[22]The wave velocities were obtained from the phonon curves by computing phonon energies and dividing by the wave vector. Thus dispersion has some effect as can be seen from the ξ dependence of the Kr 2.5 °K results. However, dispersion causes $C^S > C^O$ which therefore tends to reduce the effect discussed in this paper.

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Theory of Resonant Raman Scattering in Crystals: A Generalized Bare-Exciton Approach*

Bernard Bendow† and Joseph L. Birman
Physics Department, New York University, Bronx, New York 10453
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The bare-exciton theory of light scattering in crystals is generalized to include dispersive effects, and to incorporate damping in a first-principles calculation. The theory is applied to exciton-mediated Raman scattering; expressions for the first- and second-order Raman cross sections due to a single discrete exciton level are derived, and the resonance behavior investigated. For small couplings and intermediate dampings the predictions of the present generalized theory are very similar to available bare-exciton and undamped-polariton predictions, while differing, however, for large couplings. The cross sections are resonant when the incoming or outgoing photon frequencies lie near an exciton frequency, and peak sharply for small photon-exciton couplings and dampings. Actual calculations are presented for various choices of the parameters, among them parameters appropriate to CdS. A comparison of the present theory with other theories and with experiment is carried out.

I. INTRODUCTION: HAMILTONIAN, BACKGROUND EFFECTS, AND GENERAL CONSIDERATIONS

A. Introductory Remarks

Encouraged by recent advances in laser technology, Raman scattering (RS) from crystals at optical frequencies has emerged as a useful tool for studying the electronic, as well as the lattice, properties of crystals.[1] A fundamental class of electronic excitations in a large variety of crystals (including ionic, molecular, and semiconducting ones) are interacting electron-hole pairs, or excitons. RS enables an investigation of exciton energy levels and the nature of their interactions with light and lattice vibrations.[2]

A number of papers have employed, in various forms, a "bare-exciton," or perturbation-theory, approach[3] to light-scattering problems, which has the advantages of being relatively simple and intuitively appealing. Toyozowa's treatment of light absorption,[4] and Ganguly and Birman's (GB) treatment[2] of RS, provide examples of the application of this approximate procedure. Its major advantage, as will be seen later, lies in enabling a fairly straightforward analysis of certain of the seemingly more complex aspects of a given problem. We will develop the bare-exciton framework here because we believe it leads to a useful approximate theory of resonance RS, in a form which may be followed by experimentalists and nonexperts in the field. In this situation, we feel, its full exposition and exploitation constitutes a highly desirable adjunct to the development and implementation of more rigorous and more elegant approaches.

An example of a more elegant (and, from a *computational* point of view, much more complicated) approach to light-scattering problems is that of polariton (composite-quasiparticle) theory.[5-7] We have, e.g., applied polariton theory to certain aspects of RS in insulators, in a parallel paper.[6] The purpose of the present work, on the other hand, is (a) the generalization of the bare-exciton framework in a number of ways especially relevant for calculations of resonance phenomena; (b) a detailed application of the theory to first- and second-order RS in insulators in the optical frequency regime.

The results of the present approach, which will, from here on, be referred to as "generalized-exciton theory," will be contrasted with those of polariton theory[6,7] for certain special cases.

The present generalizations include:

(a) A derivation of a formalism which accounts for background effects, including, as well, the presence of background absorption. This is important in reducing the complexity of various calculations by allowing one to concentrate on a limited number of interactions of interest (cf. Secs. II B and II C).

(b) An introduction of scattering theory so as to include damping effects from first principles. Such a procedure is essential in the resonance regime, where, if damping were omitted, the resonances would appear as singularities in the cross section,[2] thus limiting the usefulness of the results (cf. Sec. II A and Appendix).

(c) A proposal of an empirically introduced, but physically motivated, procedure to account for dispersion of light near resonance, which may be shown to lead to results in agreement with more ex-

act theory for certain cases where more exact results are available (cf. Sec. II B).

In the application of the theory to resonant RS, we focus attention on the model problem of discrete weakly dispersive exciton levels, interacting weakly with light. We present, for this case, various calculations of the RS cross section as a function of incident photon frequency, and compare the results with other theories and with experiment. In numerical computations parameters appropriate to insulators such as CdS will be employed.

B. Light-Scattering Hamiltonian

To describe light interacting with a crystal, we employ a model Hamiltonian[2] as discussed in detail by GB, involving photons, phonons, and excitons, and their mutual interactions $V^{(i)}$:

$$H = H_0 + \sum_{i=1}^{4} V^{(i)} \ . \tag{1.1}$$

Let $a^{\pm}_{\vec{q}}$ be Bose creation-destruction operators, where $\vec{q}$ is the wave vector, for photons of frequency qc; let $(b^{\pm}_{\vec{q}s},\ \omega_{0s}(\vec{q}))$ and $(B^{\pm}_{\vec{q}\lambda},\ E(\vec{q}\lambda))$ be the analgous quantities for phonons and excitons, respectively, where s and λ are branch indices; in $E(\vec{q})$, $\vec{q}$ is the wave vector associated with the center-of-mass motion of the exciton. Let $\vec{k}$ and $\vec{p}$ indicate wave vectors as well. Also, let us use e for exciton, L for phonon, and R for radiation in labeling interactions. Employing simplified forms appropriate to a single-photon polarization, the unperturbed (free-field) Hamiltonian H_0 and the interactions $V^{(i)}$ may then be written as ($\hbar = 1$)

$$H_0 = \sum_{\vec{q}} qc\, a^{+}_{\vec{q}} a^{-}_{\vec{q}} + \sum_{\vec{q}s} \omega_{0s}(\vec{q})\, b^{+}_{\vec{q}s}\, b^{-}_{\vec{q}s} + \sum_{\vec{q}\lambda} E(\lambda\vec{q})\, B^{+}_{\vec{q}\lambda}\, B^{-}_{\vec{q}\lambda} \ ,$$

$$V^{(2)} = \sum_{\vec{q}\lambda\pm} g^{\pm\pm}_{eR}(\vec{q}\lambda)\, a^{\pm}_{\mp\vec{q}}\, B^{\pm}_{\pm\vec{q},\lambda} + \sum_{\vec{q}\lambda s\pm} g^{\pm\pm}_{eL}(\vec{q}\lambda s)\, B^{\pm}_{\mp\vec{q},\lambda}\, b^{\pm}_{\pm\vec{q},s} \ ,$$

$$\begin{aligned} V^{(3)} = \sum_{\vec{k}\vec{q}\lambda\lambda' ss',\pm} & \big[g^{\pm}_{eeL}(\vec{q}\vec{k}\lambda\lambda' s)\, b^{\pm}_{\pm\vec{q}s}\, B^{+}_{\vec{k}-\vec{q},\lambda}\, B^{-}_{\vec{k}\lambda'} \\ & + g^{\pm}_{eeR}(\vec{q}\vec{k}\lambda\lambda')\, a^{\pm}_{\pm\vec{q}}\, B^{+}_{\vec{k}-\vec{q},\lambda}\, B^{-}_{\vec{k}\lambda'} \\ & + g^{\pm\pm\pm}_{eLL}(\vec{q}\vec{k}\lambda ss')\, B^{\pm}_{\mp\vec{q}\lambda}\, b^{\pm}_{\pm(\vec{k}+\vec{q}),s}\, b^{\pm}_{\mp\vec{k},s'} \big] \ , \end{aligned} \tag{1.2}$$

$$\begin{aligned} V^{(4)} = \sum_{\vec{k}\vec{q}\vec{p}\lambda\lambda' ss',\pm} & g^{\pm\pm}_{eeLL}(\vec{k}\vec{q}\vec{p}\lambda\lambda' ss') \\ & \times B^{\pm}_{\vec{q}+\vec{k},\lambda}\, B^{-}_{\vec{k}\lambda'}\, b^{\pm}_{\mp(\vec{q}+\vec{p}),s}\, b^{\pm}_{\pm\vec{p},s'} \ . \end{aligned}$$

The g's are appropriate coupling functions; these, as well as additional interaction terms in a Hamiltonian of more general form, are given by GB, for example. Following GB the photon-exciton couplings are taken of the form (long-wave limit)

$$|g_{eR}(\vec{k})|^2 \cong |g_{eR}|^2 (\hbar c k)^{-1} \ ,$$

and

$$|g_{eeR}(\vec{q}\vec{k})|^2 \cong |g_{eeR}|^2 (\hbar c k)^{-1} \ ,$$

where the g_{eR} and g_{eeR} are appropriate constants (we set $\hbar = 1$ in what follows). Various terms with $\pm$'s come in with factors of $\pm i$ in H (cf. GB).

In the calculations it will be assumed that the various coupling functions g_α appearing in H all satisfy $|g_\alpha|^2 \ll \omega$, where ω is an optical frequency; throughout the calculations we take the variable ω to refer to optical frequencies.

To maintain a parallel with GB, the contribution of the A^2 term from the vector potential[3] is not included explicitly. For frequencies lying in the optical regime, and for small coupling of light to excitons, it may be included formally by shifting the refractive index and photon-exciton coupling functions.[8] Also omitted in this idealized model (and because we are concerned with optical frequencies) is the direct photon-phonon coupling; for reasons of simplicity, trilinear exciton[9] and phonon anharmonicities[10] are omitted as well.

We emphasize an important convention which will be employed throughout the calculations: The occupancy of phonons will be treated at finite temperatures, while the effects of finite temperature on photons and excitons will be neglected. This will lead to the appearance of factors involving the phonon-occupancy function $n_{s\vec{q}}(\beta) = (e^{\omega_{0s}(\vec{q})\beta} - 1)^{-1}$, where β is the inverse temperature, in the expressions for the cross section.

C. Notational Coventions

We will employ the following conventions and notation regarding the state occupancies of various quasiparticles: no tilde, photon; single tilde, exciton; straight bar, phonon. The occupancies will be always ordered photon, exciton, phonon, from left to right. Vector notation will be omitted in indicating the exciton and phonon occupancies, but the vector character is to be understood. Illustrations are (a) the state $|2k,\ \tilde{k}'\rangle$ contains two photons of wave vector $\vec{k}$, and one exciton of wave vector $\vec{k}'$; (b) the state $|k,\ \tilde{k}',\ \bar{k}''\rangle$ contains one photon $\vec{k}$, one exciton $\vec{k}'$ and one phonon $\vec{k}''$; (c) the state $|\tilde{k},\ \bar{k}',\ \bar{k}''\rangle$ contains one exciton $\vec{k}$ and two phonons $\vec{k}'$ and $\vec{k}''$; (d) $\langle\tilde{k}|V|\tilde{k}';\ \bar{k}-\bar{k}',\ s\rangle$ is the matrix element for scattering via V, of an exciton $\vec{k}$ to an exciton $\vec{k}'$, accompanied by the creation of a phonon $\vec{k}-\vec{k}'$ from branch s.

