Exciton absorption in disordered crystals with a singular spectrum (the Urbach problem)

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The state-density tails in disordered crystals with a singular exciton spectrum exhibit an Urbach behavior at $k = 0$, $\ln \rho(E) \propto E$. This behavior is caused by an increase in the dimension of space resulting from the singular term in the spectrum.

Pekar[1] showed the long-range dipole forces in uniaxial and biaxial crystals always lead to a nonanalytic term in the exciton spectrum. In the case of an isolated exciton band, the spectrum for small values of k has the form

$$\epsilon(\mathbf{k}) = \frac{k^2}{2m} + \delta\cos^2\theta \tag{1a}$$

or

$$\epsilon(\mathbf{k}) = \frac{k^2}{2m} + \delta\sin^2\theta , \tag{1b}$$

where θ is the angle between the wave vector $\mathbf{k}$ and the symmetry axis z. The first equation is valid for a band in which the dipole moment of the transition, $\mathbf{P}$, is polarized along the z axis (i.e., $\mathbf{P}\|z$) and the second equation is valid for $\mathbf{P}\perp z$. Here m is the effective mass, and δ is the magnitude of longitudinal-transverse splitting.

The nonanalytic second term in Eqs. (1a) and (1b) leads to an effective increase in the dimension of space.[2,3] Rashba[4] showed that this property of the spectrum changes the frequency dependence of the impurity absorption in the Rashba effect. In the present letter we show that the spectral dependence of the absorption tails can be changed and the Urbach rule for disordered semiconductors can be satisfied by effectively increasing the dimension of space.

Let us consider a solid solution with allowance for fluctuations in the concentration n. We will analyze the Gaussian fluctuations, whose probability $W[n]$ is

$$W[n] \propto \exp\left[-\int \frac{n^2 d^3r}{2n_0 x(1-x)}\right], \tag{2}$$

where x is the index of the composition of the solid solution, and n_0 is the total concentration of the atoms.

To calculate the state-density tail, we will use the maximum-fluctuation method.[5–7] We can then write the Schrödinger equation for the Frenkel exciton with spectrum (1a)

$$-\frac{\Delta\Psi}{2m} + \delta\partial_{zz}W - \frac{\alpha n(\mathbf{r})}{n_0}\Psi = -E\Psi , \tag{3}$$

where $\Delta W = \Psi$, and

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$$n(r) = \beta\alpha x(1-x)\Psi^2 \equiv \frac{n_0\gamma}{\alpha}\Psi^2,$$

where $\alpha = dE_g/dx$, E_g is the width of the energy gap of the solid solution, and $\beta = \beta(E)$ is the Lagrangian multiplier.

We make the replacement of variables $\Psi \rightarrow Bp^{1/2}\Psi, W \rightarrow B^{-1}p^{1/2}W, E = (B^2/2m)\epsilon, \rho \rightarrow B\rho$, where ρ is the polar radius, and $z \rightarrow pz$, where $B = (\delta/2m\gamma^2)^{1/4}$, and $2p = 1/m\gamma$. We replace (3) with

$$-(\Delta_2\Psi + \mu\partial_{zz}\Psi) + \partial_{zz}W - \Psi^3 = -\epsilon\Psi, \tag{4}$$

where $\Delta_2 W + \mu[(\partial^2 W/\partial z^2)] = \Psi$, and

$$\mu = 1/\gamma(2m)^{3/2}\delta^{1/2} \tag{5}$$

is the small parameter of the theory. (We will show below that this parameter is $\mu \propto [\ln(4\delta/E)]^{-1}$.) We calculate $\epsilon = \epsilon(\mu)$ and then find from it $\beta = \beta(E)$. The use of virial theorem shows that at $\mu = 0$ we have $\epsilon = 0$. We must therefore use here the method of two-scale division.[8] In the k representation for $k_\rho, k_z \ll 1$ the solution of (4) is

$$\Psi = C_1[\epsilon + k_\rho^2 + \mu k_z^2 + k_z^2/(k_\rho^2 + \mu k_z^2)]^{-1}, \tag{6}$$

where C_1 is determined from the condition of the normalizability of Ψ:

