Theoretical treatment of the processes involving the dipole transitions to the lowest exciton states in hexagonal semiconductors

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Abstract. The treatment of the two-photon transitions to the $A_{n=1}$ exciton level and the resonant Raman scattering of light by LO-phonons is given for the hexagonal semiconductors $A_2B_6$, taking into account the influence of the complex top valence band and anisotropy of the exciton effective mass.

1. Introduction
In the semiconductor crystals of the wurtzite structure the top valence band is known to be split into three closely-lying subbands. The transitions from them to the lowest conduction band lead to the excitonic hydrogen-like series A, B and C in the absorption spectra [1,2]. And the energy difference between the upper subbands is less than the exciton Rydberg for some crystals [2]. Taking into account the influence of anisotropy and the complicated structure of the top valence band by the perturbation theory, for the hexagonal semiconductors $A_2B_6$ the wave functions and the energies in a first approximation were reported to be obtained for the $A_{n=1}$ and $B_{n=1}$ excitonic levels under assumption of the zero wave vector of an exciton [3]. In this work the first order corrections to the energy and the wave functions of the $A_{n=1}$ exciton level with the small nonzero wave vector $K$ were derived. Taking them into account, the treatment of the two-photon dipole transitions to the $A_{n=1}$ level and the resonant Raman scattering of light by LO-phonons is given for the hexagonal semiconductors $A_2B_6$.

2. Theoretical model
The exciton with the wave vector $K$ is assumed to be formed by an electron with the degenerate conduction band $c$ and by a hole from the degenerate (or almost generate) valence band $v$ [4,5]. The pertinent wave functions of the relative electron-hole motion $\Phi_{j_e,j_h}^\varepsilon(r;K)$ are supposed to satisfy the system of equations of the effective mass approximation (EMA) [4-6]. Here and henceforth the indices $j_e$ and $j_h$ denote the states in the conduction band $c$ and the valence band $v$, respectively. In the case of the hexagonal semiconductors $A_2B_6$ one can introduce the wave function $\tilde{\chi}_{j,j}^{(1)}(r)$ for which the system of the EMA equations is reduced to the form [5]
\[
\left[ \frac{1}{2\mu_{\perp,j_h}} \left( \hat{p}_x^2 + \hat{p}_y^2 \right) + \frac{1}{2\mu_{\parallel,j_h}} \hat{p}_z^2 + U_{\alpha}(r) \right] \tilde{z}^{(\alpha)}_{j_{\perp},j_{\parallel}}(r) + \sum_K \left( \delta_{j_{\perp},j_{\parallel}} - 1 \right) \tilde{V}_{j_{\perp},j_{\parallel}}(r) \tilde{z}^{(\alpha)}_{j_{\perp},j_{\parallel}}(r) = \left( E_j(K) - \varepsilon_{j_{\perp},j_{\parallel}}(K) \right) \tilde{z}^{(\alpha)}_{j_{\perp},j_{\parallel}}(r)
\]

where \( \hat{p}_a = -i\hbar d/dr_a \), \( (m_{j_{\perp}})^{-1} + (m_{j_{\parallel}})^{-1} \), \( m_{j_{\perp}} \) and \( m_{j_{\parallel}} \) are the effective masses of an electron and a hole, \( U_{\alpha}(r) \) is the Coulomb energy of the electron-hole interaction, \( E_j(K) \) is the exciton level energy, \( \varepsilon_{j_{\perp},j_{\parallel}}(K) \) has the form

\[
\varepsilon_{j_{\perp},j_{\parallel}}(K) = \varepsilon_{j_{\perp},j_{\parallel}} + \frac{\hbar^2 (K_{\parallel}^2 + K_{\perp}^2)}{2(m_{j_{\perp}}^2 + m_{j_{\parallel}}^2)} + \frac{\hbar^2 K_{\perp}^2}{2(m_{j_{\perp}}^2 + m_{j_{\parallel}}^2)}
\]

where \( \varepsilon_{j_{\perp},j_{\parallel}} \) is the energy gap. Here it is assumed that \( Ka \) is considerably smaller than unit where \( a \) is the exciton radius. The operator \( \tilde{V}_{j_{\perp},j_{\parallel}} \) is given by