We note again the previously mentioned conventions regarding the labels e, L, and R; some examples are: g_{eR} is the coupling between an exciton and a photon; V_{eeL} is an interaction involving two excitons and one phonon, etc.

D. Roles of Various Interaction Terms

In the present work we will employ the Hamiltonian H, which is appropriate to an infinite crystal, to describe light scattering involving photons incident from, and scattered to, the outside of a

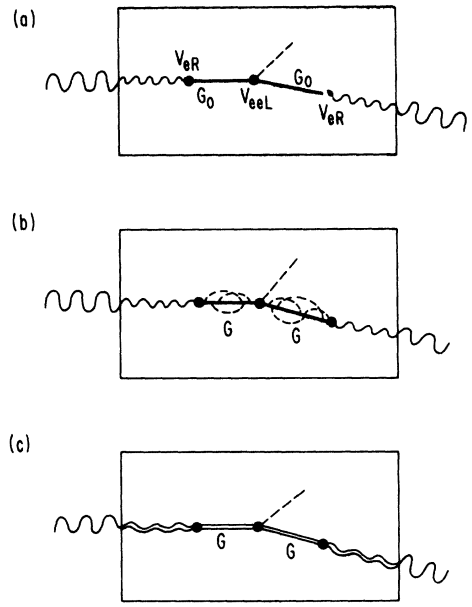

FIG. 1. Typical RS1 process, viewed in different degrees of approximation. G's indicate GF, or propagators, as introduced in Sec. II. A wavy line indicates a photon; a straight solid line, an exciton; a dashed line, a phonon. (a) Totally "bare" view of scattering: A photon incident from exterior, which is dispersed only by the background, creates an exciton, which subsequently scatters producing a phonon; a reverse process then leads to a scattered photon. G_0 represents the bare-exciton propagator. (b) Inclusion of interaction effects on G_0. While the remainder of the previous picture is unchanged, inclusion of "complex self-energy" effects of the electron-phonon interactions lead to the replacement of the bare-exciton propagator G_0 with the new propagator G (cf. Sec. II for details). (c) Inclusion of photon dispersion: The photon line (not a propagator here) is dispersed as discussed in Sec. II and as illustrated in Fig. 2, and is now represented by double wavy lines. Double straight lines indicate the new exciton propagator G as in (b).

finite crystal. As such, when applying perturbation theory to H_0, it is useful to distinguish between physically distinct roles which various interactions are assumed to play. Specifically, we adopt the following views.

As indicated schematically in Fig. 1, we consider photon-exciton interactions to act in the dual role of transforming photons incident from outside the crystal to excitons in the interior (and vice versa), and in altering the photon's dispersion (relation between $\vec{k}$ and ω inside the crystal). We consider the propagation of excitons to be altered, rather, by their interaction with the lattice, i.e., via the exciton-phonon interaction. The physical picture of a scattering process corresponding to the above description is indicated schematically in Fig. 1.

It may easily be seen that these conventions are entirely equivalent to those implicit (and essential) in carrying out the developments of a number of well-known treatments.[3,4,11] But more significantly, these assumptions will be shown to lead to results which agree with certain well-known or more exact ones, in certain limiting cases where the latter are available—a fact which argues strongly for their adoption.

II. ABSORPTION CROSS SECTION AND COMPLEX DIELECTRIC FUNCTION; GREEN'S FUNCTIONS

In this section we present a calculation of the absorption cross section and complex dielectric function in the system described by H [Eq. (1.2)], quantities to be made use of later. The calculation also introduces the philosophy and methods to be employed in treating RS, including the use of scattering Green's functions (GF) and the concomitant incorporation of damping effects. The calculation leads to a familiar form for the dielectric function ϵ.

We begin by considering the absorption cross section σ_A^1 due to a single discrete exciton level $E(\vec{k})$. More specifically, one first computes $\sigma_A^1(\vec{k}, \omega)$ (although we may suppress the $\vec{k}$ for notational simplicity), where the relation between $\vec{k}$ and ω near resonance is, due to interactions, no longer simply $k = \omega/c$, but of a more general form to be specified in the development. However, once the relationship between $\vec{k}$ and ω has been specified, σ_A^1 becomes a function of the external photon energy ω alone.

A. Calculation of σ_A

The absorption cross section $\sigma_A(\omega)$, i.e., the probability per unit length of crystal of absorption of a photon of frequency ω, may be expressed by use of the optical theorem[12] as

$$\sigma_A(\vec{k}\,\omega) = [2/v(k)]\,[-\mathrm{Im}\,T_{\vec{k}\vec{k}}(\omega)]\,, \tag{2.1}$$

where $v = \partial(kc)/\partial k = c$ is the velocity associated with photon $\vec{k}$. The quantity $T_{\vec{k}\vec{k}}$ is the diagonal matrix element in the photon state $\vec{k}$ of the scattering operator T, given by

$$\begin{aligned} &T \equiv V + V G V\,, \\ &V \equiv H - H_0\,, \quad G \equiv (E - H + i\varepsilon)^{-1}\,. \end{aligned} \tag{2.2}$$

The matrix elements of this operator yield transition amplitudes for the various possible light-scattering processes in the system.

We consider the case of a single exciton level $E(\vec{k})$ interacting with light. The lowest-order contributions in (2.1) arise from the term T_A in T, where

$$T_A \equiv V_{eR}^{(2)} G\, V_{eR}^{(2)}\,. \tag{2.3}$$

One has, employing Ref. 14,

$$(T_A)_{\vec{k}\vec{k}} = |\langle k| V_{eR}^{(2)} |\tilde{k}\rangle|^2 G_-(\vec{k}E) + |\langle k| V_{eR}^{(2)} |\tilde{k}, 2k\rangle|^2 G_+(\vec{k}E), \quad (2.4)$$

where G_- and G_+ are GF, or propagators, defined by

$$G_- \equiv \langle \tilde{k}| G |\tilde{k}\rangle, \quad G_+ \equiv \langle \tilde{k}, 2k| G |\tilde{k}, 2k\rangle. \quad (2.5)$$

The explicit evaluation of these functions proceeds in the manner outlined in the Appendix, upon incorporating the considerations discussed in Sec. ID regarding the roles of the various interaction terms. For the weak coupling case under discussion, one has

$$G_\pm(\vec{k}E) = \mp[E \pm E(\vec{k}) \pm \Delta(\vec{k}E) + \tfrac{1}{2} i\Gamma(\vec{k}E)]^{-1}, \quad (2.6)$$

where, in lowest order $[E \gg \omega_{0s}(\vec{k})]$,

$$\Gamma(\vec{k}E) \cong 2\pi \sum_{s\vec{q}\pm} |\langle \tilde{k}| V_{e\sigma L}^{(3)} |\tilde{k} - \tilde{q}, \bar{q}s\rangle|^2 (\delta_- + n_{\vec{q}s}) \times \delta(E - E(\vec{k} - \vec{q}) \pm \omega_{0s}(\vec{q})),$$

$$\Delta(\vec{k}E) \cong \sum_{\pm s} |\langle \tilde{k}| V_{eL}^{(2)} |\tilde{k}\rangle|^2 (\delta_- + n_{\vec{k}s}) [E \pm \omega_{0s}(\vec{k})]^{-1} + \mathrm{pp} \sum_{s\vec{q}\pm} |\langle \tilde{k}| V_{e\sigma L}^{(3)} |\tilde{k} - \tilde{q}\rangle|^2 [E - E(\vec{k} - \vec{q}) \pm \omega_{0s}(\vec{q})]^{-1}, \quad (2.7)$$

where pp indicates principal parts; δ_- is unity for the minus sign and zero for plus; and $n_{\vec{q}s}$ is the thermal phonon occupancy (cf. the end of Sec. IB). Δ and Γ are called the energy shift and damping functions, respectively. These forms for Δ and Γ correspond to the physical picture indicated in Fig. 1(b).

Using in (2.4) the explicit form for the matrix elements as given following Eq. (1.2) in Sec. IB, one finally obtains

$$-\mathrm{Im}(T_A)_{\vec{k}\vec{k}} = \tfrac{1}{2} |g_{eR}^{(2)}|^2 Q(\vec{k}\omega)(ck)^{-1}, \quad (2.8)$$

where

$$Q(\vec{k}\omega) \equiv 4\Gamma\omega E'(\vec{k}) \{[\omega^2 - E'(\vec{k})^2]^2 + [\omega^2 + E'(\vec{k})^2] \times \tfrac{1}{2}\Gamma^2 + \tfrac{1}{16}\Gamma^4\}^{-1} \quad (2.9)$$

and where $E'(\vec{k}) = E(\vec{k}) + \Delta$. We then have for the cross section σ_A^1 due to the single level $E(\vec{k})$

$$\sigma_A^1(\omega) = |g_{eR}^{(2)}|^2 Q(\vec{k}\omega) c^{-2} k^{-1}. \quad (2.10)$$

B. Dispersion Theory

In the present treatment we evaluate various cross sections as functions of both wave vectors $\vec{k}_i$ and frequencies ω_i associated with the photons involved in the scattering.[13] We note, however, that only the frequencies are supplied parameters (fixed by external measurements) in the present problem. Consequently, the most natural procedure to follow[14] in determining the explicit frequency dependence of a given cross section would be to express all k_α as functions of frequency, i.e., $k_\alpha = k_\alpha(\omega_\alpha)$. The σ_A, for example, would then become just a function of the frequency of the externally incident photon alone.

If dispersive effects are sufficiently weak, then far from the exciton energies involved, the free-space approximation $k = \omega/c$ is appropriate; various perturbation-theory corrections may, in principle, be calculated as well. However, for $\omega \cong E(0)$, or if $E(\vec{k})$ is strongly dependent on $\vec{k}$, k may differ substantially from ω/c, and perturbation theory is inapplicable.[5]

In treating the strong-dispersion problem with ω as the supplied parameter, it seems best suited to adopt the semiclassical approach to dispersion detailed in various places, such as Refs. 3 and 10. In this picture, an isotropic crystal, for example, is characterized[10] by a complex dielectric function $\epsilon(k\omega)$, which is directly related to $\sigma_A(k\omega)$, in a fashion to be specified below in Sec. IIC. A photon normally incident in the x direction, say, is characterized[10] by the wave function $\psi_0 \sim e^{i\omega c^{-1} x}$ outside the crystal, and by $\psi_c \sim e^{ikx}$ inside, where k satisfies the relation

$$k^2 = \epsilon(k\omega)\omega^2 c^{-2}. \quad (2.11a)$$

More specifically, one obtains, in general, a number of solutions for k^2, each of which may be expressed in the form

$$k_i^2 = \epsilon_i(\omega)\omega^2 c^{-2}, \quad (2.11b)$$

where ϵ_i, a function of ω alone, is the dielectric function characterizing the ith mode of excitation in the crystal. The relations (2.11) are, of course, equivalent to the familiar polariton dispersion relations exhibited in a variety of places.[5] In Fig. 2 we indicate schematically the sorts of interactions which are involved, and which we will include, in the evaluation of ϵ.

