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ON THE THEORY OF ABSORPTION EDGES IN AMORPHOUS SOLIDS

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Относительно теории края поглощения в аморфных телах

Дан вывод "однородного микрополевого представления" Редфильда для коэффициента поглощения аморфными телами с гауссовым случайным потенциалом и гауссовыми корреляционными функциями.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Дубна 1975

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On the Theory of Absorption Edges in Amorphous Solids

The derivation of Redfield's "uniform microfield representation" for absorption coefficient of amorphous solids with Gaussian random potential, Gaussian correlation function and large correlation lengths is presented. The exponential behaviour of the absorption edges in both cases with the inclusion of the Coulomb interaction (excitonic transitions) and neglecting that (interband transitions) has been found. The mean-square-root of the internal random electric fields $\bar{F} = \frac{c}{m/\mu\epsilon_0 a_0} \frac{0,86}{\Gamma}$ has been expressed in terms of experimental quantities.

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1. INTRODUCTION

The theory of the optical absorption edge proposed by Redfield /1, 2/ and by Dow and Redfield /3, 4/ results in the unified theory of Urbach's absorption edge. The theory bases on the assumption of the existence of random internal electric fields of various physical origin (phonons, impurities, defects, etc.), which can ionize excitons. The electric fields are supposed to be uniform in some macroscopic but sufficiently small ranges so that the absorption coefficient can be expressed as an average of the local absorption coefficients over all fields

$$\alpha(\omega) = \int \alpha(\omega, \vec{F})\, P(\vec{F})\, d\vec{F}. \qquad (1)$$

This formula is the principal assumption of Dow's and Redfield's theory. Proceeding from the results for absorption coefficient in homogeneous electric fields Dow and Redfield /5/ deduce Urbach's absorption edge in cases with Coulomb bound of the electron and the hole and Franz-Keldysh absorption edge in cases with the absence of this bound /3, 4/. In view of these theories Mott and Davis /6, 7/ suggest the possibility of explanation of Urbach's edges in amorphous semiconductors by the existence of internal random electric fields and they ask about the origin of these fields. Indeed, it has been shown by many authors (e.g., /8, 9/) that in spite of doubtless role of phonons in the interpretation of the Urbach's absorption edge at higher temperatures it persists at low temperatures as well with temperature independent slope but depending on the structure. The semiclassical theory of optical absorption by Bonch-Brujevich[10] and by Esser[11] including phonons, as well as the theory of absorption by Efros[12] lead to the approximately exponential absorption edge.

The theory proposed in this paper (the preliminary version is given in[13]) yields the derivation of the representation (1) of the absorption coefficient for the amorphous solid characterized by the Gaussian random potential with large correlation length L and with the Gaussian form of the correlation function. Sect. 2 is devoted to the derivation of the random field representation of the two-particle (electron-hole) density matrix. In Sect. 3 the exact derivation of formula (1) for the exciton absorption is presented and in Sect.4 the same for the interband absorption. Further, the absorption edges have been found for both cases and the mean-square-root of the internal fields has been estimated. The used formalism permits a simple inclusion of the Coulomb interaction, if the exciton radius ρ satisfies the relation $\rho < L - D_e$, $D_e = (\frac{2\hbar^2\beta}{m})^{1/2}$ is a diffusion length of the electron.This condition quarantees also the relative stability of the internal state of the exciton[14,16].Moreover, the center of mass is not influenced by the disorder in this case;it exhibits a free particle-like motion[16].The assumption quoted above limits the range of validity of the formula (1) for amorphous solid. The use of the effective mass approximation is also consistent with the supposal of the large correlation lengths, $L > 50\,\mathring{A}$ which is reasonable for number of cases.

2. *RANDOM ELECTRIC FIELD REPRESENTATION*

The absorption coefficient $\alpha(\omega) = \frac{4\pi}{cn} \mathrm{Re}\,\sigma(\omega)$ in amorphous solid with sufficiently large correlation length (in order to justify the effective mass approximation) can be written in the form

$$\mathrm{Re}\,\sigma_{\alpha\beta}(\omega) = \left(\frac{e}{2m}\right)^2 \frac{1}{\omega} \mathrm{Re} \int_0^\infty dt\, e^{i\omega t} \iint d\vec{x}\, d\vec{y} \times$$

$$\times \lim_{\substack{\vec{x}' \to \vec{x} \\ \vec{y}' \to \vec{y}}} (\sigma^*_{x_\alpha} + \sigma_{x'_\alpha})(\sigma_{y_\beta} + \sigma^*_{y'_\beta}) < R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t) > . \qquad (2)$$

