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Dispersion theory of surface-exciton polaritons

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Surface-exciton polaritons with spatial dispersion are investigated theoretically. We give a complete physical description of these eigenstates of the interface between a crystal having spatial dispersion and an adjacent medium. We show a detailed picture of the electric fields on either side of the boundary, derive the dispersion relation, and explore its solutions by an extensive numerical evaluation. The excitonic Brewster-angle condition is shown to be connected with the dispersion relation of surface-exciton polaritons. Finally, we derive the response function for surface-exciton polaritons. The discussion yields an extended understanding of the coupling to these modes, their damping mechanism, and their different behavior compared with surface-phonon polaritons.

I. INTRODUCTION

Surface-exciton polaritons are electromagnetic modes propagating along the surface of a crystal which has Wannier-type excitons as bulk excitation. These surface modes are eigenstates of the interface between the crystal and the adjacent medium. They are associated with macroscopic electromagnetic fields which decrease exponentially in amplitude with distance from the surface. We are dealing here only with Wannier-type excitons in semiconductors which are delocalized in the crystal.

Surface-exciton polaritons have recently become an active field of research. Experimentally, the attenuated-total-reflection technique has been employed for the excitation of these modes.[1-5] The excitation by a nonlinear process has been reported also.[6] For a discussion of localized Frenkel-type excitons in molecular crystals see Ref. 7. Maradudin and Mills[8] introduced the basic theoretical concept of Wannier-type surface-exciton polaritons and described some of the fundamental properties. Simultaneously, Agarwal[9] calculated a dispersion relation of surface-exciton polaritons. Many authors followed these ideas and extended the theoretical knowledge about surface-exciton polaritons.[2,3,10-17]

The theoretical problems associated with surface-exciton polaritons arise mainly from spatial dispersion, i.e., the wave-vector dependence of the dielectric function. The total energy of the bulk exciton consists of the eigenenergy *and* the wave-vector-dependent kinetic energy of the exciton. This wave-vector dependence results in a coexistence of two transverse waves with different wave vectors at the same frequency within the crystal.

Figure 1 shows the schematic energy versus real wave-vector dispersion relations in the bulk for phonon polaritons without spatial dispersion (upper part) and for exciton polaritons with spatial dispersion (lower part). The phonon energy is wave-vector independent. Thus, the lower (1) and upper (2) polariton branches are well separated in energy. This separation occurs no longer for exciton polaritons with spatial dispersion (lower part of Fig. 1).

The coexistence of two transverse waves at the same frequency implies that the reflectivity and the surface-exciton-polariton dispersion relation

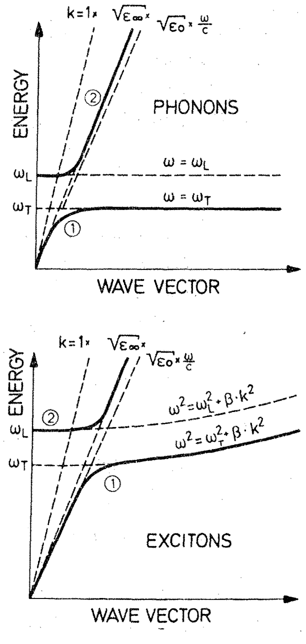

FIG. 1. Schematic energy vs real wave-vector dispersion relations for phonon polaritons without spatial dispersion (upper part) and exciton polaritons with spatial dispersion (lower part). (ϵ_0 signifies, *only* in this figure, $\epsilon = \epsilon_0$ for $\omega \to 0$; throughout the rest of the paper ϵ_0 is the dielectric constant of the adjacent medium).

of a spatially dispersive medium cannot be calculated from Maxwell equations and Maxwell boundary conditions alone. Additional information is required about the microscopic behavior of the dielectric function at the surface. This behavior can be described in macroscopic terms by so-called additional boundary conditions, which have been discussed for long time in the literature.[18]

In the present paper we search for the eigenstates of the boundary between a spatially dispersive medium with excitons and an adjacent medium. We give a complete physical description of surface-exciton polaritons which are these eigenstates. We investigate the properties of the electric fields on either side of the boundary and compare it with the much simpler case of surface-phonon polaritons.

After general remarks and definitions (Sec. II A) we start with the Maxwell boundary conditions (Sec. II B). In Sec. II C we introduce the additional boundary condition of Pekar[19] and Hopfield and Thomas.[20] They proposed that the excitonic polarization vanishes at the boundary. The formalism used in the present paper, however, could as well be used in connection with other additional boundary conditions. The Maxwell and additional boundary conditions lead to the dispersion relation in Sec. II D.

In Sec. III, we give a detailed discussion of the dispersion curve for surface-exciton polaritons obtained from our derivation. Further, we discuss in Sec. IV the dispersion curve for the excitonic Brewster-angle condition which is connected with the dispersion relation for surface-exciton polaritons.

In Sec. V, we turn finally to a calculation of the response function for surface-exciton polaritons. This function is useful to discuss the excitation of the complex surface eigenstate with real and imaginary parts by only real frequency and real wave vector, which is relevant for experiments.

II. FROM BOUNDARY CONDITIONS TO DISPERSION RELATION

In this section, we define the dielectric function of the crystal in the exciton energy region and the electromagnetic fields to be used. The Maxwell and additional boundary conditions lead to the dispersion relation.

A. General remarks

The dielectric behavior of a crystal with one excitonic resonance showing spatial dispersion is characterized for given wave vector k and frequency ω by the dielectric function ϵ (Ref. 20):

$$\epsilon(\omega, k) = \epsilon_\infty[1 + (\omega_L^2 - \omega_T^2)/(\omega_T^2 - \omega^2 + \beta k^2 - i\omega\Gamma)], \quad (1)$$

with ϵ_∞ being a frequency- and wave-vector-independent background dielectric constant ($\epsilon = \epsilon_\infty$ for $\omega \to \infty$), ω_T and ω_L the transverse and longitudinal resonance frequencies at $k = 0$, and Γ the empirical damping constant ($i = \sqrt{-1}$). The influence of spatial dispersion is described by $\beta k^2 = (\hbar\omega_T/M)k^2$, where M is the effective exciton mass and $\hbar$ is Planck's constant divided by 2π.

