the conductivity of TCNQ salts

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The temperature dependence of the electrical admittance of TCNQ salts with quinoline and acridizine, in which there is structural disorder, was investigated. An interpretation is proposed, based on the concept that the phonons influence the one-dimensional localization of the electrons, with some phonon groups enhancing it and others suppressing it.

Among the TCNQ salts with high electric conductivity of the quasi-one-dimensional type there are compounds with structural disorder due to the random orientation of the asymmetric cations.[1] In these compounds it is natural to expect a clear-cut manifestation of one-dimensional localization of the electrons.[2] We present the results of measurements of the conductivity $\sigma(T)$ and of the dielectric constant $\epsilon'(T)$ of complex TCNQ salts with quinoline (Qn) and acridizine (Adz)[1] and analyze these results on the basis of[3,4], where a theory of electronic localization was constructed and the complex conductivity on a one-dimensional metal was calculated for weak interaction of the electrons with the impurities and phonons. The temperature dependences of σ and ϵ' can be explained by recognizing that phonons of various types can exert entirely different influences on the localization pictures, causing it to be lost in some cases and enhanced in others.

The dc conductivity σ_{dc} of the single crystal was measured in the interval 10–300 °K by the procedure of[5]. To determine σ and ϵ' at 27.7 GHz in the interval 80–360 °K we used a modification of the method described in[6], of measuring the electric admittance of single crystal samples in the form of needles placed at the center of a waveguide perpendicular to its broad wall. Samples of 15–25 μ diameter were secured to the walls with silver solder. The errors in the measurements of the absolute values of σ and ϵ', estimated from the scatter of the data for various samples, were 15–20 and 25–30%, respectively. The temperature dependences were obtained with much better accuracy; this is seen in Figs. 1–3, on which the data for various crystals, referred to the corresponding mean values,[2] are shown

In the interpretation of the results we started from the fact that there are no phase transitions in salts of this type above 20 °K.[7–10] Therefore the rapid growth of σ with increasing T at $T > 20$ °K (Figs. 1 and 2) can be naturally regarded as a manifestation of one-dimensional localization. The behavior $\sigma \sim \exp[-(T_0/T)^{1/2}]$[11,12] agrees with this model and seems to indicate that percolation effects play a role at low temperatures. At higher temperatures, where these effects are negligible, we can use for the low-frequency ϵ' and σ the theory of[3,4]:

$$\epsilon' = 32\zeta(3)e^2 l_i^2 / \hbar S v_F, \qquad \sigma = 8\zeta(3)e^2 l_i^2 \, \overline{l_{ph}^{-1}}(T) / \pi \hbar S, \qquad (1)$$

where v_F is the Fermi velocity, l_i and l_{ph} are the mean free paths for the scattering by the impurities and phonons, and S is the number of filaments per cm^2. Formulas (1) were obtained under the assumption that the Fermi energy of the electrons ϵ_F and the phonon frequency ω_{ph} exceed $\hbar/\tau_i$ ($\tau_i = l_i/V_F$), $l_{ph} \gg l_i$, and $l_i \gg b$, where b is the constant of the one-dimensional lattice. Satisfaction of these criteria can be verified by determining v_F from the magnetic susceptibility,[13,14] assuming it to be of the Pauli type, and by determining l_i and l_{ph} from (1) at $T \sim T_{max}$. This yields $v_F = 7 \times 10^6$ cm/sec, $l_i \approx 9$ Å $\approx 2.5b$, and $l_{ph} \approx 240b$ for Qn(TCNQ)$_2$ and $v_F = 6.4 \times 10^6$ cm/sec, $l_i \approx 17$ Å $\approx 4.5b$, and $l_{ph} \approx 350b$ for Adz(TCNQ)$_2$. It is seen that $l_{ph} \gg l_i$ and l_i/b amounts to several units. The localization length $l_{loc} = 4l_i$, determined from the asymptotic electron density $|\psi|^2$,[4] is even larger, so that the assumption that the scattering is weak is qualitatively confirmed. However, the random potential at the site, defined as $\overline{V}^2 = \hbar^2 v_F/b\tau_i$ (cf. formula (15) of[4]) amounts to 800 °K for Qn(TCNQ)$_2$ and 550 °K for Adz(TCNQ)$_2$ and is comparable with the corresponding $\epsilon_F = 580$ and 430 °K calculated from the given v_F for a band with a cosine dispersion law, filled to 1/4. Therefore the Born approximation used in[3,4]
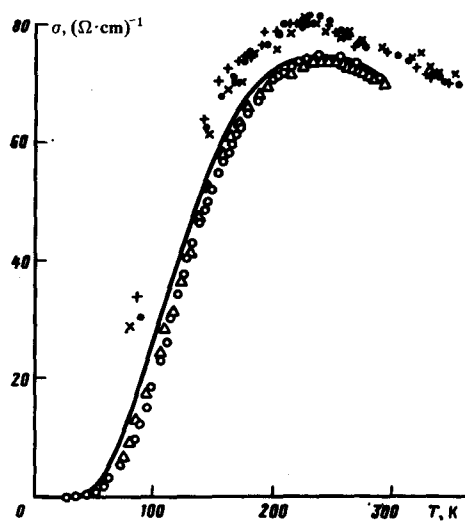