Here $\sigma_{x_\alpha} = e^{i\vec{k}\cdot\vec{x}} P_\alpha$ and $<R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t)>$ is the averaged two-particle (electron-hole) density matrix. The last quantity can be expressed by means of the Feynman path integral formalism[16] as

$$<R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t)> = N \exp\left(-\frac{it}{h} E_g\right) \iint D\vec{r}_e(u)\, D\vec{r}_h(u) \times$$

$$\times \exp\left\{\frac{i}{h} \int_0^t \left(\frac{m^*_1}{2} \dot{\vec{r}}^2_e(u) + \frac{m^*_2}{2} \dot{\vec{r}}^2_h(u) + \frac{e^2}{\epsilon\, |\vec{r}_e(u) - \vec{r}_h(u)|}\right) du\right\} \times$$

$$\times < \exp\left\{-\frac{i}{h} \int_0^t du [\eta_1 V_1(\vec{r}_e(u)) + \eta_2 V_2(\vec{r}_h(u))]\right\} > . \qquad (3)$$

Under the assumption of a Gaussian distribution of a random potential $V(\vec{r})$, the correlation term is

$$< \exp\{\ \} > = \exp\left\{-\frac{\eta^2}{2\hbar^2} \int_0^t \int_0^t du' du'' [W(\vec{r}_e(u') - \vec{r}_e(u'')) +\right.$$

$$\left. + W(\vec{r}_h(u') - \vec{r}_h(u'')) \pm 2W(\vec{r}_e(u') - \vec{r}_h(u''))]\right\} . \qquad (4)$$

The sign in the last formula depends on whether the valence and conduction bands are parallely (–) ($\eta_1 = -\eta_2 = \eta$) or antiparallely (+) ($\eta_1 = \eta_2 = \eta$) fluctuating. Further, for large correlation lengths L the harmonic approximation of the Gaussian correlation function

$$W(\vec{r}' - \vec{r}'') = \exp\left(-\frac{(\vec{r}' - \vec{r}'')^2}{L^2}\right) \approx 1 - \frac{|\vec{r}' - \vec{r}''|^2}{L^2},$$

can be used in eq. (4). Due to the condition $|\vec{\rho}(u)| < L - D_e$ the electron-hole correlations $W(\vec{r}_e(u') - \vec{r}_h(u''))$ are important in the formula (4) as well[16]. Then, for the usual case of parallelly fluctuating bands, the correlation (4) turns out to be

$$< \exp\{\ \} > = \exp\left\{-\frac{\eta^2}{h^2 L^2} \sum_{i=1}^{3} \left(\int_0^t du\, \rho^{(j)}(u)\right)^2\right\}, \tag{5}$$

where $\vec{\rho} = \vec{r}_e - \vec{r}_h$.

By means of the transformation of the formula (5)

$$\int_{-\infty}^{\infty} \exp\left\{-\frac{q_j^2}{4} - iM_j q_j\right\} dq_j = 2\sqrt{\pi} \exp(-M_j^2), \quad j = 1, 2, 3, \tag{6}$$

with $M_j^2 = \frac{\eta^2}{h^2 L^2} \left(\int_0^t du\, \rho^{(j)}(u)\right)^2$, which has been introduced in[17] (see also[18]) we can go over to the "electric field representation" of the density matrix $< R^{(2)}_{e-h} >$

$$< R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t) > = \frac{1}{(2\sqrt{\pi})^3} \iiint_{-\infty}^{\infty} dq\, e^{-\frac{q^2}{4}} R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t, \vec{q}). \tag{7}$$

Here we have used the notation

$$R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t, \vec{q}) = N e^{-\frac{i}{h} t E_g} \iint D\vec{r}_e D\vec{r}_h \times \tag{8}$$

$$\times \exp\left\{\frac{i}{h} \int_0^t du \left[\frac{1}{2} m_1^* \dot{\vec{r}}_e^{\,2}(u) + \frac{1}{2} m_2^* \dot{\vec{r}}_h^{\,2}(u) + \frac{e^2}{\epsilon\, \rho(u)} + e\vec{F}(q) \cdot \vec{\rho}(u)\right]\right\}.$$

The electric field $\vec{F}(q)$ occuring in the probability density of the density matrix $R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', t, \vec{q})$ represents a random function introduced by Barta[17]

$$\vec{F}(q) = \frac{\eta}{eL} \vec{q}, \tag{9}$$

with the Gaussian distribution

$$P(q) = \frac{1}{(2\sqrt{\pi})^3} e^{-\frac{q^2}{4}} = \frac{1}{(2\sqrt{\pi})^3} e^{-\frac{3}{2} \frac{F^2}{\bar{F}^2}},$$

where

$$\bar{F} \equiv \sqrt{< F^2 >} = \frac{\eta}{eL} \sqrt{6}, \tag{10}$$

is a mean-square-root of the electric field $\vec{F}(q)$. In what follows we shall distinguish two cases:

