Electrodynamics of the phonon-mediated optical Stark effect

A. L. Ivanov and D. F. Nelson
Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609
(Received 24 November 1997)

The electrodynamics of three-wave polariton-phonon interactions with spatial dispersion is developed and applied to the phonon-mediated optical Stark effect in bulk polar semiconductors. This electrodynamics is formulated within three macroscopic equations, which describe the coupled probe light field, excitonic polarization, and LO phonons of a semiconductor virtually excited by the pump light. We analyze how the incident probe light reflects (transmits) from a boundary of the crystal in the presence of an intense coherent polariton. A Poynting theorem, which clarifies the structure of the total energy flux of the probe wave resonantly coupled to the pump polariton through Raman interaction, is derived. In order to calculate the reflectivity of the probe light from the boundary of a virtually excited crystal, we apply the recently developed wave-vector-space method [B. Chen and D.F. Nelson, Phys. Rev. B **48**, 15 372 (1993)]. The transient excitonic spectra of the phonon-mediated Stark effect are analyzed and calculated numerically for bulk CdS. [S0163-1829(98)01727-5]

I. INTRODUCTION

An excitonic polariton is one of the central concepts of semiconductor optics.[1–6] If the exciton-photon interaction is dominant, the polariton representation gives an adequate description of the resonantly interacting excitons and photons which form a conservative, closed system in a direct-band-gap bulk semiconductor (for a review of the polariton physics see, e.g., Ref. 7). Due to the momentum conservation in the optical transition ''photon $\leftrightarrow$ exciton,'' an incoming photon with momentum $\mathbf{p}$ can be many times resonantly reabsorbed and reemitted by the excitons with the same momentum. Within the polariton picture, this process is coherent and does not lead to a ''true optical absorption'' (in the dissipative sense) due to the excitonic resonance. Classical polariton electrodynamics requires the macroscopic polariton equations,[4,5] a corresponding energy theorem,[8–10] and an additional boundary condition (ABC) to calculate the optical reflectivity/transmissivity in the spectral vicinity of the exciton resonance.[2,4,5,7,9]

There are two energy parameters Ω_c and ω_{lt} in the polariton optics. The polariton parameter Ω_c is the oscillator strength of the exciton-photon coupling. The longitudinal-transverse splitting ω_{lt} characterizes the spectral width of an excitonic line at the low temperatures. Because $\Omega_c = \sqrt{2\omega_{lt}\omega_t} \gg \omega_{lt}$, the pump light with frequency $\omega_{\mathbf{k}}$ from the spectral band $\omega_t - \Omega_c \leqslant \omega_{\mathbf{k}} \leqslant \omega_t - \omega_{lt}$ does not undergo absorption but virtually creates excitons ($\hbar\omega_t$ is the energy of an exciton at rest, i.e., characterizes the spectral position of the exciton line). This important feature of the polariton eigenwaves, which was recognized by Hopfield,[11] actually gives rise to the optical Stark effect.

An exciton optical Stark effect (OSE) is the shift and shape change of an exciton line, which follow dynamically the intensity of the pump light. The classical OSE manifests itself as a dynamical blueshift of the exciton level ω_t in the presence of a high-intensity ($I_0 \simeq 1\,\mathrm{GW/cm^2}$) pump light of the frequency $\omega < \omega_t$ and partly results from the exciton-exciton Coulombic interaction.[12] A *phonon-mediated* optical Stark effect (PMOSE) of excitons in direct-band-gap bulk semiconductors, which has been analyzed theoretically[13–18] and observed experimentally,[15,19–21] stems from the exciton-phonon interaction.

The intense coherent light of the frequency $\omega_{\mathbf{k}}$ from the transparency band $\omega_t - \Omega_c \leqslant \omega_{\mathbf{k}} \leqslant \omega_t - \omega_{lt}$ induces the pump polariton with wave vector $\mathbf{k}$. The excitonic component of the pump polariton characterizes the concentration $N_0 \propto I_0$ of the coherent virtual excitons. The virtual excitons with momentum $\mathbf{k}$ couple resonantly with optical phonons of the frequency Ω_0. This interaction gives rise to the PMOSE which develops at the anti-Stokes resonance $\omega_{\mathbf{k}} + \Omega_0$ of the pump polariton and results in a drastic line shape change (for $10\ \mathrm{MW/cm^2} \leqslant I_0 \ll 1\ \mathrm{GW/cm^2}$) and a significant dynamical shift (for $I_0 \simeq 1\ \mathrm{GW/cm^2}$) of the exciton line. Both redshift (for $\omega_{\mathbf{k}} > \omega_t + \omega_{lt} - \Omega_0$) and blueshift (for $\omega_{\mathbf{k}} < \omega_t - \omega_{lt} - \Omega_0$) of the exciton level can be realized by varying the frequency $\omega_{\mathbf{k}}$ of the pump light.

The PMOSE is a manifestation of the *phonoriton* spectrum of a bulk semiconductor in the presence of a pump polariton.[13,14,16–18] This spectrum originates from the mutual hybridization and unification of the initial exciton polariton and phonon dispersions, similarly to how the polariton dispersion develops from the exciton and photon spectra. A phonoriton is the corresponding three-component, photon, exciton, and phonon, eigenstate of the semiconductor virtually excited by the pump light. Both the exciton-photon coupling and the pump-induced exciton-phonon interaction are included to construct the phonoriton eigenwaves.

So far, the PMOSE has been analyzed mainly with respect to the pump-induced changes of the *electronic* (excitonic) properties, i.e., within the corresponding phonoriton dispersion equation. In experiments, the probe light of the frequency ω tests the PMOSE in reflectivity or transmissivity of the exciton resonance (see Fig. 1, where the pump and probe light counterpropagate). Similar to the polariton picture, the incident probe light induces two frequency-degenerate phonoritons of the same direction of propagation. The further mixing of an optical phonon with the polariton does not increase the number of the frequency degenerate excitations

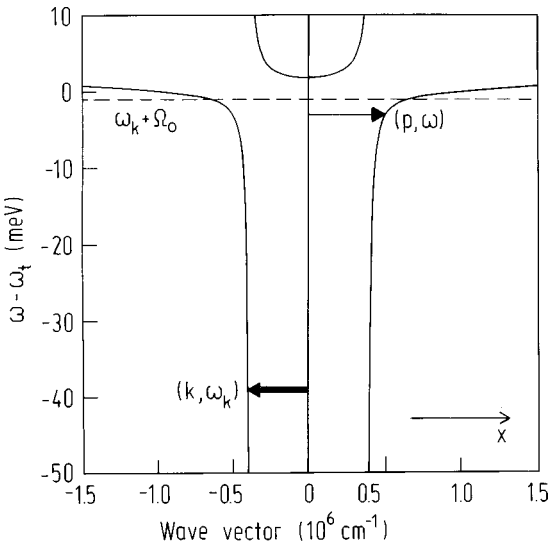

FIG. 1. Energy-momentum diagram of the LO-phonon-mediated Raman interaction of the polaritons in CdS. One-dimensional configuration $\mathbf{p}\|\mathbf{k}\|\mathbf{x}$ axis, where $(\mathbf{p},\omega)$ and $(\mathbf{k},\omega_{\mathbf{k}})$ refer to the probe and pump polaritons, respectively.

because an optical phonon is nonpropagating in the long wavelength limit. Therefore, the *optics* of the PMOSE needs a generalized polariton analysis. In the present paper, we develop the electrodynamics of the PMOSE within the macroscopic phonoriton equations applied to a bounded polar semiconductor.

In the resonant Raman triplet, the probe polariton, the pump polariton, and the phonon field, the pump polariton is treated as a given classical field. Thus the three macroscopic phonoriton equations deal with the electromagnetic and excitonic components of the probe polariton and the phonon field which couples the pump and probe polaritons. The pump polariton propagates as a free polariton. The probe light of the frequency $\omega\simeq\omega_{\mathbf{k}}+\Omega_0$, which tests the phonoriton spectrum of the PMOSE, does not influence the pump polariton. On the other hand, we assume no pump depletion due to Stokes scattering. In principle, Stokes scattering leads to an instability of the pump polariton and results in stimulated Raman scattering of the pump light.[22,23] However, these processes develop much more slowly than the PMOSE and in our case can indeed be neglected.[23]

It seems that II–VI direct-band-gap polar semiconductors, e.g., CdS and CdSe, with the well-developed polariton effect and strong exciton–LO-phonon Fröhlich interaction are optimal for the effective realization of the PMOSE. The numerical calculations of this paper refer to bulk CdS with the polariton parameter $\hbar\Omega_c=98.5$ meV, the longitudinal-transverse splitting $\hbar\omega_{lt}=1.9$ meV, and the LO-phonon frequency $\hbar\Omega_0=38$ meV. Because $\Omega_c\gg\Omega_0$, these parameters are well suited for the PMOSE. An observation of the PMOSE in CdS was reported in Ref. 19.

