

# Second Order Resonant Raman Scattering

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A theoretical model for resonant Raman scattering by two optical phonons in zincblende-type semiconductors is presented. The effect of Coulomb interaction between electrons and holes is taken into account by introducing discrete and continuous excitonic intermediate states. The model can be applied for laser frequencies below and above the band gap. We consider deformation potential and Fröhlich interaction for the electron-one-phonon coupling. The absolute value of the scattering efficiency is evaluated for the two-*LO*-phonons, *TO*- plus *LO*-phonon and two-*TO*-phonons Raman processes, around the  $E_0$  absorption edge of II-VI compound semiconductors. Comparison with the electron-hole uncorrelated theory and experimental data emphasizes the role of the excitonic effects.

## I. Introduction

Many theoretical attempts to interpret experimental results of resonant Raman scattering (RRS) have followed since the pioneering works in the early sixties<sup>[1]</sup>. More recently, absolute value measurements of first- and second-order RRS in III-V and II-VI semiconductors have become available. It has been only during the last ten years that a systematic experimental work on this direction has been performed<sup>[2]</sup>. In particular, a complete set of measurements of one- and two-phonon RRS measurements around the  $E_0$  and  $E_0 + \Delta_0$  critical points (cp's) in several semiconductor compounds of zincblende structure is available at present. To reproduce the experimental profiles of the measured Raman scattering efficiency (RSE) is a challenge for every theoretical model since it allows to select the most adequate. Moreover, from a quantitative comparison with the experiment, detailed information about the electron-phonon interactions can be extracted and the role of the intermediate electronic states involved in the scattering process can be clarified. Theoretical models covering most of the aspects

of one-phonon RRS, which take into account excitonic effects for the intermediate states of the electronic system, have been subsequently developed<sup>[3]</sup>. The models reproduce the experimental absolute values of the Raman efficiency as well as the resonance profiles (scattering efficiency vs incident photon energy) for several III-V and II-VI semiconductor compounds. It is well known, however, that second-order RRS presents distinctive features as compared to first-order RRS. The main peculiarity is that, whereas in the latter process only phonons with nearly equal zero wave vector participate in the scattering process, in the former one the phonon wave vectors are only restricted to have equal magnitude and opposite directions. Therefore, second-order RRS covers a wider range of phonon wave vectors and the RSE profiles are affected by the  $\mathbf{q}$ -dependence of the electron-phonon coupling. The aim of the present work is to develop a theoretical model for the RRS by two optical phonons. Of particular significance is the choice of exciton states as virtual intermediate states in the Raman process.

We consider a crystalline solid, with electronic and

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vibrational subsystems, under the action of a transverse electromagnetic radiation field. The unperturbed

Hamiltonian describing these three noninteracting subsystems can be generally written as:

$$\hat{H}_0 = \sum_{\kappa, e_\sigma} \hbar\omega(\kappa) \hat{a}_{e_\sigma}(\kappa)^\dagger \hat{a}_{e_\sigma}(\kappa) + \sum_{q, \nu} \hbar\omega_\nu(\mathbf{q}) \hat{b}_\nu(\mathbf{q})^\dagger \hat{b}_\nu(\mathbf{q}) + \sum_{\mathbf{K}, \alpha} E_\alpha(\mathbf{K}) \hat{d}_\alpha(\mathbf{K})^\dagger \hat{d}_\alpha(\mathbf{K}). \quad (1)$$

The first term is related with the isotropic radiation field (photons with wave vector  $\kappa$ , unit polarization vector  $\mathbf{e}_\sigma$ , and frequency  $\omega(\kappa) = |\kappa|\bar{c}/\eta$ , where  $\bar{c}$  is the velocity of light in vacuum and  $\eta$  is the refractive index). The second term describes the lattice vibrations (phonons belonging to the branch  $\nu$ , with wave vector  $\mathbf{q}$  and energy  $\hbar\omega_\nu(\mathbf{q})$ ) while the third one represents the excitations of the electronic subsystem, which we suppose to be Wannier-Mott excitons, characterized by a well defined wave vector  $\mathbf{K}$  and other quantum numbers labelled by  $\alpha \equiv (v, c, \lambda)$ ,  $v$  and  $c$  indicating the valence and conduction bands forming the exciton and  $\lambda$  being the quantum number associated with the relative motion between the electron and the hole. The energy  $E_\alpha(\mathbf{K})$  of these excitations can be expressed as:

$$E_\alpha(\mathbf{K}) \equiv E_\lambda^{(vc)}(\mathbf{K}) = E_g^{(vc)} + \Delta E_\lambda^{(vc)} + \frac{\hbar^2 K^2}{2M^{(vc)}}. \quad (2)$$