When the exciton levels $E_i(\vec{k})$ are either nondis-

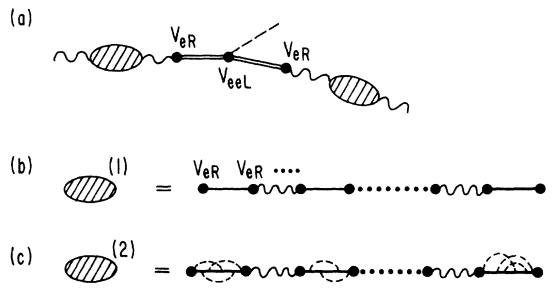

FIG. 2. Inclusion of photon dispersion in scattering processes (Ref. 14) (cf. Fig. 1 for meaning of various lines). (a) Photon dispersion is indicated in RS1 process via an interaction blob. (b) In lowest order the blob contains all possible interactions via V_{eR}. (c) Inclusion of exciton damping yields a further refinement to the interactions considered in (b).

persive (independent of $\vec{k}$) or very weakly dispersive, then one can show[6,8] that just a single solution with $|\mathrm{Re}\,k| \gg |\mathrm{Im}\,k|$ exists at any given value of ω. In the presence of dispersive $E_i(\vec{k})$, however, a multiplicity of solutions for k may, in general, arise. However, it can be shown[6] that for almost all frequencies, only a single mode from among these is transmitted at the crystal boundary with a sizable probability. For simplicity, we therefore limit ourselves to the case where k^2 is a single-valued function of ω. Should it be desired, one may straightforwardly generalize the present considerations to apply to the multiple-mode case as well.[6]

We now briefly outline the semiclassical interpretation of the propagation described by (2.11). Since k is, in general, complex, one has $\psi_c \sim e^{i n\omega c^{-1} x} e^{-\kappa\omega c^{-1} x}$, where $n + i\kappa \equiv \epsilon^{1/2}$, for the previously introduced example. Clearly, ψ_c describes pure propagation with real wave vector $n\omega c^{-1}$, coupled with a simultaneous exponential decrease with distance of the wave's amplitude (attenuation with coefficient $2\kappa\omega c^{-1}$). Evidently the quantities κ and σ_A are closely related, a fact which is exploited in Sec. IIC. Note that both n and κ include the effects of exciton damping (cf. above), once these have been incorporated into ϵ, as will be done in Sec. IIC.

Let us employ the above observations to extend the cross sections obtained here to apply to scattering of excitations characterized by complex values of the wave vector. We introduce the following fundamental assumption: Scattering events in the crystal proceed via just the propagating (unattenuated) portion of the ψ's (e.g., $e^{i n\omega c^{-1} x}$ in the previous example). Consequently, all cross sections are now to refer to just the unattenuated scattering, disregarding any concomitant spatial attenuation of the scattering waves. Once the details of the scattering geometry are specified for a particular actual experiment, one may proceed to incorporate spatial attenuation (and reflections at the boundaries as well) via well-known techniques [cf. discussions and references given following Eq. (3.11)]. The latter corrections enable the direct comparison of the theoretically predicted cross section with experimental results. The theoretical cross section is, then, obtained as a function of frequencies alone by employing for k's just the real part of the solutions following from (2.11) (i.e., $k \to n\omega c^{-1}$).

In the present approach, then, we have assumed that scattering in the case of complex k may be calculated by treating the spatial attenuation of the beams entirely separately from the scattering via their unattenuated portions. We believe this procedure is consistent with the semiclassical picture detailed above; since we have not presented a rigorous justification of the present procedure, we will characterize it as "empirical." In what follows, we will demonstrate that the present assumptions do, in fact, lead to results in agreement with various familiar existing ones.

We now proceed to introduce the concept of background absorption, which turns out to be of considerable convenience for treating scattering problems.

In a system with many levels, each one contributes a term $\sigma_A^{(i)}(\omega)$, similar to σ_A^1, to the total absorption cross section σ_A, so that

$$\sigma_A(\omega) = \sum_i \sigma_A^{(i)}(\omega) + \sigma_A^1(\omega) \ . \tag{2.12}$$

Now very often we are interested only in the scattering due to a particular level or group of levels in a system. All other levels may then be lumped into a background which may include not only all levels outside the particular frequency range being dealt with (which lead to a nearly constant, i.e., nondispersive, background), but all levels which simply are not involved in the particular scattering process under consideration (and which may lie within the frequency range, and do contribute to dispersion). We then take, say, $\sigma_A^1(\omega)$ due to a single level E, and a background $\sigma_A^0(\omega)$, with total $\sigma_A(\omega) = \sigma_A^1(\omega) + \sigma_A^0(\omega)$. The σ_A^0 might be obtained in a parallel fashion to σ_A^1, experimentally measured, or approximated in some other fashion.

We now proceed in evaluating $\epsilon(\vec{k}\omega)$.

C. Compex Dielectric Function

In order to obtain $\epsilon \equiv \epsilon_1 + i\epsilon_2$, we use the fact that σ_A is, in fact, the absorption rate of the incoming beam per unit length, so that it may be related to ϵ_2 via $[k = k(\omega)]$

$$\sigma_A(k\omega) = 2\omega c^{-1}\kappa(k\omega) = \omega c^{-1}\epsilon_2(k\omega) n^{-1}(k\omega) \tag{2.13}$$

or

$$\epsilon_2(k\omega) = \omega^{-2} \left| g_{eR}^{(2)} \right|^2 Q(\vec{k}\omega) + \epsilon_2^0(k\omega) \ , \tag{2.14}$$

where ϵ_2^0 is the background contribution to ϵ_2, i.e.,

$$\epsilon_2^0(k\omega) = c\omega^{-1}\sigma_A^0(\omega) n(k\omega) \ . \tag{2.15}$$

Using the Kramers-Kronig relations[15] to obtain ϵ_1, the full $\epsilon(\vec{k}\omega)$ follows as

$$\epsilon(\vec{k}\omega) = \epsilon^0(\vec{k}\omega) - [4 \left| g_{eR}^{(2)} \right|^2 E'(\vec{k})/\omega^2] \times [\omega^2 - E'(\vec{k})^2 - \tfrac{1}{4}\Gamma^2 + i\omega\Gamma]^{-1} \ . \tag{2.16}$$

If one takes $\Gamma^2 = 0$ at this point, one arrives at the classical form[16] for $\epsilon(k\omega)$. The present result for ϵ_2 differs in the appearance of Γ^4 terms, and in the coefficient of Γ^2, from classical theory and the Toyozowa[4] results; the latter, however, can be made to agree with the present result once antiresonant terms [cf. Eqs. (2.4)–(2.6)] are included in the analysis, as indeed they must be to satisfy causality, i.e., so that

$$\epsilon_2(\omega) = -\epsilon_2(-\omega), \qquad \epsilon_1(\omega) = \epsilon_1(-\omega) \ . \tag{2.17}$$

However, while ϵ would then be identical in the two

theories, the present results for σ_A are still more general due to the inclusion of dispersion, i.e., the appearance of dispersive n in σ_A [Eq. (2.10)]. The necessity of including "self-dispersion" in computing the absorption was, in fact, pointed out, [4] but not treated by Toyozowa; our procedure accounts for just this effect. We have computed σ_A, and found that its frequency dependence, for values of $\Gamma/E \sim 10^{-4}$, agrees generally with the Toyozowa predictions, although the dispersion of n in our theory does lead to some differences in the shape of the absorption line in the two theories.

One thus obtains familiar results for ϵ employing the techniques introduced above. In Sec. III, we extend these techniques to the calculations of RS cross sections.

III. FIRST-ORDER RAMAN SCATTERING (RS1)

In this section we obtain the cross section for first-order Stokes RS (one-phonon creation) in generalized exciton theory, and investigate its resonance properties. The resonance behavior is dominated by discrete exciton states, [17] and we therefore specialize to the consideration of such states. For simplicity, we consider in detail the contribution due to a single such discrete level; we will present actual calculations for various choices of the parameters in the theory. For definiteness, we will consider the cross section for LO-phonon RS; the principal origin of exciton damping may be considered to be interaction with acoustic phonons. [4]

Definition of cross section. In RS1 an incident photon $(\omega, \vec{k})$ is scattered to a final photon $(\omega', \vec{k}')$ with production of a phonon $(\omega_0, \vec{k}-\vec{k}')$ in the process (cf. Fig. 1). The differential cross section for Stokes RS of a photon $\omega \to \omega'$ is, by the golden rule, [12]

$$\frac{d\sigma_{\mathrm{RS1}}(\omega, \omega')}{d\Omega} = 2\pi v^{-1}(\vec{k}) \left| \langle k | T | k', \bar{k}-\bar{k}' \rangle \right|^2 \times [1 + n_{\vec{k}-\vec{k}'}(\beta)] \rho(\vec{k}, \vec{k}') , \quad (3.1)$$

where $v(\vec{k})$ is the velocity; T is the scattering operator (cf. Sec. II); $\rho(k, k')$ is the density of final states; and $n_{\vec{k}}$ is the LO-phonon occupancy (cf. Sec. IB).

The part of T contributing in lowest order to RS1 is $T_1 \equiv T_{11} + T_{12} + T_{13}$, where

$$T_{11} = V_{eR}^{(2)} G_1 V_{eeL}^{(3)} G_2 V_{eR}^{(2)} ,$$
$$T_{12} = V_{eR}^{(2)} G_1 V_{eeR}^{(3)} G_2 V_{eL}^{(2)} , \quad (3.2)$$
$$T_{13} = V_{eL}^{(2)} G_1 V_{eeR}^{(3)} G_2 V_{eR}^{(2)} .$$

Here G_1 may be chosen as either G or $\tilde{G}$, with the complementary choice for G_2 (cf. the following discussion) where

$$G \equiv (E - H + i\varepsilon)^{-1} , \quad \tilde{G} \equiv (E - \tilde{H} + i\varepsilon)^{-1} ,$$
$$\tilde{H} \equiv H_0 + V^{(2)} ,$$
$$G = \tilde{G} + \tilde{G} V^{(3)} G = \tilde{G} + G V^{(3)} \tilde{G} . \quad (3.3)$$

We have employed these relations between G and $(\tilde{G}, V, G)$ to obtain [8] Eq. (3.2). In considering LO-phonon RS we employ in T those parts of V which involve *only* LO phonons; for simplicity, we will omit the subscript s when the LO phonon is being referred to, but include it when other phonons are referred to.