In Sec. II, we analyze the macroscopic phonoriton equations which describe the electromagnetic, polarization, and LO-phonon components of the probe wave in a semiconductor virtually excited by the pump light. The phonoriton dispersion and the corresponding frequency-degenerate phonoriton eigenwaves are discussed in detail.

In Sec. III, we derive from the macroscopic phonoriton equations the Poynting energy theorem for the PMOSE in polar semiconductors. The structure of the total energy flux of the probe wave coupled with the pump polariton by the LO-phonon resonant Raman interaction is analyzed.

In Sec. IV, as a means of studying the optics of the PMOSE, we calculate the reflectivity and transmissivity of the incident probe light from a boundary of a bulk semiconductor in the presence of a pump polariton. For this purpose, the wave-vector-space method[24] is applied to the macroscopic phonoriton equations. This method derives Pekar's ABC, which puts the excitonic polarization equal to zero at the crystal boundary and does not involve the phonon component of the phonoritons induced by the probe light.

In Sec. V, the electrodynamics of the PMOSE is examined with respect to the continuity of the energy flux of the incident probe light at the boundary of the crystal. The numerical evaluations of the PMOSE in the exciton reflectivity are given for CdS.

II. PHONORITON EIGENWAVES

The closed set of the macroscopic phonoriton equations for the positive-frequency components of the electric field $\mathbf{E}(\mathbf{r},t)$, excitonic polarization $\mathbf{P}(\mathbf{r},t)$, and LO-phonon scalar potential $\Phi(\mathbf{r},t)$ is given by[14]

$$\left[\frac{\varepsilon_b}{c^2}\frac{\partial^2}{\partial t^2}-\Delta\right]\mathbf{E}^{(+)}(\mathbf{r},t)=-\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}^{(+)}(\mathbf{r},t), \tag{1a}$$

$$\left[\frac{\partial^2}{\partial t^2}+2\gamma^x\frac{\partial}{\partial t}+\omega_t^2-\frac{\hbar\omega_t}{M_x}\Delta\right]\mathbf{P}^{(+)}(\mathbf{r},t) =\omega_t^2\beta\mathbf{E}^{(+)}(\mathbf{r},t)-2\omega_t\sqrt{\rho}L\mathbf{P}_{\mathbf{k}}^{(+)}(\mathbf{r},t)\Delta\Phi^{(+)}(\mathbf{r},t), \tag{1b}$$

$$\left[\frac{\partial^2}{\partial t^2}+2\gamma^{\mathrm{ph}}\frac{\partial}{\partial t}+\Omega_0^2\right]\Phi^{(+)}(\mathbf{r},t) =\frac{2L}{\sqrt{\rho}\omega_t\beta}\mathbf{P}_{\mathbf{k}}^{(-)}(\mathbf{r},t)\cdot\mathbf{P}^{(+)}(\mathbf{r},t), \tag{1c}$$

where ε_b is the background dielectric constant for the exciton resonance, M_x is the exciton translational mass, ρ is the crystal reduced mass density, γ^x and γ^{ph} are the rates of incoherent scattering of excitons and LO phonons, respectively. The latter one, i.e., the inverse lifetime of LO phonons, is mainly due to the lattice anharmonicity which leads to the decay ''LO phonon $\rightarrow$ 2 LA phonons.'' The LO-phonon scalar potential $\Phi^{(+)}(\mathbf{r},t)$ determines the corresponding lattice displacement field $\mathbf{u}^{(+)}(\mathbf{r},t)$ by $\mathbf{u}^{(+)}(\mathbf{r},t)=\nabla\Phi^{(+)}(\mathbf{r},t)$ and $\mathbf{P}_{\mathbf{k}}$ is the polarization of the pump polariton. The dimensionless oscillator strength β of the exciton-photon interaction relates to the polariton parameter Ω_c by $\Omega_c^2=4\pi\beta\omega_t^2/\varepsilon_b$.

Macroscopic equations (1a)–(1c) refer to the phonoritons in polar semiconductors. In this case, the LO-phonon resonant Raman scattering of polaritons is mainly determined by the Fröhlich mechanism.[25–27] The corresponding matrix element of the exciton-phonon interaction is $M_{x\text{-ph}}(\mathbf{q})=L(\hbar/2\Omega_0V)^{1/2}|\mathbf{q}|$, where $\mathbf{q}$ is the LO-phonon wave vector,

V is the volume of a crystal, and the parameter L is given by $L=[\Omega_0(m_e-m_h)/M_x][\pi(\varepsilon_s/\varepsilon_\infty-1)(a_x^3/\mu)]^{1/2}$.[28,29] Here, $m_e(m_h)$ is the electron (hole) mass, $M_x=m_e+m_h$ and $\mu=m_e m_h/M_x$ are the translational and reduced exciton masses, respectively, ε_s is the static dielectric constant, ε_∞ is the high-frequency dielectric constant for the LO-phonon frequency Ω_0, and a_x is the exciton Bohr radius. The pump-induced terms on the right-hand side (RHS) of Eqs. (1b) and (1c) are proportional to L.

Equation (1a) is the Maxwell wave equation for the light coupled with the excitonic resonance, i.e., with the source of photons on the RHS due to the excitonic polarization. The left-hand side (LHS) of Eq. (1b) describes the excitonic polarization with a quadratic wave vector dispersion. The first term on the RHS of Eq. (1b) refers to an inverse process to Eq. (1a), i.e., to the generation of excitons by the photons. The second term on the RHS is due to the LO-phonon-mediated Raman coupling between excitons of the probe wave and the pump polariton. Finally, Eq. (1c) describes the generation of LO phonons in the resonant Raman interaction of the two polaritons. Because the excitonic polarization $\mathbf{P_k}(\mathbf{r},t)$ of the pump polariton is taken as a given coherent field, Eqs. (1a)–(1c) are *linear* with respect to the fields $\mathbf{E}$, $\mathbf{P}$, and Φ of the probe wave. Moreover, macroscopic equations (1a)–(1c) are valid even for an operator representation of the fields and, therefore, are independent of the photon statistics of the probe light. With decreasing Raman coupling, i.e., if $L\mathbf{P_k}\rightarrow 0$, Eqs. (1a) and (1b) reduce to Hopfield's polariton equations[4,5] while the dynamic equation (1c) describes the free LO phonons.

Macroscopic equations (1a)–(1c) are derived for a semiconductor which is isotropic in the long wavelength limit. In particular, the analyzed intraband exciton-LO-phonon Fröhlich coupling occurs only for the diagonal Raman scattering, i.e., is proportional to the scalar product $\mathbf{P}\cdot\mathbf{P_k}$. This assumption is valid irrespective of the crystal symmetry, if excitons are supposed to be isotropic.[25] Furthermore, Eqs. (1a)–(1c) imply that the carrier frequency ω of the probe wave belongs to the spectral vicinity of the anti-Stokes resonance $\omega_{\mathbf{k}}+\Omega_0$ of the pump polariton (see Fig. 1). For the resonant Raman interaction of the probe and pump waves, only the ground-state exciton resonance is treated. This assumption denotes that $\Omega_c \gg \Omega_0$ and holds, e.g., for CdS.

