PHYSICAL REVIEW B VOLUME 7, NUMBER 6 15 MARCH 1973

Effect of Spatial Dispersion on the Properties of a Semi-Infinite Dielectric

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(Received 27 June 1972)

In this paper, we explore the properties of a model of a semi-infinite nonlocal dielectric to assess the effect of spatial dispersion on the reflectivity of the material and on the properties of surface polaritons. For the model, the nonlocal form of Maxwell's equations may be solved exactly. The additional boundary conditions follow from Maxwell's equations, and it is not necessary to introduce microscopic considerations to complete the theory. We exhibit closed expressions for the reflectivity of the material, for the case where the electric field is parallel to the plane of incidence, and for the case where it is perpendicular to the plane of incidence. At non-normal incidence, when the electric field vector is parallel to the plane of incidence, structure which owes its origin to spatial-dispersion effects appears in the reflectivity. We show that in the presence of spatial dispersion, the surface polaritons acquire a finite lifetime even in the case where the dielectric is lossless; i.e., in the presence of spatial dispersion the surface polaritons become virtual surface waves. In the quasistatic limit, we obtain an analytic expression for the dependence of the real and imaginary part of the surface-polariton frequency on wave vector in the long-wavelength limit. We then present the theory of frustrated internal reflection of radiation from a prism and crystal configuration similar to that employed in several recent experiments. In a final section, we present the results of some numerical calculations of the reflectivity of the crystal, and the width and position of the dip observed in the frustrated-internal-reflection method, for parameters characteristic of the fundamental exciton line in ZnSe.

I. INTRODUCTION

The experimental study of the interaction of electromagnetic radiation with solids has provided quantitative information about a variety of elementary excitations in solids. Quite frequently, the magnitude and phase of the reflection coefficient may be studied as a function of the frequency Ω of the incident radiation. If one assumes that the complex dielectric constant of the medium is a function only of the frequency Ω, and if the medium is isotropic, then in principle one may extract values for both the real and imaginary parts of the dielectric constant from such data.[1]

In principle, the complex dielectric constant is a function of the wave vector $\vec{k}$ of the radiation in the medium, as well as of its frequency. One says that in this case spatial dispersion is present in the dielectric constant. In many instances, when the incident radiation is in the visible or infrared portion of the spectrum, the dependence of the dielectric tensor $\epsilon_{ij}(\vec{k}, \Omega)$ on $\vec{k}$ may be safely ignored, since the wavelength of the radiation is very long compared to the interatomic separation. The dielectric tensor then becomes a function only of frequency, and if the medium is isotropic or cubic, the dielectric tensor $\epsilon_{ij}(\vec{0}, \Omega)$ is diagonal, and the material is described by a single scalar dielectric constant.

However, there are many instances where the wave-vector dependence of the dielectric tensor produces striking effects in the reflectivity, even when the wavelength of the radiation is long compared to the interatomic separation. As an example, we cite the experimental and theoretical studies of CdS carried out by Hopfield and his collaborators.[2] In this case, one observes structure in the reflectivity at low temperatures from three sharp exciton series, when the frequency of the incident radiation is close to the fundamental absorption edge of the crystal. The structure in the reflectivity differs markedly from that expected from a model which considers only the frequency dependence of the dielectric constant in the exciton regime. A quantitative interpretation of the data may be obtained from a model which employs the wave-vector dependence of the dielectric constant of the material as an essential feature.[2]

The purpose of this paper is to explore in detail a number of properties of a semi-infinite isotropic dielectric medium with a dielectric constant that depends on wave vector. For the dielectric constant, we choose a model form that is applicable to cubic crystals that contain a single electric-dipole-active exciton level or optical-phonon branch with a frequency that exhibits a quadratic dependence on wave vector $\vec{k}$ in the long-wavelength limit. The model will be described in detail below. We show that for this model the nonlocal Maxwell equations may be solved exactly in closed form. We then study several aspects of electromagnetic wave propagation in the material. We consider radiation incident on the material from the vacuum, and we obtain closed expressions for

the reflectivity which fully include spatial-dispersion effects for the case where the electric field of the incident radiation is plane polarized perpendicular to the plane of incidence, and also for the case where the radiation is plane polarized with the electric vector parallel to the plane of incidence. We then examine the effect of spatial dispersion on the properties of surface polaritons. As we shall see, one effect of the presence of spatial dispersion is to allow the energy stored in the surface mode to leak into the interior of the crystal. The surface polaritons thus become virtual surface states when spatial dispersion is present. Finally, we present a theory of the effect of spatial dispersion on the position of the reflectivity minima produced by excitation of surface polaritons across a gap between two dielectrics for the configuration used recently by several groups[3] to study the properties of surface polaritons on dielectric surfaces.

While our work was in its final stages, two papers by Agarwal, Pattanayak, and Wolf[4] appeared. These authors have studied the properties of precisely the same model we use here, and their solutions are also exact. The two approaches appear identical, and the results of these two independent studies are equivalent, as far as we can see. However, we have emphasized different aspects of the theory than they have, and we regard our paper to be complementary to their work. As stated above, we have studied the effect of spatial dispersion on the properties of surface polaritons, while Agarwal *et al.* have confined their attention mainly to the reflection and refraction of radiation by a slab, and they have not studied the properties of surface waves in the model. We also treat the reflection and refraction of radiation by a plane surface. In the discussion presented below, we have chosen to stress some features of the theory contained in the work of Agarwal *et al.* but not discussed in detail by them. We also present a series of numerical calculations of the effect of spatial dispersion on the reflectivity of materials, for parameters characteristic of the semiconductor ZnSe.

The outline of the present paper is as follows: In Sec. II we begin with some general qualitative remarks about past treatments of the effects of spatial dispersion on the reflectivity, and on the physical picture provided by the present theory, and that of Agarwal and co-workers.[4] Sections III–V are devoted to an analysis of the reflectivity, the theory of surface polaritons in the presence of spatial dispersion, and an analysis of the coupling between electromagnetic radiation and surface polaritons (in the presence of spatial dispersion) in the frustrated-internal-reflection technique employed in recent studies of surface polaritons.[3] The results of our numerical calculations are presented in Sec. VI.

II. GENERAL REMARKS

We first recall some features of the theory of the reflection of radiation from a semi-infinite isotropic dielectric, for the case where the dielectric constant depends on frequency, but not on the wave vector. For simplicity, consider a medium characterized by an excitation of transverse polarization (an exciton, or a TO phonon), which is electric dipole active at $\vec{k}=0$. For frequencies Ω near the frequency Ω_T of the excitation, the dielectric constant may be approximated by the form

$$\epsilon(\Omega)=\epsilon_0+\frac{\Omega_p^2}{\Omega_T^2-\Omega^2} \quad , \tag{2.1}$$

in the absence of dissipation. The background dielectric constant ϵ_0 is, in general, complex and a function of frequency, although the frequency dependence of ϵ_0 may frequently be ignored so long as we are interested only in frequencies very close to Ω_T. If the excitation is a TO phonon in an ionic crystal the frequency Ω_p is the ion plasma frequency multiplied by $\epsilon_0^{1/2}$; if it is an exciton, Ω_p is a measure of its electric dipole oscillator strength.

The electromagnetic waves which propagate in the medium are often called polaritons, and are characterized by the dispersion relation

$$c^2k^2/\Omega^2=\epsilon(\Omega) \, . \tag{2.2}$$

The well-known polariton dispersion curves for this case are plotted in Fig. 1(a). The frequency Ω_L is the frequency for which $\epsilon(\Omega)$ vanishes. Explicitly, for the model form in Eq. (2.1),

$$\Omega_L^2=\Omega_T^2+\Omega_p^2/\epsilon_0 \quad .$$

Now suppose a wave of frequency Ω_0 is incident on the crystal surface. For simplicity, assume the wave is plane polarized, and normally incident on the surface. Some fraction of the incident energy is reflected from the surface, and the remainder transmitted. The transmitted energy is carried by the polariton with the wave vector given by Eq. (2.2), for $\Omega=\Omega_0$. When $\Omega_0>\Omega_L$, the polariton which carries the transmitted energy is illustrated graphically by the point P in Fig. 1(a). The frequency region between Ω_T and Ω_L is a stop band within which no propagating modes of the bulk dielectric exist. As a consequence, the reflection coefficient R of the model dielectric is unity when $\Omega_T<\Omega_0<\Omega_L$.

For general values of Ω_0, the reflection coefficient may be obtained by applying the boundary conditions on $\vec{E}$ and $\vec{H}$ obtained from Maxwell's equations to the problem. Given the amplitude of the incident wave, one needs to find the amplitude of the reflected and the transmitted wave. Any

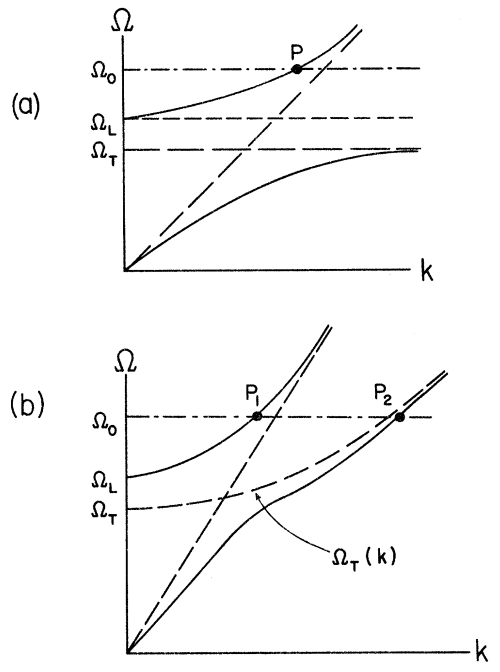

FIG. 1. (a) Polariton-dispersion relation in the absence of spatial dispersion, in a dielectric described by the dielectric constant given in Eq. (2.1). (b) Polariton-dispersion relation in the presence of spatial dispersion, where $\epsilon(\vec{k}, \omega)$ is given by Eq. (2.5).

two of the four boundary conditions obtained from Maxwell's equations suffice to determine the amplitude of the transmitted and reflected wave. If any two boundary conditions are satisfied (say, conservation of tangential $\vec{E}$ and tangential $\vec{H}$), the fact that the waves satisfy Maxwell's equations ensures that the remaining boundary conditions are satisfied, of course. From this procedure, one obtains for R the expression well known from elementary dielectric theory:

$$R = \left| \frac{\epsilon(\Omega)^{1/2} - 1}{\epsilon(\Omega)^{1/2} + 1} \right|^2 . \tag{2.3}$$

Next consider the effect of spatial dispersion on the reflectivity of radiation normally incident on the crystal. For Ω near Ω_T, an important source of wave-vector dependence of the dielectric constant comes from the dependence of the frequency Ω_T on the wave vector $\vec{k}$ of the excitations. For small values of $|\vec{k}|$, in cubic crystals, $\Omega_T(\vec{k})$ varies quadratically with $\vec{k}$. We write for small $\vec{k}$,

$$\Omega_T^2(\vec{k}) = \Omega_T^2 + Dk^2 , \tag{2.4}$$

where D measures the curvature in the dispersion relation at $\vec{k} = 0$ and Ω_T is the value of $\Omega_T(\vec{k})$ at $\vec{k} = 0$. With application to exciton problems in mind, we take $D > 0$ in this paper, although the discussion goes through in a very similar fashion when $D < 0$. If we neglect other sources of the $\vec{k}$ dependence of the dielectric constant, we may take the model form

$$\epsilon(\vec{k}, \Omega) = \epsilon_0 + \frac{\Omega_p^2}{\Omega_T^2 + Dk^2 - \Omega^2} \tag{2.5}$$

for $\epsilon(\vec{k}, \omega)$. This form is a special limiting case of the model considered below. In our quantitative discussion, we include damping effects by adding the term $-i\Omega\gamma$ to the denominator on the right-hand side of Eq. (2.5).

In the presence of spatial dispersion, the polariton dispersion relation becomes

$$\frac{c^2 k^2}{\Omega^2} = \epsilon_0 + \frac{\Omega_p^2}{\Omega_T^2 + Dk^2 - \Omega^2} . \tag{2.6}$$

The dispersion relation is sketched in Fig. 1(b).

Now consider reflection of an incident wave with frequency $\Omega_0 > \Omega_L$ from the surface. As one can see from Fig. 1(b), there are now two propagating polariton modes in the medium with the frequency Ω_0. The two modes are indicated by the points P_1 and P_2 in the figure. The incident wave thus will excite a linear combination of the two waves when it strikes the crystal surface. Thus, given the amplitude of the incident wave, we now have three unknowns to determine: the amplitude of the reflected wave, and the amplitude of each of the polaritons P_1 and P_2 in Fig. 1(b). A problem now arises, since the two independent boundary conditions associated with Maxwell's equations are insufficient to determine the three unknowns. A third boundary condition is required.

It has been argued in the literature[5] that to obtain the additional boundary condition it is necessary to construct a microscopic model of the crystal including the surface region. The additional boundary condition then results when a full account of the surface region and the effect of the low symmetry of the surface region are incorporated into the theory. In this work, and in the papers by Agarwal *et al.*, it is shown that in the presence of spatial dispersion the nonlocal form of the macroscopic Maxwell equations contain all the information required to calculate the reflection coefficient uniquely. For the dielectric constant displayed in Eq. (2.5) with dissipation added, the nonlocal macroscopic equations may be solved exactly, and a closed expression for the reflection coefficient is obtained. The additional boundary condition is contained in the nonlocal Maxwell equations, and there is no reason in principle that requires one to resort to a microscopic theory to deduce a new boundary condition to supplement the ones that follow from the macroscopic theory.

Before we proceed with the present discussion, one important point must be made. In the present work, and the work of Agarwal *et al.*, the proper-

ties of a homogeneous semi-infinite slab of material are studied. In this case, we show that Maxwell's equations provide a full and complete description of the interaction of radiation with the material, and one is not required to resort to a microscopic theory to discuss the reflectivity problem. However, in practice, microscopic inhomogeneities near the surface, perhaps of intrinsic origin, may influence the reflectivity in important qualitative ways. That this is so in the case of CdS seems clear from the work of Hopfield and his collaborators.[2] The presence of the microscopic inhomogeneities will modify the boundary conditions derived here and by Agarwal *et al.* Of course, a microscopic theory is required to obtain anything other than a phenomenological description of these effects.

We next describe the physical picture of the radiation in the medium that results from the present work, and that of Agarwal *et al.* First consider the case where $\Omega_0 > \Omega_L$, as indicated in Fig. 1(b). The additional boundary condition obtained from the nonlocal form of Maxwell's equations allows one to compute the amplitudes of the two propagating waves P_1 and P_2 as well as that of the reflected wave, as stated above.

For incident frequencies Ω_0 below Ω_L, Fig. 1(b) indicates that only one propagating mode exists. In some discussions in the literature, it is assumed that in this frequency region the normal two independent boundary conditions used in the local theory suffice to determine the reflectivity, since in the presence of only one propagating mode these boundary conditions contain enough information to determine uniquely the amplitude of the reflected wave and the single transmitted wave in the medium, just as in the case where ϵ depends only on frequency and not on wave vector. However, the additional boundary condition we obtain does not apply only for $\Omega_0 > \Omega_L$, but for all values of the frequency, even $\Omega_0 < \Omega_L$. If this is so, and there is only one wave in the medium when $\Omega_0 < \Omega_L$, the problem is overdetermined. There must be a second wave in the medium, even for $\Omega_0 < \Omega_L$. In the work of Agarwal *et al.*, and in the present work, it is found that for all values of the incident frequency Ω_0 one must couple the plane wave normally incident on the material into two internal waves. In the absence of dissipation, when $\epsilon(\vec{k}, \Omega)$ is real, for $\Omega_0 > \Omega_L$ both waves propagate as indicated in Fig. 1(b). For $\Omega_0 < \Omega_L$, one of the waves is spatially damped [i.e., the wave vector determined from Eq. (2.6) is purely imaginary for this mode], while only one of the modes is a propagating mode characterized by a real value of the wave vector. Thus, for $\Omega_0 < \Omega_L$, energy is transported into the crystal by only the propagating wave, but one must make up the electric field in the medium by constructing a linear superposition of the propagating and the spatially damped wave to satisfy Maxwell's equations with the additional boundary condition.

The above remarks apply to the case where plane-polarized radiation is normally incident on the crystal. If we consider oblique incidence, then when the electric field vector is perpendicular to the plane of incidence, a similar situation obtains. Two waves are always present. If k is the magnitude of the vacuum wave vector of the incident wave, and $k_\parallel = k \sin\theta$, where θ is the angle of incidence, then for $\Omega_0 > \Omega_L(k_\parallel)$ two propagating modes in the medium are excited by the incident radiation, where

$$\Omega_L^2(k_\parallel) = \Omega_L^2 + Dk_\parallel^2 .$$

If $\Omega_0 < \Omega_L(k_\parallel)$, only one mode has a real wave vector (in the absence of dissipation) and one mode is spatially damped.

If the electric field vector is parallel to the plane of incidence, two additional boundary conditions obtain for non-normal incidence and, in general, three waves in the medium are excited by the incident field. The third wave is an irrotational wave (the electric field has vanishing curl), and is a longitudinal mode for $\Omega > \Omega_L(k_\parallel)$, and a spatially damped oscillation of irrotational character for $\Omega < \Omega_L(k_\parallel)$.

