Raman scattering of light by polaritons in thin films; surface polaritons and size effects

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(Received 2 September 1975)

In this paper, we present a general theory of Raman scattering of light by polaritons in thin films. We consider both forward and back scattering of light from a film laid on a transparent substrate. With the assumption that the light couples with polaritons in the film via the Raman tensor and electro-optic coupling within the film, we relate the Raman cross section to the spectral density of the electic field fluctuations in the film. The spectral density functions are constructed from electromagnetic Green's functions derived previously. Our expressions for the Raman cross section describe scattering by volume LO phonons, by volume TO polaritons, and by surface polaritons associated with the substrate-film-vacuum structure. We apply the general formulas to simple special cases, and examine the form of the cross section for both forward and back scattering from surface polaritons, along with the nature of size-dependent corrections to the cross sections for scattering from volume excitations. We present numerical calculations of the shape of the cross section for both forward and back scattering from the film. We also discuss a number of qualitative features of the scattering process, such as the origin of the large forward-backward asymmetry in the surface-polariton cross.

I. INTRODUCTION

There is currently active interest in the study of the surface polaritons which propagate along the interface between two dielectric media. A surface polariton is an electromagnetic wave which propagates along the interface, under a variety of conditions.[1] The electromagnetic fields associated with the surface polariton decay to zero exponentially as one moves away from the interface into either medium.

For the simple case of the plane surface between vacuum and a lossless isotropic dielectric, surface polaritons may propagate wherever the (frequency dependent) dielectric constant $\epsilon(\Omega)$ is negative. For an insulator or semiconductor with a single infrared-active TO phonon, the dielectric constant is negative between the TO and LO phonon frequency. Thus, the modes exist at infrared frequencies. While the conditions that must be met for surface polaritons to propagate are less simple for more complex interface configurations,[1] these modes exist at infrared frequencies for many interesting physical situations.

Quite generally, at the interface between a dielectric and vacuum, the dispersion relation of the surface polariton requires $cQ_{\parallel} > \Omega$, where c is the vacuum velocity of light, $Q_{\parallel}$ the wave vector of the surface polariton parallel to the surface, and Ω its frequency. This condition is required for the electromagnetic field of the wave to decay to zero exponentially as one moves away from the interface into the vacuum. Because $cQ_{\parallel} > \Omega$, one cannot couple to the surface polariton via a linear coupling to a plane electromagnetic wave incident from the vacuum onto a smooth plane interface.

Two methods have been used widely either to generate surface polaritons, or to study their dispersion relation. One is the method of attenuated total reflection (ATR), in which a prism is used to upshift the wave vector of the incident electromagnetic wave,[2] and energy is transferred to the surface polariton across a gap between the prism and the sample under study. A second is the use of a grating ruled on the surface. While both methods of studying these modes have proved most useful, in each case the method of coupling to the mode perturbs the surface on which the mode propagates.

Since surface polaritons are elementary excitations of bounded media, they must appear in the Raman spectra of the system, as Ruppin and Englmann have pointed out.[3] A number of experimental investigators have searched without success for surface polaritons in the Raman spectrum of light *back scattered* from semi-infinite materials opaque to the incident radiation. The first successful experimental study of surface polaritons by Raman spectroscopy was reported by Evans, Ushioda, and McMullen.[4] These authors examined the Raman spectrum of light scattered from a GaAs film 2500 Å thick on a sapphire substrate. The sapphire substrate was transparent to the incident radiation and, in contrast to earlier studies, the experiment examined light scattered in the near *forward direction* with the laser beam incident through the sapphire substrate.[5]

In a previous publication,[6] we presented a quantitative theory of the surface polariton line intensity which explained the very large forward-backward asymmetry observed experimentally, and which provides an excellent account of the line intensities observed by Evans *et al.* in the near for-

ward direction.

