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Polariton Theory of Raman Scattering in Insulating Crystals. II.*

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A formal theory of polariton Raman scattering in insulators is developed, utilizing both the equation-of-motion and scattering-operator techniques, and the temperature-dependent cross section is obtained. Explicit forms are derived for polariton dispersions and transformation coefficients, and for the Raman cross section, for various specific cases, among them a nondispersive hydrogenic exciton-band model. Numerical calculations are carried out for the latter model; the resulting cross section displays considerable variation with incoming frequency, displaying, among other things, in-out resonances with discrete states, and interference between discrete and continuum contributions to scattering. Comparison with other results and with experiment is given.

I. INTRODUCTION; MODEL HAMILTONIAN

The success of recent light scattering experiments in insulating crystals[1–4] has led to increased interest in the theory of the Raman effect. One framework within which such descriptions have been advanced is the "polariton," or composite light-crystalline quasiparticle, point of view.[5–10] The emphasis in existing literature, for the most part, has been on formal and qualitative aspects of the theory, rather than on actual calculations. However, numerical calculations in the present instance are, in fact, of interest not only in themselves, but because they facilitate comparison of theory with existing data, while encouraging experiment where data are presently unavailable.

The theory of polariton Raman scattering (RS) is here developed via a three-step sequence:

(a) Polariton dispersions and transformation coefficients are obtained by the equation-of-motion method.
(b) General forms for the RS cross section are obtained via a scattering-operator formalism.
(c) The results of (a) and (b) are combined to yield explicit forms for specific cases of interest.

The present procedure, it is believed, is more direct and physically motivated than a strictly Green's-function approach,[6,7] and leads most naturally and easily to both temperature-dependent cross sections and outgoing photon line shapes,[3] dependences of significance in actual experiments.

Special attention is directed to the simplified case where a single polariton dominates in both the incoming and outgoing scattering channels. When spatial (exciton) dispersion is included in the theory, degeneracy of polariton waves at the in and outgoing channels may, in principle, have a significant effect on the scattering cross section. This possibility is considered in some detail in Ref. 10, but will not be treated here.

Numerical calculations are carried out for a hydrogen-like exciton-band model,[11] discrete and continuum levels included. While such calculations have not been previously carried out within polariton theory, we note the bare-exciton-approach calculation in Ref. 12, which did not, however, concern itself with the actual details in the structure of the RS cross section in the resonance regime.

Model Hamiltonian

For reasons of simplicity, we employ a model Hamiltonian containing a restricted number of quasiparticle

fields and interactions. The extension of the present theory to more general cases will be clear from the development.

The Hamiltonian contains the following free boson fields.[13,14]

(a) An exciton band with discrete levels $E_\lambda(\mathbf{k})$, $\lambda=1, 2, \cdots, \infty$, and continuous levels $E_\eta(\mathbf{k})$, where $\boldsymbol{\eta}$ is the relative motion wave vector of an electron-hole pair. For small $\mathbf{k}$ and $\boldsymbol{\eta}$ and nearly spherical bands, one has[14]

$$E_\lambda(\mathbf{k})=E_\lambda(0)+\tfrac{1}{2}\alpha k^2,$$
$$E_\eta(\mathbf{k})=E_g+\alpha k^2+\tfrac{1}{2}\alpha_R\eta^2, \tag{1.1}$$

where E_g is the energy gap; $\alpha\equiv(m_e+m_h)^{-1}$ and $\alpha_R\equiv m_e^{-1}+m_h^{-1}$, where m_e and m_h are the electron and hole effective masses, respectively. The creation-annihilation operators corresponding to the various levels are denoted by $B_{\lambda,\eta}^{\pm}(\mathbf{k})$.

(b) The phonon field $[\omega_0(s,\mathbf{k}), b_s^{\pm}(\mathbf{k})]$, with s the phonon polarization index.

(c) A single polarization of light $(kc, a^{\pm}(\mathbf{k}))$.

The model interactions of importance for optical scattering are considered to be

(a) bilinear photon-exciton couplings,
(b) exciton-phonon interactions leading to the scattering of a single exciton with the simultaneous creation or destruction of n phonons,
(c) trilinear phonon anharmonicity.

Although strictly speaking one would, in the general case, also include bilinear photon-phonon and exciton-phonon interactions, the major effect on the polariton dispersion in the optical region arises from interaction (a), and it is therefore expedient to restrict the bilinear couplings to (a). Also omitted is the exciton-exciton interaction[5] arising because excitons are not perfect bosons; such terms, if desired, may be treated similarly to those which are included in our model.

The above-described system has the Hamiltonian

$$H=H_0+\sum_n V^{(n)}+V_{\text{anh}}, \tag{1.2}$$

where H_0 is the bilinear Hamiltonian [$\omega_p^2\equiv 4\pi ne^2/m_e$, plasma frequency squared ($n\equiv$electron density)]

$$H_0=\sum_{\mathbf{k}} kca^+(\mathbf{k})a^-(\mathbf{k})+\sum_{\mathbf{k}\lambda\eta} E_{\lambda,\eta}(\mathbf{k})B_{\lambda,\eta}^+(\mathbf{k})B_{\lambda,\eta}^-(\mathbf{k})$$
$$+\sum_{sk}\omega_0(s,\mathbf{k})b_s^+(\mathbf{k})b_s^-(\mathbf{k})$$
$$+\sum_{\pm\mathbf{k}}(\pm)(\omega_p^2/k)a^{\pm}(\mathbf{k})a^{\pm}(\mp\mathbf{k})$$
$$+i\sum_{\pm\mathbf{k}\lambda\eta}(\pm)(|g_{\mathbf{k}\lambda\eta}|/k^{1/2})a^{\pm}(\mathbf{k})B_{\lambda,\eta}^{\pm}(\mp\mathbf{k}). \tag{1.3}$$

V_{anh} is taken to have form[15]

$$V_{\text{anh}}=\sum_{\mathbf{k}\mathbf{k}'ss's''} h(\mathbf{k}\mathbf{k}'ss's'')\beta_s(\mathbf{k})\beta_{s'}(-\mathbf{k}-\mathbf{k}')\beta_{s''}(\mathbf{k}'), \tag{1.4}$$

where

$$\beta_s(\mathbf{k})\equiv b_s^+(\mathbf{k})+b_s^-(-\mathbf{k}). \tag{1.5}$$

$V^{(n)}$ is the exciton-phonon interaction involving $n-2$ phonons, of the form

$$V^{(n)}=\sum_{\mathbf{k}\mathbf{q}\mathbf{q}_1\mathbf{q}_2\cdots\mathbf{q}_{n-2}\cdot\lambda\lambda'\eta\eta'} f^{(n)}(\mathbf{k}\mathbf{q}\mathbf{q}_1\cdots\mathbf{q}_{n-2};\lambda\eta\lambda'\eta')$$
$$\times B_{\lambda,\eta}^+(\mathbf{k})B_{\lambda',\eta'}^-(\mathbf{k}-\mathbf{q})\beta(\mathbf{q}_1)\beta(\mathbf{q}_2)\cdots\beta(\mathbf{q}_{n-2})$$
$$\times\delta(\mathbf{q}+\mathbf{q}_1+\cdots+\mathbf{q}_{n-2}). \tag{1.6}$$

Various coupling functions for certain cases of interest are detailed in Refs. 13–15; general considerations regarding relative orders of magnitude in an adiabatic system are discussed in Ref. 9. Certain of the interactions employed here are appropriate only in the long-wavelength limit. Finally, we note the especially significant relationship between coupling functions in an insulator, namely, the sum rule[16]

$$\omega_p^2=\sum_{\lambda\eta}|g_{\lambda,\eta}(0)|^2/E_{\lambda,\eta}(0). \tag{1.7}$$

II. POLARITON EIGENFREQUENCIES AND TRANSFORMATION COEFFICIENTS

This section will be devoted exclusively to obtaining the dispersion $\omega=\omega(\mathbf{k})$ of the eigenmodes of the hamiltonian H_0, the "polaritons," and to obtaining in detail the transformation from the free fields to the polariton fields. The equation-of-motion formalism has been used previously in this connection by Refs. 16 and 17, for example. A new feature in our presentation is the explicit inclusion of continuum as well as discrete excitons throughout the calculations of the polariton dispersion and transformations.

The theory of continuous systems interacting with discrete fields is discussed in Ref. 18. One may conclude from the latter treatment that for a given $\mathbf{k}$ one obtains for the eigenfrequencies of H_0 the identical exciton continuum of eigenvalues as in the free system, plus a set of new discrete eigenfrequencies, which we proceed to derive. The corresponding eigenfunctions in the perturbed system, however, all differ from those of the unperturbed system.