We conclude this section with a few qualitative remarks about the effects of spatial dispersion on surface waves. It is now well known that surface electromagnetic waves propagate down the surface of the dielectric-vacuum interface. For a beautiful experimental study of this type of wave, we refer the reader to the work of Marschall and Fisher.[3] For a given value of the wave vector $k_\parallel$ parallel to the surface, these surface electromagnetic waves (surface polaritons) have a frequency $\Omega_s(k_\parallel)$ that lies between Ω_T and Ω_L, in the absence of spatial dispersion. For the dielectric-vacuum interface, the dispersion relation assumes the form[3]

$$\frac{c^2 k_\parallel^2}{\Omega_s^2} = \frac{\epsilon(\Omega_s)}{1+\epsilon(\Omega_s)} \quad . \tag{2.7}$$

In the absence of spatial dispersion, the surface polaritons exist only for wave vectors to the right of the light line, i.e., only for values of Ω_s and $ck_\parallel$ such that $ck_\parallel > \Omega_s$. They also exist only between the frequencies Ω_T and Ω_L, as mentioned above. The first condition ensures that the energy stored in the surface polariton cannot radiate into the vacuum, since no propagating electromagnetic disturbance in the vacuum can be phase matched to the surface polariton. The second condition ensures that the energy stored in the surface wave cannot radiate into the interior of the dielectric, since no propagating modes of the dielectric medium occur within the stop band between Ω_T and Ω_L.

Thus, crudely speaking, when these conditions are satisfied the energy trapped in a wave localized to the surface must remain there, and the surface waves have infinite lifetime in the absence of dissipative forces in the medium.

When spatial dispersion is present, there is no longer a stop band between Ω_T and Ω_L, as one can see from Fig. 1(b). If one attempts to excite a mode in which the fields are localized to the surface, the energy will leak into the interior of the crystal, and the amplitude of the surface wave damps out in time, even in the absence of dissipation. If the leakage rate is low, the surface wave may propagate a large number of wavelengths before its amplitude decays. In this instance, the surface mode behaves like a weakly damped normal mode of the crystal. We refer to these weakly damped modes as virtual surface modes.

To speak more precisely, in the absence of spatial dispersion the surface polariton is characterized by an electric field which decays to zero in a purely exponential fashion as one penetrates into either the vacuum or the medium from the surface. In the presence of spatial dispersion, the presence of additional boundary conditions means that a single damped exponential wave no longer fully satisfies the set of boundary conditions. In fact, for $\Omega > \Omega_T$, the boundary conditions admix the bound exponential wave with the bulk polariton associated with the lower branch of Fig. 1(b). Thus, the electric field in the wave is no longer bound to the surface, but its amplitude is nonzero even in the interior by virtue of the admixture of the bulk wave into the surface mode.

III. REFLECTION OF PLANE ELECTROMAGNETIC WAVES FROM THE SURFACE OF A SPATIALLY DISPERSIVE MEDIUM

We shall study the properties of a semi-infinite dielectric medium. Let the surface of the dielectric lie in the xy plane of the coordinate system. The dielectric will be assumed to occupy the upper half-space $z > 0$, and the half-space $z < 0$ is the vacuum found below the dielectric surface. The magnetic permeability will be taken to be unity in the medium, so that $\vec{B} = \vec{H}$ everywhere.

In this section and in Secs. IV and V we study either the interaction of external radiation with the dielectric, or the propagation of surface waves along the dielectric-vacuum interface. In both instances, we suppose the electromagnetic waves propagate with wave vector parallel to the xz plane. We shall look for solutions of Maxwell's equations in which the αth Cartesian component of the electric field has the form

$$E_\alpha(\vec{x}, t) = E_\alpha(z)\, e^{ik_{\parallel}x} e^{-i\Omega t}\,, \tag{3.1a}$$

while similar relations obtain for the displacement field $\vec{D}$ and the magnetic field $\vec{H}$,

$$D_\alpha(\vec{x}, t) = D_\alpha(z)\, e^{ik_{\parallel}x} e^{-i\Omega t}\,, \tag{3.1b}$$

$$H_\alpha(\vec{x}, t) = H_\alpha(z)\, e^{ik_{\parallel}x} e^{-i\Omega t}\,. \tag{3.1c}$$

If these forms are substituted into Maxwell's equations, we find (with $\vec{B} = \vec{H}$)

$$ik_{\parallel} D_x(z) + \frac{\partial D_z(z)}{\partial z} = 0\,, \tag{3.2a}$$

$$ik_{\parallel} H_x(z) + \frac{\partial H_x(z)}{\partial z} = 0 \tag{3.2b}$$

from the fact that $\nabla \cdot \vec{D} = \nabla \cdot \vec{H} = 0$, and the relations [suppressing explicit reference to the dependence of $E_\alpha(z)$ and $H_\alpha(z)$ on z]

$$-\frac{\partial E_y}{\partial z} = +i\frac{\Omega}{c} H_x\,, \tag{3.3a}$$

$$\frac{\partial E_x}{\partial z} - ik_{\parallel} E_z = +i\frac{\Omega}{c} H_y\,, \tag{3.3b}$$

$$k_{\parallel} E_y = \frac{\Omega}{c} H_z \tag{3.3c}$$

and

$$\frac{\partial H_y}{\partial z} = i\frac{\Omega}{c} D_x\,, \tag{3.4a}$$

$$\frac{\partial H_x}{\partial z} - ik_{\parallel} H_z = -i\frac{\Omega}{c} D_y\,, \tag{3.4b}$$

$$k_{\parallel} H_y = -\frac{\Omega}{c} D_z \tag{3.4c}$$

from the $\nabla \times \vec{E}$ and $\nabla \times \vec{H}$ equations, respectively.

To complete the set of equations, one needs a functional relationship between $\vec{D}$ and $\vec{E}$. The most general linear relationship between $\vec{D}(\vec{x}, t)$ and $\vec{E}(\vec{x}, t)$ consistent with the homogeneity of time is

$$D_\alpha(\vec{x}, t) = \sum_\beta \int d^3x' \int dt'\, \epsilon_{\alpha\beta}(\vec{x}, \vec{x}'; t - t')\, E_\beta(\vec{x}', t')\,. \tag{3.5a}$$

The integration on the right-hand side of this equation extends over all times t' [$\epsilon_{\alpha\beta}(\vec{x}, \vec{x}'; t - t')$ vanishes identically for $t' > t$], and in the spatial integration $\vec{x}'$ is restricted to the volume occupied by the dielectric material.

We have written the dielectric tensor in Eq. (3.5a) as a function of the spatial coordinates $\vec{x}$ and $\vec{x}'$ separately. This is a consequence of the fact that although the semi-infinite crystal retains infinitesimal translational invariance in directions parallel to its surface, it has lost it in the direction normal to the surface. Consequently, $\epsilon_{\alpha\beta}(\vec{x}, \vec{x}'; t - t')$ is a function of the coordinates x, x', y, y' through the differences $x - x'$ and $y - y'$, but it depends on z and z' separately.

However, in what follows we will make the sim-

plifying assumption that $\epsilon_{\alpha\beta}(\vec{x}, \vec{x}'; t-t')$ depends on z and z' through their difference, as is the case for an infinitely extended medium. The effects of a surface, therefore, enter our calculations only through the restriction of the range of integration over z' in Eq. (3.5a) to $z' > 0$. This assumption is equivalent to setting

$$\epsilon_{\alpha\beta}(\vec{x}, \vec{x}'; t-t') = \theta(z)\,\theta(z')\,\epsilon_{\alpha\beta}(\vec{x}-\vec{x}', t-t') , \quad (3.5b)$$

where $\theta(z)$ is the Heaviside unit step function. Our neglect of surface corrections to the dielectric constant itself is consistent with the assumption that the decay length of the excitations we consider here is long enough that these excitations are insensitive to variations in the dielectric constant on a scale small in comparison, an assumption which underlies the macroscopic theory of wave propagation in dielectrics.

For the moment, we assume $\vec{x}$ lies inside the dielectric. We may write

$$\epsilon_{\alpha\beta}(\vec{x}-\vec{x}', t-t') = \int \frac{d^3q\,d\Omega}{(2\pi)^4}\,\epsilon_{\alpha\beta}(\vec{q}, \Omega) \times e^{i\vec{q}\cdot(\vec{x}-\vec{x}')}\,e^{-i\Omega(t-t')} . \quad (3.6)$$

For the purpose of analyzing the planar geometry considered here, it will be convenient to introduce the partially transformed dielectric tensor, defined as follows:

$$\epsilon_{\alpha\beta}(\vec{q}_{\parallel}\Omega; z-z') = \int_{-\infty}^{+\infty} \frac{dq_z}{2\pi}\,\epsilon_{\alpha\beta}(\vec{q}, \Omega)\,e^{iq_z(z-z')} .$$

Now suppose the electric field has the space and time dependence exhibited in Eq. (3.1a). It is a short exercise to demonstrate that for $z > 0$,

$$D_\alpha(\vec{x}, t) = e^{i(k_{\parallel}x-\Omega t)} \sum_\beta \int_0^\infty dz'\,\epsilon_{\alpha\beta}(\hat{x}k_{\parallel}, \Omega; z-z')\,E_\beta(z') ,$$

or for the function $D_\alpha(z)$ defined in Eq. (3.1b),

$$D_\alpha(z) = \sum_\beta \int_0^\infty dz'\,\epsilon_{\alpha\beta}(\hat{x}k_{\parallel}, \Omega; z-z')\,E_\beta(z') . \quad (3.7a)$$

This relation applies for $z > 0$, where the point z is inside the medium.

To proceed with a specific calculation, one needs an explicit form for the wave vector and frequency-dependent dielectric tensor that enters Eq. (3.6). We shall suppose that the dielectric is a scalar even for finite $\vec{q}$ [i.e., $\epsilon_{\alpha\beta}(\vec{q}, \Omega) = \delta_{\alpha\beta}\epsilon(\vec{q}, \Omega)$], and furthermore we suppose that $\epsilon_{\alpha\beta}(\vec{q}, \omega)$ depends only on the magnitude of the wave vector $\vec{q}$. Then Eq. (3.7a) assumes the simple form for $z > 0$,

$$D_\alpha(z) = \int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega; z-z')\,E_\alpha(z') , \quad (3.7b)$$

while in the vacuum, for $z < 0$, of course, $D_\alpha(z) = E_\alpha(z)$.

For the function $\epsilon(q, \Omega)$ we take the model discussed in Sec. II, and we include in addition a phenomenological damping term in the resonance denominator. We use the model

$$\epsilon(q, \Omega) = \epsilon_0 + \frac{\Omega_p^2}{\Omega_T^2 + Dq^2 - \Omega^2 - i\Omega\gamma} . \quad (3.8)$$

When $D = 0$, the form in Eq. (3.8) reduces to the well-known phenomenological form employed frequently in the literature to analyze reflectivity and absorption data for frequencies in the vicinity of an electric-dipole-active exciton absorption line, or in the vicinity of an absorption peak in the infrared produced by an infrared-active TO phonon. In the present work we assume ϵ_0 to be real, although in the general results exhibited below one may insert a complex value for ϵ_0 directly.

The term proportional to Dq^2 in the denominator is responsible for the spatial-dispersion effects analyzed here. We assume $D > 0$, the sign expected if the q^2 term in the denominator arises from the wave-vector dependence of the exciton dispersion relation. Again, the general formulas exhibited below may be directly applied when $D < 0$, although some of the comments and interpretation offered in Sec. II and the following must be changed in detail if $D < 0$.

The great virtue of the model form for $\epsilon(q, \Omega)$ exhibited in Eq. (3.8) is that a simple closed analytic expression for the kernel in Eq. (3.7b) may be obtained. To see this, introduce the quantity

$$\Gamma(q_{\parallel}) = \left(\frac{\Omega^2 - \Omega_T^2 - Dq_{\parallel}^2 + i\Omega\gamma}{D}\right)^{1/2} , \quad (3.9)$$

where in Eq. (3.9) the square root with positive imaginary part is chosen. Then we can write

$$\epsilon(q, \Omega) = \epsilon_0 + \frac{\Omega_p^2}{D}\,\frac{1}{[q_z + \Gamma(q_{\parallel})][q_z - \Gamma(q_{\parallel})]} \quad (3.10)$$

and, after an elementary integration,

$$\epsilon(k_{\parallel}\Omega; z-z') = \epsilon_0\,\delta(z-z') + i\,\frac{\Omega_p^2}{2D\Gamma(k_{\parallel})} \times e^{i\Gamma(k_{\parallel})|z-z'|} . \quad (3.11)$$

When $\Gamma(k_{\parallel})$ is chosen to have a positive imaginary part, as remarked above, $\epsilon(k_{\parallel}\Omega; z-z')$ vanishes as $|z-z'| \to \infty$. The imaginary part of $\Gamma(k_{\parallel})$ thus controls the range of the nonlocal dielectric constant in our model. Equation (3.7b) now becomes

$$D_\alpha(z) = \epsilon_0 E_\alpha(z) + \frac{i\Omega_p^2}{2D\Gamma(k_{\parallel})} \int_0^\infty dz'\,e^{i\Gamma(k_{\parallel})|z-z'|}\,E_\alpha(z') . \quad (3.12)$$

This relation, along with the Maxwell's equations, contain the information required to discuss the reflectivity of the semi-infinite dielectric, and the effect of spatial dispersion on surface polaritons. In this section we first study the reflection

of plane-polarized radiation with electric vector perpendicular to the plane of incidence from the surface; then we turn to the case where $\vec{E}$ is parallel to the plane of incidence.

A. Reflection or Plane-Polarized Radiation from the Surface; Case where Electric Field is Perpendicular to Plane of Incidence

In the geometry described in this section, the xz plane is the plane of incidence. In this section we examine the nonlocal form of Maxwell's equations for solutions with the electric field directed in the y direction, perpendicular to the plane of incidence. Thus, with $E_x = E_z = 0$ and $H_y = 0$, Eqs. (3.2)–(3.4) reduce to

$$ik_{\parallel} H_x + \frac{\partial H_z}{\partial z} = 0 , \qquad \frac{\partial E_y}{\partial z} + i\frac{\Omega}{c} H_x = 0 ,$$

$$k_{\parallel} E_y = \frac{\Omega}{c} H_z , \qquad \frac{\partial H_x}{\partial z} - ik_{\parallel} H_z = -i\frac{\Omega}{c} D_y ,$$

where for $z > 0$,

$$D_y(z) = \epsilon_0 E_y(z) + \frac{i\Omega_p^2}{2D\Gamma(k_{\parallel})} \int_0^{\infty} dz' \, e^{i\Gamma(k_{\parallel})|z-z'|} E_y(z') ,$$

and for $z < 0$,

$$D_y(z) = E_y(z) .$$

These equations may be rearranged to yield an equation for E_y alone. One finds that for $z > 0$,

$$\left[\frac{\partial^2}{\partial z^2} + \left(\epsilon_0 \frac{\Omega^2}{c^2} - k_{\parallel}^2\right)\right] E_y(z) + i\frac{\Omega_p^2 \Omega^2}{2Dc^2\Gamma(k_{\parallel})} \int_0^{\infty} dz' \, e^{i\Gamma(k_{\parallel})|z-z'|} E_y(z') = 0 , \tag{3.13a}$$

while in the vacuum, for $z < 0$,

$$\left[\frac{\partial^2}{\partial z^2} + \left(\frac{\Omega^2}{c^2} - k_{\parallel}^2\right)\right] E_y(z) = 0 . \tag{3.13b}$$

Our task is to solve Eq. (3.13) subject to boundary conditions appropriate to the reflectivity problem. Since tangential components of $\vec{E}$ are conserved, $E_y(z)$ must be continuous at $z = 0$. Furthermore, as one can see from the relations above, if $\partial E_y/\partial z$ is continuous at $z = 0$, we ensure conservation of tangential components of $\vec{H}$. Thus, we solve the integro-differential equation subject to the boundary condition that E_y and $\partial E_y/\partial z$ are continuous.

First consider the case $z > 0$, and the nature of the solutions to Eq. (3.13a). We shall make repeated use of a simple identity employed earlier in a different physical context.[6] Note that

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2\right) e^{i\Gamma|z-z'|} = 2i\Gamma\,\delta(z - z') . \tag{3.14}$$

If the operator $\partial^2/\partial z^2 + \Gamma^2$ is applied to Eq. (3.13a), the integro-differential equation may be reduced to a fourth-order differential equation. One finds

$$\left(\frac{\partial^2}{\partial z^2} + \Gamma^2(k_{\parallel})\right)\left[\frac{\partial^2}{\partial z^2} + \left(\epsilon_0 \frac{\Omega^2}{c^2} - k_{\parallel}^2\right)\right] E_y(z) - \frac{\Omega_p^2 \Omega^2}{Dc^2} E_y(z) = 0 . \tag{3.15}$$

Equation (3.15) possesses plane-wave solutions with $E_y(z) = E_y e^{iqz}$. Upon inserting this form into Eq. (3.15), we find q is a solution of

$$[\Gamma^2(k_{\parallel}) - q^2]\left(\epsilon_0 \frac{\Omega^2}{c^2} - k_{\parallel}^2 - q^2\right) = \frac{\Omega^2}{c^2}\frac{\Omega_p^2}{D} . \tag{3.16a}$$

This result may be rearranged into a familiar form if the definition of $\Gamma(k_{\parallel})$ is recalled. One finds

$$\frac{c^2}{\Omega^2}(k_{\parallel}^2 + q^2) = \epsilon_0 + \frac{\Omega_p^2}{\Omega_T^2 - \Omega^2 + D(k_{\parallel}^2 + q^2) - i\Omega\gamma} . \tag{3.16b}$$

Consider first the case where damping is ignored, so $\gamma = 0$. Then Eq. (3.16) is simply a particular case of the polariton dispersion relation discussed in Sec. II. If we consider a polariton which propagates at an oblique angle relative to the surface, and if the projection of the polariton's wave vector on the xy plane has magnitude $k_{\parallel}$, then the value of q obtained from Eq. (3.16) is the z component of the polariton wave vector.

