Theoretical investigation of the hyper-Raman scattering in hexagonal semiconductors under two-photon excitation near resonance with the $A_{n=2}$ exciton level

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Abstract. The hyper-Raman scattering of light by LO-phonons under two-photon excitation near resonance with the $A_{n=2}$ exciton level in the wurtzite semiconductors $A_2B_6$ was theoretically investigated, taking into account the influence of the complex structure of the top valence band.

1. Introduction

The experimental investigations of the hyper-Raman scattering (HRS) of light in the conditions of proximity of the doubled energy of incident photons to the band gap $E_{cv}$ in the semiconductors $A_2B_6$ were reported in a number of publications [1-4]. The HRS features observed were explained within the framework of the excitonic model where the hydrogen-like Wannier excitons are considered as intermediate virtual states of an electronic system [5-6]. In accordance with this model the main contribution to the HRS of light by LO-phonons is given by the sequence of intermediate virtual excitonic states, $s-p-s$. The hyper-Raman process appropriate to it is induced by the intraband Frohlich exciton-lattice interaction and is described within the framework of the two-band model. And its contribution depends on the scattering geometry.

The goal of this work is theoretical investigation of the resonant HRS of light by LO-phonons in the hexagonal crystals $A_2B_6$ in which the top valence band is split into three closely-lying subbands [7-8]. Consequently, the dipole transitions between the excitons related to the same subband as well as the different ones can participate in the hyper-Raman process. Besides, of special interest is the HRS under two-photon excitation near the $A_{n=2}$ level if the influence of the complex structure of the top valence band on it is taken into account by the use of the perturbation theory.

2. Basic formulas

When the doubled frequency of exciting radiation is close to the fundamental absorption edge of a semiconductor, the hyper-Raman scattering is described by the following sequence of processes: absorption of two incident photons with the wave vector $q_L$, energy $h\omega_L$ and polarization $\varepsilon_L$, a creation of a phonon with the wave vector $q$ and energy $h\omega_p$ and an emission of a photon of scattered light ($q_S$, $h\omega_S$, $\varepsilon_S$) [5,6]. In the initial and final states an electron system of a crystal is assumed to be in the ground state $|\Psi_0\rangle$, but its intermediate virtual states are the Wannier excitons formed by the...
transition of an electron from the degenerate (or almost degenerate) valence band $\nu$ to the excitonic level $E_{\nu}(K)$ near the conduction band $c$ [9]

$$
|\Psi_{A}(K)\rangle = \sum_{j_{c}, j_{v}} \int \, dK' A_{\nu}^{(j)}(k; K) \hat{\psi}_{j_{c}}^{\dagger}(k) \hat{\psi}_{j_{v}}(k - K) |\Psi_{0}\rangle
$$

(1)

where $K$ is the exciton wave vector, $\hat{\psi}_{j_{c}}^{\dagger}(k)$ and $\hat{\psi}_{j_{v}}(k)$ are the operators of creation and annihilation of an electron with the wave vector $k$ in the $n$ band, the indices $j_{c}$ and $j_{v}$ denote the states in the valence band $\nu$ and the conduction band $c$, $s_{c}$ and $s_{v}$ are their degeneracy multiplicities.

Because the wave vectors of the photons and the phonons ($q_{p} = 2q_{L} - q_{s}$), which participate in the HRS, are small, the scattering process is assumed to occur in the Brillouin zone center ($K = 0$).

The cross section of the resonant hyper-Raman scattering can be written as [6]

$$
\frac{d\sigma}{d\Omega} = \frac{2\pi e^{2} n_{0} \omega_{s}^{2} (N_{p} + 1)V N_{L}}{m^{4} c^{4} \omega_{s}^{4} n_{L}^{2}} |B|^{2}
$$

(2)

where $e$ and $m$ are the charge and the mass of an electron, $c$ is the light speed, $n_{L(8)}$ is the refractive index for the frequency $\omega_{L(8)}$, $V$ is the crystal volume, $N_{L}$ is the density of exciting radiation, $N_{p}$ is the a number of phonons, $B$ has a form

$$
B = e_{\alpha}^{(L)} e_{\beta}^{(L)} \sum_{A_{\alpha}, A_{\beta}} \frac{P^{\alpha}_{A_{\alpha}, A_{\beta}} P^{\beta}_{A_{\beta}, A_{\alpha}}}{E_{A_{\alpha}} - \hbar \omega_{s}^{(L)}} \frac{E_{A_{\beta}} - 2\hbar \omega_{s}^{(L)}}{(E_{A_{\alpha}} - \hbar \omega_{s}^{(L)})}
$$

(3)

Here the sum runs over all intermediate virtual exciton states $A = (c, v, \lambda)$.

