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THEORETICAL INVESTIGATION OF THE RESONANT HYPER-RAMAN SCATTERING BY OPTICAL PHONONS

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A theoretical model for the resonant hyper-Raman scattering in semiconductor crystals is presented. The Wannier excitons are considered as intermediate states. The expressions for the resonant hyper-Raman scattering cross section are obtained. The theoretical model developed allows taking into account different mechanisms of the exciton–photon and exciton–phonon interactions.

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1. INTRODUCTION

The Raman scattering (RS) is a powerful technique in the study of excitations in semiconductors and their interactions. The hyper-Raman scattering (HRS) is a nonlinear optical process where two incident photons are absorbed simultaneously and one photon of scattered light and a phonon are created [1–4]. Because the HRS is a three-photon process, it has other selection rules comparing to that of the Raman scattering, and therefore allows obtaining information that is inaccessible to RS methods.

Of special interest is the resonant HRS where the energy of two incident photons or scattered photon is close to that of electronic excitations [2, 5, 6]. In this case, the HRS allows obtaining additional information on electron–photon and electron–lattice interactions and on some parameters of electronic transitions. The resonant HRS by optical phonons was first observed in a CdS crystal where resonant conditions were provided by a temperature variation of the energy gap with a fixed frequency of the exciting radiation [7]. Recently, the resonant HRS by optical phonons in a cadmium sulfide was studied by means of a frequency tunable optical parametric oscillator using a KTP crystal [8]. Resonant effects in the HRS were also reported in $SrTiO_3$ [9, 10], TiO_2 [11, 12], ZnSe [13, 14], and Cu_2O [15]. But publications devoted to theoretical investigations of the resonant HRS in semiconductor crystals are very scarce up to now. Some mechanisms of the HRS were theoretically studied for the CdS crystal [16–19]. In the paper by Garsía-Cristóbal et al. [20], the HRS process mediated by a dipole-allowed Fröhlich interaction was analyzed in detail and the HRS efficiency was calculated with the excitonic effects taken into account.

In this paper, a theoretical model for the resonant HRS by optical phonons is given for semiconductor crystals. We assume that virtual intermediate states in the scattering process are the Wannier excitons. We consider different mechanisms for the HRS in the framework of the three-band model, i.e., we also take transitions in higher-lying conduction bands and from deeper valence bands into account. In Sec. 2, the basic formulas for the HRS cross section are given. In Sec. 3, expressions for the HRS tensor are derived using the Green's function formalism. Section 4 is devoted to a discussion of different scattering mechanisms and their contributions to the HRS efficiency.

2. BASIC FORMULAS

From a microscopic point of view, the first-order HRS process can be described as follows: two incident photons with the wave vector $\mathbf{q}_L$, frequency ω_L, and polarization $\boldsymbol{\varepsilon}_L$ are absorbed simultaneously, a phonon with the wave vector $\mathbf{q}_P$ and frequency ω_P is then created, and a scattered photon ($\mathbf{q}_S$, ω_S, $\boldsymbol{\varepsilon}_S$) is finally emitted. Using time-dependent perturbation theory, the differential cross section for the one-phonon HRS can be written as [21]

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$$\frac{d\sigma}{d\Omega} = \frac{\omega_S^3 \eta_S^3 \eta_L V}{4\pi^2 \hbar^2 c^4 \omega_L N_L} \sum_{\mathbf{q}_P} \left| \sum_{l_1,l_2,l_3} \frac{\langle f|\hat{H}_{ER}|l_3\rangle\langle l_3|\hat{H}_{EL}|l_2\rangle\langle l_2|\hat{H}_{ER}|l_1\rangle\langle l_1|\hat{H}_{ER}|i\rangle}{(E_{l_3} - \hbar\omega_S)(E_{l_2} - 2\hbar\omega_L)(E_{l_1} - \hbar\omega_L)} \right|^2, \quad (1)$$

where $\hat{H}_{ER}$ and $\hat{H}_{EL}$ are the Hamiltonians of the electron–photon and electron–lattice interactions, V is the crystal volume, $N_L = n_L/V$ is the photon density of incident radiation, η_L (η_S) is the refractive index for the frequency ω_L (ω_S), $|i\rangle$ and $|f\rangle$ are the initial and final states, $|l_j\rangle$ ($j = 1, 2, 3$) are the intermediate virtual states, and E_{l_j} are the corresponding energies of the electronic system. We assume that in the initial and final states, the electronic system of a semiconductor is in the ground state, but the virtual intermediate states are the Wannier excitons.

In the dipole approximation, the matrix element for a transition from the ground state to an excitonic state is given by [22]

$$\langle n_L - 1; \mathbf{K}, \Lambda|\hat{H}_{ER}|i\rangle = \\ = \frac{(2\pi)^2 e}{m\eta_L} \sqrt{\frac{\hbar N_L}{\omega_L}}\, \delta(\mathbf{K} - \mathbf{q}_L)\varepsilon_\alpha^L \Pi_{\Lambda 0}^\alpha \quad (2)$$

$$\Pi_{\Lambda 0}^\alpha = \left\{ \pi_{cv}^\alpha - M_{cv}^{\alpha'\alpha} p_{\alpha'} \right\} \left(\chi_{cv}^\lambda(\mathbf{r})\right)^* \Big|_{r=0}, \quad (3)$$

where $\hat{p}_\alpha = -i\hbar\partial/\partial r_\alpha$, e and m are the charge and mass of the electron, π_{cv} is the interband matrix element of the momentum operator, $\chi_{cv}^\lambda(\mathbf{r})$ is the hydrogenic wave function of relative electron–hole motion, $\mathbf{K}$ is the exciton wave vector, $\Lambda = (c, v, \lambda)$ describes an exciton belonging to the valence band v and the conduction band c, and $\lambda = (\zeta, \ell, m)$ denotes a set of inner quantum numbers of the exciton: the principal quantum number ζ is n for the discrete spectrum or k for the continuous spectrum. In expression (3), the first term in the curly brackets describes the allowed dipole transitions to s-excitonic states. The second term corresponds to another type of the dipole transitions (weakly forbidden transitions) that cause an excitation of p-excitons [22, 23]. The parameter $M_{cv}^{\alpha'\alpha}$ is defined by [22]

$$M_{cv}^{\alpha'\alpha} = \frac{1}{m}{\sum_n}' \left[\frac{\pi_{cn}^{\alpha'}\pi_{nv}^{\alpha}}{E_c - E_n} + \frac{\pi_{cn}^{\alpha}\pi_{nv}^{\alpha'}}{E_v - E_n} \right], \quad (4)$$