We now evaluate the matrix elements of the T_{1i}, which will be used to obtain the full cross section $d\sigma/d\Omega$ defined by Eq. (3.1). Rather than study the explicit form for the full $d\sigma/d\Omega$, however, we will use the T_{1i} elements to obtain cross sections appropriate to each acting alone, independently of the others. This enables us to more simply investigate details of resonance behavior and frequency dependence. We will here give special attention to the T_{11} contribution, which is often the only one considered [6-8] in treatments of RS1.

T_{11} cross section. We study the various factors in Eq. (3.1) via a detailed treatment of the T_{11} contribution. The transition element becomes

$$\langle k | T_{11} | k' \bar{k} - \bar{k}' \rangle = \langle k | V_{eR}^{(2)} | \vec{k} \rangle G_e(\vec{k} E) \times \langle k | V_{eeL}^{(3)} | \vec{k}', \bar{k} - \bar{k}' \rangle G_{eL}(\vec{k}\vec{k}' E) \times \langle \vec{k}', \bar{k} - \bar{k}' | V_{eR}^{(2)} | k' \bar{k} - \bar{k}' \rangle , \quad (3.4)$$

where, as noted above, either G_e or G_{eL} must be taken with a tilde. We have retained only diagonal matrix elements of the operators $(E-H)^{-1}$ and $(E-\tilde{H})^{-1}$, a practice we shall follow throughout. This approximation is equivalent to replacing H by H_0 everywhere except where the denominator could blow up. [18]

We determine the choice of G and $\tilde{G}$ in the following manner: For the small coupling case, such a choice could be important *only* near the resonances (singularities in energy) of the operator $G_0 = (E - H_0)^{-1}$. Since the two GF's in our case are singular at values of the energy differing by an optical-phonon energy, one can choose the full G for whichever one of the factors is nearest to resonance. For simplicity in notation, this choice will always be understood in what follows. All of the various GF's encountered are defined and evaluated in the Appendix.

We give special attention to the damping function Γ in each GF, when a singularity occurs in the absence of Γ. Returning to T_{11}, the Γ_e is given in Eq. (2.7); Γ_{eL} is similarly given by

$$\Gamma_{eL}(\vec{k}\vec{k}' E)/2\pi = \left| \langle \vec{k}', \bar{k} - \bar{k}' | V_{eeL}^{(3)} | \vec{k} \rangle \right|^2 \delta[E - E(\vec{k})] + \sum_{s\vec{q}\pm} \left| \langle \vec{k}', \bar{k} - \bar{k}' | V_{eeL}^{(3)} | \vec{k}' - \vec{q}, \vec{q}s, \bar{k} - \bar{k}' \rangle \right|^2 (\delta_{-} + n_{\vec{q}s})$$

$$\times \delta[E - E(\vec{k}' - \vec{q}) - \omega_0(\vec{k} - \vec{k}') \pm \omega_{0s}(\vec{q})] \ . \quad (3.5)$$

Strictly speaking, phonon anharmonicity is expected to contribute to damping effects in all GF's involving phonons.[19] As noted previously, we omit this interaction for reasons of simplicity, but it may be incorporated in an exactly parallel fashion as the other interactions (cf. Ref. 20).

Employing Eq. (3.4) and the Appendix, one has

$$\frac{d\sigma_{RS1}(\omega, \omega', T_{11})}{d\Omega} = 2\pi v^{-1}(\vec{k}\omega)\left|\langle k| V_{eR}^{(2)} |\vec{k}\rangle\right|^2 \times \left|\langle k'| V_{eR}^{(2)} |\vec{k}'\rangle\right|^2 \left| V_{eeL}^{(3)}(\vec{k}, \vec{k}')\right|^2 \times \{[\omega - E(\vec{k}) - \Delta_e]^2 + \tfrac{1}{4}\Gamma_e^2\}^{-1} \times \{[\omega - E(\vec{k}') - \omega_0(\vec{k} - \vec{k}') - \Delta_{eL}]^2 + \tfrac{1}{4}\Gamma_{eL}^2\}^{-1} \rho(\vec{k}\vec{k}') \ , \quad (3.6)$$

where

$$V_{eeL}^{(3)}(\vec{k}, \vec{k}') \equiv \langle \vec{k}| V_{eeL}^{(3)} |\vec{k}', \bar{k} - \bar{k}'\rangle \quad (3.7)$$

and where the energy conservation condition

$$kc = k'c + \omega_0(\vec{k} - \vec{k}') \quad (3.8)$$

is obeyed for the pair $\vec{k}$, $\vec{k}'$. Taking

$$\rho(\vec{k}\vec{k}') = (2\pi)^{-3}c^{-1}(k')^2 \quad (3.9)$$

and combining Eqs. (3.6) and (3.9), one finally arrives at the result for $d\sigma/d\Omega$

$$\frac{d\sigma(T_{11})}{d\Omega} = (2\pi)^{-2}\left(\frac{k'}{k}\right)\left| g_{eR}^{(2)}\right|^4 \left| V_{eeL}^{(3)}(k, k')\right|^2 \times [(\omega - E(\vec{k}) - \Delta_e)^2 + \tfrac{1}{4}\Gamma_e^2]^{-1} \times [(\omega' - E(\vec{k}') - \Delta_{eL})^2 + \tfrac{1}{4}\Gamma_{eL}^2]^{-1} \ . \quad (3.10)$$

One notes that two resonances occur, at

$$\omega = E(\vec{k}) + \Delta_e \quad \text{and} \quad \omega' = E(\vec{k}') + \Delta_{eL} \ , \quad (3.11)$$

corresponding to incoming and outgoing photon frequencies lying near the shifted bare-exciton levels.

To complete the actual evaluation of $d\sigma/d\Omega$, here as in all cases, we must employ the relation between k and ω given in Sec. II, which accounts both for background dispersion, as well as the dispersion due to the self-same levels involved in the scattering event. Note also, that when relating theory to experiment, one needs to incorporate two other considerations (which we do not treat explicitly here). First of all, the absorption σ_A must be accounted for (cf., e.g., Ref. 21); second, the reflection of the initial and scattered beams at their respective boundaries should be accounted for (cf., e.g., Ref. 22). The $d\sigma/d\Omega$ defined and calculated here provides only the cross section inside the crystal for scattering by the propagating (unattenuated) part of the photon beam.

We assume, as discussed in Sec. IIB, that the exciton $E(\vec{k})$ depends very weakly on $\vec{k}$; otherwise the appearance of "extra waves"[23] complicates the above given correspondence in the frequency range spanned by the exciton.

Let us consider polariton theory results for the T_{11} cross section.[6,7] First-principles calculations of the cross section have been carried out in explicit form only for $\Gamma = 0$. Comparison of the present results with polariton results, for $\Gamma = 0$ and $E(\vec{k}) \approx E(0)$, shows that the predictions of the two theories are identical for this case.[24] In addition, of course, the present theory predicts the variation in $d\sigma/d\Omega$ for $\Gamma \neq 0$ as well, but results of more exact theory are not available for comparison.

Numerical computations. The dependence of $d\sigma/d\Omega$ on the coupling function $g_{eR}^{(2)}$, and on the damping function Γ, is illustrated in Figs. 3 and 4, respectively. These calculations have included, as indicated, a nondispersive background dielectric constant ϵ_1^0. One notes the in-out double resonance mentioned above; as expected, the resonances become very peaked and narrow for small g and Γ. The resonances broaden as these parameters are increased, and, in addition, for large enough g, one observes structure on the high-energy side of

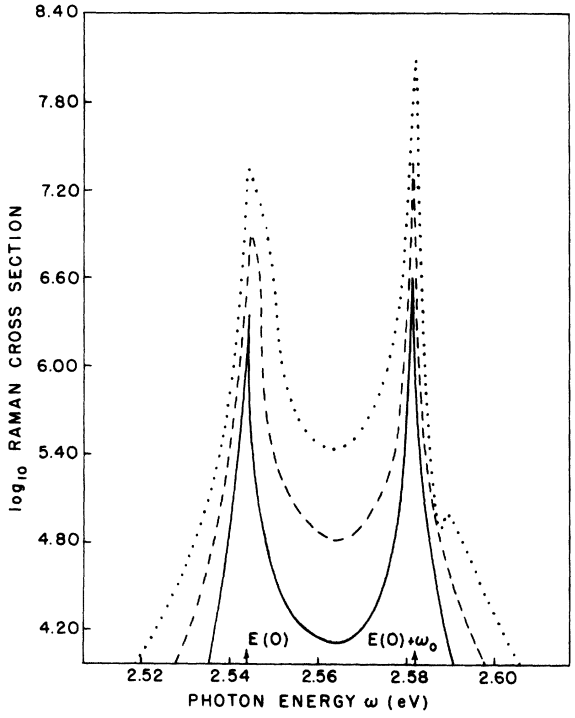

FIG. 3. Log_{10} of generalized-exciton cross section for RS1 (arbitrary units) vs photon energy ω, for various values of the photon-exciton coupling $|g|$; $E(0) = 2.544$ eV, $m^* = 4.3 \times 10^5$ eV, $\Gamma = 6 \times 10^{-4}$ eV, $\epsilon_0 = 8.0$. Solid line: $|g| = 0.2$ eV$^{3/2}$; dashed line: $|g| = 0.3$ eV$^{3/2}$; dotted line: $|g| = 0.4$ eV$^{3/2}$.

the outgoing resonance. The dependence of $d\sigma/d\Omega$ on $\epsilon_0 \equiv \epsilon_1^0$ is illustrated in Fig. 5.