FIG. 1. Electric conductivity of Qn(TCNQ)$_2$: ○, △—dc measurements; ●, +, ×—measurements at 27.7 GHz. Solid curve—theory at $\omega_{ph}^0 = 350$ °K, $\omega_{ph}' = 500$ °K, and $\Delta_\omega = 750$ °K.[3]

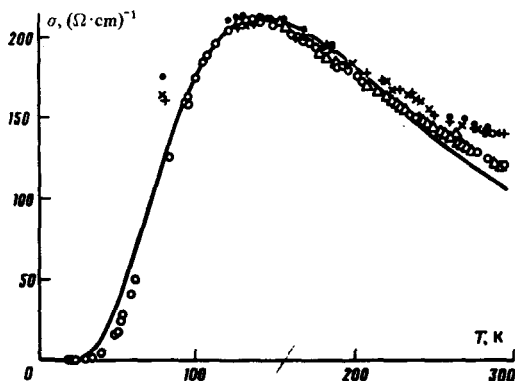FIG. 2. Electric conductivity of Adz(TCNQ)$_2$; $\circ, \triangle$— dc measurements; $\bullet, +, \times$—measurements at 27.7 GHz. Solid curve—theory at $\omega_{ph}^0 = 225\,°K$, $\omega_{ph}' = 405\,°K$, $\Delta_\omega = 800\,°K$.[3]

is at the borderline, and formulas (1) can result in a noticeable error.

The growth of σ at $T < T_{max}$ is connected with the destruction of the localization as a result of scattering by phonons. The effective ω_{ph}^0 determined from the dependence of $\log\sigma_{dc}$ on $1/T$[5] in the region $T_{max} \gtrsim T\,60\,°K$ turns out to be $\approx 300\,°K$. Since the Debye frequency is $\omega_D \approx 70\,°K$,[14] this means that in the discussed temperature region the scattering by the lattice phonons is small in comparison with the scattering by the low-frequency intramolecular phonons. These phonons should be of the fully-symmetric (FS) type, for which the electron-phonon coupling is linear. The ineffectiveness of the lattice phonons in the scattering agrees with the estimates made above: since $\hbar/\tau_i$ 350 °K greatly exceeds ω_D, the lattice phonons are adiabatic and cause transitions only between relatively remote centers with intensity $\propto (\omega_D\tau_i)^2 \ll 1$ (in analogy with the well known $\sigma \propto \omega^2$ law in conductivity).

The decrease of σ at $T > T_{max}$ is not connected with the loss of the localization and with the return to the usual phonon mechanism. In fact: 1) at $T \sim T_{max}$ we still have $l_{ph} \gg l_i$; 2) the mean free path estimated from the formula $l = \pi\hbar\sigma S/2e^2$ turns out to be ~ 1 Å $< b$, thus indicating that the usual kinetic equation does not hold[5]; 3) this is also evidenced by the observed fact that $\epsilon' \gg 1$. We assume that the decrease of σ at $T > T_{max}$ is due to the decrease of the localization length with increasing T and propose two mechanisms that ensure such a decrease.