From Eq. (3.16a), it is apparent that there are four values of q which satisfy Eq. (3.16), since it is a quadratic equation in q^2. We denote the four roots by $\pm q_1$ and $\pm q_2$, respectively. It is a straightforward matter to show that when

$$\Omega^2 > \Omega_L^2(k_{\parallel}) = \Omega_T^2 + \frac{\Omega_p^2}{\epsilon_0} + Dk_{\parallel}^2 ,$$

both q_1 and q_2 are real. (We still consider the case $\gamma = 0$ for simplicity.)

For $\Omega > \Omega_L(k_{\parallel})$, there are two propagating polaritons in the material with wave-vector component $k_{\parallel}$ in the xy plane. At $k_{\parallel} = 0$, one can readily see this from Fig. 1(b) and the discussion in Sec. II. When $\Omega < \Omega_L(k_{\parallel})$, there are still two distinct roots q_1 and q_2 of Eq. (3.16). However, one root (say, q_2) is purely imaginary with $q_2^2 < 0$, while the second root q_1 is real. Thus, for $\Omega < \Omega_L(k_{\parallel})$, there is one propagating wave that emerges as a solution of Eq. (3.13a) [see Fig. 1(b) for $\Omega < \Omega_L$], and also a second, spatially damped, wave. From this discussion, it is clear that Maxwell's equations in the spatially dispersive medium yield two distinct solutions for *all* values of the frequency Ω, not only for $\Omega > \Omega_L(k_{\parallel})$. These two solutions must be superposed to obtain the solution to the reflectivity problem.

When γ is finite, of course, q_1 and q_2 have an imaginary part for all values of Ω, by virtue of the

dissipation present. In our discussion of the reflectivity, we select from the pairs $\pm q_1$ and $\pm q_2$ the two roots q_1 and q_2 with a positive imaginary part, since these two roots describe solutions of Eq. (3.13a) in which the amplitude of the electric field decays to zero as one penetrates into the crystal. The most general solution to Eq. (3.13a) has the form

$$E_y(z) = \mathcal{E}_1 e^{iq_1 z} + \mathcal{E}_2 e^{iq_2 z}, \quad z > 0 \tag{3.17a}$$

where again

$$\mathrm{Im}(q_1) > 0, \tag{3.17b}$$

$$\mathrm{Im}(q_2) > 0. \tag{3.17c}$$

We must match the expression for $E_y(z)$ to the electric field in the vacuum. If a wave of unit amplitude is incident on the crystal, then for $z < 0$,

$$E_y(z) = e^{ik_z z} + R e^{ik_z z}, \tag{3.18}$$

where R is the reflection coefficient. If θ is the angle between the wave vector of the incident wave and the normal to the crystal surface, then

$$k_z = (\Omega_0/c)\cos\theta$$

and, of course,

$$k_\parallel = (\Omega_0/c)\sin\theta .$$

We must make E_y and $\partial E_y/\partial z$ continuous at $z = 0$, as discussed earlier. At this point, we encounter the problem described in Sec. II. There are two boundary conditions, but three constants $\mathcal{E}_1$, $\mathcal{E}_2$, and R which need to be determined. The main point is that while the function in Eq. (3.17a) satisfies the fourth-order differential equation (3.15) for arbitrary values of $\mathcal{E}_1$ and $\mathcal{E}_2$, it satisfies the original integro-differential equation (3.13a) for only one unique value of the ratio $\mathcal{E}_1/\mathcal{E}_2$. To see this, one may substitute the form in Eq. (3.17a) back into Eq. (3.13a). After a straightforward calculation, one finds that for the form given in Eq. (3.17a),

$$\left[\frac{\partial^2}{\partial z^2} + \left(\epsilon_0 \frac{\Omega^2}{c^2} - k_\parallel^2\right)\right] E_y(z) + i \frac{\Omega_p^2 \Omega^2}{2Dc^2\Gamma(k_\parallel)} \int_0^\infty dz'\, e^{i\Gamma(k_\parallel)|z-z'|} E_y(z') = \frac{\Omega_p^2\Omega^2}{2Dc^2\Gamma(k_\parallel)} e^{i\Gamma(k_\parallel)z}\left(\frac{\mathcal{E}_1}{\Gamma(k_\parallel) - q_1} + \frac{\mathcal{E}_2}{\Gamma(k_\parallel) - q_2}\right). \tag{3.19}$$

Thus, the form in Eq. (3.17a) satisfies the nonlocal Maxwell's equations in the dielectric only if the quantity in large parentheses on the right-hand side of Eq. (3.19) vanishes identically:

$$\frac{\mathcal{E}_1}{\Gamma(k_\parallel) - q_1} + \frac{\mathcal{E}_2}{\Gamma(k_\parallel) - q_2} = 0 . \tag{3.20}$$

When this statement is combined with the earlier requirement that E_y and $\partial E_y/\partial z$ be continuous at the surface, we now have enough information to compute the reflection coefficient.

The statement in Eq. (3.20) is equivalent to an additional boundary condition imposed on the dipole-moment density at $z = 0$. To see this, we may rewrite Eq. (3.20) to read

$$\frac{(\Gamma + q_1)}{(\Gamma^2 - q_1^2)} \mathcal{E}_1 + \frac{(\Gamma + q_2)}{(\Gamma^2 - q_2^2)} \mathcal{E}_2 = 0 . \tag{3.21}$$

But now in terms of the quantity Γ,

$$\epsilon(q, \Omega) = \epsilon_0 + \frac{\Omega_p^2}{D[q^2 - \Gamma^2]} = \epsilon_0 + 4\pi\chi(q, \Omega),$$

where $\chi(q, \Omega)$ is the wave-vector- and frequency-dependent susceptibility which describes the contribution to the electric-dipole-moment density from the excitation responsible for the resonance in $\epsilon(q, \Omega)$. Equation (3.21) may then be written in the form

$$[q_1 + \Gamma(k_\parallel)]\,\chi(\vec{k}_\parallel q_1; \Omega)\mathcal{E}_1 + [q_2 + \Gamma(k_\parallel)]\,\chi(\vec{k}_\parallel q_2; \Omega)\mathcal{E}_2 = 0,$$

where the function $\chi(q, \Omega)$ evaluated for the wave vector $\vec{q} = \vec{k}_\parallel + \hat{z}q_1$ is denoted by $\chi(\vec{k}_\parallel q_1; \Omega)$, in this last statement. Now the quantity $\chi(\vec{k}_\parallel q_1; \Omega)\mathcal{E}_1$ is the amplitude P_1 of the dipole-moment density carried by the mode characterized by the wave vector $\vec{k}_\parallel + \hat{z}q_1$. Thus, Eq. (3.20) becomes

$$[q_1 + \Gamma(k_\parallel)]\,P_1 + [q_2 + \Gamma(k_\parallel)]\,P_2 = 0,$$

or if

$$P(z) = P_1 e^{iq_1 z} + P_2 e^{iq_2 z}$$

is the total dipole-moment density carried by the wave, Eq. (3.20) becomes

$$\left.\frac{\partial P}{\partial z}\right|_{z=0+} + i\Gamma(k_\parallel)\,P(0+) = 0 . \tag{3.22}$$

Thus, the additional boundary condition we obtain is equivalent to the constraint on the polarization field displayed in Eq. (3.22). Hopfield[7] has presented qualitative arguments that suggest, quite generally, that one expects the additional boundary condition to assume the form

$$A\,P(0+) + B\left.\frac{\partial P}{\partial z}\right|_{z=0+} = 0 . \tag{3.23}$$

The result in Eq. (3.22) is then a special case of this condition. We again point out that we have not required the use of a microscopic model to obtain Eq. (3.22), however. It follows directly from the nonlocal form of Maxwell's equations, for the semi-infinite dielectric with spatial dispersion. Incidentally, we shall see in Sec. III B that when the electric field vector is parallel to the plane of incidence, *two* additional boundary conditions emerge from the nonlocal Maxwell equations.

It is now a straightforward matter to find an explicit expression for the reflection coefficient by using the three boundary conditions introduced above. We find that

$$R=\frac{\Omega\cos\theta - c\,[q_1+q_2-\Gamma(k_{\parallel})]}{\Omega\cos\theta + c\,[q_1+q_2-\Gamma(k_{\parallel})]}\ . \tag{3.24}$$

Recall that q_1, q_2, and $\Gamma(k_{\parallel})$ are to be chosen to have positive imaginary parts.

B. Reflection of Plane-Polarized Radiation from the Surface; Case where Electric Field is Parallel to Plane of Incidence

We now seek solutions to the nonlocal Maxwell equations with E_x and E_z nonzero, but $E_y=0$. For this case Eqs. (3.2)–(3.4) become

$$\frac{\partial E_x}{\partial z} - ik_{\parallel}E_z = +i\frac{\Omega}{c}H_y\ , \tag{3.25a}$$

$$\frac{\partial H_y}{\partial z} = +i\frac{\Omega}{c}D_x\ , \tag{3.25b}$$

$$k_{\parallel}H_y = \frac{\Omega}{c}D_z\ , \tag{3.25c}$$

and

$$ik_{\parallel}D_x + \frac{\partial D_z}{\partial z} = 0\ , \tag{3.25d}$$

where again for $z>0$,

$$D_\alpha(z) = \epsilon_0 E_\alpha(z) + i\frac{\Omega_p^2}{2D\Gamma(k_{\parallel})}\int_0^\infty dz'\, e^{i\Gamma(k_{\parallel})|z-z'|}E_\alpha(z')\ . \tag{3.26}$$

We can find the form of the magnetic field $H_y(z)$ in the medium. To do this, first let z be replaced by z' in Eq. (3.25a). Then multiply the result by $\epsilon(k_{\parallel}\Omega\,;z-z')$ and integrate on z' from 0 to ∞. One finds

$$\int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega\,;z-z')\frac{\partial E_x(z')}{\partial z'} - ik_{\parallel}D_z(z) = +i\frac{\Omega}{c}\int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega\,;z-z')H_y(z')\ . \tag{3.27}$$

But now after a partial integration,

$$\int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega\,;z-z')\frac{\partial E_x(z')}{\partial z'} = -\epsilon(k_{\parallel}\Omega\,;z)E_x(0) - \int_0^\infty dz'\,E_x(z')\frac{\partial}{\partial z'}\epsilon(k_{\parallel}\Omega\,;z-z') = -\epsilon(k_{\parallel}\Omega\,;z)E_x(0) + \frac{\partial D_x}{\partial z}\ ,$$

where to arrive at the last statement, note that

$$\frac{\partial}{\partial z'}\epsilon(k_{\parallel}\Omega\,;z-z') = -\frac{\partial}{\partial z}\epsilon(k_{\parallel}\Omega\,;z-z')\ .$$

Thus, Eq. (3.27) becomes

$$\frac{\partial D_x(z)}{\partial z} - ik_{\parallel}D_z(z) - i\frac{\Omega}{c}\int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega\,;z-z')H_y(z') = \epsilon(k_{\parallel}\Omega\,;z)E_x(0)\ .$$

But now D_x and D_z on the left-hand side of this equation may be eliminated through the use of Eqs. (3.25b) and (3.25c). We then obtain an inhomogeneous integro-differential equation for $H_y(z)$. One has, for $z>0$,

$$\left(\frac{\partial^2}{\partial z^2}-k_{\parallel}^2\right)H_y(z) + \frac{\Omega^2}{c^2}\int_0^\infty dz'\,\epsilon(k_{\parallel}\Omega\,;z-z')H_y(z') = i\frac{\Omega}{c}\epsilon(k_{\parallel}\Omega\,;z)E_x(0)\ .$$

Upon noting the explicit form of $\epsilon(k_{\parallel}\Omega\,;z-z')$ given in Eq. (3.11), we have for $z>0$,

$$\left(\frac{\partial^2}{\partial z^2}+\epsilon_0\frac{\Omega^2}{c^2}-k_{\parallel}^2\right)H_y + i\frac{\Omega_p^2\Omega^2}{2Dc^2\Gamma(k_{\parallel})}\int_0^\infty dz'\,e^{i\Gamma(k_{\parallel})|z-z'|}H_y(z') = -\frac{\Omega_p^2\Omega}{2D\Gamma(k_{\parallel})c}\,e^{+i\Gamma(k_{\parallel})z}E_x(0)\ . \tag{3.28}$$

The integro-differential operator on the left-hand side of Eq. (3.28) is the same as the operator in (3.13a). We proceed to convert the integral equation to a differential equation for H_y by operating on both sides with $[\partial^2/\partial z^2+\Gamma^2(k_{\parallel})]$ and employing the identity in Eq. (3.14). This operation shows that $H_y(z)$ satisfies precisely the same differential equation [Eq. (3.15)] as the electric field $E_y(z)$ for the case where the electric field in the incident wave is normal to the plane of incidence. From this fact, for $z>0$, the magnetic field $H_y(z)$ in the material has the form

$$H_y(z) = h_1 e^{iq_1z} + h_2 e^{iq_2z}\ , \tag{3.29}$$

where q_1 and q_2 are found from Eq. (3.16b), again with $\mathrm{Im}(q_1)>0$ and $\mathrm{Im}(q_2)>0$.

We now proceed exactly as before. The expression in Eq. (3.29), while it satisfies the differential equation (3.15), does not satisfy the original integro-differential equation (3.27) for arbitrary values of h_1 and h_2. To satisfy Eq. (3.27) we find h_1 and h_2 must obey the constraint

$$\frac{\Omega}{c}\left(\frac{h_2}{q_1-\Gamma(k_{\parallel})}+\frac{h_2}{\Gamma(k_{\parallel})-q_2}\right)=E_x(0)\ . \tag{3.30}$$

This statement is one of the two additional boundary conditions required to determine the reflectivity in the present case.

We next turn to a study of the form of the electric field $\vec{E}$ and the displacement field $\vec{D}$ in the medium for this geometry. Upon eliminating $H_y(z)$ from Eq. (3.25a) by the use of Eq. (3.25c),

and noting Eq. (3.25d) we obtain two coupled homogeneous differential equations for E_x and E_z which take the form

$$ik_{\parallel}\frac{\partial E_x}{\partial z}+\left(k_{\parallel}^2-\epsilon_0\frac{\Omega^2}{c^2}\right)E_z - i\frac{\Omega_p^2\Omega^2}{2Dc^2\Gamma(k_{\parallel})}\int_0^{\infty}dz'\,e^{i\Gamma(k_{\parallel})|z-z'|}E_z(z')=0 \quad (3.31a)$$

and

$$ik_{\parallel}\epsilon_0 E_x-\frac{\Omega_p^2 k_{\parallel}}{2D\Gamma(k_{\parallel})}\int_0^{\infty}dz'\,e^{i\Gamma(k_{\parallel})|z-z'|}E_x(z') +\epsilon_0\frac{\partial E_z}{\partial z}+i\frac{\Omega_p^2}{2D\Gamma(k_{\parallel})}\frac{\partial}{\partial z}\int_0^{\infty}dz'\,e^{i\Gamma(k_{\parallel})|z-z'|}E_z(z')=0. \quad (3.31b)$$

Now, as before, we operate on both equations with the differential operator $[\Gamma^2(k_{\parallel})+\partial^2/\partial z^2]$ to obtain two coupled differential equations. One has

$$+ik_{\parallel}\left(\frac{\partial^2}{\partial z^2}+\Gamma^2(k_{\parallel})\right)E_x +\left[\left(k_{\parallel}^2-\epsilon_0\frac{\Omega^2}{c^2}\right)\left(\frac{\partial^2}{\partial z^2}+\Gamma^2(k_{\parallel})\right)+\frac{\Omega_p^2\Omega^2}{Dc^2}\right]E_z=0, \quad (3.32a)$$

$$\epsilon_0\left(\frac{\partial^2}{\partial z^2}+\Gamma^2-\frac{\Omega_p^2}{\epsilon_0 D}\right)\left(\frac{\partial E_z}{\partial z}+ik_{\parallel}E_x\right)=0. \quad (3.32b)$$

We seek solutions to Eqs. (3.31) of the form

$$E_{x,z}(z)=\mathcal{E}_{x,z}e^{iqz}.$$

Then after setting the determinant formed from the coefficients of $\mathcal{E}_x$ and $\mathcal{E}_z$ equal to zero, one can show that the values of q are determined from the condition

$$\epsilon(\vec{k}_{\parallel}q,\ \Omega)\left(\frac{c^2(k_{\parallel}^2+q^2)}{\Omega^2}-\epsilon(\vec{k}_{\parallel}q,\ \Omega)\right)=0, \quad (3.33a)$$

where $\epsilon(\vec{k}_{\parallel}q,\ \Omega)$ is the dielectric constant $\epsilon(\vec{q},\ \Omega)$ evaluated for $\vec{q}=\vec{k}_{\parallel}+\hat{z}q$.

