

Electron localization near a band edge and dielectric constant of TCNQ salts with strong structural disorder

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Electron localization near a band edge in one-dimensional disordered systems is investigated at arbitrary values of the parameter $p_F l \sim 1$. The Berezinskii diagram technique is used. It is shown that near $p_F l$ the localization length l_{loc} and the static dielectric constant ϵ' decrease by one or two orders in a narrow interval of the parameter $p_F l$. This abrupt transition explains the temperature dependence of ϵ' in TCNQ salts with asymmetric cations.

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1. INTRODUCTION

Interest in the theory of Mott localization of electrons in one-dimensional disordered systems has increased markedly in the last few years, both in connection with the possibility of obtaining exact solutions of this problem and with the interesting experimental data on the electric properties of quasi-one-dimensional organic conductors $\text{Qn}(\text{TCNQ})_2$ and $\text{Adz}(\text{TCNQ})_2$ with strong structural disorder.^{1–3} Among the interesting results obtained in this field are the large value and strong temperature dependence of the static dielectric constant ϵ' (Refs. 1–3) and its high sensitivity to radiation defects.⁴ The large value $\epsilon' \sim 10^3$ and its decrease in the region $T > 150$ K can be easily explained with the aid of a localization theory that takes phonon defects into account.² This theory, however, did not explain the low-temperature decrease of $\epsilon'(T)$, wherein ϵ' decreases by 3–5 times compared with its maximum value.^{1–4} In addition, the very strong sensitivity of ϵ' to relatively small densities of radiation defects remained unexplained (the value of ϵ' decreases by one-half at $c_{\text{irrad}} = 0.6\%$).

It is shown in the present paper that these facts can be explained within the framework of the localization theory developed by Berezinskii,⁵ with account taken of the large impurity density ($c = 50\%$) and the relative proximity of the Fermi level $\epsilon_F \approx 500\text{--}600$ K to the edge of the band (one-quarter of the band is filled in $\text{Qn}(\text{TCNQ})_2$ and $\text{Adz}(\text{TCNQ})_2$). The reciprocal free-path time in these compounds, estimated by various methods^{2,3} is $\tau^{-1} \approx 400\text{--}600$ K and it is necessary to take into account in the localization theory the corrections in powers of $(\epsilon_F \tau)^{-1} \sim (p_F l)^{-1} \sim 1$, which were discarded in Ref. 5. Allowance for these effects decreases greatly the electron localization length l_{loc} in a narrow energy interval near the edge of the band. This leads to strong decreases of the polarizability of the localized states and explains the strong dependence of ϵ' on the temperature T (Refs. 1–3) and on the density c_{irrad} of the radiation defects.⁴ To calculate the localization length l_{loc} and dielectric constant ϵ' we use the Berezinskii technique.⁵ For simplicity we consider in the present paper a continual model of a one-dimensional disordered system with a potential of the “white noise” type and with a quadratic electron dispersion.

This model admits of an exact solution, which makes it possible to calculate the dependences of l_{loc} and ϵ' on the parameter $p_F l$. It turns out that near $p_F l \approx 1$ the values of l_{loc} and ϵ' decrease sharply by one or two orders of magnitude, corresponding to a strong decrease of the characteristic dimension of the electronic states. This transition is interpreted as the boundary between the usual bound states and the Mott localized states.⁵ It is interesting to note that the transition point $p_F l$ corresponds to the Ioffe-Regel' criterion.⁶

2. DERIVATION OF THE BASIC EQUATIONS

We consider a one-dimensional gas of non-interacting electrons with a dispersion law $\epsilon(p) = p^2/2m^*$, located in a random potential $V(x)$ produced by randomly disposed δ functions of equal amplitude u_0 and density c . In the Born approximation, such a potential is described by the pair correlator

$$\langle V(x)V(x') \rangle = cu_0^2 \delta(x-x'), \quad (1)$$

where the angle brackets denote averaging over the realizations of the random potential.

We shall assume that the relation between the electron momentum p_F and the reciprocal electron mean free path $l^{-1} = cu_0^2/v_F^2$ is arbitrary.

To determine the characteristics of the localized electron states it is necessary to calculate the correlation functions of the density and current operators $j^0(x)$ and $j^1(x)$. These correlation functions are expressed at the frequency ω in terms of mean products of exact Green's functions $G^\pm = (\epsilon - H \pm i0)^{-1}$ (Ref. 5):

$$\begin{aligned} X_{\pm}^a(\epsilon, \omega, k) &= \int_{-\infty}^{\infty} \frac{d(x-x')}{(2m^*)^{2a}} e^{ik(x'-x)} \\ &\times \left\langle \left(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2} \right)^a \left(\frac{\partial}{\partial x_1'} - \frac{\partial}{\partial x_2'} \right)^a \right|_{\substack{x_1=x_2=x \\ x_1'=x_2'=x'}} \\ &\times G^{\pm} \left(\epsilon - \frac{\omega}{2}, x_1', x_1 \right) G^{\pm} \left(\epsilon + \frac{\omega}{2}, x_2, x_2' \right) \rangle. \end{aligned} \quad (2)$$

It will be shown later that X_+ makes no contribution to the static characteristics, and will be omitted hereafter.

In diagram language, these mean values are represented in the form of a polarization loop, in the vertices of which are

located the operators

$$j^a(x) = \frac{1}{(2m^*)^a} \left(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial x_2} \right)^a \Big|_{x_1=x_2=x} \psi^+(x_1) \psi(x_2).$$

The diagram expansion in terms of V is constructed in the usual manner in the coordinate-energy representation, using the zero Green's functions

$$G_0^\pm(\varepsilon, x, x') = \mp \frac{i}{v} \exp(\pm ip|x-x'|),$$

where $p = (2m^*\varepsilon)^{1/2}$ and $v = p/m^*$. On the diagrams, the Green's functions G_0^+ and G_0^- are represented respectively by single and double lines. When averaging over the impurity positions, i.e., when integrating over their coordinates, we shall use diagrams ordered along the x axis. The Green's functions $G_0^\pm(\varepsilon, x, x')$ can therefore be represented in factorized form:

$$G_0^\pm(\varepsilon, x, x') = \mp \left(\frac{i}{v} \right)^{1/2} e^{\pm ipx} \left(\frac{i}{v} \right)^{1/2} e^{\mp ipx'}, \quad x > x'.$$

The corresponding factors can be included in the impurity vertices.