We analyze a case when the coherent pump polariton is a cw plane wave, i.e., $\mathbf{P}_{\mathbf{k}}^{(+)}(\mathbf{r},t)=\mathbf{P}_{0\mathbf{k}}^{(+)}\exp(-i\omega_{\mathbf{k}}t+i\mathbf{k}\cdot\mathbf{r})$, where $\mathbf{P}_{0\mathbf{k}}^{(+)}=\text{const}$ is the positive-frequency amplitude of the excitonic polarization of the pump wave. Then, the phonoriton eigenwaves can be found by substitution $\mathbf{E}^{(+)}(\mathbf{r},t)=\mathbf{E}_0^{(+)}\exp(-i\omega t+i\mathbf{p}\cdot\mathbf{r})$, $\mathbf{P}^{(+)}(\mathbf{r},t)=\mathbf{P}_0^{(+)}\exp(-i\omega t+i\mathbf{p}\cdot\mathbf{r})$, and $\Phi^{(+)}(\mathbf{r},t)=\Phi_0^{(+)}\exp[-i(\omega-\omega_{\mathbf{k}})t+i(\mathbf{p}-\mathbf{k})\cdot\mathbf{r}]$, where $\mathbf{E}_0^{(+)}$, $\mathbf{P}_0^{(+)}$, and $\Phi_0^{(+)}$ are the constant positive-frequency amplitudes. In order to simplify Eqs. (1a)–(1c), we treat the one-dimensional geometry with $\mathbf{P_k}\|\mathbf{P}$ and $\mathbf{k}\|\mathbf{p}\|\mathbf{x}$ axes (see Fig. 2). For example, macroscopic equations (1a)–(1c) can be applied to the one-dimensional geometry of Raman scattering in CdS or CdSe if, in addition, $\mathbf{P_k}\|\mathbf{P}\perp\mathbf{c}$ and $\mathbf{x}\perp\mathbf{c}$. Here, $\mathbf{c}$ is the main crystallographic axis of these uniaxial semiconductors.

For the one-dimensional geometry, one gets from Eqs. (1a)–(1c) the phonoriton dispersion equation

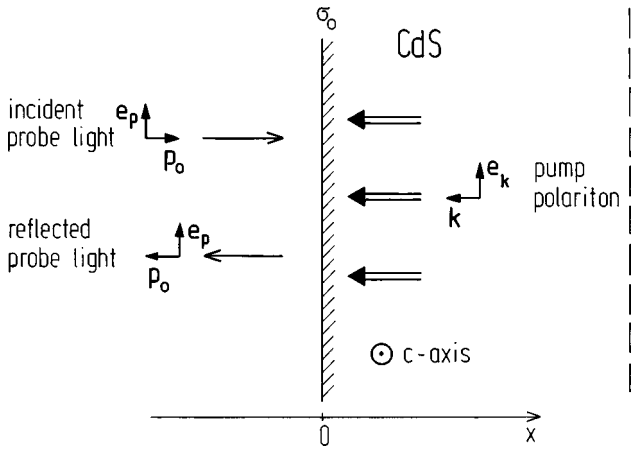

FIG. 2. Counterpropagating configuration of the pump-probe resonant Raman interaction in CdS. The pump polariton is characterized by the wave vector $\mathbf{k}$, frequency $\omega_{\mathbf{k}}$, and linear polarization $\mathbf{e_k}$. The normally incident probe light of the frequency ω, wave vector $\mathbf{p_0}$ ($p_0=\omega/c$), and linear polarization $\mathbf{e_p}$ ($\mathbf{e_p}\|\mathbf{e_k}\perp\mathbf{c}$ axis and $\mathbf{p_0}\|\mathbf{k}\|\mathbf{x}$ axis) induces the probe polariton $(\mathbf{p},\omega)$ (in the absence of the pump light) or two frequency degenerate phonoritons $(\mathbf{p_1},\omega)$ and $(\mathbf{p_2},\omega)$ (in the presence of the pump polariton).

$$\left[\omega^2+2i\gamma^x\omega-\omega_t^2-\hbar\omega_t\frac{p^2}{M_x}\right]\left(p^2-\frac{\varepsilon_b}{c^2}\omega^2\right)[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\mathrm{ph}}(\omega-\omega_{\mathbf{k}})-\Omega_0^2]-4Q^2(\mathbf{p}-\mathbf{k})\Omega_0\omega_t\times\left(p^2-\frac{\varepsilon_b}{c^2}\omega^2\right)+\frac{\varepsilon_b}{c^2}\omega^2\Omega_c^2\times[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\mathrm{ph}}(\omega-\omega_{\mathbf{k}})-\Omega_0^2]=0, \tag{2}$$

where

$$Q^2(\mathbf{p}-\mathbf{k})=N_0L^2\frac{\hbar(\mathbf{p}-\mathbf{k})^2}{2\Omega_0} \tag{3}$$

is proportional to the concentration N_0 of the virtual coherent excitons induced by the pump light. The concentration N_0 is given through the intensity I_0 of the pump light by

$$N_0=\frac{2}{\hbar\omega_t\beta}|\mathbf{P}_{0\mathbf{k}}^{(+)}|^2=\frac{I_0}{\hbar\omega_{\mathbf{k}}}\frac{\sqrt{\varepsilon_b}}{c}\frac{\Omega_c^2}{(\omega_t-\omega_{\mathbf{k}})^2}\frac{1}{(1+\sqrt{\varepsilon_b})^2}, \tag{4}$$

where the reflection from a crystal surface is taken into account for normal incidence of the pump light.

Macroscopic Eqs. (1a)–(1c) and dispersion equation (2) characterize the three-component phonoriton eigenwaves. The phonoriton is a coherent admixture of excitons, photons, and LO phonons which occurs in a spectral vicinity of the anti-Stokes resonance $\omega_{\mathbf{k}}+\Omega_0$ of the pump polariton. The underlying physical picture of the phonoritons is the following one. The incoming probe light creates resonantly an exciton with momentum $\mathbf{p}$. The exciton $\mathbf{p}$ undergoes a stimulated Raman transition to the pump polariton $\mathbf{k}$ with an emission of the LO phonon with the wave vector $\mathbf{p}-\mathbf{k}$. In turn, the created LO phonon can be reabsorbed by excitons of the pump (macroscopic) polariton and gives rise to the inverse process. Within the phonoriton picture the se-

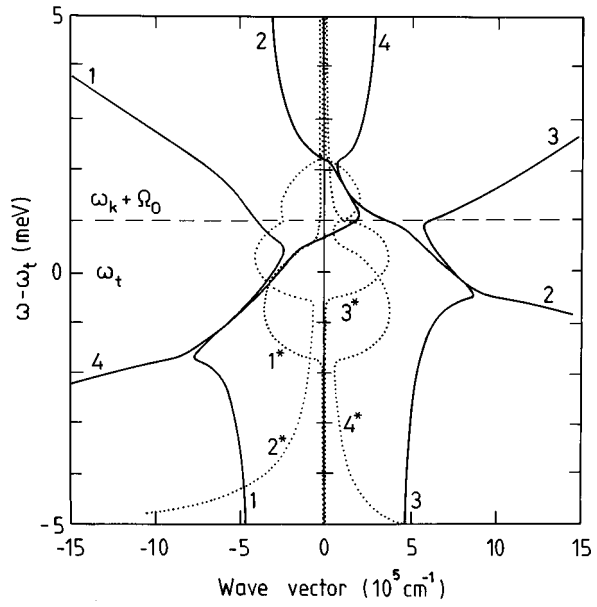

FIG. 3. The phonoriton dispersion curves for the concentration $N_0=5\times10^{18}\mathrm{cm}^{-3}$ of virtual excitons $\mathbf{k}$ induced by the coherent pump light. The following CdS parameters are used in the numerical evaluations: $\hbar\omega_t=2.552$ eV, $\hbar\omega_{lt}=1.9$ meV, $a_x=28$ Å, $m_e=0.2m_0$, $m_h=m_{h\perp}=0.7m_0$, $\varepsilon_b=\varepsilon_s=9.3$, and $\varepsilon_\infty=5.81$. The frequency of the pump light (pump polariton) corresponds to $\hbar\omega_{\mathbf{k}}=2.515$ eV, i.e., $\hbar(\omega_{\mathbf{k}}+\Omega_0-\omega_t)=1$meV. The phonoriton dispersion branches 1-2 (3-4) refer to the backscattering (forwardscattering) interaction of the counterpropagating (copropagating) probe and pump polaritons, $p'_{i=1,2,3,4}=\mathrm{Re}\{p_{i=1,2,3,4}(\omega)\}$ (solid lines 1–4) and $p''_{i=1,2,3,4}=\mathrm{Im}\{p_{i=1,2,3,4}(\omega)\}$ (dotted lines 1*–4*). The damping constants are given by $\hbar\gamma^x=0.01$ meV and $\hbar\gamma^{\mathrm{ph}}=0.1$ meV.

quence ''exciton $\mathbf{p}\rightarrow$exciton $\mathbf{k}+$LO phonon $\mathbf{p}-\mathbf{k}\rightarrow$exciton $\mathbf{p}\rightarrow\cdots$'' is a coherent process. The coherent phonon-mediated oscillations between the probe and pump waves result in the development of a split at the anti-Stokes resonance of the pump polariton, i.e., at frequency $\omega_{\mathbf{k}}+\Omega_0$. This picture is similar to the polariton one. The phonoriton eigenwaves are a generalization of Hopfield's concept to three-particle coherent interactions.

