ON THE RADIATIONLESS DECAY OF A DIRECT EXCITON IN AN INDIRECT GAP SEMICONDUCTOR

The theory of a radiationless dissociation of exciton in a semiconductor with the indirect forbidden gap is developed. It is shown that in GaAs, GaP and Ge under a pressure the main mechanism of exciton decay is the short-wave phonon-assisted scattering inside the conduction band.

Key words: semiconductors, exciton, electron-phonon interaction, density functional method.

1. Introduction

In several optical experiments the discrete levels of a direct exciton in the diamond and zincblende structure semiconductors are observed at the background of the uniform spectrum of single-electronic states [1–3]. In these cases they turn out to be resonance levels with finite lifetimes and hence the radiationless dissociation of a direct exciton becomes possible. This is just a case of direct exciton in the indirect band gap semiconductor GaP [1]. In the direct band gap GaAs the lifetime of direct exciton sharply decreases under the external uniform pressure where GaAs became the indirect one [2]. In indirect Ge the lifetime of direct exciton strongly depends on the external uniform pressure [3]. The decay mechanism of exciton’s state in all these cases is invoked by emission or absorption of short-wave phonons with large wave-vectors close to the crystal Brillouine zone edges.

A theory of exciton-phonon interaction is developed in the book [4] but it concerns to the long-wave phonons only. We present here a generalization of this theory [4] for the case of the exciton interaction with short-wave phonons.

2. General theory of the radiationless exciton decay

A multi-particle wave function of a free non-interacting electron-hole pair according to [4] can be written as an antisymmetrized product of single-particle states [4]

\[ \Phi_{cv}^{σ'}(k_h, k_e, \{ξ\}) = \hat{A}_c k_{σ} (ξ_1) \psi_{k_{α}}(ξ_2) \psi_{k_{β}}(ξ_3) \psi_{k_{σ}}(ξ_4) \cdots \]

Here one of the valence electron from a single-electron state \( \psi_{k_{σ}}(ξ_{n}) \) with a wave-vector \( k_{σ} \) and spin \( σ \) is removed from a multi-particle crystal ground state and instead one in a conduction state \( \psi_{k_{σ'}}(ξ_{m}) \) is added with a wave-vector \( k_{σ'} \) and spin \( σ' \). Here \( ξ = (r, s) \); \( \psi_{λk}(ξ_n) = \varphi_{λk}(r) χ_σ(s) \) are the single-electronic Bloch states. Band index \( λ \) has values \((c,v)\) for conduction and valence bands correspondingly; \( s \) is a spin variable; a spin projection \( σ \) has two possible values \( α \) and \( β \). The operator \( \hat{A} \) means antisymmetrization by arguments \( ξ_1, ξ_2, \ldots, ξ_n \). The removal of this valence electron is equivalent to the creation of a hole with the spin \((-σ)\) and a wave vector \((-k_{σ})\). Certainly due to the double occupation of energy levels in the multi-particle ground state the single electronic state \( \psi_{k_{σ'}}(ξ_{m}) \) is still occupied by another valence electron in the valence band with the same vector \( k_{σ} \) but with the opposite spin projection \((-σ)\).

Following to [4] let us introduce the basis of electron-hole excitations in the “excitonic” representation:

\[ \Theta_{cv}^{σ'}(K, R_L, \{ξ\}) = \frac{1}{\sqrt{N}} \sum_{k} e^{-iK \cdot r} \Phi_{cv}^{σ'}(k - K, k, \{ξ\}). \]

Here \( K \) is the wave vector of the electron-hole couple as a whole. The center of gravity of the couple is placed into the lattice vector \( R_L \). By definition \( k_{σ} = k - K \) and \( k_{σ} = k \) so \( K = k_{σ} - k_{σ} \). In what follows the indices \( c,v \) are omitted. In addition the electron-phonon interaction can not change a spin so \( σ = σ' \) and the spin indices also can be omitted.

