{-2}, $\nu_0 = 40$ cm^{-1}, $\Gamma_0 = 30$ cm^{-1} (we used in the data reduction for the high-frequency dielectric constant the value $\varepsilon^\infty = 40$ taken from Ref. 25). Our measurements showed no relaxation of this mode with rise of temperature. Note that the mode in question is located in the same region of the spectrum (with smaller strength S) and in a certain temperature interval $T > T_c$.

We observed in the course of the measurments that the submillimeter spectra of TTF-TCNQ in longitudinal polarization are substantially altered by thermal cycling of the specimens. Figure 2a shows, together with the spectra 1 measured prior to the first cooling of the specimen, the spectra 2 measured after twice cooling it to helium temperature and heating to room temperature. It can be seen that thermal cycling decreases the conductivity and increases appreciably the dielectric constant. The $\varepsilon'_{\parallel}(\nu)$ spectrum acquires, in addition, a frequency dependence of relaxation type. Note that a degradation of the same type was observed also in the measurement of the static conductivity of TTF-TCNQ.[26]

Figure 3 shows the temperature dependences of the submillimeter conductivity in transverse polarization **E**$\perp$**b** (**E**$\parallel$**a**) together with the data of Ref. 17 on the static and microwave conductivity. It can be seen that $\sigma_{\perp}$ (10 cm^{-1}) varies strongly with temperature in the interval $T = -300$ K, whereas $\varepsilon'_{\perp}$ (submm) remains practically constant: $\varepsilon'_{\perp}$ (10 cm^{-1}) ≈ 10. There was practically no dispersion in the $\varepsilon'_{\perp}(\nu)$ and $\sigma_{\perp}(\nu)$ spectra in the range $\nu = 8$–30 cm^{-1} at all the temperatures used.

Our measured $\varepsilon'_{\perp}$ and $\sigma_{\parallel}$ do not accord with the anomalously high reflection coefficient $R_{\parallel}(10\,\mathrm{cm}^{-1}) = 97\%$ mea-

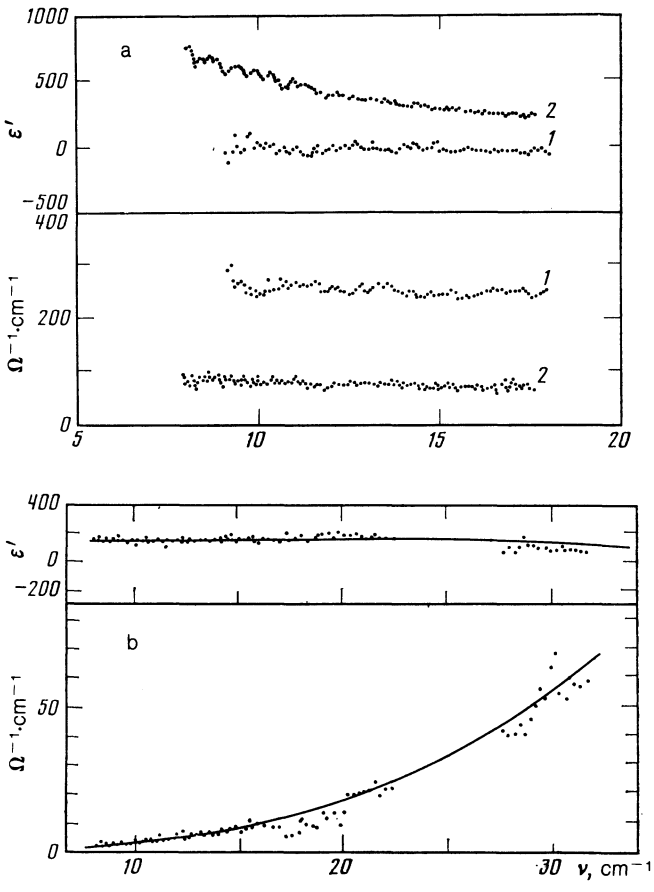

FIG. 2. Submillimeter spectra of the dielectric constant and conductivity of MTPA(TCNQ)$_2$ for longitudinal polarization **E**$\|$**b**. a) $T = 300$ K: 1—to first cooling, 2—after twice cooling to helium temperature and heating to room temperature. b) $T = 5$ K; solid lines — least square reduction using Eq. (1).

sured in Ref. 27 with an IR spectrometer. To ascertain the causes of the discrepancy between the data we have also measured the reflection coefficient $R_\parallel$ of TTF–TCNQ specimens in **E**$\|$**b** orientation at frequencies in the 10 cm^{-1} region. We measured at room temperature the reflection coefficient of a mosaic made up to "thick" (natural thickness) TTF-TCNQ single crystals with natural (a) and polished (b) surfaces. The results were the same in both cases,