The Berezinskii diagram technique⁵ was based on retention of only those diagrams in which the rapidly oscillating factors of the type $\exp(ip_F x)$ cancel out. This corresponds to a diagram-selection criterion $(p_F l)^{-1} \ll 1$. In the present paper we wish to sum a series in powers of this parameter, which is assumed to be not small. Therefore, in addition to the impurity vertices that were taken into account by Berezinskii⁵ (see Fig. 1), we should also take into account all other vertices (see Fig. 2) in which no cancellation of the oscillating multipliers takes place. The multipliers corresponding to these vertices are indicated in the figure captions. The correlators of the impurity potential (1) are shown in Figs. 1 and 2 by wavy lines. By not assuming smallness of the reciprocal free path time $\tau^{-1} = v/l$ compared with the electron energy ε , we do not assume smallness of the external frequency compared with ε .

We must next calculate the polarization loop with the operators $j^a(x)$ and $J^a(x')$ in the entrance and exit vertices. The number of impurity vertices of the type of Figs. 1 and 2 that can be inserted in this loop is arbitrary. It can be easily seen that the numbers of pairs of single and double lines in the vertical sections of the diagrams need not be equal to each other, since additional vertices of the type shown in Fig. 2 alter them in an asymmetric manner, unlike the vertices of

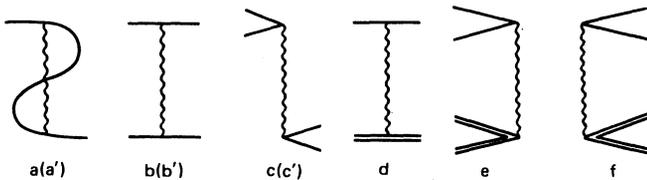


FIG. 1. Impurity vertices with cancellation of the main phase factors. A prime denotes replacement of single lines by double ones. The vertices correspond to the following factors (we have introduced for brevity the notation $p_1 = p(\varepsilon + \omega/2)$, $p_2 = p(\varepsilon - \omega/2)$, $l_1 = l(\varepsilon + \omega/2)$, $l_2 = l(\varepsilon - \omega/2)$: a, b, c - $(-l_1)^{-1}$; a', b', c' - $(-l_2)^{-1}$; d - $(l_1 l_2)^{-1/2}$; e - $(l_1 l_2)^{-1/2} \exp(2ix(p_1 - p_2))$; f - $(l_1 l_2)^{-1/2} \exp(2ix(p_2 - p_1))$.

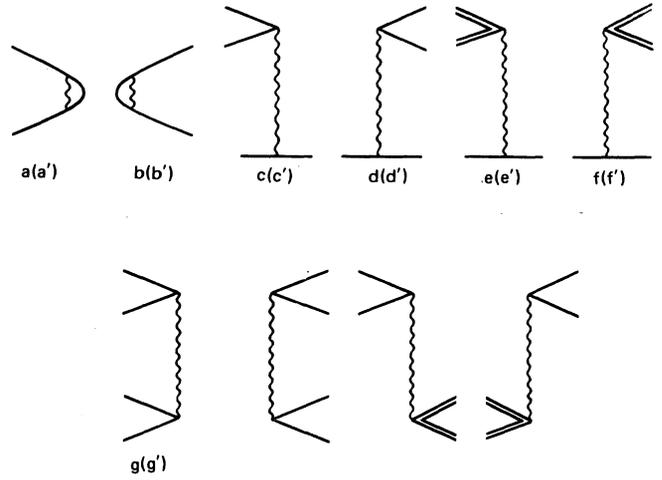


FIG. 2. Impurity vertices containing rapidly oscillating factors. A prime denotes replacement of single lines by double ones and vice versa, meaning complex conjugation and interchange of the indices 1 \leftrightarrow 2. The vertices correspond to the following factors: a, c - $(-l_1)^{-1} \exp(2ip_1 x)$; e - $(l_1 l_2)^{-1/2} \exp(-2ip_2 x)$; g - $(-l_1)^{-1} \exp(4ip_1 x)$; i - $(l_1 l_2)^{-1/2} \exp(2ix(p_1 + p_2))$. The expressions for the vertices b, d, f, h, j are obtained from the corresponding expressions for the vertices a, c, e, g, and i by complex conjugation.

the type shown in Fig. 1. It is therefore necessary to introduce separately in each section of the diagram m_1 and m_2 single and double lines. We note that a similar situation arises when account is taken of the discreteness of the lattice and of the commensurability of the electron wavelength with the lattice period.⁷ Subdividing now at $x > x'$ the diagram into three parts, namely righthand (to the right of x), central (between x and x') and left hand (to the left of x'), we obtain for the corresponding diagram sums $R_{m_1, m_2}(x)$, $Z_{m_1, m_2}^i(x', x)$, $\tilde{R}_{m_1, m_2}^i(x')$ Dyson equations that take on, after separating the coordinate dependences of the right-hand sides (Refs. 5 and 7)

