Theory of Lattice Raman Scattering in Insulators*

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The theory of Raman scattering by phonons in perfect insulator crystals is developed here. The Hamiltonian for the interacting system of electrons, phonons, and photons is written in second-quantized form, and a canonical transformation is performed to remove the lowest-order interactions. In the resulting transformed Hamiltonian, the terms causing Raman scattering can be identified. The basic electron-system eigenstates are taken in the Wannier exciton representation, including bound and continuum states. The frequency dependence of the components of the Raman tensor is obtained for single-phonon and two-phonon overtone scattering. As a function of incident photon energy, the Raman tensor has poles at energies corresponding to creation of quasiparticles (e.g., virtual excitons). This produces a particularly important effect in resonance Raman scattering, where the creation of virtual excitons dominates the scattering process. Some numerical estimates for single and overtone resonant-Raman-scattering efficiencies are given for CdS and GaAs, and are compared with available experiments. The use of the resonance Raman effect as a probe of quasiparticles is suggested.

I. INTRODUCTION

WE have reformulated the theory of lattice Raman effect[1] in perfect crystals. In the Raman effect in crystals, a photon is scattered producing a change in the vibrational state of the lattice, but the electronic states remain unchanged. However, the virtual intermediate states involve the excitation of the electrons. We assume that the virtual intermediate states are the exciton states because the Coulomb interaction is always present between the electrons and the holes. Each elementary Raman scattering consists of the three real transitions: (1) the absorption of the incident photon, (2) the emission or absorption of phonons, and (3) the emission of the scattered photon. These real transitions are accompanied by virtual exciton transitions in which an exciton is created, then the exciton is scattered, and finally it is destroyed returning the electronic system to its ground state. The real transitions can occur in any time order. In his theory, Loudon[2] assumes that the virtual intermediate states are free-electron–hole pairs. Grechko and Ovander[3] explained the Raman scattering in molecular crystals as the decay of the polaritons.

The Hamiltonian is written in Sec. II in the second quantized form for electrons, photons, and phonons. The electrons are represented in Wannier exciton representation. A canonical transformation[4] is performed to remove the lowest-order interaction terms in the Hamiltonian, and the remaining Hamiltonian is then taken as producing transitions between states of the free Hamiltonian.

In Sec. III we obtain the first-order Raman tensor and show its frequency dependence and symmetry. In Sec. IV we derive the second-order Raman tensor for the overtones only. We then discuss our theory and compare with the meager experiments now available. We make specific recommendations for the experiments to be carried out.

II. THE HAMILTONIAN AND METHOD OF CANONICAL TRANSFORMATION

We consider an insulator with two ions[5] per unit cell of mass M_1 and M_2. The total Hamiltonian is taken as

$$H=H^{(0)}+H^{(1)}+H^{(2)}+H^{(3)}, \tag{1}$$

where the unperturbed Hamiltonian $H^{(0)}$ is

$$H^{(0)}=H_e+H_L+H_R, \tag{2}$$

with[5a]

$$H_e=\sum_{cv\lambda\mathbf{K}} E_{\lambda\mathbf{K}}(c,v)a_{\lambda\mathbf{K}}{}^{\dagger}(cv)a_{\lambda\mathbf{K}}(cv), \tag{3}$$

$$H_L=\sum_{\eta\xi} \hbar\omega_{\eta\xi}(b_{\eta\xi}{}^{\dagger}b_{\eta\xi}+\tfrac{1}{2}), \tag{4}$$

$$H_R=\sum_{\chi\epsilon} \hbar\omega_{\chi\epsilon}(A_{\chi\epsilon}{}^{\dagger}A_{\chi\epsilon}+\tfrac{1}{2}). \tag{5}$$

Here $a_{\lambda\mathbf{K}}{}^{\dagger}(cv)$ and $a_{\lambda\mathbf{K}}(cv)$ are the creation and the annihilation operators for the excitons having inner quantum-number λ and wave vector $\mathbf{K}$ formed from conduction band c and valence band v. $E_{\lambda\mathbf{K}}(cv)$ denotes the energy of the excitons. For parabolic bands, $E_{\lambda\mathbf{K}}(cv)$ is given by

$$E_{n,\mathbf{K}}(cv)=Eg+\hbar^2|\mathbf{K}|^2/2(m_e{}^*+m_h{}^*)-R/n^2, \tag{6a}$$

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[1] J. L. Birman and A. K. Ganguly, Phys. Rev. Letters **17**, 647 (1966).

[2] R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963).

[3] L. G. Grechko and L. N. Ovander, Fiz. Tverd. Tela **4**, 157 (1961) [English transl.: Soviet Phys.—Solid State **4**, 112 (1962)].

[4] J. L. Birman, J. Phys. Radium **26**, 735 (1965). Preliminary results of the present approach were presented at the International Conference on Scattering Spectra of Solids, 1965, Paris (unpublished) and the abstract indicates the approach used.

[5] For crystals with more than two ions per unit cell, but having two sublattices, our theory is applicable to those modes of lattice vibrations in which ions of each sublattice move together.

[5a] Owing to typographical limitations, the vector subscripts $\boldsymbol{\epsilon}$, $\boldsymbol{\chi}$, $\boldsymbol{\eta}$, $\boldsymbol{\xi}$ will be printed in light face throughout this paper.

for discrete states with $n=1, 2, 3, \cdots$, and

$$E_{\mathbf{k},\mathbf{K}}(cv)=Eg+\hbar^2|\mathbf{K}|^2/2(m_e^*+m_h^*)+\hbar^2|\mathbf{k}|^2/2\mu \quad (6b)$$

for continuum. The exciton rydberg $R=\mu e^4/2\hbar^2\kappa^2$, where κ is the dielectric constant. The reduced mass is $1/\mu=1/m_e^*+1/m_h^*$, where m_e^* and m_h^* are the effective masses of the electron and the hole. Eg is the energy gap between the c and v bands. χ, ε, and ω_χ stand, respectively, for the wave vector, unit polarization vector, and frequency of the photons. The corresponding quantities for the phonons are denoted by η, ξ, and ω_η. We assume that in the optical branch ω_η is independent of η for small wave vectors. $\omega_\chi=(c/\kappa_\infty^{1/2})|\chi|$, where κ_∞ is the optical dielectric constant and c is the velocity of light in vacuum. $b_{\eta\xi}^\dagger$, $b_{\eta\xi}$ and $A_{\chi\epsilon}^\dagger$, $A_{\chi\epsilon}$ are the creation and the annihilation operators of the phonons and the photons. The commutation relations for the operators are

$$[b_{\eta\xi},b_{\eta'\xi'}^\dagger]=\delta_{\eta\eta'}\delta_{\xi\xi'}, \quad (7a)$$

$$[A_{\chi\epsilon},A_{\chi'\epsilon'}^\dagger]=\delta_{\chi\chi'}\delta_{\epsilon\epsilon'}, \quad (7b)$$

$$[a_{\lambda\mathbf{K}}(cv),a_{\lambda'\mathbf{K}'}^\dagger(c'v')]=\delta_{cc'}\delta_{vv'}\delta_{\lambda\lambda'}\delta_{\mathbf{K}\mathbf{K}'}+0\left(\frac{\text{number of electron-hole pairs}}{N}\right). \quad (7c)$$

We will assume the excitons to be almost bosons since the number of excitons will be zero or unity in the electronic states of interest to us. The perturbation terms $H^{(1)}$, $H^{(2)}$, and $H^{(3)}$ are given by

$$H^{(1)}=H_{eL}^{(1)}+H_{eR}^{(1)}, \quad (8a)$$

$$H^{(2)}=H_{eL(1)}{}^{(2)}+H_{eL(2)}{}^{(2)}+H_{eR}^{(2)}, \quad (8b)$$

$$H^{(3)}=H_{eL}^{(3)}, \quad (8c)$$

where H_{eL} is the exciton-phonon interaction and H_{eR} is the exciton-radiation interaction. $H_{eL}^{(1)}$ is linear in both exciton and phonon operators; this term creates or annihilates an exciton emitting a phonon. $H_{eL(1)}{}^{(2)}$ is linear in phonon operator but bilinear in exciton operators; this term scatters an exciton and emits a phonon. $H_{eL(2)}{}^{(2)}$ is bilinear in phonon operators but linear in exciton operators which creates two phonons simultaneously and creates or annihilates an exciton. $H_{eL}^{(3)}$ is bilinear in both phonon and exciton operators. $H_{eR}^{(1)}$ is linear in both exciton and photon operators, whereas $H_{eR}^{(2)}$ is linear in photon but bilinear in exciton operators. The specific forms of the interaction terms are given below.