\[
\tilde{V}_{j_{\perp},j_{\parallel}} = D^{\parallel\alpha}_{j_{\perp},j_{\parallel}} \left( \hat{p}_a - hK_a \frac{m_{j_{\perp}}^{\alpha\alpha} + m_{j_{\parallel}}^{\alpha\alpha}}{m_{j_{\perp}}^{\alpha\alpha} + m_{j_{\parallel}}^{\alpha\alpha}} \right) \left( \hat{p}_\mu - hK_{\mu} \frac{m_{j_{\perp}}^{\beta\mu} + m_{j_{\parallel}}^{\beta\mu}}{m_{j_{\perp}}^{\beta\mu} + m_{j_{\parallel}}^{\beta\mu}} \right)
\]

where \( D^{\parallel\alpha}_{j_{\perp},j_{\parallel}} \) are the effective mass parameters [4]. For the wurtzite crystals the nonzero parameters \( D^{\parallel\alpha}_{j_{\perp},j_{\parallel}} \) can be found due to the known zone structure and the symmetry selection rules. Neglect of the coupling between the subbands (\( \tilde{V}_{j_{\perp},j_{\parallel}} = 0 \)) and the influence of anisotropy can reduce the equation (1) to the hydrogen-like equation for which the wave functions \( \chi_{j_{\perp},j_{\parallel}}^{(\xi\eta\mu)}(r) \) are known [7]. Here \( (\xi\eta\mu) \) is the proper set of quantum numbers for the relative electron-hole motion.

Taking into account the terms associating the equations for the different subbands (\( \tilde{V}_{j_{\perp},j_{\parallel}} \cdot j_{\perp} \neq j_{\parallel} \)) and anisotropy of the excitonic effective mass \( m_{j_{\perp},j_{\parallel}} \) by the perturbation theory, the wave functions and the energies in a first approximation were obtained for the \( A_{n-1} \) exciton level. The first order corrections to the energy are independent on the wave vector \( K \) and lead to the level shift.

The obtained first order corrections to the wave functions \( \sum_{\xi,\eta,\mu} \chi_{j_{\perp},j_{\parallel}}^{(\xi\eta\mu)}(r) \) involve some nonzero coefficients \( b_{j_{\perp},j_{\parallel}}^{(\xi\eta\mu)} \), as distinct from the case \( K=0 \). This can in particular lead to the added sequences of the intermediate exciton states in the processes of the two-photon absorption and the Raman scattering (RS). The expressions for the nonzero coefficients \( b_{j_{\perp},j_{\parallel}}^{(\xi\eta\mu)} \) are too cumbersome and are not presented here.

3. Results and discussion

It is well known that the two-photon dipole transition to the exciton state of the \( s \)-type can be described within the framework of the two-band as well as three-band model [8,9]. In the first case absorption of a photon is accompanied by the weakly-forbidden dipole transition from the ground state to an exciton of the \( p \)-type, then the intraband dipole transition to the \( s \)-exciton occurs when another photon is absorbed. The sequence of the intermediate excitonic states \( p-s \) corresponds to this process. In accordance with the three-band model the intermediate states are assumed to be the \( s \)-excitons belonging to the some higher-lying conduction band and the top valence band or to the lowest conduction band and the deeper-lying valence band. However the inclusion of the first order corrections to the exciton wave functions can lead to the added two-photon transition mechanism which is described by following sequence of processes: the allowed dipole transition to the \( s \)-exciton of the \( B \) or \( C \) series and the dipole transition to the \( A_{n-1} \) level. Thus this process is described within the framework of the two-band model and includes the allowed dipole transitions. Moreover the
contributions of the two-band and three-band models are opposite in sign [8,10]. In consequence of this, it was possible to assume that the role of this process can be non-negligible.