where the prime on the summation indicates that the terms with vanishing denominators are omitted. The matrix element describing the transitions between excitonic states can be written as [24]

$$\langle n_L - 1; \mathbf{K}', \Lambda'|\hat{H}_{ER}|n_L; \mathbf{K}, \Lambda\rangle = \\ = \frac{e}{m\eta_L} \sqrt{\frac{2\pi\hbar N_L}{\omega_L}}\, \delta(\mathbf{K}' - \mathbf{K} - \mathbf{q}_L)\varepsilon_\beta^L \Pi_{\Lambda'\Lambda}^\beta, \quad (5)$$

$$\Pi_{\Lambda'\Lambda}^\beta = \left(\pi_{c'c}^\beta \delta_{v'v} - \pi_{vv'}^\beta \delta_{c'c}\right) \langle \chi_{c'v'}^{\lambda'}|\chi_{cv}^\lambda\rangle + \\ + \delta_{c'c}\delta_{v'v} \left(M_{c'c}^{\beta'\beta} - M_{vv'}^{\beta'\beta}\right) \langle \chi_{c'v'}^{\lambda'}|\hat{p}_{\beta'}|\chi_{cv}^\lambda\rangle. \quad (6)$$

In expression (6), the first term corresponds to the transitions between excitonic states belonging to different pairs of bands (interband transitions), whereas the second term describes the intraband dipole transitions between excitonic states.

It is known that there are two types of electron–lattice interactions [25]. This is the deformation potential interaction, which is due to scattering of electrons by perturbations of a periodic potential caused by the displacement of atoms of the lattice. For longitudinal optical (LO) phonons, the deformation potential interaction is supplemented by the Fröhlich interaction due to the electric field associated with these phonons. In the general case, the matrix element of the exciton–lattice interaction can be written as [26]

$$\langle n_P + 1; \mathbf{K}', \Lambda'|\hat{H}_{EL}|n_P; \mathbf{K}, \Lambda\rangle = \\ = \frac{\gamma\sqrt{n_P + 1}}{\sqrt{V}}\, \delta(\mathbf{K}' + \mathbf{q}_P - \mathbf{K})\, P_{\Lambda'\Lambda}, \quad (7)$$

$$P_{\Lambda'\Lambda} = \langle \chi_{c'v'}^{\lambda'}|\hat{P}|\chi_{cv}^\lambda\rangle = \\ = \langle \chi_{c'v'}^{\lambda'}|\Theta_{c'c}\delta_{vv'} \exp(-i\alpha_e \mathbf{q}_P \cdot \mathbf{r}) - \\ - \Theta_{vv'}\delta_{cc'} \exp(i\alpha_h \mathbf{q}_P \cdot \mathbf{r})|\chi_{cv}^\lambda\rangle, \quad (8)$$

where n_P is the phonon number. For the deformation potential interaction in a crystal with two atoms per unit cell,

$$\Theta_{n'n} = \Xi_{n'n} \quad (9)$$

and

$$\gamma = \gamma_D = \sqrt{\frac{\hbar\Omega}{2\omega_P d^2 M^*}}, \quad (10)$$

where Ω is the cell volume, M^* is the reduced mass of atoms in the cell, d is the lattice constant [25, 26], and $\Xi_{n'n}$ is the deformation potential defined by Bir and Pikus [27]. For the Fröhlich interaction, $\Theta_{n'n}$ and γ are given by

$$\Theta_{n'n} = \hat{q}_j r_{n'n}^j (1 - \delta_{n'n}) + iq_P^{-1}\delta_{n'n} \quad (11)$$

and

$$\gamma = \gamma_F = \sqrt{2\pi\hbar\omega_P e^2 \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)}, \qquad (12)$$

where $\hat{\mathbf{q}}$ is the unit vector in the direction of $\mathbf{q}_P$, and ε_∞ and ε_0 are the optical and static dielectric constants, respectively [26]. The parameter $\alpha_{e(h)}$ is determined by $\alpha_{e(h)} = m^*_{h(e)}/(m^*_e + m^*_h)$ where m^*_e and m^*_h are the effective masses of electrons and holes.

After the substitution of (2), (5), and (7) in expression (1), the HRS cross section becomes

$$\frac{d\sigma}{d\Omega} = \frac{2\pi\hbar e^6 \eta_S \omega_S^2 (n_P + 1)}{m^6 c^4 \eta_L^3 \omega_L^3} \times \times N_L V \left|\varepsilon^S_\gamma \varepsilon^L_\beta \varepsilon^L_\alpha \beta_{\alpha\beta\gamma}(2\mathbf{q}_L - \mathbf{q}_S)\right|^2, \qquad (13)$$

where the HRS tensor $\beta_{\alpha\beta\gamma}(\mathbf{q})$ is given by

$$\beta_{\alpha\beta\gamma}(\mathbf{q}) = \gamma \sum_{\Lambda_1,\Lambda_2,\Lambda_3} \frac{\Pi^\gamma_{0\Lambda_3} P_{\Lambda_3\Lambda_2} \Pi^\beta_{\Lambda_2\Lambda_1} \Pi^\alpha_{\Lambda_1 0}}{[E_{\Lambda_3}(\mathbf{q}_S) - \hbar\omega_S]\,[E_{\Lambda_2}(2\mathbf{q}_L) - 2\hbar\omega_L]\,[E_{\Lambda_1}(\mathbf{q}_L) - \hbar\omega_L]}. \qquad (14)$$

Here, the exciton energy is

$$E_\Lambda(\mathbf{q}) = E_{cv} + \frac{\hbar^2 q^2}{2M} + \Delta E_\lambda, \qquad (15)$$

where $M = m^*_e + m^*_h$, E_{cv} is the energy gap, and $\Delta E_\lambda = \Delta E_\zeta$ is the energy associated to the relative motion of the electron and the hole (i.e., $\Delta E_n = -R/n^2$ or $\Delta E_k = Rk^2$, where R is the Rydberg constant of an exciton). Because the photon wave vector is small, we assume that $E_\Lambda(\mathbf{q}) = E_\Lambda(0)$ in what follows.