According to dispersion equation (2), there are two basic parameters Ω_c and $Q(\mathbf{p}-\mathbf{k})$ characterizing the exciton-photon interaction and the pump-induced Raman transitions, respectively. With decreasing pump intensity I_0 the Raman coupling $Q(\mathbf{p}-\mathbf{k})\rightarrow0$ and the phonoriton $\mathbf{p}$ decouples into the polariton $\mathbf{p}$ and LO phonon $\mathbf{p}-\mathbf{k}$. An increase of the damping processes, i.e., γ^x and γ^{ph}, also relaxes the phonoriton picture. Because $Q(\mathbf{p}-\mathbf{k})$ is proportional to the value $|\mathbf{p}-\mathbf{k}|$ of the transferred phonon momentum, the largest phonoriton split at $\omega_{\mathbf{k}}+\Omega_0$ occurs for the backscattering configuration when the pump and probe light counterpropagate (see Figs. 1 and 2).

The phonoriton dispersion calculated with Eq. (2) for $N_0=5\times10^{18}\mathrm{cm}^{-3}$ in CdS is plotted in Fig. 3. The corresponding Mott factor $N_0a_x^3\simeq0.1$ is still considerably less than unity. Because the dispersion equation (2) is fourth order with respect to the wave vector p, there are four phonoriton dispersion branches 1–4. In order to classify the dispersion branches we preserve the finite damping, i.e., the imaginary terms in Eq. (2). For the counterpropagating configuration, the probe wave of frequency ω induces two frequency degenerate phonoritons with wave vectors $p_1(\omega)$ and $p_2(\omega)$ of branches 1 and 2, respectively. The phonoriton amplitudes decrease with propagation, according to the damping. For forwardscattering, when the macroscopic polariton and the probe light copropagate, the phonoritons with wave vectors $p_3(\omega)$ and $p_4(\omega)$ of branches 3 and 4 are excited. The sectors of anomalous dispersion of branches 1 and 3 correspond to the pump-induced split (see Fig. 3). For branch 1 (backscattering) the split is considerably more developed in comparison with that of branch 3 (forwardscattering).

With decreasing pump intensity $I_0\rightarrow0$ the upper sectors of branches 2 and 4 and branches 1 and 3 evolve to the upper and lower polariton dispersions, respectively, while the lower sectors of branches 2 and 4 yield the LO-phonon dispersion calculated from the frequency $\omega_{\mathbf{k}}$, i.e., a horizontal line $\omega_{\mathbf{k}}+\Omega_0$. The phonoriton modification of the initial LO-phonon term is accompanied by a finite LO-phonon mass, because according to Eq. (3) $Q^2(\mathbf{p}-\mathbf{k})\propto|M_{x\text{-ph}}(\mathbf{p}-\mathbf{k})|^2\propto(\mathbf{p}-\mathbf{k})^2$. The finite pump-induced mass can be estimated from the dispersion equation (2) as

$$M_{\mathrm{ph}}^{\mathrm{eff}}=M_{\mathrm{ph}}^{\mathrm{eff}}(I_0,\omega)=\frac{\Omega_0(\omega^2-\omega_t^2)}{2\omega_tN_0L^2}. \tag{5}$$

Simultaneously, one gets a pump-induced renormalization of the bare exciton mass M_x. This renormalization can be easily seen for the monochromatic spatially inhomogeneous waves of Eqs. (1a)–(1c), i.e., for $\mathbf{E}^{(+)}(\mathbf{r},t)=\mathbf{E}_\omega^{(+)}(\mathbf{r})\exp(-i\omega t)$, $\mathbf{P}^{(+)}(\mathbf{r},t)=\mathbf{P}_\omega^{(+)}(\mathbf{r})\exp(-i\omega t)$, and $\Phi^{(+)}(\mathbf{r},t)=\Phi_{\omega-\omega_{\mathbf{k}}}^{(+)}(\mathbf{r})\exp[-i(\omega-\omega_{\mathbf{k}})t]$. With substitution of $\Phi^{(+)}(\mathbf{r})$ from Eq. (1c) in Eq. (1b), the initial macroscopic equations reduce to

$$\left[\frac{\varepsilon_b}{c^2}\omega^2+\Delta\right]\mathbf{E}_\omega^{(+)}(\mathbf{r})=-\frac{4\pi}{c^2}\omega^2\mathbf{P}_\omega^{(+)}(\mathbf{r}), \tag{6a}$$

$$\left[-\omega^2-2i\gamma^x\omega_t+\omega_t^2-\frac{\hbar\omega_t}{M_x}\Delta-\frac{\hbar\omega_t}{M_x^{\mathrm{eff}}}(\nabla-i\mathbf{k})^2\right]\mathbf{P}_\omega^{(+)}(\mathbf{r})=\omega_t^2\beta\mathbf{E}_\omega^{(+)}(\mathbf{r}), \tag{6b}$$

where the pump-induced effective mass M_x^{eff} is given by

$$M_x^{\mathrm{eff}}=M_x^{\mathrm{eff}}(I_0,\omega)=\frac{1}{2\omega_tN_0L^2}[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\mathrm{ph}}(\omega-\omega_{\mathbf{k}})-\Omega_0^2]. \tag{7}$$

The extrema of the pump-induced LO-phonon dispersion with $M_{\mathrm{ph}}^{\mathrm{eff}}$ of Eq. (5) and of the additional excitonic dispersion with M_x^{eff} of Eq. (7) refer to the same point $\mathbf{k}$ (wave vector of the pump polariton) in momentum space. For the well-separated Raman and excitonic resonances, i.e., when $|\omega_{\mathbf{k}}+\Omega_0-\omega_t|\geqslant\omega_{lt}$, one gets from Eqs. (5) and (7) the approximate relationship

$$M_{\rm ph}^{\rm eff}(I_0,\omega\simeq\omega_{\mathbf{k}}+\Omega_0)=-M_x^{\rm eff}(I_0,\omega\simeq\omega_t)$$
$$=\frac{\Omega_0}{N_0L^2}(\omega_{\mathbf{k}}+\Omega_0-\omega_t). \qquad (8)$$

According to Eq. (8), the sign of the pump-induced effective LO-phonon mass depends upon the position of the Raman resonance $\omega_{\mathbf{k}}+\Omega_0$ with respect to the exciton level ω_t. The assumed proportionality of the matrix element $M_{x\text{-ph}}(\mathbf{p}-\mathbf{k})$ to $|\mathbf{p}-\mathbf{k}|$, which gives rise to finite $M_{\rm ph}^{\rm eff}$ and $M_x^{\rm eff}$, is valid provided that $|\mathbf{p}-\mathbf{k}|a_x<1$. This inequality holds for the optical range of Fig. 3.

III. THE POYNTING THEOREM FOR A CRYSTAL VIRTUALLY EXCITED BY PUMP LIGHT

The Poynting theorem is a continuity relation between the time rate of change of the stored electromagnetic energy, the outgoing flow of energy, and its dissipation. In our case, the energy theorem clarifies a structure and an origin of the energy flow of a probe wave coupled with the pump polariton through the LO-phonon-assisted Raman interaction. The energy theorem is formulated within the macroscopic Eqs. (1a)–(1c). Mainly, we are interested in the total energy flux $\mathbf{S}$ of the probe wave, because conservation of its normal component at a surface of the virtually excited polar semiconductor is a natural constraint for any set of the boundary conditions.