The Hamiltonian of interest is

$$\tilde{H}\equiv H_0-H_L, \tag{2.1}$$

where H_L is the free phonon Hamiltonian [cf. Eq. (1.3)], which commutes with $\tilde{H}$ and may be diagonalized separately. We thus obtain the "photoexciton polaritons" characterizing the system. These eigenmodes of $\tilde{H}$ may be obtained by defining the operators $A_{\lambda,\eta}^{\pm}(\mathbf{k})$ for each and every $\mathbf{k}$ by the relation

$$A_{\lambda,\eta}^+(\mathbf{k})=\chi_0(\mathbf{k})a^+(\mathbf{k})+\sum_{\lambda,\eta}\chi_{\lambda,\eta}(\mathbf{k})B_{\lambda,\eta}^+(\mathbf{k})$$
$$+\phi_0(\mathbf{k})a^-(-\mathbf{k})+\sum_{\lambda,\eta}\phi_{\lambda,\eta}(\mathbf{k})B_{\lambda,\eta}^-(-\mathbf{k}), \tag{2.2}$$

where we now drop the explicit $\mathbf{k}$ dependence, for

notational simplicity. The discrete frequencies satisfy simultaneously the equations of motion,[16] for all λ, η,

$$[H, A_{\lambda,\eta}^{\pm}]=\pm\omega A_{\lambda,\eta}^{\pm}. \tag{2.3}$$

These conditions take the explicit form

$$\begin{aligned}
&(kc+2\omega_p^2/kc)\chi_0+\sum_{\lambda\eta} g_{\lambda,\eta}k^{-1/2}\chi_{\lambda,\eta}+(2\omega_p^2/kc)\phi_0 \\
&\qquad +\sum_{\lambda\eta} g_{\lambda,\eta}^{*}k^{-1/2}\phi_{\lambda,\eta}=\omega\chi_0, \\
&g_{\lambda,\eta}^{*}k^{-1/2}\chi_0+E_{\lambda,\eta}\chi_{\lambda,\eta}+g_{\lambda,\eta}^{*}k^{-1/2}\phi_0=\omega\chi_{\lambda,\eta}, \qquad (2.4)\\
&(2\omega_p^2/kc)\chi_0+\sum_{\lambda\eta} g_{\lambda,\eta}k^{-1/2}\chi_{\lambda,\eta}+(kc+2\omega_p^2/kc)\phi_0 \\
&\qquad +\sum_{\lambda\eta} g_{\lambda,\eta}^{*}k^{-1/2}\phi_{\lambda,\eta}=-\omega\phi_0, \\
&g_{\lambda,\eta}k^{-1/2}\chi_0+g_{\lambda,\eta}k^{-1/2}\phi_0+E_{\lambda,\eta}\phi_{\lambda,\eta}=-\omega\phi_{\lambda,\eta},
\end{aligned}$$

where we have reabsorbed the factor i in the photon-exciton coupling [cf. Eq. (1.3)] back into $g_{\lambda,\eta}$.

Using Eqs. (2.4) and (1.7), one obtains the condition for the solution of this homogeneous set of equations:

$$\begin{aligned}
\epsilon(\mathbf{k},\omega)&\equiv k^2c^2/\omega^2 \\
&=1+\sum_{\lambda}\frac{4\mid g_\lambda\mid^2}{E_\lambda(E_\lambda^2-\omega^2)}+\sum_{\eta}\frac{4\mid g_\eta\mid^2}{E_\eta(E_\eta^2-\omega^2)}, \qquad (2.5)
\end{aligned}$$

the eigenvalue equation for the discrete polariton frequencies $\omega(\mathbf{k})$. For $g_\eta=0$, all η, the result is the well-known polariton spectrum as illustrated in the figures in Refs. 10 and 19, for example. In the general case, when E depends on $\mathbf{k}$, one has a transcendental equation for ω^2, the solution of which may become especially tedious. Further on in this section we compute the solution for the dispersion relation for a model system.

The new polariton Hamiltonian is characterized by discrete frequencies $\omega(\mathbf{k},\lambda)$, and continuous frequencies identical with the unperturbed band of frequencies; then one has the normal-mode Hamiltonian

$$H_0=\sum_{\mathbf{k}\lambda\eta}\omega(\mathbf{k}\lambda\eta)A_{\lambda,\eta}^{+}(\mathbf{k})A_{\lambda,\eta}^{-}(\mathbf{k}). \tag{2.6}$$

The transformation coefficients (χ,ϕ) for the $[\alpha,\omega(\mathbf{k},\alpha)]$ polariton follow as $[\omega(\mathbf{k}\alpha)=\omega]$

$$\begin{aligned}
\chi_{\lambda,\eta}&=(\omega-E_{\lambda,\eta})^{-1}g_{\lambda,\eta}^{*}\omega^{-1/2}\gamma(\mathbf{k}\omega), \\
\phi_{\lambda,\eta}&=-(\omega+E_{\lambda,\eta})^{-1}g_{\lambda,\eta}\omega^{-1/2}\gamma(\mathbf{k}\omega), \qquad (2.7)\\
\chi_0&=2(kc+\omega)(k\omega)^{-1/2}\gamma(\mathbf{k}\omega), \\
\phi_0&=2(kc-\omega)(k\omega)^{-1/2}\gamma(\mathbf{k}\omega),
\end{aligned}$$

where

$$\gamma^{-1}(\mathbf{k}\omega)=[1+\sum_{\lambda\eta}4E_{\lambda,\eta}\mid g_{\lambda,\eta}\mid^2(\omega^2-E_{\lambda,\eta}^2)^{-2}]^{1/2}. \tag{2.8}$$

For the simplified case of a single dispersive level $E_1(\mathbf{k})$, one has

$$\begin{aligned}
\chi_1&=g_1^{*}\omega^{-1/2}(\omega+E_1)\alpha(\mathbf{k}\omega), \\
\phi_1&=-g_1\omega^{-1/2}(\omega-E_1)\alpha(\mathbf{k}\omega), \qquad (2.9)\\
\chi_0&=2(kc+\omega)(k\omega)^{-1/2}(\omega^2-E_1^2)\alpha(\mathbf{k}\omega), \\
\phi_0&=2(kc-\omega)(k\omega)^{-1/2}(\omega^2-E_1^2)\alpha(\mathbf{k}\omega),
\end{aligned}$$

where

$$\alpha^{-1}(\mathbf{k}\omega)=[(\omega^2-E_1^2)^2+4E_1\mid g_1\mid^2]^{1/2}. \tag{2.10}$$

This result is in the form given in the model of Ref. 16.

For the case where $E_{\lambda,\eta}$ is independent of $\mathbf{k}$, one has

$$\begin{aligned}
\gamma^{-1}(\mathbf{k}\omega)&=[\partial(\omega^2\epsilon(\omega))/\partial\omega^2]^{1/2} \\
&=[kc^2/\omega v_g(\omega)]^{1/2}, \qquad (2.11)
\end{aligned}$$

where $v_g(\omega)$ is the polariton group velocity

$$v_g(\omega)\equiv\partial\omega/\partial k. \tag{2.12}$$

In this case

$$\chi_{\lambda,\eta}=(\omega-E_{\lambda,\eta})^{-1}g_{\lambda,\eta}^{*}c^{-1}k^{-1/2}v_g^{1/2}, \text{ etc.} \tag{2.13}$$

The various eigenfunctions obtained above have been given previously, in an equivalent but slightly different form, in Ref. 20. The latter work considers the transformation between the old and new canonical coordinates of the interacting system; those coefficients are, to within a constant, equal to $(\chi_i^2-\phi_i^2)^{1/2}$. Various explicit forms for the coefficients, and other details of the transformation relating to discrete versus continuum behavior, however, were not emphasized in Ref. 20.

In actual computations one needs to extend the above results to account for a background dielectric constant,[3] i.e., to approximate the effect of levels far from the frequencies of interest by a constant contribution ϵ_0 to $\epsilon(\omega)$. This may be done by noting that if $1\to\epsilon_0$ in Eq. (2.5), we may retain the original relation via the replacements

$$g_{\lambda,\eta}\to g_{\lambda,\eta}\epsilon_0^{-1/2}, \qquad c\to c\epsilon_0^{-1/2}, \tag{2.14}$$

so that the corresponding changes in (χ,ϕ) will account for ϵ_0. We omit these factors in developing the formalism, but account for them in the various computations in the paper.