3. THEORETICAL MODEL

3.1. Scattering mechanisms

We consider the resonant HRS process, i.e., the process where the double frequency of the exciting radiation is close to the energy gap E_{cv}. If only the dipole-allowed transitions are taken into account, the absorption of the incident photon leads to the excitation of an s-excitonic state, while another photon induces an intraband transition to a p-exciton or an interband transition to an s-exciton belonging to the higher lying conduction band or the lower valence band. In case of the resonant HRS, where $2\hbar\omega_L \sim E_{cv}$, the two-photon transition to a p-exciton is of interest. It is known that for the first-order HRS, the phonon wave vector is small and the scattering process can be considered in the Brillouin zone centre. In the approximation of the zero wave vector of the phonon, the intraband Fröhlich interaction reduces to

$$P_{\Lambda'\Lambda} \approx \delta_{c'c}\delta_{vv'} \langle \chi^{\lambda'}_{c'v'} | \hat{\mathbf{q}} \cdot \mathbf{r} | \chi^{\lambda}_{cv} \rangle \qquad (16)$$

and therefore leads to transitions between the s- and p-excitonic states. When $q_P \approx 0$, the corresponding matrix elements of the deformation potential and interband Fröhlich interactions are given by

$$P_{\Lambda'\Lambda} \approx \{\Theta_{c'c}\delta_{vv'} - \Theta_{vv'}\delta_{cc'}\} \langle \chi^{\lambda'}_{c'v'} | \chi^{\lambda}_{cv} \rangle \qquad (17)$$

and therefore connect states with the same parity. Thus, in the HRS process considered, the deformation potential or interband Fröhlich interaction leads to the transition to a p-exciton, but the intraband Fröhlich coupling causes the transition to an s-state. Because the transition from the p-excitonic state to the ground state is weakly forbidden, the intraband Fröhlich mechanism plays a leading role in the scattering. The corresponding HRS tensor is therefore given by

$$\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q}) = \gamma \pi^\gamma_{vc} \pi^\alpha_{cv} \left[M^{\beta'\beta}_{cc} - M^{\beta'\beta}_{vv}\right] \sum_{\lambda_3,\lambda_2,\lambda_1} \frac{\chi^{\lambda_3}_{cv}(0) \langle \chi^{\lambda_3}_{cv} | \hat{P} | \chi^{\lambda_2}_{cv} \rangle \langle \chi^{\lambda_2}_{cv} | \hat{p}_{\beta'} | \chi^{\lambda_1}_{cv} \rangle \left(\chi^{\lambda_1}_{cv}(0)\right)^*}{(E_{cv} + \Delta E_{\lambda_3} - \hbar\omega_S)(E_{cv} + \Delta E_{\lambda_2} - 2\hbar\omega_L)(E_{cv} + \Delta E_{\lambda_1} - \hbar\omega_L)}. \qquad (18)$$

If the HRS is considered in the framework of the three-band model and the weakly forbidden dipole transitions to the p-excitons belonging to the highest valence band v and the lowest conduction band c are taken into account, we can also identify two other scattering mechanisms including two-photon transitions to s-excitonic states. The exciton–lattice interaction then causes the transition to a p-exciton belonging to the same pair of bands (the intraband Fröhlich coupling) or induces the interband transition to another s-excitonic state (the deformation potential or interband Fröhlich interaction). The corresponding HRS tensors $\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})$ and $\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q})$ are given by

$$\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q}) = \gamma \sum_{\lambda_3,\lambda_2} \frac{M^{\gamma'\gamma^*}_{cv}\hat{p}_{\gamma'}\chi^{\lambda_3}_{cv}(\mathbf{r})\big|_{r=0}\langle\chi^{\lambda_3}_{cv}|\hat{P}|\chi^{\lambda_2}_{cv}\rangle A_{\alpha\beta}(\lambda_2,\omega_L)}{(E_{cv}+\Delta E_{\lambda_3}-\hbar\omega_S)(E_{cv}+\Delta E_{\lambda_2}-2\hbar\omega_L)} \tag{19}$$

and

$$\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q}) = \gamma \sum_{c'',v''}\sum_{\lambda_3,\lambda_2} \frac{\pi^{\gamma}_{v''c''}\chi^{\lambda_3}_{c''v''}(0)\langle\chi^{\lambda_3}_{c''v''}|\hat{P}|\chi^{\lambda_2}_{cv}\rangle A_{\alpha\beta}(\lambda_2,\omega_L)}{(E_{c''v''}+\Delta E_{\lambda_3}-\hbar\omega_S)(E_{cv}+\Delta E_{\lambda_2}-2\hbar\omega_L)}\,, \tag{20}$$

where $A_{\alpha\beta}(\lambda_2,\omega_L)$ describes the two-photon transition to the s-excitonic state,

$$\begin{aligned} A_{\alpha\beta}(\lambda_2,\omega) = \left(M^{\beta'\beta}_{cc} - M^{\beta'\beta}_{vv}\right)\left(-M^{\alpha'\alpha}_{cv}\right) \times \\ \times \sum_{\lambda_1} \frac{\langle\chi^{\lambda_2}_{cv}|\hat{p}_{\beta'}|\chi^{\lambda_1}_{cv}\rangle\hat{p}_{\alpha'}\left(\chi^{\lambda_1}_{cv}(\mathbf{r})\right)^*\big|_{r=0}}{E_{cv}+\Delta E_{\lambda_1}-\hbar\omega} + \\ + \sum_{c',v'}\left(\pi^{\beta}_{cc'}\delta_{vv'} - \pi^{\beta}_{v'v}\delta_{cc'}\right)\pi^{\alpha}_{c'v'} \times \\ \times \sum_{\lambda_1} \frac{\langle\chi^{\lambda_2}_{cv}|\chi^{\lambda_1}_{c'v'}\rangle\left(\chi^{\lambda_1}_{c'v'}(0)\right)^*}{E_{c'v'}+\Delta E_{\lambda_1}-\hbar\omega}\,. \end{aligned} \tag{21}$$

The first term in (21) describes the two-photon excitation of the s-exciton in the framework of the two-band model where the absorption of the first photon is accompanied by the weakly forbidden transition to a p-excitonic state. The intraband dipole transition to the s-excitonic state occurs when the second photon is absorbed. The second term in (21) describes the contribution of the three-band model where the intermediate state is assumed to be an s-exciton composed of an electron from some higher lying conduction band c' and a hole from the valence band v, or an exciton belonging to the conduction band c and a deeper valence band v'. In this case, the second photon induces the interband transition of the electron or the hole.