$$H_{eL}^{(1)}=\sum_{\substack{c,v,\lambda,\mathbf{K}\\ \eta,\xi}}\{g_{\eta,\xi}(cv\lambda\mathbf{K})a_{\lambda,\mathbf{K}}^\dagger(cv)b_{\eta\xi}^\dagger\delta_{\mathbf{K},-\eta}+g_{\eta,\xi}^*(cv\lambda\mathbf{K})a_{\lambda,\mathbf{K}}(cv)b_{\eta,\xi}^\dagger\delta_{\mathbf{K},\eta}\}, \quad (9a)$$

$$H_{eL(1)}{}^{(2)}=\sum_{\substack{cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}'\\ \eta\xi}}G_{\eta,\xi}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')a_{\lambda\mathbf{K}}^\dagger(cv)a_{\lambda'\mathbf{K}'}(c'v')b_{\eta\xi}^\dagger\delta_{\mathbf{K}-\mathbf{K}',-\eta}, \quad (9b)$$

$$H_{eL(2)}{}^{(2)}=\sum_{\substack{cv\lambda\mathbf{K}\\ \eta\xi\eta'\xi'}}\{d_{\eta\xi,\eta'\xi'}(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}^\dagger(cv)b_{\eta\xi}^\dagger b_{\eta'\xi'}^\dagger\delta_{\mathbf{K},-(\eta+\eta')}+d_{\eta\xi\eta'\xi'}^*(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}(cv)b_{\eta\xi}^\dagger b_{\eta'\xi'}^\dagger\delta_{\mathbf{K},\eta+\eta'}\}, \quad (9c)$$

$$H_{eL}^{(3)}=\sum_{\substack{cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}'\\ \eta\xi\eta'\xi'}}D_{\eta\xi\eta'\xi'}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')a_{\lambda\mathbf{K}}^\dagger(cv)a_{\lambda'\mathbf{K}'}(c'v')b_{\eta\xi}^\dagger b_{\eta'\xi'}^\dagger\delta_{\mathbf{K}-\mathbf{K}',-(\eta+\eta')}, \quad (9d)$$

and the exciton-photon interaction is

$$H_{eR}^{(1)}=\sum_{\substack{cv\lambda\mathbf{K}\\ \chi\epsilon}}\{f_{\chi,\epsilon}(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}^\dagger(cv)A_{\chi\epsilon}\delta_{\mathbf{K},\chi}+f_{\chi\epsilon}^*(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}(cv)A_{\chi\epsilon}\delta_{\mathbf{K},-\chi}\}+\text{c.c.} \quad (9e)$$

$$H_{eR}^{(2)}=\sum_{\substack{cv\lambda\mathbf{K}\\ c'v'\lambda'\mathbf{K}'\\ \chi,\epsilon}}\{F_{\chi\epsilon}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')a_{\lambda\mathbf{K}}^\dagger(cv)a_{\lambda'\mathbf{K}'}(c'v')A_{\chi\epsilon}\delta_{\mathbf{K}-\mathbf{K}',\chi}+F_{\chi\epsilon}^*(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')a_{\lambda\mathbf{K}}(cv)a_{\lambda'\mathbf{K}'}^\dagger(c'v')A_{\chi\epsilon}\delta_{\mathbf{K}-\mathbf{K}',-\chi}\}+\text{c.c.} \quad (9f)$$

The perturbation terms (9a) and (9b) will give Stokes's lines. To get anti-Stokes's lines, we have to include terms with $b_{\eta\xi}$ in H_{eL}.

Assume that the perturbations affect H only through single-particle interactions. Thus we write the coupling parameters using Toyozawa's[6] procedure

$$g_{\eta\xi}(cv\lambda\mathbf{K})=\frac{1}{N^{1/2}}\sum_{\beta,\mathbf{k}}U_{cv\lambda\mathbf{K}}^*(\beta)e^{i\mathbf{k}\cdot\beta}\int\Psi_c^*(\mathbf{r},\mathbf{k})\delta\phi\Psi_v(\mathbf{r},\mathbf{k}-\mathbf{K})d\mathbf{r} \quad (10)$$

[6] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **20**, 53 (1958).

and

$$G_{\eta\xi}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=\frac{1}{N}\sum_{\beta,\beta',\mathbf{k}}U_{cv\lambda\mathbf{K}}{}^{*}(\beta)U_{c'v'\lambda'\mathbf{K}'}(\beta')e^{i(\mathbf{K}-\mathbf{K}')\cdot\beta'+i\mathbf{k}\cdot(\beta-\beta')}\int\Psi_{c}{}^{*}(\mathbf{r},\mathbf{k})\delta\phi\Psi_{c'}(\mathbf{r},\mathbf{k}-\mathbf{K}+\mathbf{K}')d\mathbf{r}\,\delta_{vv'}$$

$$-\frac{1}{N}\sum_{\beta,\beta',\mathbf{k}}U_{cv\lambda\mathbf{K}}{}^{*}(\beta)U_{c'v'\lambda'\mathbf{K}'}(\beta')e^{i(\mathbf{k}+\mathbf{K})\cdot(\beta-\beta')}\int\Psi_{v'}{}^{*}(\mathbf{r},\mathbf{k}+\mathbf{K}-\mathbf{K}')\delta\phi\Psi_{v}(\mathbf{r},\mathbf{k})d\mathbf{r}\,\delta_{cc'},\quad(11)$$

where $\Psi(\mathbf{r},\mathbf{k})$ are one-electron Bloch functions and $\delta\phi$ is the usual electron-lattice interaction for which deformation potential and polar interaction will be used. N is the number of unit cells in the crystal, and β is the electron-hole separation. $U_{cv\lambda\mathbf{K}}(\beta)$ is the wave function for the relative motion of the electron and the hole.

For long-wavelength optic mode of a lattice with two atoms per unit cell, the electron lattice interaction (Bir and Pikus)[7] is

$$\int\Psi_{n}{}^{*}(\mathbf{r},\mathbf{k})\delta\phi\Psi_{n'}(\mathbf{r},\mathbf{k}')d\mathbf{r}=\left(\frac{\hbar}{2MN\omega_{\eta}}\right)^{1/2}\frac{1}{a}\sum_{i}\xi_{\eta}{}^{(i)}\langle n\mathbf{k}|D^{(i)}|n',\mathbf{k}-\boldsymbol{\eta}\rangle,\quad 1/M=1/M_1+1/M_2.\quad(12)$$

$\xi^{(i)}$ are the x, y, and z components of $\boldsymbol{\xi}$. The deformation potential

$$D^{(i)}=\partial\phi_0/\partial(u_i/a),$$

where ϕ_0 is the equilibrium lattice potential and $\mathbf{u}=\mathbf{u}_1-\mathbf{u}_2$ is the relative displacement of the two sublattices; a is the lattice constant. If the wave vector dependence of the matrix elements of $D^{(i)}$ is neglected, then for long-wavelength optic phonons, we get

$$g_{\eta\xi}{}^{(\mathrm{op})}(cv\lambda\mathbf{K})=N^{1/2}\left(\frac{\hbar}{2MN\omega_{\eta\xi}}\right)^{1/2}\frac{1}{a}\sum_{i}\xi_{\eta}{}^{(i)}\langle c|D^{(i)}|v\rangle U_{cv\lambda\mathbf{K}}{}^{*}(0)\quad(13)$$

and

$$G_{\eta\xi}{}^{(\mathrm{op})}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=\left(\frac{\hbar}{2MN\omega_{\eta\xi}}\right)^{1/2}\frac{1}{a}\sum_{i}\xi_{\eta}{}^{(i)}[\langle c|D^{(i)}|c'\rangle q_{e}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\delta_{vv'}$$

$$-\langle v'|D^{(i)}|v\rangle q_{h}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\delta_{cc'}],\quad(14)$$

where

$$q_{e}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=\sum_{\beta}U_{cv\lambda\mathbf{K}}{}^{*}(\beta)U_{c'v'\lambda'\mathbf{K}'}(\beta)e^{i(\mathbf{K}-\mathbf{K}')\cdot\beta},\quad(15)$$

$$q_{h}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=\sum_{\beta}U_{cv\lambda\mathbf{K}}{}^{*}(\beta)U_{c'v'\lambda'\mathbf{K}'}(\beta).\quad(16)$$

If $c=c'$, $v=v'$, Ansel'm and Firsov[8] have shown that q_e and q_h depend on $\mathbf{K}-\mathbf{K}'$ only due to translational invariance; and in the limit $\mathbf{K}-\mathbf{K}'\to 0$, the following completeness relation is obtained:

$$q_{e}(cv\lambda\mathbf{K},cv\lambda'\mathbf{K}')=q_{h}(cv\lambda\mathbf{K},cv\lambda'\mathbf{K}')=1\text{ if }\lambda=\lambda'$$
$$=0\text{ if }\lambda\neq\lambda'.\quad(17)$$

Similarly, making the long-wave and momentum-independence assumptions,

$$d_{\eta\xi,\eta'\xi'}{}^{(\mathrm{op})}(cv\lambda\mathbf{K})=N^{1/2}\frac{\hbar}{2MN(\omega_{\eta\xi}\omega_{\eta'\xi'})^{1/2}}\frac{1}{a^2}\sum_{ij}\xi_{\eta}{}^{(i)}\xi_{\eta'}{}^{(j)}\langle c|D^{(ij)}|v\rangle U_{cv\lambda\mathbf{K}}{}^{*}(0)\quad(18)$$

and

$$D_{\eta\xi,\eta'\xi'}{}^{(\mathrm{op})}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=\frac{\hbar}{2MN(\omega_{\eta\xi}\omega_{\eta'\xi'})^{1/2}}\frac{1}{a^2}\sum_{ij}\xi_{\eta}{}^{(i)}\xi_{\eta'}{}^{(j)}[\langle c|D^{(ij)}|c'\rangle q_{e}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\delta_{vv'}$$

$$-\langle v'|D^{(ij)}|v\rangle q_{h}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\delta_{cc'}].\quad(19)$$

Here the deformation potential is

$$D^{(ij)}=\frac{\partial^2\phi_0}{\partial(u_i/a)\partial(u_j/a)}.$$

[7] G. L. Bir and G. E. Pikus, Fiz. Tverd. Tela **2**, 2287 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2039 (1961)].
[8] A. I. Ansel'm and Iu. A. Firsov, Zh. Eksperim. i Teor. Fiz. **28**, 151 (1955) [English transl.: Soviet Phys.—JETP **1**, 139 (1955)].

