Exciton-Phonon Bound State and the Vibronic Spectra of Solids

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The final-state interaction between an optically excited LO phonon and an exciton is studied within the framework of a simple two-state model of the exciton. Criteria for the existence of a bound state (EPBS) of the exciton-phonon system are derived, and binding energies and oscillator strengths are computed for various values of the parameters which characterize the model. Our results are consistent with the optical data reported recently for a wide class of ionic crystals with shallow excitons.

I. INTRODUCTION

Vibronic spectra have recently been resolved in a large class of ionic insulators with shallow excitons.[1] Surprisingly, the first phonon sideband (SB) corresponding to simultaneous creation of an exciton and an LO phonon has a *peak* at or *below* the expected threshold $E_1+\omega_0$, where E_1 is the exciton energy at $\mathbf{K}=0$ and ω_0 the LO-phonon energy. According to second-order perturbation theory the peak should occur somewhat *above* threshold, while absorption very near threshold rises as the three-halves power of the energy difference. Thus, if the observed peak occurs on energy $\delta\omega_0$ below $E_1+\omega_0$, the *real* discrepancy with perturbation theory is $(\delta+\nu)\omega_0$, where ν depends on the ratio of electron and hole masses and the effective Bohr radius of the exciton, and $\nu\lesssim 1$. The absence of this discrepancy for low-temperature *emission* in AgBr: I though $\delta\approx 0.3$ in *absorption* led us to study the final-state interaction of the exciton-phonon pair produced by the optical transition.[2] While this interaction may produce a bound SB in absorption, the SB in emission, corresponding to a final state in which only a phonon and a photon are present, should be describable by perturbation theory. Simple model calculations demonstrated the possibility of a bound-state split off from the one-phonon continuum, or exciton-phonon bound state (EPBS).

Shallow excitons, with Coulomb energy ϵ_B near the LO-phonon energy ω_0 at $k=0$, have internal excited states that are degenerate, or nearly degenerate, with one-phonon states associated with the exciton ground state ($1s$). The exciton-phonon interaction derived from Fröhlich's Hamiltonian creates and destroys phonons, causing excitation energy to resonate between the overlapping manifolds. In certain cases a wave packet of states representing a mixed mode of lattice and electronic excitations can be constructed for which the electrostatic interaction energy overcomes the kinetic energy; such a wave packet corresponds to a bound state of an exciton and an LO phonon, or EPBS. The optical transition-matrix element has two components associated with the zero- and one-phonon amplitudes of the EPBS. Thus the oscillator strength contains an interference term, and the intensity ratio f with the zero-phonon line is bounded by the SB strength g in perturbation theory. The latter is of order unity in the systems studied, and the EPBS width due to acoustic-phonon scattering is an order of magnitude smaller than ω_0; thus the EPBS, when it exists, can be observed at low temperature as a distinct peak in the absorption spectrum.

Another solution of the final-state problem has been studied by Toyozawa.[3] In this case a quasibound state (EPQBS) is formed below the one-phonon emission threshold but decays into the electron-hole continuum, or quasicontinuum of Rydberg states, with which it is degenerate. The Auger width must be added to the acoustic-phonon width (and inhomogeneous broadening) to determine the spectral line shape of the EPQBS. It was suggested that this model may be useful for the interpretation of the spectra of TlCl, TlBr, ZnO, and the Cd chalcogenides, where the exciton state $\epsilon_B\lesssim\omega_0$. The EPBS solution may be useful when the Rydberg-state energy is larger, but not too much larger, than ω_0; e.g., BeO, MgO, and the bound exciton in AgBr:I. For completeness we mention the reflection experiments of several authors,[4] where the SB spectra of several alkali halides have been resolved for the first time. Here the Coulomb energy is an order of magnitude larger than the LO energy, and the SB peaks occur above $E_1+\omega_0$, as expected in lowest-order perturbation theory. Thus it appears that final-state interaction is important only near resonance $\epsilon_B\sim\omega_0$ between electronic and lattice excitation.

In the present paper we describe more fully the physical and mathematical content of the theory and present new results based on more accurate treatment of the exciton-phonon interaction. We begin in Sec. II with the definition of the model Hamiltonian underlying our work, and the spectral shape of the first SB is calculated within the second-order Born approximation in Sec. III. Final-state interaction is taken up in Sec. IV; EPBS binding energies are presented for two models of the exciton internal structure. In Sec. V the optical transition rate to the EPBS is derived, and a summary of our conclusions and comments pertaining to the optical data are included in Sec. VI.

II. HAMILTONIAN

In this section we derive an effective exciton-phonon interaction for the case $\epsilon_B\sim\omega_0$. Consider the Fröhlich interaction[5] for electron-phonon scattering,

$$\mathcal{H}_I(\mathbf{r}_e)=\sum_{\mathbf{q}} iV_{\mathbf{q}}\{b_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}_e)-b_{\mathbf{q}}^{\dagger}\exp(-i\mathbf{q}\cdot\mathbf{r}_e)\},\quad(2.1)$$

where the $b_{\mathbf{q}}^{\dagger}(b_{\mathbf{q}})$ are creation (destruction) operators

for LO phonons of wave vector $\mathbf{q}$, and $\mathbf{r}_e$ is the position vector of the electron; transverse lattice modes do not give rise to a potential field. The electron-phonon vertex is

$$V_q=[2\pi\omega_0(\kappa_\infty^{-1}-\kappa_s^{-1})]^{1/2}\,|\,\mathbf{q}\,|^{-1}, \tag{2.2}$$

where $\kappa_\infty(\kappa_s)$ is the optical (static) dielectric constant; the quantity in parentheses, $1/\bar{\kappa}$, is the inverse ionic susceptibility. Shallow excitons $\epsilon_B\sim\omega_0$ are coupled to long-wavelength phonons $|\,\mathbf{q}\,|d\ll 1$ where d is the lattice parameter; thus the phonon dispersion relation $\omega(\mathbf{q})$ may be replaced by ω_0, as assumed in the Fröhlich model. On the other hand, exciton kinetic energy $\mathbf{q}^2/2M$ is not omitted in our analysis. The hole-phonon interaction differs from (2.1) only by a change of sign corresponding to the positive charge of the hole. Transforming to center-of-mass coordinates of the exciton the electron and hole position vectors are given by