Equation (1) leads to the energy versus wave-vector dispersion relation of an exciton polariton with spatial dispersion propagating in the bulk of the crystal. The dielectric functions of the transverse lower polariton branch (1) and upper polariton branch (2) in the bulk are determined as solutions of the condition

$$\epsilon(\omega, k) = k^2c^2/\omega^2 . \quad (2)$$

For given ω, Eq. (2) is quadratic in k^2. There are two transverse modes 1 and 2 with dielectric functions ϵ_1 and ϵ_2, which may propagate in the same direction of the crystal and with the same polarization and frequency (c is the vacuum velocity of light).

The longitudinal solution is defined by

$$\epsilon_L(\omega, k) = 0 \quad (3a)$$

or after rearranging by

$$\omega^2 = \omega_L^2 + \beta k^2 \quad (3b)$$

which leads to one longitudinal mode at a given frequency in the bulk.

Let us now consider the boundary between a homogeneous insulating crystal of the described behavior and an adjacent medium of frequency-independent dielectric constant $\epsilon_0 = n_0^2$ (for vacuum: $n_0 = 1$) which both fill up infinite half-spaces.

We search for the eigenstates of this boundary between the crystal with excitons having spatial dispersion and the adjacent medium. The eigenstates of the boundary are electromagnetic waves, one transverse mode outside the crystal (called mode "0") obeying the dispersion relation $k_0 = n_0\omega/c$, and three modes inside the crystal belonging to the two transverse polariton modes (called mode "1" and "2") and to the longitudinal one (called mode "L"). All these modes are matched together at the crystal surface by the Maxwell and additional boundary conditions to form the eigenstate of the boundary. We call this eigenstate of the boundary a surface-exciton polariton, if the mode "0" is localized at the boundary and is traveling nearly parallel to it.

The Brewster angle of reflection in case of excitons is described by the second solution of the eigenstate condition of the boundary which yields a nonlocalized mode "0" outside the crystal: only one traveling incoming wave, but no reflected wave.

The surface-exciton polariton and the excitonic Brewster angle are solutions of the same eigenstate condition, but with different interpretations depending on the localization or nonlocalization of the waves at the boundary. This connection was already pointed out for phonon polaritons whose dielectric function, however, leads to only one transverse and no longitudinal polariton mode inside the crystal.[21]

It should be noted, that the behavior of the surface eigenstates is determined only by the dielectric function of the crystal bulk and by the refractive index of the adjacent medium. In the dielectric continuum theory there is no need of a special dielectric function close to the crystal surface for Wannier-type excitons considered in this paper. The eigenstate arises by the existence of the boundary and may be determined in the framework of Maxwell's theory.

B. Maxwell boundary conditions

Before we define the electric fields of the polariton modes we split the wave vectors into components parallel and perpendicular to the surface. The component $k_\parallel$ parallel to the surface is the same for all waves outside and inside the crystal because of the phase-matching condition. This common $k_\parallel$ together with the dielectric functions of all modes describe the eigenstate of the boundary. Therefore, $k_\parallel$ is usually plotted in energy versus wave-vector dispersion relations of surface polaritons and of the Brewster angle.

The components perpendicular to the surface are then given by

$$k_{j\perp}^2 = k_j^2 - k_\parallel^2 = \epsilon_j k_v^2 - k_\parallel^2 \quad (j=0,1,2,L), \tag{4}$$

with the wave vector in vacuum being $k_v = \omega/c$.

If $k_{j\perp}^2$ is negative and therefore $k_{j\perp}$ imaginary, the corresponding mode j is exponentially decaying perpendicular to the surface and periodically traveling parallel to the surface, thus being localized at the boundary. If $k_{j\perp}^2 > 0$, then mode j is not localized.

According to Fig. 2, we define the electric field amplitudes $\vec{E}_0$ of the transverse mode "0" outside the crystal, the amplitudes $\vec{E}_1$ and $\vec{E}_2$ of the transverse modes, and $\vec{E}_L$ of the longitudinal mode in the crystal. The electric fields are all polarized parallel to the x-z plane because only this geometry yields eigenstates of the boundary:

$$\begin{aligned}\vec{E}_j &= E_j(-k_{j\perp}/k_j, 0, k_\parallel/k_j)e^{ik_\parallel x}\, e^{ik_{j\perp}z}\, e^{-i\omega t}\,,\\ \vec{E}_L &= E_L(-k_\parallel/k_L, 0, -k_{L\perp}/k_L)e^{ik_\parallel x}\, e^{ik_{L\perp}z} e^{-i\omega t}\,,\end{aligned} \tag{5}$$

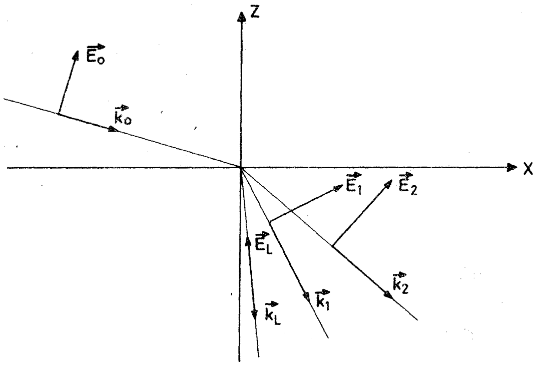

FIG. 2. Boundary between the crystal ($z<0$) and the adjacent medium ($z>0$). The wave vectors $\vec{k}$ and the electric field amplitudes $\vec{E}$ of one wave outside the crystal (mode "0") and three waves inside the crystal (modes "1", "2", and "L") are shown.

for ($j=0,1,2$). These are waves traveling in $+x$ and $+z$ direction if $\mathrm{Re}k_\parallel > 0$ and $\mathrm{Re}k_\perp > 0$.

The conservation of the tangential component of the electric field amplitude and of the magnetic field amplitude are the two Maxwell boundary conditions of the considered eigenstate. They connect the electric field amplitudes at the crystal surface of one wave outside and three waves inside the crystal which all have the same $k_\parallel$ but different $k_\perp$.