1. The exciton absorption which realizes by the inclusion of the Coulomb term in (8).
2. Interband absorption.

3. THE EXCITON ABSORPTION

The usual formula for the density matrix

$$R(\vec{\rho}, \vec{\rho}', t, \vec{q}) = \sum_i \Phi_i(\vec{\rho}, \vec{q})\, \Phi_i^*(\vec{\rho}', \vec{q})\, e^{-\frac{i}{h} E_i(q)\, t}, \tag{11}$$

together with the formula (8) introduces the local dynamics of the internal exciton motion. Evidently, eqs. (8) and (11) imply the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \Lambda_\rho - \frac{e^2}{\epsilon\, \rho} - e\vec{F}(\vec{q}) \cdot \vec{\rho}\right) \cdot \Phi_i^{exc}(\vec{q}) = E_i^{exc}(\vec{q}) \cdot \Phi_i^{exc}(\vec{q}). \tag{12}$$

Inserting the equation

$$< R^{(2)}_{e-h}(\vec{x}, \vec{x}', \vec{y}, \vec{y}', \vec{t}) > = e^{-\frac{i}{h} F_i t}\, R(\vec{R}, \vec{R}', t) \times$$

$$\times \frac{1}{(2\sqrt{\pi})^3} \int_0^{\infty} e^{-\frac{q^2}{4}} 4\pi q^2\, dq\, R(\rho, \rho', q, t), \tag{13}$$

where

$$R(\vec{R}, \vec{R}', t) = \frac{1}{V} \sum_{\vec{k}} \exp\left[i\vec{k}(\vec{R} - \vec{R}') - \frac{it}{h} E(\vec{k})\right],$$

together with $R(\vec{\rho},\vec{\rho}\,',t,\vec{q})$ given by eq. (11) into eq. (2), we obtain for the absorption coefficient the formula

$$\alpha^{exc}(\omega)=\frac{1}{(2\sqrt{\pi})^3}\iiint_{-\infty}^{\infty}dq_1 dq_2 dq_3\, e^{-\frac{q^2}{4}}\alpha^{exc}(\omega,\vec{q}), \tag{14}$$

where

$$\alpha^{exc}(\omega,\vec{q})=\left(\frac{2\pi e}{m}\right)^2\frac{1}{\omega c n}\Sigma\,|\langle\Phi_{\vec{k}i}(\vec{q})\,|e^{i\vec{k}\cdot\vec{r}}\,\vec{\epsilon}\cdot\vec{p}|\,0\rangle|^2\times$$

$$\times\,\delta(h\omega-E_g-E_i^{exc}(q)),$$

or, in dipole approximation,

$$\alpha^{exc}(\omega,\vec{q})=\left(\frac{2\pi e}{m}\right)^2\frac{1}{\omega cn}|\langle v\vec{k}\,|\vec{\epsilon}\cdot\vec{p}|\,c\vec{k}_0\rangle|^2\times$$
$$\times\sum_i|\Phi_i(0,\vec{q})|^2\,\delta(\hbar\omega-E_g-E_i^{exc}(a)). \tag{15}$$

Here,

$$\Phi_{\vec{k}i}(\vec{R},\vec{\rho})=\frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{R}}\,\Phi_i(\vec{\rho},\vec{q}) \quad \text{and} \quad \Phi_i(\vec{\rho},\vec{q}),\,E_i^{exc}(\vec{q})$$

are the solutions of eq. (12).

Hence, the "local" absorption coefficient $\alpha^{exc}(\omega,\vec{q})$ has the same form as the absorption coefficient of a crystal in the external uniform electric field $F=\vec{F}(q)$. So the formula (14) is identical with the "uniform microfield approximation" by Dow and Redfield /4/ for the case of amorphous solid with Gaussian distribution of the random potential, Gaussian correlation function and large correlation lengths.

Using the results for the exciton absorption coefficient in external electric fields for large $\Delta=E_g-h\omega$ /5/ we have

$$\alpha^{exc}(\omega,\vec{q})=\left(\frac{2\pi e}{m}\right)^2\frac{1}{cn\omega}|\langle c\vec{k}_0|\vec{\epsilon}\cdot\vec{p}\,|v\vec{k}_0\rangle|^2\,e^{-\frac{c\Delta L}{\eta a q}}.$$

Then,

$$\alpha^{exc}(\omega)=\frac{\alpha}{2\sqrt{\pi}}\int_0^{\infty}dq\,q^2\,e^{-\frac{q^2}{4}-\frac{c\Delta L}{a\eta q}}$$

c is a constant, $a=\epsilon_0\frac{m}{\mu}a_0$ is a radius of the exciton. Numerical calculation of the last integral yields

$$\alpha^{exc}(\omega)\approx\alpha_0^{exc}\cdot\exp\left(-\frac{0{,}86\,c\Delta}{e\bar{F}a}\right)\equiv\alpha_0^{exc}\exp(-\Gamma\Delta). \tag{16}$$