In this paper the hyper-Raman scattering of light is considered within the framework of the two-band model, and only the dipole-allowed transitions between excitonic states are taken into account. Because of this, the matrix elements of the exciton-photon interaction are described as [9-11]

$$
\Pi_{A_{0}}^{a} = \sum_{j_{c}, j_{v}} \pi_{j_{c}, j_{v}}^{a} \phi_{j_{c}, j_{v}}^{(a)}(0)
$$

(4)

and

$$
\Pi_{A_{0} A_{0}}^{a} = \sum_{j_{c}, j_{v}} \left[ M^{\beta}_{j_{c}, j_{v}} \delta_{j_{c}, j_{v}} - M^{\beta}_{j_{c}, j_{v}} \delta_{j_{c}, j_{v}} \right] \phi_{j_{c}, j_{v}}^{(a)}(0) \phi_{j_{c}, j_{v}}^{(a)}(0)
$$

(5)

where $\hat{p}_{a} = -i\hbar d/dr_{a}$, $\pi_{a}$ is the interband matrix element of the momentum operator, $\phi_{j_{c}, j_{v}}^{(a)}(r)$ is the wave function of the relative electron-hole motion. The parameter $M^{a\beta}_{\rho}$ is determined by [9,12]

$$
M^{a\beta}_{\rho} = \frac{1}{m} \sum_{i} \left[ \frac{\pi_{a}^{\rho} \pi_{\mu}^{\beta}}{E_{\rho i}^{(a)}} + \frac{\pi_{\mu}^{\rho} \pi_{a}^{\beta}}{E_{\rho i}^{(a)}} \right].
$$

(6)

In the equation (3) the matrix element of the intraband Frohlich exciton–lattice interaction $P_{\tau A}$ is considered in the approximation of the zero wave vector of the phonon [13].

The wave functions of the relative motion of an electron and a hole $\phi_{j_{c}, j_{v}}^{(a)}(r)$ are assumed to satisfy a system of the effective mass approximation equations [9,14-15].

As may be seen from the equation (5), the matrix element can describe the dipole transitions between the excitons related to the same and different series.
3. Exciton wave functions

With allowance made for anisotropy and the complex valence band of hexagonal semiconductors, the wave functions and the energies in the first approximation for the $A_{n=1}$ and $B_{n=1}$ exciton levels are reported in Ref. [16] to be obtained. In this paper the analogous approach is applied to find the first order corrections to the wave functions and the energy of the $A_{n=2}$ level. In the case of the wurtzite semiconductors $A^3B^6$ the set of the equations for the wave functions $\Phi_{j,n}^{(k)}(r)$ can be written as [16]

$$
\left\{ \frac{1}{2\mu_{j,n}^{a}} \left( \hat{p}_{x}^{2} + \hat{p}_{y}^{2} + \frac{1}{2\mu_{j,n}^{l}} \hat{p}_{z}^{2} + U_{eh}(r) \right) \right\} \Phi_{j,n}^{(k)}(r) - \sum_{j' \neq j} D_{j'j}^{(k)} \hat{p}_{x}^{a} \hat{p}_{x}^{b} \Phi_{j',n}^{(l)}(r) = \left( E_{j,n} - e_{j,n} \right) \Phi_{j,n}^{(k)}(r)
$$

(7)

where $E_{j} = E_{j}(0)$, $e_{j,n}$ is the energy gap in the Brillouin zone center, $\mu_{j,n}^{a}$ is the excitonic effective mass, $U_{eh}(r)$ is the Coulomb energy of the electron-hole interaction, $D_{j'j}^{(k)}$ are the effective mass parameters [9]

$$
D_{j'j}^{(k)} = \frac{1}{2m} \delta_{j'j}^{a} \delta_{j'j}^{b} + \frac{1}{m^{2}} \sum_{n} \frac{\pi_{j}^{a} \pi_{j'}^{b}}{e_{j,n}}.
$$

(8)

Based on the band structure of the considered crystals and the selection rules the nonzero parameters $D_{j'j}^{(k)}$ can be found.