We replace E_2 and E_L by the amplitude ratios F_{21p} and F_{L1} as introduced by Skettrup[22]:

$$F_{21p} = E_2/E_1, \quad F_{L1} = (k_\parallel/k_{0\perp})(E_L/E_1)\,. \tag{6}$$

The division of the first by the second Maxwell boundary equation gives the condition for an eigenstate of the boundary

$$\frac{\epsilon_1 k_{0\perp} - \epsilon_0 k_{1\perp}}{k_1} + \frac{\epsilon_2 k_{0\perp} - \epsilon_0 k_{2\perp}}{k_2} F_{21p} - \frac{\epsilon_0 k_{0\perp}}{k_L} F_{L1} = 0\,. \tag{7}$$

Equation (7) is the dispersion relation between the wave vector $k_\parallel$ and the frequency ω of surface-exciton polaritons and of the Brewster-angle condition. The dispersion relation in this form contains the still unknown parameters F_{21p} and F_{L1}.

The same dispersion relation can be obtained by setting the reflectivity in the exciton energy region[23] equal to zero. Setting the amplitude ratios F_{21p} and F_{L1} equal to zero in Eq. (7) yields the well-known dispersion relation for surface phonon polaritons.[24]

C. Additional boundary conditions

Spatial dispersion leads to more than two unknown electric field amplitudes at the boundary. More equations are required to solve the system, the so-called additional boundary conditions (ABC).

The ABC connect the electric field amplitude of the upper transverse and the longitudinal polariton branch with that of the lower transverse polariton branch.

The explicit behavior of the surface eigenstate depends on the chosen ABC. One special ABC yields, for example, the dispersion relation obtained by Maradudin and Mills.[8] The appropriate ABC may be found empirically or derived more generally as a consequence of the Maxwell equations and the properties of the boundary. A recent publication by García-Moliner and Flores[15] about spatial dispersion summarizes different additional boundary conditions.[25]

We use the ABC proposed by Pekar[19] and applied also by Hopfield and Thomas,[20] who claimed that the excitonic polarization vanishes at the surface. We consider this ABC to be reasonable for Wannier-type excitons in view of a comparison between our experimental attenuated-total-reflection spectra on ZnO and calculated spectra.[2] However, a definite decision about the appropriate ABC based on measured surface-exciton-polariton dispersion curves is not yet possible. The available experimental results are confined to small wave vectors where dispersion curves calculated with different ABC still coincide. A comparison of such calculated dispersion curves is given in a forthcoming review.[26] Attenuated-total-reflection spectra at small wave vectors may yield information about the ABC only by a careful line-shape analysis, which is in progress in this laboratory.

The ABC proposed by Pekar yields two equations for the eigenstate of the boundary after splitting the polarization and thus the electric field vectors into components parallel and perpendicular to the surface:

$$\frac{E_1(\epsilon_1-\epsilon_\infty)k_{1\perp}}{k_1}+\frac{E_2(\epsilon_2-\epsilon_\infty)k_{2\perp}}{k_2}-\frac{E_L\epsilon_\infty k_\parallel}{k_L}=0\,; \tag{8}$$

$$\frac{E_1(\epsilon_1-\epsilon_\infty)k_\parallel}{k_1}+\frac{E_2(\epsilon_2-\epsilon_\infty)k_\parallel}{k_2}+\frac{E_L\epsilon_\infty k_{L\perp}}{k_L}=0\,. \tag{9}$$

Thus, the amplitude ratios F_{21p} and F_{L1} have the following forms[27]:

$$F_{21p}=\frac{E_2}{E_1}=-\frac{\epsilon_1-\epsilon_\infty}{\epsilon_2-\epsilon_\infty}\;\frac{k_2}{k_1}\;\frac{k_\parallel^2+k_{L\perp}k_{1\perp}}{k_\parallel^2+k_{L\perp}k_{2\perp}}\,; \tag{10}$$

$$F_{L1}=\frac{k_\parallel}{k_{0\perp}}\;\frac{E_L}{E_1}=\frac{\epsilon_1-\epsilon_\infty}{\epsilon_\infty}\;\frac{k_L}{k_1}\;\frac{k_\parallel^2}{k_{0\perp}}\;\frac{k_{1\perp}-k_{2\perp}}{k_\parallel^2+k_{L\perp}k_{2\perp}}\,. \tag{11}$$

D. Dispersion relation

We obtain the dispersion relation of surface-exciton polaritons and of the excitonic Brewster-angle condition from Eqs. (7), (10), and (11):

$$\begin{aligned}&\epsilon_1(\epsilon_2-\epsilon_\infty)(\epsilon_\infty k_{0\perp}-\epsilon_0 k_{1\perp})k_\parallel^2\\&\quad-\epsilon_2(\epsilon_1-\epsilon_\infty)(\epsilon_\infty k_{0\perp}-\epsilon_0 k_{2\perp})k_\parallel^2\\&\quad+\epsilon_\infty k_{L\perp}[\epsilon_1(\epsilon_2-\epsilon_\infty)k_{0\perp}k_{2\perp}\\&\qquad-\epsilon_2(\epsilon_1-\epsilon_\infty)k_{0\perp}k_{1\perp}+\epsilon_0(\epsilon_1-\epsilon_2)k_{1\perp}k_{2\perp}]=0\,.\end{aligned} \tag{12}$$

The excitonic dispersion relation cannot be given in an explicit equation of $k_\parallel^2$, which is possible in the case of phonons. A rearrangement of Eq. (12) yields a polynomial of twelfth order in $k_\parallel^2$ which is, however, rather cumbersome.

