

THEORY OF ENHANCED RAMAN SCATTERING AND VIRTUAL QUASIPARTICLES IN CRYSTALS*

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(Received 15 July 1966)

The purpose of this paper is to provide an explanation for the enhanced Raman-scattering cross sections in CdS recently reported by Leite and Porto and to point out the likely generality of the phenomenon involved.

We have reformulated the theory of the first-order Raman scattering in crystals. In the existing theory of Loudon,¹ the intermediate states are the free electron and hole Bloch functions. In our theory, we use the exciton representation, where the electron-hole Coulomb interaction is always present. This will be relevant to explain the enhanced Raman scattering recently reported by Leite and Porto.²

The total Hamiltonian of the system can be taken as

$$\mathcal{H}_{\text{tot}} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)}, \quad (1)$$

where

$$\begin{aligned} \mathcal{H}^{(0)} &= \mathcal{H}_{\text{exciton}} + \mathcal{H}_{\text{phonon}} + \mathcal{H}_{\text{radiation}}, \\ \mathcal{H}^{(1)} &= \mathcal{H}_{\text{ep}}^{(1)} + \mathcal{H}_{\text{er}}^{(1)}, \\ \mathcal{H}^{(2)} &= \mathcal{H}_{\text{ep}}^{(2)} + \mathcal{H}_{\text{er}}^{(2)}. \end{aligned}$$

$\mathcal{H}_{\text{exciton}}$, $\mathcal{H}_{\text{phonon}}$, and $\mathcal{H}_{\text{radiation}}$ are the uncoupled exciton, phonon, and photon Hamiltonians. We use the formalism of second quantization, and the Hamiltonian is written in terms

of the destruction and creation operators for exciton, phonon, and photon. $\mathcal{H}_{\text{er}}^{(1)}(\mathcal{H}_{\text{ep}}^{(1)})$ is the exciton-radiation (exciton-phonon) interaction term, which is linear in both exciton and photon (phonon) operators. $\mathcal{H}_{\text{er}}^{(2)}(\mathcal{H}_{\text{ep}}^{(2)})$ is the interaction term, which is bilinear in exciton operator but linear in photon (phonon) operators. Deformation potential approximation is used for \mathcal{H}_{ep} . The coupling parameters for the various interactions are obtained by a procedure similar to that of Toyozawa.³

We now make a canonical transformation of the total Hamiltonian such that the terms linear in exciton operators are eliminated. The transformed Hamiltonian $\hat{\mathcal{H}}$ is

$$\begin{aligned} \hat{\mathcal{H}} &= e^{-iS} \mathcal{H}_{\text{tot}} e^{+iS} \\ &= \mathcal{H}_{\text{tot}} - i[S, \mathcal{H}_{\text{tot}}] - \frac{1}{2}[S, [S, \mathcal{H}_{\text{tot}}]] \\ &\quad + (i/6)[S, [S, [S, \mathcal{H}_{\text{tot}}]]] - \dots, \quad (2) \end{aligned}$$

where S is chosen such that

$$i[S, \mathcal{H}^{(0)}] = \mathcal{H}^{(1)}. \quad (3)$$

Then

$$\begin{aligned} \hat{\mathcal{H}} &= \mathcal{H}^{(0)} + \mathcal{H}^{(2)} - (i/2)[S, \mathcal{H}^{(1)}] - i[S, \mathcal{H}^{(2)}] - \frac{1}{3}[S, [S, \mathcal{H}^{(1)}]] \\ &\quad - \frac{1}{2}[S, [S, \mathcal{H}^{(2)}]] + (i/6)[S, [S, \mathcal{H}^{(1)}]] + (i/6)[S, [S, [S, \mathcal{H}^{(2)}]]] - \dots. \quad (4) \end{aligned}$$

First-order Raman effect occurs due to the terms in the commutator⁴ $[S, [S, \mathcal{H}^{(2)}]]$.

The initial state of the system will be specified by $|i\rangle = |n_i; n_s; n_0; 0\rangle$, where n_i , n_s , and n_0 are the numbers of the incident photons, the scattered photons, and phonons. The zero in the ket refers to the ground electronic state, where no excitons are present. The final state after Raman scattering will be $|f\rangle = |n_i - 1; n_s + 1; n_0 + 1; 0\rangle$. Since we consider spontaneous Raman scattering, n_s will be taken to be zero. The transition probability per unit time from the initial to the final state in the case of nonpolar optic vibration is

$$W = \frac{2\pi}{\hbar^2} \sum_{\vec{\eta}, \vec{\chi}_S} |\langle f | \frac{1}{2}[S, [S, \mathcal{H}^{(2)}]] | i \rangle|^2 \delta(\omega_i - \omega_s - \omega_0). \quad (5)$$