The inverse transformation to that in Eq. (2.2) may be shown to be[21]

$$\begin{aligned}
a^{+}&=\chi_0^{*}(\omega_0)A_0^{+}+\sum_{\lambda'\eta'}\chi_0^{*}(\omega_{\lambda',\eta'})A_{\lambda',\eta'}^{+} \\
&\qquad -\phi_0^{*}(\omega_0)A_0^{-}-\sum_{\lambda'\eta'}\phi_0^{*}(\omega_{\lambda',\eta'})A_{\lambda',\eta'}^{-}, \qquad (2.15)\\
B_{\lambda,\eta}^{+}&=\chi_{\lambda,\eta}^{*}(\omega_0)A_0^{+}+\sum_{\lambda'\eta'}\chi_{\lambda,\eta}^{*}(\omega_{\lambda',\eta'})A_{\lambda',\eta'} \\
&\qquad -\phi_{\lambda,\eta}^{*}(\omega_0)A_0^{-}-\sum_{\lambda'\eta'}\phi_{\lambda,\eta}^{*}(\omega_{\lambda',\eta'})A_{\lambda',\eta'}^{-}.
\end{aligned}$$

Calculation of Polariton Dispersion for a Model System

We calculate polariton frequency as a function of wave vector from Eq. (2.5), for a simplified model of a hydrogenic exciton band. Because of the computational difficulties it would introduce, we omit spatial dispersion effects, and take $E_{\lambda,\eta}$ independent of $\mathbf{k}$. The differences in the spectrum for only discrete levels resulting from

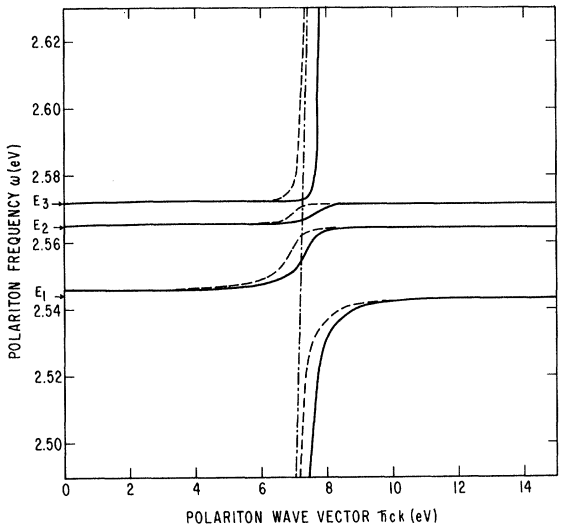

FIG. 1. Polariton frequency versus wave vector, for CdS A-exciton parameters (cf. Sec. II). Solid line: full result; dashed line: result in absence of continuum; dash-dotted line: photon line $\omega=\hbar kc\epsilon_0^{-1/2}$.

inclusion of spatial dispersion are noted, e.g., in Refs. 10 and 22.

Because of the rapid convergence of the discrete levels onto the gap E_g, we collapse, in our model, all energy levels but the two lowest onto E_g. We employ the $\boldsymbol{\eta}$ dependence of Eq. (1.1); the sum over $\boldsymbol{\eta}$ is transformed into an integration cutoff at $E_m=2E_g$, as in Ref. 12. The coupling constants $g_{\lambda,\eta}$ are related to g_1 by[11]

$$|g_\lambda|^2=|g_1|^2\lambda^{-3}, \qquad |g_\eta|^2=|g_c|^2\eta^{-2}F(\eta), \quad (2.16)$$

where

$$F(\eta)\equiv\eta[1-\exp(-A/\eta)]^{-1},$$
$$A\equiv 2\pi(2R/\alpha_R)^{1/2}, \quad (2.17)$$
$$|g_c|^2\equiv\pi a_0^3 A\,|g_1|^2.$$

The constants involved above, and their approximate values for the A exciton in CdS, are[14] as follows (eV units except where indicated otherwise): Exciton frequencies $E_1=2.544$, $E_2=2.565$, $E_\lambda(\lambda\geq 3)=E_g=2.572$; exciton Rydberg $R=0.028$; background dielectric constant $\epsilon_0=8$; effective masses $m_h^*/m_e=0.65$ and $m_e^*/m_e=0.25$ (m_e=electronic mass); exciton Bohr radius $a_0=27.5$ Å; coupling constant[22] $g_1=0.2$. Various other quantities are defined in Sec. I.

Equation (2.5) becomes

$$k^2c^2/\omega^2=\epsilon_0+4\sum_{\lambda=1,2}|g_\lambda|^2E_\lambda^{-1}(E_\lambda^2-\omega^2)^{-1}$$
$$+4(0.0771)E_g^{-1}(E_g^2-\omega^2)^{-1}$$
$$+|g_c'|^2\omega^{-2}[Z(-\omega)+Z(\omega)-2Z(0)], \quad (2.18)$$

where

$$Z(\omega)=\int_0^{\eta_m}d\eta\,F(\eta)(\eta^2+2(E_g+\omega)/\alpha_R)^{-1},$$
$$|g_c'|^2=2\,|g_c|^2(\hbar c)^{-3}(\alpha\pi^2)^{-1}, \quad (2.19)$$

where principal parts are to be understood when applicable.

The results of the calculation are shown in Fig. 1. The dotted line indicates the result when the continuum contributions are absent; in this instance the polariton dispersion above E_g never crosses the photon line $\omega=kc\epsilon_0^{-1/2}$, as does the full result. The detailed behavior of the polariton spectrum is of central importance in the calculation of RS cross sections, as will be demonstrated in the following sections.

III. GENERAL RESULTS FOR TEMPERATURE-DEPENDENT RAMAN CROSS SECTION

In this section we demonstrate how various nth order (n phonon) contributions to the temperature-dependent RS cross section may be obtained: One first obtains the total cross section for scattering from an initial polariton state $(\mathbf{k},\omega(\mathbf{k}))$ to all final states by use of the optical theorem[23]; one then proceeds to identify contributions to nth order scattering, and, specifically, the corresponding differential cross sections for scattering into solid angle $d\Omega$ and outgoing polariton wave vector spread dk'.

The following points must be emphasized:

(a) The cross section as defined here will refer only to polaritons inside the crystal, so that the actually observed cross section is obtained by incorporating the transmittivities associated with the incident and scattered polariton beams at the crystalline boundary.[7]

(b) In the exciton regime, damping (attenuation) of the incident and scattered polaritons cuts down the observed cross section, and should be taken into account before comparison with experiment is made.

Both the above considerations[10,24] may be incorporated by well-known techniques, and will not be discussed further here. Our attention will be directed solely to the scattering of "undamped" polaritons inside the crystal.

The total cross section σ at temperature $T=0°$K follows from the optical theorem[23] $[\omega(\mathbf{k})=\omega]$:

$$\sigma(\mathbf{k})=-[2/v(\mathbf{k})]\,\mathrm{Im}\langle\mathbf{k}\,|\,T(\omega)\,|\,\mathbf{k}\rangle, \quad (3.1)$$

where Im indicates imaginary part, and where $T(\omega)$ is the scattering operator defined by

$$T(\omega)\equiv V+VG(\omega)V,$$
$$G(\omega)\equiv(E-H+i\epsilon)^{-1}; \qquad V\equiv H-H_0. \quad (3.2)$$

$v(\mathbf{k})$ is the polariton velocity, taken to be[5] the group velocity $v_g=\partial\omega/\partial k$.

We extend this result to the case of temperatures where a thermal distribution of phonons exists, but where the number of excitons present is negligibly small. In this case we take[25]

$$\sigma(\mathbf{k},T)=-[2/v(\mathbf{k})]\,\mathrm{Im}\langle\langle\mathbf{k}\,|\,T(\{E\})\,|\,k\rangle\rangle\rangle, \quad (3.3)$$

where

$$\langle\langle\theta\rangle\rangle \equiv \mathrm{Tr}[\exp(-\beta H_L)\theta]/\mathrm{Tr}\exp(-\beta H_L), \quad (3.4)$$

where H_L is the free field Hamiltonian of the phonons alone [cf. Eq. (1.3)], and where E is the total initial system energy of both phonons and polariton $\mathbf{k}$; E takes on different values as the trace over all distributions is carried out.

First-Order RS

The first-order RS (RS1) cross section arises, in lowest order, from keeping only the $V^{(3)}$ terms in V. One finally obtains for the RS1 cross section σ_1

$$\sigma_1(\mathbf{k}, T) = -[2/v(\mathbf{k})] \sum_{\pm,\mathbf{k}_\alpha,\alpha} \{|\, V^{(3)}(\mathbf{k}; \mathbf{k}_\alpha\alpha)|^2 \times \mathrm{Im}G_1^{\pm}(\mathbf{k}; \mathbf{k}_\alpha\alpha)(\delta_+ + n_{\mathbf{k}-\mathbf{k}_\alpha})\} + (\mathbf{k}, \mathbf{k}_\alpha \text{ time ordering reversed}), \quad (3.5)$$

where δ_+ is unity for the plus sign in G and zero for the minus; and α is the polariton branch index. Other quantities appearing above are defined as

$$\langle \mathbf{k} \mid V^{(3)} \mid \mathbf{k}_\alpha\alpha\rangle \equiv (b_{\mathbf{k}-\mathbf{k}_\alpha}{}^{+} + b_{-(\mathbf{k}-\mathbf{k}_\alpha)}{}^{-}) V^{(3)}(\mathbf{k}; \mathbf{k}_\alpha\alpha),$$
$$n_{\mathbf{q}} \equiv \langle\langle b_{\mathbf{q}}{}^{+} b_{\mathbf{q}}{}^{-}\rangle\rangle, \quad (3.6)$$
$$G_1^{\pm}(\mathbf{k}; \mathbf{k}_\alpha\alpha) \equiv \{\omega - [\omega(\mathbf{k}_\alpha\alpha) \pm \omega_0(\mathbf{k}-\mathbf{k}_\alpha)] + \tfrac{1}{2} i\Gamma^{\pm}(\mathbf{k}_\alpha\alpha)\}^{-1}.$$