$$\mathbf{r}_e=\mathbf{R}+s_e\mathbf{r}, \qquad \mathbf{r}_h=\mathbf{R}-s_h\mathbf{r} \tag{2.3}$$

in terms of the center-of-mass vector $\mathbf{R}$ and electron-hole relative coordinate $\mathbf{r}$; the kinematic parameters

$$\begin{aligned} s_{e,h}&=m_{h,e}/(m_e+m_h)\\ &=\tfrac{1}{2}\{1\pm[1-(4\mu/M)]^{1/2}\}, \end{aligned} \tag{2.4}$$

where $m_e(m_h)$ is the electron (hole) band mass and $\mu(M)$ is the reduced (total) effective mass of the exciton. Typically $m_h\sim 10m_e$ for ionic insulators, and $s_e\sim 10s_h$ (note that $s_e+s_h=1$). With these definitions the total Hamiltonian for the exciton-phonon system may be written[6]

$$\begin{aligned} &\mathcal{H}=\mathcal{H}_{\rm ex}+\mathcal{H}_{\rm ph}+\mathcal{H}_I,\\ &\mathcal{H}_{\rm ex}=E_G+(\mathbf{P}^2/2M)+(\mathbf{p}^2/2\mu)-(\kappa_\infty r)^{-1},\\ &\mathcal{H}_{\rm ph}=\omega_0\sum_{\mathbf{q}} b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}},\\ &\mathcal{H}_I=\sum_{\mathbf{q}} iV_q\exp(i\mathbf{q}\cdot\mathbf{R})\{\rho_{\mathbf{q}}(\mathbf{r})b_{\mathbf{q}}-\rho_{\mathbf{q}}^{*}(\mathbf{r})b_{\mathbf{q}}^{\dagger}\}, \end{aligned} \tag{2.5}$$

where $\mathcal{H}_{\rm ex}$ and $\mathcal{H}_{\rm ph}$ are the exciton and phonon kinetic energies and the interaction term $\mathcal{H}_I$ contains the exciton charge density operator

$$\rho_{\mathbf{q}}(\mathbf{r})=\exp(is_e\mathbf{q}\cdot\mathbf{r})-\exp(-is_h\mathbf{q}\cdot\mathbf{r}). \tag{2.6}$$

In $\mathcal{H}_{\rm ex}$ we have used the notation $\mathbf{p}(\mathbf{P})$ for the internal (total) momentum of the electron-hole pair and E_G is the energy gap. We note that charge neutrality of the exciton implies $\rho_{\mathbf{q}}(\mathbf{r})\to 0$ as $\mathbf{q}\to 0$, so that the long-range character of the Fröhlich interaction is removed. Finally κ_∞ appears in $\mathcal{H}_{\rm ex}$ since the valence charge polarization field has characteristic energy $E_G\gg\epsilon_B$. As noted in a previous publication,[6] the total momentum $\mathbf{K}$ of the system (exciton plus phonon field) is a constant of the motion, and the canonical transformation[7]

$$S=\exp[i(\mathbf{K}-\sum_{\mathbf{q}}\mathbf{q}b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}})\cdot\mathbf{R}] \tag{2.7}$$

leads to the effective Hamiltonian for momentum $\mathbf{K}$,

$$\begin{aligned} S^{-1}\mathcal{H}S=&(\mathbf{K}-\sum_{\mathbf{q}}\mathbf{q}b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}})^2/2M+\omega_0\sum_{\mathbf{q}}b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}\\ &+E_G+\mathbf{p}^2/2\mu-1/\kappa_\infty r+\sum_{\mathbf{q}} iV_q\{\rho_{\mathbf{q}}^{(r)}b_{\mathbf{q}}-\rho_{\mathbf{q}}^{*(r)}b_{\mathbf{q}}^{\dagger}\}, \end{aligned} \tag{2.8}$$

where the first term is the exciton kinetic energy (not a constant of the motion) and the center-of-mass coordinate $\mathbf{R}$ has been eliminated from the problem.

To treat the SB spectra we are concerned with the ground state of (2.8) and the first excitations lying on energy ω_0 above the ground state (we take $\mathbf{K}=0$ since the photon wavelength is long compared with a lattice constant). The ground-state wave function is approximated by the Hartree form

$$\Phi_1(b\mathbf{r})=\psi_{1s}(\mathbf{r})U(b)|\,0\rangle, \quad U(b)=\exp[\sum_{\mathbf{q}} d_q(b_{\mathbf{q}}^{\dagger}+b_{\mathbf{q}})], \tag{2.9}$$

where d_q is the variational displacement of the phonon mode $\mathbf{q}$ due to the exciton form factor

$$\rho_{\mathbf{q}1s,1s}=\int\psi_{1s}^{*}(\mathbf{r})\rho_{\mathbf{q}}(\mathbf{r})\psi_{1s}(\mathbf{r})d^3r \tag{2.10}$$

and $|\,0\rangle$ is the phonon vacuum at $T=0$. The self-consistent equations for ψ_{1s} and d_q are

$$\begin{aligned} &\mathcal{H}_1\psi_{1s}=E_0\psi_{1s}, \qquad \mathcal{H}_2U=\epsilon U,\\ &\mathcal{H}_1=E_G+\mathbf{p}^2/2\mu-1/\kappa_\infty r\\ &\qquad\qquad+\sum_{\mathbf{q}} iV_q\{d_q\rho_{\mathbf{q}}(\mathbf{r})-d_q^{*}\rho_{\mathbf{q}}^{*}(\mathbf{r})\},\\ &\mathcal{H}_2=(1/2M)(\sum_{\mathbf{q}}\mathbf{q}b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}})^2+\omega_0\sum_{\mathbf{q}}b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}\\ &\qquad\qquad+\sum_{\mathbf{q}} iV_q\{\rho_{\mathbf{q}1s,1s}b_{\mathbf{q}}-\rho_{\mathbf{q}1s,1s}^{*}b_{\mathbf{q}}^{\dagger}\}. \end{aligned} \tag{2.11}$$

We first solve for $U(d_q)$ in the presence of $\rho_{\mathbf{q}1s,1s}$; from the variational theorem we obtain

$$d_q=\frac{iV_q\rho_{\mathbf{q}1s,1s}}{\omega_0+\mathbf{q}^2/2M}. \tag{2.12}$$

Thus we have the self-consistent Hamiltonian for the exciton problem

$$\mathcal{H}_1(\psi_{1s})=E_G+\frac{\mathbf{p}^2}{2\mu}-(\kappa_\infty r)^{-1}-2\sum_{\mathbf{q}}\frac{V_q^2\rho_{\mathbf{q}1s,1s}}{\omega_0+\mathbf{q}^2/2M}\rho_{\mathbf{q}}(\mathbf{r}). \tag{2.13}$$