Using the explicit forms of S and $\mathcal{H}^{(2)}$, we finally get

$$W = \frac{4\pi^3 e^4}{\hbar^3 m^2 a_0^2 \kappa^2 M N} \sum_{\vec{\eta}, \vec{\chi}_S} \frac{n_i (n_0 + 1)}{\omega_i \omega_s \omega_0} \left| \sum_{j=x,y,z} \xi_0^{(j)} R_{is}^{(j)} \right|^2 \frac{(2\pi)^3}{V} \delta(\vec{\chi}_i - \vec{\chi}_s - \vec{\eta}) \delta(\omega_i - \omega_s - \omega_0), \quad (6)$$

where a_0 is the lattice constant, V the volume of the crystal, κ the dielectric constant, and N the number of unit cells. $1/M = 1/M_1 + 1/M_2$, where M_1 and M_2 are the masses of the two sublattices; $\vec{\eta}$, $\vec{\chi}_i$, $\vec{\chi}_s$ are the wave vectors of phonon, the incident photon, and the scattered photon respectively; and ω_0 , ω_i , ω_s , and $\vec{\epsilon}_i$, $\vec{\epsilon}_s$, $\vec{\xi}_0$ are the corresponding frequencies and unit polarization vectors, respectively. $R_{is}^{(j)}$ in Eq. (6) is the Raman tensor which is given by

$$R_{is}^{(j)}(-\omega_i, \omega_s, \omega_0) = \frac{N\hbar^2}{V} \sum_{\substack{\lambda, c, v \\ \lambda', c', v'}} \left\{ U_{c, v, \lambda, \vec{\chi}_s}^{(0)} U_{c', v', \lambda', \vec{\chi}_i}^{*(0)} \right. \\ \left. \times \frac{\langle v | \vec{\epsilon}_s \cdot \vec{p} | c \rangle \langle c | D^{(j)} | c' \rangle q_e \delta_{vv'} - \langle v | D^{(j)} | v' \rangle q_h \delta_{cc'}}{[E_{\lambda, \vec{\chi}_s}(c, v) - \hbar\omega_s][E_{\lambda', \vec{\chi}_i}(c', v) - \hbar\omega_i]} + \text{five other terms} \right\}, \quad (7)$$

where $U_{cv\lambda\vec{K}}$ and $E_{\lambda\vec{K}}(c, v)$ are the wave function and the energy, respectively, of the exciton with inner quantum number λ and wave vector \vec{K} . The conduction and the valence bands are denoted by c and v , and q_e and q_h are given by

$$q_e = \sum_{\vec{\beta}} U_{cv\lambda\vec{K}}(\vec{\beta}) U_{c'v'\lambda'\vec{K}'}(\vec{\beta}) e^{i(\vec{K}-\vec{K}')\cdot\vec{\beta}}, \quad q_h = \sum_{\vec{\beta}} U_{cv\lambda\vec{K}}^*(\vec{\beta}) U_{c'v'\lambda'\vec{K}'}(\vec{\beta}).$$

When $c=c'$, $v=v'$, and $\vec{K}-\vec{K}' \rightarrow 0$, it can be shown that $q_e=q_h=1$. In Eq. (7), $\vec{\chi}_i$, $\vec{\chi}_s$, and $\vec{\eta}$ will be assumed to be zero, which is a good approximation for first-order Raman effect. Further, the wave-vector dependence of the matrix elements of the deformation potential (Bir and Pikus⁵) $D^{(j)}$ and $\vec{\epsilon} \cdot \vec{p}$ are neglected. We have shown only the dominant term in the expression for $R_{is}^{(j)}$.

We calculate $R_{is}^{(j)}$ approximately for a two-band model involving the highest valence band and the lowest conduction band. Assume that the bands are parabolic. We may then use hydrogenic wave functions and eigenvalues for U and E . Thus we obtain

$$R_{is}^{(j)} \sim [\langle v | \epsilon_s \cdot p | c \rangle \langle c | D^{(j)} | c \rangle - \langle v | D^{(j)} | v \rangle \langle c | \vec{\epsilon}_i \cdot \vec{p} | v \rangle] \left\{ \frac{\hbar^2}{\pi a^3} \sum_n \frac{1}{n^3 (\hbar\omega_g - R/n^2 - \hbar\omega_s) (\hbar\omega_g - R/n^2 - \hbar\omega_i)} \right. \\ \left. + \frac{1}{4\pi\omega_0} \left(\frac{2\mu}{\hbar} \right)^{3/2} \left(\frac{2\pi R}{\hbar} \right)^{1/2} \left[\left(1 - \exp \left[- \left(\frac{2\pi R}{\hbar\omega_g - \hbar\omega_s} \right)^{1/2} \right] \right)^{-1} - \left(1 - \exp \left[- \left(\frac{2\pi R}{\hbar\omega_g - \hbar\omega_i} \right)^{1/2} \right] \right)^{-1} \right] \right\}, \quad (9)$$

where $\hbar\omega_g$ is the band gap. R , μ , and a are the Rydberg exciton, effective exciton mass, and exciton Bohr radius for $n=1$. The first term inside the curly bracket in Eq. (9) arises from the discrete exciton states and the second term from the continuum.