The formula (16) expresses the following fact: The internal random electric field with the mean square root $\bar{F}$ has the same effect on the absorption in the edge range as has an external electric field $F_{ext}\approx\bar{F}/0{,}86\approx\eta/eL\cdot 2{,}85$ on the absorption edge of the respective crystal. The value of $\bar{F}$ can be estimated from the experimental values of Γ:

$$\bar{F}=\frac{c}{\frac{m}{\mu}\epsilon_0 a_0}\cdot\frac{0{,}86}{\Gamma}\,[\,V\ cm^{-1}\,]. \tag{17}$$

The value of c is determined by the dependence of the absorption on the external fields in crystals /5/, $c\approx 2$. For $\Gamma\approx 17\ (eV)^{-1}$ /7/, $\mu\approx m$ and $\epsilon_0\approx 10$ we obtain the value $\bar{F}\approx 1.7.10^6\ V\,cm^{-1}$ (The Esser's estimation /11/ gives the value $\bar{F}\approx 10^6\ V\,cm^{-1}$, too). This value takes place, e.g., for $L\approx(50\text{–}100)$ Å and $\eta\approx(0{,}5\text{–}1)$ *eV*.

4. INTERBAND ABSORPTION

If we neglect the Coulomb term in eq. (8), then the density matrix separates on the electron and the hole part. Using the same method as in Sect. 3, we obtain the "local" Schrödinger equations

$$\left(-\frac{\hbar^2}{2m_1^*}\Delta_x-e\vec{F}(q)\cdot\vec{x}\right)\Phi_i^{(e)}(\vec{q})=E_i(\vec{q})\cdot\Phi_i^{(e)}(\vec{q}),$$
$$\left(-\frac{\hbar^2}{2m_2^*}\Delta_y+e\vec{F}(\vec{q})\cdot\vec{y}\right)\Phi_j^{(h)}(\vec{q})=E_j(q)\cdot\Phi_j^{(h)}(\vec{q}). \tag{18}$$

For not too strong fields the interband matrix elements are exponentially small so that the solutions of eqs. (18) are Airy functions. For the absorption coefficient we obtain the formula (14) again, with the local absorption coefficient

$$a(\omega,\vec{q}) = \left(\frac{2\pi e}{m}\right)^2 \frac{1}{\omega c n} \sum_{i,j} |\langle\Phi_i^{(e)}(\vec{q})\,|\vec{\epsilon}\,\vec{p}|\Phi_j^{(e)}(\vec{q})\rangle|^2 \times$$

$$\times\,\delta(h\omega - E_g + E_i(\vec{q}) + |E_j(\vec{q})|)\,. \qquad (19)$$

The "local" absorption coefficient (19) is identical with the interband absorption coefficient of a crystal in an external electric field. Then, we can use the standard results for the Franz-Keldysh absorption given by the known formula[19]

$$a(\omega,\vec{q}) \approx \frac{f^{1/3}}{4\pi}\left(|A_i(z)|^2 - zA_i^2(z)\right) \approx$$

$$\approx \frac{f}{32\pi^2 E}\exp\left(-\frac{4}{3}E^{3/2}/f\right), \quad \text{for large } E.$$

Here is

$$f = \frac{eFa}{R},\quad E = \frac{\Delta}{R},\quad R = \frac{e^2}{2\epsilon_0 a_0},\quad Z = \frac{E}{f^{2/3}}.$$

Putting $\vec{F} = \frac{\eta}{eL}\vec{q}$, we have

$$a(\omega) \approx \frac{\eta a}{32\pi^2\Delta L}\cdot\frac{1}{2\sqrt{\pi}}\int_0^\infty dq\, q^3 \exp\left(-\frac{q^2}{4} - \frac{A}{q}\right), \qquad (20)$$

where

$$A = \frac{4}{3}\,\frac{LR}{\eta a}E^{3/2}.$$

The integral in eq. (20) can be calculated approximately by the saddle point method*. It yields

$$a(\omega) \approx \frac{E^{1/2}}{12\sqrt{3}\,\pi^2}\exp\left\{-2\left(\frac{3}{2\bar{f}}\right)^{2/3} E\right\}. \qquad (21)$$

Here

$$\bar{f} = \frac{\eta a}{LR}\sqrt{6}.$$

The formula (21) gives Urbach type of the absorption edge again. So the "statistical" Franz-Keldysh effect given by eqs. (1) and (19) results, after averaging, in exponential absorption edge.

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