$$R_{m_1, m_2}(x) = R_{m_1, m_2} \exp[2ix(m_1 p_1 - m_2 p_2)] \quad (3)$$

for R_{m_1, m_2} the form

$$\begin{aligned} & 2i(m_2 p_2 - m_1 p_1) R_{m_1, m_2} \\ &= R_{m_1, m_2} \left[\frac{4m_1 m_2}{(l_1 l_2)^{1/2}} - \frac{3m_1^2}{l_1} - \frac{3m_2^2}{l_2} \right] + R_{m_1 - 1, m_2 - 1} \frac{m_1 m_2}{(l_1 l_2)^{1/2}} \\ &+ R_{m_1 + 1, m_2 + 1} \frac{m_1 m_2}{(l_1 l_2)^{1/2}} + R_{m_1 - 1, m_2} m_1 \left[\frac{2m_2}{(l_1 l_2)^{1/2}} - \frac{2m_1 - 1}{l_1} \right] \\ &+ R_{m_1, m_2 - 1} m_2 \left[\frac{2m_1}{(l_1 l_2)^{1/2}} - \frac{2m_2 - 1}{l_2} \right] \\ &+ R_{m_1 + 1, m_2} m_1 \left[\frac{2m_2}{(l_1 l_2)^{1/2}} - \frac{2m_1 + 1}{l_1} \right] + R_{m_1, m_2 + 1} m_2 \\ &\times \left[\frac{2m_1}{(l_1 l_2)^{1/2}} - \frac{2m_2 + 1}{l_2} \right] - R_{m_1 - 2, m_2} \frac{m_1(m_1 - 1)}{2l_1} \\ &- R_{m_1, m_2 - 2} \frac{m_2(m_2 - 1)}{2l_2} - R_{m_1 + 2, m_2} \frac{m_1(m_1 + 1)}{2l_1} \\ &- R_{m_1, m_2 + 2} \frac{m_2(m_2 + 1)}{2l_2} + R_{m_1 - 1, m_2 + 1} \frac{m_1 m_2}{(l_1 l_2)^{1/2}} + R_{m_1 + 1, m_2 - 1} \frac{m_1 m_2}{(l_1 l_2)^{1/2}}. \end{aligned} \quad (4)$$

Equation for $Z_{m_1, m_2}^{m_1', m_2'}(x', x)$ with allowance for the trivial boundary condition

$$Z_{m_1, m_2}^{m_1', m_2'}(x=0, x) = \delta_{m_1, m_1'} \delta_{m_2, m_2'}$$

can be easily transformed^{5,7} by introducing the quantities

$$P_{m_1, m_2}^a = \frac{1}{2} (R_{m_1, m_2} + R_{m_1+1, m_2+1} + R_{m_1+1, m_2} + R_{m_1, m_2+1}),$$

$$P_{m_1, m_2}^i = \frac{p_1 + p_2}{2p} (R_{m_1, m_2} - R_{m_1+1, m_2+1}) + \frac{p_1 - p_2}{2p} (R_{m_1, m_2+1} - R_{m_1+1, m_2})$$

(The appearance of the terms R_{m_1, m_2+1} and R_{m_1+1, m_2} is due to allowance for the entering vertices in which the double and single lines are oppositely directed),

$$Q_{m_1, m_2}^a = \frac{1}{l} \sum_{m_1', m_2'=0}^{\infty} \int_{x'}^{\infty} dx e^{ik(x'-x)} Z_{m_1', m_2'}^{m_1, m_2}(x', x)$$

$$\times P_{m_1', m_2'} \exp[2i((m_1 p_1 - m_2 p_2)x - (m_1' p_1 - m_2' p_2)x')] \quad (6)$$

to the form

$$-i((2m_1+1)p_1 - (2m_2+1)p_2) Q_{m_1, m_2}^a = \frac{1}{l} P_{m_1, m_2}$$

$$- ik Q_{m_1, m_2}^a + Q_{m_1, m_2}^a \left[\frac{(2m_1+1)(2m_2+1)}{(l_1 l_2)^{1/2}} - \frac{3m_1(m_1+1)+1}{l_1} - \frac{3m_2(m_2+1)+1}{l_2} \right] + Q_{m_1-1, m_2-1}^a \frac{m_1 m_2}{(l_1 l_2)^{1/2}}$$

$$+ Q_{m_1+1, m_2+1}^a \frac{(m_1+1)(m_2+1)}{(l_1 l_2)^{1/2}} + Q_{m_1-1, m_2}^a m_1 \left[\frac{2m_2+1}{(l_1 l_2)^{1/2}} - \frac{2m_1}{l_1} \right] + Q_{m_1, m_2-1}^a m_2 \left[\frac{2m_1+1}{(l_1 l_2)^{1/2}} - \frac{2m_2}{l_2} \right]$$

$$+ Q_{m_1+1, m_2}^a \left[\frac{(2m_2+1)(m_1+1)}{(l_1 l_2)^{1/2}} - \frac{2(m_1+1)^2}{l_1} \right] + Q_{m_1, m_2+1}^a \left[\frac{(2m_1+1)(m_2+1)}{(l_1 l_2)^{1/2}} - \frac{2(m_2+1)^2}{l_2} \right]$$

$$- Q_{m_1-2, m_2}^a \frac{m_1(m_1-1)}{2l_1} - Q_{m_1, m_2-2}^a \frac{m_2(m_2-1)}{2l_2}$$

$$- Q_{m_1+2, m_2}^a \frac{(m_1+1)(m_1+2)}{2l_1}$$

$$- Q_{m_1, m_2+2}^a \frac{(m_2+1)(m_2+2)}{2l_2} + Q_{m_1-1, m_2+1}^a \frac{m_1(m_2+1)}{(l_1 l_2)^{1/2}}$$

$$+ Q_{m_1+1, m_2-1}^a \frac{m_2(m_1+1)}{(l_1 l_2)^{1/2}}. \quad (7)$$

The correlation functions $X_{-}^a(\varepsilon, \varepsilon, k)$ are expressed in terms of the quantities P_{m_1, m_2}^a and Q_{m_1, m_2}^a , in accordance with the equations^{5,7}

$$X_{-}^a(\varepsilon, \omega, k)$$

$$= \frac{2l}{(v_1 v_2)^{1/2}} \left[\frac{v}{2} \right]^{2a} \sum_{m_1, m_2=0}^{\infty} P_{m_1, m_2}^a(\varepsilon, \omega) [Q_{m_1, m_2}^a(\varepsilon, \omega, k) + Q_{m_1, m_2}^a(\varepsilon, \omega, -k)]. \quad (8)$$

Equations (4) and (7) enable us to calculate the main characteristics of localized electron states near a band edge. We

note that the quantities R_{m_1, m_2} must satisfy the trivial boundary condition $R_{00} = 1$.