For any frequency Ω, there are *three* values of q which satisfy Eq. (3.33a). Two values of q follow upon requiring that the factor in large parentheses vanish:

$$\frac{c^2q^2}{\Omega^2}=\epsilon(\vec{k}_{\parallel}q,\ \Omega)\equiv\epsilon_0+\frac{\Omega_p^2}{\Omega_T^2-\Omega^2+D(k_{\parallel}^2+q^2)-i\Omega\gamma}.$$

These two values of q are, of course, just the two quantities q_1 and q_2 that appear in the expression for the magnetic field, Eq. (3.29). The third value for the propagation constant is the solution of

$$\epsilon(\vec{k}_{\parallel}q,\ \Omega)=\epsilon_0+\frac{\Omega_p^2}{\Omega_T^2-\Omega^2+D(k_{\parallel}^2+q^2)-i\Omega\gamma}=0. \quad (3.33b)$$

We denote this third root by q_3. Again, we select only the one root of Eq. (3.33b) with $\mathrm{Im}(q_3)>0$. From the equations for the amplitudes $\mathcal{E}_x$ and $\mathcal{E}_z$, one readily sees that for the wave characterized by the attenuation constant q_3, $\nabla\cdot\vec{E}\neq0$, while the two roots characterized by q_1 and q_2 have $\nabla\cdot\vec{E}=0$ always. If we neglect dissipation in the medium (set the damping constant $\gamma=0$), then for $\Omega>\Omega_L(k_{\parallel})$ all three attenuation constants q_1, q_2, and q_3 are real. Then the roots q_1 and q_2 are associated with the transverse polaritons of Fig. 1(b), while the mode q_3 is a longitudinal wave with $\vec{E}$ parallel to the wave vector $k_{\parallel}\hat{x}+q_3\hat{z}$, and $\nabla\cdot\vec{E}\neq0$ (of course, $\nabla\cdot\vec{D}\equiv0$ always). When $\Omega<\Omega_L(k_{\parallel})$, q_3 becomes pure imaginary, as does one of the pair q_1 and q_2. When $\Omega<\Omega_L(k_{\parallel})$, $\nabla\cdot\vec{E}=0$ for the modes q_1 and q_2, but $\nabla\cdot\vec{E}$ is still nonvanishing for the mode q_3. For all values of Ω, the mode q_3 has zero magnetic field associated with it, while as we have seen explicitly, q_1 and q_2 have nonzero magnetic fields.

The relative amplitudes of the various field components in the medium are interrelated by the Maxwell equations (3.25), the differential equations (3.31), and by Eq. (3.26). If we write

$$E_x=\mathcal{E}_x^{(1)}e^{iq_1z}+\mathcal{E}_x^{(2)}e^{iq_2z}+\mathcal{E}_x^{(3)}e^{iq_3z}, \quad (3.34a)$$

then from these relations we find

$$E_z=-\sum_{i=1,2}\frac{k_{\parallel}}{q_i}\mathcal{E}_x^{(i)}e^{iq_iz}+\frac{q_3}{k_{\parallel}}\mathcal{E}_x^{(3)}e^{iq_3z}, \quad (3.34b)$$

$$H_y=+\frac{\Omega}{c}\sum_{i=1,2}\frac{\epsilon_i}{q_i}\mathcal{E}_x^{(i)}e^{iq_iz}, \quad (3.34c)$$

$$D_x=\sum_{i=1,2}\epsilon_i\mathcal{E}_x^{(i)}e^{iq_iz}, \quad (3.34d)$$

and

$$D_z=-\sum_{i=1,2}\frac{\epsilon_i k_{\parallel}}{q_i}\mathcal{E}_x^{(i)}e^{iq_iz}. \quad (3.34e)$$

In these expressions, the quantity ϵ_i is an abbreviated notation for the quantity $\epsilon(\vec{k}_{\parallel}q_i,\ \Omega)$ of Eqs. (3.33). For the mode q_3, the displacement field vanishes identically.

We now find the additional constraints imposed on the solutions by the requirements that the original integro-differential be satisfied. If we write

$$E_x(z)=\sum_i\mathcal{E}_x^{(i)}e^{iq_iz}$$

and

$$E_z(z)=\sum_i\mathcal{E}_z^{(i)}e^{iq_iz},$$

where the coefficients $\mathcal{E}_z^{(i)}$ are displayed in terms of $\mathcal{E}_x^{(i)}$ in Eq. (3.34b), then when we require Eqs. (3.31a) and (3.31b) be satisfied, two additional boundary conditions are obtained:

$$\sum_{i=1}^{3}\frac{\mathcal{E}_x^{(i)}}{\Gamma(k_{\parallel})-q_i}=0 \quad (3.35a)$$

and

$$\sum_{i=1}^{3}\frac{\mathcal{E}_z^{(i)}}{\Gamma(k_{\parallel})-q_i}=0. \quad (3.35b)$$

We now have three additional boundary conditions, when we include Eq. (3.29) with Eqs. (3.35). However, it is a straightforward matter to express h_1 and h_2 in terms of $\mathcal{E}_x^{(1)}$ and $\mathcal{E}_x^{(2)}$ via Eq. (3.34c), then insert these quantities into Eq. (3.30), and demonstrate that Eq. (3.30) is the same as Eq. (3.35a). Thus, we employ the two conditions, Eqs. (3.35), in the remainder of this section.

If we multiply the numerator and denominator of each term in Eqs. (3.35) by $[\Gamma(k_\parallel)+q_i]$, and note the relationship between the electric-dipole-moment density and the electric field given in the discussion which precedes Eq. (3.22), then Eqs. (3.35) become

$$\left.\frac{\partial P_{x,z}}{\partial z}\right|_{z=0+} + i\Gamma(k_\parallel)P_{x,z}\Big|_{0+} = 0 ,$$

where P_α is the αth Cartesian component of the dipole-moment density.

There is now only one independent constant, say, $\mathcal{E}_x^{(1)}$, in terms of which the relative amplitudes of all the waves of the medium may be expressed, once Eqs. (3.35a) and (3.35b) are used. Then, by matching the internal fields to the vacuum fields through the use of two of the usual boundary conditions (conservation of tangential $\vec{E}$ and tangential $\vec{H}$, for example), one may compute the reflection coefficient. We find for the amplitude of the reflected wave the expression

$$R = \frac{\cos\theta - Q}{\cos\theta + Q} , \tag{3.36a}$$

where

$$Q = \Gamma(k_\parallel) - \frac{k_\parallel^4 + k_\parallel^2(q_1^2 + q_1q_2 + q_2^2) + (q_1+q_2)q_1q_2q_3}{k_\parallel^2(q_1+q_2-q_3) + q_1q_2q_3} . \tag{3.36b}$$

We have carried out a series of numerical calculations of the effect of spatial dispersion on the reflectivity, for parameters characteristic of cubic ZnSe at low temperatures. The results of these calculations are described in Sec. VI.

IV. THEORY OF SURFACE POLARITONS IN THE PRESENCE OF SPATIAL DISPERSION

In this section, we obtain the dispersion relation for surface polaritons on the surface of the model nonlocal dielectric studied in Sec. III.

In the absence of spatial dispersion (the parameter $D=0$ in the model used here) and in the absence of dissipation in the medium ($\gamma=0$), Maxwell's equations admit solutions which have the character of surface waves. The electric and magnetic fields associated with the wave, as well as the electric-dipole-moment density in the medium, are localized near the surface when the surface wave is excited. The dispersion relation for the surface waves which propagate along the interface between an isotropic local dielectric and the vacuum is given in Eq. (2.7). Some properties of the surface waves were also summarized in Sec. II. The surface wave exists only for values of the wave vector $k_\parallel$ (which is parallel to the surface) which satisfy $ck_\parallel > \Omega_s(k_\parallel)$, since it is only in this limit that the electromagnetic field in the vacuum region remains localized near the surface. Furthermore, the surface waves exist only in the stop band between Ω_T and Ω_L, where no bulk polaritons exist and where the dielectric constant is negative. The electric field associated with the wave lies in the plane formed by the wave vector of the wave and the normal to the surface of the dielectric. If, as in Sec. III, the surface lies in the xy plane, and if the surface polariton propagates in the x direction, then E_x and E_z are nonzero, while $E_y=0$ identically. The magnetic field is in the y direction.

In this section we explore the effect of spatial dispersion on the properties of surface polaritons, within the framework of the model employed in Sec. III. The principal results of this investigation were discussed in Sec. II from a qualitative point of view.

We suppose that the surface polariton propagates along the surface, parallel to the x axis. The αth Cartesian component of the electric field then has the form

$$E_\alpha(\vec{x}, t) = E_\alpha(z)e^{ik_\parallel x}e^{-i\Omega_s t} , \tag{4.1}$$

with a similar variation for $\vec{H}$ and for $\vec{D}$. In this instance, Maxwell's equations (3.2)–(3.4) may be used to describe the variation of the fields in the z direction. In the vacuum region ($z<0$), $\vec{E}=\vec{D}$, while in the crystal ($z>0$) the relation between $\vec{E}$ and $\vec{D}$ is given in Eq. (3.12), for the model.

We consider waves with a field configuration similar to that present in the absence of spatial dispersion; i.e., we look for solutions of Maxwell's equations with $E_y=0$. Consider first the electromagnetic field in the vacuum region $z<0$. Since the wave is bound to the surface, we seek solutions with

$$E_x(z) = \mathcal{E}_x^< e^{\alpha_0 z} , \quad E_z(z) = \mathcal{E}_z^< e^{\alpha_0 z} ,$$

where α_0 is assumed real and positive. Upon noting that $\vec{D}=\vec{E}$ for $z<0$, then using Eq. (3.2a), one finds

$$\mathcal{E}_z^< = -i\frac{k_\parallel}{\alpha_0}\mathcal{E}_x^< .$$

Then from Eqs. (3.3a) and (3.4c) one finds a relation between α_0, the wave vector $k_\parallel$, and the frequency Ω_s of the surface wave:

$$\alpha_0^2 = k_\parallel^2 - \Omega_s^2/c^2 . \tag{4.2}$$

The attenuation constant α_0 is real only if $ck_\parallel > \Omega_s$.

It is only in this region of frequencies and wave vectors that Maxwell's equations admit solutions for which the electromagnetic fields in the vacuum decay to zero as one moves away from the crystal. The electric field in the vacuum outside the crystal thus has the form for $z < 0$,

$$\vec{E}(z) = \mathcal{E}^{<}[\hat{x} - i(k_{\parallel}/\alpha_0)\hat{z}]\, e^{\alpha_0 z}\,, \tag{4.3}$$

with α_0 given by Eq. (4.2).

We now match the vacuum field in Eq. (4.3) to the fields in the crystal. This will lead to a dispersion relation from which the frequency Ω_s of the surface polariton may be computed, given the wave vector $k_{\parallel}$.

Within the crystal, we search for solutions with

$$E_x(z) = \mathcal{E}_x^{>} e^{-\alpha z}\,, \quad E_z(z) = \mathcal{E}_z^{>} e^{-\alpha z}\,, \tag{4.4}$$

and $\mathrm{Re}(\alpha) > 0$.

The nature of the solutions for the field within the crystal may be studied by precisely the mathematical methods we employed in Sec. III. Indeed, the two coupled differential equations (3.32a) and (3.32b) were derived quite generally for the model, with no assumption about the nature of the z dependence of the electric field in the medium. Thus, we can substitute the fields in Eq. (4.4) into Eqs. (3.32) to obtain the values of α allowed for a given value of $k_{\parallel}$ and Ω_s, and the relation between the amplitudes $\mathcal{E}_x^{>}$ and $\mathcal{E}_z^{>}$ for a given value of α. Indeed, the algebra in the present case is identical to that in Sec. III B, provided we replace q by $i\alpha$. The allowed values of α associated with a given $k_{\parallel}$ and Ω_s are thus determined from the condition

$$\epsilon(\vec{k}_{\parallel} i\alpha, \Omega_s)\left(\frac{c^2(k_{\parallel}^2 - \alpha^2)}{\Omega_s^2} - \epsilon(\vec{k}_{\parallel} i\alpha, \Omega_s)\right) \equiv 0\,, \tag{4.5}$$

where

$$\epsilon(\vec{k}_{\parallel} i\alpha, \Omega_s) = \epsilon_0 + \frac{\Omega_p^2}{\Omega_T^2 - \Omega_s^2 + D(k_{\parallel}^2 - \alpha^2) - i\Omega\gamma}\,.$$

For a given value of Ω_s and $k_{\parallel}$, there are three solutions to Eq. (4.5) with $\mathrm{Re}(\alpha) > 0$. It will be necessary to construct an expression for the electromagnetic field in the crystal that is a linear combination of all three solutions, to satisfy the constraints imposed by the nonlocal Maxwell equations and to match the vacuum fields at the surface.

Although the discussion in this section will be phrased in general terms, the limit $\gamma \to 0$ where the dielectric is lossless is of particular interest, since we can easily compare the qualitative properties of the surface polaritons with and without spatial dispersion in this case. Furthermore, since the surface polaritons exist in the region of frequencies $\Omega_T < \Omega_s < \Omega_L$ in the absence of spatial dispersion, we will be primarily interested in the frequency region for which $\Omega_T(k_{\parallel}) < \Omega_s < \Omega_L(k_{\parallel})$, where $\Omega_T^2(k_{\parallel}) = \Omega_T^2 + Dk_{\parallel}^2$ and $\Omega_L^2(k_{\parallel}) = \Omega_T^2(k_{\parallel}) + \Omega_p^2/\epsilon_0$. Consider the nature of the roots to Eq. (4.5) in this frequency region, with attention to the case $\gamma \to 0$.

The dielectric function $\epsilon(\vec{k}_{\parallel} i\alpha, \Omega_s)$ vanishes when $\alpha = \alpha_3$, where

$$\alpha_3 = +D^{-1/2}\left[\Omega_L^2(k_{\parallel}) - \Omega_s^2 - i\Omega_s\gamma\right]^{1/2}\,. \tag{4.6}$$

As $\gamma \to 0$, when $\Omega_s < \Omega_L(k_{\parallel})$, α_3 is real and positive. The fields associated with this wave decay to zero exponentially, as one proceeds into the interior of the crystal from the surface. For this wave, if $\mathcal{E}_x^{(3)>}$ and $\mathcal{E}_z^{(3)>}$ are the z and x components of the electric field in the wave, from Eqs. (3.31) one finds

$$\mathcal{E}_z^{(3)>} = i(\alpha_3/k_{\parallel})\mathcal{E}_x^{(3)>}\,.$$

Next consider the roots of the quantity in large parentheses in Eq. (4.5). We call the two roots α_2 and α_1. It is straightforward to obtain simple analytic expressions for these two roots from Eq. (4.5), since to find the two roots one needs to find the roots of a quadratic equation in the quantity α^2. The general expression is quite cumbersome and not very illuminating, however. In the limit $\gamma \to 0$; the properties of the two roots are readily displayed by graphical means. If the quantity in large parentheses in Eq. (4.5) is set equal to zero, the expression may be rearranged to read (for $\gamma = 0$)

$$\frac{c^2}{\epsilon_0 D\Omega_s^2}(D\alpha^2 - Dk_{\parallel}^2) = \frac{\Omega_L^2(k_{\parallel}) - \Omega_s^2 - D\alpha^2}{D\alpha^2 + \Omega_s^2 - \Omega_T^2(k_{\parallel})}\,. \tag{4.7}$$

For the case $\Omega_T(k_{\parallel}) < \Omega_s < \Omega_L(k_{\parallel})$ of interest here, the right- and left-hand sides of Eq. (4.7) are sketched in Fig. 2, and the position of the two

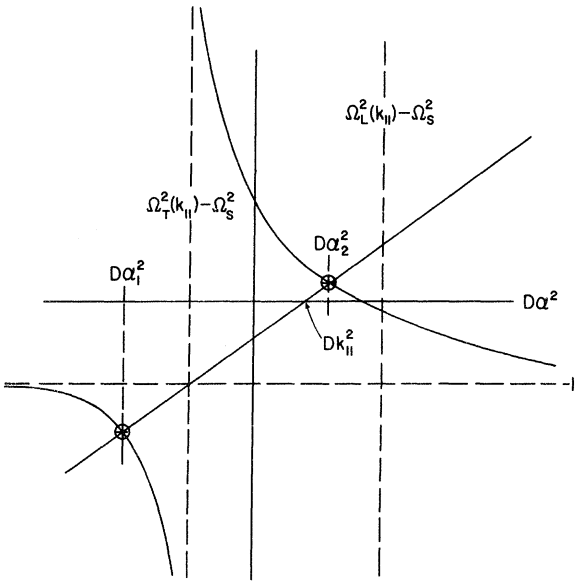

FIG. 2. Plot of the left- and right-hand side of Eq. (4.7). The solid straight line is the left-hand side. The position of the two roots is indicated by the circles.

roots are indicated and labeled. There is one root α_2 for which α_2^2 is positive and α_2 is real. However, as one can see from the graph, for the second root α_1, the quantity α_1^2 is negative. Thus, for $\gamma = 0$, one root with α pure imaginary exists.