The first is connected with the influence of the not-fully-symmetrical (NFS) intramolecular phonons.[6] The Hamiltonian of their interaction with the electron $(\Delta_\omega/2)a_{\bf a}^* a_{\bf a}(c_{\bf a}^* + c_{\bf a})^2$ at $T < \omega_{ph}'$ reduces to $\Delta_\omega a_{\bf a}^* a_{\bf a} c_{\bf a}^* c_{\bf a}$; here ω_{ph}' is the frequency of the NFS phonon, and Δ_ω is the frequency shift on going from the molecule to the ion. In this approximation, the prescence of NFS phonons leads to the appearance of scattering centers with potential Δ_ω and with a concentration determined by the Planck value $\bar{N}(\omega_{ph}')$. As a result, the effective impurity mean free path is given by $l^{-1}(T) = l_i^{-1} + (l_{ph}')^{-1}$, with $1/l_{ph}' = b\Delta_\omega^2 \bar{N}/\hbar^2 v_F^2$. The value of Δ_ω for TCNQ is known only for several oscillations; according to[17], the maxi-

mum measured value is $\Delta_\omega \approx 200\,°K$.

The second mechanism consists in the fact that the adiabatic lattice phonons produce a random quasistatic field that decreases the localization length. In this case (in analogy with formula (15) of[4]) we have

$$1/l_{ph}' = (1/\hbar v_F)^2 \int_{-\infty}^{\infty} < H_{int}(x)\,H_{int}(0) > \exp(2i\,k_F\,x)\,dx\,, \qquad (2)$$

where H_{int} is the potential produced by the displacement of the nuclei. In the deformation-potential approximation we have

$$\frac{1}{l_{ph}'} = \frac{C^2}{2\hbar\rho v_F^2} \int \frac{d^2 {\bf q}_\perp}{(2\pi)^2}\,\frac{q^2}{\omega_q}\,(2N_q + 1) \sim \frac{C^2 T}{\hbar^2 \rho S v_F^2}\left(\overline{\frac{q}{\omega_q}}\right)^2\,, \qquad (3)$$

where ${\bf q} = (2k_F, {\bf q}_\perp)$, ρ is the density, and C is the deformation potential. At $C \sim 1$ eV and $T \sim 300$ °K, Eq. (3) yields the reasonable value $l_{ph}' \sim 10$ Å. The relatively large role of this mechanism in narrow-band systems is connected with the fact that v_F, together with the width of the band, is exponentially small in terms of the overlap, but C does not have this smallness.

The theoretical curves on Figs. 1–3 correspond to the scheme in which there is one FS phonon that suppresses the localization, and one NFS phonon that enhances it. The main qualitative regularities in $\sigma(T)$, and also the decrease of $\epsilon'(T)$ at high temperatures, are described by them correctly. The parameters are chosen for a best fit of theory to experiment. In view of the highly simplified character of the scheme, one can hardly expect a better agreement. What is unnaturally large, however, is the value $\Delta_\omega \approx 800$ °K; this
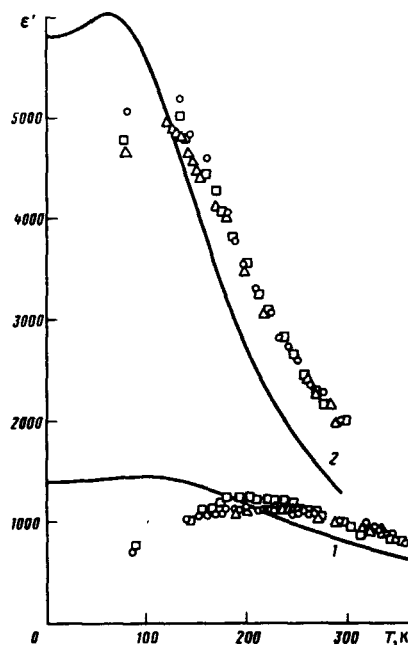

FIG. 3. Dielectric constants of Qn(TCNQ)$_2$ (1) and of Adz(TCNQ)$_2$ (2). The different symbols denote the data for different crystals. Solid curves—theory. The corrections relative to the parameter T/ϵ_F were taken into account in the data reduction.

cludes contributions from many NFS phonons, and in part by the contribution of the lattice phonon. The only qualitative regularity, the origin of which is not clear, is the decrease of ϵ towards lower temperature.

Thus, the concept of electron localization with large lengths, on the order of twenty lattice constants, in conjunction with the mechanisms of the phonon enhancement and suppression of this localization, enables us to interpret a large number of experimental data, including the large values of ϵ' and the temperature dependences of σ and ϵ'.

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