In perturbation theory[26] (neglecting V_{anh})

$$\Gamma^{\pm}(\mathbf{k}_\alpha\alpha) \cong 2\pi \sum_{(\pm),\mathbf{k}_\beta\beta} \{|\, V^{(3)}(\mathbf{k}_\alpha\alpha; \mathbf{k}_\beta\beta)|^2 (\delta_{(+)} + n_{\mathbf{k}_\alpha - \mathbf{k}_\beta}) \times \delta\{\omega - [\omega(\mathbf{k}_\beta\beta) + (\pm)\omega_0(\mathbf{k}_\alpha - \mathbf{k}_\beta) \pm \omega_0(\mathbf{k}-\mathbf{k}_\alpha)]\}\} + 2\pi \sum_\gamma \{|\, V^{(3)}(\mathbf{k}_\alpha\alpha; \mathbf{k}\gamma)|^2 \delta[\omega - \omega(\mathbf{k}\gamma)]\}. \quad (3.7)$$

In arriving at Eq. (3.6) we have kept only diagonal elements of the operator $G(E)$, as is consistent for obtaining the lowest-order contribution in $V^{(3)}$. For simplicity, we have not explicitly included the second-order perturbation-theory energy shift[26] in $\omega(\mathbf{k}\alpha)$ in the denominator of G, but shall understand $\omega(\mathbf{k}\alpha)$ to include this assumed small shift. Our result also notes the necessity for including[13,14] the time ordering where the polariton $(\mathbf{k}_\alpha\alpha)$ is emitted temporally prior to the polariton $\mathbf{k}$; this term may be obtained from the given one operationally by simply changing the sign in front of the brackets in G from minus to plus. This term does not lead to the resonance behavior in the optical region, and therefore in what follows we will often omit including it explicitly when writing formulas for cross sections.

If one now introduces the integration over $\mathbf{k}_\alpha$ as $(2\pi)^{-3}\int k'^2 dk' d\Omega$ then one may identify $d^2\sigma/dk'd\Omega$ directly as

$$d^2\sigma_1(\mathbf{k}, T)/dk'd\Omega = (2\pi)^{-3}[k'^2/v(k)] \sum_\alpha \{|\, V^{(3)}(\mathbf{k}; \mathbf{k}'\alpha)|^2 \times [\mathrm{Im}(-2G_1^{+}(\mathbf{k}; \mathbf{k}'\alpha))(1 + n_{\mathbf{k}-\mathbf{k}'}) + \mathrm{Im}(-2G_1^{-}(\mathbf{k}; \mathbf{k}'\alpha)) n_{\mathbf{k}-\mathbf{k}'}]\}. \quad (3.8)$$

Since (suppressing various dependences in our notation)

$$\mathrm{Im}(-2G_1^{\pm}) = \Gamma\{[\omega - (\omega(\mathbf{k}'\alpha) \pm \omega_0)]^2 + \tfrac{1}{4}\Gamma^2\}^{-1}, \quad (3.9)$$

then in the limit of small Γ one has two sharply peaked contributions in the cross section corresponding to Stokes and anti-stokes scattering, i.e., to creation and destruction of a phonon, about the energy-conservation frequencies

$$\omega(\mathbf{k}'\alpha) = \omega(\mathbf{k}) \pm \omega_0(\mathbf{k}-\mathbf{k}'). \quad (3.10)$$

Clearly, only Stokes scattering contributes at $T = 0°\mathrm{K}$. The line shapes are nearly Lorentzian when $\Gamma(\mathbf{k}'\alpha)$ and $V^{(3)}(\mathbf{k}; \mathbf{k}'\alpha)$ are slowly varying near the region of energy conservation.

For notational simplicity we adopt, from this point on, the symbol $d\sigma/d\Omega$ for the differential cross section as defined above.

Second-Order RS

The differential cross section for second-order Raman scattering (RS2) follows in an exactly analogous fashion to that for RS1. One term arises from $V^{(4)}GV^{(4)}$ in Eq. (3.2); the others result from the term G_0VGVG_0 in the expansion of the operator G as

$$G = G_{(0)} + G_{(0)}VG_{(0)} + G_{(0)}VGVG_{(0)},$$
$$G_{(0)} \equiv (E - H_0 + i\epsilon)^{-1}. \quad (3.11)$$

The lowest-order result for RS2 follows as (Wick's theorem[27] has been used for taking thermal averages of phonon operators)

$$d\sigma_2(\mathbf{k}, T)/d\Omega = (2\pi)^{-3}[k'^2/v(\mathbf{k})] \times \sum_{\mathbf{k}''\beta\pm} \{\{|\, V^{(4)}(\mathbf{k}; \mathbf{k}'\alpha, \mathbf{k}'')|^2 + 2\sum_\gamma [P(\mathbf{k}''\beta)P(\mathbf{k}''\gamma) + P(\mathbf{k}''\beta)P(\mathbf{k}''-\mathbf{k}'-\mathbf{k}, \gamma)] + \sum_s |\, V^{(3)}(\mathbf{k}; \mathbf{k}'\alpha)|^2 |\, V_{\mathrm{anh}}([\mathbf{k}-\mathbf{k}', s]; [\mathbf{k}-\mathbf{k}''], [\mathbf{k}''-\mathbf{k}'])|^2 \times [G_{(0),1}^{\pm}(\mathbf{k}; \mathbf{k}'\alpha)]^2 (\delta_+ + n_{\mathbf{k}-\mathbf{k}',s})(1 + 2n_{\mathbf{k}-\mathbf{k}',s})\} \times \{\mathrm{Im}(-2G_2^{\pm}(\mathbf{k}; \mathbf{k}'\alpha))(\delta_+ + n_{\mathbf{k}-\mathbf{k}''})(\delta_+ + n_{\mathbf{k}''-\mathbf{k}'})\}\} + (\text{time reversed contribution}), \quad (3.12)$$

where

$$P(\mathbf{k}''\beta) \equiv |\, V^{(3)}(\mathbf{k}; \mathbf{k}''\beta) V^{(3)}(\mathbf{k}''\beta, \mathbf{k}'\alpha)|\, G_{(0),1}(\mathbf{k}, \mathbf{k}''\beta),$$

where we have indicated phonon occupancy with brackets, and where we have included V_{anh} to the same order as $V^{(3)}$, although this may not be necessary in general, if the adiabatic approximation strictly applies.[9] The three types of terms for RS2 arise from the three processes indicated diagrammatically in Fig. 2. G_2 is now a two-phonon line-shape function; the small-coupling perturbation-theory result, employing for G_2 the two-phonon analog of G_1 in Eq. (3.6) is

$$\mathrm{Im}(-2G_2^{\pm}) = \Gamma\{[\omega - (\omega(\mathbf{k}'\alpha) \pm \omega_0(\mathbf{k}-\mathbf{k}'') \pm \omega_0(\mathbf{k}''-\mathbf{k}'))]^2 + \tfrac{1}{4}\Gamma^2\}^{-1}. \quad (3.13)$$

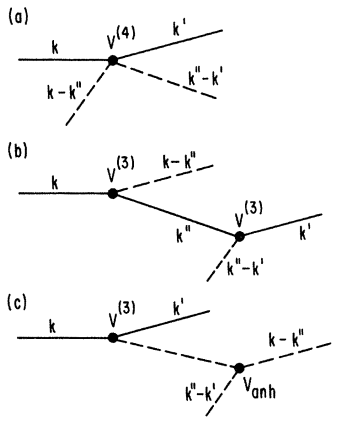

FIG. 2. RS2 scattering processes. Contributions from (a) $V^{(4)}$, (b) $V^{(3)}GV^{(3)}$, (c) $V^{(3)}GV_{\text{anh}}$. Solid line: polariton; dashed line: phonon.

Higher-order differential RS cross sections follow similarly, but because of the multiplicity of interactions involved little is gained in the way of clarity by detailing the nth-order term in general form. Rather, it would appear that a detailed investigation of the properties and interrelation of the RS1 and RS2 cross sections is more useful. This program is carried out in Sec. IV.