Here,  $E_g^{(vc)}$  is the gap energy between the bands forming the pair,  $M^{(vc)} = m_v + m_c$  the total exciton mass ( $m_v$  and  $m_c$  are the effective masses of the hole and the electron, respectively) and  $\Delta E_\lambda^{(vc)}$  is an energy term associated with the relative motion of the exciton. The

bands are assumed to be isotropic and parabolic.

The perturbation Hamiltonian  $\hat{H}_I$ , containing the interaction terms, can be decomposed as:

$$\hat{H}_I = \hat{H}_{E-R} + \hat{H}_{E-L}, \quad (3)$$

where  $\hat{H}_{E-R}$  corresponds to the interaction between the electronic system and the radiation field and  $\hat{H}_{E-L}$  is the interaction Hamiltonian of the electronic system with the lattice vibrations. The form of the matrix element for the interaction between the excitons and the radiation field, for allowed direct transitions, is<sup>[4]</sup>

$$T_\alpha^{(e\sigma)}(\kappa) = \left( \frac{e}{m_0} \right) \sqrt{\frac{2\pi\hbar}{\omega(\kappa)\eta^2}} \langle c | \mathbf{e}_\sigma \cdot \hat{\mathbf{p}} | v \rangle \varphi_\alpha(0)^* \quad (4)$$

$\varphi_\alpha(\mathbf{r})$  is the exciton envelope wave function,  $m_0$  and  $-e$  are the free electron mass and charge.

For the interaction between the excitons and long-wavelength optical phonons, the coupling factor  $S_{\alpha, \alpha'}^{(\nu)}(\mathbf{K}, \mathbf{K}')$  can be written in terms of the usual electron-phonon interaction potential  $\delta\phi^{(\nu)}$ , following Toyozawa's procedure<sup>[1,5]</sup>:

$$S_{\alpha, \alpha'}^{(\nu)}(\mathbf{K}, \mathbf{K}') = \langle c' | \delta\phi^{(\nu)} | c \rangle \delta_{v, v'} I_{\alpha, \alpha'}(-\mathbf{q}^{(e)}) - \delta_{c', c} \langle v | \delta\phi^{(\nu)} | v' \rangle I_{\alpha, \alpha'}(\mathbf{q}^{(h)}) \quad (5)$$

The first term in Eq. (5) refers to the scattering by the electron and the second one corresponds to the scattering by the hole. The vectors  $\mathbf{q}^{(e)}$  and  $\mathbf{q}^{(h)}$  are defined as:

$$\mathbf{q}^{(e)} = \frac{m_v}{m_v + m_c} \mathbf{K} - \frac{m_{v'}}{m_{v'} + m_{c'}} \mathbf{K}' \quad ; \quad \mathbf{q}^{(h)} = \frac{m_c}{m_v + m_c} \mathbf{K} - \frac{m_{c'}}{m_{v'} + m_{c'}} \mathbf{K}' \quad (6)$$

The matrix element between the envelope functions is:

$$I_{\alpha,\alpha'}(\mathbf{q}) = \int d^3\mathbf{r} \varphi_{\lambda'}^{(v'c')}(\mathbf{r})^* e^{i\mathbf{q}\cdot\mathbf{r}} \varphi_{\lambda}^{(vc)}(\mathbf{r}) \quad (7)$$

Two kinds of electron-phonon interaction of very different nature are taken into account ( $\delta\phi^{(\nu)} = \delta\phi_{DP}^{(\nu)} + \delta\phi_F^{(LO)}\delta_{\nu,LO}$ ). On one hand, we have the deformation potential interaction,  $\delta\phi_{DP}^{(\nu)}$  ( $\nu = LO, TO$ ), related to

$$\langle v' | \delta\phi_{DP}^{(\nu)} | v \rangle = \frac{\bar{u}_0\sqrt{3}}{2a_0} \langle v' | \hat{D}_h^{(\nu)} | v \rangle \quad ; \quad \bar{u}_0 = \sqrt{\frac{\hbar V_c}{2VM^*\omega_\nu}} \quad , \quad (8)$$