3. STATE DENSITY

We note first that Eq. (4) with $m_2 = 0$ describes the averaging of the exact electron Green's function $G^+(\varepsilon + \omega/2, x, x)$ at coinciding points⁷ and determines thus at $\omega = 0$ the electronic state density distribution $\rho(\varepsilon)$ in accord with the known formula

$$\rho(\varepsilon) = -\frac{1}{\pi} \text{Im} \langle G^+(\varepsilon, x, x) \rangle. \quad (9)$$

The expression for $\rho(\varepsilon)$ in terms of $R_m(\varepsilon) = R_{m0}(\varepsilon)$ takes in this case the form

$$\rho(\varepsilon) = \frac{1}{\pi v} \sum_{m=-\infty}^{\infty} R_m(R_m + R_{m+1}), \quad (10)$$

where it is convenient to introduce the quantities R_m with $m < 0$ in accord with the formula $R_m = R_{-m}^*$. The quantities R_m satisfy the trivial boundary condition $R_0 = 1$.

The equation for R_m is of the form

$$2implR_m = 3m^2 R_m + m(2m+1)R_{m+1} + m(2m-1)R_{m-1} + \frac{1}{2}m(m+1)R_{m+2} + \frac{1}{2}m(m-1)R_{m-2}. \quad (11)$$

Introducing the function

$$R(\varphi) = \sum_{m=-\infty}^{\infty} e^{im\varphi} R_m,$$

we obtain for it the following equation:

$$(3 + \cos 2\varphi + 4 \cos \varphi) dR/d\varphi + (s - 2 \sin \varphi - \sin 2\varphi) R = C_1, \quad (12)$$

where $s = 2pl$ and the constant C_1 is chosen to satisfy the periodicity condition $R(0) = R(2\pi)$. The function $R(\varphi)$ must satisfy the normalization condition

$$\int_0^{2\pi} \frac{d\varphi}{2\pi} R(\varphi) = 1. \quad (13)$$

The substitutions

$$z = (s/4)^{1/2} \text{tg} \frac{\varphi}{2} \text{ and } R(\varphi) \left(1 + \text{tg}^2 \frac{\varphi}{2} \right) = \pi (s/4)^{1/2} p_0(z)$$

reduce Eq. (12) to the form

$$dp_0/dz + (z^2 + (s/4)^{1/2}) p_0 = C_3, \quad (14)$$

where the constant C_3 is determined from the condition that $p_0(z)$ decrease at infinity, $p_0(\infty) = p_0(-\infty) = 0$. This equation coincides with the known Halperin equation.⁸ Its solution, which satisfies the conditions that they decrease at infinity, is

$$p_0(z) = C s(z), \quad (15)$$

$$s(z) = \exp(-1/3 z^3 - 2Ez) \int_{-\infty}^z \exp(1/3 u^3 + 2Eu) du,$$

where

$$2E = (s/4)^{1/2} = \varepsilon (1/2 c^2 u_0^4 m^*)^{-1/2}.$$

The constant C is determined from the normalization

condition

$$\int_{-\infty}^{\infty} p_0(z) dz = 1. \quad (16)$$

The state density $\rho(\varepsilon)$ can be easily expressed in terms of $p_0(z)$:

$$\begin{aligned} \rho(\varepsilon) &= \frac{1}{\pi v} \int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} R(\varphi) R(-\varphi) (1 + \cos \varphi) \\ &= 2\rho_0 \int_{-\infty}^{\infty} p_0(z) p_0(-z) dz, \end{aligned} \quad (17)$$

where $\rho_0 = 0m^*/2cu_0^2)^{1/2}$. The expression for $\rho(\varepsilon)$ can be easily transformed into the standard equation of Frisch and Lloyd⁹:

$$\rho(\varepsilon) = \rho_0 dN/dE, \quad (18)$$

$$\begin{aligned} N(E) &= \left[\int_0^{\infty} du \left(\frac{\pi}{u} \right)^{1/2} \exp\left(-\frac{1}{12} u^3 - 2Eu\right) \right]^{-1} \\ &= \frac{1}{\pi^2} [(\text{Ai}(-2E))^2 + (\text{Bi}(-2E))^2]^{-1}, \end{aligned} \quad (19)$$

where Ai and Bi are Airy functions. The function $\rho(E)$ has a characteristic maximum at $E \approx 0.2$. The asymptotic form of $\rho(E)$ as $E \rightarrow \pm \infty$ is

$$\rho(E)/\rho_0 \approx [\pi(2E)^{3/2}]^{-1}, \quad E \rightarrow +\infty, \quad (20)$$

$$\rho(E)/\rho_0 \approx \frac{4}{\pi} |E| \exp\left(-\frac{4}{3}(2|E|)^{3/2}\right), \quad E \rightarrow -\infty. \quad (21)$$

The quantities R_m are expressed in terms of $p_0(z)$ in accord with the formula

$$R_m(\varepsilon) = (-1)^m \int_{-\infty}^{\infty} dz p_0(z) \left[\frac{z - i(2E)^{1/2}}{z + i(2E)^{1/2}} \right]^m. \quad (22)$$

Equation (22) determines, in particular, the solutions of (4) at $m_1 = 0$ and $m_2 = 0$:

$$R_{m,0} = R_{m_1}(\varepsilon + \omega/2), \quad R_{0,m_2} = R_{m_2}(\varepsilon - \omega/2). \quad (23)$$