Excited states of the form (2.9) are eigenstates of a Hamiltonian like (2.13) with $\rho_{\mathbf{q}1s,1s}$ replaced by the diagonal element $\rho_{\mathbf{q}\lambda,\lambda}$ of the density matrix:

$$\rho_{\mathbf{q}\lambda,\lambda'}=\int\psi_{\lambda}^{*}(\mathbf{r})\rho_{\mathbf{q}}(\mathbf{r})\psi_{\lambda'}(\mathbf{r})d^3r. \tag{2.14}$$

In the work reported here we make the assumption that ψ_{1s} has been determined from the above equations with eigenvalue E_1, and higher excited states ψ_λ with eigenvalues E_λ are obtained by replacing the last two terms in (2.13) by a screened Coulomb potential $\delta E_G-1/\kappa r'$,

where κ' must lie between κ_o and κ_s and δE_G is the sum of electron and hole self-energies at $\mathbf{k}=0$. For shallow excitons the Bohr radius is comparable with the polaron radius of the electron, and κ' approaches κ_s.[8] To simplify further we assume that the self-consistent displacements d_q do not depend on λ and are the result (2.12); this assumption does not affect EPBS binding energies.

Finally, the effective Hamiltonian used in this work is derived by displacing all phonon modes according to Eqs. (2.9) and (2.12):

$$\begin{aligned}
&\mathcal{H}_{\rm eff}=U^{-1}S^{-1}\mathcal{H}SU=\bar{\mathcal{H}}_{\rm ex}+\bar{\mathcal{H}}_{\rm ph}+\bar{\mathcal{H}}_I,\\
&\bar{\mathcal{H}}_{\rm ex}=\sum_\lambda E_\lambda a_\lambda^\dagger a_\lambda,\\
&\bar{\mathcal{H}}_{\rm ph}=\sum_q [\omega_0+\mathbf{q}^2/2M]b_q^\dagger b_q, \qquad (2.15)\\
&\bar{\mathcal{H}}_I=\sum_{\lambda\lambda' q}\{iV_q(\rho_{q\lambda\lambda'}-\delta_{\lambda\lambda'}\rho_{q1s,1s})a_\lambda^\dagger a_{\lambda'}b_q+\text{h.c.}\},
\end{aligned}$$

where the exciton recoil energy appears in the phonon term and nondiagonal phonon terms not retained in intermediate coupling theory are deleted; $a_\lambda^\dagger(a_\lambda)$ is the exciton creation (destruction) operator for the state λ. Within the Tamm-Dancoff one-phonon approximation introduced below the omitted phonon terms make no contribution to EPBS energies. Note that diagonal terms $\lambda=\lambda'$ in $\bar{\mathcal{H}}_I$ may be eliminated by a canonical transformation[9] which displaces the lattice field to a new configuration d_q^λ for each state λ (the term $\lambda=1=\lambda'$ was eliminated above); since we are approximating d_q^λ by the function obtained for the exciton ground state, we neglect these *intraband* terms below. Our new problem is the consideration of *interband* scattering only. This is equivalent to the omission of nonresonant energy denominators; the resonant interband processes give rise to EPBS solutions for $\epsilon_B\sim\omega_0$. We emphasize that the (nominal) zero-phonon states $\psi_\lambda SU\,|\,0\rangle$ now contain virtual phonons due to the lattice displacement field d_q around the exciton.

III. VIBRONIC SPECTRA: ONE-BAND THEORY

In this section we compute optical transition rates of the exciton-phonon system described above, omitting off-diagonal terms $\lambda\neq\lambda'$. Thus we consider final states in which the exciton internal motion is frozen in the state λ; the kinetic energy of the exciton is $\mathbf{q}^2/2M$. For allowed optical processes the (emitted) phonon wave vectors must sum to $-\mathbf{q}$ to balance the exciton momentum $\mathbf{q}$. We restrict ourselves to the lowest excition band $\lambda=1$ ($1s$ transverse exciton in a singlet spin state) and calculate the one-phonon transition rate according to the electric dipole operator

$$P=\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\psi_{1s}(0)\,(a_1^\dagger+a_1), \qquad (3.1)$$

where c and v label the conduction- and valence-band states at $\mathbf{k}=0$; we assume that the interband matrix element of the momentum is allowed, and $\psi_{1s}(0)$ is the probability amplitude for finding the electron and hole on the same lattice site.[10] Neglecting interband scattering $\lambda\neq\lambda'$ in Eq. (2.15), the one-phonon final state is simply

$$|\,\psi_q\rangle=SUa_1^\dagger b_q^\dagger\,|\,0\rangle \qquad (3.2)$$

for phonon wave vector $\mathbf{q}$. The energy of this state is

$$E_q=E_1+\omega_0+\mathbf{q}^2/2M, \qquad (3.3)$$

where the last term represents the exciton recoil energy. We obtain the optical transition rate from (3.1) and (3.2):

$$\begin{aligned}
&|\,\langle 0\,|\,P\,|\,\psi_q\rangle\,|^2=|\,\psi_{1s}(0)\,|^2\,|\,\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\,|^2\,|\,d_q\,|^2e^{-g},\\
&g=\sum_q|\,d_q\,|^2. \qquad (3.4)
\end{aligned}$$

Summing over all states $\mathbf{q}$ the one-phonon contribution to the absorption coefficient is proportional to

$$F_1(\omega)=F_0\sum_q|\,d_q\,|^2\delta(\omega-E_q), \qquad (3.5)$$

where the zero-phonon oscillator strength

$$F_0=A\,|\,\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\,|\,|\,\psi_{1s}(0)\,|^2e^{-g} \qquad (3.6)$$

contains the Debye-Waller factor e^{-g} expressing the probability that all lattice modes $\mathbf{q}$ will "tunnel" to the final state (specified by d_q) during the optical transition. From Eq. (3.5) it is easy to see that the integrated absorption strength of the first sideband is g times the zero-phonon line strength. In general the intensity ratio of the n-phonon transition and the zero-phonon line is given by the Poisson distribution

$$f_n=g^n/n!, \qquad (3.7)$$

which satisfies the sum rule on oscillator strength,

$$F_0\sum_n f_n=A\,|\,\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\,|^2\,|\,\psi_{1s}(0)\,|^2. \qquad (3.8)$$

Thus the *integrated* absorption intensity is unchanged by the electron-phonon interaction.