Equation (12) contains, in general, complex quantities because the wave vectors $k_\perp$ perpendicular to the surface may have imaginary parts even without any empirical damping Γ, as discussed earlier. Thus, the eigenstate of the boundary must have complex solutions for the wave vector $k_\parallel$ or the frequency ω, as has already been found for other additional boundary conditions.[8,12]

A complex wave vector $k_\parallel$ describes the spatial damping of the eigenstate of the boundary if the eigenstate is excited in some manner at position x. Formally, the situation is equivalent to an infinite amount of energy being supplied to the system at $x=-\infty$. The spatial damping along the boundary is the same for all four modes whereas their wave-vector components $k_{j\perp}$ perpendicular to the surface are different ($j=0,1,2,L$). The $k_{j\perp}$ have real and imaginary parts because they are given by

$$k_{j\perp}^2=\epsilon_j k_v^2-k_\parallel^2\,. \tag{13}$$

All modes must have constant electric field amplitudes along their traveling direction $\vec{k}_j=(k_\parallel,0,k_{j\perp})$ if empirical damping Γ is omitted and thus ϵ_j is real.

Introducing real and imaginary parts into Eq. (13) yields in case of spatial damping ($k_\parallel$ taken complex) with $\Gamma=0$ and thus real ϵ_j:

$$(\mathrm{Re}k_{j\perp})^2-(\mathrm{Im}k_{j\perp})^2=\epsilon_j k_v^2-(\mathrm{Re}k_\parallel)^2+(\mathrm{Im}k_\parallel)^2 \tag{14}$$

and

$$\mathrm{Re}k_{j\perp}\,\mathrm{Im}k_{j\perp}+\mathrm{Re}k_\parallel\,\mathrm{Im}k_\parallel=0\,. \tag{15}$$

We may write Eq. (15) as a scalar product of two vectors:

$$(\mathrm{Re}k_{j\perp},0,\mathrm{Re}k_\parallel)\cdot(\mathrm{Im}k_{j\perp},0,\mathrm{Im}k_\parallel)=0\,. \tag{16}$$

This relation shows that the real part of $\vec{k}_j$ is always perpendicular to the imaginary part of $\vec{k}_j$ in the case of spatial damping with $\Gamma=0$.

Temporal damping with complex frequency ω and real wave vector $k_{\parallel}$ describes the time behavior of the eigenstate of the boundary if the system is excited in some manner at a time t with constant amplitude along the surface. This situation corresponds formally to an infinite amount of energy having been supplied to the system at time $t = -\infty$.[28] In this case, all modes must have constant electric field amplitudes parallel to the boundary, whereas the imaginary part of $\vec{k}_j$ is always perpendicular to the boundary.

Several authors have already derived dispersion relations of surface-exciton polaritons using particular additional boundary conditions, but did not discuss the dispersion relation in detail.[9,13-15,17] Maradudin and Mills[8] gave an extensive discussion of the influence of spatial dispersion on the properties of surface-exciton polaritons. They developed the dispersion relation using their additional boundary condition and explained the radiation damping. Further, they discussed special limits of the dispersion relation, but they did not show explicitly an energy versus wave-vector diagram. Rimbey[12] used the method of surface impedances and presented energy versus wave-vector dispersion plots for special additional boundary conditions. The same method was applied by Fischer and Queisser[16] who, however, dealt only with the real part of the dispersion relation, which is relevant mainly for attenuated-total-reflection experiments.

What is lacking in all these publications is a detailed picture of the electromagnetic waves which build up the surface-exciton polariton, a complete evaluation of the dispersion relation for complex wave vector and frequency, and a connection between the dispersion relation of surface-exciton polaritons and the excitonic Brewster angle. This information is contained in Secs. III–V.

III. SOLUTION OF THE DISPERSION RELATION FOR SURFACE EXCITON POLARITONS

Equation (12) gives the dispersion relation of the surface eigenstate which is described for fixed frequency ω by the same wave vector $k_{\parallel}$ for all four modes j ($j = 0, 1, 2, L$) and the resulting $k_{j\perp}$ of Eq. (13). This Eq. (13) is quadratic in $k_{j\perp}$ and gives two solutions for $k_{j\perp}$:

$$k_{j\perp} = \pm(\epsilon_j k_v^2 - k_{\parallel}^2)^{1/2} . \tag{17}$$

Caution must be exercised regarding the determination of the sign of the root in Eq. (17) to find the solution of the surface eigenstate. The real part of $k_{j\perp}$ determines the traveling direction of each mode j, the imaginary part the direction of the spatial decay.

We found for the surface-exciton-polariton region that the following signs give a physically meaningful solution of the dispersion relation:

$$\begin{aligned}
&\mathrm{Re}k_{0\perp} < 0 \text{ with } \mathrm{Im}k_{0\perp} > 0 \quad \text{(outside the crystal)} ,\\
&\mathrm{Re}k_{1\perp} < 0 \text{ with } \mathrm{Im}k_{1\perp} > 0 \quad \text{(lower polariton branch)} ,\\
&\mathrm{Re}k_{2\perp} > 0 \text{ with } \mathrm{Im}k_{2\perp} < 0 \quad \text{(upper polariton branch)} ,\\
&\mathrm{Re}k_{L\perp} > 0 \text{ with } \mathrm{Im}k_{L\perp} < 0 \quad \text{(longitudinal polariton branch)} .
\end{aligned} \tag{18}$$

Other combinations seem to be unphysical because the amplitudes of their waves bound to the surface increase with increasing distance from the surface.

TABLE I. Solutions of the dispersion relation for surface-exciton polaritons of the $C1$ exciton in ZnO at $\hbar\omega = 3.43$ eV with $n_0 = 1$ and $\Gamma = 0$.

Wave vector (10^4 cm^{-1})	Decay length (nm)
$k_{\parallel} = 22.8 + 4.2i$	240
$k_{0\perp} = -6.1 + 15.5i$	65
$k_{1\perp} = -443.2 + 0.2i$	5880 (increase)
$k_{2\perp} = 3.0 - 31.8i$	31
$k_{L\perp} = 0.3 - 213.2i$	4

For illustration we made a numerical evaluation without empirical damping ($\Gamma = 0$) for the $C1$ exciton in ZnO neglecting the anisotropy of this crystal.[2] The solution of the dispersion relation and the distances in which the electric field amplitudes decrease by a factor of $1/e$ are given in Table I for fixed frequency.