Introduction of the some scalar effective mass of the exciton $\overline{\mu}_{j,n}$, as well as in Ref. [16], allows one to write the set of the equations (7) as

$$
\left\{ \frac{1}{2\overline{\mu}_{j,n}^{a}} \left( \hat{p}_{x}^{2} + \hat{p}_{y}^{2} + \frac{1}{2\overline{\mu}_{j,n}^{l}} \hat{p}_{z}^{2} + U_{eh}(r) \right) \right\} \Phi_{j,n}^{(k)}(r) + \hat{G}_{j,n} \left( \frac{1}{2\overline{\mu}_{j,n}^{a}} \left( \hat{p}_{x}^{2} + \frac{1}{2\overline{\mu}_{j,n}^{l}} \hat{p}_{z}^{2} \right) \right) \Phi_{j,n}^{(k)}(r) - \sum_{j' \neq j} D_{j'j}^{(k)} \hat{p}_{x}^{a} \hat{p}_{x}^{b} \Phi_{j',n}^{(l)}(r) = \left( E_{j} - e_{j,n} \right) \Phi_{j,n}^{(k)}(r)
$$

(9)

where

$$
\hat{G}_{j,n} = \frac{1}{2} \left\{ \left( \frac{1}{\overline{\mu}_{j,n}^{a}} - \frac{1}{\overline{\mu}_{j,n}^{l}} \right) \hat{p}_{x}^{2} + \left( \frac{1}{\overline{\mu}_{j,n}^{a}} - \frac{1}{\overline{\mu}_{j,n}^{l}} \right) \hat{p}_{z}^{2} \right\}.
$$

(10)

It is obvious that the set of the equations (9) is reduced to the individual well-known hydrogen-like equations if the second and third terms are neglected and the anisotropy effect on $U_{eh}(r)$ is ignored. In order to allow for the influence of the complex valence band and anisotropy of the excitonic effective mass, the disregarded terms can be taken into account with the use of the perturbation theory [17]. For this purpose the wave functions $\Phi_{j,n}^{(k)}(r)$ are expanded over the hydrogen-like wave functions $\chi_{j,n}^{(\xi,m)}(r)$ [17]

$$
\Phi_{j,n}^{(k)}(r) = \sum_{\xi,m} \chi_{j,n}^{(\xi,m)}(r).
$$

(11)

where $\chi_{j,n}^{(\xi,m)}$ is the set of quantum numbers characterizing the relative electron-hole motion. After the substitution of the expansion (11), each from the equations of the set (9) is multiplied by $\chi_{j,n}^{(\xi,m)}(r)^{*}$ and then the integration over $r$ is carried out. Thus, the system of the equations for coefficients $\chi_{j,n}^{(\xi,m)}$ is obtained. These coefficients are considered here as $\chi_{j,n}^{(\xi,m)} = a_{j,n}^{(\xi,m)} + b_{j,n}^{(\xi,m)}$ where $a_{j,n}^{(\xi,m)}$ and $b_{j,n}^{(\xi,m)}$ correspond to the zero and first approximation. In order to find the first order corrections to the $A_{n=2}$ energy level the coefficients $a_{j,n}^{(\xi,m)}$ related to the B and C exciton series are taken to be equal to zero,
but in the case of the A series $a_{j,k}^{(zm)} = 0$ if $\xi \neq 2$. If $\xi'$ is assumed to be equal to 2 and the second approximation terms are discarded in the obtained system of equations, then the first order corrections to the A$_{n-2}$ level can be derived. In this case the splitting into three sublevels is found. If the discarded terms associated this level with others are taken into account, the A$_{n-2}$ level splits into four sublevels, for which the wave functions in the first approximation were derived. Because the obtained expressions are too cumbersome, they are not present in this paper.