For polar crystals, there is an additional Fröhlich[9] electron lattice interaction for long-wavelength longitudinal optic phonons given by

$$\int \Psi_{n\mathbf{k}}^*(\mathbf{r})\delta\phi\Psi_{n'\mathbf{k}'}(\mathbf{r})d\mathbf{r}=\sum_{\boldsymbol{\eta}}\frac{ie}{|\boldsymbol{\eta}|}\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)^{1/2}\left(\frac{2\pi\hbar\omega_l}{V}\right)^{1/2}\langle n\mathbf{k}|e^{i\boldsymbol{\eta}\cdot\mathbf{r}}|n'\mathbf{k}'\rangle,$$

where V is the volume of the crystal, ω_l is the frequency of the longitudinal phonon, and κ_0 is the static dielectric constant. Because of translational symmetry, $\mathbf{k}'=\mathbf{k}+\boldsymbol{\eta}$, and if we let $\eta\to 0$, then the matrix element becomes diagonal in electron states. In such a case $g_{\eta\xi}^{(\mathrm{pol})}(cv\lambda\mathbf{K})=0$ and also

$$G_{\eta\xi}^{(\mathrm{pol})}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=G_{\eta\xi}^{(\mathrm{pol})}(cv\lambda\mathbf{K},cv\lambda'\mathbf{K}')\delta_{cc'}\delta_{vv'}=0,$$

using Eq. (17). As pointed out by Loudon,[2] we should expand $e^{i\boldsymbol{\eta}\cdot\mathbf{r}}$ and retain the term of lowest order in $\boldsymbol{\eta}$. Thus

$$g_{\eta_l}^{(\mathrm{pol})}(cv\lambda\mathbf{K})=ie\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)^{1/2}\left(\frac{2\pi\hbar\omega_l}{V}\right)^{1/2}N^{1/2}U_{cv\lambda\mathbf{K}}^*(0)\frac{\hbar\langle c|\hat{\boldsymbol{\eta}}\cdot\mathbf{p}|v\rangle}{m(\mathcal{E}_c-\mathcal{E}_v)},\tag{20}$$

and

$$G_{\eta_l}^{(\mathrm{pol})}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=ie\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)^{1/2}\left(\frac{2\pi\hbar\omega_l}{V}\right)^{1/2}\Bigg[q_e(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K})\frac{\hbar\langle c|\hat{\boldsymbol{\eta}}\cdot\mathbf{p}|c'\rangle}{m(\mathcal{E}_c-\mathcal{E}_{c'})}\delta_{vv'}-q_h(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\frac{\langle v'|\boldsymbol{\eta}\cdot\mathbf{p}|v\rangle}{m(\mathcal{E}_v-\mathcal{E}_{v'})}\delta_{cc'}\Bigg].\tag{21}$$

Here $\hat{\boldsymbol{\eta}}$ is a unit vector in the direction of $\boldsymbol{\eta}$. $\mathcal{E}_n$ is the energy at the bottom of band n. Since $\mathbf{p}$ has no in-band matrix elements, $G^{(\mathrm{pol})}=0$ if simultaneously $c=c'$ and $v=v'$. This behavior of $G^{(\mathrm{pol})}$ is to be contrasted with the behavior of $G^{(\mathrm{op})}$, which does not vanish if $c=c'$ and $v=v'$, because the deformation potential can have in-band matrix elements. As we shall see later, because of this difference in the structure of $G^{(\mathrm{op})}$ and $G^{(\mathrm{pol})}$, the deformation-potential interaction contributes to the Raman-scattering tensor while the polar interaction does not when we assume a simple two-band model for excitons.

The coupling parameters f and F are of the same form as that of g and G in Eqs. (6) and (7), but now

$$\int \Psi_{n,\mathbf{k}}^*(\mathbf{r})\delta\phi\Psi_{n',\mathbf{k}'}(\mathbf{r})d\mathbf{r}=-\frac{e}{m}\left(\frac{2\pi\hbar}{V\kappa_\infty\omega_{\chi,\epsilon}}\right)^{1/2}\int u_{n,\mathbf{k}}^*(\mathbf{r})\boldsymbol{\epsilon}\cdot\mathbf{p}u_{n',\mathbf{k}-\chi}(\mathbf{r})d\mathbf{r},$$

where we have used the translational property of Bloch waves,

$$\Psi_{n,\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n,\mathbf{k}}(\mathbf{r}).$$

Assuming the matrix element of $\boldsymbol{\epsilon}\cdot\mathbf{p}$ to be independent of $\mathbf{k}$, we have

$$f_{\chi,\epsilon}(cv\lambda\mathbf{k})=-N^{1/2}(e/m)(2\pi\hbar/V\kappa_\infty\omega_{\chi,\epsilon})^{1/2}\times U_{cv\lambda\mathbf{K}}^*(0)\langle c|\boldsymbol{\epsilon}\cdot\mathbf{p}|v\rangle\tag{22}$$

and

$$F_{\chi,\epsilon}(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')=-(e/m)(2\pi\hbar/V\kappa_\infty\omega_{\chi,\epsilon})^{1/2}\Big[q_e(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\times\langle c|\boldsymbol{\epsilon}\cdot\mathbf{p}|c'\rangle\delta_{vv'}-q_h(cv\lambda\mathbf{K},c'v'\lambda'\mathbf{K}')\times\langle v'|\boldsymbol{\epsilon}\cdot\mathbf{p}|v\rangle\delta_{cc'}\Big].\tag{23}$$

F vanishes if simultaneously $c=c'$ and $v=v'$.

[9] H. Fröhlich, Advan. Phys. 3, 325 (1954).

We make a canonical transformation of the total Hamiltonian H such that the term $H^{(1)}$ is eliminated. The transformed Hamiltonian $\hat{H}$ is

$$\hat{H}=e^{-iS}He^{iS}=H-i[S,H]-\tfrac{1}{2}[S,[S,H]]+(i/6)[S,[S,[S,H]]]+\cdots,\tag{24}$$

where S is chosen such that

$$i[S,H^{(0)}]=H^{(1)}.\tag{25}$$

Then

$$\hat{H}=H^{(0)}+H_{eL(1)}{}^{(2)}+H_{eL(2)}{}^{(2)}+H_{eR}{}^{(2)}+H_{eL}{}^{(3)}-\tfrac{1}{2}i[S,H^{(1)}]-i[S,H_{eL(1)}{}^{(2)}+H_{eR}{}^{(2)}]-i[S,H_{eL(2)}{}^{(2)}]-i[S,H_{eL}{}^{(3)}]-\tfrac{1}{3}[S,[S,H^{(1)}]]-\tfrac{1}{2}[S,[S,H_{eL(1)}{}^{(2)}+H_{eR}{}^{(2)}]]-\tfrac{1}{2}[S,[S,H_{eL(2)}{}^{(2)}]]-\tfrac{1}{2}[S,[S,H_{eL}{}^{(3)}]]+\cdots.\tag{26}$$

Writing S in the form

$$S=(1/i)[Q+Q'+P+P'],\tag{27}$$

and using the condition (25), we find

$$Q=-\sum_{\substack{cv\lambda\mathbf{K}\\ \chi\epsilon}}\frac{f_{\chi\epsilon}(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}{}^\dagger(cv)A_{\chi\epsilon}}{E_{\lambda\mathbf{K}}(cv)-\hbar\omega_{\chi\epsilon}}\delta_{\mathbf{K},\chi}+\text{c.c.},\tag{28a}$$

$$Q'=\sum_{\substack{cv\lambda\mathbf{K}\\ \chi\epsilon}}\frac{f_{\chi\epsilon}{}^*(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}(cv)A_{\chi\epsilon}}{E_{\lambda\mathbf{K}}(cv)+\hbar\omega_{\chi\epsilon}}\delta_{\mathbf{K},-\chi}-\text{c.c.},\tag{28b}$$

$$P=-\sum_{\substack{cv\lambda\mathbf{K}\\ \eta\xi}}\frac{g_{\eta\xi}(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}{}^\dagger(cv)b_{\eta\xi}{}^\dagger}{E_{\lambda\mathbf{K}}(cv)+\hbar\omega_{\eta\xi}}\delta_{\mathbf{K},-\eta},\tag{28c}$$

$$P'=\sum_{\substack{cv\lambda\mathbf{K}\\ \eta\xi}}\frac{g_{\eta\xi}{}^*(cv\lambda\mathbf{K})a_{\lambda\mathbf{K}}(cv)b_{\eta\xi}{}^\dagger}{E_{\lambda\mathbf{K}}(cv)-\hbar\omega_{\eta\xi}}\delta_{\mathbf{K},\eta}.\tag{28d}$$

The commutators in Eq. (26) signify different types of photon and phonon processes. In Sec. III we will identify the terms giving rise to the first- and second-order Raman transitions.