Figure 3 shows a picture of the electromagnetic waves which build up the surface-exciton polariton for complex wave vector $k_{\parallel}$ and real frequency ω at fixed time. The upper part represents the half-space of the adjacent medium which is separated by the boundary from the crystal in the lower half-space. The thicknesses of the wave fronts represent the electric field amplitudes.

The upper part of Fig. 3 shows the mode "0" outside the crystal. This mode is nearly an evanescent wave propagating along and bound to the surface with constant amplitude along the propagation direction $\mathrm{Re}\vec{k}_0$. The electric field amplitude is decreasing weakly along the surface and decreasing strongly perpendicular to the surface. The propagation direction $\mathrm{Re}\vec{k}_0$ is not exactly parallel to the surface but slightly tilted with respect to the surface, because of the complex wave vector $k_{\parallel}$. It must be tilted to the surface because the amplitude is constant along the propagation direction, but is decreasing with the complex wave vector $k_{\parallel}$ along the surface.

The lower part of Fig. 3, which represents the crystal, is split for clarity into three internal sec-

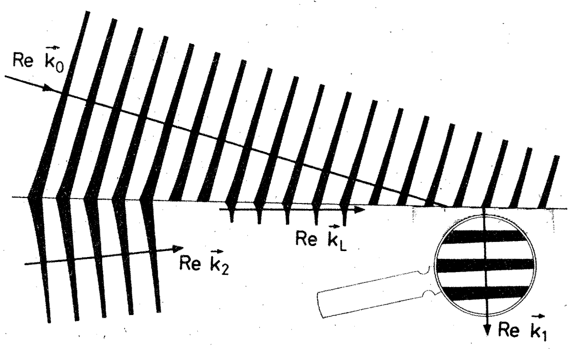

FIG. 3. Picture at fixed time of the electromagnetic waves which build up the surface-exciton polariton for complex wave vector $k_{\parallel}$ and real frequency ω. Upper part: adjacent medium. Lower part: crystal with waves of the three modes which have to be extended throughout the whole crystal and have to be superimposed.

tions. However, the waves of all three sections have to be extended throughout the half-space of the crystal and have to be superimposed. The relative amplitudes of all waves are chosen to be equal at the boundary. In reality, they have to be calculated from the additional boundary conditions.

On the left-hand side and in the middle of Fig. 3 the evanescent bound waves of mode "2" and mode "L" are shown. They are also slightly tilted with respect to the surface, and they have the same behavior as mode "0" outside the crystal.

Mode "1" is shown on the right-hand side of Fig. 3. This mode gives the eigenstate a contribution which is mainly periodic in the direction perpendicular to the surface because $\mathrm{Re}k_{1\perp} \gg \mathrm{Im}k_{1\perp}$. Parallel to the surface the amplitude is slightly decreasing as shown in the magnified inset. This periodic mode is responsible for the damping of the surface-exciton polariton because it carries energy from the surface into the crystal bulk. The propagation directions of the other modes bound to the surface are tilted to the surface because their amplitudes are coupled to that of mode "1" at the surface by the boundary conditions. The amplitudes have to decrease because of the energy transport by mode "1".

Surface-phonon polaritons which are damped by an empirical damping parameter show a similar behavior. The propagation directions inside and outside the crystal are also tilted to the surface, because the energy dissipates in the crystal due to the damping. In the case of excitons this tilting occurs even without empirical damping.

Recently, García-Moliner and Flores[15] showed that the surface-exciton polariton is not damped by the periodical mode "1" if the vanishing derivative of the excitonic polarization at the surface is taken as an additional boundary condition.

We add one detail concerning the choice of the sign in Eq. (17). The positive imaginary part of $k_{1\perp}$ describes an amplitude which is exponentially increasing perpendicular to the surface (see Table I). This increase seems at first glance not to be physically meaningful. However, the amplitude at a point (x, z) originates from the point $(x-\delta, 0)$ at the boundary. The amplitude at $(x-\delta, 0)$ has already been greater than at $(x, 0)$ because the amplitude is decreasing along the surface from $(x-\delta, 0)$ to $(x, 0)$. Therefore, the positive imaginary part of $k_{1\perp}$ is an artifact of splitting the wave vectors into components.

Changing the frequency yields a change of all real and imaginary parts of the wave vectors which solve the surface eigenstate condition of Eq. (12). We evaluated the dispersion relation for varied frequency with both complex wave vector $k_{\parallel}$ and complex frequency ω. In this section we restrict ourselves to the surface-exciton-polariton region where $k_{\parallel} > k_0$, which excludes radiation into the adjacent medium. The results are given in Figs. 4–6.

Figure 4 shows the dispersion relation projected into the real-ω real-k^2 plane. The dashed and dotted lines give the energy versus wave-vector dispersion relations of three bulk modes and asymptotic curves as explained in Fig. 4. The full lines show the dispersion relation of the surface eigenstate solution: the real part of the wave vector $k_{\parallel}$ versus the real part of the frequency ω.

The dispersion of the surface-exciton polariton lies at frequencies above the transverse resonance frequency ω_T and at wave vectors above that of the mode "0" because they are localized at the surface. The dispersion relation splits in this region of Fig. 4 into two parts, for complex $k_{\parallel}$ and for

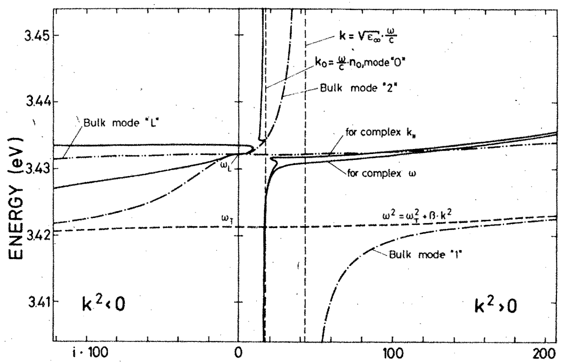

FIG. 4. Real parts of energy vs wave vector of the dispersion relation for the surface eigenstate including spatial dispersion (full lines for complex ω and $k_{\parallel}$). ($n_0 = 1$; $\Gamma = 0$. For parameters see Ref. 2).