4. Discussion

Let us consider the resonant HRS by LO-phonons in the wurtzite semiconductors on the assumption that the hydrogen-like Wannier excitons participate in the scattering process. The polarization of the incident radiation is supposed to be perpendicular to the axis $z$. If the dipole transitions between the subbands are ignored, then the contributions of the A, B and C series to the HRS cross section depends on the scattering geometry as $B \propto (\epsilon_{O}^{(S)} + \epsilon_{O}^{(S)z}) \left( \epsilon_{x}^{(b)} \hat{q}_{x} + \epsilon_{y}^{(b)} \hat{q}_{y} \right)$ where $\hat{q}$ is the unit vector in the direction of the phonon wave vector.

As may be seen from the equations (6) and (8), the parameters $M_{\alpha\beta}^{v'v}$ ($v' \neq v$) can be associated with $D_{\alpha\beta}^{v}$ by the correlation $M_{\alpha\beta}^{v'v} = m(D_{\alpha\beta}^{v} + D_{\alpha\beta}^{v'})$. Consequently, if the nonzero parameters $D_{\alpha\beta}^{v}$ for the wurtzite crystals are known, analysis of the contributions of the transitions between the excitons of the different series to the HRS can be performed. Because of this, of some interest are the scattering geometries $z(xx,y')x'$ and $z(xx,z)x'$ when the incident radiation with the polarized $\epsilon_{L} \parallel x$ is traveling along the $z$ axis and the scattered light propagates normally on $z$ and at the angle $\phi_{L} = \pi/4$ to the $x$ axis. In this case the sequences of the exciton states related to the same series participate in the hyper-Raman process if $\epsilon_{L} \perp z$. But due to the inclusion of the dipole transitions between the excitons of different series the considered HRS is possible when $\epsilon_{L} \parallel z$. In this case the pertinent hyper-Raman process is described as the two-photon transition to the $p$-exciton state of the B or C series and the indirect transition to the ground state. And its contribution grows as the doubled frequency of exciting radiation is approached to resonance with the B$_{n-2}$ exciton level. Besides, it was found that allowance made for the transitions between the $s$- and $p$-excitons related to the different subbands leads to the hyper-Raman scattering for the scattering geometry $y(xx,y)z$.

The frequency dependences of the HRS cross section $d\sigma/d\Omega$ for CdS and CdSe were obtained. The results are present in Fig. 1 where the curves (1) and (2) illustrate $d\sigma/d\Omega$ calculated for the scattering geometry $z(xx,y')x'$ as a function of the doubled energy of incident photons if the transitions between the excitons associated with the different subbands are ignored (1) and are taken into account (2). The curves (3) and (4) show the cross section computed for the geometries $z(xx,z)x'$ and $y(xx,y)z$, respectively. Calculations were performed for the following parameters of semiconductors: $R_{A} = R_{B} = 0.028$ eV, $R_{C} = 0.026$ eV [7], $E_{c}^{A} = 2.578$ eV, $E_{c}^{B} = 2.593$ eV, $E_{c}^{C} = 2.656$ eV [18], $\hbar\omega_{k} = 0.038$ eV [19], $\Gamma_{A} = 0.004$ eV, $\Gamma_{B} = 0.005$ eV, and $\Gamma_{C} = 0.026$ eV [8] for CdS and $R_{A} = 0.0158$ eV, $R_{B} = R_{C} = 0.0161$ eV, $E_{c}^{A} = 1.833$ eV, $E_{c}^{B} = 1.8571$ eV, $E_{c}^{C} = 2.272$ eV [8], $\hbar\omega_{k} = 0.027$ eV [19], $\Gamma_{A} = 0.004$ eV, $\Gamma_{B} = 0.006$ eV, and $\Gamma_{C} = 0.080$ eV [8] for CdSe where $\Gamma_{A(B,C)}$ and $R_{A(B,C)}$ are the lifetime broadening of the exciton states and the Rydberg of the A (B, C) series. $E_{cv}$ is the energy gap. The data on the effective masses of an electron and a hole in CdS were used from Ref. [18]. In the case of CdSe the exciton effective masses are assumed to little differ in a magnitude. Besides, it is supposed that the terms including the transitions between the nearest bands give the main contribution to the parameters $D_{\alpha\beta}^{v}$. Under summation over the intermediate virtual states the Green’s function approach was applied [6,20].
For the scattering geometries to the A-series corrections approximately twice for the cross section. The approximate relationship to the A-series related to the A-series do not participate in the HRS contribution with \[2\]. As an example too weak enhancement was reported in the experimental investigation of the HRS in ZnSe on the frequency dependence of the scattering intensity considerably less than the one of the dominant sequence of the intermediate states \[6\]. However, under experimental investigation of the HRS in ZnSe on the frequency dependence of the scattering intensity a weak enhancement was reported to be found for the two-photon resonance with the 1s exciton state \[2\]. Thus, the hyper-Raman processes taking into account the transitions between the subbands along with the scattering mechanisms including the two-photon transitions to the s-excitonic states can give a contribution to the cross section when the sequence of the intermediate excitonic states s-p-s of the same series do not participate in the HRS.