III. FIRST-ORDER RAMAN TENSOR

$[S,[S,H_{eL(1)}{}^{(2)}+H_{eR}{}^{(2)}]]$ is the lowest-order commutator that contributes to the first-order Raman effect. The initial state of the system will be specified by $|i\rangle=|n_1;n_2;n_0;0\rangle$, where n_1, n_2, and n_0 are the number of incident photons, the scattered photons, and the phonons. The zero in the ket refers to the ground state of the electrons where no excitons are present. The final state after Raman scattering is

$$|f\rangle=|n_1-1,n_2+1,n_0+1,0\rangle.$$

Since we consider spontaneous Raman scattering, n_2 will be taken to be zero. In the following, ω_1, $\varkappa_1$, ε_1 and ω_2, $\varkappa_2$, ε_2 will refer to the incident and scattered photons; ω_0 will denote phonon frequency. Expanding the commutator $-\frac{1}{2}[S,[S,H_{eL(1)}{}^{(2)}+H_{eR}{}^{(2)}]]$ in Eq. (26), we find that the contribution to the first-order Raman effect comes from the six terms $Q'H_{eR}{}^{(2)}P$, $Q'H_{eL(1)}{}^{(2)}Q'$, $QH_{eR}{}^{(2)}P$, $QH_{eL(1)}{}^{(2)}Q$, $P'H_{eR}{}^{(2)}Q'$, and $P'H_{eR}{}^{(2)}Q$ corresponding to the various time orderings of the absorption of the incident photon, the emission of the phonon, and the emission of the scattered photon accompanied by three virtual exciton transitions. The other terms do not contribute because (i) $a_{\lambda K}|0\rangle=0$, (ii) we cannot return to the ground electronic state, and (iii) processes do not involve two photons and one phonon.

By first-order time-dependent perturbation theory, the transition probability per unit time from the initial to the final state in the case of nonpolar optic vibration is

$$W=\frac{2\pi}{\hbar^2}\sum_{\eta,\varkappa_2}|\langle f|[Q'H_{eL(1)}{}^{(2)}Q'+Q'H_{eR}{}^{(2)}P+QH_{eR}{}^{(2)}P+QH_{eL(1)}{}^{(2)}Q+P'H_{eR}{}^{(2)}Q'+P'H_{eR}{}^{(2)}Q|i\rangle|^2\delta(\omega_1-\omega_2-\omega_0)$$

$$=\frac{4\pi^3e^4}{\hbar^3m^4a^2\kappa_\infty{}^2MN}\sum_{\eta,\varkappa_2}\frac{n_1(n_0+1)}{\omega_0\omega_1\omega_2}|\sum_i\xi^{(i)}R_{12}{}^{(i)}|^2\frac{(2\pi)^3}{V}\delta(\varkappa_1-\varkappa_2-\boldsymbol{\eta})\delta(\omega_1-\omega_2-\omega_0), \tag{29}$$

where the Raman tensor $R_{12}{}^{(i)}$ is given by

$$\begin{aligned}R_{12}{}^{(i)}(-\omega_1,\omega_2,\omega_0)=\frac{N\hbar^2}{V}\sum_{\substack{\lambda cv\\ \lambda'c'v'}}&\frac{U_{cv\lambda\varkappa_2}(0)U_{c'v'\lambda'\varkappa_2+\eta}{}^*(0)\langle v|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c\rangle\{q_e\langle c|\mathfrak{D}^{(i)}|c'\rangle\delta_{vv'}-q_h\langle v'|\mathfrak{D}^{(i)}|v\rangle\delta_{cc'}\}\langle c'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|v'\rangle}{[E_{\lambda\varkappa_2}(cv)-\hbar\omega_1+\hbar\omega_0][E_{\lambda'\varkappa_2+\eta}(c'v')-\hbar\omega_1]}\\
&+\frac{U_{cv\lambda,-\varkappa_1}(0)U_{c'v'\lambda',\eta-\varkappa_1}{}^*(0)\langle v|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|c\rangle\{q_e\langle c|\mathfrak{D}^{(i)}|c'\rangle\delta_{vv'}-q_h\langle v'|\mathfrak{D}^{(i)}|v\rangle\delta_{cc'}\}\langle c'|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|v'\rangle}{[E_{\lambda,-\varkappa_1}(cv)+\hbar\omega_2+\hbar\omega_0][E_{\lambda',\eta-\varkappa_1}(c'v')+\hbar\omega_2]}\\
&+\frac{U_{cv\lambda,-\varkappa_1}(0)U_{c'v'\lambda'\varkappa_2-\varkappa_1}{}^*(0)\langle v|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c\rangle\{q_e\langle c|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c'\rangle\delta_{vv'}-q_h\langle v'|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|v\rangle\delta_{cc'}\}\langle c'|\mathfrak{D}^{(i)}|v'\rangle}{[E_{\lambda,-\varkappa_1}(cv)+\hbar\omega_2+\hbar\omega_0][E_{\lambda',\varkappa_2-\varkappa_1}(c'v')+\hbar\omega_0]}\\
&+\frac{U_{cv\lambda\varkappa_2}(0)U_{c'v'\lambda',\varkappa_2-\varkappa_1}{}^*(0)\langle v|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c\rangle\{q_e\langle c|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|c'\rangle\delta_{vv'}-q_h\langle v'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|v\rangle\delta_{cc'}\}\langle c'|\mathfrak{D}^{(i)}|v'\rangle}{[E_{\lambda\varkappa_2}(cv)-\hbar\omega_1+\hbar\omega_0][E_{\lambda',\varkappa_2-\varkappa_1}(c'v')+\hbar\omega_0]}\\
&+\frac{U_{cv\lambda\eta}(0)U_{c'v'\lambda',\eta-\varkappa_1}{}^*(0)\langle v|\mathfrak{D}^{(i)}|c\rangle\{q_e\langle c|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|c'\rangle\delta_{vv'}-q_h\langle v'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|v\rangle\delta_{cc'}\}\langle c'|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|v'\rangle}{[E_{\lambda\eta}(cv)-\hbar\omega_1+\hbar\omega_2][E_{\lambda',\eta-\varkappa_1}(c'v')+\hbar\omega_2]}\\
&+\frac{U_{cv\lambda\eta}(0)U_{c'v'\lambda'\varkappa_2+\eta}{}^*(0)\langle v|\mathfrak{D}^{(i)}|c\rangle\{q_e\langle c|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c'\rangle\delta_{vv'}-q_h\langle v'|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|v\rangle\delta_{cc'}\}\langle c'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|v'\rangle}{[E_{\lambda\eta}(cv)-\hbar\omega_1+\hbar\omega_2][E_{\lambda',\varkappa_2+\eta}(c'v')-\hbar\omega_1]}.\end{aligned} \tag{30}$$

$\varkappa_1$, $\varkappa_2$, and $\boldsymbol{\eta}$ are very small, and they will be assumed to be zero in Eq. (30). The subscripts on $R_{12}{}^i$ indicate the photon-polarization directions and the superscripts refer to the phonon-polarization direction. In the summation over $\varkappa_2$, the direction of the scattered wave vector is restricted to a small solid angle $d\Omega$ determined by the geometry of the detector. The Raman-scattering efficiency[2] is defined to be the ratio of the number N_2 of the scattered photons into solid angle $d\Omega$ about the direction of observation per unit cross-sectional area of the crystal per unit time to the number N_1 of the incident photons crossing unit area per unit time, and is given by

$$\sigma^{(1)}d\Omega=\frac{N_2}{N_1}=\frac{e^4LV(n_0+1)(\omega_1-\omega_0)d\Omega}{2\hbar^3MNm^4a^2c^4\omega_0\omega_1}|\sum_{\delta,\gamma=x,y,z}\epsilon_1{}^\delta R_{\delta\gamma}(-\omega_1,\omega_1-\omega_0,\omega_0)\epsilon_2{}^\gamma|^2, \tag{31}$$

where L is the crystal thickness and $R_{\delta\gamma}=\sum_i \xi^{(i)}R_{\delta\gamma}{}^{(i)}$. In obtaining (31) from (29), we have converted the sums over $\boldsymbol{\eta}$ and $\varkappa_2$ into integrals.

In order to obtain the transition probability with the absorption of phonons (anti-Stokes's line) we have simply to replace $\boldsymbol{\eta}$ and ω_η by $-\boldsymbol{\eta}$ and $-\omega_\eta$ in Eqs. (9a), (9b), (28c), (28d), (29), and (31). Also, (n_0+1) in Eq. (29) should be replaced by n_0.