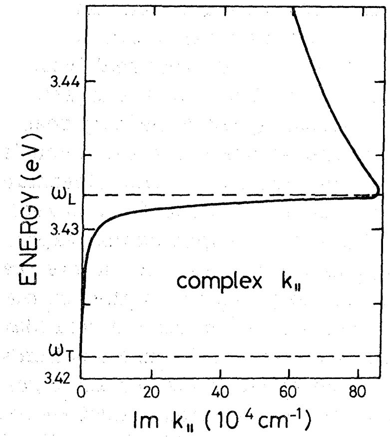

FIG. 5. Imaginary part of the wave vector $k_\parallel$ vs the energy for real ω corresponding to Fig. 4.

complex ω. This splitting is due to the projection of a function of two complex variables into a two-dimensional plane along the real $k_\parallel$ or real ω axes. Similar effects are known from surface-phonon polaritons with damping.[29] This connection shows again the similar behavior of damped phonons and undamped excitons with spatial dispersion.

At higher wave vectors the dispersion relation crosses the dispersion curve of mode "L". Mode "L" of the surface-exciton polariton becomes radiative like mode "1". However, one has to consider also the imaginary parts of $k_\parallel$ and ω. The imaginary part of the wave vector $k_\parallel$ is plotted for real frequency ω in Fig. 5, whereas the imaginary part of the frequency ω is plotted for real wave vector $k_\parallel$ in Fig. 6. These figures show that the solution of the surface eigenstate becomes more complex with higher wave vectors and thus takes off from the real-ω real-k plane. In this region the plot of Fig. 4 alone is no longer meaningful and one always has to include the imaginary parts. This consideration is also relevant for the different dispersion relations shown by Rimbey[12] which approach at large wave vectors the mode "L" or lie at lower frequencies than this mode.

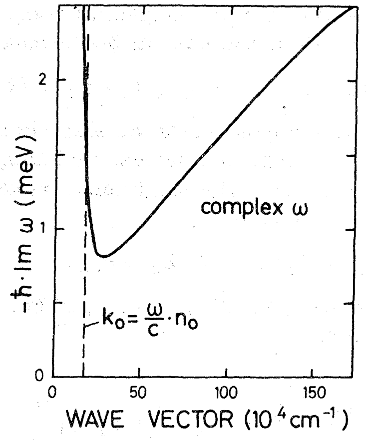

FIG. 6. Imaginary part of the frequency ω vs the wave vector $k_\parallel$ for real $k_\parallel$ corresponding to Fig. 4.

A deeper understanding of the properties of the surface eigenstate will be reached in Sec. V where we consider the possibility of exciting the surface eigenstate.

IV. SOLUTION OF THE DISPERSION RELATION FOR THE EXCITONIC BREWSTER ANGLE

The ansatz of electric field amplitudes in Sec. II includes only one wave outside the crystal. Such an ansatz yields the excitonic Brewster-angle condition in addition to the dispersion relation of the surface-exciton polariton. The reflectivity of a crystal with excitons is—by definition—equal to zero for fixed frequency at the excitonic Brewster angle α of incidence. The corresponding wave vector is given by $k_\parallel = (n_0\omega/c)\sin\alpha$. The Brewster angle changes with frequency according to the Brewster-angle condition. The solution of the surface eigenstate condition in the Brewster-angle case describes waves which are not bound to the surface outside the crystal because their wave vector Re$k_\parallel$ parallel to the surface is smaller than the wave vector k_0.

The solid line in Fig. 4 describes at frequencies lower than the transverse resonance frequency ω_T the dispersion relation of the excitonic Brewster angle. The corresponding wave vectors have an imaginary part too in case of excitons because the modes "2" and "L" have negative dielectric functions and thus mainly imaginary wave vectors in this energy region. The signs of Eq. (17) are the same as for surface-exciton polaritons [see Eq. (18)]. Mode "0" and "1" are mainly periodically propagating with small imaginary parts of their wave vectors; mode "2" and "L" are mainly evanescent, having small real parts of their wave vectors, and are bound to the surface.

This behavior causes the experimental reflectivity in the exciton energy region to stay above zero at the Brewster angle below ω_T, since the experiment probes the reflectivity only at real wave vectors k^2 and real frequencies ω.

The situation is quite different for frequencies above the longitudinal resonance frequency ω_L and for wave vectors $k_\parallel$ with $0 < k_\parallel < k_0$. In this frequency region all wave vectors have only real parts in Eq. (17). Thus, the dispersion relation Eq. (12) is purely real, and all waves are periodically propagating in $-z$ direction. The upper part of Fig. 4 shows the corresponding dispersion relation of the Brewster angle (full lines). There are two frequencies possible with zero reflectivity for given angle of incidence α or wave vector $k_{\parallel}$ except for a small gap. These two frequencies have already been found in calculated excitonic reflection spectra.[30]

However, it should be noticed that the Brewster angle near ω_L yields a very sharp minimum in calculated reflection spectra. This minimum is damped out by introducing even a small empirical damping and is thus not experimentally relevant. The two Brewster angles with $k_{\parallel} \lesssim k_0$ at frequencies above ω_L lead in calculated reflection spectra to two flat minima which cannot be distinguished experimentally.

The back bending of the dispersion relation at frequencies just above ω_L is a consequence of the complicated system including spatial dispersion. A gap develops between the two branches of the Brewster-angle dispersion curve. In this gap the involved waves are obviously not able to suppress a reflected wave.

The upper curve of the Brewster-angle condition ends in Fig. 4 at the crossing point of mode "0" and bulk mode "2". It is not clear if there does not exist a continuation or if we were unable to find any because of the complicated structure of the dispersion relation in Eq. (12).

Finally, we have to discuss some special cases with $k^2 < 0$ at the left-hand side of Fig. 4. There is a part of the dispersion relation at frequencies above ω_L which has a purely imaginary wave vector $k_{\parallel}$ and resulting purely real wave vectors $k_{j\perp} < 0$ $(j = 0, 1, 2, L)$. This dispersion describes zero reflectivity for normal incidence of light. All involved waves have to decrease exponentially perpendicular to their direction of periodical propagation.