The first real root α_2 describes a wave for which the field decays to zero exponentially as one penetrates into the medium. For the second root α_1, since $\alpha_1^2 < 0$ and α_1 is purely imaginary, the field oscillates and does not damp out with z. In fact, if one remembers that the quantity $i\alpha$ is the propagation constant q of Sec. III, then one sees that the undamped wave is the bulk polariton associated with the lower branch of Fig. 1(b), with frequency Ω_s below the onset $\Omega_L(k_\parallel)$ of the upper branch.

In general, to construct a wave which satisfies the nonlocal form of Maxwell's equations, and to match the fields in the medium to the attenuated field in the vacuum, all three waves α_1, α_2, and α_3 will need to be superposed, as we shall see. Thus, in the presence of spatial dispersion, no gap in the frequency spectrum of the dielectric exists between Ω_L and Ω_T, and the boundary conditions admix the purely attenuated surface wave with the bulk polariton. The resulting state is not a true surface polariton, but rather is a virtual surface state.

When $\gamma \neq 0$, α_1, α_2, and α_3 all become complex. In particular, α_2 acquires a real part that vanishes as $\gamma \to 0$. Since the waves must damp out in space and not increase exponentially, one must select only the α's that satisfy Eq. (4.7) and for which $\mathrm{Re}(\alpha) > 0$ always. Since Eq. (4.7) involves only α^2, for each α^2 that satisfies Eq. (4.7), there is one value of $(\alpha^2)^{1/2}$ with positive real part, and one with negative real part. Thus, for finite γ, there are three and only three solutions of Eq. (4.7) with $\mathrm{Re}(\alpha) > 0$.

If we denote the x and z components of the electric field for the modes α_1 and α_2 in the medium by $\mathcal{E}_x^{(i)>}$, $\mathcal{E}_z^{(i)>}$, where $i = 1$ or 2, then one easily finds that

$$\mathcal{E}_z^{(i)>} = i(k_\parallel/\alpha_i)\mathcal{E}_x^{(i)>}, \quad i = 1, 2 . \tag{4.8}$$

From the discussion given above, we see that the most general solution to the differential equations (3.32) in the medium $z > 0$ assumes the form (with a small change in notation)

$$E_x(z) = \sum_{i=1,2} \mathcal{E}_{(i)}^{>} e^{-\alpha_i z} + \mathcal{E}_{(3)}^{>} e^{-\alpha_3 z} \tag{4.8'}$$

and

$$E_z(z) = \sum_{i=1,2} i\frac{k_\parallel}{\alpha_i}\mathcal{E}_{(i)}^{>} e^{-\alpha_i z} + i\frac{\alpha_3}{k_\parallel}\mathcal{E}_{(3)}^{>} e^{-\alpha_3 z} . \tag{4.8''}$$

While these forms satisfy the differential equations (3.32), they will satisfy the original set of coupled integro-differential equations [Eqs. (3.32)] from which these differential equations are derived only for certain particular values of the admixture coefficients $\mathcal{E}_{(i)}^{>}$, as explained in detail in Sec. III. In the present case, the constraint equations analogous to Eqs. (3.35) assume the forms

$$\frac{\mathcal{E}_{(1)}^{>}}{\Gamma(k_\parallel) - i\alpha_1} + \frac{\mathcal{E}_{(2)}^{>}}{\Gamma(k_\parallel) - i\alpha_2} + \frac{\mathcal{E}_{(3)}^{>}}{\Gamma(k_\parallel) - i\alpha_3} = 0 \tag{4.9a}$$

and

$$\frac{k_\parallel}{\alpha_1}\frac{\mathcal{E}_{(1)}^{>}}{\Gamma(k_\parallel) - i\alpha_1} + \frac{k_\parallel}{\alpha_2}\frac{\mathcal{E}_{(2)}^{>}}{\Gamma(k_\parallel) - i\alpha_2} + \frac{\alpha_3}{k_\parallel}\frac{\mathcal{E}_{(3)}^{>}}{\Gamma(k_\parallel) - i\alpha_3} = 0 . \tag{4.9b}$$

The constraints in Eq. (4.9) allow the internal field to be determined to within one multiplicative constant. We must now match the internal field to the vacuum field in Eq. (4.3). Conservation of tangential components of $\vec{E}$ at the boundary gives the relation

$$\mathcal{E}_{(1)}^{>} + \mathcal{E}_{(2)}^{>} + \mathcal{E}_{(3)}^{>} - \mathcal{E}^{<} = 0 . \tag{4.10}$$

As a second boundary condition, we require that the normal component of $\vec{D}$ be conserved. The form of D_z is given in the dielectric by Eq. (3.34e). This expression can be adapted to the present circumstance by recalling that $q_i = i\alpha_i$. Then conservation of normal components of D leads to the condition

$$\frac{\epsilon_1 k_\parallel}{\alpha_1}\mathcal{E}_{(1)}^{>} + \frac{\epsilon_2 k_\parallel}{\alpha_2}\mathcal{E}_{(2)}^{>} + \frac{k_\parallel}{\alpha_0}\mathcal{E}^{<} = 0 , \tag{4.11}$$

where as before $\epsilon_1 = \epsilon(\vec{k}_\parallel, i\alpha_i; \Omega_s)$.

We now have four homogeneous equations in the four amplitudes $\mathcal{E}^{<}$, $\mathcal{E}_{(1)}^{>}$, $\mathcal{E}_{(2)}^{>}$, and $\mathcal{E}_{(3)}^{>}$ [Eqs. (4.9)–(4.11)]. For a given value of $k_\parallel$, the equations admit a solution only if the coefficient determinant vanishes. We find the surface-polariton dispersion relation from this condition.

After some manipulation, the following implicit equation may be obtained for Ω_s as a function of $k_\parallel$:

$$\begin{aligned}&\alpha_1(i\Gamma + \alpha_1)(k_\parallel^2 - \alpha_3\alpha_2) - \alpha_2(i\Gamma + \alpha_2)(k_\parallel^2 - \alpha_3\alpha_1)\\ &\quad + k_\parallel^2(i\Gamma + \alpha_3)(\alpha_2 - \alpha_1) + \alpha_0[\epsilon_1(i\Gamma + \alpha_1)(k_\parallel^2 - \alpha_3\alpha_2)\\ &\quad - \epsilon_2(i\Gamma + \alpha_2)(k_\parallel^2 - \alpha_3\alpha_1)] \equiv D(k_\parallel, \Omega_s) = 0 .\end{aligned} \tag{4.12}$$

Unfortunately, Eq. (4.12) is cumbersome and unwieldy. It does have one important qualitative feature that results from the admixture of the bulk polariton into the surface wave. For real values of the wave vector $k_\parallel$, the frequency Ω_s that emerges as the solution to Eq. (4.12) has an imaginary part. The presence of the imaginary part means that the amplitude of a plane wave of wave vector $k_\parallel$ set up at time zero decays away to zero in a lifetime τ given by $\tau^{-1} = \mathrm{Im}[\Omega_s(k_\parallel)]$. Crudely speaking, the amplitude of the wave decays in time because the energy stored near the

surface leaks into the crystalline interior via the coupling to the bulk polariton which results when $D \neq 0$.

To see this effect, we explore a special limit of Eq. (4.12). We consider values of $k_\parallel$ such that $ck_\parallel \gg \Omega_s$. Then retardation effects can be ignored. Formally, we may take the limit $c \to \infty$ in Eq. (4.12) if we wish to obtain the form of Eq. (4.12) in the quasistatic region where retardation effects are unimportant. The root α_3 is given in Eq. (4.6), and this root is unaffected by the presence of retardation. The behavior of α_1 and α_2 is readily deduced from Fig. 2. As $c \to \infty$, the slope of the straight line in Fig. 2 [a plot of the left-hand side of Eq. (4.7)] approaches infinity. Then one sees that

$$\lim_{c\to\infty} \alpha_2 = k_\parallel \ , \tag{4.13a}$$

$$\lim_{c\to\infty} \alpha_1 = i\,\frac{[\Omega_s^2 - \Omega_T(k_\parallel)]^{1/2}}{D^{1/2}} = -i\Gamma(k_\parallel) \ , \tag{4.13b}$$

and

$$\lim_{c\to\infty} \alpha_0 = k_\parallel \ . \tag{4.13c}$$

We have also specialized to the case $\gamma = 0$, and the last relation holds only then. In order to recover the dispersion relation in the absence of retardation from Eq. (4.12), the limit $c \to \infty$ must be taken quite carefully. In fact, it is more straightforward to take the limit $c \to \infty$ directly from the boundary conditions. We begin by eliminating $\mathcal{E}^{>}_{(1)}$ from Eq. (4.9a) to obtain a relation between $\mathcal{E}^{>}_{(2)}$ and $\mathcal{E}^{>}_{(3)}$:

$$\frac{1 - \alpha_1/\alpha_2}{\Gamma - i\alpha_2}\,\mathcal{E}^{>}_{(2)} + \frac{1 - \alpha_1\alpha_3/k_\parallel^2}{\Gamma - i\alpha_3}\,\mathcal{E}^{>}_{(3)} = 0 \ .$$

Upon employing the limiting forms in Eqs. (4.13), one obtains

$$\frac{k_\parallel \mathcal{E}^{>}_{(2)}}{k_\parallel^2 + i\Gamma\alpha_3} + \frac{\mathcal{E}^{>}_{(3)}}{\alpha_3 + \Gamma} = 0 \ . \tag{4.14a}$$

Now from Eq. (4.9a), one has

$$\mathcal{E}^{>}_{(1)} = -\left(\frac{\Gamma - i\alpha_1}{\Gamma - i\alpha_2}\right)\mathcal{E}^{>}_{(2)} - \left(\frac{\Gamma - i\alpha_1}{\Gamma - i\alpha_3}\right)\mathcal{E}^{>}_{(3)} \ . \tag{4.14b}$$

When $c \to \infty$ and $\alpha_1 \to -i\Gamma$, this equation shows that

$$\lim_{c\to\infty} \mathcal{E}^{>}_{(1)} = 0 \ .$$

Equation (4.10) then reads

$$\mathcal{E}^{>}_2 + \mathcal{E}^{>}_3 - \mathcal{E}^{<} = 0 \ . \tag{4.15}$$

Equation (4.11) must be handled with care, since as $c \to \infty$, $\mathcal{E}^{>}_1 \to 0$ but at the same time $\epsilon_1 \to \infty$. Note that

$$\epsilon_1 = \epsilon(k_\parallel\, i\alpha_1, \Omega_3) = \epsilon_0 + \frac{\Omega_p^2}{D}\,\frac{1}{(\Gamma - i\alpha)(\Gamma + i\alpha)}$$

$$\to \frac{\Omega_p^2}{2D\Gamma}\,\frac{1}{\Gamma - i\alpha} \qquad \text{as } \alpha \to -i\Gamma \ .$$

Thus Eq. (4.11) becomes, as $c \to \infty$,

$$i\left(\frac{k_\parallel}{\Gamma}\right)\frac{\Omega_p^2}{2D\Gamma}\,\frac{\mathcal{E}^{>}_{(1)}}{\Gamma - i\alpha_1} + \epsilon_0(\Omega_s)\mathcal{E}^{>}_2 + \mathcal{E}^{<} = 0 \ , \tag{4.16}$$

where as $\alpha_2 \to k_\parallel$, the quantity $\epsilon_2 = \epsilon(\tilde{k}_\parallel i\alpha_2, \Omega_s)$ approaches the local dielectric constant $\epsilon_0(\Omega_s)$ given in Eq. (2.1). Now, the quantity $\mathcal{E}^{>}_{(1)}/(\Gamma - i\alpha_1)$ may be expressed entirely in terms of $\mathcal{E}^{>}_{(2)}$ through the use of Eqs. (4.14). This allows us to write Eq. (4.16) in the form

$$\mathcal{E}^{>}_{(2)}\left(\epsilon_0(\omega) + i\,\frac{\Omega_p^2}{2D\Gamma}\,\frac{k_\parallel(k_\parallel - \alpha_3)}{(k_\parallel + i\Gamma)(k_\parallel^2 + i\Gamma\alpha_3)}\right) + \mathcal{E}^{<} = 0 \ . \tag{4.17}$$

With Eqs. (4.14a), (4.15), and (4.17), we may obtain the surface-polariton dispersion relation. If Eq. (4.14a) is used to eliminate $\mathcal{E}^{>}_{(3)}$ from Eq. (4.15), a second relation between $\mathcal{E}^{>}_{(2)}$ and $\mathcal{E}^{<}$ is obtained:

$$\frac{(k_\parallel - i\Gamma)(k_\parallel - \alpha_3)}{(k_\parallel^2 + i\Gamma\alpha_3)}\,\mathcal{E}^{>}_{(2)} - \mathcal{E}^{<} = 0 \ . \tag{4.18}$$

Now upon combining Eqs. (4.17) and (4.18), one finds after a bit of manipulation that

$$\epsilon_0(\Omega_s) + 1 = \frac{k_\parallel}{i\alpha_3\Gamma + k_\parallel^2}\left[i\Gamma + \alpha_3 + i\,\frac{\Omega_p^2}{2D\Gamma}\left(\frac{\alpha_3 - k_\parallel}{k_\parallel i\Gamma}\right)\right] . \tag{4.19}$$

Consider the behavior of the various quantities in Eq. (4.19) as $k_\parallel \to 0$. In this limit, both Γ and α_3 remain finite, with

$$\lim_{k_\parallel\to 0} \Gamma = \left(\frac{\Omega_s^2 - \Omega_T^2}{D}\right)^{1/2} \tag{4.20a}$$

and

$$\lim_{k_\parallel\to 0} \alpha_3 = \left(\frac{\Omega_L^2 - \Omega_s^2}{D}\right)^{1/2} . \tag{4.20b}$$

Thus, the right-hand side of Eq. (4.19) vanishes linearly with $k_\parallel$ as $k_\parallel \to 0$. Then as $k_\parallel \to 0$, in the absence of retardation, the surface-polariton frequency is obtained as the solution of

$$\epsilon(\Omega_s) + 1 = 0 \ . \tag{4.21}$$

The well-known result displayed in Eq. (4.21) also follows at once from Eq. (2.7), upon taking the limit $c \to \infty$.

From Eq. (4.19), we can readily find the form of the surface-polariton dispersion relation as $k_\parallel \to 0$. As $Dk_\parallel^2 \to 0$, all quantities on the right-hand side may be replaced by their limiting forms at $k_\parallel = 0$, and Ω_s may be replaced by the value obtained from Eq. (4.21). This gives, as $k_\parallel \to 0$,

$$\epsilon(\Omega_s(k_\parallel)) + 1 = \frac{k_\parallel}{i\Gamma\alpha_3}\left[\alpha_3\left(1 + \frac{\Omega_p^2}{2D\Gamma^2}\right) + i\Gamma\right] , \tag{4.22a}$$

where Γ and α_3 are given by Eqs. (4.20). After some straightforward manipulation, we find that Eq. (4.21) may be written

$$\epsilon(\Omega_s(k_\parallel))+1=\frac{D^{1/2}k_\parallel}{\Omega_p}(1+\epsilon_0)^{1/2}\left[\epsilon_0^{1/2}-i\left(\frac{\epsilon_0+3}{2}\right)\right]. \tag{4.22b}$$

We now write

$$\Omega_s(k_\parallel)=\Omega_s(0)+\Delta\Omega(k_\parallel),$$

where $\Omega_s(0)$ is the frequency which satisfies Eq. (4.21). Then to first order in $k_\parallel$,

$$\Delta\Omega_s(k_\parallel)=\frac{D^{1/2}k_\parallel(1+\epsilon_0)^{1/2}}{\Omega_p(d\epsilon/d\Omega)|_{\Omega_s}}\left[\epsilon_0^{1/2}-i\left(\frac{\epsilon_0+3}{2}\right)\right].$$

After a bit of manipulation, this result may be written in the form

$$\Delta\Omega_s(k_\parallel)=D^{1/2}k_\parallel\left(\frac{(\epsilon_s-\epsilon_0)^{1/2}}{2(1+\epsilon_0)^{3/2}}\,\frac{\Omega_T(0)}{\Omega_s(0)}\right)\times\left[\epsilon_0^{1/2}-i\left(\frac{\epsilon_0+3}{2}\right)\right]. \tag{4.23}$$

In this expression, $\epsilon_s=\epsilon_0+\Omega_p^2/\Omega_T^2$ is the static dielectric constant of the medium, while $\Omega_T(0)$ is the frequency of the bulk transverse excitation at $k_\parallel=0$, and $\Omega_s(0)$ is the solution of Eqs. (4.20), i.e., the frequency of the surface polariton at $k_\parallel=0$, neglecting retardation.

Several comments are in order at this point. First, we remind the reader that Eq. (4.23) is valid only for small $k_\parallel\cong 0$, and in the absence of retardation.