In order to get the energy theorem, one starts from the well-known consequence of Maxwell's equations

$$\frac{c}{4\pi}\nabla\cdot(\mathbf{E}\times\mathbf{H})+\frac{1}{4\pi}\left(\varepsilon_b\mathbf{E}\cdot\frac{\partial\mathbf{E}}{\partial t}+\mathbf{H}\cdot\frac{\partial\mathbf{H}}{\partial t}+4\pi\mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}\right)=0, \qquad (9)$$

where $\mathbf{H}$ is the magnetic field of the light. Substituting an expression for $\mathbf{E}$ in terms of $\mathbf{P}$ and $\Delta\Phi$ from Eq. (1b) into the term $4\pi\mathbf{E}\cdot\partial\mathbf{P}/\partial t$ of Eq. (9) and performing some vector algebra, which involves Eq. (1c), we derive

$$\frac{\partial W}{\partial t}+\nabla\cdot\mathbf{S}+\Theta=0, \qquad (10)$$

where W is the density of a total stored energy, Θ is the energy dissipation rate, and $\mathbf{S}$ is the total energy flux given by

$$\mathbf{S}=\mathbf{S}_\gamma+\mathbf{S}_x+\mathbf{S}_{x\text{-LO}},\quad \mathbf{S}_\gamma=\frac{c}{16\pi}[\mathbf{E}^{(-)}\times\mathbf{H}^{(+)}+\text{H.c.}], \qquad (11a)$$

$$\mathbf{S}_x=-\frac{\hbar}{4\omega_t\beta M_x}\left[\frac{\partial\mathbf{P}^{(-)}}{\partial t}\times(\nabla\times\mathbf{P}^{(+)})+(\nabla\cdot\mathbf{P}^{(+)})\frac{\partial\mathbf{P}^{(-)}}{\partial t}+\text{H.c.}\right], \qquad (11b)$$

$$\mathbf{S}_{x\text{-LO}}=\frac{L\rho^{1/2}}{8\omega_t\beta}\left[\left(\frac{\partial\mathbf{P}^{(-)}}{\partial t}\cdot\mathbf{P}_{\mathbf{k}}^{(+)}\right)\nabla\Phi^{(+)}+\text{H.c.}\right]. \qquad (11c)$$

According to Eqs. (11a)–(11c), the total energy flux consists of three components. The first one $\mathbf{S}_\gamma$ is an electromagnetic flux given by the Poynting vector of the probe wave. The second one $\mathbf{S}_x$ of Eq. (11b) characterizes a ''mechanical'' flow due to the translational motion of excitons of the probe wave. Finally, the vector $\mathbf{S}_{x\text{-LO}}$ of Eq. (11c) describes a flow of coherent LO phonons generated in the stimulated Raman transitions of excitons of the probe wave into the pump polariton $\mathbf{k}$. With decreasing pump intensity I_0, the flux $\mathbf{S}_{x\text{-LO}}$ disappears. Physically, the three contributions to $\mathbf{S}$ originate from the three components (exciton, photon, and LO phonon) of the phonoriton. Both, the excitonic flux $\mathbf{S}_x$ and the pump-induced phonon flux $\mathbf{S}_{x\text{-LO}}$ slow down the energy propagation of the probe wave.

The total energy density W is given by

$$W=W_\gamma+W_x+W_{\rm LO}+W_{x\text{-LO}},$$

$$W_\gamma=\frac{1}{16\pi}[\varepsilon_b(\mathbf{E}^{(+)}\cdot\mathbf{E}^{(-)})+\mathbf{H}^{(+)}\cdot\mathbf{H}^{(-)}], \qquad (12a)$$

$$W_x=\frac{1}{4\omega_t^2\beta}\left[\frac{\partial\mathbf{P}^{(+)}}{\partial t}\cdot\frac{\partial\mathbf{P}^{(-)}}{\partial t}+\omega_t^2\mathbf{P}^{(+)}\cdot\mathbf{P}^{(-)}+\left(\frac{\hbar\omega_t}{M_x}\right)(\nabla\times\mathbf{P}^{(+)})\cdot(\nabla\times\mathbf{P}^{(-)})\right], \qquad (12b)$$

$$W_{\rm LO}=\frac{\rho}{4}\left[\Omega_0^2(\nabla\Phi^{(+)})\cdot(\nabla\Phi^{(-)})+\left(\frac{\partial}{\partial t}\nabla\Phi^{(+)}\right)\cdot\left(\frac{\partial}{\partial t}\nabla\Phi^{(-)}\right)+i\omega_{\mathbf{k}}\left(\frac{\partial}{\partial t}\nabla\Phi^{(+)}\right)\cdot(\nabla\Phi^{(-)})-i\omega_{\mathbf{k}}\left(\frac{\partial}{\partial t}\nabla\Phi^{(-)}\right)\cdot(\nabla\Phi^{(+)})\right], \qquad (12c)$$

$$W_{x\text{-LO}}=-\frac{L\rho^{1/2}}{8\omega_t\beta}\{\nabla[\mathbf{P}^{(-)}\cdot\mathbf{P}_{0\mathbf{k}}^{(+)}\exp(-i\omega_{\mathbf{k}}t+i\mathbf{k}\cdot\mathbf{r})]\cdot\nabla\Phi^{(+)}+\text{H.c.}\}. \qquad (12d)$$

Here, W_γ and W_x are the densities of the electromagnetic energy and of the energy of the excitonic polarization, respectively. The density of the phonon energy $W_{\rm LO}$ of Eq. (12c) refers to the LO-phonon frequency Ω_0 calculated from the frequency $\omega_{\mathbf{k}}$ of the pump polariton, i.e., $W_{\rm LO}=(\rho/4)(\Omega_0+\omega_{\mathbf{k}})^2\mathbf{u}^{(+)}\cdot\mathbf{u}^{(-)}$. Physically, this is because in the stimulated Raman decay ''probe wave $\rightarrow$ pump polariton + LO phonon'' the phonon energy $\hbar\Omega_0$ is accompanied by the ''hidden'' energy $\hbar\omega_{\mathbf{k}}$ which refers to the pump polariton. Finally, $W_{x\text{-LO}}$ is the energy density of the exciton-phonon coupling induced by the macroscopic polariton.

The energy dissipation rate Θ is

$$\Theta=\frac{\gamma^x}{\omega_t^2\beta}\left(\frac{\partial\mathbf{P}^{(+)}}{\partial t}\cdot\frac{\partial\mathbf{P}^{(-)}}{\partial t}\right)+\gamma^{\rm ph}\frac{\rho}{2}\left[2\left(\frac{\partial}{\partial t}\nabla\Phi^{(+)}\right)\cdot\left(\frac{\partial}{\partial t}\nabla\Phi^{(-)}\right)+i\omega_{\mathbf{k}}\left(\frac{\partial}{\partial t}\nabla\Phi^{(+)}\right)\cdot(\nabla\Phi^{(-)})-i\omega_{\mathbf{k}}\left(\frac{\partial}{\partial t}\nabla\Phi^{(-)}\right)\cdot(\nabla\Phi^{(+)})\right]. \qquad (13)$$

The incoherent scattering of excitons proportional to γ^x and the decay of LO phonons given by $\gamma^{\rm ph}$ contribute to the energy dissipation. Similarly to the term $W_{\rm LO}$ of Eq. (12c),

the phonon dissipation term of Eq. (13) refers to the effective energy $\hbar(\Omega_0+\omega_{\mathbf{k}})\gg\hbar\Omega_0$, due to the presence of the pump polariton.

An energy flux $\mathbf{S}_{\rm ph}$, which corresponds to the phonon energy density $W_{\rm LO}$ given by Eq. (12c), does not contribute to the total flux $\mathbf{S}$ because the group velocity of LO phonons, unperturbed by the pump polariton, is equal to zero. The energy flux $\mathbf{S}_{x\text{-LO}}$ of the coherent LO phonons originates from a pump-induced finite mass $M_{\rm ph}^{\rm eff}$ [see Eq. (5)]. With the pump intensity $I_0\to 0$, the polariton system decouples from the LO-phonon one. In this case, Eqs. (11a), (11b) and Eqs. (12a), (12b) are identical to those derived in Ref. 8.

IV. EXCITONIC SPECTRA OF THE PHONON-MEDIATED OPTICAL STARK EFFECT

The PMOSE changes the reflectivity (transmissivity) of the probe light from a crystal. These modifications refer to the Raman resonance $\omega_{\mathbf{k}}+\Omega_0$ and follow dynamically the intensity I_0 of the pump light. In order to find the PMOSE in the transient excitonic spectra, one needs to analyze how the incident probe light reflects, propagates, and transmits in and from a crystal in the presence of a pump polariton. In the present paper, we apply a recently developed wave-vector-space method[24] to macroscopic phonoriton Eqs. (1a)–(1c). A *macroscopic* approach is used, i.e., Eqs. (1a)–(1c) are supposed to be valid up to an abrupt crystal boundary σ_0 at $x=0$ (see Fig. 2). No changes of the parameters of Eqs. (1a)–(1c) due to the surface effects are assumed. Derived quantities such as the susceptibility are affected near the surface by the nonlocal interactions. Since these effects occur in a surface layer that is narrow compared to a wavelegth, they arise naturally as surface distributions of fields in the long wavelength or macroscopic theory. We consider a normal incidence of the probe light on the crystal from a spatially nondispersive media (e.g., from air or vacuum).