The dispersion relation at frequencies below ω_L with $k_{\parallel}^2 < 0$ belongs to a surface-exciton polariton which is overdamped along the surface. Modes "0", "1", and "2" are mainly periodical and have propagation directions away from the surface, whereas only mode "L" is localized at the surface. The surface wave decays by radiation into the crystal and into the adjacent medium. A similar behavior for $k_{\parallel}^2 < 0$ is known for surface-phonon polaritons.[21]

V. RESPONSE FUNCTION OF SURFACE-EXCITON POLARITONS

A basic question in the case of surface-exciton polaritons with spatial dispersion is how to excite such a complex surface eigenstate and how to determine the dispersion relation. An experimental excitation causes a driven oscillation of the surface eigenstate at the driving real frequency and real wave vector. The complex eigenstate condition of the boundary cannot be fully reached. Therefore, one always measures a coupling strength of the complex surface eigenstate to an excitation with real frequency ω and real wave vector k^2. It may be expected that experimentally measured dispersion relations in this real plane deviate from the projection of the complete complex dispersion relation into the real plane.

We want to derive a response function which describes the response of the surface eigenstate in the case of surface-exciton polaritons to an excitation with real ω and real k^2. Generally, such a response function has to be considered for each special experimental arrangement, for instance, for an attenuated total reflection (ATR) experiment. The reflectivity of the ATR multilayer would be one such response function.[31]

However, it is desirable to obtain a more general knowledge of surface-exciton polaritons considering the response of the surface eigenstate with constant driving force over the ω-k^2 plane and without additional external influences, such as from the ATR prism. Therefore, we use the method of response functions developed by Barker[32] for surface-phonon polaritons, although this method does not directly correspond to a special experimental arrangement.[31]

As driving force we consider an externally applied polarization with a component $P_{\mathrm{ext}\perp}$ perpendicular to the surface

$$P_{\mathrm{ext}\perp} = P_{\mathrm{ext}} e^{i(k_{\parallel}x - \omega t)} \delta(z) . \tag{19}$$

This polarization is periodical along the surface. The δ function $\delta(z)$ specifies that $P_{\mathrm{ext}\perp}$ is a surface polarization at the boundary $z = 0$. P_{ext} is a constant.

The conservation of the tangential component of the electric field amplitudes at the boundary yields

$$E_{0\perp} k_{0\perp}/k_{\parallel} = E_{1\perp} k_{1\perp}/k_{\parallel} + E_{2\perp} k_{2\perp}/k_{\parallel} - E_{L\perp} k_{\parallel}/k_{L\perp} . \tag{20}$$

The normal components of the electric displacement also have to be continuous, including the external polarization. The longitudinal mode carries no electric displacement.

$$\epsilon_0 \tilde{\epsilon}_0 E_{0\perp} = \epsilon_1 \tilde{\epsilon}_0 E_{1\perp} + \epsilon_2 \tilde{\epsilon}_0 E_{2\perp} + P_{\mathrm{ext}} . \tag{21}$$

We introduce again F_{21p} and F_{L1} of Eq. (6) and find a function T:

$$T \equiv \tilde{\epsilon}_0 \frac{E_{0\perp}}{P_{\mathrm{ext}}} = -\left(\frac{k_{1\perp}}{k_1} + \frac{k_{2\perp}}{k_2} F_{21p} + \frac{k_{0\perp}}{k_L} F_{L1}\right)\left[\frac{k_{0\perp}}{k_v^2}(k_1 + k_2 F_{21p}) - \epsilon_0\left(\frac{k_{1\perp}}{k_1} + \frac{k_{2\perp}}{k_2} F_{21p} + \frac{k_{0\perp}}{k_L} F_{L1}\right)\right]^{-1} . \tag{22}$$

Im(T) is the response function for surface-exciton polaritons.[32] F_{21p} and F_{L1} again are determined by the additional boundary condition which connect E_1, E_2, and E_L. Thus, T depends not only on $E_{0\perp}$, but also on the other electric field amplitudes.

The wave vectors $k_{j\perp}$ ($j=0,1,2,L$) in Eq. (22) are either purely real or purely imaginary because we are dealing in this section with real wave vector $k_\parallel$ and real frequency ω. The signs of the roots in Eq. (17) have to be chosen similar to those of Eq. (18):

$$\begin{aligned} &k_{0\perp}=\mathrm{Im}k_{0\perp}>0 \ \text{(outside the crystal)},\\ &k_{1\perp}=\mathrm{Re}k_{1\perp}<0 \ \text{(lower polariton branch)},\\ &k_{2\perp}=\mathrm{Im}k_{2\perp}<0 \ \text{(upper polariton branch)},\\ &k_{L\perp}=\mathrm{Im}k_{L\perp}<0 \ \text{(longitudinal polariton branch)}. \end{aligned} \tag{23}$$

For convenience, we introduce an effective refractive index n_{eff} which describes the crystal with spatial dispersion. Writing Eq. (2) of Ref. 2 with the terms used in the present paper yields for n_{eff}:

$$n_{\mathrm{eff}}^2=[1\pm(1-4A^2k_\parallel^2/k_v^2)^{1/2}]/2A^2, \tag{24}$$

with

$$A^2=k_v^2\left(\frac{k_{1\perp}}{k_1}+\frac{k_{2\perp}}{k_2}F_{21p}+\frac{k_{0\perp}}{k_L}F_{L1}\right)^2(k_1+k_2F_{21p})^{-2}. \tag{25}$$

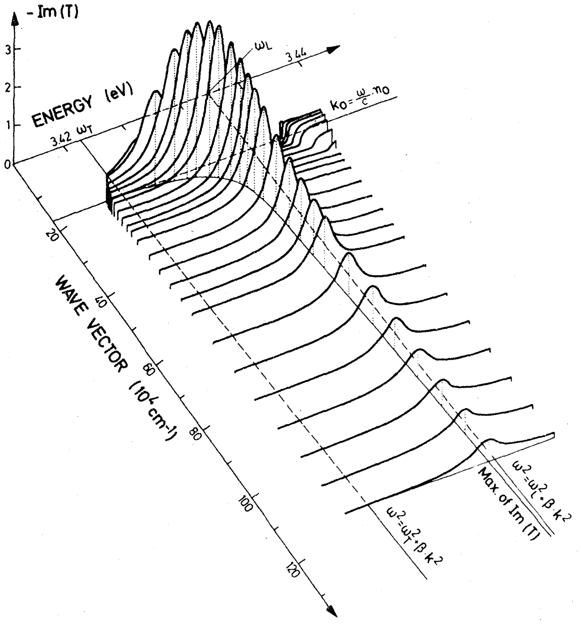

FIG. 7. Response function Im(T) of surface-exciton polaritons vs wave vector and energy. ($n_0=1$.)