A remaining consideration in the evaluation of the RS cross section in the present case is the evaluation of polariton matrix elements. Using Eq. (2.15) the contribution of the operator

$$B_\lambda{}^+(\mathbf{q})B_{\lambda'}{}^-(\mathbf{q}')+B_\lambda{}^-(-\mathbf{q})B_{\lambda'}{}^+(-\mathbf{q}')$$

to the $(\mathbf{k}, \mathbf{k}')$ polariton matrix element is

$$[\chi_\lambda{}^*(\mathbf{q})\chi_{\lambda'}(\mathbf{q}')+\phi_\lambda{}^*(\mathbf{q})\phi_{\lambda'}(\mathbf{q}')]\delta(\mathbf{k}-\mathbf{q})\delta(\mathbf{k}'-\mathbf{q}'). \tag{3.14}$$

This relation enables one to express polariton matrix elements of exciton operators in terms of the polariton transformation coefficients obtained in Sec. II.

IV. FIRST- AND SECOND-ORDER RS CROSS SECTIONS FOR MODEL SYSTEMS

First-Order RS

Consider the scattering of a single polariton $\mathbf{k}$ to a single polariton $\mathbf{k}'$, where we suppress the branch indices in our notation. Then from Eqs. (3.8), (1.6), and (3.14), one obtains for the RS1 cross section ($f=f^{(3)}$)

$$d\sigma_1/d\Omega=(2\pi)^{-3}[k'^2/v(\mathbf{k})]\left|\sum_{\pm\lambda\eta\lambda'\eta'} f(\mathbf{k}\mathbf{k}'\lambda\eta\lambda'\eta')U(\lambda\eta\lambda'\eta')\right|^2 \times[-2\,\mathrm{Im}G_1{}^\pm(\mathbf{k};\mathbf{k}')](\delta_+ + n_{\mathbf{k}'-\mathbf{k}}), \tag{4.1}$$

where

$$U(\lambda,\eta;\lambda',\eta)=\chi_{\lambda,\eta}{}^*(\omega)\chi_{\lambda',\eta'}(\omega')+\phi_{\lambda,\eta}{}^*(\omega)\phi_{\lambda',\eta,}(\omega'). \tag{4.2}$$

From this point on, we introduce the approximation[14]

$$f(\mathbf{k}\mathbf{k}'\lambda\eta\lambda'\eta')=f(\mathbf{k}\mathbf{k}'\lambda\eta)\,\delta_{\lambda,\lambda'}\delta_{\eta,\eta'}, \tag{4.3}$$

which is exact only for $\mathbf{k}=\mathbf{k}'$. Then only the $U(\lambda\eta, \lambda\eta)$ terms contribute in Eq. (4.1).

Limits of $\Gamma\to 0$, $E_\lambda(k)$ *Independent of* $\mathbf{k}$, $T=0°\mathrm{K}$. In the limit where $E_\lambda(k)\approx$const. (no spatial dispersion) and $\Gamma\to 0$ in G, the cross section takes an especially simple form. The scattered spectrum is composed of two lines at the Stokes and anti-Stokes frequencies, with only the Stokes contribution at $T=0°\mathrm{K}$. The expression for $d\sigma/d\Omega$ reveals the dependence of the intensity of the scattered line with incoming photon frequency. The result at $T=0°\mathrm{K}$, with the above approximation, follows from Eqs. (4.1), (2.13), and (3.9) as ($c=1$)

$$(d\sigma_1/d\Omega)_0=(2\pi)^{-2}(k'/k)\left|\sum_{\lambda\eta} f(\mathbf{k}\mathbf{k}'\lambda\eta)\right|g_{\lambda,\eta}\,|^2 \times(\omega-E_{\lambda,\eta})^{-1}(\omega'-E_{\lambda,\eta})^{-1}+[(\omega+E)\text{ terms}]|^2, \tag{4.4}$$

where $\mathbf{k}'$ satisfies

$$\omega(\mathbf{k})=\omega(\mathbf{k}')+\omega_0(\mathbf{k}-\mathbf{k}'). \tag{4.5}$$

This result is similar to those given by Ref. 7, e.g., but is, however, free of velocity factors, and of a rather more transparent form. For ω, $\omega'\to E_\lambda$ the cross section diverges; this is due to neglecting both spatial-dispersion and polariton-damping effects.[10,28,7]

The finite-temperatures results for $\Gamma=0$ are simply

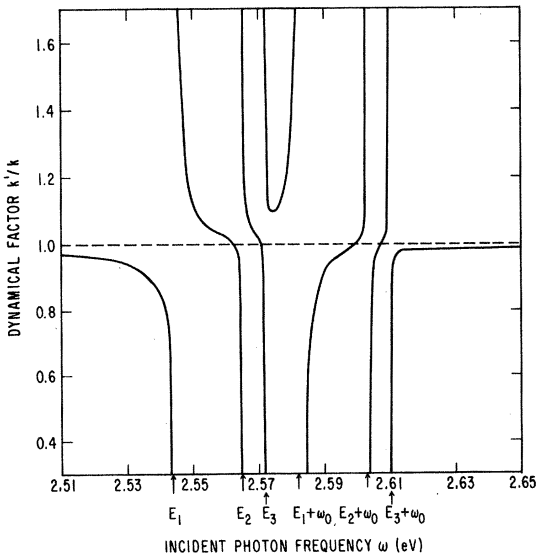

FIG. 3. Dynamical factor k'/k versus photon frequency for CdS A-exciton parameters (cf. Sec. II).

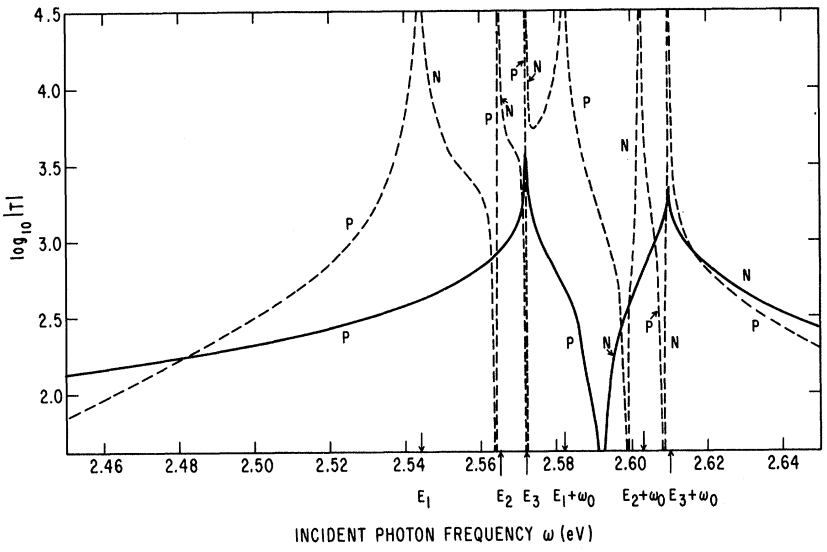

FIG. 4. Log_{10} of contributions to Raman tensor (arbitrary units) versus photon frequency (CdS parameters). Solid line: continuum contribution T_C; broken line: discrete-state contribution T_D. "P" indicates portions where T is positive, while "N" indicates portions where T is negative.

lines of intensity

$$(d\sigma/d\Omega)(1+n_{k_S'-k}) \quad \text{and} \quad (d\sigma/d\Omega)(k_A'/k_S')n_{k_A'-k}$$

at the Stokes and anti-Stokes frequencies $\omega'=\omega\pm\omega_0$, respectively, where k_S' and k_A' are the corresponding outgoing wave vectors.

RS1 Calculations for a Nondispersive Exciton Model. Calculations of the RS1 cross section due to a single discrete exciton level have been carried out previously within both the bare-exciton and polariton approaches.[10,28] A calculation including also the continuum has been carried out for bare-exciton theory[12]; however, the detailed variation due to a series of levels, for both the in and outgoing resonances, was not demonstrated.

The present calculation yields the differential cross section for Stokes LO phonon scattering due to an exciton band of an insulator, employing the model detailed in Sec. II. We assume[14] $f(\mathbf{k}\mathbf{k}'\lambda\eta)\approx \text{const}=f$, for the optical wave vectors of interest. In this model one has for $d\sigma/d\Omega$

$$d\sigma/d\Omega=(4\pi)^{-2}(k'/k)\,|\,T_D+T_C\,|^2\,|\,f\,|^2,$$

$$T_D=\sum_{\lambda=1}^{\infty}4\,|\,g_\lambda\,|^2(\omega\omega'+E_\lambda^2)(\omega^2-E_\lambda^2)^{-1}(\omega'^2-E_\lambda^2)^{-1}, \tag{4.6}$$

$$T_C=\,|\,g_R\,|^2[Z(-\omega)-Z(-\omega')+Z(\omega')-Z(\omega)],$$

where

$$|\,g_R\,|^2=(2\omega_0)^{-1}\,|\,g_C'\,|^2; \qquad \omega'=\omega-\omega_0, \tag{4.7}$$

with ω_0 the LO phonon frequency, approximated to be independent of wave vector ($\omega_0\approx 0.038$ eV for CdS). T_D and T_C are the discrete and continuum contributions to the "Raman tensor," respectively; g_λ and E_λ are detailed in Sec. II, as is the explicit form of the function Z.