Two limiting cases may now be considered: (i) When $\hbar\omega_g - \hbar\omega_i \gg 2\pi R$, we get

$$R_{is}^{(j)} \sim p_{0\alpha}^{(s)} \sum_{\alpha\alpha}^{(j)} p_{\alpha 0}^{(i)} \left\{ \pi a^3 (\omega_g - \omega_i) (\omega_g - \omega_i + \omega_0)^{-1} \sum_n \frac{1}{n^3} \right. \\ \left. + \frac{1}{4\pi\omega_0} \left(\frac{2\mu}{\hbar} \right)^{3/2} [(\omega_g - \omega_i + \omega_0)^{1/2} - (\omega_g - \omega_i)^{1/2}] \right\}, \quad (10)$$

where the matrix elements are written in Loudon's¹ notation. In this limit the first term is small compared with the second, and we obtain Loudon's result.

(ii) $\hbar\omega_g - \hbar\omega_i \cong R$. In this limit all terms in Eq. (9) are finite, except the term with $n=1$ (in the summation), and $R_{is}^{(j)}$ diverges as

$$R_{is}^{(j)} \sim [p_{0\alpha}^{(s)} \sum_{\alpha\alpha}^{(j)} p_{\alpha 0}^{(i)} / \pi a^3][(\omega_g - R/\hbar - \omega_i + \omega_0) (\omega_g - R/\hbar - \omega_i)]^{-1}, \quad (11)$$

which agrees with the result of Grecho and Ovander⁶ without damping, but does not agree with Loudon's result.

For transverse polar optic vibration, the Raman tensor is the same as in Eq. (7), but for longitudinal polar optic vibration, there is an additional contribution to the Raman tensor due to the associated electric field. This can be accounted for by using Frohlich⁷ interaction for H_{ep} . The transition probability per unit time due to this term alone is found to be

$$W' = \frac{(2\pi)^4 e^6}{\hbar^3 m^6 \kappa^2 V} \left(\frac{1}{\kappa} - \frac{1}{\kappa_0} \right) \sum_{\vec{\eta}, \vec{\chi}_S} \frac{n_i (n_l + 1) \omega_l}{\omega_i \omega_s} |p_{is}^{\vec{\eta}}(-\omega_i, \omega_s, \omega_l)|^2 \frac{(2\pi)^3}{V} \delta(\vec{\chi}_i - \vec{\chi}_s - \vec{\eta}) \delta(\omega_i - \omega_s - \omega_l), \quad (12)$$

where

$$p_{is}^{\vec{\eta}} = \frac{N \hbar^3}{V} \sum_{\substack{\lambda c v \\ \lambda' c' v'}} \left\{ \text{terms similar to that of Eq. (7) in which } \langle n | D^{(i)} | n' \rangle \text{ is replaced by } \frac{\langle n | \hat{\eta} \cdot \vec{p} | n' \rangle}{E_n - E_{n'}} \right\}.$$

Here κ_0 is the static dielectric constant, $\hat{\eta}$ is a unit vector in the direction of $\vec{\eta}$, and \sum' means that the term with $c=c'$, $v=v'$ simultaneously is omitted. So we cannot make a simple two-band calculation for $p_{is}^{\vec{\eta}}$. However, near resonance, $p_{is}^{\vec{\eta}}$ will diverge as $(\omega_g - R/\hbar - \omega_i)^{-1}$ in disagreement with both Ovander and Grechko, who predict a $(\omega_g - \omega_i)^{-2}$ divergence, and Loudon, who predicts a $(\omega_g - \omega_i)^{1/2}$ behavior.

Equation (11) explains the experimental results of Leite and Porto² on CdS. The value of 2.521 eV at 77°K that they obtained for the intermediate state should correspond to the intermediate exciton state according to our theory. Thomas, Hopfield, and Powell⁸ obtained a value of 2.544 eV at 77°K for the exciton states in CdS from absorption experiments. The discrepancy between the two values suggests that the intermediate state involved in Raman scattering in CdS may not be simple exciton states, but some other elementary excitation such as coupled exciton phonon. Investigation along that line is proceeding.

We have also calculated the variation of the intensity of the scattered radiation from CdS when the incident energy of the photons is increased from 2.41 to 2.53 eV. We find that the intensity increases by a factor of 10^2 , whereas according to Loudon's theory the intensity increases by a factor of 4. Leite and Porto² report an appreciable increase in intensity ("at least one order of magnitude"). Accurate measurements of scattered intensity for various frequencies near resonance and for different materials are necessary to decide the

correct theory. We are applying our theory to other materials such as GaAs, Ge, etc., for which no experimental results have yet been reported.

We believe that the enhanced Raman scattering near resonance will provide a means of obtaining information about the intermediate quasiparticle states involved in the Raman scattering and the coupling among and between these states (e.g., electron-phonon, exciton-phonon, etc.). The details of our calculations will soon be sent for publication.

*This work supported in part by the Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson Air Force Base, Ohio, under Contract No. AF(33)(615)-1746 and the U. S. Army Research Office (Durham) under Grant No. DA-ARO-D-31-124-G792.

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