We calculate $R_{12}{}^{(i)}$ approximately using a very simple model. We assume that the exciton spectrum is given by Eq. (6). Further, we consider electronic transitions between the highest valence band v_0 and the lowest conduction band c_0 only. We observe that the first term on the right-hand side of Eq. (30) has the strongest divergence. For the two-band model, only the first and the second terms in the right-hand side of Eq. (30) survive, and when $\hbar\omega_1$ is close to the band gap, the first term will be the most important. Assuming $\varkappa_1\to 0$ and $\varkappa_2\to 0$, the first term of $R_{12}{}^{(i)}$ becomes, after using (17),

$$\frac{N\hbar^2}{V}\sum_\lambda |U_\lambda(0)|^2 \frac{\langle v_0|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c_0\rangle\{\langle c_0|\,\mathfrak{D}^{(i)}\,|c_0\rangle-\langle v_0|\,\mathfrak{D}^{(i)}\,|v_0\rangle\}\langle c_0|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v_0\rangle}{[E_{\lambda,0}(c_0v_0)-\hbar\omega_2][E_{\lambda,0}(c_0v_0)-\hbar\omega_1]}. \tag{32}$$

Using λ for discrete and continuum states of excitons, we get

$$R_{12}{}^{(i)}\sim p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(i)}p_{\alpha 0}{}^{(1)}\left\{\frac{N}{V}\sum_n \frac{\hbar^2|U_n(0)|^2}{\left[E_g-\frac{R}{n^2}-\hbar\omega_2\right]\left[E_g-\frac{R}{n^2}-\hbar\omega_1\right]}\right.$$
$$\left.+\frac{N\hbar^2}{(2\pi)^3}\int d\mathbf{k}\frac{|U_k(0)|^2}{\left(E_g+\frac{\hbar^2k^2}{2\mu}-\hbar\omega_2\right)\left(E_g+\frac{\hbar^2k^2}{2\mu}-\hbar\omega_1\right)}\right\}, \tag{33}$$

where the matrix elements have been written in the notation of Loudon[2] and the sum over $\mathbf{k}$ has been replaced by an integral. Now $|U_n(0)|^2=V_0/\pi a_0{}^3n^3$, where V_0 is the volume of the unit cell and exciton 'Bohr' radius $a_0=\kappa\hbar^2/\mu e^2$ and $|U_k(0)|^2=(1/N)\pi\alpha e^{\pi\alpha}/\sinh\pi\alpha$, where $\alpha=|R/(\hbar^2k^2/2\mu)|^{1/2}$. Using these values of $|U_n(0)|^2$ and $|U_k(0)|^2$, we obtain

$$R_{12}{}^{(i)}\sim p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(i)}p_{\alpha 0}{}^{(1)}\left\{\frac{1}{\pi a_0{}^3}\sum_n \frac{1}{n^3\left(\omega_g-\frac{R'}{n^2}-\omega_2\right)\left(\omega_g-\frac{R'}{n^2}-\omega_1\right)}\right.$$
$$\left.+\frac{1}{(2\pi)^3}\int_0^\infty d\mathbf{k}\frac{\pi\alpha e^{\pi\alpha}}{\sinh\pi\alpha}\frac{1}{\left(\omega_g-\omega_2+\frac{\hbar k^2}{2\mu}\right)\left(\omega_g-\omega_1+\frac{\hbar k^2}{2\mu}\right)}\right\},$$

$$=p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(i)}p_{\alpha 0}{}^{(1)}\left\{\frac{1}{\pi a_0{}^3}\sum_n \frac{1}{n^3}\frac{1}{\left(\omega_g-\frac{R'}{n^2}-\omega_2\right)\left(\omega_g-\frac{R'}{n^2}-\omega_1\right)}\right.$$
$$\left.+\frac{1}{4\pi\omega_0}\left(\frac{2\mu}{\hbar}\right)^{3/2}(4\pi^2R')^{1/2}\left[\left\{1-\exp\left(-\frac{4\pi^2R'}{\omega_g-\omega_2}\right)^{1/2}\right\}^{-1}-\left\{1-\exp\left(-\frac{4\pi^2R'}{\omega_g-\omega_1}\right)^{1/2}\right\}^{-1}\right]\right\}, \tag{34}$$

where $\omega_g=E_g/\hbar$ and $R'=R/\hbar$.

If $\omega_g-\omega_1\gg 4\pi^2R'$, we can neglect R'/n^2 in the first term of (34) and in the second term we use the approximation $1-e^{-x}\approx x$ for small x and get

$$R_{12}{}^{(i)}\sim\left\{\frac{1}{\pi a^3\omega_0}\left[\frac{1}{\omega_g-\omega_1}-\frac{1}{\omega_g-\omega_1+\omega_0}\right]\sum_{n=1}^{\infty}\frac{1}{n^3}+\frac{1}{4\pi\omega_0}\left(\frac{2\mu}{\hbar}\right)^{3/2}[(\omega_g-\omega_1+\omega_0)^{1/2}-(\omega_g-\omega_1)^{1/2}]\right\}p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(i)}p_{\alpha 0}{}^{(1)}. \tag{35}$$

In this limit the first term in (35) is very small compared to the second and we obtain Loudon's[2] result.

When $\omega_1 \cong \omega_g - R'$, all terms in (34) except the term with $n=1$ in the summation are finite and $R_{12}^{(i)}$ becomes

$$R_{12}^{(i)} \sim \frac{p_{0\alpha}^{(2)} \Xi_{\alpha\alpha}^{(i)} p_{\alpha 0}^{(1)}}{\pi a_0^3} \times \frac{1}{(\omega_g - R' - \omega_1 + \omega_0)(\omega_g - R' - \omega_1)}. \quad (36)$$

$R_{12}^{(i)}$ diverges as ω_1 approaches resonance. In this respect, our result agrees with that of Grechko and Ovander[3] without damping. However, the result of Grechko and Ovander does not contain the second energy factor in the denominator of $R_{12}^{(i)}$, as in our theory. The presence of this second factor in the denominator is necessary to explain the experimental results, as will be discussed later. The difference between our theory and that of Loudon[2] arises because of the different density of states for the intermediate states in the two theories. The density of the initial and the final states are the same in the two theories.

In polar semiconductors, the Raman efficiency for the transverse-optic phonon will be given by Eq. (31) but for the longitudinal-optic phonon there will be additional contributions due to the terms given in Eqs. (20) and (21). The contribution to the transition probability per unit time due to these new terms alone will be

$$W' = \frac{(2\pi)^4 e^6}{\hbar^3 m^6 \kappa_\infty^2 V}\left(\frac{1}{\kappa_\infty} - \frac{1}{\kappa_0}\right) \times \sum_{\eta, \chi_2} \frac{n_1(n_l+1)\omega_l}{\omega_1 \omega_2} |P_{12}^{\hat{\eta}}(-\omega_1, \omega_2, \omega_l)|^2 \frac{(2\pi)^3}{V} \times \delta(\chi_1 - \chi_2 - \eta)\delta(\omega_1 - \omega_2 - \omega_l). \quad (37)$$

n_l, ω_l are the number and frequency of the longitudinal phonons. $P_{12}^{\hat{\eta}}$ contains terms similar to that of Eq. (30) in which $\langle m|\mathfrak{D}^{(i)}|m'\rangle$ is replaced by $\hbar\langle m|\hat{\boldsymbol{\eta}}\cdot\mathbf{p}|m'\rangle/(E_m - E_{m'})$.

$$P_{12}^{\hat{\eta}}(-\omega_1, \omega_2, \omega_l) = \frac{N\hbar^3}{V} \sum_{\substack{\lambda cv \\ \lambda' c' v'}}{}' \frac{U_{cv\lambda\chi_2}(0) U^*_{c'v'\lambda'\chi_1}(0)\langle v|\boldsymbol{\varepsilon}_2\cdot\mathbf{p}|c\rangle}{[E_{\lambda\chi_2}(cv) - \hbar\omega_2][E_{\lambda'\chi_1}(c'v') - \hbar\omega_1]} \times \left\{\frac{q_e\langle c|\hat{\boldsymbol{\eta}}\cdot\mathbf{p}|c'\rangle\delta_{vv'}}{E_c - E_{c'}} - \frac{q_h\langle v'|\hat{\boldsymbol{\eta}}\cdot\mathbf{p}|v\rangle\delta_{cc'}}{E_v - E_{v'}}\right\}\langle c'|\boldsymbol{\varepsilon}_1\cdot\mathbf{p}|v'\rangle \quad (+\text{five other terms}). \quad (38)$$

$\sum'$ means that the term with $c=c'$, $v=v'$ is to be omitted as explained in Sec. II. As seen in Eq. (38), $P_{12}^{\hat{\eta}}$ involves three momentum matrix elements. Therefore, we need virtual electronic transitions between three different bands. So $P_{12}^{\hat{\eta}}$ does not make any contribution to Raman scattering if we assume a simple two-band model. We do not possess knowledge of the exciton structures formed from pairs of at least three different bands between which optical transitions are allowed. However, we observe from Eq. (38) that $P_{12}^{\hat{\eta}}$ will diverge as $(E_g - R - \hbar\omega_1)^{-1}$ near to resonance, in disagreement with both Loudon's theory,[2] which predicts a nondivergent $(E_g - \hbar\omega_1)^{1/2}$ behavior and that of Grechko and Ovander, which predicts a $(E_g - \hbar\omega_1)^{-2}$ divergence as $\hbar\omega_1 \to E_g$. The symmetry properties of $R_{12}^{(i)}$ and $P_{12}^{\hat{\eta}}$ are the same as those enumerated by Loudon.[2]

IV. SECOND-ORDER RAMAN EFFECT

The second-order Raman effect consists of three types of processes.