Our main result, Eq. (3.5), is similar to that obtained by Dillinger *et al.*[1] in Born approximation except that we have allowed for self-consistent (Hartree) renormalization of the exciton ground state. The presence of virtual phonons surrounding the exciton (in addition to the real phonons emitted in the optical transition) is essential, since it gives rise to the Debye-Waller factor and, hence, satisfies the sum rule (3.8).

We now introduce the dimensionless parameters specifying the exciton-phonon system:

$$\gamma\equiv\kappa'/\bar{\kappa}, \qquad \Delta\equiv\epsilon_B/\omega_0, \qquad \eta=4\mu/M. \qquad (3.9)$$

The coupling constant γ is a ratio of dielectric constants, $\kappa'\equiv a(\mu/m)$ where m is the free-electron mass and a the effective Bohr radius in atomic units, and $(\bar{\kappa})^{-1}=\kappa_o^{-1}-\kappa_s^{-1}$; Δ is the Coulomb binding energy in units of the phonon energy, and η is a kinematic parameter which varies between zero (bound exciton) and one ($m_e=m_h$). In the latter case the total charge density $\rho_q(\mathbf{r})$ of the exciton is zero everywhere, and the coupling with the phonon system vanishes. Figure 1

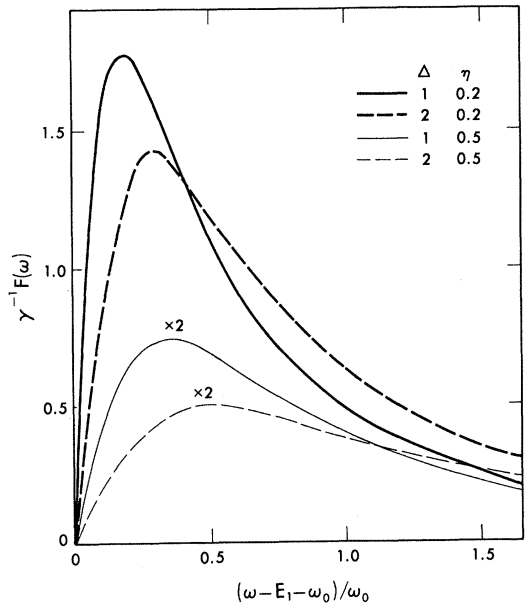

FIG. 1. One-phonon sideband $F(\omega)$ according to second-order perturbation theory. The peak position corresponds to the most probable exciton recoil energy $\nu\omega_0$. The parameters are defined in the text.

shows calculated one-phonon spectra $F_1(\omega)$ associated with the exciton ground state. The important features are (a) $F_1(\omega)$ is proportional to γ; (b) the threshold behavior is characterized by a three-halves power law arising from the charge neutrality and definite parity of the $1s$ exciton

$$(|\, d_q\,|^2\alpha\,|\,q^{-1}\rho_{q1s,1s}\,|^2\alpha q^2 \text{ near threshold } q\to 0);$$

(c) the peak occurs on energy $\nu\omega_0$ above threshold $E_{\rm th}=E_1+\omega_0$, where ν scales roughly with $\Delta\eta$; $\nu\omega_0$ is the most probable recoil energy of the exciton (it vanishes for bound excitons); and (d) absorption drops off at high energy owing to exciton recoil and the finite size of the hole. At still higher energy the absorption is cut off by the boundaries of the Brillouin zone.

IV. EXCITON-PHONON BOUND STATE (EPBS)

The real discrepancy between the SB picture presented in Sec. III and recent observation presented in the Introduction is not $\delta\omega_0$ but rather $(\delta+\nu)\omega_0$, where $\nu\lesssim 1$. In a recent paper[2] Toyozawa and the present author considered the final-state interaction between an exciton and an LO phonon created by photon absorption, for $\Delta\gtrsim 1$. We demonstrated the possibility of bound states with appreciable oscillator strength occurring below $E_{\rm th}$. These mixed modes of the exciton-lattice system were computed using an approximate charge density

$$\rho_q^0(\mathbf{r})=\exp(i\mathbf{q}\cdot\mathbf{r})-1, \tag{4.1}$$

which is strictly valid only for $\eta=0$. In this approximation the hole density is replaced by a point charge at the origin; in reality the hole describes an s-state "orbit" around the exciton center of mass (only spherically symmetric envelope functions ψ_λ are optically allowed), with effective radius $s_h a$. The positive charge density overlaps the electronic density, with effective radius $s_e a(s_e+s_h=1)$, and charge cancellation for $\eta>0$ reduces the effective strength of the exciton-phonon interaction. Here we present improved model calculations in which the exact density (2.6) was used. In addition we have completed the calculation of EPBS oscillator strength f(EPBS) for $\eta>0$ (mobile excitons) as well as $\eta=0$ (bound excitons). Finally, integrated sideband intensities g have been computed; according to the sum rule, $f(\text{EPBS})\leq gF_0$.

Two models of the internal structure of the exciton were used to study the resonant exciton-phonon system $\Delta\sim 1$: (I) a two-level model in which only hydrogenic $1s$ and $2s$ states are included; this is the simplest possible treatment of a polarizable exciton ($2p$ states are electric-dipole forbidden); (II) a variational extension of I, with $\bar{\psi}_{2s}=c(3-(1+\beta)(r/a))\exp(-\beta r/a)$, permitting substantially increased polarizability of the exciton and hence stronger exciton-phonon interaction. For all values of β, $\bar{\psi}_{2s}$ is orthogonal to ψ_{1s}. In the Coulomb field $-1/\kappa' r$, $\bar{\psi}_{2s}$ has the energy

$$\bar{E}_{2s}=E_1+\epsilon_B[1+\tfrac{1}{3}\beta(7\beta^3-10\beta^2+7\beta-3)/(\beta^2-\beta+1)]. \tag{4.2}$$

Model I is obtained by putting $\beta=\frac{1}{2}$ in $\bar{\psi}_{2s}$; then $\bar{E}_{2s}=E_1+\frac{3}{4}\epsilon_B$. More localized excited states $\beta>\frac{1}{2}$ enhance the (negative) potential energy due to exciton-phonon scattering, but $\bar{E}_{2s}>E_{2s}$, and minimization of the sum of kinetic and potential energies determines the value of β. A third exciton model discussed in Ref. 2 was used to check the results obtained from models I and II, but is less useful for estimating oscillator strengths. In this model, energy denominators $(E-E_\lambda)$ are replaced by their smallest value $(E-E_{2s})$ and the closure relation is used to evaluate exciton-phonon matrix elements; since this necessarily overestimates the exciton polarizability it generates upper bounds for EPBS binding energies. A lower bound is obtained from model I; we assert that the real situation is well represented by model II unless $\Delta<1$. The latter case has been investigated by Toyozawa,[3] who demonstrated the possibility of exciton-phonon quasibound states (EPQBS) which decay into the electron-hole continuum.