where  $a_0$  is the lattice constant,  $V_c = a_0^3/4$  the volume of the primitive cell,  $V$  the crystal volume,  $M^*$  the reduced mass of the atoms contributing to the optical mode, and  $\hat{D}_h^{(\nu)}$  the deformation potential as defined by Bir and Pikus<sup>[6]</sup>. For Fröhlich interaction:

$$\langle j | \delta\phi_F^{(LO)} | j' \rangle = \frac{1}{\sqrt{V}} \frac{C_F^*}{|\mathbf{q}|} \delta_{j,j'} \quad ; \quad C_F = -i \sqrt{2\pi\hbar\omega_{LO}e^2 \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right)} \quad , \quad (9)$$

$\varepsilon_0$  and  $\varepsilon_\infty$  being the low frequency (static) and high frequency (optic) limits of the dielectric function, respectively. In covalent semiconductors, such as Si and Ge,  $\delta\phi_F^{(LO)}$  vanishes and  $\delta\phi^{(\nu)}$  becomes  $\delta\phi_{DP}^{(\nu)}$ .

The Raman process by two phonons can be interpreted as an elementary quantum transition between the initial state

$$|I\rangle = |I\rangle_R \otimes |I\rangle_L \otimes |0\rangle_E \quad (10)$$

and the final state

$$|F\rangle = \hat{a}_{e_s}(\kappa_s)^\dagger \hat{b}_{\nu_2}(\mathbf{q}_2)^\dagger \hat{b}_{\nu_1}(\mathbf{q}_1)^\dagger \hat{a}_{e_l}(\kappa_l) |I\rangle \quad . \quad (11)$$

$|I\rangle_R$  and  $|I\rangle_L$  are the initial states of the radiation field and the vibrational system, respectively, in the occupation number representation,  $|0\rangle_E$  the electronic ground

state (a set of filled valence bands and empty conduction bands) and the subscripts  $l$  and  $s$  refer to laser and scattered radiation, respectively.

The measured quantity in a Raman scattering experiment is the scattering efficiency, which can be written in terms of  $\mathcal{P}_{FI}$ , the probability per unit time for the quantum transition from  $|I\rangle$  to  $|F\rangle$ <sup>[7]</sup>:

$$\frac{d^2S}{d\Omega_s d\omega_s} = \frac{V}{(2\pi)^3} \frac{\omega_s^3}{\omega_l} \frac{\eta_l \eta_s^3}{c^4} \sum_F \mathcal{P}_{FI} \quad . \quad (12)$$

The sum over final states, in the case of second-order RRS, is a sum over phonon wave vectors ( $\sum_F = \sum_{\mathbf{q}}$ ); in the dipole approximation  $\kappa_l \simeq 0 \simeq \kappa_s$ . A second-order Raman process can be treated in fourth-order perturbation theory, and the probability amplitude  $W_{FI}$  is then given by

$$W_{FI} = \left\langle F \left| \hat{H}_I \frac{1}{\hbar\omega_l - \hat{H}_0} \hat{H}_I \frac{1}{\hbar\omega_l - \hat{H}_0} \hat{H}_I \frac{1}{\hbar\omega_l - \hat{H}_0} \hat{H}_I \right| I \right\rangle \quad ,$$

which is related to  $\mathcal{P}_{FI}$  through the Fermi Golden rule.

The final expression for the RSE is:

$$\frac{dS}{d\Omega_s} = r_e^2 \left( \frac{\omega_s}{\omega_l} \right)^2 \frac{\eta_s}{\eta_l} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \left| \mathcal{W}^{(\nu_1, \nu_2)}(\mathbf{q}) \right|^2 \quad , \quad (13)$$