(a) This process consists of the transitions in which the incident photon is absorbed creating an exciton, then two phonons are simultaneously created scattering the exciton to a different state, and finally the scattered photon is emitted annihilating the exciton. The absorption of the incident photon, the emission of the phonons, and the emission of the scattered photon can occur in any time order. This process contributes six terms to the Raman tensor. Two of these terms arise from the cumulator $[S,[S,H_{eL}^{(3)}]]$ treated in the first-order perturbation theory. The remaining four terms arise from when the commutators $[S,H_{eR}^{(2)}]$ and $H_{eL(2)}^{(2)}$ are treated in the second-order perturbation theory.

(b) This process involves the absorption of the incident photon, the emission of the two phonons separately (owing to H_{eL} acting twice), and the emission of the scattered photon. These four real transitions are accompanied by four virtual exciton transitions. This process results from the commutator $[S,[H_{eL(1)}^{(2)} + H_{eR}^{(2)}]]$ treated in the second-order perturbation theory and contributes 24 terms to the Raman tensor.

(c) Second-order Raman transition also occurs by the iteration of the first-order process. Six virtual exciton transitions and a virtual photon or phonon now occur with the absorption of the incident photon, the separate emission of the two phonons, and the emission of the incident photon. This process contributes 36 terms to the Raman tensor from the commutator $[S,[S,H_{eL(1)}^{(2)}+H_{eR}^{(2)}]]$ treated in the second-order perturbation theory.

The wave vector selection rule for the second-order Raman effect allows phonons of all wave vectors so long as the two phonons have equal and opposite wave vectors. However, the coupling parameters g, G, d, and D for the electron-phonon interaction were calculated only for small wave vectors. These parame-

ters for large $\boldsymbol{\eta}$ are not known. Therefore, we will consider only the overtones, i.e., the emission of two phonons with wave vectors at the center of the Brillouin zone. The final state for the second-order Raman transition is denoted by $|f\rangle=|n_1-1, n_2+1, n_0+2, 0\rangle$. For spontaneous process, $n_2=0$.

The transition probability per unit time for process (a) in the case of nonpolar optic phonons is

$$W=\frac{2\pi}{\hbar^2}\sum_{\eta,\eta',\chi_2}\Big|\langle f|\Big\{QH_{eL}{}^{(3)}Q+Q'H_{eL}{}^{(3)}Q'+\sum_b\frac{H_{eL(2)}{}^{(2)}|b\rangle\langle b|(H_{eR}{}^{(2)}Q+H_{eR}{}^{(2)}Q')\rangle}{E_b-E_i}$$
$$+\sum_b\frac{(QH_{eR}{}^{(2)}+Q'H_{eR}{}^{(2)})|b\rangle\langle b|H_{eL(2)}{}^{(2)}}{E_b-E_i}\Big\}|i\rangle\Big|^2\delta(\omega_1-\omega_2-2\omega_0)$$
$$=\frac{2\pi^3e^4}{\hbar^2m^4a^4\kappa_\infty{}^2M^2N^2}\sum_{\eta,\eta',\chi_2}\frac{n_1(n_0+1)(n_0+2)}{\omega_1\omega_2\omega_0{}^2}\Big|\sum_{i,j}\xi^{(i)}\xi^{(j)}R_{12}{}^{(ij)}(-\omega_1,\omega_2,2\omega_0)\Big|^2\frac{(2\pi)^3}{V}$$
$$\times\delta(\chi_1-\chi_2-\boldsymbol{\eta}-\boldsymbol{\eta}')\delta(\omega_1-\omega_2-2\omega_0), \quad (39)$$

where $|b\rangle$ denotes the intermediate states and the second-order Raman tensor $R_{12}{}^{(ij)}$ is given by

$$R_{12}{}^{(ij)}(-\omega_1,\omega_2,2\omega_0)=\frac{N\hbar^2}{V}\sum_{\substack{\lambda cv\\ \lambda'c'v'}}\Big[\frac{U_{cv\lambda\chi_2}(0)U_{c'v'\lambda'\chi_1}{}^*(0)\langle v|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c\rangle\{q_e\langle c|\,\mathfrak{D}^{(ij)}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\mathfrak{D}^{(ij)}\,|v\rangle\delta_{cc'}\}\langle c'|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v'\rangle}{[E_{\lambda\chi_2}(cv)-\hbar\omega_2][E_{\lambda'\chi_1}(c'v')-\hbar\omega_1]}$$
$$+\frac{U_{cv\lambda\eta+\eta'}(0)U_{c'v'\lambda'\chi_1}(0)^*\langle v|\,\mathfrak{D}^{ij}\,|c\rangle\{q_e\langle c|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|v\rangle\delta_{cc'}\}\langle c'|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v'\rangle}{[E_{\lambda'\chi_1}(c',v')-\hbar\omega_1][E_{\lambda,\eta+\eta'}(cv)-\hbar(\omega_\eta+\omega_{\eta'})]}$$
$$+\frac{U_{cv\lambda\eta+\eta'}(0)U_{c'v'\lambda',-\chi_2}(0)^*\langle v|\,\mathfrak{D}^{(ij)}\,|c\rangle\{q_e\langle c|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v\rangle\delta_{cc'}\}\langle c'|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|v'\rangle}{[E_{\lambda',-\chi_2}(c'v')+\hbar\omega_2][E_{\lambda,\eta+\eta'}(cv)-\hbar(\omega_\eta+\omega_{\eta'})]}$$
$$+\frac{U_{cv\lambda,-\chi_1}(0)U_{c'v'\lambda',-\chi_2}(0)^*\langle v|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|c\rangle\{q_e\langle c|\,\mathfrak{D}^{(ij)}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\mathfrak{D}^{(ij)}\,|v\rangle\delta_{cc'}\}\langle c'|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|v'\rangle}{[E_{\lambda,-\chi_1}(cv)+\hbar\omega_1][E_{\lambda',-\chi_2}(c'v')+\hbar\omega_2]}$$
$$+\frac{U_{cv\lambda,-\chi_1}(0)U_{c'v'\lambda',-(\eta+\eta')}(0)^*\langle v|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|c\rangle\{q_e\langle c|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|v\rangle\delta_{cc'}\}\langle c'|\,\mathfrak{D}^{(ij)}\,|v'\rangle}{[E_{\lambda,-\chi_1}(cv)+\hbar\omega_1][E_{\lambda',-(\eta+\eta')}(c'v')+\hbar(\omega_\eta+\omega_{\eta'})]}$$
$$+\frac{U_{cv\lambda\chi_2}(0)U_{c'v'\lambda',-(\eta+\eta')}(0)^*\langle v|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c\rangle\{q_e\langle c|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|c'\rangle\delta_{vv'}-q_h\langle v'|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v\rangle\delta_{cc'}\}\langle c'|\,\mathfrak{D}^{ij}|v'\rangle}{[E_{\lambda,\chi_2}(cv)-\hbar\omega_2][E_{\lambda',-(\eta+\eta')}(c'v')+\hbar(\omega_\eta+\omega_{\eta'})]}\Big]. \quad (40)$$