3.2. The Green's function approach

To evaluate the HRS tensors obtained, it is necessary to calculate the matrix elements and the sums over all the intermediate discrete and continuous excitonic states. The problem can be considerably simplified using the Green's function method [28]. This approach was earlier used in theoretical investigation of the two-photon absorption [24, 29] and the first-order resonant RS [26]. We have also applied the Green's functions for a theoretical treatment of the two-photon resonant RS [30, 31]. In accordance with this method, the sums over intermediate states can be expressed as Whittaker functions $W_{\kappa,\mu}(z)$ [28, 29],

$$\begin{aligned} \sum_{\lambda} \frac{\chi^{\lambda}_{cv}(\mathbf{r})\left(\chi^{\lambda}_{cv}(0)\right)^*}{E_{cv}+\Delta E_{\lambda}-\hbar\omega_L} = \\ = \frac{\mu\Gamma(1-\kappa_L)}{2\pi\hbar^2 r} W_{\kappa_L,1/2}\left(\frac{2r}{\kappa_L a}\right) \end{aligned} \tag{22}$$

and

$$\begin{aligned} \frac{\partial}{\partial r'_j}\sum_{\lambda} \frac{\chi^{\lambda}_{cv}(\mathbf{r})\left(\chi^{\lambda}_{cv}(\mathbf{r}')\right)^*}{E_{cv}+\Delta E_{\lambda}-\hbar\omega_L}\bigg|_{r'=0} = \\ = \frac{\mu\Gamma(2-\kappa_L)}{2\pi\hbar^2\kappa_L a}\frac{r_j}{r^2} W_{\kappa_L,3/2}\left(\frac{2r}{\kappa_L a}\right), \end{aligned} \tag{23}$$

where $\Gamma(z)$ is the gamma function, and a and μ are the Bohr radius and the reduced mass of the exciton. The parameter κ_L is defined as $\kappa_L = \sqrt{R/(E_{cv}-\hbar\omega_L)}$. Hereafter, the respective indices «L» and «S» correspond to the incident and scattered light. The Whittaker function has the integral representation [32]:

$$\begin{aligned} W_{\kappa,\mu}(z) = \frac{z^{\mu+1/2}e^{-z/2}}{\Gamma(1/2-\kappa+\mu)} \times \\ \times \int_0^{\infty} e^{-zt}t^{-1/2-\kappa+\mu}(1+t)^{-1/2+\kappa+\mu}dt, \\ \mathrm{Re}(\mu-\kappa) > -\frac{1}{2}. \end{aligned} \tag{24}$$

Because the frequency of the incident radiation is away from the excitonic resonance for the resonant HRS ($\kappa_L \ll 1$), the Green's function approach enables us to reduce the sum over λ_1 to the integral. Further, after the substitution of explicit expressions for the hygrogenic wave function [33] and the $\mathbf{r}$ integration, the sums over the intermediate states λ_1 can be calculated. Taking the results obtained in [24, 29] into account, we

write

$$\sum_{\lambda'} \frac{\langle \chi_{cv}^{(\zeta 1m)} | \hat{p}_j | \chi_{cv}^{\lambda'} \rangle \left(\chi_{cv}^{\lambda'}(0) \right)^*}{E_{cv} + \Delta E_{\lambda'} - \hbar\omega_L} =$$

$$= \left(\hat{p}_j \chi_{cv}^{(\zeta 1m)}(\mathbf{r}) \big|_{r=0} \right)^* \kappa_L^2 R^{-1} \begin{cases} J_4(n, \kappa_L), & \zeta = n, \\ J_4(i/k, \kappa_L), & \zeta = k \end{cases} \tag{25}$$

and

$$A_{\alpha\beta}(\lambda, \omega_L) =$$

$$= \left(\chi_{cv}^{\lambda}(0) \right)^* \begin{cases} B_{\alpha\beta}(n, \omega_L), & \zeta = n, \\ B_{\alpha\beta}(i/k, \omega_L), & \zeta = k, \end{cases} \tag{26}$$

where [34]

$$B_{\alpha\beta}(n, \omega_L) = \mu M_{cv}^{\alpha'\alpha} \left(M_{cc}^{\beta'\beta} - M_{vv}^{\beta'\beta} \right) \times$$

$$\times \delta_{\alpha'\beta'} J_2(n, \kappa_L) +$$

$$+ \sum_{c', v'} \frac{(\pi_{cc'}^{\beta} \delta_{vv'} - \pi_{v'v}^{\beta} \delta_{cc'}) \pi_{c'v'}^{\alpha}}{E_{c'v'} - \hbar\omega_L} J_1(n, \kappa_L'). \tag{27}$$

Here, κ_L' is defined for $E_{c'v'}$: $\kappa_L' = \sqrt{R'/(E_{c'v'} - \hbar\omega_L)}$. The integrals $J_1(n, \kappa')$, $J_2(n, \kappa)$, and $J_4(n, \kappa)$ are given in [24, 29]:

$$J_1(n, \kappa') = 4 \int_0^\infty dt \left(\frac{1+t}{t} \right)^{\kappa'} \left(\frac{2t + 1 - \kappa'/nb}{2t + 1 + \kappa'/nb} \right)^n \times$$

$$\times \frac{2t + 1 - \kappa'/b}{\left[(2t+1)^2 - (\kappa'/nb) \right]^2}, \tag{28}$$

$$J_2(n, \kappa) = \frac{16}{3} \kappa \int_0^\infty dt\, t^{1-\kappa} (1+t)^{1+\kappa} \left(\frac{2t+1-\kappa/n}{2t+1+\kappa/n} \right)^n \times$$

$$\times \frac{3(2t+1)^2 + 3(\kappa/n)^2 - 2\kappa(2t+1)(1+2n^{-2})}{\left[(2t+1)^2 - (\kappa/n)^2 \right]^3}, \tag{29}$$

$$J_4(n, \kappa) = 4 \int_0^\infty dt \left(\frac{t+1}{t} \right)^{\kappa} \left(\frac{2t + 1 - \kappa/n}{2t + 1 + \kappa/n} \right)^n \times$$

$$\times \frac{2t + 1}{\left[(2t+1)^2 - (\kappa/n)^2 \right]^2}, \tag{30}$$

where $b = a/a'$ (R' and a' are the Rydberg constant and the Bohr radius of the exciton belonging to the pair of bands, c' and v').