The bounded \( i - \)th state of an exciton which moves with a quasi-momentum \( K \) can be presented as a decomposition onto the basis of the states of virtual electron-hole pairs:

\[ \Psi_{i}(K, \{ξ\}) = \sum_{R} U_{i}^{K}(R_L) \Theta(k_e - k_h, R_L, \{ξ\}) \delta_{K,k_{σ} - k_{σ}}. \]

The weights \( U_{i}^{K}(R_L) \) of virtual electron-hole pair \( \Theta(k_e - k_h, R_L, \{ξ\}) \) inside the bounded state can be found from the equation [4]

\[ \sum_{R} \left( \Phi(K, R_L) \right)^{\dagger} \hat{H}_0 \Phi(K, R_L) U_{i}^{K}(R_L) = E_{i}(K) U_{i}^{K}(R_L). \]

Here \( \hat{H}_0 \) is the multi-particle Hamiltonian of electron subsystem in the equilibrium lattice, \( E_{i}(K) \) is...
the energy of an exciton with a wave vector \( \mathbf{K} \). For the Wannier exciton the envelope approximation is justified and it is shown in [4] that

\[
U_{\text{nlm}}^{\mathbf{K}}(\mathbf{R}_L) = \exp(i - \frac{m_e}{m_c + m_h} \mathbf{K} \mathbf{R}_L) F_{\text{nlm}}(\mathbf{R}_L).
\]

The envelope function \( F_{\text{nlm}}(\mathbf{R}_L) \) is equal to the hydrogenic one \( \varphi_{\text{nlm}}(\rho) \) at lattice vectors

\[
F_{\text{nlm}}(\mathbf{R}_L) = \varphi_{\text{nlm}}(\rho_{\mathbf{L} \cdot \mathbf{R}_L}) = \frac{m_e}{m_c + m_h} \mathbf{K} \mathbf{R}_L.
\]

Here, \( \rho = (m_e \mathbf{r}_e + m_h \mathbf{r}_h)/(m_e + m_h) \); \( \mathbf{r}_e, \mathbf{r}_h \) are the coordinates of a conduction electron and a hole in the real space, \( m_e, m_h \) are their effective masses. For the energy of a bound state one has

\[
E_{\text{nlm}}(\mathbf{K}) = E_{\text{band}} + + \mu^{-1} - \frac{m_e^2 + m_h^2}{2(m_e + m_h)}
\]

Here \( \mu^{-1} = m_e^{-1} + m_h^{-1} \); \( e^2 / \epsilon_0 \); \( \epsilon_0 \) is a dielectric constant of a crystal, \( E_{\text{band}} \) is the sum of valence band energies, \(-\mu e^2/2n^2\hbar^2\) is the discrete energy levels of bounded exciton state. The last term is the kinetic energy. The normalization condition for the envelope is

\[
\int_{\mathbf{R}_L} \left| F_{\text{nlm}}(\mathbf{R}_L) \right|^2 d\mathbf{R}_L = 1.
\]

Next it is convenient to rewrite the multi-particle wave functions in the form [4]:

\[
\Psi_{s}^{\pm}(\mathbf{K}, \{\xi\}) = \sum_{\mathbf{R}_L} F_{\text{nlm}}(\mathbf{R}_L) \times \Phi(\mathbf{k} - \mathbf{K}, \mathbf{k}_s, \{\xi\})
\]

Here \( F_{\text{nlm}}(\mathbf{Q}) \) is the Fourier transformation of the envelope

\[
F_{\text{nlm}}(\mathbf{Q}) = \frac{1}{N} \sum_{\mathbf{R}_L} F_{\text{nlm}}(\mathbf{R}_L) e^{-i\mathbf{Q} \cdot \mathbf{R}_L}.
\]

The normalization condition for the envelope is reduced to

\[
\sum_{\mathbf{Q}, \mathbf{R}_L} \left| F_{\text{nlm}}(\mathbf{Q}) \right|^2 = 1.
\]

3. Exciton-phonon interaction in indirect gap band structure

For the Wannier exciton due to weak link between the electron and the hole one can treat their interaction with phonons independently. Hence the multi-particle operator of the electron-phonon interaction is:

\[
\Delta \hat{H} = \sum_{\mathbf{q}, \mathbf{k}_s} \hat{\omega}'(\mathbf{k}_s) \hat{\delta} \hat{h}_\mathbf{q}(\mathbf{r}_e) \times \Phi(\mathbf{k} - \mathbf{K}, \mathbf{k}_s, \{\xi\})
\]