The considerable variation in magnitude of the dynamical factor $S(k)\equiv k'/k$, and the variation in both sign and magnitude of T_D and T_C, is behavior strongly reflected in the variation of $d\sigma/d\Omega$ with frequency. The variation of $S(k)$ reflects the variation in the polariton dispersion relation as a function of frequency (cf. Fig. 1).

Numerical results for S, and T_D and T_C, are illustrated in Figs. 3 and 4, for the case of parameters approximately appropriate to the A-exciton band in CdS. As noted in Ref. 12, e.g., discrete state effects dominate in resonance regions where ω, $\omega'\sim E_\lambda$, while far from resonance continuum effects dominate.[7] The resulting cross section for CdS parameters is given in Fig. 5, with the detail in the resonance region shown in Fig. 6. Prominent features of the results for $d\sigma/d\Omega$ are (a) the structure associated with both incoming and outgoing resonances[3] and (b) the interplay of discrete and continuum effects in $d\sigma/d\Omega$. These results are discussed in more detail in Sec. V.

Note that there is only one independent photoexciton coupling constant in the model, once a hydrogenic structure is assumed, which we take to be $|\,g_1\,|$. To investigate the dependence of $d\sigma_1/d\Omega$ with g_1, we first of all note that $|\,T_D+T_C\,|^2$ is simply proportional to $|\,g_1\,|^4$. As for k'/k, note that as g_1 is increased, the polariton dispersion curves demonstrate smoother bending, moving off further from the bare levels and showing larger splittings (cf., e.g., Ref. 20). This behavior is reflected in k'/k so that one has all together, as $g_1(1)$ is increased to $g_1(2)$, an over-all enhancement in $d\sigma_1/d\Omega$ by a factor of $|\,g_1(2)\,|^4/|\,g_1(1)\,|^4$, while the onset to resonance occurs at an energy nearly $|\,g_1(2)\,|^2/|\,g_1(1)\,|^2$ further below E_1 than previously; in the resonance

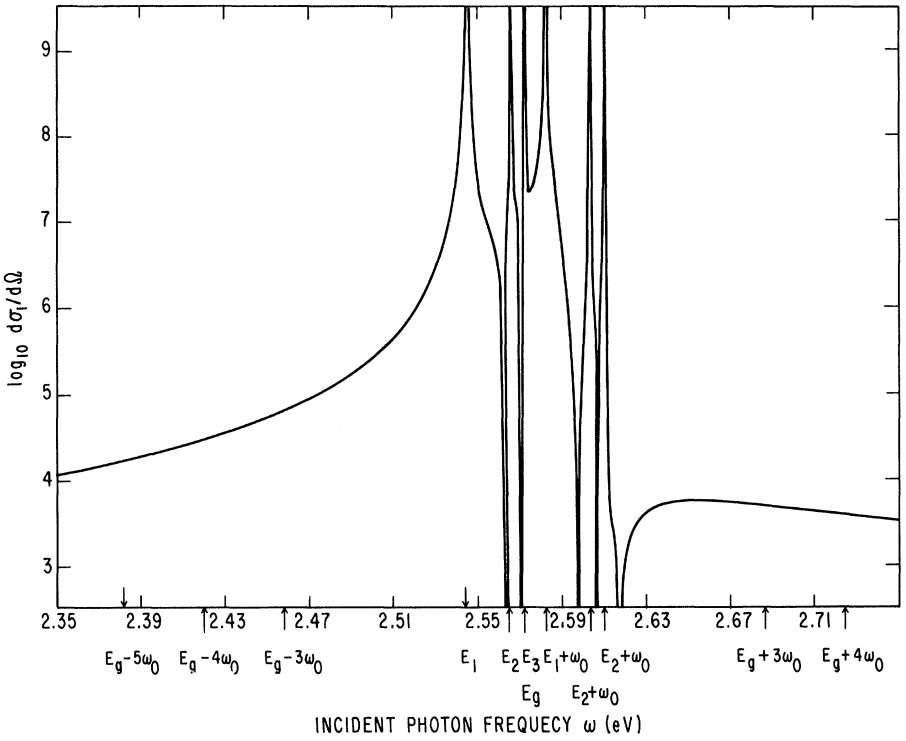

FIG. 5. Log_{10} RS1 cross section versus photon frequency (CdS parameters).

region the cross section varies more smoothly, but shows larger regions of splitting.

RS1, Dispersive Exciton Case. In this case the coefficients (χ, ϕ) are of somewhat complicated form; it is most useful to demonstrate the cross section due to simply a single exciton level $E_1(\mathbf{q})$. The $\Gamma=0$, $T=0°\text{K}$ cross section follows from Eqs. (4.1) and (2.10) as

$$d\sigma/d\Omega=(2\pi)^{-2}k'^2(v_g v_g'\omega\omega')^{-1}\,|f|^2\,|g_1|^4F(\mathbf{k}\omega;\,\mathbf{k}'\omega'), \tag{4.8}$$

where f has been introduced above Eq. (4.6), and where [cf. Eq. (2.10)]

$$F(\mathbf{k}\omega;\,\mathbf{k}'\omega')=\alpha^2(\mathbf{k}\omega)\alpha^2(\mathbf{k}'\omega') \times 4[\omega\omega'+E_1(\mathbf{k})E_1(\mathbf{k}')]^2. \tag{4.9}$$

From this form one easily discerns various previously noted properties of the single-branch cross section for the dispersive case.[8,9] In particular, one notes the saturation of $d\sigma/d\Omega$ as ω is increased through $E_1(0)$; this occurs since $\omega^2-E_1^2(q)\to 0$, while $v_g,\ v_g'\propto k'$ for large enough k. Results for CdS for the single-branch cross section for this simplified model are given in Ref. 10.

Second-Order RS2

We consider the $T=0°\text{K}$ (pure Stokes) RS2 cross section in the limit $\Gamma\to 0$ in the nondispersive exciton case described above for RS1. Inspection of Eq. (3.12) reveals three types of contributions ($V^{(4)}$, $V^{(3)}GV^{(3)}$, and $V^{(3)}GV_{\text{anh}}$), which yields the final result

$$d\sigma_2/d\Omega=(2\pi)^{-2}(k'/k)\,(S_1+S_2+S_3), \tag{4.10}$$

with [$f_{\text{anh}}\equiv h$ in Eq. (1.4)]

$$S_1\equiv |f^{(4)}|^2\mathcal{S}^2(\omega,\omega'),$$

$$S_2\equiv 2\,|f^{(3)}|^4\sum_{\mathbf{q}}[\mathcal{K}^2(\omega,\omega',\mathbf{q}) +\mathcal{K}(\omega,\omega',\mathbf{q})\mathcal{K}(\omega,\omega',\mathbf{q}-\mathbf{k}'-\mathbf{k})], \tag{4.11}$$

$$S_3\equiv |f^{(3)}|^2\,|f_{\text{anh}}|^2\,\mathcal{S}^2(\omega,\omega'),$$

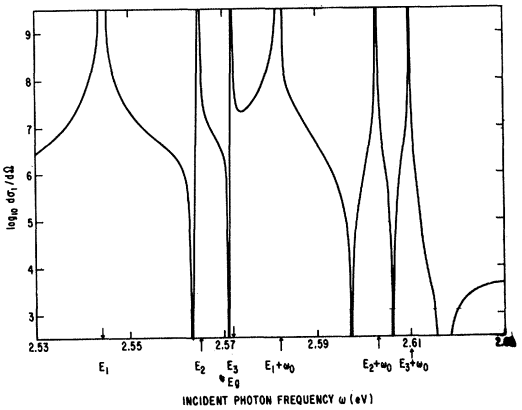

FIG. 6. Detail of RS1 cross section of Fig. 5, in the resonance regime.

where

$$\mathcal{K}(\omega,\omega',\mathbf{q})\equiv\sum_{\alpha}\mathcal{S}(\omega,\omega(\mathbf{q}\alpha))\mathcal{S}(\omega(\mathbf{q}\alpha),\omega')\times[\mathbf{q}(\omega-\omega(\mathbf{q}\alpha)-\omega_0)]^{-1},$$

where

$$\mathcal{S}(\omega,\omega')\equiv|\sum_{\lambda\eta}(E_{\lambda,\eta}-\omega)^{-1}(E_{\lambda,\eta}-\omega')^{-1}|\,g_{\lambda,\eta}\,|^2+[(E+\omega)\text{ terms}]|. \quad (4.12)$$

We have here taken the trilinear coupling functions independent of λ, η, and wave vector, as was done for RS1 above. The $\omega+E$ terms have been isolated because their recombination with $\omega-E$ terms substantially complicates the expressions for the S's, while in fact these terms do not contribute to the resonance behavior ($\omega,\omega'\sim E_\lambda$), which is the principal concern.