When the energy of the scattered photon is below the excitonic resonances ($\kappa_S < 1$), we can also apply the Green's functions to calculate the sums over λ_3 in expressions (18) and (20). In the works devoted to the second-order resonant RS, we calculated the sums over λ_3 similar to the ones in expressions (18) and (20) for the intraband Fröhlich interaction [30, 31]. In the general case, taking the results obtained in [30] into account, we can write

$$\sum_{\lambda_3} \frac{\chi_{c'v'}^{\lambda_3}(0) \langle \chi_{c'v'}^{\lambda_3} | \hat{P} | \chi_{cv}^{(\zeta \ell m)} \rangle}{E_{c'v'} + \Delta E_{\lambda_3} - \hbar\omega_S} =$$

$$= \frac{Y_{\ell m}(\vartheta_q, \varphi_q) \kappa_S'^2}{(2\ell+1)! \sqrt{a}\, (E_{c'v'} - \hbar\omega_S)} \begin{cases} \dfrac{2^{\ell+2}}{n^{\ell+2}} \sqrt{\dfrac{(n+\ell)!}{(n-\ell-1)!}}\, J_\ell^{(\Theta)}(qa, \kappa_S', n), & \zeta = n, \\ \sqrt{\dfrac{a^3}{V}}\, 2^{\ell+2} k^{\ell+1} e^{\pi/2k} \left| \Gamma\left(\ell + 1 - \dfrac{i}{k} \right) \right| J_\ell^{(\Theta)}\left(qa, \kappa_S', \dfrac{i}{k} \right), & \zeta = k, \end{cases} \tag{31}$$

where

$$J_\ell^{(\Theta)}(Q, \kappa', n) = \frac{i^\ell}{a} \left\{ (-1)^\ell \Theta_{c'c} \delta_{vv'} \frac{I_\ell^{(\Theta)}(\alpha_e Q, \kappa', n)}{(\alpha_e Q)^{\ell+1}} - \Theta_{vv'} \delta_{cc'} \frac{I_\ell^{(\Theta)}(\alpha_h Q, \kappa', n)}{(\alpha_h Q)^{\ell+1}} \right\}, \tag{32}$$

$Q = qa$, $Y_{\ell m}(\vartheta_q, \varphi_q)$ is a spherical function of the angular coordinates of the phonon wave vector. The integral

$I_\ell^{(\Theta)}(Q,\kappa',n)$ is given by

$$I_\ell^{(\Theta)}(Q,\kappa',n)=\frac{b}{2^{\ell+2}\kappa'^3}\int\limits_0^\infty dt\left(\frac{1+t}{t}\right)^{\kappa'}\sum_{v=0}^{\ell}\frac{(\ell+v)!(\ell+1-v)}{v!}\left(\frac{\kappa' Q}{b}\right)^{\ell-v}\times$$
$$\times\,\mathrm{Re}\left\{(-i)^{\ell-v+1}\left(t+\frac{1}{2}+\frac{\kappa'}{2nb}-i\frac{\kappa' Q}{2b}\right)^{v-\ell-2}\times\right.$$
$$\left.\times\,F\left(-n+\ell+1,\ell-v-2;2\ell+2;\ \frac{\kappa'/nb}{t+\frac{1}{2}+\frac{\kappa'}{2nb}-i\frac{\kappa' Q}{2b}}\right)\right\},\quad(33)$$

where $F(a,b;c;z)$ is the hypergeometric function.

To calculate the sum over λ_3 in expression (19), we applied the method that was previously used by us in [30, 31], and obtained the expression (for the intraband Fröhlich interaction and $\kappa_S<2$)

$$\sum_{\lambda_3}\hat{p}_\gamma\chi_{cv}^{\lambda_3}(\mathbf{r})\big|_{r=0}\frac{\langle\chi_{cv}^{\lambda_3}|\hat{P}|\chi_{cv}^{(\zeta 00)}\rangle}{E_{cv}+\Delta E_{\lambda_3}-\hbar\omega_S}=\frac{-i\hbar\hat{q}_\gamma}{E_{cv}-\hbar\omega_S}\chi_{cv}^{(\zeta 00)}(0)\begin{cases}\mathrm{Jp}(qa,\kappa_S,n), & \zeta=n,\\ \mathrm{Jp}(qa,\kappa_S,i/k), & \zeta=k,\end{cases}\quad(34)$$

where

$$\mathrm{Jp}(Q,\kappa,n)=\frac{1}{Q}\left[\frac{\mathrm{Ip}(\alpha_e Q,\kappa,n)}{(\alpha_e Q)^2}+\frac{\mathrm{Ip}(\alpha_h Q,\kappa,n)}{(\alpha_h Q)^2}\right]\quad(35)$$

and

$$\mathrm{Ip}(Q,\kappa,n)=\frac{1}{\kappa^3}\int\limits_0^\infty dt\,t^{1-\kappa}(1+t)^{1+\kappa}\left\{\mathrm{Im}\left[\frac{\left(t+\frac{1}{2}-\frac{\kappa}{2n}-i\frac{\kappa Q}{2}\right)^{n-1}}{\left(t+\frac{1}{2}+\frac{\kappa}{2n}-i\frac{\kappa Q}{2}\right)^{n+1}}\right]-\right.$$
$$\left.-\,\kappa Q\,\mathrm{Re}\left[\frac{\left(t+\frac{1}{2}-\frac{\kappa}{2n}-i\frac{\kappa Q}{2}\right)^{n-2}}{\left(t+\frac{1}{2}+\frac{\kappa}{2n}-i\frac{\kappa Q}{2}\right)^{n+2}}\ \left(t+\frac{1}{2}-\frac{\kappa}{2}-i\frac{\kappa Q}{2}\right)\right]\right\}.\quad(36)$$