4. LOCALIZATION LENGTH

The stationary distribution of the density of a localized electronic state is known^{5,10} to be determined by the low-frequency asymptotic form of the electron-density correlator $X^0(\varepsilon, \omega, k)$. In the limit of small $\omega \ll \tau^{-1}$ the important role in Eqs. (4) and (7) is assumed by large $m_1, m_2 \sim \partial\omega\tau)^{-1} \gg 1$, so that we can transform from difference to differential equations. It is convenient to introduce for this purpose new discrete variables $M = m_1 + m_2$ and $m = m_1 - m_2$, and, using the condition $M \gg 1$, expand Eqs. (4) and (7) in powers of $M^{-1} \ll 1$ up to the first term. Introducing now the continuous variable $q = -ivM$ and $v = \omega\tau \ll 1$, we obtain after simple transformations the equations:

$$\begin{aligned} 0 &= (-q + i\kappa - 3m^2)R_m + q^2 \frac{d^2 R_m}{dq^2} + \frac{q^2}{s^2} \left(\frac{3}{4}R_m + \frac{1}{2}R_{m-1} + \frac{1}{2}R_{m+1} \right. \\ &\quad \left. + \frac{1}{8}R_{m-2} + \frac{1}{8}R_{m+2} \right) + \frac{iq}{s} (3mR_m + (2m-1)R_{m-1} + (2m+1)R_{m+1} \\ &\quad + 2(m-1)R_{m-2} + 2(m+1)R_{m+2}) + (2m-1)q \frac{dR_{m-1}}{dq} - m(2m-1)R_{m-1} \\ &\quad + (2m+1)q \frac{dR_{m+1}}{dq} - m(2m+1)R_{m+1} + \frac{1}{2}q^2 \left(\frac{d^2 R_{m-2}}{dq^2} + \frac{d^2 R_{m+2}}{dq^2} \right) \\ &\quad + (m-1)q \frac{dR_{m-2}}{dq} + (m+1)q \frac{dR_{m+2}}{dq} - \frac{m(m-1)}{2}R_{m-2} - \frac{m(m+1)}{2}R_{m+2}, \end{aligned} \quad (24)$$

$$\begin{aligned} 0 &= (-i\kappa - q + i\kappa s - 3m^2)Q_m^a + q^2 \frac{d^2 Q_m^a}{dq^2} + 2q \frac{dQ_m^a}{dq} + P_m^a + \frac{q^2}{s^2} \left(\frac{3}{4}Q_m^a \right. \\ &\quad \left. + \frac{1}{2}Q_{m-1}^a + \frac{1}{2}Q_{m+1}^a + \frac{1}{8}Q_{m-2}^a + \frac{1}{8}Q_{m+2}^a \right) + i \frac{q}{s} (3mQ_m^a + 2(m-1)Q_{m-1}^a \\ &\quad + 2(m+1)Q_{m+1}^a + \left(2m - \frac{5}{2}\right)Q_{m-2}^a + \left(2m + \frac{5}{2}\right)Q_{m+2}^a) + (2m-1)q \frac{dQ_{m-1}^a}{dq} \\ &\quad + (2m+1)q \frac{dQ_{m+1}^a}{dq} - (m-1)(2m-1)Q_{m-1}^a - (m+1)(2m+1)Q_{m+1}^a \\ &\quad + \frac{1}{2}q^2 \left(\frac{d^2 Q_{m-2}^a}{dq^2} + \frac{d^2 Q_{m+2}^a}{dq^2} \right) + (m-1)q \frac{dQ_{m-2}^a}{dq} + (m+1)q \frac{dQ_{m+2}^a}{dq} \\ &\quad - \frac{1}{2}(m-1)(m-2)Q_{m-2}^a - \frac{1}{2}(m+1)(m+2)Q_{m+2}^a, \end{aligned} \quad (25)$$

where

$$\begin{aligned} \kappa &= kl, \quad P_m^0 = R_m + \frac{1}{2}(R_{m+1} + R_{m-1}), \\ P_m^1 &= 2(-iv) \left[-\frac{dR_m}{dq} + \frac{i}{2s}(R_{m-1} - R_{m+1}) \right]. \end{aligned} \quad (26)$$

The expression for the correlators X^a in terms of P_m^a and Q_m^a takes as $\omega \rightarrow 0$ the form

$$\begin{aligned} X^a(\varepsilon, \omega, k) &\approx \frac{l}{-ivv} \left[\frac{v}{2} \right]^{2a} \int_0^{\infty} dq \sum_{m=-\infty}^{\infty} (Q_m^a(q, \kappa) + Q_m^a(q, -\kappa)) P_m^a(q). \end{aligned} \quad (27)$$

We note that at $q = 0$ Eq. (24) goes over into Eq. (11), therefore the functions $R_m(q)$ satisfy the boundary condition

$$R_m(0) = R_m, \quad (28)$$

where R_m is defined by (22).

It is easily seen that for the density correlator $X^0(\varepsilon, \omega, k)$ expression (27) takes the form

$$X^0(\varepsilon, \omega, k) \approx \frac{f(\kappa) + f(-\kappa)}{-i\omega}, \quad (29)$$

$$f(\kappa) = \int_0^{\infty} dq \sum_{m=-\infty}^{\infty} Q_m^0(q, \kappa) P_m^0(q).$$

This means that in the time representation the density correlator $X^0(\varepsilon, t, x)$ has as $t \rightarrow \infty$ a stationary distribution that determines the density distribution $p_{\infty}(x)$ of the localized electron state. It must be emphasized that the very presence of the stationary density distribution $p_{\infty}(x)$ follows directly already from the general structure of Eqs. (4) and (7), as manifest in their "nondimensionalization" upon introduction of the continuous parameter $q = -iv(m_1 + m_2)$ at large $m_1, m_2 \gg 1$. We note that an analogous structure is possessed also by the corresponding equations for the correlator

$X_+^0(\varepsilon, \omega, k)$. This correlator, however, is an even function of ω , so that its expansion in powers of ω as $\omega \rightarrow 0$ begins not with the term $\sim (-i\omega)^{-1}$, as for $X_-^0(\varepsilon, \omega, k)$ (see (29)), but with a constant. Therefore $X_+^0(\varepsilon, \omega, k)$ makes no contribution to the stationary distribution of the electron density as $t \rightarrow \infty$, and influences only the time dependences and the rate at which this distribution is reached. In the calculation of the static characteristic the contribution of X_+^0 can therefore be omitted.