If we assume $\Gamma \approx 10^{-3}$–10^{-4} eV for CdS, values in general agreement with available reflectivity data,[25] then the expected behavior of the contribution of the $n=1$ level of the A exciton in CdS is given approximately by the solid line in Fig. 3, the dotted line in Fig. 4, and the solid line in Fig. 5. The predictions are meaningful only close to resonance, where interference with the continuum and other levels can be neglected.[17]

Contributions of T_{12} and T_{13} to $d\sigma/d\Omega$. One has, for T_{12}, the transition element

$$\langle k | T_{12} | k', \bar{k} - \bar{k}' \rangle = \langle k | V_{eR}^{(2)} | \bar{k} \rangle G_e(\vec{k}E) \times V_{eeR}^{(3)}(k, k' - k) G_{eR}(k', \bar{k} - \bar{k}', E) V_{eL}^{(2)}(k - k') , \quad (3.12)$$

where

$$V_{eL}^{(2)}(k - k') \equiv \langle \bar{k} - \bar{k}' | V_{eL}^{(2)} | \bar{k} - \bar{k}' \rangle \quad (3.13)$$

and G_e has been discussed with regard to the T_{11} contribution. G_{eR}, a nondivergent factor, will be approximated as (cf. Appendix) (employing a prime to indicate an energy-shifted exciton)

$$G_{eR} \cong [\omega_0 - E'(\vec{k} - \vec{k}')]^{-1} . \quad (3.14)$$

The result for T_{12} acting alone, employing (3.12)

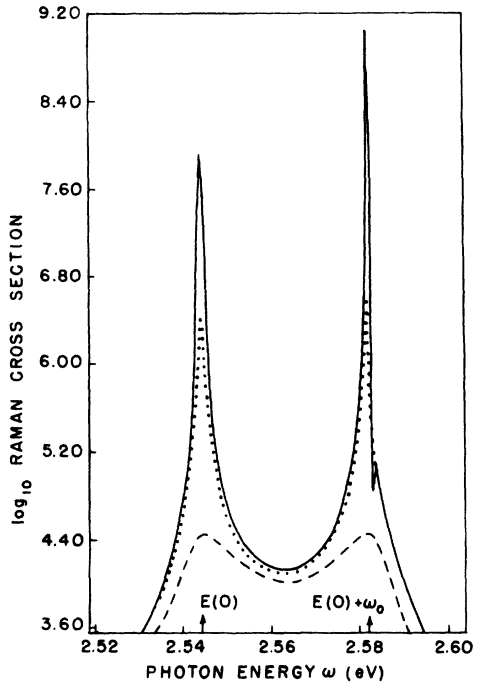

FIG. 4. Log_{10} of RS1 cross section vs ω, as in Fig. 3, for various values of damping Γ, for $|g| = 0.2$ eV$^{3/2}$, and the other parameters as in Fig. 3. Dashed line: $\Gamma = 6\times10^{-3}$ eV; dotted line: $\Gamma = 6\times10^{-4}$ eV; solid line: $\Gamma = 6\times10^{-5}$ eV.

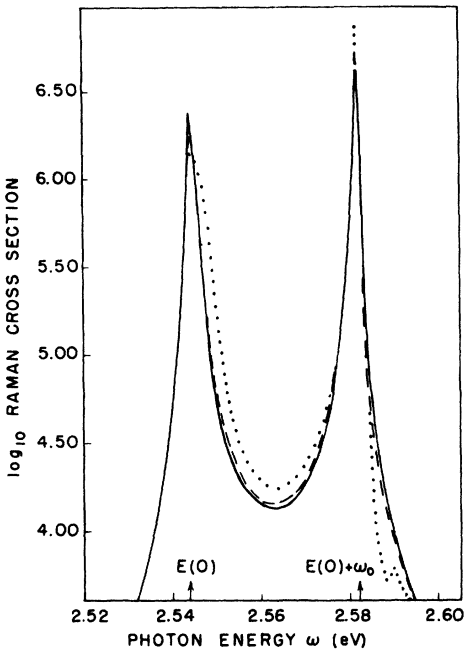

FIG. 5. Log_{10} of RS1 cross section vs ω, as in Fig. 3, for various values of the background dielectric constant ϵ_0, for $|g| = 0.2$, and other parameters as in Fig. 3. Solid line: $\epsilon_0 = 8$; dashed line: $\epsilon_0 = 4$; dotted line: $\epsilon_0 = 2$.

and the various results of the T_{11} discussion, becomes

$$\frac{d\sigma(T_{12})}{d\Omega} = (2\pi)^{-2}\left(\frac{k'}{k}\right) |g_{eR}^{(2)}|^2 |V_{eL}^{(2)}(k - k')|^2 \times |g_{eeR}^{(3)}(k, k')|^2 \{[\omega - E'(\vec{k})]^2 + \tfrac{1}{4}\Gamma_e^2\}^{-1} \times [\omega_0 - E'(\vec{k} - \vec{k}')]^{-2} . \quad (3.15)$$

We note that the T_{12} contribution is resonant only at $\omega \approx E'(\vec{k})$.

Similarly, one has for T_{13}

$$\langle k | T_{13} | k', \bar{k} - \bar{k}' \rangle = V_{eL}^{(2)}(k - k') G_{ReL}(k, \bar{k}' - \bar{k}, \bar{k} - \bar{k}') \times \langle k, \bar{k}' - \bar{k}, \bar{k} - \bar{k}' | V_{eeR}^{(3)} | \bar{k}', \bar{k} - \bar{k}' \rangle G_{eL}(k'kE) \times \langle \bar{k}', \bar{k} - \bar{k}' | V_{eR}^{(2)} | k', \bar{k} - \bar{k}' \rangle . \quad (3.16)$$

Approximating for the nondivergent factor G_{ReL} as in the Appendix, one obtains the contribution of T_{13} acting alone as

$$\frac{d\sigma(T_{13})}{d\Omega} = \frac{d\sigma(T_{12}; k, \omega \to k', \omega'; \omega_0 \to -\omega_0; \Gamma_e \to \Gamma_{eL})}{d\Omega} . \quad (3.17)$$

The only resonance for the T_{13} contribution is at $\omega' \approx E'(\vec{k}')$.

The complete differential cross section may be constructed directly from the various matrix elements obtained in the text as

$$\frac{d\sigma}{d\Omega} = (2\pi)^{-2}\left(\frac{k'}{k}\right)\left|\left|g_{eR}^{(2)}\right|^2 V_{eeL}^{(3)}(k,k')\right.$$
$$\times[\omega - E(\vec{k}) - \Delta_e + \tfrac{1}{2}i\Gamma_e]^{-1}[\omega' - E(\vec{k}') - \Delta_{eL} + \tfrac{1}{2}i\Gamma_{eL}]^{-1}$$
$$+ g_{eR}^{(2)} V_{eL}^{(2)}(k-k') g_{eeR}^{(3)}(k,k')\{[\omega - E'(\vec{k}) + \tfrac{1}{2}i\Gamma_e]^{-1}$$
$$\times[\omega_0 - E'(\vec{k}-\vec{k}')]^{-1} - [\omega' - E'(\vec{k}') + \tfrac{1}{2}i\Gamma_{eL}]^{-1}$$
$$\times[\omega_0 + E'(\vec{k}-\vec{k}')]^{-1}\}\Big|^2 . \quad (3.18)$$

It is clear that all told there are two resonances, one at $\omega = E(\vec{k}) + \Delta_e$ and the other at $\omega' = E(\vec{k}) + \Delta_{eL}$. All contributions are finite at resonance; for small couplings, various contributions may remain approximately Lorentzian about either of the two resonances. In general, various contributions may interfere either constructively or destructively, depending on the relative signs and magnitudes of the various coupling constants, complicating the dependence of $d\sigma/d\Omega$ on ω.

IV. SECOND-ORDER RAMAN SCATTERING (RS2)

In this section we investigate second-order Raman scattering (RS2) in a manner analogous to the treatment of first-order scattering in Sec. III. After demonstrating how various parts of the scattering operator T contribute to Stokes LO-phonon RS2, we investigate resonance properties and specific examples of the contributions to the cross section. We conclude with a brief discussion of how the inclusion of the exciton's spatial dispersion changes the character of intermediate resonances.

Fundamental considerations. RS2 is defined as a process in which an incident photon $(\vec{k}, \omega)$ is scattered to a final photon $(\vec{k}', \omega')$, with the production of two phonons $\vec{k} - \vec{k}''$ and $\vec{k}'' - \vec{k}'$ in the process. We assume that the two phonons are approximately dispersionless, so that conservation of energy determines the allowed $\vec{k}'$ uniquely. In this section, the methods of Sec. III in handling RS1 are employed. The contributions to RS2 are different from those of GB, where an equivalent to the expansion $G = G_0 + G_0 V G_0 + \cdots$ was employed.[2] The present section restricts all expansions to the operators G and $\tilde{G}$, of the forms

$$G - \tilde{G} - \tilde{G}V\tilde{G} = \tilde{G}VG V\tilde{G}$$
$$= \tilde{G}V\tilde{G}VG = GV\tilde{G}V\tilde{G} . \quad (4.1)$$

The lowest-order contributions to RS2 are taken to arise from either one quadrilinear interaction or two trilinear interactions, where any set of interactions involve two phonon operators all told. With the appropriate scattering operator

$$T_2 = \sum_{i=1}^{9} T_{2i} , \quad (4.2)$$

one has for the cross section

$$\frac{d\sigma_{RS2}(\omega,\omega')}{d\Omega} = (2\pi)^{-2}(k')^2 c^{-2}$$
$$\times \left|\langle k | T_2 | k', \vec{k} - \vec{k}'', \vec{k}'' - \vec{k}'\rangle\right|^2$$
$$\times [1 + n_{\vec{k}-\vec{k}''}(\beta)][1 + n_{\vec{k}''-\vec{k}'}(\beta)], \quad (4.3)$$

where integration over $\vec{k}''$, and the energy conservation δ function, will be understood.