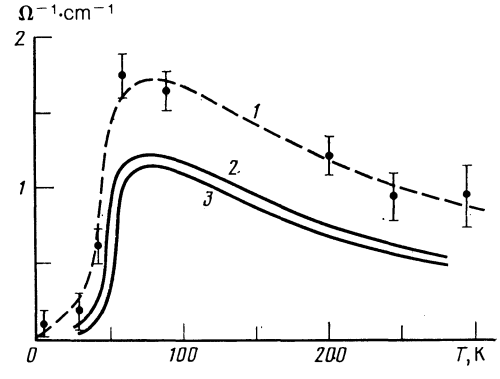

FIG. 3. Temperature dependence of submillimeter ($\nu = 10$ cm^{-1}) conductivity of TTF-TCNQ (1A) for transverse polarization **E**$\perp$**b**. (**E**$\|$**a**). The plots for the microwave (2) ($\nu = 10.4$ GHz) and static (3) conductivities were taken from Ref. 17.

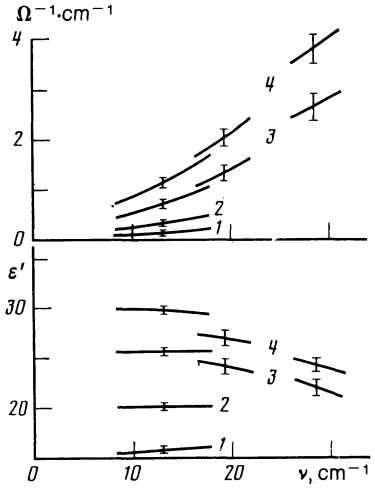

FIG. 4. Submillimeter spectra of dielectric constant and conductivitiy of MTPA(TCNQ)$_2$ for longitudinal polarization **E**$\|$**b** at the temperatures: 1 — 86 K, 2 — 208 K, 3 — 295 K, 4 — 330 K. The spectra for $\nu > 18$ cm^{-1} and $\nu < 18$ cm^{-1} were measured with different samples.

$R_\parallel(10\ \text{cm}^{-1}) = 93 \pm 1\%$, in agreement with the value of $R_\parallel$ calculated on the basis of the values $\varepsilon'_\parallel(300\ \text{K}) = 0$ and $\sigma_\parallel(300\ \text{K}) = 250\ \Omega^{-1}\cdot\text{cm}^{-1}$ measured for a "thin" specimen prepared by us. This leads to the conclusion, first, that the far-infrared measurement data[27] are too high and, second, that our specimen-production procedure causes no noticeable change in the electrodynamic properties of TTF-TCNQ in the submillimeter band.

2. MTPA(TCNQ)$_2$, MTPP(TCNQ)$_2$, MEM(TCNQ)$_2$. Figures 4–6 show the frequency dependences of $\varepsilon'_\parallel$ and $\sigma_\parallel$ of the MTPA, MTPP, and MEM salts. The MTPA(TCNQ)$_2$ spectra (Fig. 4) show a clearly pronounced relaxation whose strength increases with temperature (Fig. 7a). The temperature dependence of the relaxation contribution $\varepsilon'_\parallel - \varepsilon^\infty$ (ε^∞ was assumed equal to 15, see Figs. 4 and 7) is shown in Fig. 8. It can be seen that it is exponential with an activation energy $E_a \approx 0.05$ eV. The spectra of the MTPP and MTPA salts in longitudinal polar-

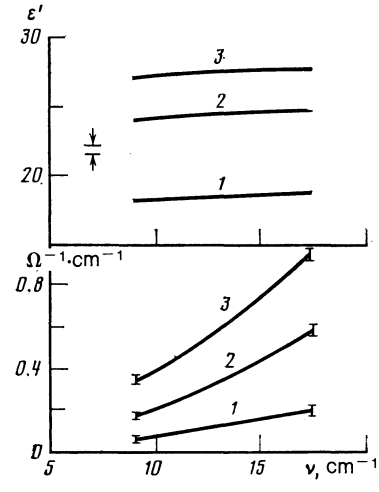

FIG. 5. Submillimeter spectra of dielectric constant and conductivity of MTPP(TCNQ)$_2$ for longitudinal polarization **E**$\|$**b** at the temperatures: 1—153 K, 2—269 K, 3—296 K. The arrows mark the experimental errors.