One important feature of Eq. (4.23) is that in the presence of spatial dispersion, for real values of $k_\parallel$, the surface-polariton frequency is complex. As explained earlier, this is because in the presence of spatial dispersion, there is no longer a gap in the frequency spectrum of the dielectric between Ω_T and Ω_L. Furthermore, the boundary conditions admix the waves bound to the surface with the bulk-polariton mode indicated as the lower branch in Fig. 1(b). As a consequence, energy stored near the surface leaks off into the interior, and the surface mode acquires a finite lifetime.

Notice that $\Delta\Omega(k_\parallel)$ is proportional to $k_\parallel$ and not $k_\parallel^2$. Also, it is clear that the expansion parameter that enters for small $Dk_\parallel^2$ in the calculation of corrections to local dielectric theory is $D^{1/2}k_\parallel$. These two features indicate that even when $Dk_\parallel^2$ is small the effects of spatial dispersion can be significant. A dimensionless measure of the importance of spatial dispersion is provided by the quantity

$$\Delta=\epsilon_0 D/c^2.$$

For excitons in ZnSe, we shall see that $\Delta\sim 5\times 10^{-5}$. Then $\Delta^{1/2}\sim 10^{-2}$ to 10^{-3}, so spatial-dispersion effects can be expected to exert an influence on the optical properties of exciton levels in semiconductors, since a very narrow range of frequencies very close to Ω_T is of interest in this case. We shall explore spatial-dispersion effects in our model in Sec. VI for parameters characteristic of ZnSe.

Finally, we point out the similarity of the expression in Eq. (4.23) to the dispersion relation of surface plasmons in metals.[8] The surface-plasmon frequency is also complex for small $k_\parallel$ as $k_\parallel\to 0$. Experimental evidence for this linear shift in wave vector of the surface-plasmon frequency has been provided by studies of the inelastic scattering of low-energy electrons from the surface of aluminum.[9]

V. OBSERVATION OF SURFACE POLARITONS BY THE METHOD OF FRUSTRATED TOTAL INTERNAL REFLECTION

It is not possible to observe surface polaritons in a conventional light-absorption experiment. If the incident light strikes the crystal at non-normal incidence, then the frequency of the incident photon is $c(k_\parallel^2+k_z^2)^{1/2}$. If the incident photon is absorbed with the creation of a surface polariton with wave vector $\vec{k}_\parallel$ parallel to the surface, then conservation of energy requires

$$c(k_\parallel^2+k_z^2)^{1/2}=\Omega_s(\vec{k}_\parallel), \tag{5.1}$$

while at the same time, in Sec. IV we have seen that the electromagnetic fields associated with the surface wave can be localized to the surface only if

$$\Omega_s(\vec{k}_\parallel)<ck_\parallel. \tag{5.2}$$

The two conditions (5.1) and (5.2) can be reconciled only if $k_z^2<0$, that is, if the electromagnetic field of the light incident on the crystal surface is damped along the z direction. Such an electromagnetic field can be produced by the method of attenuated total reflection (ATR) first proposed by Otto[10] as the means for the experimental study of surface plasmons in metals. This method has been used subsequently in investigations of other kinds of surface excitations.[3]

In this section we present the theory of the ATR method, with a view toward the use of this method to explore the effects of spatial dispersion on surface polaritons discussed in Sec. IV. In this method, one measures the reflection coefficient of an electromagnetic wave incident on the interface between two media, a prism and a gap, constituting a plane of total internal reflection. The presence of the crystal being studied at a distance from this interface destroys the conditions necessary for total internal reflection, and, as a consequence, the reflection coefficient departs from unity. From structure in the reflection coefficient as a function of the frequency of the incident light, the dispersion relation for surface polaritons can be obtained. We now turn to a calculation of the re-

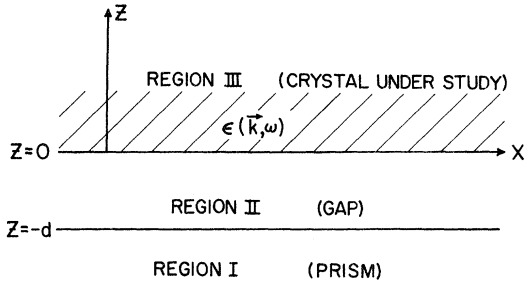

FIG. 3. Configuration employed in the frustrated-internal-reflection method.

flection coefficient.

The geometry we consider is illustrated in Fig. 3. To simplify the problem, we have assumed that the prism (region I) and the crystal (region III) occupy semi-infinite portions of the z axis. The electric and magnetic fields in the prism will be written in a form similar to the form used in the preceding sections:

$$E_\alpha^{(1)}(\vec{x},t)=E_\alpha^{(1)}(z)e^{ik_{\parallel}x}e^{-i\Omega t}\ , \tag{5.3a}$$

$$H_\alpha^{(1)}(\vec{x},t)=H_\alpha^{(1)}(z)e^{ik_{\parallel}x}e^{-i\Omega t}\ , \tag{5.3b}$$

where the superscript (1) refers to region I of Fig. 3. We assume the electric vector is in the xz plane, since this is the only configuration which gives rise to coupling between the incident radiation and the surface polariton. Then $E_y^{(1)}(z) = H_x^{(1)}(z) = H_z^{(1)}(z) \equiv 0$.

The nonzero components of the electric and magnetic fields in the region of the prism can be written in the form

$$E_z^{(1)}(z)=e^{i\gamma_1 z}+R\,e^{-i\gamma_1 z}\ , \tag{5.4a}$$

$$E_x^{(1)}(z)=\frac{\gamma_1}{k_{\parallel}}\left(-e^{i\gamma_1 z}+R\,e^{-i\gamma_1 z}\right)\ , \tag{5.4b}$$

and

$$H_y^{(1)}(z)=-\frac{\epsilon_p\Omega}{ck_{\parallel}}\left(e^{i\gamma_1 z}+R\,e^{-i\gamma_1 z}\right)\ , \tag{5.4c}$$

where

$$\gamma_1=(\epsilon_p\Omega^2/c^2-k_{\parallel}^2)^{1/2} \tag{5.5}$$

and ϵ_p is the dielectric constant of the prism, which we take to be real, isotropic, and independent of the incident frequency Ω. The first term on the right-hand sides of Eqs. (5.4) describes the incident field, while the second describes the reflected field.

The time-averaged flux of energy in an electromagnetic wave is given by the real part of the complex Poynting vector[11]

$$\vec{S}=(c/8\pi)\vec{E}\times\vec{H}^*\ . \tag{5.6}$$

If we use the expressions for $\vec{E}$ and $\vec{H}$ given by Eqs. (5.4) and (5.5), the magnitudes of the energy flux in the incident and reflected waves are given by

$$|\mathrm{Re}\vec{S}|_{\mathrm{inc}}=\frac{\epsilon_p^{3/2}}{8\pi}\frac{\Omega^2}{c^2k_{\parallel}^2} \tag{5.7a}$$

and

$$|\mathrm{Re}\vec{S}|_{\mathrm{ref}}=\frac{\epsilon_p^{3/2}}{8\pi}\frac{\Omega^2}{c^2k_{\parallel}^2}|R|^2\ . \tag{5.7b}$$

The fraction F of the incident energy reflected from the interface between the prism and the gap is then

$$F=\frac{|\mathrm{Re}\vec{S}|_{\mathrm{ref}}}{|\mathrm{Re}\vec{S}|_{\mathrm{inc}}}=|R|^2\ . \tag{5.8}$$

The value of R is determined from the boundary conditions satisfied by the electromagnetic fields at the interfaces between the prism and the gap, and the gap and the crystal under study.

In the gap (region II of Fig. 3), the electric and magnetic fields have the nonzero components

$$E_x^{(2)}(z)=A_1e^{-\gamma_2 z}+A_2e^{+\gamma_2 z}\ , \tag{5.9a}$$

$$E_z^{(2)}(z)=-\frac{k_{\parallel}}{i\gamma_2}\left(A_1e^{-\gamma_2 z}-A_2e^{+\gamma_2 z}\right)\ , \tag{5.9b}$$

$$H_y^{(2)}(z)=-\frac{\epsilon_g\Omega}{ic\gamma_2}\left(A_1e^{-\gamma_2 z}-A_2e^{+\gamma_2 z}\right)\ , \tag{5.9c}$$

where

$$\gamma_2=\left(k_{\parallel}^2-\epsilon_g\frac{\Omega^2}{c^2}\right)^{1/2}\ , \tag{5.10}$$

and ϵ_g is the dielectric constant of the gap, which we also take to be real, isotropic, and independent of frequency.

The conservation of the tangential components of $\vec{E}$ and the normal components of $\vec{D}$ at the plane $z=-d$ yields the pair of equations

$$\frac{\gamma_1}{k_{\parallel}}\left(-e^{-i\gamma_1 d}+R\,e^{+i\gamma_1 d}\right)=A_1e^{\gamma_2 d}+A_2e^{-\gamma_2 d} \tag{5.11a}$$

and

$$\epsilon_p\left(e^{-i\gamma_1 d}+R\,e^{+i\gamma_1 d}\right)=-\frac{\epsilon_g k_{\parallel}}{i\gamma_2}\left(A_1e^{\gamma_2 d}-A_2e^{-\gamma_2 d}\right)\ . \tag{5.11b}$$

Of course, the conservation of the components of $\vec{H}$ across the plane $z=d$ yields no new conditions.

Equations (5.1) can be solved for the amplitudes A_1 and A_2 with the results that

$$A_1=-\tfrac{1}{2}e^{-\gamma_2 d}\left(\frac{\gamma_1}{k_{\parallel}}+i\frac{\gamma_2}{k_{\parallel}}\frac{\epsilon_p}{\epsilon_g}\right)e^{-i\gamma_1 d} + \tfrac{1}{2}e^{-\gamma_2 d}\left(\frac{\gamma_1}{k_{\parallel}}-i\frac{\gamma_2}{k_{\parallel}}\frac{\epsilon_p}{\epsilon_g}\right)R\,e^{+i\gamma_1 d} \tag{5.12a}$$

and

$$A_2=-\tfrac{1}{2}e^{+\gamma_2 d}\left(\frac{\gamma_1}{k_{\parallel}}-i\frac{\gamma_2}{k_{\parallel}}\frac{\epsilon_p}{\epsilon_g}\right)e^{-i\gamma_1 d}$$

$$+\tfrac{1}{2}e^{+\gamma_2 d}\left(\frac{\gamma_1}{k_\parallel}+i\,\frac{\gamma_2}{k_\parallel}\,\frac{\epsilon_p}{\epsilon_g}\right)R\,e^{+i\gamma_1 d}\quad . \tag{5.12b}$$

It only remains to satisfy the boundary conditions at the plane $z=0$, the interface between the gap and the crystal. Upon combining Eq. (5.9a) with Eq. (4.8a), we obtain, from the conservation of the tangential components of $\vec{E}$ across the plane $z=0$,

$$A_1+A_2=\mathcal{E}^{>}_{(1)}+\mathcal{E}^{>}_{(2)}+\mathcal{E}^{>}_{(3)}\ . \tag{5.13a}$$

Combining Eq. (5.9b) with Eq. (3.34c), we obtain, from the conservation of normal components of $\vec{D}$ at the plane $z=0$,

$$\frac{\epsilon_g k_\parallel}{\gamma_2}(A_1-A_2)=\frac{k_\parallel\epsilon_1}{\alpha_1}\mathcal{E}^{>}_{(1)}+\frac{k_\parallel\epsilon_2}{\alpha_2}\mathcal{E}^{>}_{(2)}\ , \tag{5.13b}$$

where we write this expression in terms of the parameters α_i used in the discussion of surface polaritons in Sec. III. Recall that the quantities ϵ_i which appear on the right-hand side of Eq. (5.13b) are $\epsilon(\vec{k}_\parallel i\alpha_i\,,\ \Omega)$, where $\epsilon(\vec{k}_\parallel k_z\,,\ \Omega)$ is the frequency- and wave-vector-dependent dielectric constant of the crystal.

The conservation of the tangential component of $\vec{H}$ across the plane $z=0$ yields no new condition. The two additional boundary conditions (4.9) may be used to eliminate $\mathcal{E}^{>}_2$ and $\mathcal{E}^{>}_3$ from Eqs. (5.13). The resulting expressions become

$$A_1+A_2=M(k_\parallel,\Omega)\mathcal{E}^{>}_{(1)} \tag{5.14a}$$

and

$$A_1-A_2=N(k_\parallel,\Omega)\mathcal{E}^{>}_{(2)}\ , \tag{5.14b}$$

where in the notation of Sec. IV

$$M(k_\parallel,\Omega)=1-\frac{\alpha_2}{\alpha_1}\left(\frac{k_\parallel^2-\alpha_1\alpha_3}{k_\parallel^2-\alpha_2\alpha_3}\right)\left(\frac{i\Gamma+\alpha_2}{i\Gamma+\alpha_1}\right)+\frac{k_\parallel^2}{\alpha_1}\left(\frac{\alpha_2-\alpha_1}{k_\parallel^2-\alpha_2\alpha_3}\right)\left(\frac{i\Gamma+\alpha_3}{i\Gamma+\alpha_1}\right) \tag{5.15a}$$

and

$$N(k_\parallel,\Omega)=\frac{\gamma_2}{\epsilon_g\alpha_1}\left[\epsilon_1-\epsilon_2\left(\frac{k_\parallel^2-\alpha_1\alpha_3}{k_\parallel^2-\alpha_2\alpha_3}\right)\left(\frac{i\Gamma+\alpha_2}{i\Gamma+\alpha_1}\right)\right]\ . \tag{5.15b}$$

It follows that

$$\frac{A_1+A_2}{A_1-A_2}=\frac{M(k_\parallel,\Omega)}{N(k_\parallel,\Omega)}\quad . \tag{5.16}$$

In view of Eqs. (5.12), Eq. (5.16) can be regarded as the equation determining the amplitude R, and hence the reflection coefficient F. Combining Eqs. (5.12) and (5.16), we find that

$$R=\frac{A_1^{(1)}+A_2^{(1)}-(M/N)(A_1^{(1)}-A_2^{(1)})}{A_1^{(2)}+A_2^{(2)}-(M/N)(A_1^{(2)}-A_2^{(2)})}\quad , \tag{5.17}$$

where

$$A_1^{(1)}=\tfrac{1}{2}e^{-\gamma_2 d}\left(\frac{\gamma_1}{k_\parallel}+i\,\frac{\gamma_2}{k_\parallel}\,\frac{\epsilon_p}{\epsilon_g}\right)e^{-i\gamma_1 d}\ , \tag{5.18a}$$

$$A_1^{(2)}=\tfrac{1}{2}e^{-\gamma_2 d}\left(\frac{\gamma_1}{k_\parallel}-i\,\frac{\gamma_2}{k_\parallel}\,\frac{\epsilon_p}{\epsilon_g}\right)e^{+i\gamma_1 d}\ , \tag{5.18b}$$

$$A_2^{(1)}=\tfrac{1}{2}e^{+\gamma_2 d}\left(\frac{\gamma_1}{k_\parallel}-i\,\frac{\gamma_2}{k_\parallel}\,\frac{\epsilon_p}{\epsilon_g}\right)e^{-i\gamma_1 d}\ , \tag{5.18c}$$

$$A_2^{(2)}=\tfrac{1}{2}e^{+\gamma_2 d}\left(\frac{\gamma_1}{k_\parallel}+i\,\frac{\gamma_2}{k_\parallel}\,\frac{\epsilon_p}{\epsilon_g}\right)e^{+i\gamma_1 d}\ . \tag{5.18d}$$

This result may be written in the form

$$R=e^{-i2\gamma_1 d}\left(\frac{1-iQ}{1+iQ}\right)\ , \tag{5.19a}$$

where

$$Q=\frac{\epsilon_p}{\epsilon_g}\,\frac{\gamma_2}{\gamma_1}\,\frac{(M/N)+\tanh\gamma_2 d}{1+(M/N)\tanh\gamma_2 d}\quad . \tag{5.19b}$$

Suppose for the moment the width d of the gap is allowed to be very large, so that $\gamma_2 d\gg 1$. Then if the conditions of the experiment are such that both γ_1 and γ_2 are real (the electromagnetic wave propagates in the transparent prism, with its amplitude exponentially attenuated in the gap region), then Q is purely real, and the reflection coefficient F equals unity.

When $\gamma_2 d$ is the order of unity, the wave interacts with the crystal, and F drops below unity. If the angle of incidence is θ, then

$$k_\parallel=\frac{\Omega}{c}\,\epsilon_p^{1/2}\sin\theta\ .$$

Thus, if the frequency Ω of the incident wave is fixed, and the angle of incidence θ is varied, $k_\parallel$ may be swept through a large range of values. The experimental work cited earlier shows that for fixed Ω, the reflectivity suffers a sharp dip when

$$\Omega=\Omega_s(k_\parallel)\ ,$$

where $\Omega_s(k_\parallel)$ is the surface-polariton frequency. Then by observing the position of the reflectivity dip for various frequencies, the dispersion relation $\Omega_s(k_\parallel)$ may be mapped out. This is the technique used by Marschall and Fischer[3] to obtain the dispersion relation of the surface polariton in GaP, in the region between the TO-phonon and LO-phonon frequency.