Here \( \hat{\omega}'(\mathbf{k}_s) \) is a single-particle operator of interaction of phonon with the wave vector \( \mathbf{q} \) and the \( \mathbf{k}_s \) electron. We are looking for the dissociation that is for a decay of exciton to the uncoupled electron and hole pair. The initial state here is a ground \( s \)-state of exciton \( \Psi_{s}^{\pm}(\mathbf{K}, \{\xi\}) \) with its energy \( E_s(\mathbf{K}) \). The final state is uncoupled state of electron and hole with wave vectors \( \mathbf{k}_s' \) and \( \mathbf{k}_h' \) correspondingly. This last state is described by a pair wave function \( \Phi(\mathbf{k}_s', \mathbf{k}_h, \{\xi\}) \). The energy of this state is \( E_{\text{free}} = E_{\text{band}} + E_{\text{e}}(\mathbf{k}_s') - E_{\text{e}}(\mathbf{k}_h') \pm \hbar \omega_\mathbf{q} \).

The energy conservation rule for the phonon-assisted dissociation should be written as:

\[
E_s(\mathbf{K}) = E_{\text{band}} + E_{\text{e}}(\mathbf{k}_s') - E_{\text{e}}(\mathbf{k}_h') \pm \hbar \omega_\mathbf{q}.
\]

Here \( \hbar \omega_\mathbf{q} \) is the phonon energy. The matrix element of the phonon-assisted transition from \( \Psi_{s}^{\pm}(\mathbf{K}, \{\xi\}) \) to \( \Phi(\mathbf{k}_s', \mathbf{k}_h', \{\xi\}) \) is:

\[
M(\mathbf{k}_s', \mathbf{k}_h', \mathbf{K}) = \int \Psi_{s}^{\pm}(\mathbf{K}, \{\xi\}) \times \Phi(\mathbf{k}_s', \mathbf{k}_h', \{\xi\}) d^2\xi.
\]

At absolute temperatures close to zero we can neglect the kinetic energy of exciton and take \( \mathbf{K} = 0 \). The calculation reduces to the calculation of the matrix elements between the virtual electron-hole (e - h) states \( \Phi(\mathbf{k}_s', \mathbf{k}_h', \{\xi\}) \) with “vertical” excitation \( \mathbf{k}_s = \mathbf{k}_h = \mathbf{k} \) which enters into the bounded states with a weight \( F_{\text{nlm}}(\mathbf{K}) \), and the final state of free pair \( \Phi(\mathbf{k}_s', \mathbf{k}_h', \{\xi\}) \). Keeping in mind that

\[
\int d^2\xi = \sum_{\mathbf{k}_s} \int d\mathbf{r}_k \int d\mathbf{r}_c \int d\mathbf{r}_v \int d\mathbf{r}_e,
\]

one gets after some algebra

\[
M(\mathbf{k}_s', \mathbf{k}_c', \mathbf{K}) = A_{\nu\nu}(\mathbf{k}_s, \mathbf{k}_c, \mathbf{K}) + A_{\nu\e}(\mathbf{k}_h, \mathbf{k}_e, \mathbf{K})
\]

Here

\[
A_{\nu\nu}(\mathbf{k}_s, \mathbf{k}_c, \mathbf{K}) = \delta_{\mathbf{k}_s, \mathbf{k}_c} \delta_{\mathbf{K}, \mathbf{q}} \times \Phi(\mathbf{k}_s, \mathbf{K}) \int \Psi_{\nu}(\mathbf{k}_s, \mathbf{q}) \Phi(\mathbf{k}_c, \mathbf{q}) d\mathbf{q}/A_{\nu\e}(\mathbf{k}_h, \mathbf{k}_e, \mathbf{K})
\]

is the matrix element of a transition with the emission of phonon with the wave vector \( \mathbf{q} \) between the virtual (e-h) pair with “vertical” excitation of electron having the quasi-momentum \( \mathbf{k}_h = \mathbf{k}_e = \mathbf{k} \) and the uncoupled free electron with the wave vector \( \mathbf{k}_e' = \mathbf{k} \) and the
hole with $k'_h = \pm k \pm q$. For a Wannier exciton the weight $F_s(k)$ is a delta-shaped function and so the lengths of $k$ and $k$ are restricted by values $|k| < 2\pi / a$. It is easy to find by inspection (Fig. 1) that the configurations of a valence band in the indirect semiconductors do not give an opportunity to find a wave vector $k'_{v}$ in order to satisfy both energy and momentum conservation rules. So $(h-h)$ scattering inside a valence band is impossible in this configuration.