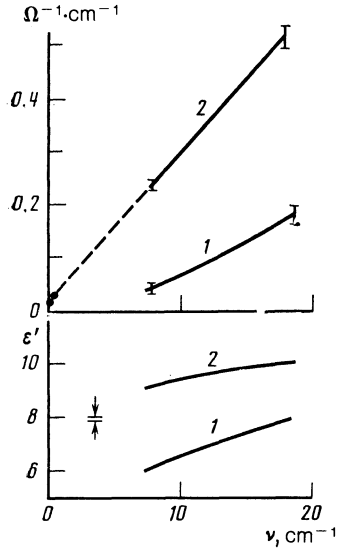

FIG. 6. Submillimeter spectra of dielectric constant and conductivity of $MEM(TCNQ)_2$ for longitudinal polarization E‖c at temperatures: 1–5 K, 2–316 K. The static and microwave data (dark points) were taken from Ref. 19. The arrows show the experimental errors.

ization and in the range $\nu = 9$–$18\ cm^{-1}$ differ very little, as seen from Figs. 4 and 5 from Figs. 7a and b. Figure 6 shows the $\varepsilon'_{\parallel}(\nu)$ and $\sigma_{\parallel}(\nu)$ spectra of $MEM(TCNQ)_2$ together with the static and microwave conductivity data from Ref. 10. In contrast to the MTPA and MTPP salts, the dielectric constant of $MEM(TCNQ)_2$ increases noticeably with increase of frequency.

Figure 7 shows the temperature dependences of the dielectric constant and of the conductivity of all three salts. The values of $\varepsilon_{\perp}$, not shown in the figure, remain constant in the entire employed temperature interval ($\varepsilon'_{\perp}(MTPP) \approx \varepsilon'_{\perp}(MTPA) \approx 3.7$; $\varepsilon'_{\perp}(MEM) \approx 4.0$), not-

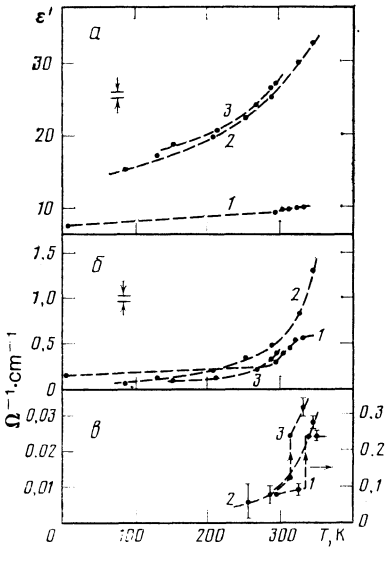

FIG. 7. Temperature dependence of submillimeter conductivity and dielectric constant for longitudinal (a, b) and transverse (c) polarizations: 1—$MEM(TCNQ)_2$, $\nu = 17\ cm^{-1}$; 2—$MTPA(TCNQ)_2$, $\nu = 10\ cm^{-1}$; 3—$MTPP(TCNQ)_2$, $\nu = 10\ cm^{-1}$. The dielectric constant of all three salts at transverse polarization are independent of temperature in the indicated ranges: $\varepsilon'_{\perp}(MTPP) \approx \varepsilon'_{\perp}(MTPA) \approx 3.7$; $\varepsilon'_{\perp}(MEM) \approx 4$. The arrows show the experimental errors.

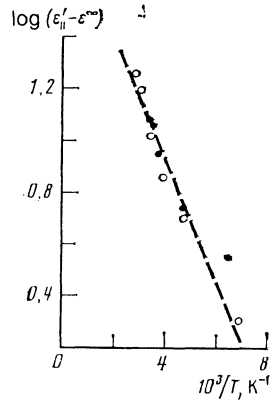

FIG. 8. Temperature dependence of the relaxation contribution $\varepsilon'_{\parallel} - \varepsilon^{\infty}$ to $MTPA(TCNQ)_2$ (○) and $MTPP(TCNQ)_2$ (●); $\nu = 10\ cm^{-1}$, $\varepsilon^{\infty} = 15$. The dashed line corresponds to an activation energy $E_a = 0.05$ eV.

withstanding the noticeable change of conductivity $\sigma_{\perp}$, including the jumps (in $MTPP(TCNQ)_2$ and $MEM(TCNQ)_2$) at the phase-transition points. In the case of $MEM(TCNQ)_2$ the values of $\varepsilon'_{\perp}$ and $\sigma_{\parallel}$ vary very little in the wide temperature interval $T = 5$–300 K. The region near 17 K (the spin-Peierls phase-transition temperature in $MEM(TCNQ)_2$) was investigated by us in particular detail. However, no anomalies were observed in the submillimeter spectra at the PT point.