$$C_1 = [16\pi \ln^{-1}(4/(\epsilon\mu))]^{1/2}.$$

On the other hand, since ϵ is small in the parameter μ, for $k_z \gg \mu$ and $k_\rho \gg \mu^{1/2}$ the wave function Ψ must satisfy the equation

$$-\Delta_2\Psi - \mu\partial_{zz}\Psi + \partial_{zz}W - \Psi^3 = 0, \tag{7}$$

$$\Delta_2 W + \mu\partial_{zz}W = \Psi.$$

The solution of this equation

$$\Psi(\mathbf{k}) = \int \Psi^3(\mathbf{r})e^{i\mathbf{kr}}d^3r[k_\rho^2 + \mu k_z^2 + k_z^2/(k_\rho^2 + \mu k_z^2)]^{-1} \tag{8}$$

is matched with (6) in the region $\mu \ll k_z \ll 1$, $\mu^{1/2} \ll k_\rho \ll 1$. The matching condition is

$$\int \Psi^3(\mathbf{r})d^3r = [16\pi/\ln(4/\mu\epsilon)]^{1/2}. \tag{9}$$

Eliminating μ from (9), we find instead of (9)

$$C_3\mu^{1/2} = [16\pi/\ln(4/\mu\epsilon)]^{1/2}, \tag{10}$$

where $C_3 = \int\varphi^3(\mathbf{r})d^3(r)$, and $\varphi(\mathbf{r})$ satisfies the dimensionless equation

$$-\Delta\varphi + \partial_{zz}\Phi - \varphi^3 = 0, \tag{11}$$

$$\Delta\Phi = \varphi.$$

From (9) we find ϵ

$$\epsilon = \frac{4}{\mu} \exp\left(-\frac{16\pi}{\mu C_3^2}\right). \tag{12}$$

From (5) and (12) we find $\beta = \beta(E)$, which must be substituted into the general expression for the state-density tail $\rho(E)$ (see Ref. 9, for example). We finally find

$$\rho(E) \propto \exp\left[-\frac{\delta^{1/2} n_0}{\alpha^2 x(1-x)(2m)^{3/2}}\left(\frac{C_4}{2} + \frac{C_3^2}{16\pi}\frac{E}{\delta}\ln\left(\frac{4\delta}{E}\right)\right)\right], \tag{13}$$

where $C_4 = 33.48$, and $C_3 = 40.37$.

A similar analysis of the exciton that corresponds to spectrum (1b) gives rise to maximum-fluctuation equations

$$-\partial_{zz}\Psi - \lambda\Delta_2\Psi + \Delta_2 W - \Psi^3 = -\epsilon\Psi, \tag{14}$$

$$\partial_{zz} W + \lambda\Delta_2 W = \Psi,$$

where λ is a small parameter. At $\lambda = 0$ Eq. (14) has no solutions with $\epsilon > 0$ (Ref. 10).

The method of two-scale division cannot be used here, since the normalizing integral sits on the small scale. There is a critical value $\lambda = \lambda_c$ such that $E(\lambda_c) = 0$. For $\lambda < \lambda_c$ Eq. (14) has no solutions. For $\lambda \gg \lambda_c$ near λ_c the energy $\epsilon \propto (\lambda - \lambda_c)^2$, just as the energy of a weakly coupled state. The value of λ_c is determined from the solution of Eq. (14) with $\epsilon = 0$. Solving this equation and substituting λ_c into the general expression for $\rho(E)$ (Ref. 9), we find that the state density in the tail is

$$\rho(E) \propto \exp\left[-\frac{\delta^{1/2} n_0}{\alpha^2 x(1-x)(2m)^{3/2}}\left(\frac{C_4}{2} + \frac{30E}{\delta}\right)\right], \tag{15}$$

where $C_4 \approx 18.4$.

The exciton-absorption coefficient $k(\epsilon)$ is determined by Eqs. (13) and (15): $k(\epsilon) \propto \rho(\epsilon)$. If the singularity in the spectrum is ignored, we find the usual dependence[5-7] $\rho(\epsilon) \propto \exp(-\epsilon/\epsilon_0)^{1/2}$.

We should point out that at low photon energy deficit, Δ, the polariton effects are important. In this case the scales of the maximum fluctuations are comparable to the wavelength of light L. Equations (13) and (15) can therefore be used for $\Delta \gg 1/mL^2$.

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