χ_1 and χ_2 will be assumed to be zero. Then $\boldsymbol{\eta}'=-\boldsymbol{\eta}$, and we consider only the case where $\boldsymbol{\eta}=0$. After performing the $\boldsymbol{\eta},\boldsymbol{\eta}'$, and χ_2 integrations, the Raman-scattering efficiency is given by

$$\sigma_\alpha{}^{(2)}d\Omega=\frac{e^4LV^2(n_0+1)(n_0+2)(\omega_1-2\omega_0)}{4\hbar^2N^2M^2m^4a^4c^4\omega_1\omega_0{}^2}d\Omega\frac{Z_\xi(2\omega_0)d\omega_0}{V_0}\Big|\sum_{\delta,\gamma=x,y,z}\epsilon_2{}^{(\delta)}R_{\delta\gamma}(-\omega_1,\omega_1-2\omega_0,2\omega_0)\epsilon_1{}^{(\gamma)}\Big|^2, \quad (41)$$

where $Z_\xi(2\omega_0)d\omega_0$ is the fractional number of modes of frequency $2\omega_0$ in the interval $d\omega_0$ and

$$R_{\delta\gamma}=\sum_{i,j}\xi^{(i)}\xi^{(j)}R_{\delta\gamma}{}^{(ij)}.$$

Proceeding exactly as in Sec. III, we find that

$$R_{12}{}^{(ij)}(-\omega_1,\omega_1-2\omega_0,2\omega_0)\sim p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(ij)}p_{\alpha0}{}^{(1)}\Big\{\frac{1}{\pi a_0{}^3}\sum_n\frac{1}{n^3}\cdot\frac{1}{\Big(\omega_g-\dfrac{R'}{n^2}-\omega_1+2\omega_0\Big)\Big(\omega_g-\dfrac{R'}{n^2}-\omega_1\Big)}$$
$$+\frac{1}{8\pi\omega_0}\Big(\frac{2\mu}{\hbar}\Big)^{3/2}(4\pi^2R')^{1/2}\Big[\Big\{1-\exp\Big(-\frac{4\pi^2R'}{\omega_g-\omega_1+2\omega_0}\Big)^{1/2}\Big\}^{-1}-\{1-\exp(-4\pi^2R'/(\omega_g-\omega_1))^{1/2}\}^{-1}\Big]\Big\},$$

and in the limit $\omega_1 \approx \omega_g - R'$, we get

$$R_{12}^{(ij)} \sim [p_{0\alpha}^{(2)} \Xi_{\alpha\alpha}^{(ij)} p_{\alpha 0}^{(1)} / \pi a_0^3][(\omega_g - R' - \omega_1 + 2\omega_0)(\omega_g - R' - \omega_1)]^{-1}. \tag{42}$$

The ratio of efficiencies for the first- and second-order Raman scattering for incident frequencies near the absorption edge is

$$\frac{\sigma^{(1)}}{\sigma_\alpha^{(2)}} = \frac{2Ma^2\omega_0(\omega_1 - \omega_0)\Xi_{\alpha\alpha}^2}{\hbar(\omega_1 - 2\omega_0)\Xi_{\alpha\alpha}'^2(n_0+2)Z_\xi(2\omega_0)d\omega_0}\left[1 + \frac{\omega_0}{\omega_\beta + \omega_0 - \omega_1}\right]^2, \tag{43}$$

where $\omega_\beta = \omega_g - R'$, $\Xi_{\alpha\alpha} = \sum_i \xi^{(i)} \Xi_{\alpha\alpha}^{(i)}$ and $\Xi_{\alpha\alpha}' = \sum_{i,j} \xi^{(i)}\xi^{(j)} \Xi_{\alpha\alpha}^{(ij)}$.

The transition probability per unit time for process of type (b) is

$$W = \frac{2\pi^3 e^4}{\hbar^2 m^4 a^4 \kappa_\infty^2 M^2 N^2} \sum_{\eta, \eta', \chi_2} \frac{(2\pi)^3}{V} \frac{n_1(n_0+1)(n_0+2)}{\omega_1 \omega_2 \omega_0^2} \left| \sum_{i,j} \xi^{(i)}\xi^{(j)} R_{12}^{(ij)} \right|^2 \delta(\varkappa_1 - \varkappa_2 - \eta - \eta')\delta(\omega_1 - \omega_2 - 2\omega_0), \tag{44}$$

where

$$R_{12}^{(ij)}(-\omega_1, \omega_2, 2\omega_0)$$

$$= \frac{N\hbar^2}{V} \sum_{\substack{cv\lambda \\ c_1 v_1 \lambda_1 \\ c'v'\lambda'}} \left\{ \frac{U_{cv\lambda\chi_2}(0) U_{c'v'\lambda'\chi_1}{}^*(0) \langle v | \boldsymbol{\varepsilon}_2 \cdot \mathbf{p} | c \rangle G(cv\lambda\varkappa_2, c_1 v_1 \lambda_1 \eta' + \varkappa_2) G(c_1 v_1 \lambda_1 \eta' + \varkappa_2, c'v'\lambda'\varkappa_1) \langle c' | \boldsymbol{\varepsilon}_1 \cdot \mathbf{p} | ' \rangle}{[E_{\lambda\chi_2}(cv) - \hbar\omega_{\chi_2}][E_{\lambda'\chi_1}(c'v') - \hbar\omega_{\chi_1}][E_{\lambda_1\eta'+\chi_2}(c_1 v_1) - \hbar\omega_{\chi_1} + \hbar\omega_\eta]} \right.$$

$$\left. + 23 \text{ other terms} \right\}. \tag{45}$$

The Raman-scattering efficiency is then

$$\sigma_b^{(2)} d\Omega = \frac{e^4 L V^2 d\Omega (n_0+1)(n_0+2)(\omega_1 - 2\omega_0)}{4\hbar^2 N^2 M^2 m^4 a^4 c^4 \omega_1 \omega_0^2} \frac{Z_\xi(2\omega_0) d\omega_0}{V_0} \left| \sum_{\delta,\gamma} \epsilon_2^{(\delta)} R_{\delta,\gamma}(-\omega_1, \omega_1 - 2\omega_0, 2\omega_0) \epsilon_1^{(\gamma)} \right|^2. \tag{46}$$

For the two-band model using the same approximations as in Sec. III and employing Eq. (17), we obtain

$$R_{12}^{(ij)}(-\omega_1, \omega_1 - 2\omega_0, 2\omega_0)$$

$$\cong p_{0\alpha}^{(2)} \Xi_{\alpha\alpha}^{(i)} \Xi_{\alpha\alpha}^{(j)} p_{\alpha 0}^{(1)} \left\{ \frac{1}{\pi\hbar a_0{}^3} \sum_n \frac{1}{n^3(\omega_g - R'/n^2 - \omega_1 + 2\omega_0)(\omega_g - R'/n^2 - \omega_1)(\omega_g - R'/n^2 - \omega_1 + \omega_0)} \right.$$

$$+ \frac{1}{8\pi\hbar\omega_0^2} \left(\frac{2\mu}{\hbar}\right)^{3/2} (4\pi^2 R')^{1/2} \left[\frac{2}{1 - \exp(-4\pi^2 R'/(\omega_g - \omega_1 + \omega_0))^{1/2}} - \frac{1}{1 - \exp(-4\pi^2 R'/(\omega_g - \omega_1))^{1/2}} \right.$$

$$\left. \left. - \frac{1}{1 - \exp(-4\pi^2 R'/(\omega_g - \omega_1 + 2\omega_0))^{1/2}} \right] \right\}, \tag{47}$$

and in the limit $\omega_1 \approx \omega_g - R'$, we have

$$R_{12}^{(ij)} \sim (p_{0\alpha}^{(2)} \Xi_{\alpha\alpha}^{(i)} \Xi_{\alpha\alpha}^{(j)} p_{\alpha 0}^{(1)} / \pi\hbar a_0{}^3)[(\omega_g - R' - \omega_1 + 2\omega_0)(\omega_g - R' - \omega_1)(\omega_g - R' - \omega_1 + \omega_0)]^{-1}. \tag{48}$$

Finally, we obtain for the ratio of the efficiencies, in this case

$$\frac{\sigma^{(1)}}{\sigma_b^{(2)}} = \frac{2Ma^2\omega_0(\omega_1 - \omega_0)\Xi_{\alpha\alpha}^2}{(\omega_1 - 2\omega_0)\Xi_{\alpha\alpha}''^2(n_0+2)Z_\xi(2\omega_0)d\omega_0} \hbar(\omega_g - R' - \omega_1 + 2\omega_0)^2, \tag{49}$$

where

$$\Xi_{\alpha\alpha}'' = \sum_{i,j} \xi^{(i)}\xi^{(j)} \Xi_{\alpha\alpha}^{(i)} \Xi_{\alpha\alpha}^{(j)}.$$

In this case there is no pole in the ratio.

The transition probability per unit time for process (c) is given by

$$W=\frac{8\pi^5e^8}{\hbar^6a^4m^8\kappa_\infty{}^4M^2N^2}\sum_{\eta,\eta',\chi_2,\chi',\epsilon'}\frac{n_1(n_0+1)(n_0+2)}{\omega_{\chi_1}\omega_{\chi'}{}^2\omega_{\chi_2}\omega_\eta\omega_{\eta'}(\omega_{\chi'}+\omega_\eta-\omega_{\chi_1})^2}\left|\sum_{i,j}\xi^{(i)}\xi^{(j)}R_{12}{}^{(ij)}\right|^2\delta_{\chi_1,\chi'+\eta}\delta_{\chi',\chi_2+\eta'}\delta(\omega_1-\omega_2-2\omega_0), \quad (50)$$

where

$$R_{12}{}^{(ij)}(-\omega_1,\omega_2,2\omega_0)=\frac{N^2\hbar^4}{V^2}\sum_{\substack{c_1'v_1'\lambda_1'\\ c_1v_1\lambda_1\\ cv\lambda\\ c'v'\lambda'}}\Bigg\{U_{c_1v_1\lambda_1\chi_2}(0)U^*{}_{c_1'v_1'\lambda_1'\chi_1-\eta}(0)U_{cv\lambda\chi_1-\eta}(0)U^*{}_{c'v'\lambda'\chi_1}(0)$$