The conductivity and transverse polarization spectra for all three salts are shown in Fig. 9. The conductivity is seen to increase with frequency in all cases. The $\sigma_{\perp}(\nu)$ dependences for $MEM(TCNQ)_2$ are well extrapolated to the static data of Ref. 20: $\sigma_{\perp}(330\ K) \approx 0.002\ \Omega^{-1}\cdot cm^{-1}$ and $\sigma_{\perp}(340\ K) \approx 0.06\ \Omega\cdot cm^{-1}$. In the entire frequency range, the values of $\varepsilon'_{\perp}$ (MTPA, MTPP, MEM) remained constant withi the limits of measurement error; they are not shown in the figure.

DISCUSSION OF MEASUREMENT RESULTS

1. TTF–TCNQ. The absence of dispersionin the $\varepsilon'_{\parallel}(\nu)$ and $\sigma_{\parallel}(\nu)$ spectra at $T = 300$ K (Fig. 2a) is evidence in favor of the Drude mechanism of dynamic conduction (in the low-frequency limit) by free carriers. The temperature dependence of the conductivity (Fig. 1) is of the activation (semiconductor) type. This behavior of $\varepsilon'_{\parallel}(\nu, T)$ and $\sigma_{\parallel}(\nu, T)$ can be explained by assuming that the submilli-

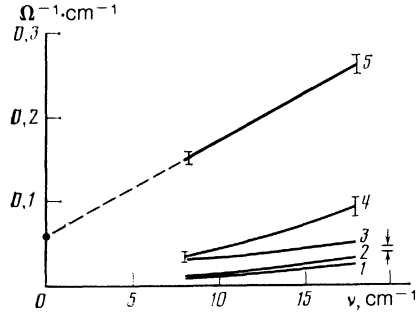

FIG. 9. Submillimeter conductivity spectra of the salts: 1—$MTPA(TCNQ)_2$; $T = 290$ K; 2, 3—$MTPP(TCNQ)_2$, 2—$T = 308$ K, 3—$T = 334$ K; 4,5—$MEM(TCNQ)_2$, 4—$T = 330$ K, 5—$T = 340$ K. Transverse polarization. The static conductivity of $MEM(TCNQ)_2$ was taken from Ref. 20. The arrows show the experimental errors.

meter electrodynamic properties of TTF-TCNQ at room temperature are determined by free carriers that are thermally activated via the Peierls pseudogap 2Δ that exists already at $T = 300$ K. In this case the temperature dependence of the conductivity is determined by the usual expression for semiconductors.[28]

$$\sigma_{\parallel}(10\ \text{см}^{-1}) = \sigma^{\infty} F_{1/2}(-2\Delta/2kT)/F_{1/2}(0), \qquad (2)$$

where

$$F_{1/2}(y) = \int_0^{\infty} \frac{x^{1/2}\,dx}{e^{x-y}+1} \approx \frac{2\pi^{1/2}e^{y}}{4+e^{y}},$$

and k is Boltzmann's constant. The conductivity σ^{∞} corresponds to $T \to \infty$, when all the carriers are excited into the conduction band; its value can be calculated by the Drude model using the equation $\sigma^{\infty} = (\omega_{\parallel}^{p})^2/4\pi\Gamma_{\parallel} = 810\ \Omega^{-1}\cdot\text{cm}^{-1}$, where the cyclic plasma frequency $\omega_{\parallel}^{p} = 1.8\cdot 10^{15}\ \text{s}^{-1}$ and the damping $\Gamma_{\parallel} = 3.5\cdot 10^{14}\ \text{s}^{-1}$ (the parameters of the Drude plasma) were calculated on the basis of the IR reflection spectrum.[29] Knowing $\sigma_{\parallel}(10\ \text{cm}^{-1}) = 250 \pm 20\ \Omega^{-1}\cdot\text{cm}^{-1}$, we determine with the aid of (2) the Peierls pseudogap $2\Delta = 460 \pm 50\ \text{cm}^{-1}$ ($T = 300$ K) and the characteristic transition temperature $T_p = 190 \pm 20$ K, the latter connected with 2Δ in the molecular field approximation by the relation $2\Delta = 3.5kT_p$ (Ref. 1). This value of T_p agrees well with the estimates $T_p = 150$–200 K obtained from x-ray scattering experiments, and also from measurement of the thermoelectric power, of the pressure dependence of the static conductivity, and of the nonlinearity of the IVC characteristics (see the brief review[6]).