Only one-phonon states associated with the $1s$ exciton (ground state) were considered; nonresonant states in which both the exciton and the lattice are excited will not appreciably modify our results, for $\Delta\sim 1$. Thus we look for an EPBS solution [ground state of Eq. (2.15)] by applying the variational theorem within the subspace spanned by $\bar{\psi}_{2s}\,|\,0\rangle$ and $\psi_{1s}\,|\,1_q\rangle$, where the latter form a continuum above $E_{\rm th}$, and the former has the discrete energy $\bar{E}_{2s}$. Denoting

the zero-phonon probability amplitude by t, and the one-phonon amplitude by s_q, we make the ansatz[2]

$$\chi=\sum_q s_q a_1^\dagger \mid 1_q\rangle+t\bar{a}_2^\dagger \mid 0\rangle, \tag{4.3}$$

where $\bar{a}_2^\dagger$ creates the variational state $\bar{\psi}_{2s}$. The "real" wave function appropriate to Eq. (2.5) is then

$$\Psi=SU\chi. \tag{4.4}$$

To illustrate the mixed-mode problem we have sketched in Fig. 2 the zero-order excitation energy $\epsilon_{2s}=E_{2s}-E_1$ belonging to ψ_{2s} (model I) as a function of Δ. The interaction of this discrete-level and the one-phonon SB produces two branches, 1 and 2. The lower branch is the bound state for $\Delta<\Delta_c$; for deeper excitons it passes into the continuum and acquires a width due to decay. Strictly speaking, branch 2 is always quasibound since it is degenerate with the background of one-phonon states; however, the matrix element for decay decreases monotonically above $(1+\nu)\omega_0$ due to the finite size of the exciton. For large Δ, the second branch may be viewed as a renormalized $2s$ exciton state. Similarly, for $\Delta<1$, branch 1 is a renormalized $2s$ state. We note that oscillator strength sufficient to satisfy the sum rule is withdrawn from the one-phonon background. Finally, higher-order resonant behavior occurs near $\Delta_n=\frac{4}{3}n$, where n is an integer greater than 1, corresponding to multiphonon processes. Since the exciton-phonon interaction is linear in phonon operators these processes are not expected to yield observable effects.

Minimizing the energy $E=\langle\chi \mid \mathcal{H}_{\rm eff} \mid \chi\rangle$ we find the simultaneous equations for s and t

$$\begin{aligned}(E_1+\omega_0+\mathbf{q}^2/2M-E)s_q-iV_q\rho_{q1s,2\bar{s}}t=0,\\ (\bar{E}_{2s}-E)t+i\sum_q V_q\rho_{q1s,2\bar{s}}s_q=0,\end{aligned} \tag{4.5}$$

subject to the normalization condition

$$\sum_q \mid s_q\mid^2+\mid t\mid^2=1. \tag{4.6}$$

Eliminating s_q from (4.5) we obtain the secular equation for the energy

$$\bar{E}_{2s}+\mathrm{Re}\,\Sigma_{1s,2\bar{s}}(E)=E, \tag{4.7}$$

where

$$\Sigma_{1s,2\bar{s}}(E)=\sum_q \frac{\mid V_q\rho_{q1s,2\bar{s}}\mid^2}{E^+-E_1-\omega_0-\mathbf{q}^2/2M}, \qquad E^+=E+i\delta^+$$

is the exciton-phonon self-energy for zero total momentum, δ^+ is a positive infinitesimal needed to satisfy causality (Im $\Sigma=0$ for $E<E_{\rm th}$), and

$$\begin{aligned}\rho_{q1s,2\bar{s}}&=\langle\psi_{1s}\mid\rho_q\mid\bar{\psi}_{2s}\rangle\\ &=32\beta^{5/2}[3^{1/2}(1+\beta)^3(\beta^2-\beta+1)^{1/2}]^{-1}\\ &\quad\times[p_e^4q^2(p_e^2+q^2)^{-3}-p_h^4q^2(p_h^2+q^2)^{-3}],\\ p_{e,h}&=s_{e,h}(1+\beta)/a.\end{aligned} \tag{4.8}$$

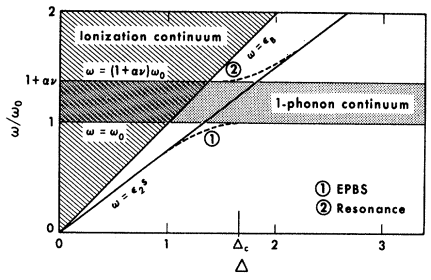

FIG. 2. Zero-order energies corresponding to basis states mixed by the exciton-phonon interaction. ϵ_{2s} is the first excitation energy of the exciton internal motion and the band of states between ω_0 and $(1+\alpha\nu)\omega_0$ ($\alpha\approx3$) represents the one-phonon states described in the text. The electron-hole binding energy ϵ_B in units of the LO-phonon energy is represented by Δ. The mixed-mode problem gives rise to two branches, 1 and 2, as a function of Δ. All energies are measured relative to the zero-phonon line at E_1.

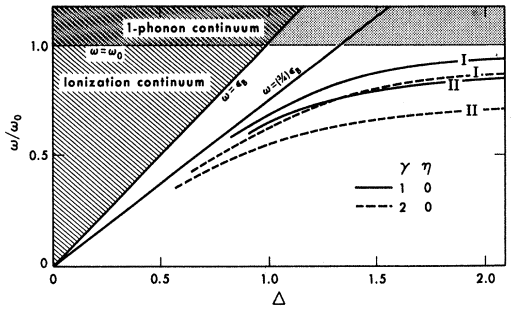

FIG. 3. EPBS energies in units of ω_0, measured from the zero-phonon line. Results are presented for $\eta=0$ (bound exciton or impurity state) and several values of γ; the theory is useful for $\Delta>1$.