Next, after the substitution of the relations obtained for the sums over λ_3 and λ_1 in expressions (18)–(20), we have

$$\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})=i\frac{2\hbar\gamma_F\pi_{vc}^{\gamma}\pi_{cv}^{\alpha}\left(M_{cc}^{\beta'\beta}-M_{vv}^{\beta'\beta}\right)\hat{q}_j\delta_{j\beta'}}{3\pi R^3a^3}\times$$
$$\times\,\kappa_L^2\kappa_S^4\left\{\sum_{n=2}^{\infty}\frac{n^2-1}{n^5}\,\frac{J_1^F(qa,\kappa_S,n)J_4(n,\kappa_L)}{\xi(\omega_L)-n^{-2}-i\gamma_n}+\right.$$
$$\left.+\int\limits_0^\infty\frac{dk\,k(1+k^2)}{1-e^{-2\pi/k}}\,\frac{J_1^F(qa,\kappa_S,i/k)J_4(i/k,\kappa_L)}{\xi(\omega_L)+k^2-i\gamma_k}\right\},\quad(37)$$

$$\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})=-i\frac{\hbar\gamma_F M_{cv}^{\gamma'\gamma^*}\hat{q}_j\delta_{j\gamma'}}{\pi R^2a^3}\kappa_S^2\times$$
$$\times\left\{\sum_{n=1}^{\infty}\frac{1}{n^3}\,\frac{\mathrm{Jp}(qa,\kappa_S,n)}{\xi(\omega_L)-n^{-2}-i\gamma_n}B_{\alpha\beta}(n,\omega_L)+\int\limits_0^\infty\frac{dk\,k}{1-e^{-2\pi/k}}\,\frac{\mathrm{Jp}(qa,\kappa_S,i/k)}{\xi(\omega_L)+k^2-i\gamma_k}\,B_{\alpha\beta}\left(\frac{i}{k},\omega_L\right)\right\}\quad(38)$$

and

$$\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q}) = \frac{2\gamma}{\pi R a^2} \sum_{c''v''} \frac{\pi^{\gamma}_{v''c''} \kappa''^2_S}{E_{c''v''} - \hbar\omega_S} \times$$

$$\times \left\{ \sum_{n=1}^{\infty} \frac{1}{n^3} \frac{J_0^{(\Theta)}(qa, \kappa''_S, n)}{\xi(\omega_L) - n^{-2} - i\gamma_n} B_{\alpha\beta}(n, \omega_L) + \int_0^{\infty} \frac{dk\, k}{1 - e^{-2\pi/k}} \frac{J_0^{(\Theta)}(qa, \kappa''_S, i/k)}{\xi(\omega_L) + k^2 - i\gamma_k} B_{\alpha\beta}\left(\frac{i}{k}, \omega_L\right) \right\}, \quad (39)$$

where $\xi(\omega) = (E_{cv} - 2\hbar\omega)/R$, $\gamma_n = \Gamma_n/R$, Γ_n is an exciton damping, and $J^F_\ell(Q, \kappa, n)$ is the integral $J^{(\Theta)}_\ell(Q, \kappa, n)$ defined for the intraband Fröhlich interaction, i.e., for $\Theta_{nn'} = iq^{-1}\delta_{nn'}$.

We note that the expressions obtained for the HRS tensors can be simplified. As mentioned above, in the case of resonant HRS, the energy of the incident photon is far from the resonance ($E_{cv} - \hbar\omega_L \gg R$), and the parameters κ_L and κ'_L are therefore considerably smaller than unity. Further, it is not difficult to show that $J_1(n, \kappa)$, $J_4(n, \kappa) \approx \left[1 - (\kappa/n)^2\right]^{-1}$ for $\kappa \ll 1$.

We note that expression (37) obtained via the Green's function method is applicable for the computation of the resonant HRS cross section only if the scattered frequency is below excitonic resonances, i.e. for $\hbar\omega_S < E_{cv} - R$ ($\kappa_S < 1$). As a result of using the Green's functions for the summation over λ_3, expressions (38) and (39) can be used only when $\kappa_S < 2$ and $\kappa'_S < 1$. For higher frequencies of the incident radiation, the exciton–lattice matrix elements must be calculated and summation over all the intermediate excitonic states λ_2 and λ_3 must be performed. This approach was used by Garsía-Cristóbal et al. [20] to calculate the efficiency of the HRS induced by the two-photon excitation of a p-exciton followed by the transition to an s-exciton due to the Fröhlich interaction. We therefore do not consider this case here. Although the expression obtained using the Green's function method has a limited applicability range with respect to the photon energy, this method considerably simplifies cumbersome computations of the HRS cross section and at the same time enables one to take all the intermediate discrete and continuous excitonic states into account. Moreover, because the phonon wave vector is small, an approximation of the above expressions can be obtained. In [30, 31, 35], it was shown that $J^F_1(Q, \kappa, n)$ weakly depends on Q for $\kappa Q \ll 1$ and in the limit as $Q \to 0$ coincides with [8, 16]

$$J_5(n, \kappa) = 4 \int_0^{\infty} dt \left(\frac{t+1}{t}\right)^{\kappa} \left(\frac{2t + 1 - \kappa/n}{2t + 1 + \kappa/n}\right)^n \times$$

$$\times \frac{4t + 2 - \kappa}{\left[(2t+1)^2 - (\kappa/n)^2\right]^3}. \quad (40)$$

It can also be shown that as $\kappa Q \to 0$, $\mathrm{Jp}(Q, \kappa, n) \to J_3(n, \kappa)$, where [16, 18]

$$J_3(n, \kappa) = \frac{2^5}{3} \int_0^{\infty} dt\, t^{1-\kappa} (1+t)^{1+\kappa} \left(\frac{2t + 1 - \kappa/n}{2t + 1 + \kappa/n}\right)^n \times$$

$$\times \frac{3(2t + 1 - \kappa)\left[(2t+1)^2 + (\kappa/n)^2 - 2\kappa(2t+1)\right] - \kappa^3(1 - n^{-2})}{\left[(2t+1)^2 - (\kappa/n)^2\right]^4}. \quad (41)$$

Expanding $I^{(\Theta)}_0(Q, \kappa, n)$ in a series in Q, we have

$$J^{(\Theta)}_0(Q, \kappa', n) \approx \frac{1}{2\kappa'^2 a} \left(\Theta_{c'c}\delta_{vv'} - \Theta_{vv'}\delta_{cc'}\right) J_1(n, \kappa') \quad (42)$$

for $Q \ll 1$. Thus, the approximation of the zero wave vector of the phonon allows considerable simplifying the computations. In addition, the phonon energy is often greater than the exciton Rydberg, $\hbar\omega_p > R$, and the expressions obtained via the Green's function approach can therefore be applicable in a sufficiently wide frequency range.

4. DISCUSSION

In the general case, different mechanisms of electron–photon and electron–phonon interactions can be involved in the resonant HRS process. Their contributions depend on the electronic structure and parameters of the crystal, the incident frequency, the selection rules, and the scattering geometry. Specifically, if the one-photon dipole transition is allowed ($\pi_{cv} \neq 0$) and the two-photon transition is forbidden in the semiconductor, the HRS process is described by the tensor $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$ corresponding to the intraband Fröhlich scattering. Therefore, the LO lines are dominant in the resonant HRS spectra.