The sign in Eq. (24) has to be chosen such that Im(n_{eff}) > 0.

The response function of Eq. (22) may then be rearranged in the same way as for surface-phonon

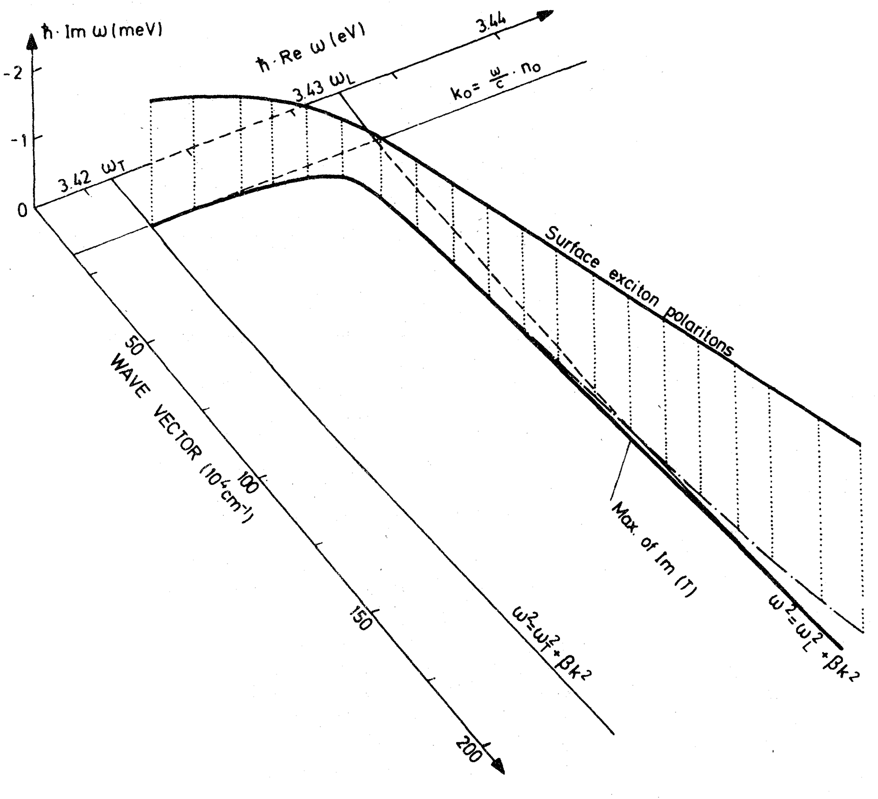

FIG. 8. Comparison of the curve representing the response-function maxima for fixed real $k_\parallel$ with the surface-exciton-polariton dispersion relation for complex ω and real $k_\parallel$. (Note the different scales in Figs. 7 and 8.)

polaritons:

$$T \equiv \tilde{\epsilon}_0 \frac{E_{0\perp}}{P_{\mathrm{ext}}} = \frac{(n_{\mathrm{eff}}^2 k_v^2 - k_\parallel^2)^{1/2}}{n_{\mathrm{eff}}^2(\epsilon_0 k_v^2 - k_\parallel^2)^{1/2} + \epsilon_0 (n_{\mathrm{eff}}^2 k_v^2 - k_\parallel^2)^{1/2}} , \tag{26}$$

with positive signs of the roots.

Figure 7 shows a three-dimensional plot of the response function Im(T) for surface-exciton polaritons over the real energy versus wave-vector plane. The full lines represent profiles through the Im(T) function with constant wave vector $k_\parallel$.

The Im(T) mountain describes the response of the surface eigenstate to a driving force at any point in the real ω-$k_\parallel$ plane. The halfwidth of the mountain parallel to the energy or to the wave-vector axis is related to the radiation damping caused by spatial dispersion. One has to choose the related profiles according to different experimental arrangements in which the energy or the wave vector are changed.

The height of the Im(T) mountain in Fig. 7 is finite even without an empirical damping constant. It is not possible to reach the complex resonance condition for surface-exciton polaritons completely by an experiment with only real frequency and real wave vector. Therefore, an attenuated-total-reflection spectrum always shows finite half-width and at most several percent of outcoupled intensity.[3] Surface-phonon polaritons show this behavior only with empirical damping which causes the solution of the dispersion relation to become complex.

The curve which describes the positions of the maxima of Im(T) for fixed $k_\parallel$ is also given in Fig. 7. Figure 8 shows again this curve in the real-ω real-$k_\parallel$ plane. Additionally, the dispersion relation for surface-exciton polaritons is plotted for real wave vector $k_\parallel$ and complex frequency ω. The curve of the response-function maxima approaches at large wave vectors the curve $\omega^2 = \omega_L^2 + \beta k^2$ and deviates remarkably from the projection of the complex dispersion relation into the real ω-$k_\parallel$ plane. This behavior shows that the coupling from the real ω-$k_\parallel$ plane to the complex surface eigenstate need not be strongest at values in the real ω-$k_\parallel$ plane which are equal to Reω and Re$k_\parallel$ of the complex dispersion relation. The deviation occurs in case of surface-exciton polaritons with spatial dispersion and thus with radiation damping, whereas the deviation is negligible in case of surface-phonon polaritons with small empirical damping. Therefore, a measured dispersion relation must not be equal to the real part of the surface-eigenstate dispersion relation. The experimental results which have been obtained up to now are all confined to the region at small $k_\parallel$ where the dispersion curves still coincide.

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