EPBS energies are determined for model II by solving (4.7) graphically for different values of β and drawing a smooth curve through the points E versus β. The minimum energy $E(\beta_{\rm min})$ is the variational solution; typically $\beta_{\rm min}\approx0.6$ or 0.7. In model I the restriction $\beta=\frac{1}{2}$ diminishes the exciton polarizability and $E(\beta=\frac{1}{2})>E(\beta_{\rm min})$. Figure 3 shows EPBS energies $\omega=E-E_1$ relative to the zero-phonon line, for bound excitons $\eta=0$. The relationship of the solutions of the mixed-mode problem and the unperturbed energies $\omega=\epsilon_{2s}=\frac{3}{4}\epsilon_B=\frac{3}{4}\Delta\omega_0$ and $\omega=\omega_0$ is seen from the figure. Perfect resonance (degeneracy) of the electronic and lattice excitations occurs at $\Delta=\frac{4}{3}$. Results for mobile excitons $\eta=\frac{1}{2}$ are shown in Fig. 4. Comparison of our results and those of Ref. 2 shows that the screening effect due to the finite size of the hole [included in $\rho_q(\mathbf{r})$ but not in $\rho_q^0(\mathbf{r})$] weakens the EPBS binding energy. Important trends manifest in Figs. 3 and 4 (and in other results not presented here) are: (1) The binding energy increases with coupling strength γ; (2) recoil effects and self-screening, whose importance increases with η, weaken the binding; (3) except for the special case $\eta=0$, exciton-phonon interaction leads to bound states only in a finite interval $0<\Delta<\Delta_c$, where Δ_c increases with γ but decreases with

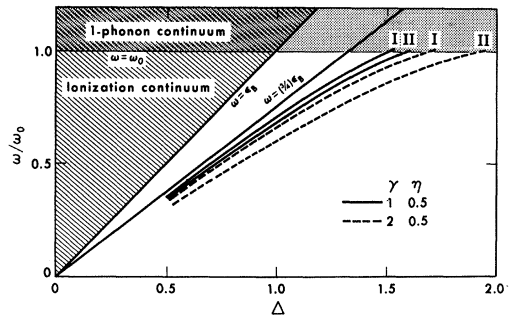

FIG. 4. EPBS energies for $\eta=0.5$ (mobile excitons).

η; for small $\Delta<1$ the solutions may be regarded as renormalized $2s$ exciton states, since $|t|^2>\frac{1}{2}$. When $\eta=0$ all one-phonon states $|1_q\rangle$ fall at the energy E_{th}, and an EPBS exists for arbitrarily deep excitons $\Delta\gg1$, though the binding energy approaches zero asymptotically (and so does the oscillator strength). We emphasize that our results pertain to optically active final states, for which the total momentum is zero. EPBS dispersion has not been considered; however it seems likely that the kinetic energy $\mathbf{K}^2/2M^*$ will exceed the binding energy $\delta\omega_0$ for rather small momentum $\mathbf{K}$ of the bound state, leading to decay into the one-phonon continuum above E_{th}.

The existence criterion for the bound state $\omega<\omega_0$ may be represented in parameter space by the relation

$$f(\eta)\geq\gamma^{-1}\xi, \tag{4.9}$$

where $\xi=\frac{3}{4}\Delta-1$ is a resonance parameter equal to zero at $\Delta=\frac{4}{3}$. The function f is determined from the equation

$$\bar{E}_{2s}+\sum_{1s,2\bar{s}}(E_{th})=E_{th}=E_1+\omega_0. \tag{4.10}$$

As before, β is chosen to minimize the total energy (model II) or is set equal to $\frac{1}{2}$ (model I). For small η, the recoil energy $\langle q^2\rangle/2M$ is small compared with ω_0 and $\rho_q(\mathbf{r})$ may be replaced by $\rho_q{}^0(\mathbf{r})$ since the hole orbit is much smaller than the electon orbit. Then the existence criterion may be written

$$\begin{aligned} f_0(\eta)&\geq\gamma^{-1}\xi, && \eta\ll1\\ &=0.091/\eta, && \text{model I}\\ &=0.128/\eta, && \text{model II.}\end{aligned} \tag{4.11}$$

For η near unity, exciton recoil and the finite size of the hole must be included rigorously. We obtain the result for model I

$$f(\eta)=f_0(\eta)[1-\eta^2(3\eta+4)/7]. \tag{4.12}$$

To derive an approximate result for model II we interpolated smoothly the known behavior of $f(\eta)$ in the limits $\eta\to0$ and $\eta\to1$. The functions $f(\eta)$ and $f_0(\eta)$ are shown in Fig. 5. As expected, these results show EPBS solutions are favored for strong coupling $\gamma\gtrsim1$, near resonance $|\xi|\ll1$, and narrow exciton bands $\eta\ll1$. No bound state is possible for $\eta=1$, owing to perfect charge cancellation $\rho_q=0$. Finally, model II, which contains virtual admixtures of the ns excited states of the exciton, leads to EPBS existence in a larger volume of parameter space than does the more restrictive model I.

V. EPBS OSCILLATOR STRENGTH

Optical (electric dipole) transitions to the final state $\Psi=SU\chi$ are now considered. We will show that EPBS transitions have intensity comparable to the zero-phonon line in favorable cases; since the same lifetime mechanisms are present for the former and the latter, both should be observable in certain crystals by high-resolution spectroscopy. Electron and hole Bloch functions c and v at the band edge have opposite parity in most ionic crystals, and only s states of the exciton internal motion are optically-active. The dipole operator is proportional to[10]

$$P=\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\sum_\lambda\psi_\lambda(0)(a_\lambda{}^\dagger+a_\lambda), \tag{5.1}$$

where $\boldsymbol{\varepsilon}\cdot\mathbf{p}$ is the component of the electron momentum operator parallel to the polarization vector of the incident phonon and $\psi_\lambda(0)$ is the probability amplitude, for the internal state λ, that the electron and hole occupy the same lattice site. For $\mathbf{K}=0$ the "real" EPBS state vector may be written

$$\begin{aligned}\Psi=SU\chi=\exp[-i\sum_q b_q{}^\dagger b_q\mathbf{q}\cdot\mathbf{R}]\exp[\sum_q d_q(b_q{}^\dagger+b_q)]\\ \times\{\sum_q s_q b_q{}^\dagger a_1{}^\dagger+t\bar{a}_2{}^\dagger\}\,|\,0\rangle,\end{aligned} \tag{5.2}$$

where $|\,0\rangle$ is the phonon vacuum. In the calculation of the transition matrix element $\langle0\,|\,P\,|\,\Psi\rangle$ the first