Note that in the resonance regions ($\omega,\omega'\sim E_\lambda$) the S_2 contribution tends to dominate $d\sigma/d\Omega$, since $\chi\sim1$ when $\omega(\mathbf{k}'')\sim\omega-\omega_0$, while $\chi\sim0$ for $\omega(\mathbf{k}'')\sim\omega-\omega_0$ outside resonance regions. Outside the resonance region the various terms may be expected to compete, and the extent of phonon anharmonicity, especially at high temperatures, may play a significant role.

We now investigate the ratios R, U defined as

$$R(\omega)\equiv\frac{d\sigma_2}{d\Omega}\Big/\left(\frac{d\sigma_1}{d\Omega}\right)^2,\qquad U(\omega)\equiv\frac{d\sigma_2}{d\Omega}\Big/\frac{d\sigma_1}{d\Omega} \quad (4.13)$$

in the resonance region $E_1-\omega\ll\omega_0$ (for the case $\Gamma=0$ and $T=0°\mathrm{K}$) for a single level E_1, neglecting spatial dispersion. In this instance it is a very good approximation to keep only $E_1-\omega$ terms in the cross sections. For the case where S_2 dominates one has

$$R(\omega)\approx(kk_2'/k_1'^2)\mathcal{F}(\omega)/\mathcal{S}^2(\omega,\omega_1'),$$
$$U(\omega)\approx(2\pi)^{-2}(k_2'/k_1')\,|f^{(3)}\,|^2\mathcal{F}(\omega), \quad (4.14)$$
$$\mathcal{F}(\omega)\equiv\tfrac{1}{2}(2\pi)^2\sum_{\mathbf{k}''\alpha\beta}\{\chi^2(\mathbf{k}''\alpha)[\omega-\omega(\mathbf{k}''\alpha)-\omega_0]^{-1}\times[\chi^2(\mathbf{k}''\beta)(\omega-\omega(\mathbf{k}''\beta)-\omega_0)^{-1}+(\mathbf{k}''\to\mathbf{k}''-\mathbf{k}'-\mathbf{k})]\},$$

where k_1' and k_2' are the outgoing Stokes wave vectors for RS1 and RS2, respectively. For photoexciton couplings of the order of those in CdS the ratio k_2'/k_1', for $\omega\to E_1$, is approximately $1-2\omega_0/\omega\approx1$. So except for a constant, the experimentally measurable ratio $U(\omega)$ is fully determined near resonance by just the function $\mathcal{F}(\omega)$. We will see in Sec. V that if S_2 indeed dominates $d\sigma/d\Omega$, measurements then imply that the function R is nearly unity and independent of frequency for LO phonon scattering as $\omega\to E_1$, in CdS.

V. DISCUSSION AND COMPARISON WITH EXPERIMENT

Properties of RS1 Cross Section

Among the prominent features of the polariton theory RS1 cross section are the nature of the resonances, and the competition between continuum and discrete contributions to scattering. We now proceed to discuss these properties.

The in-out photon resonances occur whenever $\omega,\omega'\sim E_\lambda$, a discrete bare exciton frequency [cf. Eq. (4.4) and Fig. 5]. Inclusion of spatial dispersion shifts the resonances to $\omega,\omega'\sim\omega_{l,\lambda}$ (cf. below). Singular behavior near resonance in the nondispersive model is in fact removable by inclusion of spatial dispersion[10,7] and/or damping effects.[28]

Continuum and discrete contributions compete throughout the resonance regime[7] (cf. Sec. IV and Fig. 4). Far enough below E_1 ($\sim E_1-2\omega_0$ in CdS) and above E_g ($\sim E_g+2\omega_0$ in CdS), the continuum terms dominate.[12] In the resonance regime the magnitude of T_C varies considerably, peaking at E_g and $E_g+\omega_0$, and changing sign from positive to negative near $E_g+\frac{1}{2}\omega_0$; T_D oscillates in both magnitude and sign throughout. The minima in the cross sections correspond to the opposite sign crossings of T_D and T_C; except for the minimum above $E_g+\omega_0$, which is absent when T_D is omitted, the other minima are only slightly shifted by the inclusion of T_C.

Of special significance is the fixed interrelation between discrete and continuum effects once the hydrogenic band model is adopted. The shape of $|\,T_D+T_C\,|^2$ is entirely independent of the photoexciton coupling g_1 (cf. Sec. IV). As such, arguments of the sort presented in Ref. 7, e.g., associating the difference in $d\sigma/d\Omega$ with differences in relative couplings for discrete and continuum states for different mechanisms (such as TO versus LO phonon coupling), do not seem applicable for the hydrogenic model as employed here and elsewhere[11,29] in discussing exciton properties of CdS (also cf. below).

The enhancement of $d\sigma/d\Omega$ as $\omega\to E_1$ has been observed in various experiments[1–4] in diverse insulators and semiconductors, among them CdS, CdSe, ZnTe, and GaP. The relative cross section has been compared with theory[12] for LO phonon scattering in CdS, e.g., where measurements up to about $\frac{1}{4}\omega_0$ below E_1 have been carried out. The nearly identical predictions of the polariton and bare-exciton (including damping) theories in this case[10] yield good fits for the data; free (noninteracting) electron-hole theory[13] does not. Only isolated points above the gap have been recorded; bare-exciton and polariton predictions are nearly equal in this region and both are an order of magnitude lower than the observed data. The disagreement suggests further inquiry regarding the effects of spatial dispersion and excitation of real-continuum polaritons, and the possibility of contributions to the observed cross section due to bound exciton scattering.

The outgoing photon resonances have not been observed directly as a function of incoming photon frequency, but analysis of outgoing spectra indicates their existence (cf. below).

Less satisfactory from the point of view of the present theory is the interpretation of TO phonon data.[2] In

CdS the TO phonon scattering saturates as $\omega \rightarrow E_1$, and no scattering at all is observed above the gap. Qualitative interpretations of these features await the rigorous demonstration of such behavior within a fundamental microscopic model. Suggested differences in discrete versus continuum couplings for different mechanisms, and variations in coupling constants with frequency, are not inherent in the present model; neither have the suggestive effects of damping been incorporated into polariton theory in a fundamental fashion (cf. below).

Polariton versus Bare-Exciton Predictions

Comparison of the RS1 cross section of Eq. (4.4) with the results of bare-exciton theory, as given by Eq. (33) of Ref. 14, or Eq. (3) of Ref. 12, e.g., demonstates that for the nondispersive model the polariton cross section $d\sigma_p/d\Omega$ and the corresponding bare-exciton cross section $d\sigma_b/d\Omega$ are related simply as

$$(d\sigma_p/d\Omega) = (d\sigma_b/d\Omega)\,(k'/k), \tag{5.1}$$

where the function k'/k is illustrated for CdS parameters in Fig. 3. We note the present results obtain in the limit of vanishing outgoing linewidth, and neglecting any contributions to RS due to excitation of real continuum polaritons (real interacting electron-hole pairs). In the case of no spatial dispersion this neglect is motivated for small k by noting that all such contributions proceed via nondiagonal values of $f(\lambda\eta;\lambda'\eta')$ in Eq. (4.1); but the off-diagonal elements[30] are of order k^2, and consequently small for small k.

The function k'/k varies enormously with incoming photon frequency within the resonance regime (bounded approximately by $E_1-\frac{1}{2}\omega_0$ and $E_g+\omega_0$ for CdS parameters), and is nearly unity outside this region, where RS1 is adequately described by bare-exciton theory alone[7]; within the resonance region we need to know, in addition to the bare-exciton results, the behavior of k'/k. We note also that polariton theory in this case yields results identical (neglecting damping factors) to those of the generalized bare-exciton theory of Ref. 28, which semiempirically accounts for the dispersion of the $e''m$ field in the crystal.

Comparison of the various theories in the case of spatial dispersion cannot be made as simply as for the nondispersive case. The treatment of Ref. 10, in conjunction with the present work, allows one to conclude that the various theories predict nearly similar results as in the nondispersive case to within millivolts below E_1, while above E_1, and into the continuum, the theories may differ substantially depending on details of the exciton dispersion and couplings.

General Characteristics of nth-Order RS

The present treatment allows one to draw certain general conclusions about the theoretically predicted behavior of the nth-order RS cross section, among them the following.

(a) The appearance of resonances associated with in and outgoing photons ω and ω', occurring whenever either

$$\omega,\ \omega' \sim E_\lambda, \qquad \omega-\omega' = \pm n\omega_0, \tag{5.2}$$

where E_λ is a discrete frequency, with n the order of the scattering, and with $\pm$ referring to Stokes and anti-Stokes scattering. The identical conclusions follow from a bare-exciton approach.[14] Intermediate-state resonances may appear, in principle, but the sums over these states of the form in Eq. (4.12) for RS2, e.g., would be expected, in general, to weaken such behavior.

(b) The outgoing spectrum is composed of narrow lines centered about energy-conservation frequencies $\bar{\omega}$ for systems with small polariton damping Γ, with broad lines for large Γ. The line shapes depend on the frequency variation of the factor $[k'/v(\mathbf{k})]\,|V^{(3)}(\mathbf{k},\mathbf{k}')|^2$ in the cross section, in addition to the Lorentzian-like shape arising from G. The cross section resonates strongly when $\bar{\omega}$ lies near a discrete bare-exciton frequency.