$$\mathcal{W}^{(\nu_1, \nu_2)}(\mathbf{q}) = \sum_{\alpha_1, \alpha_2, \alpha_3} \frac{\langle c_1 | e_l \cdot \hat{\mathbf{p}} | v_1 \rangle \langle v_3 | e_s^* \cdot \hat{\mathbf{p}} | c_3 \rangle}{m_0} \frac{\varphi_{\alpha_1}(0)^*}{\hbar\omega_l - \tilde{E}_{\alpha_1}(0)} \frac{\varphi_{\alpha_3}(0)}{\hbar\omega_s - \tilde{E}_{\alpha_3}(0)} \times \left[ \frac{S_{\alpha_1, \alpha_2}^{(\nu_1)}(0, -\mathbf{q}) S_{\alpha_2, \alpha_3}^{(\nu_2)}(-\mathbf{q}, 0)}{\hbar\omega_l - \hbar\omega_{\nu_1} - \tilde{E}_{\alpha_2}(-\mathbf{q})} + \left( \begin{matrix} \nu_1 \leftrightarrow \nu_2 \\ \mathbf{q} \leftrightarrow -\mathbf{q} \end{matrix} \right) \right], \quad (14)$$

where  $r_e = e^2/m\tilde{c}^2$  is the classical electron radius and the complex energies  $\tilde{E}_\alpha(\mathbf{K}) \equiv E_\alpha(\mathbf{K}) - i\Gamma_\alpha(\mathbf{K})$  include the broadening  $\Gamma_\alpha(\mathbf{K})$  of the excitonic states. The conservation of energy,  $\hbar\omega_s = \hbar\omega_l - \hbar\omega_{\nu_1} - \hbar\omega_{\nu_2}$ , is implicitly understood. This expression allows to treat in a unified manner the Raman scattering by *LO* and *TO*-phonons. Three cases can be distinguished experimentally because of their different Raman shifts:

#### A. RRS by one *LO*- and one *TO*-phonon.

The *TO*-phonon is necessarily emitted via deformation potential interaction, but there are two possibilities for the *LO*-phonon emission. It can occur i) via deformation potential (*LO(DP)* + *TO(DP)*) or ii) via Fröhlich interaction (*LO(F)* + *TO(DP)*).

#### B. RRS by two *LO*-phonons.

In this case, several possibilities exist: i) the two *LO*-phonons can be emitted via the same interaction, either Fröhlich (*2LO(F)*) or deformation potential interaction (*2LO(DP)*) or ii) each phonon is scattered via a different interaction mechanism (*LO(F)* + *LO(DP)*).

#### C. RRS by two *TO*-phonons.

Here the scattering of the two phonons is necessarily via deformation potential interaction (*2TO(DP)*). The *2TO(DP)* process is isomorphic to the *2LO(DP)* one: if the bands mediating the process are the same, one does not expect different features as far as the shape of the resonance profile is concerned. The only difference is that in the Raman spectrum the corresponding Stokes shifts would be different.

To illustrate the theoretical results we choose the parameters of a zincblende compound semiconductor, namely ZnSe<sup>[8]</sup>. A zincblende semiconductor has three valence bands: heavy holes (*hh*), light holes (*lh*) and

split-off holes (*so*). Thus, three different excitonic branches (heavy, light and split-off excitons) participate in the scattering process. Fig. 1 shows the resonance profile calculated around the  $E_0$  cp for three kinds of Raman processes described above (*2LO(F)*, *LO(F)* + *TO(DP)* and *2TO(DP)*). We observe in all of them a weak incoming resonance when the laser energy matches the *1s* level of the exciton ( $\hbar\omega_l = E_{1s} = E_0 - R_{hh}$ ,  $R_{hh}$  being the binding energy of the heavy exciton) and a stronger outgoing resonance ( $\hbar\omega_s = E_{1s}$ ), that occurs at different laser energies depending on the Raman process considered, due to the fact that the phonons involved have different energies. We note also the relative importance of Fröhlich interaction as compared to deformation potential: the most intense resonance profile corresponds to *2LO(F)*.