The relationship of the position of the reflectivity dip to the frequency and wave vector of the surface polariton follows from the preceding results. Suppose that the gap between the crystal and the prism is an air gap. Then $\epsilon_g=1$, and the parameter $\gamma_2=\alpha_0$, where α_0 is the parameter encountered in Sec. IV [see Eq. (4.2)]. Furthermore, suppose d is sufficiently large that $\gamma_2 d\gg 1$. Then the quantity Q is well approximated by the expression (for $\epsilon_g=1$ and $\gamma_2=\alpha_0$)

$$Q\equiv\frac{\alpha_0\epsilon_p}{\gamma_1}\left[1+2\Delta(k_\parallel,\Omega)\,e^{-2\gamma_2 d}\right]\ ,$$

where

$$\Delta(k_{\parallel},\Omega)=\frac{M(k_{\parallel},\Omega)-N(k_{\parallel},\Omega)}{M(k_{\parallel},\Omega)+N(k_{\parallel},\Omega)} \quad . \tag{5.20}$$

Then after a short calculation, one finds for the amplitude R of the reflected wave

$$R=R_0\left[1-\left(\frac{4\alpha_0\gamma_1\epsilon_p}{\gamma_1^2+\alpha_0^2\epsilon_p^2}\right)i\Delta(k_{\parallel},\Omega)e^{-2\gamma_2 d}\right] \quad ,$$

where

$$R_0=e^{-i2\gamma_1 d}\left(\frac{\gamma_1-i\alpha_0\epsilon_p}{\gamma_1+i\alpha_0\epsilon_p}\right) \quad .$$

Under the conditions where the incident wave suffers total internal reflection, $|R_0|^2=1$. Then in this case,

$$F=|R|^2=1+\left(\frac{8\alpha_0\gamma_1\epsilon_p}{\gamma_1^2+\alpha_0^2\epsilon_p^2}\right)e^{-2\gamma_2 d}\,\mathrm{Im}[\Delta(k_{\parallel},\Omega)] \quad . \tag{5.21}$$

All of the information about the properties of the crystal under investigation are stored in the quantity $\Delta(k_{\parallel},\Omega)$. From Eq. (5.20) it is a short calculation to demonstrate that

$$\Delta(k_{\parallel},\Omega)=S(k_{\parallel},\Omega)/D(k_{\parallel},\Omega) \quad , \tag{5.22}$$

where the function $D(k_{\parallel},\Omega)$ is defined in Eq. (4.12), and

$$S(k_{\parallel},\Omega)=\alpha_1(i\Gamma+\alpha_1)(k_{\parallel}^2-\alpha_3\alpha_2)$$

$$-\alpha_2(i\Gamma+\alpha_2)(k_{\parallel}^2-\alpha_3\alpha_1)+k_{\parallel}^2(i\Gamma+\alpha_3)(\alpha_2-\alpha_1)$$

$$+\alpha_0[\epsilon_2(i\Gamma+\alpha_2)(k_{\parallel}^2-\alpha_3\alpha_1)-\epsilon_1(i\Gamma+\alpha_1)(k_{\parallel}^2-\alpha_3\alpha_2)] \quad .$$

Suppose we now consider the following idealized experiment. Radiation is incident on the interface, and the frequency Ω is varied while $k_{\parallel}$ remains fixed always. (Of course, as Ω is varied, the angle of incidence θ needs to be varied if $k_{\parallel}$ is to remain constant.) The frequency dependence of the reflectivity is controlled by the frequency dependence of $\Delta(k_{\parallel},\Omega)$ in this case. We have seen in Sec. IV that for a fixed value of $k_{\parallel}$, the denominator has a pole in the lower half of the complex Ω plane. In a lossless dielectric and in the absence of spatial dispersion, this pole lies on the real axis, at the surface-polariton frequency $\Omega_s(k_{\parallel})$ given by Eq. (2.7). In the presence of spatial dispersion, the pole is shifted off the real axis (the surface polariton is now a virtual state), as we have seen in Sec. IV. In the limit that $k_{\parallel}\to 0$, and retardation effects are ignored, the pole lies close to the real axis, as one can see from Eq. (4.23). There will thus be a sharp resonant structure in the function $\Delta(k_{\parallel},\Omega)$ for Ω near the surface-state resonance. Let the pole occur at the (complex) frequency

$$\Omega_s(k_{\parallel})=\Omega_s^{(R)}(k_{\parallel})-i\Omega_s^{(I)}(k_{\parallel}) \quad .$$

Then for Ω near $\Omega_s(k_{\parallel})$, since the numerator is a slowly varying function of frequency, to a good approximation

$$\Delta(k_{\parallel},\Omega)=\frac{\alpha(k_{\parallel})}{\Omega-\Omega_s^R(k_{\parallel})+i\Omega_s^I(k_{\parallel})} \quad , \tag{5.23}$$

where

$$\alpha(k_{\parallel})=\frac{S(k_{\parallel},\Omega_s(k_{\parallel}))}{\left.\frac{\partial D}{\partial\Omega}\right|_{\Omega=\Omega_s(k_{\parallel})}} \quad .$$

The reflectivity thus exhibits a dip when Ω is near $\Omega_s(k_{\parallel})$. The dip has a Lorentzian shape only if the quantity $\alpha(k_{\parallel})$ is real. The position of the dip provides a measure of $\Omega_s^R(k_{\parallel})$, and its width provides a measure $\Omega_s^I(k_{\parallel})$.

The present work shows there are two contributions to the width $\Omega_s^I(k_{\parallel})$. If the dielectric is lossy [the parameter γ in Eq. (3.8) is nonzero], $\Omega_s^I(k_{\parallel})$ will be finite because the energy stored in the electromagnetic field is damped out by the presence of dissipation in the medium. Second, when spatial dispersion is present, the "leak" into the interior of the crystal damps out the energy in the surface wave even in the absence of dielectric loss. Thus, spatial dispersion manifests itself by an increase in width of the reflectivity minimum over that expected on the basis of the local dielectric theory, and the position of the resonance is shifted by virtue of the contribution of spatial-dispersion effects to $\Omega_s^R(k_{\parallel})$.

The structure in the reflectivity occurs near $\Omega_s(k_{\parallel})$ only in the limit $\gamma_2 d\gg 1$. When $\gamma_2 d$ is the order of unity, the presence of the prism perturbs the surface polariton and shifts the resonance position somewhat, as Marschall and Fisher have noted.

The width of the resonance is controlled by $\Omega_s^I(k_{\parallel})$ only when Ω is varied with $k_{\parallel}$ fixed, as assumed above in our analysis of the idealized experiment. In general, both frequency and the wave vector vary, if θ is fixed and Ω is varied. When the frequency is fixed, and θ is varied, then we must consider the behavior of $\Delta(k_{\parallel},\Omega)$ for fixed real frequency Ω, and varying real values of $k_{\parallel}$. The width of the reflectivity dip then measures in essence the imaginary part of the wave vector of a surface polariton excited by a driving field of fixed frequency; i.e., the width of the dip is controlled by the quantity $k_{\parallel}^{(I)}$, where

$$k_{\parallel}=k_{\parallel}^{(R)}+ik_{\parallel}^{(I)}$$

is the solution of

$$D(k_{\parallel},\Omega)=0 \quad ,$$

for real values of the frequency Ω.

VI. EFFECT OF SPATIAL DISPERSION ON THE REFLECTIVITY AND THE PROPERTIES OF SURFACE POLARITONS; NUMERICAL STUDIES

We have carried out a series of numerical calculations to explore the effects of spatial disper-

sion on the properties of the model crystal discussed in Secs. II–V. In this section we describe the results of these numerical calculations, and we compare the behavior of the reflectivity and the properties of surface polaritons in the presence of spatial dispersion with the predictions of the local dielectric theory.

We first comment on the parameters employed in the calculations. We have chosen the parameters to describe the resonance in the dielectric constant produced by the ground-state exciton in the cubic semiconductor ZnSe. The reflectivity of ZnSe for frequencies near the fundamental absorption edge has been studied by Hite, Marple, Aven, and Segall.[12] These authors have extracted the oscillator strength of this exciton state from the data, and they also provide a convenient table of properties of ZnSe.

The background dielectric constant [the ϵ_0 of Eq. (3.8)] is found to be 8.1, and the contribution of the exciton level to the static dielectric constant is 5.5×10^{-3}. Thus, for this crystal,

$$\Omega_p^2/\Omega_T^2 = 5.5\times10^{-3}\,, \tag{6.1}$$

and in electron volts,

$$\Omega_T = 2.8\ \text{eV}. \tag{6.2}$$

Next consider the parameter D. If $E_T(k)$ is the energy of the transverse exciton of wave vector k, and if the dependence of the exciton energy on k comes about only because of the center-of-mass motion, then

$$E_T(k) = E_T(0) + \frac{\hbar^2}{2(m_e+m_h)}\,k^2\,,$$

where m_e and m_h are the effective masses of the electron and hole, respectively. For ZnSe,[12] the sum m_e+m_h assumes a value very close to the free-electron mass. Then the function $\Omega_T^2(k) = \Omega_T^2+Dk^2$ of our model is given by

$$\Omega_T^2(k) = \frac{E_T(k)^2}{\hbar^2} = \frac{E_T^2(0)}{\hbar^2} + \frac{E_T(0)}{m_e+m_h}\,k^2 + \cdots\,,$$

so that

$$D = \frac{E_T(0)}{m_e+m_h}\,.$$

It is convenient to introduce a dimensionless measure of the amount of spatial dispersion present. We use a parameter Δ for this purpose, where

$$\Delta = \epsilon_0 D/c^2\,.$$

For the parameters characteristic of ZnSe, we find that

$$\Delta = 5\times10^{-5}\,. \tag{6.3}$$

All of the calculations carried out in the remainder of this section employ the numerical values given in Eqs. (6.1)–(6.3). We first describe the results of the reflectivity calculations, then we turn to a study of the properties of surface polaritons and the technique of frustrated internal reflection.

A. Reflectivity

The results of calculations of the reflectivity are displayed in Figs. 4–6. In these calculations, the parameter γ in Eq. (3.8) was set equal to $10^{-5}\Omega_T$. This value of γ is similar in magnitude to the damping constant employed by Mahan and Hopfield in their analysis of the effect of spatial dispersion on the reflectivity of CdS.[2]

In Fig. 4 we compare the reflectivity in the presence and absence of spatial dispersion, for the case where the radiation is normally incident on the surface, so that the angle of incidence θ is zero. The dashed line shows the frequency dependence of the reflectivity calculated from the local dielectric theory (with $D=0$), and the solid line shows the reflectivity computed when D assumes the value in Eq. (6.3). At normal incidence, the principal effect of spatial dispersion is to decrease the amplitude of the peak in the reflectivity by a substantial amount, while the dip in the reflectivity on the high-frequency side is not greatly affected. In fact, if in a given experiment the sharp dip is not completely resolved, so that an accurate mea-

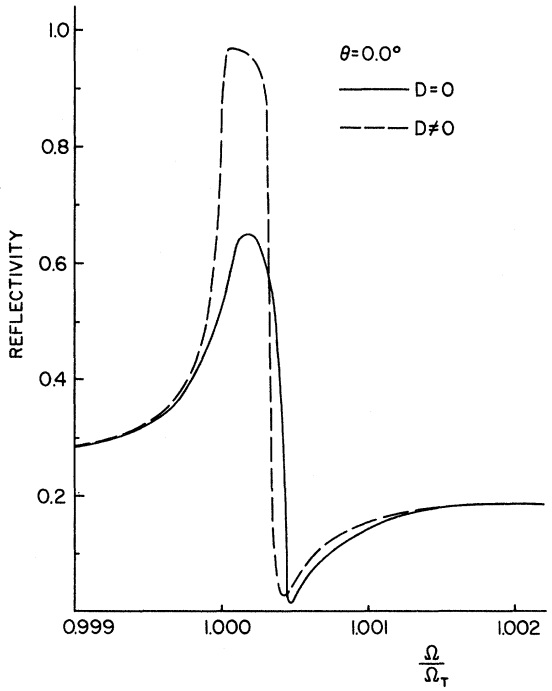

FIG. 4. Frequency dependence of the reflectivity in the presence and absence of spatial dispersion, for the case where the radiation is normally incident on the crystal.

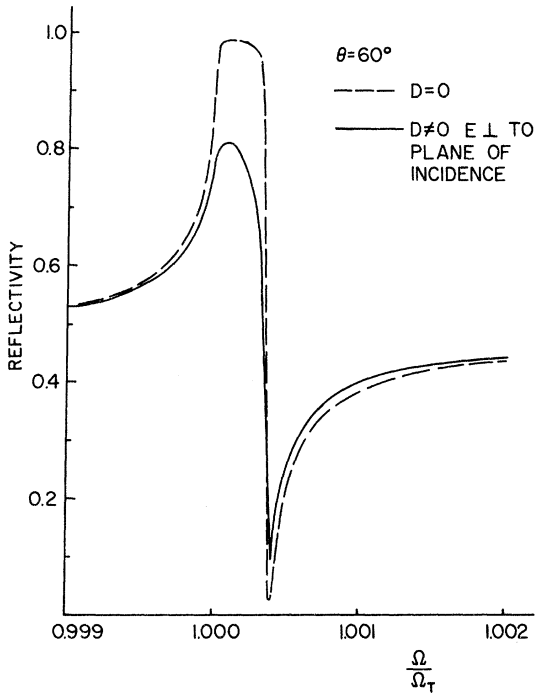

FIG. 5. Frequency dependence of the reflectivity for the case where the angle of incidence is 60°, and the electric field vector is normal to the plane of incidence.

sure of its depth is not obtained, the solid curve in Fig. 4 could be fitted rather well by the local theory, but with a value of the damping constant γ considerably larger than the true value. When data are taken at normal incidence, this result indicates that one should take note of the relative magnitudes of the height of the peak and the depth of dip in the reflectivity, to assess the importance of spatial-dispersion effects.

In Fig. 5 we show the frequency dependence of the reflectivity for the case where the angle of incidence θ is 60°, and the electric field vector is perpendicular to the plane of incidence. The effect of spatial dispersion on the reflectivity in this case is very similar to its effect at normal incidence: The height of the peak is considerably lower in the presence of spatial dispersion than expected from the local theory, while the dip above Ω_T is affected much less dramatically.

In Fig. 6 we show the frequency dependence of the reflectivity in the presence of spatial dispersion when the angle of incidence $\theta = 60°$, and now the electric field in the incident radiation is parallel to the plane of incidence. The effect of spatial dispersion is now striking, and the shape of the solid curve is now qualitatively different from the reflectivity calculated in the absence of spatial dispersion. In the presence of spatial dispersion, the location of the dip coincides very accurately with the longitudinal-exciton frequency at $k_{\parallel} = 0$, as indicated. Just above Ω_L in frequency a small but well-resolved peak in the reflectivity appears, while for frequencies above the peak the reflectivity is significantly higher than the value expected in the absence of spatial dispersion. The presence of the peak and the elevated value of the reflectivity for frequencies above the peak both arise from the presence of the third longitudinal wave excited by the incident field at non-normal incidence, when the electric field is parallel to the plane of incidence.

At this point, we should discuss the relationship of the present theory to that of Hopfield and coworkers,[2] since they also predict structure in the reflectivity above the transverse-exciton frequency. As mentioned earlier, there is a fundamental difference between the theory presented here, and theirs. We assume the dielectric material is uniform in its properties right up to the surface. They argue that in CdS there is a surface layer with a thickness the order of 100 Å, from which the bulk polarization field is excluded. The structure in the reflectivity curves they calculate depends on the presence of the surface layer, and in the range of parameters explored by them the magnitudes of the peaks above Ω_T increase as the

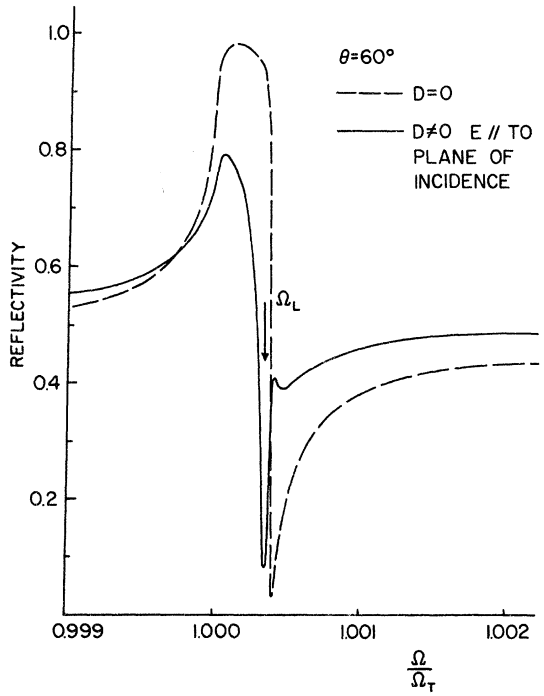

FIG. 6. Frequency dependence of the reflectivity in the presence and absence of spatial dispersion, when the electric field vector is parallel to the plane of incidence. The frequency Ω_L of the longitudinal exciton is indicated on the figure.

thickness of the surface layer increases. They also confine their attention only to the case of normal incidence, and their mechanism produces structure in this case. As one sees from Figs. 4–6, we obtain the reflectivity peak above Ω_T only for non-normal incidence, and only when the electric field is parallel to the plane of incidence.