A joint analysis of the data on submillimeter dynamics and of the results of static and microwave measurements[8,25] leads thus to the following conclusions. The conductivity of TTF-TCNQ at frequencies $\nu = 8$–$30\ \text{cm}^{-1}$ for $\mathbf{E}\|\mathbf{b}$ at room temperature is determined by the free carriers. At lower frequencies $\nu = 0.03$–$1\ \text{cm}^{-1}$ and in the static case there is an additional collective contribution due to phase fluctuations of the CDW, i.e., to the non-pinning Frohlich mode. An estimate of the mode lifetime yields $\tau \gtrsim 1/8\ \text{cm}^{-1} \approx 4\cdot 10^{-12}$ s, which agrees with the estimate based on the measurement of $R_{\parallel}(\nu)$ in the far IR region.[7,11]

It must be noted that the mode discussed makes an appreciable negative contribution to $\varepsilon_{\parallel}'$ in the microwave band and at lower frequencies, whereas according to the results of Ref. 9 $\varepsilon_{\parallel}'(\approx 1\ \text{cm}^{-1}) \approx 2500$ at room temperature. To explain the large positive value of $\varepsilon_{\parallel}'$ obtained in Ref. 9 it is necessary in the present situation to assume the existence in the TTF-TCNQ spectrum, at a finite frequency, of a certain additional excitation of as yet unknown origin.

We discuss now the influence of the thermal cycling of the TTF-TCNQ samples on their submillimeter electrodynamic properties (spectra 2 of Fig. 2a). As already indicated, it leads to a decrease of $\sigma_{\parallel}$, to an increase of $\varepsilon_{\parallel}'$, and to the appearance of a relaxation-type frequency dependence in the $\varepsilon_{\parallel}'(\nu)$ spectrum. The relaxation dispersion should, according to the Kramers-Kronig relation, correspond also to relaxation of conductivity with characteristic frequency $\nu < 8\ \text{cm}^{-1}$. The observed behavior of $\varepsilon_{\parallel}'$ and $\sigma_{\parallel}$ as functions of T and ν ina dehydrated specimen agrees qualitatively with the deductions of models that consider the mechanisms of localization and hopping conduction in one-dimensional conductors,[3,4,30] if it is assumed that thermal cycling produces in the specimen "defects" that hinder the conduction along conducting molecule chains. note that when measuring the static conductivity the thermal degradation manifests itself to a much lesser degree.[25] This means a lower sensitivity to degradation of the collective contribution to the conductivity compared with the single-frequency value. If it is recognized that the former is determined by the CDW correlation length ξ and the latter by the carrier mean free path λ (Ref. 5), this situation can be realized if $\lambda > \xi$.

The low temperature spectra $\varepsilon_{\parallel}'(\nu)$ and $\sigma_{\parallel}(\nu)$ point to the presence of a strongly damped mode at the frequency $\nu_0 = 40\ \text{cm}^{-1}$. Our calculations of the parameters of this mode agree with those previously determined from the far IR reflection spectra,[27,31] with the exception of the much larger value of the oscillator strength S obtained in Refs. 27 and 31. In these references this mode is interpreted as a Fröhlich phason. According to our measurements, however (see above), and as can be seen from the fiar IR $R_{\parallel}(\nu)$ spectra of Ref. 27, the behavior of this mode reveals features not possessed by phasons: it can be seen in spectra in a certain temperature interval $T > T_c$ and its frequency does not relax as $T \to T_c$. We believe therefore that it is more probably due to oscillations, in oppositely directed CDW, on neighboring chains of TTF and TCNQ molecules. In such oscilations the Coulomb interaction of neighboring CDW causes the corresponding mode to have a natural frequency that does not relax as $T \to T_c$. Such a mode will also have a dipole moment, and hence IR activity, so long as a CDW exists, even if not three-dimensionally correlated in the region $T_c < T < T_p$. On the other hand the dispersion due to the CDW pinning takes place in our opinion at frequencies in the region of 1 cm^{-1}, as indicated by a comparison of the low-temperature dielectric constants $\varepsilon_{\parallel}'$ (submm) $\approx 170 \ll \varepsilon_{\parallel}'(10\ \text{GHz}) = 300$–$3500$ (Refs. 15, 17).