The existence of outgoing resonances in nth order has been demonstrated in experiments reported in Refs. 1 and 3, complementing the original observations of incoming photon resonances.[1,2] The results are discussed at some length in these references; the available data allow for limited quantitative comparisons with the theory. Near resonance the predicted Lorentzian-like line shapes are in evidence. In agreement with the previous discussion, no intermediate-state resonances are observed.

Although the polariton theory accounts most rigorously for the behavior of $d\sigma/d\Omega$ in the resonance regime, it is nevertheless simpler to handle formally than bare-exciton theory in many cases, as may be easily observed through a comparison of the present RS2 results for the nondispersive case, Eq. (4.11), with the bare-exciton results of Ref. 14. For example, certain of what appear to be different processes in bare-exciton theory are actually described by a single polariton process.[4]

This advantage in the formalism is somewhat offset by the calculational difficulties for second order and higher, arising from integrations over functions of polariton wave vector.

A particular observation, noted in Ref. 4, e.g., is the value of the ratio $R(\omega)$, measured to be nearly unity near resonance, implying $k\mathfrak{F}\approx k_1'\mathcal{S}^2$ [cf. Eq. (4.14)]. This result is plausible on the basis of the considerations of Sec. III, but does not follow as a general conclusion of the theory. The relationship between nth order intensities in LO phonon scattering is also discussed in Ref. 31, from a somewhat different point of view.

Comparison with Other Recent Work

A detailed polariton treatment of RS1, within a Green's-function formalism, has been recently advanced in Ref. 7 (herewith referred to as MB). As this

is the most recent treatment, it is instructive to discuss the central aspects of this work, and to compare it with the present work.

The formalism of MB is more general in a number of ways than the present one. For example we have here begun by singling out in H [Eqs. (1.2)–(1.6)] excitons made up from a single conduction-valence-band pair. While MB do eventually specialize to the analysis of such excitons in considering RS1, they first examine the photon propagator appropriate to a multiplicity of electron bands. Also, the photon propagator is investigated in considerable detail, the RS1 cross section $d\sigma_1/d\Omega$ eventually being extracted from the imaginary part of the proper self-energy. In addition to the generality introduced in this way, these propagators are of considerable interest in themselves, since a wide variety of system properties follow once they have been obtained (cf., e.g., Ref. 6). MB also discuss the possibility of other contributions to RS1 prior to specializing to those we consider at the outset here, and indicate various ways in which spatial dispersion is expected to effect the scattering.

As regards the final results for the RS1 cross section, the case which MB finally specialize to (dispersionless excitons, etc.) is the same as the one considered here, if one takes, in the present work, the limit of perfectly sharp outgoing photon line shape (cf. Sec. IV) and omits our consideration of the anharmonic phonon interaction $V_{\rm anh}$ (in the sharp outgoing shape limit, $V_{\rm anh}$ is important only in higher-order scatterings than the first). Thus, in this limit, the Stokes portions of Eqs. (3.8) and (4.1) are the same, allowing for notational differences, as Eq. (5.3) of MB for the Raman efficiency {note that our functions $(\chi^2-\phi^2)$ (cf. Sec. II) and ϵ [Eqs. (2.5) and (2.14)] are essentially equivalent to MB's exciton strength $\mathcal{S}$ [MB's Eq. (4.14)] and ϵ [MB's Eq. (3.26)], respectively}. In the present work, however, we further simplify the expression for $d\sigma_1/d\Omega$, in the dispersionless case, to a form independent of velocity factors [Eq. (4.4)]; this form, e.g., facilitates direct comparison with perturbation-theory results (cf. above).

MB do not carry out numerical computations of $d\sigma_1/d\Omega$ in their treatment, but discuss the general properties of $d\sigma_1/d\Omega$, especially for $\omega \lesssim E_1$. They note the enhancement of $d\sigma_1/d\Omega$ for $\omega \to E_1$, and the concomitant decrease in the continuum contributions to $d\sigma_1/d\Omega$ as $\omega \to E_1$ (cf. our Figs. 3 and 4). These and various other conclusions are similar to those observed here, and demonstrated in explicit and detailed form via numerical computations for CdS parameters. In addition, we describe in some detail in our work the importance of interference between discrete and continuum contributions to RS in determining the frequency dependence of $d\sigma_1/d\Omega$ for $\omega \lesssim E_g$ (cf. Figs. 4 and 5).

We find ourselves somewhat skeptical of the conclusion reached by MB that the dominance of continuum terms leads to "broad maxima" for $\omega < E_1$, and that such dominance may help explain observed RS1 TO phonon behavior (cf. Fig. 2 of Ref. 2). As illustrated in Fig. 7, we have varied parameters in a manner simulating continuum domination. Although the curves flatten out more, we do not obtain the concave-down curvature observed in the TO phonon data; our computations lead us to believe that other considerations may be necessary to explain these experimental results (cf. above).

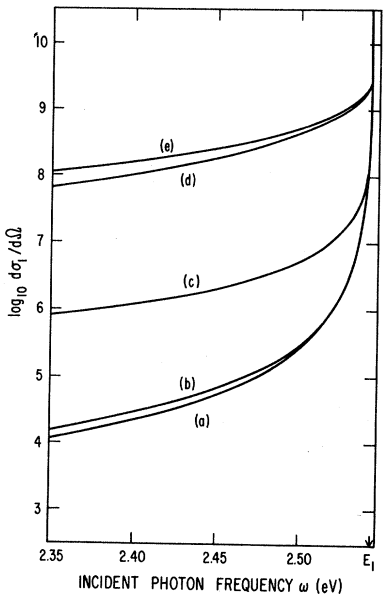

FIG. 7. $\log_{10}$ RS1 cross section versus photon frequency; dependence of $d\sigma/d\Omega$ for $\omega \lesssim E_1$ on continuum parameters. Let $(g_c/g_1)_0$ be the appropriate hydrogenic ratio of continuum to discrete couplings and E_m the energy cutoff on the continuum (cf. Sec. II). Then in (a) $(g_c/g_1)=(g_c/g_1)_0$, $E_m=2E_g$; (b) $(g_c/g_1)=(g_c/g_1)_0$, $E_m=20E_g$; (c) $(g_c/g_1)=3(g_c/g_1)_0$, $E_m=6E_g$; (d) $(g_c/g_1)=10(g_c/g_1)_0$, $E_m=2E_g$; and (e) $(g_c/g_1)=10(g_c/g_1)_0$, $E_m=20E_g$. All remaining parameters are identical with those in the previous figures.

Spatial Dispersion and Damping Effects

In bare-exciton theory it is necessary to include damping in lowest order[2,14] even in RS1 to obtain physically reasonable behavior throughout the resonance region. Spatial dispersion, on the other hand, becomes especially significant in higher-order cross sections, which involve integrations over intermediate-state vectors.[28] In RS2, for example, originally quadratic divergences are reduced to square-root divergences when spatial dispersion is accounted for.

In polariton theory, however, spatial dispersion may play a role from the start, as in this instance a multiplicity of degenerate modes are simultaneously excited at the crystal boundary[22]; contributions to scattering due to the additional "nonphotonic" modes may, in principle, be of importance. Below the frequency E_1 (cf. Fig. 1) the polariton spectrum is always non-

degenerate and such considerations are less important; in fact, below E_1 the cross sections are virtually independent of dispersive effects. Significant is the shift of all resonance behavior from $E_\lambda \rightarrow \omega_{l,\lambda}$ in the dispersive case[10]; $\omega_{l,\lambda}$ are the $k=0$ frequencies of the various polariton branches directly above the corresponding E_λ in frequency. Boundary conditions for determining the admixture of degenerate modes are discussed in Refs. 22, 32 and 33, but the theory is not sufficiently advanced to yield the discrete plus continuum admixture coefficients necessary in considering the dispersive case for frequencies above E_g. As such, one is unable to estimate the effects of including real continuum polaritons in the cross section.

Although inclusion of damping effects is merely a refinement in the case of spatial dispersion, they are most significant in the nondispersive case, where unphysical singularities and regions of splitting (perfect reflection) result in their absence. A general first-principles polariton theory including damping has not as yet been detailed, although special cases have been considered.[34]

The various experimental data referred to throughout this paper bolster aspects of the existing theory, while at the same time suggesting the necessity for further refinements. The various detailed predictions of the theory await comprehensive measurements of the variation of the cross section with both in and outgoing frequencies, throughout the entire resonance regime. In addition, it would be most desirable to have measurements of absolute scattering intensities, as such data provide information about the values of the microscopic coupling functions characterizing crystalline interactions. With recent advances in the tunability of lasers over a wide frequency range, it is reasonable to expect the availability of such data in the near future.

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