The wave-vector-space method,[24] which was originally developed to calculate an excitonic reflection (transmission) within the polariton picture, operates in momentum space and yields the reflection and transmission coefficients without any explicit use of the boundary conditions. Being applied to the macroscopic phonoriton equations, this method allows us to find the reflection coefficient $r(\omega)$ and the partial transmission coefficients $t_{1,2}(\omega)$ of the probe light. The coefficients $t_{1,2}$ describe how the transmitted intensity of the probe wave is shared between the two frequency-degenerate phonoritons $p_1(\omega)$ and $p_2(\omega)$.

In the wave-vector-space method, the macroscopic Eqs. (1a)–(1c), which are valid for $x\geqslant 0$, are supplemented by the wave equation

$$\left[\frac{1}{c^2}\frac{\partial^2}{\partial t^2}-\Delta\right]\mathbf{E}^{(+)}(\mathbf{r},t)=0, \tag{14}$$

which describes the incident and reflected probe light at $x\leqslant 0$. A combination of Eq. (14) for $x\leqslant 0$ and Eqs. (1a)–(1c) for $x\geqslant 0$ is given in terms of the step function $\Theta(x)$. Then, for the considered one-dimensional geometry, a Fourier transform $\int_{-\infty}^{+\infty}\cdots\exp(-ipx)dx$ of Eq. (14) and Eqs. (1a)–(1c) yields

$$\left(p^2-\frac{\omega^2}{c^2}\right)E_-(p)+\left(p^2-\varepsilon_b\frac{\omega^2}{c^2}\right)E_+(p)-\frac{4\pi}{c^2}\omega^2P_+(p)=0, \tag{15a}$$

$$\left(\omega_t^2-\omega^2-2i\gamma^x\omega+\frac{\hbar\omega_t}{M_x}p^2\right)P_+(p)-\beta\omega_t^2E_+(p)$$
$$-2\omega_t\sqrt{\rho}L(p+k)^2P_{0\mathbf{k}}^{(+)}\Phi_+(p+k)+\frac{\hbar\omega_t}{M_x}\frac{1}{2\pi}$$
$$\times\left[ipP^{(0)}+\left(\frac{\partial P}{\partial x}\right)^{(0)}\right]-\omega_t\sqrt{\rho}LP_{0\mathbf{k}}^{(+)}$$
$$\times\frac{1}{\pi}\left[i(p+k)\Phi^{(0)}+\left(\frac{\partial\Phi}{\partial x}\right)^{(0)}\right]=0, \tag{15b}$$

$$[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\rm ph}(\omega-\omega_{\mathbf{k}})-\Omega_0^2]\Phi_+(p+k)$$
$$+\frac{2L}{\sqrt{\rho}\omega_t\beta}P_{0\mathbf{k}}^{(-)}P_+(p)=0. \tag{15c}$$

Here, a Fourier transform F [$F=E^{(+)}(p)$, $P^{(+)}(p)$, and $\Phi^{(+)}(p+k)$] is treated as $F=F_++F_-$, where F_+ has poles only in the upper half complex $p=p'+ip''$ plane which can be shown to be those of the semiconductor ($x\geqslant 0$), while F_- has poles only in the lower half-plane which can be attributed to the incident and reflected probe light at $x\leqslant 0$. The surface values of the excitonic polarization $P^{(0)}$ and of the LO-phonon potential $\Phi^{(0)}$ and their first-order derivatives $(\partial P/\partial x)^{(0)}$ and $(\partial\Phi/\partial x)^{(0)}$ are defined by $F^{(0)}\equiv\int_{-\infty}^{+\infty}F(p)dp$ and $(\partial F/\partial x)^{(0)}\equiv\int_{-\infty}^{+\infty}ipF(p)dp$ $(F=P,\Phi)$, respectively. These quantities are still unknown at this point in the derivation. Equations (15a)–(15c) in momentum space are equivalent to Eq. (14) ($x\leqslant 0$) and Eqs. (1a)–(1c) ($x\geqslant 0$) in real space.

The functional form of the electric field in wave vector space is given by[24]

$$E_-(p)=-\frac{E_0}{2\pi i}\left[\frac{1}{p-\omega/c+i\delta}+\frac{r}{p+\omega/c+i\delta}\right],$$
$$E_+(p)=\frac{E_0}{2\pi i}\left[\frac{t_1}{p-p_1}+\frac{t_2}{p-p_2}\right], \tag{16}$$

where E_0 is the amplitude of the incident light and $\delta\to+0$. Substituting in Eq. (15a) the expressions of $\Phi_+(p+k)$ and $P_+(p)$ in terms of $E_+(p)$ found from Eqs. (15b),(15c), one gets

$$1+r-t_1-t_2=0, \tag{17a}$$

$$(\omega/c)(1-r)-t_1p_1-t_2p_2=0, \tag{17b}$$

$$\tilde{A}[t_1(p_2p_3+p_2p_4+p_3p_4)+t_2(p_1p_3+p_1p_4+p_3p_4)]$$
$$-\tilde{B}(t_1+t_2)-\tilde{C}(t_1p_1+t_2p_2)+\tilde{D}\alpha_2=0, \tag{17c}$$

$$-\tilde{A}(t_1p_2+t_2p_1)p_3p_4+\tilde{B}(t_1p_1+t_2p_2)+i\tilde{D}\alpha_1=0. \tag{17d}$$

Here,

$$\tilde{A}=\left(\frac{\hbar\omega_t}{M_x}\right)[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{ph}(\omega-\omega_{\mathbf{k}})-\Omega_0^2]+2\hbar L^2N_0\omega_t, \tag{18a}$$

$$\tilde{B}=-[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{ph}(\omega-\omega_{\mathbf{k}})-\Omega_0^2](\omega^2+2i\gamma^{\mathrm{ph}}\omega-\omega_t^2)+2\hbar k^2L^2N_0\omega_t, \tag{18b}$$

$$\tilde{C}=4\hbar kL^2N_0\omega_t, \tag{18c}$$

$$\tilde{D}=\frac{8\pi^2}{c^2}\omega^2[(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\mathrm{ph}}(\omega-\omega_{\mathbf{k}})-\Omega_0^2], \tag{18d}$$

$$\alpha_1=\omega_t\sqrt{\rho}LP_{0\mathbf{k}}^{(+)}\frac{1}{\pi}\left[ik\Phi^{(0)}+\left(\frac{\partial\Phi}{\partial x}\right)^{(0)}\right]-\frac{\hbar\omega_t}{M_x}\frac{1}{2\pi}\left(\frac{\partial P}{\partial x}\right)^{(0)}, \tag{18e}$$

$$\alpha_2=\omega_t\sqrt{\rho}LP_{0\mathbf{k}}^{(+)}\frac{1}{\pi}\Phi^{(0)}-\frac{\hbar\omega_t}{M_x}\frac{1}{2\pi}P^{(0)}. \tag{18f}$$

After the treatment described above, Eq. (15a) reduces to a cubic polynomial of the variable p. Equations (17a)–(17d) originate from the requirement that this polynomial is identical to zero and that p is arbitrary (for details of the method see Ref. 24). This procedure implies that r and $t_{1,2}$ are independent of the variable p. Formally, five unknown variables r, $t_{1,2}$, and $\alpha_{1,2}$ enter four coupled Eqs. (17a)–(17d).