To calculate the localization length l_{loc} it is necessary to find the position of the branch point of $Q_m^0(q, \kappa)$ with respect to κ , which determines the exponential asymptotic form of $p_\infty(x)$ at $|x| \gg l$.¹⁰ The position of the branch point relative to κ can be easily determined from the asymptotic form of $Q_m^0(q, \kappa)$ at small $q \ll 1$ (Ref. 11). Indeed, substituting in (25) with $a = 0$ and $q \ll 1$ the quantities $Q_m^0(q, \kappa) \approx a_m q^\lambda$, we obtain for the coefficients a_m the following linear equations:

$$\begin{aligned} 0 = & a_m(\lambda(\lambda+1) + ims - i\kappa - 3m^2) + a_{m-1}(2m-1)(\lambda-m+1) \\ & + a_{m+1}(2m+1)(-\lambda-m-1) \\ & + a_{m-2}[-\frac{1}{2}\lambda(\lambda+1) + (m-1)(\lambda+1) - \frac{1}{2}m(m-1)] \\ & + a_{m+2}[-\frac{1}{2}\lambda(\lambda+1) - (m+1)(\lambda+1) - \frac{1}{2}m(m+1)]. \end{aligned} \quad (30)$$

The position of the κ branch point is determined from the equation

$$\partial\kappa/\partial\lambda = 0. \quad (31)$$

At large $s \gg 1$ only the term with $m = 0$ are significant in (30). As a result, the equation for λ takes the form

$$\lambda(\lambda+1) - i\kappa = 0 \quad (32)$$

and the branch points located at $\kappa = i/4$ (Ref. 10). This corresponds to a localization length $l_{loc} = 4l$. We shall find it convenient to introduce a new length unit $l_0 = (2cu_0^2(m^*)^2)^{-1/3}$. In these units, $l_{loc}/l_0 \approx 16E$ at $E \gg 1$ ($s \gg 1$). The first correction to l_{loc} in terms of the parameter $s^{-1} \ll 1$ can be easily calculated by perturbation theory:

$$l_{loc} \approx 4l \left(1 + \frac{131}{8s^2} \right) = l_0 \cdot 16E \left(1 + \frac{131}{1024E^3} \right), \quad E \gg 1. \quad (33)$$

We note that this correction is relatively small only at $s > 10$ ($E > 1$). At arbitrary values of the parameter $s \sim 1$, Eqs. (30) and (31) can be easily solved by numerical methods. The corresponding plot of l_{loc}/l_0 vs E is shown in Fig. 3. It must be emphasized that the function l_{loc} has a characteristic maximum at $E \approx 0.35$ ($p_l \approx 1$) and falls off rapidly at $E < 0.35$. This rapid falloff points to the existence of a rather abrupt boundary between the localized Mott states that are produced as a result of interference of the scattered electron waves in a one-dimensional disordered system,⁵ and the usual bound states. We note that the abrupt decrease of the localization length takes place near $p_F l \approx 1$. It is curious that according to Mott's qualitative arguments^{12,13} the Anderson transitions from the localized to the delocalized states takes place in two- and three-dimensional systems at the point $p_F l \approx 1$ (the Ioffe-Regel' criterion⁶). This statement agrees well with the results of numerical calculations for three-dimensional systems (see the review¹⁴).

Thus, even in one-dimensional systems this point is the

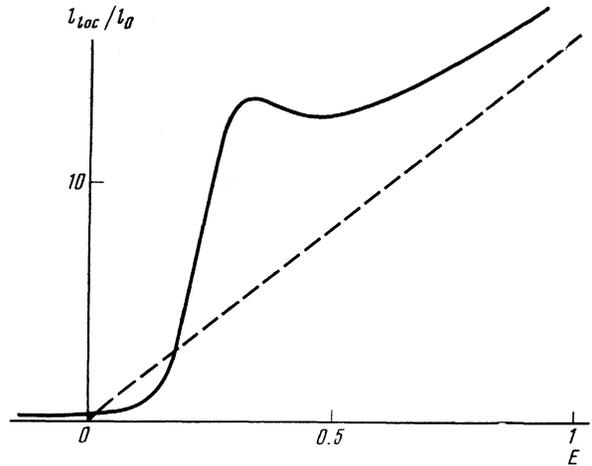


FIG. 3. Plots of the localization length l_{loc}/l_0 vs the electron energy E . The dashed line shows the asymptote $l_{loc}/l_0 = 16E$ at $E \gg 1$.

boundary between the weakly and strongly localized electronic states.

The function l_{loc} in the region of strong localization, at negative values of E , can be easily obtained by analytically continuing (30) into the region of complex values of the parameter s , in analogy with the procedure used in the preceding section.

We note, in particular, that as $E \rightarrow -\infty$ the value of l_{loc} decreases relatively more slowly: $l_{loc}(E) \propto |E|^{-1/2}$. This result agrees well with the usual ideas, advanced by I. M. Lifshitz,¹⁵ concerning the structure electronic states in a fluctuation tail.