We consider now the properties of TTF-TCNQ in transverse polarization. The spectra $\varepsilon_{\perp}(\nu)$ and $\sigma_{\perp}(\nu)$ which, as indicated above, have practically no dispersion, can be described in the Drude model (in the low-frequency limit) by

$$\sigma_{\perp}(\nu) = \sigma_{\perp}(0), \quad \varepsilon_{\perp}'(\nu) = \varepsilon_{\perp}'(0) = \varepsilon_{\perp}^{\infty} - (4\pi\sigma_{\perp}(0)/\omega_{\perp}^{p})^2, \qquad (3)$$

where the cyclic plasma frequency $\omega_{\perp}^{p}$ is connected with the static conductivity $\sigma_{\perp}(0)$ and with the damping $\Gamma_{\perp}$ by the relation $\omega_{\perp}^{p} = (4\pi\sigma_{\perp}(0)/\Gamma_{\perp})^{1/2}$, and $\varepsilon_{\perp}^{\infty}$ is the contribution made to $\varepsilon_{\perp}'$ by the higher-frequency excitations (phonons, electronic transitions). The fact that following a large change of $\sigma_{\perp}$ with temperature the value of $\varepsilon_{\perp}'$ remains practically constant indicates that the following relation should hold (see (3)) $(4\pi\sigma_{\perp}(0))^2/(\omega_{\perp}^{p})^2 \ll \varepsilon_{\parallel}^{\infty}$, i.e., $\Gamma_{\perp}^2 \gg (\omega_{\perp}^{p})^2/\varepsilon_{\parallel}^{\infty}$, which yields $\omega_{\perp}^{p} > 10^{13}\ c^{-1}$ and $\Gamma_{\perp} > \omega_{\perp}^{p}$. In other words, the plasma is excessively slowed down.

Comparison of the values of $\varepsilon_{\perp}'$ and $\sigma_{\perp}$ (submm) with the static and microwave data[10] shows that at all $5 < T < 300$ K the conductivity $\sigma_{\perp}$ increases with increase of frequency, while the dielectric constant $\varepsilon_{\perp}'$ decreases. This points to the presence of dispersion in the region $\nu = 1\ \text{cm}^{-1}$, connected, as indicated in Ref. 10, with the hopping character of the conductivity of TTF-TCNQ in this polarization.

2. $MTPA(TCNQ)_2$, $MTPP(TCNQ)_2$, $MEM(TCNQ)_2$. We begin with the result of greatest interest, in our opinion, namely the observed relaxation in the spectra $\varepsilon'_{\parallel}(\nu)$ and $\sigma_{\parallel}(\nu)$ in $MTPA(TCNQ)_2$ (Fig. 5).

Measurements of RF spectra[18] have shown that the relaxation in the $\varepsilon'_{\parallel}(\nu)$ spectrum in $MTPA(TCNQ)_2$ is observed at lower frequencies (≈ 2 MHz at room temperature), and its contribution has an activation dependence on the temperature, with an activation energy $E_{a1} = 0.41$ eV, which coincides with activation energy for the static conductivity. It was shown by the authors of Ref. 18 that the only model capable of explaining their results is the so-called model of interrupted conducting strands, developed in Refs. 32–34 for one-dimensional metals. This model was modified in Ref. 18 for the case of one-dimensional semiconductors in which the conducting strands are interrupted by defects that produce electrostatic barriers in the carrier paths. The model was further perfected in Ref. 30 and yielded for the barriers in $MTPA(TCNQ)_2$ a value $l_1 \approx 30$ μm, which agrees fully with the estimates based on experiments on nuclear and electron spin resonance.[18]

We assume that the relaxation observed in the submillimeter spectra of $MTPA(TCNQ)_2$ is also electronic and joins to unequal conduction levels: a lower one at $\nu < 8$ cm^{-1} and a higher at $\nu \gg 30$ cm^{-1}. It can be seen that in our case the relaxation takes place at a frequency $\nu_R \approx 30$ cm^{-1} which is approximately higher by five orders than the one obtained in Ref. 18. At the same time, the contribution $\varepsilon'_{\parallel} - \varepsilon^{\infty}$ of the submillimeter relaxation, as in Ref. 18, has an activation-type variation, although with a different activation energy $E_a = 0.05 \pm 0.01$ eV (see Fig. 9).

Within the framework of the model of blocked strands it is possible to explain both the presence of two relaxation frequencies in the $MTPA(TCNQ)_2$ spectra and the activation-type temperature dependence of the corresponding contributions. Obviously, the activation energy of the static and low-frequency ($\nu < 8$ cm^{-1}) conductivity should be determined by the potential barriers between the individual tetramers of the TCNQ molecules. This energy is equal to the energy difference of two configurations: a) two neighboring tetramers have two electrons each, and b) one electron on the first tetramer and three on the second (such configurations ensure a nonzero current along the tetramer chain). Thus, the conductivity in the frequency region $\nu < \nu_R \approx 30$ cm^{-1} is determined by quasi-free electrons that are thermally excited into configuration b) via the gap $E_{g1} = 2E_{a1} = 0.8$ eV $= 6500$ cm^{-1}. On the other hand, the conductivity at $\nu \gg 30$ cm^{-1} is determined by electrons that are similarly excited through a gap $E_g = 2E_a = 0.1$ eV $= 800$ cm^{-1}, corresponding to a "shallower" energy level of the electrons inside the tetramer.