The T_{2i} we shall consider are of five types:

(a) Two $V_{eR}^{(2)}$'s, one $V_{eeLL}^{(4)}$:

$$T_{21} = V_{eR}^{(2)} G V_{eeLL}^{(4)} G V_{eR}^{(2)} .$$

(b) One each of $V_{eR}^{(2)}$, $V_{eeR}^{(3)}$, and $V_{eLL}^{(3)}$:

$$T_{22} = V_{eR}^{(2)} G V_{eeR}^{(3)} G V_{eLL}^{(3)} ,$$
$$T_{23} = V_{eLL}^{(3)} G V_{eeR}^{(3)} G V_{eR}^{(2)} .$$

(c) One each of $V_{eR}^{(2)}$, $V_{eeR}^{(3)}$, $V_{eeL}^{(3)}$, and $V_{eL}^{(2)}$:

$$T_{24} = V_{eR}^{(2)} G V_{eeR}^{(3)} G V_{eeL}^{(3)} G V_{eL}^{(2)} ,$$
$$T_{25} = V_{eR}^{(2)} G V_{eeL}^{(3)} G V_{eeR}^{(3)} G V_{eL}^{(2)} ,$$
$$T_{26} = V_{eL}^{(2)} G V_{eeL}^{(3)} G V_{eeR}^{(3)} G V_{eR}^{(2)} ,$$
$$T_{27} = V_{eL}^{(2)} G V_{eeR}^{(3)} G V_{eeL}^{(3)} G V_{eR}^{(2)} .$$

(d) Two $V_{eR}^{(2)}$'s and two $V_{eeL}^{(3)}$'s:

$$T_{28} = V_{eR}^{(2)} G V_{eeL}^{(3)} G V_{eeL}^{(3)} G V_{eR}^{(2)} .$$

(e) Two $V_{eL}^{(2)}$'s and two $V_{eeR}^{(3)}$'s:

$$T_{29} = V_{eL}^{(2)} G V_{eeR}^{(3)} G V_{eeR}^{(3)} G V_{eL}^{(2)} .$$

The same remarks as in the previous Sec. III apply regarding the choice of G or $\tilde{G}$; in the present instance we may choose one factor of G and two of $\tilde{G}$, in a manner dictated by convenience [cf. Eq. (4.1)].

Transition matrix elements. We need matrix elements of the T_{2i} of the form

$$\langle k | T_{2i} | k', \vec{k} - \vec{k}'', \vec{k}'' - \vec{k}'\rangle . \quad (4.4)$$

Referring to the Appendix for the explicit form for the various GF's, and employing the previously introduced abbreviated notation for matrix elements whenever clear, one obtains

$$T_{21} = V_{eR}^{(2)}(k) G_e(k) V_{eeLL}^{(4)}(kk'k''E) G_{eLL}(k', k-k'', k''-k') V_{eR}^{(2)}(k') ,$$
$$T_{22} = V_{eR}^{(2)}(k) G_e(k) V_{eeR}^{(3)}(kk') G_{eR}(k', \tilde{k}-\tilde{k}') V_{eLL}^{(3)}(k-k', k'') ,$$
$$T_{23} = \langle k | V_{eL}^{(3)} | k, \tilde{k}'-\tilde{k}, \tilde{k}-\tilde{k}'', \tilde{k}''-\tilde{k}'\rangle G_{ReLL}(k, k'-k, k-k'', k''-k')$$
$$\times \langle k, \tilde{k}'-\tilde{k} | V_{eeR}^{(3)} | \tilde{k}'\rangle G_{eLL}(k', k-k'', k''-k') V_{eR}^{(2)}(k') ,$$

$$T_{24} = V^{(2)}_{eR}(k)G_e(k)V^{(3)}_{eeR}(k,k')G_{eR}(k',\vec{k}-\vec{k}')V^{(3)}_{eeL}(k-k',k-k'') \times G_{ReL}(k',k-k'',k''-k')V^{(2)}_{eL}(k-k'')+(k''\to k+k'-k''),$$

$$T_{25} = V^{(2)}_{eR}(k)G_e(k)V^{(3)}_{eeL}(k,k'')G_{eL}(k'',k-k'')V^{(3)}_{eeR}(k'',k') \times G_{ReL}(k',k'-k'',k-k'')V^{(2)}_{eL}(k''-k')+(k''\to k+k'-k''),$$

$$T_{26} = V^{(2)}_{eL}(k''-k')G_{ReL}(k,k'-k'',k''-k')V^{(3)}_{eeL}(k'-k'',k'-k)\ G_{ReLL}(k',k,k-k'',k''-k') \times V^{(3)}_{eeR}(k',k)G_{eLL}(k',k-k'',k''-k')V^{(2)}_{eR}(k')+(k''\to k+k'-k''),$$

$$T_{27} = V^{(2)}_{eL}(k''-k)G_{ReL}(k,k-k'',k''-k)V^{(3)}_{eeR}(k'',k)G_{eL}(k'',k-k'')V^{(3)}_{eeL}(k'',k') \times G_{eLL}(k',k-k'',k''-k')V^{(2)}_{eR}(k')+(k''\to k+k'-k''),$$

$$T_{28} = V^{(2)}_{eR}(k)G_e(k)V^{(3)}_{eeL}(k,k'')G_{eL}(k'',k-k'')V^{(3)}_{eeL}(k'',k') \times G_{eLL}(k',k-k'',k''-k')V^{(2)}_{eR}(k')+(k''\to k+k'-k''),$$

$$T_{29} = V^{(2)}_{eL}(k-k'')G_{ReL}(k,k-k'',k''-k)V^{(3)}_{eeR}(k'',k)G_{eL}(k'',k-k'')V^{(3)}_{eeR}(k'',k'-k'') \times G_{ReL}(k',k'-k'',k''-k)V^{(2)}_{eL}(k''-k')+(k''\to k+k'-k''). \quad (4.5)$$

Examples from these interactions are illustrated diagrammatically in Fig. 6.

Resonance properties. Resonant behavior appears to occur (cf. following material with regard to effects of exciton dispersion) for RS2 at the points (neglecting the shifts Δ)

$$\omega_1 \approx E(\vec{k}),\ \omega_2 \approx E(\vec{k}')+\omega_0\ ,\quad \omega_3 \approx E(\vec{k}')+2\omega_0\ . \quad (4.6)$$

The ω_1 is resonant in contributions from T_{21}, T_{22}, T_{24}, T_{25}, and T_{28}; the ω_2 is resonant in contributions from T_{25}, T_{27}, T_{28}, and T_{29}; and ω_3 is resonant in contributions from T_{21}, T_{23}, T_{26}, T_{27}, and T_{28}.

As with RS1, various contributions from the T_{2i} would show peaking about one or more of the resonant points; the total cross section is a complicated expression involving $|T_{2i}|^2$ terms as well as cross terms, which may interfere either constructively or destructively in individual cases.

Let us, for simplicity, consider the contributions one obtains from the T_{21} and T_{22} terms acting alone. One has

$$\frac{d\sigma(T_{12})}{d\Omega} = (2\pi)^{-2}(k'/k)\left|g^{(2)}_{eR}\right|^4\left|V^{(4)}_{eeLL}(\vec{k},\vec{k}',\vec{k}'')\right|^2 \times\{[\omega-E'(\vec{k})]^2+\tfrac{1}{4}\Gamma_e^2\}^{-1} \times\{[\omega-E'(\vec{k}')-2\omega_0]^2+\tfrac{1}{4}\Gamma_{eLL}^2\}^{-1}\ . \quad (4.7)$$

This result is similar in form and in the contributions at resonance, to the T_{12} contribution to RS1, when $V^{(3)}_{eeL}$ is replaced by $V^{(4)}_{eeLL}$. For T_{22} one has

$$\frac{d\sigma(T_{22})}{d\Omega} = (2\pi)^{-2}\left(\frac{k'}{k}\right)\left|g^{(2)}_{eR}\right|^2\left|g^{(3)}_{eeR}\right|^2 \times\left|V^{(3)}_{eLL}(\vec{k},\vec{k}')\right|^2\{[\omega-E'(\vec{k})]^2+\tfrac{1}{4}\Gamma_e^2\}^{-1} \times[E'(\vec{k})+2\omega_0]^{-2}\ , \quad (4.8)$$

where we have neglected damping in a nondivergent factor.

These two parts of the total RS2 cross section illustrate the typical resonant behavior. It is seen that, in general, measurements of the cross sections give us information about combinations of the various interactions $V^{(2)}$ and $V^{(3)}$. We note that as with RS1 the theory presented here gives finite results for the cross section throughout the optical region.

It is important to note that when taking the dispersion of the exciton in account, one needs to perform, in certain of the contributions, an integration over $\vec{k}''$, which plays a crucial part in determining the "intermediate" resonance behavior. For example, taking

$$E(\vec{k}) = E(0)+\tfrac{1}{2}\alpha k^2 \quad (4.9)$$

in the case of the T_{28} contribution, if one squares amplitudes and then integrates, one has, instead of

$$\{[\omega-E(0)-\omega_0]^2+\tfrac{1}{4}\Gamma^2\}^{-1}\ , \quad (4.10)$$

the contribution

$$\propto \int dk''\,k''^2\{[\omega-E(\vec{k}'')-\omega_0]^2+\tfrac{1}{4}\Gamma^2\}^{-1}\ , \quad (4.11)$$

which, if integrated 0 to ∞ yields a frequency-dependent modulation of the form

$$F(\omega) = \alpha^{-3/2}R^{-1/4}\{1+[\omega-E(0)-\omega_0]R^{-1/2}\}^{-1/2}\ , \quad (4.12)$$

where

$$R \equiv [\omega-E(0)-\omega_0]^2+\tfrac{1}{4}\Gamma^2\ . \quad (4.13)$$

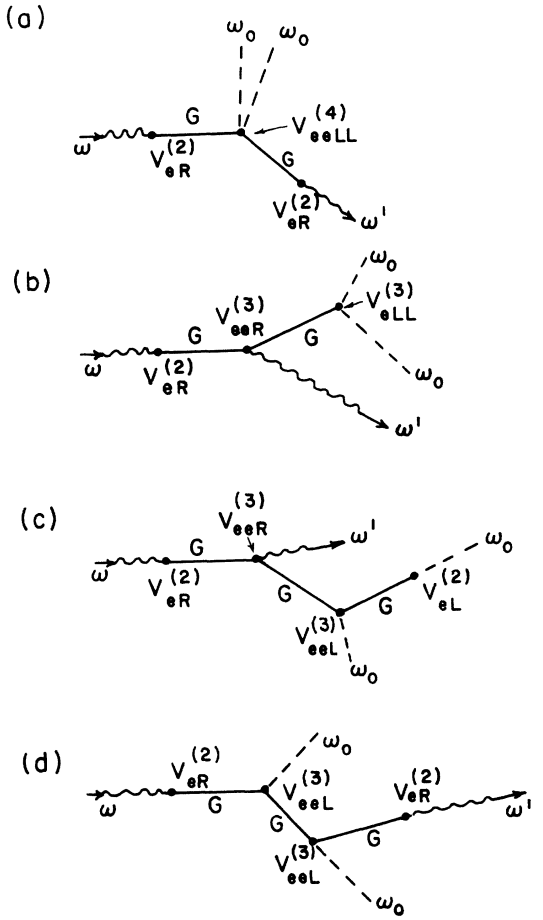

FIG. 6. Schematic diagrams representing various RS2 processes in generalized-exciton theory; contributions due to (a) T_{21}; (b) T_{22}; (c) T_{24}; (d) T_{28}.