In order to compare the added mechanism with the others, the two-photon transition to the A_{n-1} level was considered for the two monochromatic light beams incident on a CdS crystal. The first beam with the frequency \( \omega_1 \) and polarization \( \mathbf{e}_1 \parallel z \) propagates along the x axis and the second one with \( \omega_2 \) and \( \mathbf{e}_2 \parallel x \) travels along the z axis. The frequencies \( \omega_1 \) and \( \omega_2 \) are assumed be such that their sum \( \omega_1 + \omega_2 \) lies in the region of resonance with the A_{n-1} level. Consideration of the two-photon transitions was carried out for the near frequencies \( \omega_1 \) and \( \omega_2 \). In the case of the unperturbed wave functions under simultaneous absorption of the two photons \( h\omega_1 \) and \( h\omega_2 \) the transition is allowed to the exciton state of the symmetry \( \Gamma_5 \) and is described within the framework of the two-band and three-band models. Rough estimations performed have shown that the contribution of the three band model dominates. In this work comparison between the two-photon transition process, which is due to the first order corrections to the exciton wave functions, and the mechanism described by the sequence of the intermediate excitonic states p-s of the A series was performed. The terms including the transitions between the nearest bands were assumed to give the main contribution to the parameters \( D_{p}^{0} \). The estimation of the parameter of the weakly-forbidden transition \( M_{p} \), from Ref. [11] and the data on the effective masses of an electron and a hole from Ref. [12] were used. The computations were performed for the following values of the exciton Rydberg and the energy gap of the A, B and C series: \( R_A = R_B = 0.028 \) eV, \( R_C = 0.026 \) eV [1], \( E_{cv}^{A} = 2.578 \) eV, \( E_{cv}^{B} = 2.593 \) eV, \( E_{cv}^{C} = 2.656 \) eV [12]. Thus the rough estimates obtained for CdS have shown that the contribution of the added process is considerably less than the one of the sequence p-s.

The treatment of the Raman scattering of light by LO-phonons under excitation near the A_{n-1} exciton level is of interest too. The sequences of the intermediate excitonic states, s-p and s-s, are known to give a main contribution to the resonant RS [11,13]. In the first case, the intraband Frohlich exciton-lattice interaction is considered in the approximation of the zero wave vector of a phonon \( \mathbf{q}=0 \), but the scattering process includes the weakly-forbidden dipole transitions. The RS mechanism described by the sequence s-s is caused by the forbidden \( q \)-dependent Frohlich interaction [13].

If the first order corrections to the exciton wave functions are taken into account, the added scattering process, which is induced by the \( q \)-independent Frohlich interaction \( \mathbf{q}=0 \) and comprises only the allowed dipole transitions, can participate in the RS. Its contribution in the scattering cross section was compared with the one of the sequence of the intermediate states s-s for a CdS crystal. For this purpose the frequency dependences of the RS cross section \( d\sigma/d\Omega \) were computed for the

![Figure 1](image-url)  
*Figure 1*. The RS cross section calculated for the scattering mechanism including the dipole transition to the A_{n-1} exciton level in a CdS crystal as a function of the energy of incident photons. The curve \( d\sigma/d\Omega \) corresponding to the scattering geometry \( y(xy)x \) is multiplied by the factor of 100.
scattering mechanism, which includes dipole transition to the $A_{n=1}$ exciton level and the indirect transition to the ground state and dominates in the considered resonant conditions. Calculations were carried out for the two scattering configurations $x(yy)x$ and $y(xy)x$. The results obtained for the lifetime broadening of the exciton level $\Gamma = 0.004$ eV [2] are presented in Fig. 1. In the back scattering configuration $x(yy)x$ the Raman scattering is described by the sequence of the intermediate states $s-s$. And in this case the cross section was calculated for the unperturbed wave functions. For the geometry $y(xy)x$ the resonant RS is only due to inclusion of the corrections to the exciton wave functions because the sequences of the intermediate states $s-s$ and $s-p$ do not participate in it. Owing to this the frequency dependence of $d\sigma/d\Omega$ was computed for the added scattering process described above. As can be seen from Fig. 1 the RS cross section calculated with due regard for the first order corrections is considerably less than the one obtained for the $s-s$ sequence.

4. Conclusion
Taking into account the influence of the complex top valence band and anisotropy of the exciton effective mass by the perturbation theory, the wave functions and the energies in the first approximation were derived for the $A_{n=1}$ exciton level with the nonzero wave vector. The two-photon dipole transitions to the $A_{n=1}$ exciton level and the resonant Raman scattering of light by LO-phonons were considered. The inclusion of the first-order corrections to the wave functions was found to lead to the added sequences of the intermediate states in these processes. Rough estimations obtained for a CdS crystal have shown that their contributions are considerably less than the ones which were calculated for the unperturbed wave functions.

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