The presence of relaxation in the spectra is quite lucidly explained also in classical terms. At sufficiently high frequencies, the distance over which an individual electron diffuses during one half-cycle of the electromagnetic field is shorter than the distance between neighboring potential barriers. As a result, the electrons in such a field behave as free ones, and the conductivity reaches the maximum value obtainable in the absence of barriers. At frequencies much lower than $1/\tau_d$, however (τ_d is the time of diffusion between barriers), the conductivity is determined only by those electrons which surmount the barriers and is therfore lower. These two values of the conductivity combine near the frequency $1/\tau_d$, where the relaxation of $\varepsilon'_{\parallel}(\nu)$ and $\sigma_{\parallel}(\nu)$ is indeed observed.

We use the equations obtained in Ref. 30 to calculate the microscopic parameter of the carrier system in $MTPA(TCNQ)_2$, assuming that the potential barriers responsible for the submillimeter dispersion are at the "junctions" of the tetramers. According to Ref. 30, the frequency and the contribution of the relaxation are given by

$$\nu_R = 10{,}1\,(\mu_0 kT/2\pi e l^2), \tag{4}$$

$$\Delta\varepsilon = \varepsilon'(0) - \varepsilon^{\infty} = (\pi N e^2 l^2/3kT), \tag{5}$$

where μ_0 is the electron mobility inside the tetramers, e is their charge, l is the tetramer length (the lattice constant in the b direction), and N is the carrier density. Substituting in (4) and (5) $e = 4.8 \cdot 10^{-10}$ cgs and $l = 1.2 \cdot 10^{-7}$ cm from the structure data of Refs. 14 and 15, and recognizing also that $\varepsilon'(0) = 25$, $\varepsilon^{\infty} = 15$ and $\nu_R = 30$ cm^{-1}, we obtain at room temperature $N = 1.2 \cdot 10^{20}$ cm^{-3} and $\mu_0 = 95$ cgs $= 0.32$ cm^2/V·s. The total electron density (two electrons per tetramer) is $N_0 = 1.7 \cdot 10^{21}$ cm^{-3}. With the aid of expression $N = N_0 \exp(-E_a/kT)$ we get $E_a \approx 0.07$ eV ($E_g = 2E_a = 1130$ cm^{-1}), in good agreement with $E_a = 0.05 \pm 0.01$ eV ($E_a = 800$ cm^{-1}), as obtained by us from the temperature dependence of the relaxation contribution (Fig. 9). The estimates presented for E_g are in reasonable agreement also with the energy of lowest-frequency mode of charge transport $\nu_{CT} = 970$ cm^{-1}, determined from the IR reflection spectra of $MTPA(TCNQ)_2$ in Ref. 35. A theoretical analysis of the system of energy levels of two electrons in an isolated tetramer of TCNQ molecules[36] has shown that the two excitations that are lowest in enrgy are IR active. It is therefore quite natural to associate with the energies E_g and ν_{CT} that one of these excitations to which charge transport from molecule inside the tetramer corresponds.[36]

Knowing the mobility μ_0, we can determine the conductivity of the "intratetramer free-electron plasma" $\sigma_0 = Ne\mu_0 \approx 6\,\Omega^{-1}\cdot$cm^{-1}. Owing to the large plasma damping $4\pi e/m\mu_0$, a conductivity of this order should be observed at frequencies $\nu \gg 30$ cm^{-1} down to the IR band. This is indeed the case, as seen from the IR $\sigma_{\parallel}(\nu)$ spectrum of $MTPA(TCNQ)_2$.[35]

In the case of two other salts $MTPP(TCNQ)_2$ and $MEM(TCNQ)_2$, $\varepsilon'_{\parallel}$ and $\sigma_{\parallel}(\nu,T)$ dependences similar to those for $MTPA(TCNQ)_2$ are observed (Figs. 6 and 7). The noticeable growth of $\varepsilon'_{\parallel}$ (MTPP, MEM) does not agree, however, with the simple relaxation relation and can be explained by assuming that at $\nu < 8$ cm^{-1} there is one more excitation of resonant type. Since the available microwave data are contradictory, it is possible to accept or reject this hypothesis unambiguously. Favoring our assumption are the high values of the dielectric constant at 9 GHz, viz., $\varepsilon'_{\parallel}$ (MTPP) ≈ 30 (Ref. 37) and $\varepsilon'_{\parallel}$ (MEM) = 15–20 (Ref. 19). At the same time a value $\varepsilon'_{\parallel}$ (MTPP), $\nu = 10$ GHz ≈ 5 is reported in Ref. 38, which in our opinion is too small even relative to the contribution $\Delta\varepsilon \approx 10$ provided by the rich IR spectrum of $MTPP(TCNQ)_2$.[39]