For the crystal with the dipole-forbidden transition ($\pi_{cv} = 0$), the resonant HRS process can be caused by the two-photon excitation of an s-exciton. This «forbidden» HRS is described by the tensors $\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})$ and $\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q})$, and therefore, both the Fröhlich and deformation potential scattering mechanisms are involved in the resonant process. Consequently, an effect of the deformation potential interaction in the hyper-Raman spectra can be expected in this case. Such a «forbidden» resonant HRS near the energy gap was experimentally investigated in Ti_2O, which is a centrosymmetric crystal [11, 12]. Because its lowest conduction and top valence bands have the same parity, the interband dipole transition is strictly forbidden in it. In the rutile, Watanabe et al. [11, 12] observed the resonant HRS by transverse optical (TO) phonons along with a scattering by LO phonons.

At first sight, the «forbidden» resonant HRS under consideration is similar to the resonant RS in which the one-photon interband transition is replaced by a two-photon transition. As mentioned above, both the two-band and three-band models contribute to the two-photon excitation of an s-exciton. The parameter $M^{\alpha\alpha}_{cv}$ in expression (27) can be written as

$$M^{\alpha\alpha}_{cv} = \\ = -\frac{2}{m}\sum_{c',v'}\frac{(\pi^{\alpha}_{cc'}s_{c'c}\delta_{vv'} - \pi^{\alpha}_{v'v}s_{vv'}\delta_{cc'})\,\pi^{\alpha}_{c'v'}}{E_{c'v'}}, \quad (43)$$

where $s_{nn'} = 1 + E_{cv}/2E_{nn'}$. Taking into account that $M_{cc} - M_{vv} = m/\mu$, it is easy to show that the difference of the two-band and three-band contributions is contained in the expression for $B_{\alpha\alpha}(n, \omega_L)$. In particular, $B_{\alpha\alpha}(n, \omega_L)$ can be approximated by

$$B_{\alpha\alpha}(n, \omega_L) \approx \sum_{c',v'}\frac{(\pi_{cc'}\delta_{vv'} - \pi_{v'v}\delta_{cc'})\,\pi_{c'v'}}{E_{c'v'}} \times \\ \times [J_1(n, \kappa'_L) - 2J_2(n, \kappa_L)] \quad (44)$$

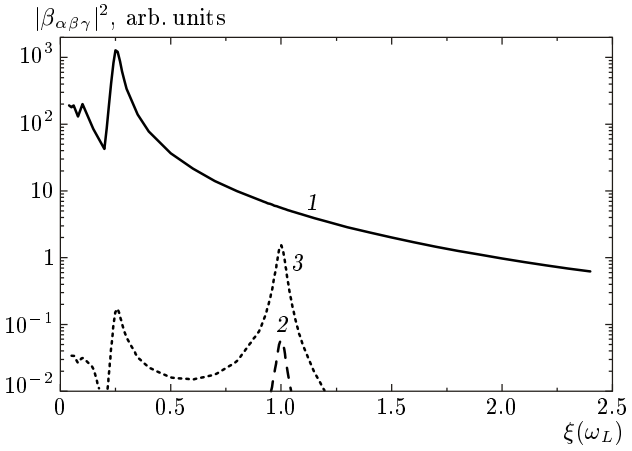
for $E_{c'c}$, $E_{vv'} \gg E_{cv}$. Owing to this, the resonance profile of the HRS can contain additional features caused by the interference of dissimilar transitions. Their appearance is governed by the semiconductor parameters and the exciton–lattice interaction mechanism.

Of special interest is the HRS if the one-photon and two-photon transitions are allowed in a crystal. In this case, the scattering mechanisms described by $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$, $\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})$, and $\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q})$ are involved in the hyper-Raman process. It is obvious that the «allowed» HRS mechanism, which is determined by $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$, gives the main contribution to the HRS intensity because it assumes only the dipole-allowed transitions and is described in the framework of the two-band model, as distinct from $\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})$ and $\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q})$. This conclusion agrees with experimental results because only the resonant HRS by LO phonons was reported in CdS and ZnSe crystals [8, 13, 14]. The «forbidden» scattering mechanisms should not be neglected, however.

Because the «forbidden» resonant HRS is due to the two-photon transition to s-excitonic states, the resonant enhancement for this scattering mechanism occurs when the doubled energy of the incident photons, $2\hbar\omega_L$, coincides with the energy level of the $1s$ exciton, E_{1s}. On the other hand, a resonant increase of the «allowed» HRS occurs for other frequencies of the incident radiation ($2\hbar\omega_L \approx E_{2p}$), i.e., the resonance sets earlier for the «forbidden» HRS than for the «allowed» scattering. In addition, a new scattering mechanism can be involved in the hyper-Raman process and can contribute to the HRS intensity. It is known that the intensive forbidden LO line was observed in the RS spectra for some semiconductors when the incident frequency was near the excitonic resonance [36, 37]. Its appearance was explained by the forbidden Fröhlich interaction that corresponds to the second term in the expansion of the intraband Fröhlich coupling matrix element,

$$P_{\Lambda'\Lambda} \approx \langle\chi^{\lambda'}_{cv}|\hat{\mathbf{q}}\cdot\mathbf{r}|\chi^{\lambda}_{cv}\rangle + \\ + \frac{i}{2q_P}\,\frac{m^*_e - m^*_h}{m^*_e + m^*_h}\langle\chi^{\lambda'}_{cv}|(\mathbf{q}_P\cdot\mathbf{r})^2|\chi^{\lambda}_{cv}\rangle, \quad (45)$$

and induces transitions between s-excitons. For the resonant HRS, a similar scattering mechanism is accompanied by the following sequence of processes: the two-photon transition to an s-excitonic state, the intraband transition between s-excitons due to the Fröhlich interaction, and the return of the electronic system to the ground state. The corresponding tensor $\beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})$ coincides with $\beta^{(3)}_{\alpha\beta\gamma}(\mathbf{q})$ for $\Theta_{n'n} = iq^{-1}\delta_{n'n}$. The estimations performed show that for $2\hbar\omega_L \approx E_{1s}$, the