5. DIELECTRIC CONSTANT

Equations (24) and (25) at $a = 1$ enable us to calculate the current correlator $X_-^1(\varepsilon, \omega, k)$ that determines, in accord with the Kubo formula, the complex conductivity $\sigma(\omega)$ of the system.⁵ It follows from these equations and from (26) and (27), in particular, that $\omega \rightarrow 0$, $X_-^1(\varepsilon, \omega) \propto (-i\nu)$ at $k = 0$ and vanishes at $\omega = 0$. Similar properties are possessed also by the equations for the correlator $X_+^1(\varepsilon, \omega)$, and this also causes it to vanish at $\omega = 0$. This correlator, however, is an even function of ω and its expansion as $\omega \rightarrow 0$ begins with the term $\sim \nu^2$ and makes no contribution to the static dielectric constant ε' , but contributes only to the low-frequency absorption. The static dielectric constant is therefore fully determined by the correlator X_-^1 and takes the form

$$\varepsilon' = \varepsilon_0 |E|^{3/2} \int_0^\infty dq \sum_{m=-\infty}^{\infty} q_m^1(q) \left(-\frac{d}{dq} R_m + \frac{i}{2s} (R_{m-1} - R_{m+1}) \right), \quad (34)$$

where the quantity $q_m^1(q)$ is the solution of Eqs. (25) at $\kappa = 0$ and when P_m^a is replaced by

$$-\frac{d}{dq} R_m + \frac{i}{2s} (R_{m-1} - R_{m+1}), \quad \text{a } \varepsilon_0 = 64\sqrt{2}e^2/Scu_0^2m^*$$

(here e is the electron charge and S is the cross-section area per conducting filament). In particular, at large $E \gg 1$ only

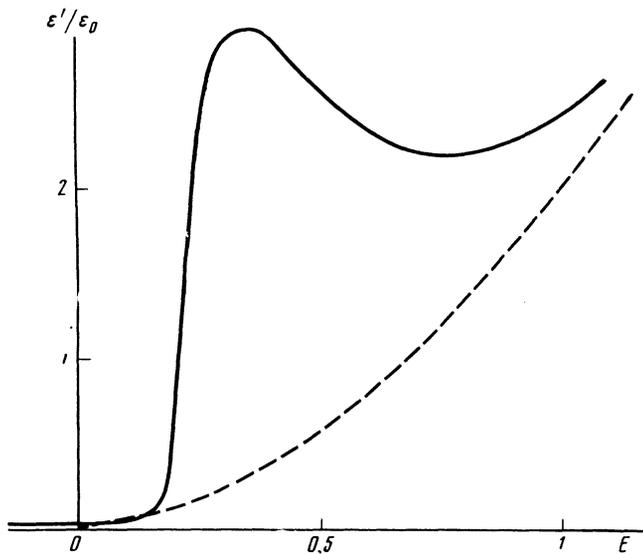


FIG. 4. Plots of the static dielectric constant ϵ'/ϵ_0 vs E . The dashed line is the asymptote of $\epsilon'/\epsilon_0 = 2\zeta(3)E^{3/2}$ at $E \gg 1$.

the terms with $m = 0$ are significant in the sums over m , and Eq. (34) takes the form

$$\epsilon' \approx \epsilon_0 E^{3/2} 2\zeta(3), \quad E \gg 1, \quad (35)$$

where $\zeta(3) \approx 1.205$ is a Riemann ζ function.

The solution of Eqs. (14) and (25) at arbitrary $pl \sim 1$ can be easily obtained by numerical method. A plot of $\epsilon'(E)$ is shown in Fig. 4. We note that this function, just as $l_{\text{loc}}(E)$, has a characteristic maximum at $E \approx 0.35$ ($pl \approx 1$). The decrease of ϵ' to the left of the maximum is even more abrupt and reaches two orders of magnitude. The presence of a steep rise of ϵ' in the region $pl < 1$ explains the substantial temperature dependence of $\epsilon'(T)$ in $\text{Qn}(\text{TCNQ})_2$ and $\text{Adz}(\text{TCNQ})_2$ at low temperatures¹⁻³ and the strong sensitivity of ϵ' to low densities of radiation defects.

We note in conclusion that at large negative E the value of ϵ' decreases rapidly, exponentially: $\ln \epsilon' \propto (-|E|^{3/2})$, owing to the exponential decrease of the density $\rho(E)$ of the electron states.

6. ANALYSIS OF EXPERIMENTAL DATA

The strong $\epsilon'(E)$ dependence near $E \approx 0.35$ leads to a substantial temperature dependence of $\epsilon'(T)$. Indeed, as shown in Ref. 2, the Fermi energy ϵ_F in $\text{Qn}(\text{TCNQ})_2$ and $\text{Adz}(\text{TCNQ})_2$ is close to 500 K. Therefore at $T \sim 100$ K the electron gas in these substances cannot be regarded as strongly degenerate and in the calculation of ϵ' it is necessary to take into account the thermal smearing of the Fermi distribution. The temperature dependence of $\epsilon'(T)$ is determined in this case by the relation^{5,10}

$$\epsilon'(T) = \int_{-\infty}^{\infty} \frac{d\epsilon}{T} \epsilon'(\epsilon) \left(2 \operatorname{ch} \frac{\epsilon - \mu}{2T} \right)^{-2}, \quad (36)$$

where μ is the chemical potential. The function $\mu(T)$ is defined by

$$\int_{-\infty}^{\infty} \frac{d\epsilon \rho(\epsilon)}{e^{(\epsilon - \mu)/T} + 1} = \text{const.} \quad (37)$$

At the present time, the most detailed data on $\epsilon'(T)$ were obtained for $\text{Qn}(\text{TCNQ})_2$ (Refs. 1-4, 16). These studies revealed an abrupt fall-off of $\epsilon'(T)$ (by approximately 5-6 times compared with the maximum $\epsilon_{\text{max}}(200 \text{ K}) \approx 1500-2000$) in the temperature interval $50 < T < 200$ K. The mean free path l estimated from the maximum of ϵ' amounts in $\text{Qn}(\text{TCNQ})_2$ to about 2.5 lattice constants b ($b \approx 3.8 \text{ \AA}$).² It can be easily seen that a similar estimate of l based on the value of $\epsilon'(0 \text{ K})$ yields $l = b$. This value is in good agreement with estimates of the impurity potential ($V \sim 0.1 \text{ eV}$) obtained by computer calculations³ of the chemical structure of $\text{Qn}(\text{TCNQ})_2$. Since the electron band in $\text{Qn}(\text{TCNQ})_2$ is $\frac{1}{4}$ -filled, we have $p_F = \pi/4b$ and $p_F l \approx 0.7-0.8$. Figure 5 shows the temperature dependence of $\epsilon'(T)$ determined from (36) at $p_F l = 0.7$ (the parameter $p_F l$ was determined at zero temperature). We note that within the limit of the scatter of the experimental data¹⁶ the agreement between theory and experiment is good enough. Thus, the noticeable decrease of ϵ' with decreasing temperature can be successfully explained within the framework of the theory of one-dimensional localization.