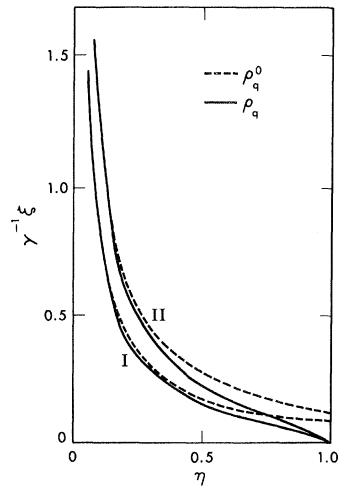

FIG. 5. EPBS existence regions in parameter space. For each model bound states exist below the line $f(\eta)$. Calculations omitting the finite size of the hole are indicated by the dashed lines.

exponential operator, involving the exciton center of mass, may be replaced by unity since the ground state at $T=0$ contains no phonons. The second factor in (5.2) can be simplified using the operator identity

$$\exp[\sum_q d_q(b_q^\dagger+b_q)]=\exp[\sum_q d_q b_q^\dagger]\exp[\sum_q d_q b_q]\times\exp\{-\tfrac{1}{2}\sum_q d_q^2[b_q^\dagger, b_q]\}. \quad (5.3)$$

The first factor in (5.3) may be replaced by unity at $T=0$ since it operates (to the left) on $|0\rangle$; also terms higher than the second in a Taylor series expansion of the second exponential make no contribution to the transition matrix element, and the last factor is the Debye-Waller factor $e^{-g/2}$ due to lattice distortion around the exciton. Finally we have the result

$$\langle 0\,|\,P\,|\,\Psi\rangle=\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle\{\psi_1(0)\sum_q s_q d_q+\bar{\psi}_2(0)t\}e^{-g/2}. \quad (5.4)$$

We have already mentioned the selection rule on ψ_λ for allowed interband transitions. The selection rule on one-phonon amplitude s_q is derived by noting that there is no preferred direction in the final state if $\mathbf{K}=0$; thus d_q is spherically symmetric, and s states s_q are allowed in the sense that the one-phonon component of $\langle 0|P|\Psi\rangle$ is nonzero. The maximum contribution of this term is $|\langle c\,|\,\boldsymbol{\varepsilon}\cdot\mathbf{p}\,|\,v\rangle|^2\,|\psi_{1s}(0)|^2 g e^{-g}$ if we neglect cross terms in $|\langle 0\,|\,P\,|\,\Psi\rangle|^2$. For bound states the first and second terms of Eq. (5.4) interfere *destructively*, and the intensity ratio f of the EPBS and the zero-phonon line

$$f\equiv f(\text{EPBS})/f(0-\text{ph})=|\sum_q s_q d_q+t_2(\bar{\psi}_2(0)/\psi_1(0))|^2 \quad (5.5)$$

is bounded by g; the unperturbed SB intensity ratio $g=f(1-\text{ph})/f(0-\text{ph})$ was derived in Sec. III. The second term in (5.4) is about one order of magnitude smaller then the first term.

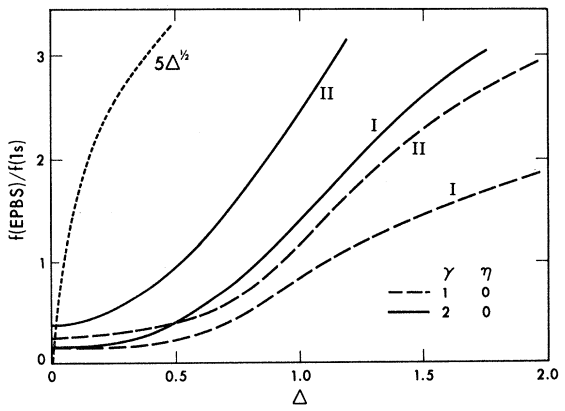

FIG. 6. EPBS transition strengths relative to the zero-phonon intensity $f(1s)$, calculated for bound excitons $n=0$. The dashed line is the total SB intensity g in the absence of final-state interactions.

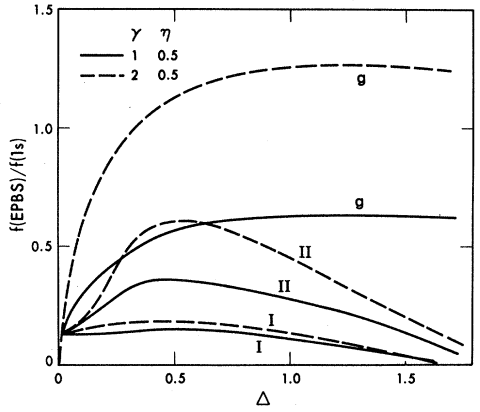

FIG. 7. EPBS transition strengths for mobile excitons $\eta=0.5$.

The intensity ratio f of the EPBS and zero-phonon transitions is given in Figs. 6 and 7 for models I and II and for parameter values $(\gamma,\eta)=(1,0)$, $(2,0)$, $(1,0.5)$, and $(2,0.5)$. As before, the reduced Coulomb energy Δ varies from 0 to about 2. Bound excitons (Fig. 6) are associated with much stronger absorption strength than are the mobile excitons (Fig. 7). This is due to (a) the importance of exciton recoil when $\eta>0$, which increases the energy denominator for exciton-phonon scattering and (b) self-screening of the electron-hole pair, which depresses the matrix element $V_q\rho_{q1s,2\bar{s}}$. As expected from trends observed in Figs. 3 and 4, EPBS intensity increases monotonically with γ. For $\eta=0$ the zero-order SB intensity ratio is