The contributions of three scattering mechanisms, $|\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})|^2$, $|\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})|^2$, and $|\beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})|^2$, to the HRS as a function of the parameter $\xi(\omega_L) = (E_{cv} - 2\hbar\omega)/R$ (curves *1*, *2*, and *3*, respectively)

contributions of the «allowed» and «forbidden» scattering mechanisms, $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$ and $\beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})$, can be comparable providing substantially different effective masses m_h^* and m_e^* and a small magnitude of γ_{1s}. As an example, Figure shows the result of the computation of the hyper-Raman tensors $|\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})|^2$, $|\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q})|^2$, and $|\beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})|^2$ for $qa = 0.15$, $m_e^*/m_h^* = 0.2$, $|\pi_{cv}| \approx \hbar/d$, $d = 5$ Å, $R = 0.03$ eV, $E_{cv} = 100R$, $\hbar\omega_P = 1.5R$, and $\Gamma = 0.02R$. In the calculation, the virtual transition in the one higher lying conduction band c' ($E_{c'c} = 1.5E_{cv}$) was only taken into account in expression (28). It can be seen from the figure that $|\beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})|^2$ sharply increases as the doubled frequency approaches the two-photon resonance with the $1s$ excitonic state. When $2\hbar\omega_L \approx E_{1s}$, the contributions of «forbidden» and «allowed» HRS become magnitudes of the same order. If the «forbidden» scattering mechanisms play an appreciable role in the resonant HRS, they can affect the frequency dependence of the HRS intensity. Such a feature was observed in a ZnSe crystal where a small enhancement was found for $2\hbar\omega_L \approx E_{1s}$ along with the increase of the HRS signal as the doubled frequency approaches the resonance with a $2p$ exciton [13]. Interesting peculiarities of the HRS in a CdS crystal were also observed [8].

The increase in the HRS intensity by LO phonons (by more than two orders of magnitude) was found in a CdS crystal when the doubled frequency of the exciting radiation approaches the excitonic resonances [8]. The signal then decreases, which was explained by attenuation of the scattered light near the fundamental absorption edge. We apply the theoretical model developed here to analyze the HRS in CdS. The 90°-scattering geometry with the incident radiation propagating along to the optical axis z of the crystal was used in the experiment [8]. In this configuration ($\boldsymbol{\varepsilon}_L$ is directed perpendiculary to the z axis), the dipole transition to the s-excitonic state is allowed for the A, B, and C series. All the three excitonic series can therefore participate in the «allowed» HRS. As regards the «forbidden» mechanisms, the two-photon transition is allowed to the dipole-forbidden s-exciton of the Γ_6 symmetry for the A series and to the dipole-allowed s-exciton for the B or C series. Therefore, in the configuration used in the experiment [8], resonant HRS caused by the two-photon transitions to s-excitons and p-excitons can contribute to the HRS intensity. We evaluated the HRS cross section as a function of the doubled energy of incident photons for the «allowed» ($\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$) and «forbidden» ($\beta^{(2)}_{\alpha\beta\gamma}(\mathbf{q}) + \beta^{(F)}_{\alpha\beta\gamma}(\mathbf{q})$) scattering mechanisms separately. In the calculation, we used the known parameters of CdS ($\hbar\omega_P = 0.038$ eV, $m_e^* = 0.2m$, $m_h^* = 1.34m$ [38]) and took the following values for the A, B, and C excitonic series: $E_{cvA} = 2.579$ eV, $E_{cvB} = 2.596$ eV, $E_{cvC} = 2.66$ eV, $R_A = 0.028$ eV, $R_B = 0.03$ eV, $R_C = 0.026$ eV [39,40], $f_{1sA} = 0.0014$, $f_{1sB} = 0.001$, and $f_{1sC} = 0.0013$ (here, f_{1s} is the oscillator strength for the transition to the $1s$ exciton state) [41]. We also used the energies of the excitons with $n = 1$ and $n = 2$ ($E_{An=1} = 2.548$ eV, $E_{Bn=1} = 2.56$ eV, and $E_{An=2} = 2.568$ eV [40]) and the damping ($\Gamma_A = 0.004$ eV, $\Gamma_B = 0.005$ eV, and $\Gamma_C = 0.026$ eV [41]) known for the temperature at which the measurements were made ($T = 80$ K) [8]. We considered the higher lying conduction band ($E_{c'v} \approx 6.2$ eV) as the intermediate band [42]. The estimations have shown that the HRS intensity enhancement caused by the «allowed» HRS is approximately an order of magnitude less than the increase measured in the experiment when the doubled energy of incident photons varies from 2.49 to 2.53 eV. On the other hand, the cross section gain calculated for «forbidden» resonant HRS was found to be comparable to the change of the HRS intensity observed. Consequently, it is plausible that the resonant HRS observed was induced by the «forbidden» scattering mechanisms. Let us consider expression (37) where we can write $M^{\beta'\beta}_{cc} - M^{\beta'\beta}_{vv} = (m/\mu)\delta_{\beta\beta'}$ for CdS. From this fact, it transpires that the scattering mechanism described by $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$ is effective if the polarization vector of the exciting radiation lies in the plane determined by the photon wave vectors (i.e., $\hat{q}_\beta \neq 0$ in this case). The «allowed» HRS mechanism is therefore forbidden

if the incident radiation is polarized along the x axis and the scattering light propagates in the y direction. Only the «forbidden» scattering mechanisms then contribute to the HRS intensity. Also the appearance of the intensive forbidden 2LO line, which is characteristic of the resonant RS in the HRS spectra near the excitonic resonance, agrees well with our assumption. The strong HRS by LO phonons in CdS for the two-photon resonance with the $2p$ exciton was reported in [13]. But the measurements were performed in the $x(yy, z+x)y$ geometry where the scattering described by $\beta^{(1)}_{\alpha\beta\gamma}(\mathbf{q})$ is allowed according to our model. The above discussion shows that additional experimental research of the resonant HRS in a CdS crystal is of great interest.

5. CONCLUSIONS

A theoretical model for the resonant hyper-Raman scattering in semiconductors was developed. The model includes the Wannier excitons as intermediate states in the scattering process. Different mechanisms of exciton–photon and exciton–lattice interactions were considered and their contributions to the HRS cross section were analyzed for the crystals with both allowed and forbidden dipole transitions. Agreement with the experimental results was found. It was shown that under the resonant conditions, the «forbidden» HRS can give the contribution compatible with the one of the «allowed» HRS. The model developed allows one to calculate the cross section for the HRS when the doubled energy of incident photons is below and in the range of excitonic resonances.

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