It is easily seen that the abrupt decrease of ϵ' in a narrow interval of the parameter $p_F l$ can explain also the decrease of ϵ' , by one order of magnitude, at a radiation-defect density $c_{\text{irrad}} \sim 10\%$ (Ref. 4).

It is easy to see that our interpretation of the strong influence of the radiation defects on the value of ϵ' is based on the assumption that the parameter $p_F l$ is close to unity; this corresponds to the region of the abrupt decrease of ϵ' and to a relatively short mean free path $l \sim b$. This estimate agrees well with the notion of strong disorder in

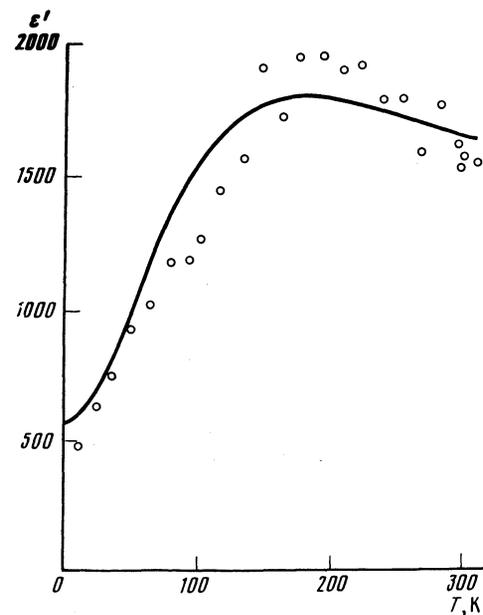


FIG. 5. Plots of the temperature dependence of $\epsilon'(T)$ in $\text{Qn}(\text{TCNQ})_2$. The circles are the experimental points.¹⁶ The solid line is theoretical for $p_F l = 7$.

$\text{Qn}(\text{TCNQ})_2$, due to the random spatial orientation of the asymmetric Qn^{++} cations. The value of the random potential V produced in this case is numerically estimated³ at approximately 0.1 eV, in agreement with the estimate $l \sim b$. These estimates agree also with the experimental data on the influence of radiative defects on the magnetic susceptibility χ in $\text{Qn}(\text{TCNQ})_2$ (Ref. 17). As seen from the plots in that reference, small densities, $\sim 2-3\%$, of radiation defects lead at not too low temperatures $T \sim 50$ K to weak changes of χ , not larger than 10%. These data point thus to a rather high density of the main defects in $\text{Qn}(\text{TCNQ})_2$ and agree with the estimate $l \sim b$. The stronger change of χ in the region of a strong singularity of the magnetic susceptibility at low temperatures $T < 20$ K can be connected with collective effects that are of no significance at higher temperatures $T > 50$ K.

7. CONCLUSION

Our present results point to the existence of two characteristic localization lengths in one-dimensional disordered system near a band edge. These scales differ by an order of magnitude, and the boundary between them lies near the value $p_F l \approx 1$, in accord with the usual Ioffe-Regel' criterion.^{6,12,13} In systems with more dimensions this point corresponds to the Anderson transition^{13,14} and separates the localized and delocalized electronic states. In one-dimensional systems it is the boundary between weakly and strongly localized states. We note that a similar phenomenon can occur also in two-dimensional systems.

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- ¹I. F. Shchegolev, Phys. Stat. Sol. (a) **12**, 9 (1972).
- ²A. A. Gogolin, S. P. Zolotukhin, V. I. Mel'nikov, É. I. Rashba, and I. F. Shchegolev, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 564 (1975) [JETP Lett. **22**, 278 (1964)].
- ³K. Holczer, G. Mihaly, A. Janossy, G. Grüner, and H. Kertesz, J. Phys. C: Sol. St. Phys. **11**, 4707 (1978).
- ⁴K. Holczer, G. Mihaly, G. Grüner, and A. Janossy, Sol. St. Comm. **31**, 145 (1979); J. Phys. C: Sol. St. Phys. **12**, 1883 (1979).
- ⁵V. L. Berezinskiĭ, Zh. Eksp. Teor. Fiz. **65**, 1251 (1973) [Sov. Phys. JETP **38**, 620 (1974)].
- ⁶A. F. Ioffe and A. R. Regel', Progr. Semicond. **4**, 237 (1960).
- ⁷A. A. Gogolin and V. I. Mel'nikov, Zh. Eksp. Teor. Fiz. **73**, 706 (1977) [Sov. Phys. JETP **46**, 369 (1977)].
- ⁸B. I. Halperin, Phys. Rev. **139**, A104 (1965).
- ⁹H. L. Frisch and S. P. Lloyd, Phys. Rev. **120**, 1175 (1960).
- ¹⁰A. A. Gogolin, V. I. Mel'nikov, and É. I. Rashba, Zh. Eksp. Teor. Fiz. **69**, 327 (1975) [Sov. Phys. JETP **42**, 168 (1975)].
- ¹¹A. A. Gogolin, Zh. Eksp. Teor. fiz. **76**, 1759 (1979) [Sov. Phys. JETP **49**, 895 (1979)].
- ¹²N. F. Mott, Adv. Phys. **16**, 49 (1967).
- ¹³N. F. Mott and E. A. Davis, Electronic Processes in Non-Crystalline Materials, Oxford, 1971.
- ¹⁴D. J. Thouless, Phys. Rep. **13**, 93 (1974).
- ¹⁵I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **53**, 743 (1967) [Sov. Phys. JETP **26**, 462 (1968)].
- ¹⁶K. Holczer and A. Janossy, Sol. State Comm. **26**, 689 (1978).
- ¹⁷J. R. Cooper, M. Miljak, and B. Karin, Chemica Scripta **17**, 79 (1981).

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