$$g=(4\gamma\Delta/\pi)[K_0 a-(11/8)\tan^{-1}\tfrac{1}{2}(K_0 a)], \quad (5.6)$$

where K_0 is a momentum-space cutoff given by $2\pi/$(lattice parameter); for shallow excitons $K_0 a\gg 1$ and the second term may be neglected. Since $a\alpha\Delta^{-1/2}$, $g\alpha\gamma\Delta^{1/2}$ where the constant of proportionality is of order 10, and variations of lattice parameter and exciton reduced mass have been neglected. The dotted line in Fig. 6 is probably a lower bound for Eq. (5.6). Thus manifestation of resonance near $\Delta=\frac{4}{3}$ occurs not in f but in the *fractional* EPBS intensity f/g drawn from the SB by exciton-phonon interaction. In the figure the resonant effect shows up as a point of inflection in f for both models. We comment that both f and f/g decrease monotonically for $\Delta>2$, approaching zero asymptotically. For deep excitons $\Delta\gtrsim 10$ momentum-space cutoff reduces f as well as g. Since the form factor $\rho_{q1s,2\bar{s}}$ decays to negligible value near K_0 for shallow excitons, we have extended the phase-space integrals to infinity and evaluated them by the method of residues.

Calculation of EPBS oscillator strength is more difficult for $\eta\neq 0$, and we have had to omit normalization

corrections that are important for $\Delta \lesssim \frac{1}{2}$. However, since this region is less interesting (the EPBS solution is simply a renormalized $2s$ exciton) we have determined approximate normalization by interpolating between the known behavior for large and small Δ. As in the case $\eta=0$, $f<g$ for all values of γ and Δ. Also, model II, which leads to larger binding energies than does model I, gives greater absorption strength as well. Both effects reflect the enhanced polarizability of the variational model. The resonance between zero- and one-phonon states is more pronounced for $\eta\neq 0$ because $g(\Delta)$ is flat above $\Delta\sim 0.5$. As in the case $\eta=0$, EPBS intensity approaches zero as $\Delta\to\infty$. The bound state passes continuously into the SB region above $E_{\rm th}$ where it is broadened by decay. The width of this quasibound state increases monotonically from zero at threshold to values comparable with the SB width as the "bare" energy passes into the continuum. Since the total intensity ratio f diminishes as the width increases, a distinct peak is probably not observable unless it occurs very near $E_{\rm th}$; this requires $\Delta \lesssim 2$.

We now discuss the mechanisms which broaden the EPBS. The matrix element coupling this state to the $1s$ exciton band was eliminated above within the subspace (2.9); indirect coupling via the higher excited states of the exciton is neglected. The most important process limiting the EPBS lifetime in a pure crystal is acoustic-phonon scattering, which we discussed in Ref. 2. Within second-order perturbation theory the decay width may be written as

$$2\Gamma_{\rm ac}=2\pi\sum_{\mathbf{K}}|\langle\mathbf{K};-\mathbf{K}\,|\,\mathcal{H}'\,|\,\text{EPBS};0\rangle|^2 \times\delta(\omega-(\mathbf{K}^2/2M)-u\,|\,\mathbf{K}\,|\,), \quad (5.7)$$

where u is the velocity of (longitudinal) sound and the matrix element of the electron-phonon interaction is taken between the EPBS state and a final state consisting of a $\lambda=1$ exciton of momentum $\mathbf{K}$ and an acoustic phonon of momentum $-\mathbf{K}$. In analogy with the matrix element for *electron*-phonon scattering[11] the squared matrix element in this equation is $E_d^2K/2\rho\mu$, where E_d is the exciton deformation potential[12] and ρ is the density. For $\Delta<\frac{4}{3}-\delta$, decay to higher exciton states provides an additional mechanism to broaden the EPBS. Converting the K-space sum in Eq. (5.7) into an integral,

$$\Gamma_{\rm ac}\sim\int_0^{K_0}K^3\delta\left(\omega-\frac{K^2}{2M}-uK\right)dK, \quad (5.8)$$

where K_0 is a characteristic Brillouin-zone dimension. Thus

$$2\Gamma_{\rm ac}=\frac{E_d^2}{2\pi\rho u}\frac{K_1^3}{u+K_1/M}. \quad (5.9)$$

Since $\omega\gg 1/2Mu^2$ the characteristic velocity $K_1/M\approx(2\omega/M)^{1/2}\gg u$ and we have the final result

$$2\Gamma_{\rm ac}=E_d^2\omega^3/2\pi\rho u^5, \quad (5.10)$$

which is smaller than ω_0 by an order of magnitude. This means that at low temperature the EPBS can be observed as a distinct peak in the absorption spectrum, provided f is sufficiently large.

VI. DISCUSSION

Our model calculations are consistent with the following general features of the optical data[1] referred to in the introduction: (a) Negative-energy shifts of observed sidebands are larger for bound excitons $\eta=0$ than for mobile excitons; (b) the static dielectric constant is generally much larger than the optical dielectric constant, implying large ionic susceptibility and strong exciton-phonon coupling; (c) the crystals which appear to contain EPBS structure satisfy the resonance condition $\Delta\sim\frac{4}{3}$; (d) the intensity ratio f, like the binding energy, is larger for bound excitons; and (e) the intensity of the observed sideband is too large to be accounted for by pure ns-exciton transitions. The abundance of experimental evidence supports the suggestion that bound states of an exciton and an LO phonon may be present in the spectra of many ionic crystals with shallow excitons. A residual sideband due to free pairs (exciton+phonon) is not detected in these crystals for several reasons: (a) Much of the oscillator strength is transferred to the bound state; (b) the SB is much broader than the EPBS; (c) it may be obscured by a stronger background absorption due to interband transitions; and (d) when the EPBS width is comparable to its binding energy the SB may merge with the bound-state absorption; in this case a single peak is observed with a threshold pelow $E_1+\omega_0$ and maximum absorption below $E_1+(1+\nu)\omega_0$.

Definitive statements regarding the region $\Delta<1$ must await further study of the EPQBS proposed by Toyozawa[3]; this state is expected to be broader than the bound state. Fong has made the interesting conjecture[13] that the first SB in CaO (see Whited and Walker[1]) is degenerate with the ionization continuum of the exciton ($\Delta\sim 1$) and is so broadened by decay that it merges with the zero-phonon structure at 6.79 eV. Indeed Toyozawa[3] has shown that the width of the quasibound state may be comparable with ω_0 in the limit $\eta\to 0$; both the EPQBS and the residual SB due to the excitation of a free pair are probably too broad to detect in this case.

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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