As can be seen from Fig.1, impossibility of participation of the sequences of the intermediate exciton states related to the same subbands in the HRS leads to the appreciable decrease in the cross section. It has been known that the hyper-Raman scattering induced by the two-photon transitions to the s-excitonic states can occur too \[2,6,21-22\]. In general case the contribution of this mechanism is considerably less than the one of the dominant sequence of the intermediate states \[6\]. However, under experimental investigation of the HRS in ZnSe on the frequency dependence of the scattering intensity a weak enhancement was reported to be found for the two-photon resonance with the 1s exciton state \[2\]. Thus, the hyper-Raman processes taking into account the transitions between the subbands along with the scattering mechanisms including the two-photon transitions to the s-excitonic states can give a contribution to the cross section when the sequence of the intermediate excitonic states s-p-s of the same series do not participate in the HRS.

In order to assess the role of the obtained the corrections to the wave functions the HRS induced by the two-photon transition to the \(A_{n=2}\) exciton level was considered for the following scattering geometries: \(z(xx,y')x'\), \(z(xx,z)x'\) and \(y(xx,y)z\). Rough estimations of the relative contributions of this hyper-Raman process to the cross section \(d\sigma/d\Omega\) were executed for the CdS, CdSe and ZnS semiconductors. As an example the results obtained for a CdS crystal are shown in Fig. 2. As mentioned above, for the configuration \(z(xx,y')x'\) the sequence of the intermediate exciton states related to the A-series dominates in the HRS. The inclusion of the corrections to the wave functions of the \(A_{n=2}\) level leads to a decrease of the relative contribution of the considered hyper-Raman process to the cross section. The approximate estimations have shown that in this case \(d\sigma/d\Omega\) decreases approximately twice for \(2\hbar\omega_L \sim E_{A_{n=2}}\). For the scattering geometry, \(z(xx,z)x'\) allowance made for the corrections to the wave functions leads to the added HRS process caused by the two-photon transition to the \(A_{n=2}\) level. However, its contribution is negligible in comparison with the one calculated for the geometry \(z(xx,y')x'\). The rough estimations have shown that in the case of the configuration \(y(xx,y)z\) the inclusion of the corrections give rise to a decrease of the relative contribution of the considered process to the cross section too.

**Figure 1.** The HRS cross section calculated for CdS \((a)\) and CdSe \((b)\) as a function of the doubled energy of incident photons.
Figure 2. The HRS cross section calculated for the scattering mechanism including the two-photon transition to the $A_{n=2}$ level in a CdS crystal as a function of the doubled energy of incident photons. Calculations were carried out for the configurations $z(xx,y')x'$, $z(xx,z)x'$ (a) and $y(xx,y)z$ (b) if the first order corrections to the wave functions are neglected (the curve 1) and are taken into account (the curves 2 and 3).

5. Conclusion

The resonant hyper-Raman scattering by LO-phonons in the wurtzite semiconductors $A^2B^6$ was treated within the framework two-band model, taking into account the Wannier excitons as the intermediate states of an electronic system. It has been shown that in certain cases the sequences of the intermediate excitonic states, $s$-$p$-$s$, can give a contribution to the HRS only due to the inclusion of the transitions between excitons related to the different series.

Taking into account the complex structure of the top valence band and the anisotropy of the exciton effective mass by the perturbation theory, the energies and the wave functions in a first approximation were obtained for the $A_{n=2}$ excitonic level. The hyper-Raman scattering of light by LO-phonons near the two-photon resonance with the $A_{n=2}$ excitonic level was theoretically investigated. Rough estimations obtained for some semiconductors have shown that allowance made for these corrections can exert perceptible influence on the contribution of the hyper-Raman process including the two-photon transition to the $A_{n=2}$ excitonic level to the cross section.

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