A second term

$$A_s(k_h, k'_v, K) = \delta_{k_h, k} \delta_{k, k + q} \times$$

$$\times F_s(k_h) \int \psi_{k_h}^*(r) \delta\hat{h}_{r+q} \psi_k(r) dr$$

is a matrix element of transition assisted by phonon with a wave vector $q$ between a virtual “vertically” excited ($e-h$) couple and a free hole with $k'_h = k$ and conduction electron with a wave vector $k'_v = k \pm q$. In the indirect semiconductor this process appears to be possible (Fig. 1) and it involves a shortwave phonon. Consequently the total probability includes only the scattering inside the conduction band and it is assisted by shortwave phonons. Phonon energies $\hbar \omega_q$, exciton’s levels and its kinetic energy are small in comparison with a forbidden gap. Neglecting them one gets a energy conservation condition in the form $\varepsilon_e(k'_v) - \varepsilon_e(k'_h) = E_G$. The total probability is written as:

$$W = \sum_q \left| F_s(k) \right|^2 \int \left| \psi_{k+q}^*(r) \delta\hat{h}_{q} \psi_k(r) \right|^2 dr \times$$

$$\times \delta(\varepsilon_e(k+q) - \varepsilon_e(k) - E_G).$$

Let us use the integral mean value theorem, then

$$W = \left( \sum_k \left| F_s(k) \right|^2 \right) \times$$

$$\times \sum_q \left|\int \psi_{k+q}^*(r) \delta\hat{h}_{q} \psi_k(r) dr \right|^2 \times$$

$$\times \delta(\varepsilon_e(k+q) - \varepsilon_e(k) - E_G).$$

Due to the delta shape of $F_s(k)$ the mean value $K$ is close to zero. Keeping in mind $\sum_k \left| F_s(k) \right|^2 = 1$ and using the Fermi golden rule one gets the probability per second of the exciton dissociation

$$W = \sum_q \left|\int \psi_{k+q}^*(r) \delta\hat{h}_{q} \psi_k(r) dr \right|^2 \times$$

$$\times \delta(\varepsilon_e(k+q) - \varepsilon_e(k)).$$

Here $\Gamma$ means that the states belong to the center of a Brillouin zone and it is used that energy in $\Gamma$-point of a conduction band is $\varepsilon_{c, \Gamma} = \varepsilon_{e, \Gamma} + E_G$.

**4. Results and conclusion**

The last expression means that the problem of the calculation of the decay probability of a direct exciton in the indirect gap material reduces to the calculation of the “horizontal” short-wave phonon-assisted transition from a single-electronic Bloch state in the centre of a Brillouin zone into aside minima (Fig.1). This theory was applied in [5, 6] to calculate the exciton decay in GaP and GaAs. Electron and phonon spectra were calculated in the density functional perturbation theory [7]. According this our calculation the linewidth of exciton in GaP is 9.2 meV in a reasonable agreement with experimental values 16 meV [2] and 12 meV [8]. The calculated life time of direct exciton in GaAs $\tau = 1.5 \pm 0.2$ ps [5, 6] also is in a good agreement with experimental 1.4 ps [9], 2.0±0.5 ps [10]. The calculated pressure dependence [11] of exciton lifetimes and the width of exciton spectral lines in Ge under the external pressure also agree satisfactorily with an existing experiment [3]. We believe, that the method developed in [5, 6, 11] for the calculating of electron-phonon scattering probabilities can be useful in the investigation of relaxation of highly excited electrons [12] and the problem of high-temperature superconductivity [13].
References


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