$$\times\frac{\langle v_1|\,\boldsymbol{\varepsilon}_2\cdot\mathbf{p}\,|c_1\rangle\{\langle c_1|\,\mathfrak{D}^{(i)}\,|c_1'\rangle\delta_{v_1v_1'}q_e-\langle v_1'|\,\mathfrak{D}^{(i)}\,|v_1\rangle\delta_{c_1c_1'}q_h\}\langle c_1'|\,\boldsymbol{\varepsilon}'\cdot\mathbf{p}\,|v_1'\rangle}{[E_{\lambda_1,\chi_2}(c_1v_1)-\hbar\omega_{\chi_2}][E_{\lambda_1',\chi_1-\eta}(c_1'v_1')-\hbar\omega_{\chi_1-\eta}]}$$

$$\times\frac{\langle v|\,\boldsymbol{\varepsilon}'\cdot\mathbf{p}\,|c\rangle\{\langle c|\,\mathfrak{D}^{(i)}\,|c'\rangle\delta_{vv'}q_e-\langle v'|\,\mathfrak{D}^{(j)}\,|v\rangle\delta_{cc'}q_h\}\langle c'|\,\boldsymbol{\varepsilon}_1\cdot\mathbf{p}\,|v'\rangle}{[E_{\lambda,\chi_1-\eta}(cv)-\hbar\omega_{\chi_1-\eta}][E_{\lambda'\chi_1}(c'v')-\hbar\omega_{\chi_1}]}+35\text{ other terms}\Bigg\}. \quad (51)$$

Here $\boldsymbol{\varepsilon}'$ is the unit polarization vector of the intermediate state photon. Under the approximations we have used so far, $R_{12}{}^{(ij)}$ becomes

$$R_{12}{}^{(ij)}(-\omega_1,\omega_2,2\omega_0)\sim p_{0\alpha}{}^{(2)}\Xi_{\alpha\alpha}{}^{(i)}p_{\alpha0}p_{0\alpha}\Xi_{\alpha\alpha}{}^{(j)}p_{\alpha0}{}^{(1)}$$

$$\times\left(\frac{N\hbar^2}{V}\right)^2\sum_{\lambda,\lambda'}|U_\lambda(0)|^2|U_{\lambda'}(0)|^2\frac{1}{(E_{\lambda',0}-\hbar\omega_1+2\hbar\omega_0)(E_{\lambda',0}-\hbar\omega_{\chi_1-\eta})(E_{\lambda,0}-\hbar\omega_{\chi_1-\eta})(E_{\lambda,0}-\hbar\omega_1)}, \quad (52)$$

Here $\hbar\omega_{\chi_1-\eta}$ is equal to $\hbar\omega_2$ in Eq. (30). Comparing Eq. (52) and the first term of (30), it is easy to see that for process of type (c) there is no pole in the ratio $\sigma^{(1)}/\sigma_c{}^{(2)}$.

V. DISCUSSION

Equation (43) agrees qualitatively and almost quantitatively with the experimental results of Leite and Porto[10] on CdS. They observed longitudinal phonons of Γ_1 symmetry. Our theory applies to this phonon mode since the Cd lattice moves against the S lattice in this particular mode. The value of 2.521 eV for the parameter $\hbar\omega_\beta$ at a temperature of 77°K that they obtained should correspond to the exciton energy according to our theory. The exact value of the exciton energy at 77°K is 2.544 eV.[11] The discrepancy between the two values might be due to the fact that the intermediate states are not pure exciton states but coupled exciton-phonon states. We have also calculated the ratio of the intensity of Raman scattering at 77°K in CdS for phonons of Γ_1 mode at the incident photon energies 2.41 and 2.53 eV using the following values: $m_e{}^*=0.6m$, $m_h{}^*=0.25m$, $a_0=27.47$ Å, $E_g=2.572$ eV, $R=0.028$ eV, $\hbar\omega_0=0.038$ eV. We find the ratio to be 2.78×10^2. The ratio calculated by Loudon's[2] theory is 3.05. Leite and Porto[10] have observed an appreciable increase in intensity ("at least one order of magnitude"). Measurement of absolute intensities are required to know the correct increase in the intensity of Raman scattering.

The exciton spectrum of GaAs has been studied by Sturge.[12] At 90°K, the exciton binding energy $R=0.0033$ eV, $E_g=1.511$ eV, $\mu=0.0651$ m, $a_0=133.128$ Å, and $\hbar\omega_0=0.0360$ eV. We would expect a pole in the ratio of the intensity of the first-order Raman effect and its overtone at 1.508 eV. The intensity of the first-order Raman effect increases by a factor 4×10^2 as the incident frequency is changed from 1.37 to 1.506 eV, whereas the corresponding factor in Loudon's[2] theory is 8.

We give a brief discussion of the relative strength of the two types of electron-phonon interaction and of the electron-radiation interaction. The ratio of the coupling parameters is approximately

$$\frac{g^{(\mathrm{pol})}}{g^{(\mathrm{op})}}\simeq\frac{2(M_1M_2)^{1/2}}{M_1+M_2}(\pi\rho)^{1/2}\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_0}\right)^{1/2}\frac{\hbar\omega_0ep}{mDE_g}$$

and

$$g^{(\mathrm{pol})}/f\simeq\kappa_\infty{}^{1/2}(1/\kappa_\infty-1/\kappa_0)^{1/2}\hbar(\omega_1\omega_0)^{1/2}/E_g.$$

ρ is the density of the material. We estimate these ratios now specifically for CdS and GaAs. For CdS, $\kappa_0=9.3$, $\kappa_\infty=5.8$, $\rho=4.82$ g/cc, $a=6.72$ Å, $p\sim3.8\times10^{-2}$, egs units, $\mathfrak{D}\sim10$ eV.[13] The $g^{(\mathrm{pol})}/g^{(\mathrm{op})}$ is found to be 1.02. For GaAs using the values of $\kappa_0=13$, $\kappa_\infty=11.6_0$ $\rho=5.4$ g/cc, $a=5.64$ Å, $p\sim8.1\times10^{-20}$ cgs units, $\mathfrak{D}\sim15$ eV,[14] we obtain $g^{(\mathrm{pol})}/g^{(\mathrm{op})}=1.08$. Polar scattering and

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deformation potential scattering are thus found to be of the same order of magnitude. On the other hand $g^{(\mathrm{pol})}/f=7.4\times10^{-2}$ for CdS and $g^{(\mathrm{pol})}/f=5\times10^{-2}$ for GaAs. Electron-radiation interaction is two orders of magnitude stronger than the electron-phonon interaction. In the perturbation theory they should really be treated in different orders. However, we have followed the common practice of treating H_{eR} and H_{eL} in the same order of perturbation theory.

VI. CONCLUSION

Virtual quasiparticles play an important part in Raman scattering as intermediate states. The Raman tensor is found to have a pole at an incident photon energy equal to the exciton binding energy, in agreement with experimental results available at present. We believe that the Raman scattering might be used as a tool to probe quasiparticles in crystals.

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X-Ray-Induced First-Stage Coloring of NaCl†‡

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The initial or first-stage F-center coloring of NaCl, irradiated with x rays at room temperature, has been carefully studied. Both Korth and Harshaw samples were used. The first-stage coloring is modified by changing the experimental conditions. These include altering the dose rate; subjecting the crystals to plastic deformation before irradiation; and cycles of coloring, bleaching, and recoloring. The observed curves of F-center concentration versus dose can be resolved into one linear and three additional components. Two of these can be considered saturating exponentials. The third, which does not occur in every curve, may also be a saturating exponential, but is too weak to characterize precisely. Changing the experimental conditions alters one or two of the exponential components but leaves the others unchanged. This suggests that each component is related to a separate process and that the resolution into components is *not* fortuitous. The linear component is unaffected by all the above-mentioned changes in experimental conditions. The exponential component which varies slowest, as a function of irradiation time, is independent of dose rate and prior coloring and bleaching. Its saturation level is increased by plastic deformation prior to irradiation, but only after the strain has exceeded a threshold value. Beyond this threshold strain, the saturation level increases linearly with strain. The saturation level of the next slowest component is unaffected by strain. However, it is increased by a coloring-bleaching-recoloring cycle and is a function of dose rate. This dose rate dependence is given by the expression: $C_1+C_2I^2$, where C_1 and C_2 are constants and I is proportional to x-ray intensity. The saturation level of the third and fastest-changing component is always less than 10% of the total exponential contribution and is too small to study in detail. In the 185- to 350-mμ region both the absorption spectrum and the behavior under the various experimental conditions differ considerably in the two types of crystals. Also, the coloring curves seem to be strongly dependent on impurity content in a way that is also different in the two types of crystals.

INTRODUCTION

THE coloring of crystals, or more explicitly, the formation of color centers by ionizing radiation, has been studied for many years. The dependence of color-center concentration on dose or irradiation time is often called a growth curve or coloration curve. In most materials these curves are influenced by numerous factors. The most important of these appear to be the impurity content,[1–7] plastic deformation,[1,8–12] ionizing radiation intensity,[1,13–16] and the presence or absence of light that can optically bleach the centers formed.[17]

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