For $\Gamma = 0$, for example, one has

$$F(\omega) \propto [\omega - E(0) - \omega_0]^{-1/2} , \qquad (4.14)$$

so that what would be originally a quadratic divergence is reduced to a square root divergence.[26]

V. DISCUSSION AND COMPARISON OF RS RESULTS; COMPARISON WITH EXPERIMENT

In this section we summarize the predictions of generalized-exciton theory as presented here for Stokes RS mediated by a discrete exciton level interacting with light. After comparison with other results and experiment, we comment briefly on the differences in approach and nature of the approximations employed in the various theories.

A. Summary and Comparison with other Predictions

The present RS results demonstrate the existence of a double resonance, corresponding to incoming or outgoing photon frequencies lying near $E'(0)$. For small photon-exciton coupling [$|g_{eR}^{(2)}|^2 \ll E'(0)$] the peaks are symmetrically disposed, with widths of order $|g_{eeL}^{(3)}|^2$. As the photon-exciton coupling increases, the peaks become asymmetrical, as illustrated in Fig. 3. In the general case of Nth order RS, resonances are predicted for incoming photon frequency $\omega \approx E'(0) + n\omega_0$, where $n = 0, 1, \ldots, N$. The existence and strengths of the intermediate resonances depend crucially on the nature of the exciton dispersion (cf. Sec. IV). The $E'(0)$ and $E'(0) + N\omega_0$ peaks are symmetrically disposed for the small coupling case.

Thus, generalized-exciton theory predicts RS resonance positions identical to those of bare-exciton theory[2] if one only replaces the bare exciton $E(\vec{k})$ with the energy-shifted exciton $E'(\vec{k})$. It turns out that the results for the cross section are nearly similar in the two theories for the case of small coupling if the GB results are modified in an *ad hoc* manner to include damping (cf. Fig. 7). Then one has a corroboration of the quantitative validity of the GB results for RS following from a more detailed treatment for the small coupling limit. As the photon-exciton coupling is increased, however, the generalized-exciton peakings, due to dispersive effects, become more asymmetrical (cf. Fig. 3), in sharp contrast to the symmetrical disposition of the peaks in the GB result.

We indicate the comparison between the results of a two-branch polariton-scattering calculation[6] and generalized-exciton theory. As pointed out previously (cf. Sec. III), the results of polariton theory for dispersionless excitons and $\Gamma = 0$ are identical with those of the present approach; results for $\Gamma \neq 0$ are not presently available. However, calculations have been carried out for $\Gamma = 0$ which include exciton dispersion[6]; although this case is not, strictly speaking, comparable with the present one in the immediate vicinities of ω, $\omega' \approx E'(0)$, it is nevertheless of interest to compare their numerical predictions, especially in view of the past implications by several sources[7] that use of polariton theory is mandatory for cases such as CdS. Reference to Fig. 8 shows that for the reasonable choice of $\Gamma \approx 0.0006$ meV (cf. Ref. 25), the three theories yield very similar predictions. It must be pointed out, however, that as $|g_{eR}^{(2)}|$ is increased, the three theories begin to differ more considerably.[6]

B. Comparison with Experiment

Let us compare the RS predictions of the bare-exciton and generalized-exciton theories with experimental data for the case of insulators such as CdS. An extensive review of experiment is given in Ref. 27, and other discussions of theory vs experiment are given in Refs. 6, 8, and 20. We note that CdS falls within our above given description of small coupling; in this region bare-exciton

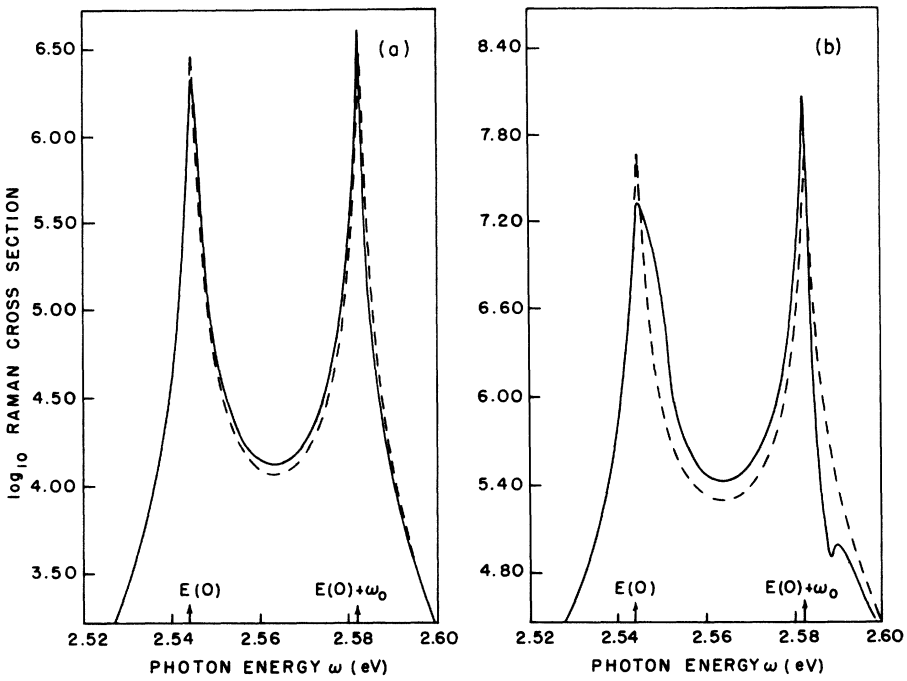

FIG. 7. Comparison of $\log_{10}$ of RS1 cross section vs ω for generalized-exciton theory and bare-exciton theory. Solid line: generalized-exciton result; broken line: bare-exciton result. (a) Small coupling (CdS): $|g| = 0.2\ \text{eV}^{3/2}$; (b) larger coupling: $|g| = 0.4\ \text{eV}^{3/2}$; other parameters identical to those given in Fig. 3.

and generalized-exciton theory yield nearly similar predictions.

The theoretically predicted enhancement of RS, as the incident photon frequency ω approaches $E'(0)$ from below, has been recently observed in a number of experiments.[28] Both LO- and TO-phonon enhancements have been observed. In Ref. 17 it is shown that the bare- (and therefore the generalized-) exciton theory provides a good fit for the LO-phonon RS data in CdS below $E'(0)$.

The peaking associated with the outgoing resonance in Nth order RS has been corroborated experimentally for LO RS in CdS.[29,30] No intermediate resonance behavior seems to have been observed as yet.

As discussed in Refs. 17 and 20, e.g., comparison of theory with experimental data outside the immediate regions of discrete resonances, such as the region above the energy gap E_g or sufficiently below $E'(0)$, ought to include the consideration of continuum contributions. Incorporation of the continuum into the bare-exciton theory, however, has failed to achieve agreement with certain limited data[17] available for $\omega > E_g$. Regarding the discrete polariton prediction in this region,[6] one notes that the full two-branch calculation shows that the contribution is actually similar to the bare-exciton prediction for small coupling (although for large coupling an extended region of enhancement results).

One may conclude that the nearly similar quantitative predictions of the three theories for RS in CdS account for the observed LO RS experimental data as regards discrete exciton effects, namely, in and outgoing resonances, and the shape of the cross section for ω below $E(0)$; no available theory accounts quantitatively for the data for $\omega > E_g$. A more complete comparison with experiment is limited by a deficiency of data in the immediate regions of $\omega \gtrsim E'(0)$ and $\omega \approx E'(0) + \omega_0$.

C. Description of Various Theories

We present a brief discussion of the validity of, and approximations involved in, the various theories. Bare-exciton theory is a purely perturbative approach which, e.g., when applied to RS as in Ref. 2, is incomplete at resonance, where the mutual interactions between excitons, photons, and phonons can no longer be treated as small.[17] The generalized-exciton approach compensates for this deficiency via the introduction of damping effects and via a prescription for including the effects of photon dispersion. The inclusion of damping in the GF's has been carried out in more or less standard fashion. However, our inclusion of photon dispersion, via a revision of the correspondence between $\vec{k}$ and ω, must be considered semiempirical in nature, and, as such, the validity of the present approximations cannot be directly assessed. Agreement of the resulting dispersive behavior with certain more exact results (cf. Sec. III), however, argues strongly in favor of at least the qualitative validity of this revision.

Certainly, polariton theory provides the most exact framework presently available within which

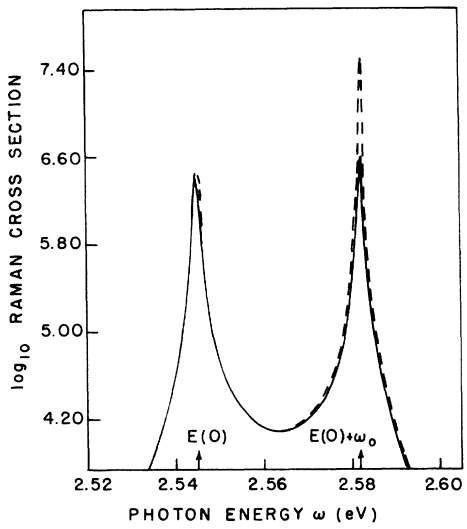

FIG. 8. Comparison of $\log_{10}$ RS1 cross section vs ω for polariton and generalized-exciton theories. Solid line: generalized exciton; broken line: polariton result. The generalized-exciton theory employs $\Gamma = 6\times10^{-4}$, while damping is omitted entirely in the polariton calculation. Other parameters are identical to those given in Fig. 3.

light-scattering problems may be investigated. We note, however, that a first-principles formulation of the theory including damping has not been given, and even the inclusion of dispersive effects[6] alone for just a single level introduces nontrivial computational complications into the cross section. In light of these practical limitations, detailed consideration of the formulation and predictions of generalized-exciton approaches to light-scattering problems seem an appropriate adjunct to the development of the more exact approaches. We have observed above, e.g., that for certain practical cases of interest various approximate descriptions within various different theories may, indeed, adequately account, even quantitatively, for certain of the observed data.

Since the various theoretical predictions differ most markedly for larger coupling, experiments on substances fulfilling this requirement would be of value in further evaluating their validity and usefulness.

We have discussed RS exclusively from the point of view of quantum-scattering theory, assuming the existence of simplified coupling interactions. While this program has been generally useful in interpreting LO RS data in CdS, only certain features of the TO RS are accounted for within this framework.[31-33] This situation emphasizes the necessity, in general, for the detailed consideration of the microscopic interaction mechanisms coupling light, electrons, and lattice vibrations in insulating crystals.

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One of us (B. B.) thanks Dr. S. C. Ying for useful discussions.