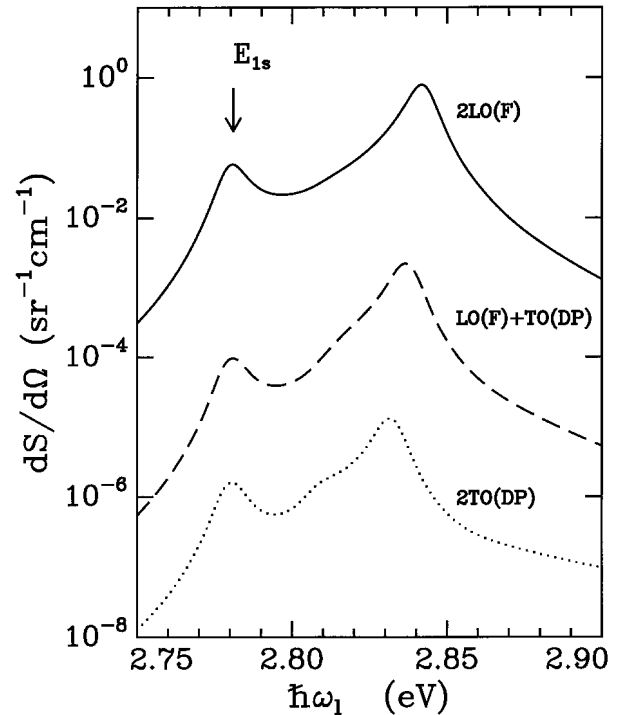


Figure 1. Calculated resonance profiles of *2LO(F)*, *LO(F)* + *TO(DP)* and *2TO(DP)* RRS. The parameters used correspond to ZnSe (Ref. [8]).

Fig. 2 shows the comparison between the theoretical model (solid lines) and the experimental results (full circles) obtained for the  $2LO(F)$  RSE in ZnTe<sup>[9]</sup>. In order to emphasize the role of excitonic effects, we represent also the results obtained by considering uncorrelated electron-hole pairs as intermediate states in the Raman process (dashed line)<sup>[10]</sup>. It is evident that the Raman efficiency obtained with the excitonic model is in much better agreement with the experimental profile, both in shape and absolute value, than the calculations for uncorrelated electrons.

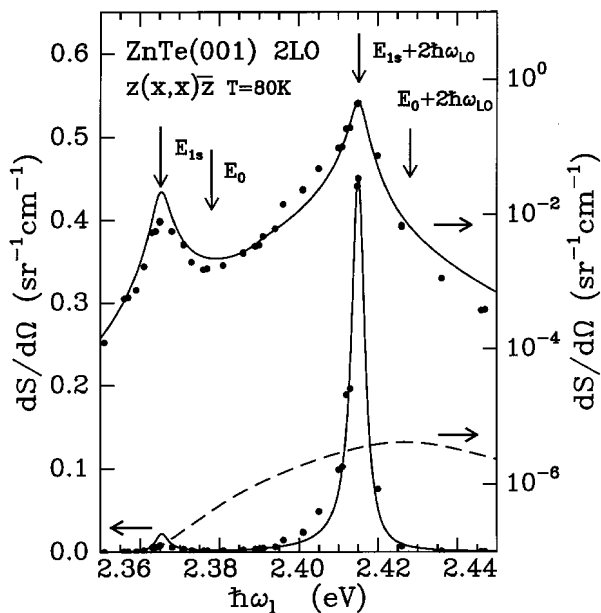


Figure 2. Resonant Raman scattering efficiency for  $2LO(F)$  RRS in ZnTe around the  $E_0$  critical point. The horizontal arrows indicate the scale (linear or logarithmic) to which the different curves refer. We need to multiply the theoretical result only by a scale factor of 1.5 in order to achieve the experimental absolute value.

In the foregoing discussion we have established a general treatment enabling us to obtain the second-order RSE including excitonic effects around the  $E_0$  and  $E_0 + \Delta_0$  cp's in III-V and II-VI semiconductor compounds. To check its validity, the model has been tested in ZnTe, where it successfully fit the experimental results.

## References

1. A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).
2. W. Kauschke, M. Cardona and E. Bauser, Phys. Rev. B **35**, 8030 (1987).
3. C. Trallero-Giner, A. Cantarero and M. Cardona, Phys. Rev. B **40**, 4030 (1989).
4. R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
5. Y. Toyozawa, Prog. Theor. Phys. **20**, 53 (1958).
6. G. L. Bir and G. E. Pikus, *Symmetry and Strain-induced Effects in Semiconductors*, (John Wiley & Sons, New York, 1974).
7. A. García-Cristóbal, A. Cantarero, C. Trallero-Giner and M. Cardona, Phys. Rev. B **49**, 13 430 (1994).
8. W. Limmer, H. Leiderer, K. Jakob, W. Gebhardt, W. Kauschke, A. Cantarero and C. Trallero-Giner, Phys. Rev. B **42**, 11 325 (1990).
9. A. García-Cristóbal, A. Cantarero, C. Trallero-Giner and W. Limmer, unpublished.
10. R. Zeyher, Phys. Rev. B **9**, 4439 (1974).