From Eq. (15c) one gets the relationships between the surface values of the phonon potential and excitonic polarization and their first-order spatial derivatives:

$$\Phi^{(0)}=\eta\nu(\omega)P^{(0)},\quad \left(\frac{\partial\Phi}{\partial x}\right)^{(0)}=\eta\nu(\omega)\left[ikP^{(0)}+\left(\frac{\partial P}{\partial x}\right)^{(0)}\right], \tag{19}$$

where

$$\eta=\eta(N_0)=-\frac{L}{\Omega_0^2}\left(\frac{2\hbar N_0}{\omega_t\beta\rho}\right)^{1/2},$$

$$\nu(\omega)=\nu'(\omega)+i\nu''(\omega)=\frac{\Omega_0^2}{(\omega-\omega_{\mathbf{k}})^2+2i\gamma^{\mathrm{ph}}(\omega-\omega_{\mathbf{k}})-\Omega_0^2}. \tag{20}$$

Taking into account Eqs. (19) and the definition $P^{(0)}=\int_{-\infty}^{+\infty}P(p)dp$, one derives from Eqs. (15b) and (15c):

$$\alpha_2=\frac{\beta\omega_t^2}{\pi(3\tilde{p}_2-\tilde{p}_1)}\left(\frac{t_1}{\tilde{p}_2-p_1}+\frac{t_2}{\tilde{p}_2-p_2}\right)+\frac{2i}{(3\tilde{p}_2-\tilde{p}_1)}\alpha_1, \tag{21}$$

where $\tilde{p}_1$ and $\tilde{p}_2$ are the solutions of the quadratic equation

$$\tilde{A}p^2+\tilde{C}p+\tilde{B}=\tilde{A}(p-\tilde{p}_1)(p-\tilde{p}_2)=0. \tag{22}$$

Equations (17a)–(17d) and Eq. (21) are five coupled linear equations which completely define the reflectivity r, the partial transmission coefficients $t_{1,2}$, and the surface terms $\alpha_{1,2}$. Then, the surface values $P^{(0)}$, $(\partial P/\partial x)^{(0)}$, $\Phi^{(0)}$, and $(\partial\Phi/\partial x)^{(0)}$ can be found from Eqs. (18e),(18f) and Eqs. (19). The solution of Eqs. (17a)–(17d) and (21) yields $P^{(0)}=0$ and

$$r(\omega)=\frac{A-B}{A+B}, \tag{23}$$

where A and B are given by

$$A=\left(\frac{\omega}{c}\right)(p_1+p_2),\quad B=\left(p_1p_2+\frac{\varepsilon_b}{c^2}\omega^2\right). \tag{24}$$

Equations (23) and (24) with the phonoriton wave vectors $p_{1,2}=p_{1,2}(\omega)$ given by Eq. (2) describe the PMOSE in reflectivity.

V. DISCUSSION

The transient excitonic spectra of the PMOSE depend on the boundary conditions for the macroscopic phonoriton Eqs. (1a)–(1c). In our case, the Maxwell equations yield the continuity of the tangential components of the electric and magnetic fields of the probe light at σ_0:[5,30]

$$\mathbf{E}_\tau^{(I)}=\mathbf{E}_\tau^{(II)}|_{\sigma_0},\quad \mathbf{H}_\tau^{(I)}=\mathbf{H}_\tau^{(II)}|_{\sigma_0}. \tag{25}$$

The Maxwellian boundary conditions (25) refer to the wave equation (1a), but are not used explicitly in the wave-vector-space method. Because the incident probe light induces two frequency-degenerate phonoritons of the same direction of propagation (along the x-axis), Eqs. (25) should be supplemented by an additional boundary condition. The problem of the ABC's is well-known in polariton optics.[2,4,5,9,24] The nonlocal dispersion of phonoritons stems both from the finite exciton mass M_x and from the wave vector dependence of the Raman interaction. Therefore, it might be expected that in this more general case the ABC deals with the excitonic polarization $\mathbf{P}$ and the phonon potential Φ at the crystal surface σ_0. The wave-vector-space method yields Eqs. (23) and (24) which correspond to Pekar's ABC:

$$\mathbf{P}|_{\sigma_0}=0. \tag{26}$$

As recognized in Ref. 9 for polariton optics, the Maxwellian boundary conditions (25) together with an additional boundary condition should satisfy the energy flux conservation at the crystal surface σ_0. In our case, for a monochromatic probe wave with $\mathbf{P}^{(+)}\propto\mathbf{E}^{(+)}\propto\exp(-i\omega t+i\mathbf{p}\cdot\mathbf{r})$ and $\Phi^{(+)}\propto\exp[-i(\omega-\omega_{\mathbf{k}})t+i(\mathbf{p}-\mathbf{k})\cdot\mathbf{r})]$ the pump-induced LO-phonon flux $\mathbf{S}_{x\text{-ph}}$ is proportional to the phonon wave vector $(\mathbf{p}-\mathbf{k})$ and $\mathbf{S}_\gamma\|\mathbf{S}_x\|\mathbf{S}_{x\text{-ph}}\|\mathbf{p}\|\mathbf{k}$. For the analyzed one-dimensional geometry of the counterpropagating pump and probe plane waves, one gets from Eqs. (11a)–(11c)

$$S(x)=|t_1|^2S^{(1)}(x)+|t_2|^2S^{(2)}(x)+[t_1t_2^*S^{(12)}(x)+\mathrm{H.c.}], \tag{27}$$

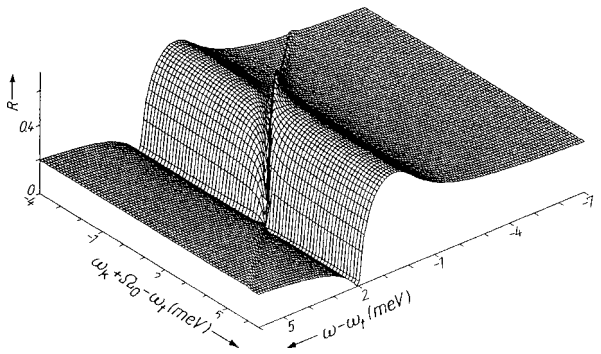

FIG. 4. The phonon-mediated optical Stark effect in the excitonic reflectivity $R=|r(\omega,\omega_{\mathbf{k}})|^2$ of CdS. The concentration of virtual coherent excitons $\mathbf{k}$ induced by the pump light is $N_0=5\times10^{17}\mathrm{cm}^{-3}$ ($I_0=1.5$ GW/cm^2).

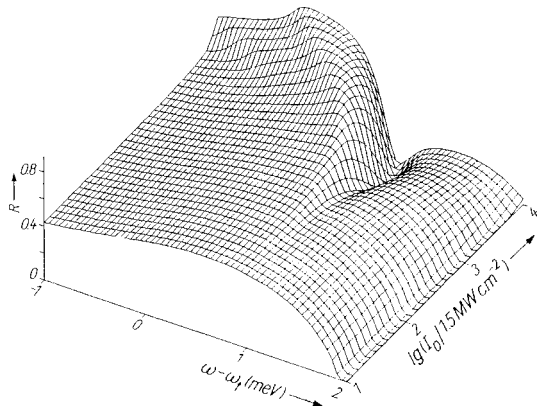

FIG. 5. The PMOSE in the excitonic reflectivity versus pump intensity I_0. The frequency $\omega_{\mathbf{k}}$ of the pump polariton corresponds to that of Fig. 3 [$\hbar\omega_{\mathbf{k}}=2.515$ eV, i.e., $\hbar(\omega_{\mathbf{k}}+\Omega_0-\omega_t)=1$ meV].

where $t_{i=1,2}$ are the partial transmission coefficients of the probe light into the two frequency-degenerate phonoritons $p_1(\omega)$ and $p_2(\omega)$ and

$$S^{(i=1,2)}(x)=\left(\frac{c}{\omega}\right)\left\{p_i'+\frac{c^2}{\varepsilon_b\Omega_c^2\omega^2}\left(p_i^2-\frac{\varepsilon_b}{c^2}\omega^2\right)\times\left((p_i^*)^2-\frac{\varepsilon_b}{c^2}\omega^2\right)\left[\left(\frac{\hbar\omega_t}{M_x}\right)p_i'+N_0\hbar\omega_t L^2\frac{1}{\Omega_0^2}\times[(p_i+k)\nu(\omega)+(p_i^*+k)\nu^*(\omega)]\right]\right\}\times\exp(-2p_i''x)|_{x\geqslant0}, \tag{28a}$$

$$S^{(12)}(x)=\frac{1}{2}\left(\frac{c}{\omega}\right)\left\{(p_1+p_2^*)+\frac{c^2}{\varepsilon_b\Omega_c^2\omega^2}\left(p_1^2-\frac{\varepsilon_b}{c^2}\omega^2\right)\times\left((p_2^*)^2-\frac{\varepsilon_b}{c^2}\omega^2\right)\left[\left(\frac{\hbar\omega_t}{M_x}\right)(p_1+p_2^*)+2N_0\hbar\omega_t L^2\times\frac{1}{\Omega_0^2}[(p_1+k)\nu(\omega)+(p_2^*+k)\nu^*(\omega)]\right]\right\}\times\exp[i(p_1-p_2^*)x]|_{x\geqslant0}. \tag{28b}$$

Here, $S^{(i=1,2)}$ are the total energy fluxes of the phonoriton waves with the real frequency ω and the complex wave vectors $p_{i=1,2}=p_{i=1,2}'+ip_{i=1,2}''$, $S^{(12)}$ is the interference flux of the two frequency-degenerate phonoritons, and the complex function $\nu(\omega)=\nu'(\omega)+i\nu''(\omega)$ is given by Eq. (20).