APPENDIX: GENERALIZED BARE-EXCITON GF

In this Appendix we evaluate various GF's (cf. definition below) appearing in the text in perturbation theory on $H_0 \equiv H - V$; as many terms as are relevant to the problems treated in the text are given. The energy E is always assumed to lie in the optical range, thereby restricting various contributions to Γ, and restricting the possibility of singularities in the GF.

The GF denoted by the symbol G are herein defined as the diagonal matrix elements of the operator $(E - H + i\varepsilon)^{-1}$. Not to be given explicitly are the GF's $\tilde{G}$ referring to the operator $(E - \tilde{H} + i\varepsilon)$; to obtain $\tilde{G}$ one simply keeps only contributions arising from $V^{(2)}$ in Γ or Δ.

The evaluation of various GF's proceeds along the lines outlined in Ref. 14, which shows that if ψ is an eigenstate of H_0, then

$$G(\psi, E) \equiv \langle\psi\,|\,(E - H + i\varepsilon)^{-1}\,|\,\psi\rangle = [E - E(\psi) - \Delta(\psi, E) + \tfrac{1}{2}i\Gamma(\psi, E)]^{-1}, \quad \text{(A1)}$$

where

$$\Delta(\psi, E) \equiv \langle\psi\,|\,V(E - QHQ)^{-1}V\,|\,\psi\rangle, \qquad \Gamma(\psi, E) \equiv \langle\psi\,|\,V\,\delta(E - QHQ)\,V\,|\,\psi\rangle, \quad \text{(A2)}$$

where Q is the projector onto the complementary subspace to ψ.

Taking note of the physical interpretation of these functions, Δ is the real energy-level shift of the "unperturbed" level ψ, while $1/\Gamma$ is the lifetime associated with it. In perturbation theory Δ and Γ have forms

$$\Delta \cong \mathrm{pp}\sum_{\psi'} |\langle\psi\,|\,V\,|\,\psi'\rangle|^2 (E - E_{\psi'})^{-1}, \qquad \Gamma \cong 2\pi\sum_{\psi'} |\langle\psi\,|\,V\,|\,\psi'\rangle|^2 \delta(E - E_{\psi'}), \quad \text{(A3)}$$

where ψ' indicates a set of accessible states for ψ to decay into, and pp indicates principal-parts integral.

We now discuss the various GF's appearing in the text, employing the considerations of Sec. ID. We are principally interested in the resonant behavior of factors divergent in the optical regime in the absence of damping; for nondivergent factors, therefore, we omit the self-energy effects described above (Δ, Γ). Let us employ the subscripts e, R, and L to indicate matrix elements between exciton, photon, and phonon states, respectively, and introduce the notation

$$G[\psi, E] \equiv \langle\psi\,|\,(E - H + i\varepsilon)^{-1}\,|\,\psi\rangle. \quad \text{(A4)}$$

The nondivergent functions are

$$G_{eR}[k', \tilde{k} - \tilde{k}', E] \cong [E - k'c - E(\tilde{k} - \tilde{k}')]^{-1},$$

$$G_{Rel}[k', \tilde{k}-\tilde{k}'', \bar{k}''-\bar{k}', E] \cong [E - k'c - E(\tilde{k}-\tilde{k}'') - \omega_0(\tilde{k}''-\tilde{k}')]^{-1},$$

$$G_{ReLL}[k, \tilde{k}'-\tilde{k}, \bar{k}-\bar{k}'', \bar{k}''-\bar{k}', E] \cong [E - k'c - E(\tilde{k}'-\tilde{k}) - 2\omega_0]^{-1}. \quad \text{(A5)}$$

The GF's which require inclusion of self-energy effects are evaluated as

(a) $$G_e[\tilde{k}, E] = [E - E(\tilde{k}) - \Delta_e + \tfrac{1}{2}i\Gamma_e]^{-1},$$

$$\Delta_e \cong \sum_{s\pm} |V^{(2)}_{eL}(\tilde{k})|^2(\delta_- + n_{s\tilde{k}})[E \pm \omega_{0s}(\tilde{k})]^{-1} + \mathrm{pp}\sum_{s\tilde{q}\pm} |V^{(3)}_{eeL}(\tilde{k}\tilde{q})|^2(\delta_- + n_{s,\tilde{k}-\tilde{q}})[E - E(\tilde{q}) \pm \omega_{0s}(\tilde{k}-\tilde{q})]^{-1},$$

$$\Gamma_e/2\pi \cong \sum_{s\tilde{q}\pm} |V^{(3)}_{eeL}(\tilde{k}\tilde{q})|^2(\delta_- + n_{s,\tilde{k}-\tilde{q}})\,\delta[E - E(\tilde{q}) \pm \omega_{0s}(\tilde{k}-\tilde{q})];$$

(b) $$G_{eL}[k', \bar{k}-\bar{k}', E] = [E - E(\tilde{k}') - \omega_0(\tilde{k}-\tilde{k}') - \Delta_{eL} + \tfrac{1}{2}i\Gamma_{eL}]^{-1},$$

$$\Delta_{eL} \cong \sum_{s\pm} |V^{(2)}_{eL}(\tilde{k}')|^2(\delta_- + n_{s\tilde{k}'})[E \pm \omega_{0s}(\tilde{k}') - \omega_0(\tilde{k}-\tilde{k}')]^{-1}$$
$$+ |V^{(2)}_{eL}(\tilde{k}-\tilde{k}')|^2[E - E(\tilde{k}-\tilde{k}') - E(\tilde{k}')]^{-1} + |V^{(3)}_{eeL}(\tilde{k}, \tilde{k}')|^2 \mathrm{Re}(G_e[\tilde{k}, E])$$
$$+ \mathrm{pp}\sum_{\tilde{q}s\pm} |V^{(3)}_{eeL}(\tilde{k}'\tilde{q})|^2(\delta_- + n_{s,\tilde{k}'-\tilde{q}})[E - E(\tilde{q}) \pm \omega_{0s}(\tilde{k}'-\tilde{q}) - \omega_0(\tilde{k}-\tilde{k}')]^{-1},$$

$$\Gamma_{eL}/2\pi \cong |V^{(3)}_{eeL}(\tilde{k}, \tilde{k}')|^2 \mathrm{Im}(G_e[\tilde{k}, E]) \quad \text{(A6)}$$
$$+ \sum_{\tilde{q}s\pm} |V^{(3)}_{eeL}(\tilde{k}', \tilde{q})|^2(\delta_- + n_{s,\tilde{k}'-\tilde{q}})\,\delta[E - E(\tilde{q}) \pm \omega_{0s}(\tilde{k}'-\tilde{q}) - \omega_0(\tilde{k}-\tilde{k}')];$$

(c) $$G_{eLL}[\tilde{k}', \bar{k}-\bar{k}'', \bar{k}''-\bar{k}', E] = [E - E(\tilde{k}') - 2\omega_0 - \Delta_{eLL} + \tfrac{1}{2}i\Gamma_{eLL}]^{-1},$$

$$\Delta_{eLL} \cong \sum_{s\pm} |V^{(2)}_{eL}(\tilde{k}')|^2(\delta_- + n_{s\tilde{k}'})[E \pm \omega_{0s}(\tilde{k}') - 2\omega_0]^{-1}$$
$$+ \{|V^{(2)}_{eL}(\tilde{k}-\tilde{k}'')|^2[E - E(k') - E(\tilde{k}-\tilde{k}'') - \omega_0]^{-1}$$
$$+ (\tilde{k}-\tilde{k}'' \to \tilde{k}''-\tilde{k}')\} + (V^{(3)}_{eeL}\ \text{terms}),$$

$$\Gamma_{eLL}/2\pi \cong \{|V^{(3)}_{eeL}(\tilde{k}', \tilde{k}'')|^2 \mathrm{Im}(G_{eL}[\tilde{k}'', \bar{k}-\bar{k}'', E]) + (\tilde{k}'' \to \tilde{k}'-\tilde{k}-\tilde{k}'')\}$$
$$\pm \sum_{s\tilde{q}\pm} |V^{(3)}_{eeL}(\tilde{k}', \tilde{q})|^2(\delta_- + n_{s,\tilde{k}'-\tilde{q}})\,\delta[E - E(\tilde{q}) - \omega_{0s}(\tilde{k}'-\tilde{q}) - 2\omega_0].$$

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out k space. Our procedure, consequently, attempts to approximate the distribution by a particular choice of k. A rigorous theory would consider contributions from all k, appropriately weighted.

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Temperature Dependence of Vibrational Spectra in Calcite by Means of Emissivity Measurement

Takemaro Sakurai and Tsutomu Satō*
The Research Institute for Scientific Measurements, Tōhoku University, Sendai, Japan
(Received 21 December 1970)

The emissivities at various temperatures from 500 to 1200 °K, together with the reflectivity at 300 °K in calcite, were measured on the spectral region 200–4000 cm^{-1}. It was found by the measurements that conspicuous changes with temperature occurred in the reststrahlen bands of the lattice and molecular vibrations. By analyzing the reststrahlen bands, the temperature dependences of vibration parameters of the lattice vibration $E_{u(3)}$, 305 cm^{-1} in frequency, and of the molecular vibrations $A_{2u(a)}$ and $E_{u(b)}$, 886 and 1416 cm^{-1} in frequency, were obtained in the temperature range 300–1000 °K. The results were interpreted in the light of the theories on anharmonic crystals. The damping constants of the lattice and molecular vibrations were found to arise from the quartic as well as the cubic anharmonicities; the contribution of quartic anharmonicity was seen to become prominent with increasing temperatures. The frequency shifts of the lattice and molecular vibrations due to anharmonicity were found to be proportional to $-T^2$; some explanations were given for this. The oscillator strength did not show any change which exceeded the experimental error as expected theoretically.

I. INTRODUCTION

The spectral emissivity is obtained by comparing the thermal radiation of a specimen with that of a black body at the same temperature, for various frequencies. When a flat plate is used as a specimen, a theoretical calculation[1] shows that the normal emissivity ϵ is given by the following equation:

$$\epsilon = (1-T)(1-R)/(1-RT), \tag{1}$$

where T and R are transmissivity and reflectivity, respectively. In the spectral region where the transmission is very small, the above equation becomes

$$\epsilon = 1 - R, \tag{2}$$

while in the region where the reflection by specimen surfaces is very small, it becomes

$$\epsilon = 1 - T = 1 - e^{-Kd}, \tag{3}$$

where K and d are the absorption coefficient and the thickness of the specimen. Thus, the measurement of the spectral emissivity gives the optical properties of the material at elevated temperatures.

The purpose of the present work is to study the optical properties of natural calcite at elevated temperatures by means of the emissivity measurement. The infrared spectra of this material have