In conclusion, we consider briefly the spectra for transverse polarization (Fig. 8). For all three salts, the dispersion of $\sigma_\perp(\nu)$ is not accompanied by any noticeable change of $\varepsilon_\perp'(\nu)$. An estimate made by us with the aid of the Kramers-Kronig relation shows in fact that the contribution made to $\varepsilon_\perp'$ by the dispersion of $\sigma_\perp$ in the entire employed frequency range is about 0.1, which is within the limits of the experimental error. The almost linear $\sigma_\perp(\nu)$ dependence together with $\sigma_\perp(\text{dc}) \neq 0$ cannot be described with the aid of the Debye relaxation model, which yields $\sigma(\nu) \to \nu^2$ as $\nu \to 0$. To explain the observed relations it is apparently necessary to invoke the hopping conduction model, which takes into account the broad distribution of the relaxation times.[40]

CONCLUSIONS

1. TTF-TCNQ. At room temperature the conductivity of TTF-TCNQ in the submillimeter band is determined at $\mathbf{E} \| \mathbf{b}$ by the dynamics of the fre electrons which are thermally excited through a Peierls gap $2\Delta = 460 \pm 50\ \text{cm}^{-1}$. The collective (Fröhlich) mechanism makes an additional contribution to the conductivity at $\nu \lesssim 1\ \text{cm}^{-1}$.

In the low-temperature ($T = 5$ K) spectra of $\varepsilon_\parallel'(\nu)$ and $\sigma_\parallel(\nu)$ there is observed a mode with characteristic frequency $\nu_0 = 40\ \text{cm}^{-1}$, which we attribute to CDW counterphase oscillations on neighboring chains of TTF and TCNQ molecules. At frequencies between 0.3 cm^{-1} and 8 cm^{-1} there should be present an additional dielectric-dispersion mechanism with a contribution $\Delta\varepsilon \approx 3000$.

At $5 < T < 300$ K the submillimeter spectra $\varepsilon_\perp'(\nu)$ and $\sigma_\perp(\nu)$, for the polarization $\mathbf{E} \perp \mathbf{b}$ ($\mathbf{E} \| \mathbf{a}$) can be described within the framework of Drude conduction by free carriers that make up an overdamped plasma condensate. At a frequency $\nu \approx 1\ \text{cm}^{-1}$ there should be observed for this polarization a relaxation connected with the hopping character of the conductivity.

In the case of thermal cycling of TTF-TCNQ crystals, degradation of the specimens takes place and leads to a decrease of $\sigma_\parallel$ (submm), an increase of $\varepsilon_\parallel'$ (submm), and appearance of relaxation in the submillimeter spectrum of $\varepsilon_\parallel'(\nu)$. The sensitivity of the submillimeter conductivity to cycling is much higher than that of static conductivity.

2. MTPA$(TCNQ)_2$, MTPP$(TCNQ)_2$, MEM$(TCNQ)_2$. The conductivity of MTPA$(TCNQ)_2$ in longitudinal polarization at frequencies lower than 30 cm^{-1} is determined mainly by the electron contribution. This is the result of the relatively high level of the local conductivity via quasifree electrons inside of the TCNQ-molecule tetramers. At millimeter and longer wavelengths, a substantial role is assumed in the carrier dynamics by the intertetramer potential barriers, that lower the conductivity substantially. Joining of two values of the conductivity (high and low) takes place in the submillimeter band and is manifested by a relaxation dispersion in the $\varepsilon_\parallel'(\nu)$ and $\sigma_\parallel(\nu)$ spectra. The model of discontinuous conducting strands was used to determine the parameters of the intratetramer electron plasma at room temperature, viz., the carrier mobility $\mu = 0.32$ $\text{cm}^2/\text{V}\cdot\text{s}$, their density $N = 1.2 \cdot 10^{20}\ \text{cm}^{-3}$, and the conductivity $\sigma = 6\ \Omega^{-1}\cdot\text{cm}^{-1}$. We obtained also the energy $E = 0.14$ eV needed to transport an electron from molecule to molecule inside a tetramer.

In the two other salts MTPP$(TCNQ)_2$ and MEM$(TCNQ)_2$, the observed temperature and frequncy dependences of $\varepsilon_\parallel'$ and $\sigma_\parallel$ are similar to those of MTPA$(TCNQ)_2$. Additional resonant excitation is possible in these salts at a frequency lower than 8 cm^{-1}.

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