

ON THE THEORY OF FREQUENCY DEPENDENCE OF CONDUCTIVITY IN DISORDERED ORGANIC SEMICONDUCTORS

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A phononless contribution to low-temperature alternating-current conductivity for a model with a diagonal disorder is calculated with consideration for quantum correlation of the levels. It is shown that a band corresponding to resonance transitions between neighboring localized states can appear in the IR absorption spectra of organic semiconductors.

The study of relaxation processes is known to be one of the principal techniques of collecting information about the mechanisms of electronic processes in organic semiconductors [1-3]. Additional information on these mechanisms can also be extracted from measurements of the frequency dependence of conductivity or photoconductivity [4]. For many organic semiconductors (e.g., of the anthracene series), the results of these measurements can be described on the assumption of the jump transfer mechanism. The theory of jump transfer in these materials has been developed by means of both analytic [5, 6] and numerical methods. This model has been used in [6] to determine the relaxation (phonon) contribution to the alternating-current conductivity. It has been shown that the major contribution, which is made by three-node clusters, results in a power frequency dependence of conductivity. In this work, we discuss the contribution from resonance transitions not involving phonons. In the mode of jump conductivity with a variable jump length, this contribution can in certain cases be substantial [7].

In the model with a diagonal disorder that we are considering (the Anderson model), the spatial arrangement of local centers is ordered while the energies of localized states are random. When the distances between the centers exceed the radius of localization, the analysis can be restricted to electron transitions between nearest neighbors [2]. Under these conditions, quantum correlation of the levels becomes important. This correlation increases the energy gap between the levels of the neighboring centers to at least $2I$, where I is the overlap integral. In the model with a simple lattice, this integral has the same value for all pairs of neighboring nodes. Quantum correlation of the levels only weakly affects the phonon contribution, because the characteristic jump-induced change in electron energy far exceeds I , $\Delta E_h \gg I$. Actually, for three-node clusters, the relaxation time $\tau_3 \approx W_0^{-1} \exp\{-\Delta E_h/kT\} \approx \omega$ and $\Delta E_h \approx kT \ln(W_0/\omega)$, where the effective pre-exponential factor $W_0 \approx W_{00} \exp\{-2\gamma a\}$, W_{00} is the pre-exponential factor for the rate of transitions, and a is the distance between neighboring centers. For the materials under consideration W_0 is on the order of 10^6 to 10^8 s⁻¹, and therefore, in the low-frequency region with $\omega \lesssim 10^6$ s⁻¹, the value of $\Delta E_h \approx kT \ln(W_0/\omega)$ far exceeds I .

On the other hand, quantum correlation of the levels imposes an obvious restriction on the frequency of phononless transitions, viz. $\hbar\omega \geq 2I$. Because the typical value of the parameter I , which determines the band width, is about 10^{-2} eV in organic crystals [2], resonance transitions between neighboring centers are only possible if $\omega \gg \omega_{cr}$, where $\omega_{cr} \approx 10^{13}$ s⁻¹. Therefore in the low-frequency region, the contribution from resonance transitions to conductivity is zero. When $\omega \geq \omega_{cr}$, this contribution is given by (cf. [7])

$$\operatorname{Re} \sigma(\omega) = \frac{e^2 I^2}{3\gamma^5 \hbar^2 \omega} \left[1 - \exp\left\{-\frac{\hbar\omega}{kT}\right\} \right] \int d\varepsilon \rho(\varepsilon) \rho(\varepsilon + \hbar\omega) \\ \times \Psi(\varepsilon, \varepsilon + \hbar\omega) n_F(\varepsilon) [1 - n_F(\varepsilon + \hbar\omega)],$$

where $\rho(\varepsilon)$ is the density of localized states, n_F is the Fermi function, and $\Psi(\varepsilon, \varepsilon') = [1 - (2I/(\varepsilon - \varepsilon'))^2]^{1/2} \theta((\varepsilon - \varepsilon') - 2I)$ is the function of correlation of the levels. At low temperatures (if $kT \ll \hbar\omega$),

this expression becomes

$$\operatorname{Re} \sigma(\omega) = \frac{e^2 I^2}{3\gamma^5 \hbar^2 \omega} \left[1 - \left(\frac{2I}{\hbar\omega} \right)^2 \right]^{1/2} \int_{F-\hbar\omega}^F d\varepsilon \rho(\varepsilon) \rho(\varepsilon + \hbar\omega) \theta(\hbar\omega - 2I).$$

If the Fermi level lies in the neighborhood of the conductivity level, the $\operatorname{Re} \sigma(\omega)$ value in the frequency range $\omega_{\text{cr}} < \omega < (\hbar d \ln \rho(F)/dF)^{-1}$ is virtually independent of frequency for a slowly varying density of states. If $\rho(\varepsilon)$ has the form of a smeared peak of width on the order of Δ , the $\operatorname{Re} \sigma(\omega)$ value decreases if $\hbar\omega > \Delta$. The frequency dependence of the resonance contribution to $\operatorname{Re} \sigma(\omega)$, which determines the frequency dependence of the absorption coefficient for electromagnetic waves α , $\alpha(\omega) = (4\pi/nc) \operatorname{Re} \sigma(\omega)$ (where n is the refractive index and c is the velocity of light), is schematically shown in Fig. 1.

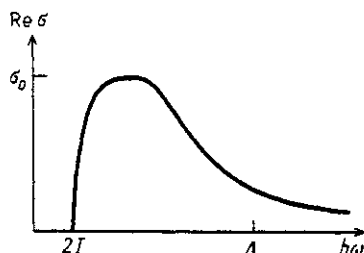


Fig. 1

The frequency dependence of the resonance contribution to conductivity; $\sigma_0 = (e^2 I^2 / 3\gamma^5 \hbar) \rho^2(F)$.

In the $\omega \geq \omega_{\text{cr}}$ region, the contribution of resonance transitions to $\sigma(\omega)$ is large compared with the relaxation contribution $\sigma^{(2)}(\omega)$ over a wide temperature range. Actually, in the frequency range under consideration, the contribution to conductivity from pairs of nodes exceeds that from three-node clusters. Using the expression for $\operatorname{Re} \sigma^{(2)}(\omega)$ obtained in [6] we find that the ratio of the phononless contribution to the phonon contribution to conductivity in the $\omega \geq \omega_{\text{cr}}$ region is about

$$\frac{\operatorname{Re} \sigma}{\operatorname{Re} \sigma^{(2)}} = \frac{I^2}{6W_0 kT} \exp \left\{ \frac{E_0 - F}{kT} \right\}.$$

For estimation purposes, we put $W_0 = 10^8 \text{ s}^{-1}$, $I = 0.01 \text{ eV}$, $T = 300 \text{ K}$. For $F = E_0$, we then obtain a ratio of about 10^4 .

To summarize, the IR absorption of electromagnetic waves in organic semiconductors under the conditions when the Fermi level lies in the neighborhood of a classically broadened conductivity level depends on resonance transitions between neighboring localized states. In this case, a band appears in the IR absorption spectrum whose width is defined by the conduction level width.

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