Thus, from an experimental point of view, it would be a straightforward matter, in principle, to distinguish between the structure present in Fig. 6 and that described by Hopfield and his collaborators. The structure in Fig. 6 disappears at normal incidence where the electric field does not excite the longitudinal wave, and at non-normal incidence the structure appears only for one polarization.

One may ask whether our model can be applied to a real material, particularly since Hopfield and his collaborators demonstrate quite clearly that in CdS the surface layer plays an important role in determining the form of the reflectivity for frequencies in the region where excitons produce structure in the dielectric constant. We feel that it is not clear that the surface layer will play an important role in all materials. In the particular case of ZnSe, at normal incidence, no anomalous structure appears in the low-temperature reflectivity data of Hite *et al.* It would be extremely interesting to examine the reflectivity of ZnSe for frequencies in the vicinity of the fundamental exciton absorption line at large angles of incidence to see if structure similar to that in Fig. 6 would appear. Indeed, we know of no reflectivity studies of exciton lines in III-V or II-VI semiconductors at non-normal incidence.

B. Method of Frustrated Internal Reflection

In this section we describe the results of our numerical studies of the reflectivity dip observed in the method of frustrated total internal reflection. The geometrical configuration utilized in such an experiment is discussed in Sec. V, where an expression for the reflection coefficient is obtained, and several of its properties are discussed from a qualitative point of view.

The numerical studies have been carried out for the case where the reflectivity dip is produced by the surface polariton formed from the ground-state exciton in ZnSe. It should be mentioned that to date all of the experiments reported so far have employed infrared radiation, and have explored the reflectivity dip produced by the surface polariton that exists in the frequency region between the $\vec{k}=0$ TO-phonon frequency and the $\vec{k}=0$ LO-phonon frequency. Thus, in this section, the frequency region we explore is in the visible, near 2.8 eV for the ground-state exciton in ZnSe. In principle, it should be possible to apply the technique of frustrated internal reflection in the visible as well as in the infrared. We choose to carry out the numerical studies for this case since spatial-dispersion effects can be significant in the study of excitons, as we have seen in the calculations of the reflection coefficient just described. However, for phonons, the damping constant γ is sufficiently large and characteristic values of $Dk_{\parallel}^2$ so small that observation of spatial-dispersion effects will prove very difficult, if not impossible.

We have carried out the numerical studies of the reflectivity dip observed in the frustrated-internal-reflection method for the parameters introduced at the beginning of this section, choosing an air gap between the prism and the sample ($\epsilon_g = 1$), and choosing the dielectric constant ϵ_p of the prism equal to 15. We choose a large value of ϵ_p so that the wave is totally reflected from the prism-gap interface for a wide range of incident angles. The value of ϵ_p chosen affects the range of $k_{\parallel}$ that may be explored by the frustrated-internal-reflection method, but for sufficiently large d, the width and position of the reflectivity dip is independent of ϵ_p, as we may see from the discussion at the end of Sec. V. The angle of incidence θ was varied from 20° to 80°, in increments of 10°, and at each angle the dependence of the reflectivity on frequency was computed. The shape of the reflectivity dip was examined for each value of θ. The thickness of the air gap was chosen so that when $\theta = 20°$, the parameter $\gamma_2 d$ of Sec. V assumed the value unity.

The reflectivity dip at $\theta = 20°$ is exhibited in Fig. (7a), and the reflectivity dip at $\theta = 80°$ is presented in Fig. 7(b). The full form for the reflectivity coefficient given in Eqs. (5.19) was used in the calculations. However, for this value of $\gamma_2 d$, the results are well approximated by the approximate form in Eqs. (5.21). As a consequence, we interpret the results in terms of this latter equation. Also, the value of the damping constant γ was set equal to an unrealistically small value, so that the shape, width, and the position of the reflectivity dip are controlled entirely by spatial-dispersion effects. We shall comment briefly on the effect of a realistic value of γ later in the present section. Next we comment on several features of the results.

First of all, since the oscillator strength of the exciton level is small, the magnitude of the reflectivity dip is much smaller than the magnitude of the dip observed in Ref. 3. At $\theta = 20°$, the maximum value of the fractional change $\Delta R/R_0$ in the reflectivity is roughly 2×10^{-5}.

The curves in Fig. (7) are not Lorentzian in shape, but are distinctly asymmetric. This is expected from the limiting form in Eq. (5.23), since the numerator in this expression is complex. This means that the position and the width of the reflectivity dip are not simply related to $\mathrm{Re}[\Delta\Omega_s(k_{\parallel})]$ and

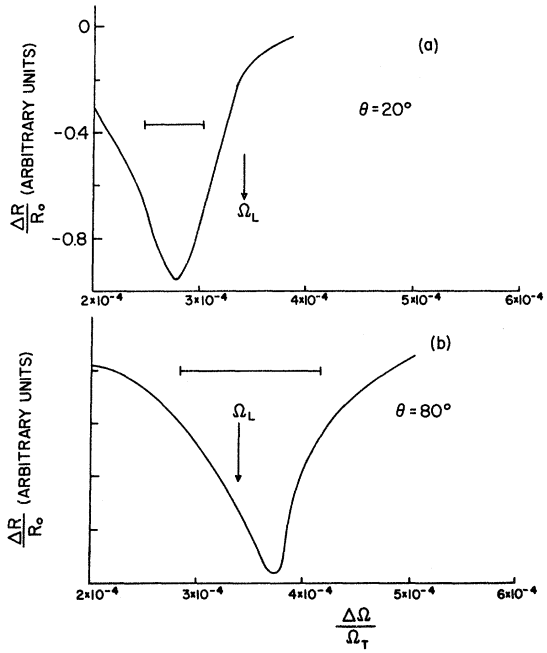

FIG. 7. Reflectivity dip appropriate to the frustrated-internal-reflection experiment for the angle of incidence θ equal to (a) 20° and (b) 80°. The parameters employed in the calculation are described in text. The position of the bulk longitudinal exciton is marked by the vertical arrow. The horizontal bar is the width of the reflectivity dip predicted from the width of the virtual-surface-polariton state predicted by Eq. (4.23).

$\mathrm{Im}[\Delta\Omega_s(k_\parallel)]$, respectively, where $\Delta\Omega_s(k_\parallel)$ is the complex shift in frequency of the surface polariton produced by the presence of spatial dispersion. An approximate expression for these quantities is given in Eq. (4. 23). Nonetheless, we do expect these two quantities to provide semiquantitative estimates of the contribution to the width and position of the dip from spatial dispersion.

The effect of spatial dispersion on the position of the reflectivity dip is particularly evident in Fig. 7(b), since the minimum in the reflectivity lies *above* the frequency of the bulk longitudinal exciton. In the absence of spatial dispersion, the frequency of the surface polariton always lies below the frequency of the bulk longitudinal exciton, in the gap between the bulk transverse- and longitudinal-exciton frequencies, as explained earlier in this paper [see Eq. (2. 7)].

In Fig. 7(a), notice the distinct change in slope of the wing of the reflectivity dip at the frequency Ω_L of the bulk longitudinal exciton. This break in slope appeared distinctly in all of the calculations for which the minimum in the reflectivity was well below Ω_L. The physical origin of the break in slope lies in the presence of the longitudinal (or irrotational) wave component present in the surface polariton, in the presence of spatial dispersion. When $\Omega = \Omega_L(k_\parallel)$ $[\approx \Omega_L(0)$ for the values of $k_\parallel$ relevant here], this irrotational wave changes from a spatially damped wave to a propagating one. This produces an increase in the width of the virtual surface polariton.

We have computed the quantity $2\mathrm{Im}[\Delta\Omega_s(k_\parallel)]$ from Eq. (4. 23) for the parameters employed here, and compared the result to the features in Fig. 7. Of course, the expression in Eq. (4. 23) was derived only after retardation effects were ignored. Furthermore, since the reflectivity dip is skewed by the presence of the imaginary part of the numerator in Eq. (5. 23), the width of the reflectivity dip is not controlled only by $\mathrm{Im}[\Delta\Omega_s(k_\parallel)]$, as remarked above. Nonetheless, the expression in Eq. (4. 23) does provide a good semiquantitative estimate of the width of the features in Fig. 7, and the variation of the width with θ. The solid horizontal bars in Fig. 7 represent the quantity $2\mathrm{Im}[\Delta\Omega_s(k_\parallel)]$ for the two values of θ.

One can see quite clearly from the expression in Eq. (4. 23), and also from the results displayed in Fig. 7, that the width of the virtual-surface-polariton state produced by the presence of spatial dispersion increases as the wave vector $k_\parallel$ or the angle of incidence θ increases. When dissipation is present in the dielectric, there is a contribution to the width of the reflectivity dip and the decay rate of the surface-polariton state simply from the presence of dissipation. This latter contribution behaves quite differently from the former as a function of θ or, equivalently, of $k_\parallel$. As θ decreases, and the surface-polariton frequency sinks toward Ω_T, the latter contribution increases, since the frequency of the surface polariton moves toward the region where the imaginary part of the dielectric constant is large. Thus, in the presence of both spatial dispersion and losses in the dielectric, the width of the reflectivity dip should be large for $k_\parallel$ small enough for the dominant contribution to the lifetime of the surface polariton to come from the dissipation present in the medium. As $k_\parallel$ is increased, and the frequency of the mode increases, the width of the reflectivity dip should decrease and pass through a minimum to begin to increase as $k_\parallel$ becomes large enough for the dominant contribution to the width of the surface polariton to arise from spatial-dispersion effects.

Next consider the contribution to the frequency of the surface polariton from spatial-dispersion effects. The frequency shift produced by spatial dispersion in the absence of retardation, and in the long-wavelength limit is given by the real part of the right-hand side of Eq. (4. 23). As remarked above, it is clear from Fig. 7(b) that there is a large contribution to the frequency of the surface wave from this effect, since the reflectivity mini-

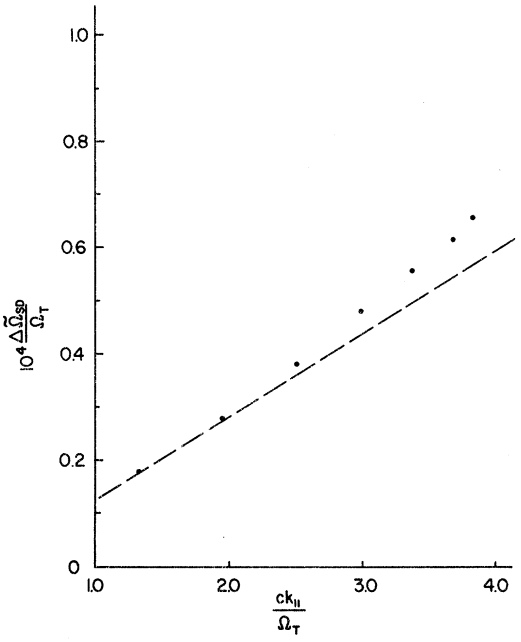

FIG. 8. The quantity $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ plotted against the parameter $ck_\parallel/\Omega_T$.

mum lies above the frequency of the bulk longitudinal exciton.

There are two distinct contributions to the variation of the frequency of the virtual surface polariton with $k_\parallel$. First of all, in the absence of spatial dispersion, the frequency $\Omega_s(k_\parallel)$ of the surface polariton increases with $k_\parallel$ simply because of retardation effects. One can see this from Eq. (2.7), which gives the form of the surface-polariton dispersion relation in the absence of spatial-dispersion curves. Then, when spatial dispersion is included, there is an additional contribution to $\Omega_s(k_\parallel)$, as we see from Eq. (4.23). Thus, a plot of the frequency of the reflectivity minimum against θ, or against $k_\parallel$, will contain contributions from these two sources. In order to extract the contribution to the frequency of the surface polariton from spatial dispersion from the numerical calculations, we have used the following approximate procedure. Let $\Delta\tilde{\Omega}(k_\parallel)$ be the shift of the reflectivity minimum above Ω_T, as determined from the numerical calculations. Then let $\Delta\tilde{\Omega}_{ret}(k_\parallel)$ be the shift in the surface-polariton frequency above Ω_T, if only retardation and not spatial dispersion is present. This quantity may be calculated from Eq. (2.7). We then define $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ from the relation

$$\Delta\tilde{\Omega}(k_\parallel) = \Delta\tilde{\Omega}_{ret}(k_\parallel) + \Delta\tilde{\Omega}_{SD}(k_\parallel) , \tag{6.4}$$

and we use $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ as a measure of the effect of spatial dispersion on the frequency of the surface polariton.

There are two assumptions in this procedure. First of all, the two contributions to the frequency of the surface polariton will be additive only for sufficiently small values of $Dk_\parallel^2$. We assume this condition is satisfied. Second, since the numerator in Eq. (5.23) is complex and the reflectivity dip is skewed as a consequence, the quantity $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ determined from Eq. (6.4) is not strictly the real part of $\Delta\Omega_s(k_\parallel)$, even if the additivity assumption is valid. The two quantities are equal only if the numerator of Eq. (5.23) is purely real, and the reflectivity dip a Lorentzian as a consequence.

The values of $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ determined in the manner just described are presented in Fig. 8, where this quantity is plotted against $ck_\parallel/\Omega_T$. From Fig. 8 it is clear that the dominant contribution to $\Delta\tilde{\Omega}_{SD}(k_\parallel)$ comes from a term linear in $k_\parallel$, as one would expect from Eq. (4.23). The dashed line in Fig. 8 is a straight line drawn through the point $k_\parallel = 0$, $\Delta\Omega_{SD}(k_\parallel) = 0$, and through the smallest values of $\Delta\Omega_s(k_\parallel)$. While a contribution quadratic in $k_\parallel$ is visible in Fig. 8, the dominent contribution comes from the term linear in $k_\parallel$. The slope of the dashed line in Fig. 8 is quite close to the value computed from the real part of the right-hand side of Eq. (4.23). The slope of the dashed line is larger than the value computed from Eq. (4.23) by 30%. We conclude that the expression in Eq. (4.23) provides a good semiquantitative estimate of the shift in frequency of the surface polariton produced by the presence of spatial dispersion.

ACKNOWLEDGMENTS

We have enjoyed many stimulating conversations with Professor E. Burstein about the material in this paper. We also are grateful to Dr. S. Cunningham for writing the computer programs employed in the numerical calculations described in Sec. VI.

*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Grant No. AFOSR 71-2018.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 6 15 MARCH 1973

Model-Pseudopotential Calculation of Electron States in Solids. I. Method*

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(Received 21 August 1972)

A model-pseudopotential method for calculating the states of a valence electron in a solid (such as a conduction or localized electron) is developed. This is done by using atomic model pseudopotentials and the expansion of the valence-electron state in terms of the complete orthonormal set of atomic model pseudo-wave-functions. By this expansion, the operation of the atomic-pseudopotential operator on the pseudo-wave-function of the valence electron is changed into the operation of the atomic pseutopotential on the atomic pseudo-wave-functions. A model pseudopotential suitable to this method is suggested. In the case of the positive ions where bound states are available, the quantum-defect data for them are used to determine the necessary parameters. In the case of a negative ion with no open cores the integro-differential equation for the electron scattering problem is solved. The necessary parameters are then determined from the solution. This method is tested in the case of a localized electron by calculating the optical ionization energy of the F center in the ground state for KCl. It is found that the method gives satisfactory results.

I. INTRODUCTION

The calculation of the states of a valence electron (i.e., a noncore electron) in a solid is a complicated problem. Among other things, one has to take into account the effect of the presence of the core electrons, such as direct and exchange interactions, correlations, etc. Since a complete solution of the many-body Schrödinger equation for the interacting electrons and nuclei is out of the question, one has to resort to different kinds of approximations.

In the usual Hartree–Fock (HF) approximation, the correlation and other minor effects, e.g., relativistic effects, have been neglected. The core states are just taken to be free-ion core states, thereby neglecting some crystal effects. Even in this approximation, the solution of the HF equation for a solid is still not easy, in that a large amount of computation has to be done. This is particularly true when the situation becomes more complicated, e.g., in impurity-state calculations.

Another method to tackle this problem is provided by the theory of pseudopotentials.[1] Already, a number of pseudopotentials have been suggested. These fall into two classes. In one, the core states are included explicitly. A well-known example is Austin's pseudopotential,[2] V_A^{ps}, which is defined by

$$V_A^{ps}|\phi\rangle = V_a|\phi\rangle - \sum_c \langle\psi_c|V_a|\phi\rangle|\psi_c\rangle \qquad (1.1)$$

for an arbitrary ket $|\phi\rangle$. Here, as in the rest of the paper, we denote the spatial one-electron core states by $|\psi_c\rangle$, and the atomic-core potential operator by V_a.

Another well-known example of this class is the Philip and Kleinman[3] pseudopotential, which is defined by

$$V_{PK}^{ps}|\phi\rangle = V_a|\phi\rangle + \sum_c (E - E_c)\langle\psi_c, \phi\rangle|\psi_c\rangle \qquad (1.2)$$

for arbitrary $|\phi\rangle$. Here E is the energy of the state $|\phi\rangle$ and E_c are the core energy levels.

For both of these, an exact form of V_a has to be known. In actual applications, V_a is usually taken as the HF potential, neglecting correlation and other minor effects. Even in this approximation, the solution of the pseudoeigenequation is by no means easy, especially in the solid case.

In the other class, it is assumed that the pseudopotential has some simple analytic form, with pa-