The continuity of the energy flux of the probe light at the crystal surface σ_0 results in the following condition:

$$1-|r|^2=S(x=0), \tag{29}$$

where $S(x)$ is given by Eq. (27) [note that $S(x)$ of Eqs. (27)–(29) is normalized by the incident flux of the probe light]. The transmission coefficients $t_{i=1,2}$ are determined by Eqs. (17a),(17b) with r of Eq. (23). Equations (17a) and (17b) are equivalent to the Maxwellian boundary conditions (25). Straightforward substitution of the coefficients r, $t_{i=1,2}$, and the phonoriton wave vectors $p_{i=1,2}$ of the dispersion Eq. (2) show that Eq. (29) is indeed valid for Pekar's ABC (26).

As it is shown above, Pekar's ABC for the phonoriton Eqs. (1a)–(1c) has been generated by the wave-vector-space method as two conditions $P|_{\sigma_0}=P^{(0)}=0$. This ABC naturally conserves the energy flux of the incident probe light across the crystal boundary, because according to Eqs. (11b) and (11c) $S_x|_{\sigma_0}\propto\omega P|_{\sigma_0}=0$ and $S_{x\text{-LO}}|_{\sigma_0}\propto\omega P|_{\sigma_0}=0$. While the exciton flux S_x and the pump-induced phonon flux $S_{x\text{-LO}}$ disappear at σ_0, the conservation of the total flux stems from the continuity of the electromagnetic flow S_γ of the probe light. The Maxwellian boundary conditions (25) are responsible for the conservation of S_γ.

The reflectivity $R(\omega,\omega_{\mathbf{k}})=|r|^2$ of the probe light from the boundary of bulk CdS in the presence of the cw pump light is plotted in Fig. 4 for the various positions of the anti-Stokes resonance $\omega_{\mathbf{k}}+\Omega_0$. The development of the PMOSE in reflectivity with the increasing pump intensity I_0 is shown in Fig. 5. The PMOSE of Fig. 5 corresponds to the most complicated case when the pump-induced Raman resonance at $\omega_{\mathbf{k}}+\Omega_0$ nearly overlaps with the spectral band of the unperturbed excitonic reflection.

VI. CONCLUSIONS

In this paper, we develop the electrodynamics of the phonon-mediated optical Stark effect for excitons in polar semiconductors. The following conclusions summarize our study.

(i) The PMOSE is formulated in terms of three macroscopic Eqs. (1a)–(1c) which describe the coupled electromagnetic, excitonic polarization, and LO-phonon fields of the probe wave in a polar semiconductor in the presence of a pump polariton. The corresponding three-component phonoriton eigenwaves originate from the pump-induced hybridization of the initial polariton and LO-phonon dispersions.

(ii) The Poynting theorem for a crystal virtually excited by the coherent pump light is derived and applied to the PMOSE. The total energy flux of the probe wave consists of the electromagnetic, excitonic, and pump-induced LO-phonon components.

(iii) In order to develop the optics of the PMOSE, we apply the wave-vector-space method to the macroscopic

phonoriton equations. We calculate reflectivity of the probe light and show that the continuity of the total energy flux at the crystal boundary is satisfied. The wave-vector-space method generates Pekar's ABC. Numerical evaluations of the transient excitonic reflectivity spectra of the PMOSE are given for bulk CdS.

ACKNOWLEDGMENTS

We appreciate valuable discussions with S.G. Tikhodeev and G.S. Vygovskii. Support of this work by the National Science Foundation Grant No. DMR-9712885 is gratefully acknowledged.

[1] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).
[2] S. I. Pekar, Zh. Éksp. Teor. Fiz. **33**, 1022 (1957) [Sov. Phys. JETP **6**, 785 (1957)]; **34**, 1176 (1958) [**7**, 813 (1958)].
[3] V. L. Ginzburg, Zh. Éksp. Teor. Fiz. **34**, 1953 (1958) [Sov. Phys. JETP **7**, 1096 (1958)].
[4] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).
[5] V. M. Agranovich and V. L. Ginzburg, *Crystal Optics with Spatial Dispersion, and Excitons*, 2nd ed. (Springer, Berlin, 1984).
[6] D. F. Nelson, *Electric, Optic, and Acoustic Interactions in Dielectrics* (Wiley, New York, 1979).
[7] J. L. Birman, in *Excitons*, edited by E.I. Rashba and M. Sturge (North-Holland, Amsterdam, 1982) p. 27; E. S. Koteles, *ibid.*, p. 83.
[8] W. C. Tait, Phys. Rev. B **5**, 648 (1972).
[9] M. F. Bishop and A. A. Maradudin, Phys. Rev. B **14**, 3384 (1976).
[10] D. F. Nelson, Phys. Rev. Lett. **76**, 4713 (1996).
[11] J. J. Hopfield, Phys. Rev. **182**, 945 (1968).
[12] S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. **57**, 2752 (1986); S. Schmitt-Rink, D. S. Chemla, and H. Haug, Phys. Rev. B **37**, 941 (1988).
[13] A. L. Ivanov and L. V. Keldysh, Zh. Éksp. Teor. Phys. **84**, 404 (1983) [Sov. Phys. JETP **57**, 234 (1983)].
[14] A. L. Ivanov, Zh. Éksp. Teor. Phys. **90**, 158 (1986) [Sov. Phys. JETP **63**, 90 (1986)]; D.Sc. thesis, Moscow State University, 1991.
[15] B. I. Greene, J. F. Mueller, J. Orenstein, D. H. Rapkine, S. Schmitt-Rink, and M. Thakur, Phys. Rev. Lett. **61**, 325 (1988); in *Proceedings of the NATO Workshop on Optical Switching in Low-Dimensional Systems* Marbella, Spain, 1988, Vol. 194 of *NATO Advanced Studies Institute Series B: Physics*, edited by H. Haug and L. Banyai (Plenum, New York, 1989), p. 97.
[16] J. L. Birman, M. Artoni, and B. S. Wang, Phys. Rep. **194**, 367 (1990); B. S. Wang and J. L. Birman, Solid State Commun. **75**, 867 (1990); Phys. Rev. B **42**, 9609 (1990).
[17] N. M. Khue, N. Q. Huong, and N. H. Quang, J. Phys.: Condens. Matter **6**, 3221 (1994).
[18] F. X. Bronold and A. R. Bishop, Phys. Rev. B **53**, 13 456 (1996).
[19] G. S. Vygovskii, G. P. Golubev, E. A. Zhukov, A. A. Fomichev, and M. A. Yakshin, Pis'ma Zh. Éksp. Teor. Phys. **42**, 134 (1985) [JETP Lett. **42**, 164 (1985)].
[20] T. Ishihara, J. Phys. Soc. Jpn. **57**, 2573 (1988).
[21] G. J. Blanchard, J. P. Heritage, A. C. Von Lehmen, M. K. Kelly, G. L. Baker, and S. Etemad, Phys. Rev. Lett. **63**, 887 (1989).
[22] A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967); R. Zeyher, C. S. Ting, and J. L. Birman, Phys. Rev. B **10**, 1725 (1974).
[23] L. V. Keldysh and S. G. Tikhodeev, Zh. Éksp. Teor. Phys. **90**, 1852 (1986) [Sov. Phys. JETP **63**, 1086 (1986)].
[24] B. Chen and D. F. Nelson, Solid State Commun. **86**, 769 (1993); Phys. Rev. B **48**, 15 365 (1993); **48**, 15 372 (1993).
[25] R. M. Martin and T. C. Damen, Phys. Rev. Lett. **26**, 86 (1971); R. M. Martin, Phys. Rev. B **4**, 3676 (1971).
[26] S. A. Permogorov and A. N. Reznitsky, Solid State Commun. **18**, 781 (1976).
[27] M. Cardona, in *Light Scattering in Solids II*, Vol. 50 of *Topics in Applied Physics*, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982), p. 19.
[28] A. I. Ansel'm and Yu. A. Firsov, Zh. Éksp. Teor. Phys. **30**, 719 (1956) [Sov. Phys. JETP **3**, 564 (1957)].
[29] Y. Toyozawa, Prog. Theor. Phys. **20**, 53 (1958).
[30] M. Born and E. Wolf, *Principles of Optics*, 2nd ed. (Pergamon, New York, 1964), Sec. 1.1.