The purpose of the present paper is to present a detailed discussion of the Raman scattering of light from polaritons (both volume and surface) in a thin film placed on a substrate transparent to the incident and scattered radiation. We consider both forward and back scattering intensities within the framework of a Green's-function method that allows study of line shapes as well as line intensities. Our earlier results, which focused on the integrated intensity of the surface polariton line, emerge as a special limit of the present analysis. Our previous paper provided a quantitative theory of the line intensities, as remarked above. Here, we confine our attention first to the task of obtaining a general expression for the shape and intensity of the frequency spectrum of light forward scattered or back scattered from the film. We then apply the formula to a special case which allows us to explore many features of the general result by analytic methods: we consider plane polarized radiation normally incident on a film of zinc-blende structure material with (100) surfaces, and examine the spectrum of radiation scattered near the normal to the film. After we discuss a number of features of the spectrum of scattered light by analytic methods, we present numerical calculations of the shape of the spectrum. In addition to lines associated with scattering from surface polaritons in the spectrum, we find that the intensities of the volume LO phonon and volume TO polaritons are size dependent.

The method we use is an extension of an earlier description of the back scattering of light from a semi-infinite opaque material.[7] We require the scattered fields outside the film produced by fluctuations $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ of the dielectric tensor of the film. The electromagnetic Green's functions required to relate the scattered field to $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ have been constructed for use in a different context.[8] We then relate $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ to the amplitude of the thermodynamic fluctuations of the electric field in the film. The cross section for Raman scattering may be related to certain spectral densities of the electric field; these spectral densities may be constructed from the same Green's functions that enter the description of the scattering process.

While this work was in its final stages, we have learned that Nkoma has also analyzed the spectrum of light scattered from surface polaritons in a three-layer geometry by extending the method used earlier by Nkoma and Loudon.[9] They employ a response function method mathematically equivalent to our Green's-function method. The two methods produce identical results, if the problem is fully solved with either method.[10] We believe the description presented here is more complete than that of Nkoma and Loudon. They examine only the contribution to the spectrum from surface polaritons, while here in addition we explore size-dependent corrections to the volume excitation (LO phonons and TO polariton) line intensities. Also, our treatment gives a more complete description of the interaction between the incident radiation, and the excitations in the film, in a sense described below.

II. GENERAL THEORETICAL DISCUSSION

We wish to analyze the Raman-scattering geometry illustrated in Fig. 1. One has a film of thickness d laid down upon a substrate. The dielectric constant of the film ϵ_1 and that of the substrate ϵ_2 are both isotropic, frequency dependent, and complex. Light is incident upon the film either from the vacuum above the film, or through the substrate under the film. Only the latter case, the configuration employed in the experiments of Ushioda and co-workers, is illustrated in the figure. We assume the substrate is transparent to the incident radiation, while (as for GaAs illuminated by the Ar ion laser), the film may be strongly absorbing. In the experiments performed by the Ushioda group, the sapphire substrate is transparent while the film was two or three optical-absorption lengths thick. The film is also surface active, in the sense that $\mathrm{Re}(\epsilon_1(\Omega))$ may be negative for frequencies Ω in the range of frequency shifts encountered in the Raman experiment. Our treatment makes no assumption about the behavior of $\epsilon_2(\Omega)$, but in the special cases

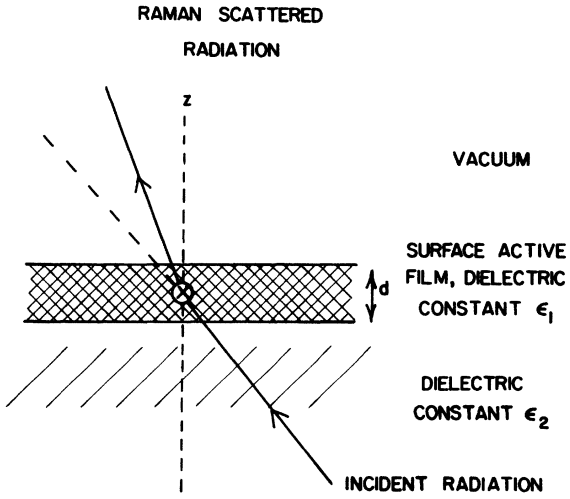

FIG. 1. Configuration analyzed in the text. One has a surface-active film of thickness d, and the incident radiation is Raman scattered into the vacuum above the crystal through coupling to fluctuations in the film. While the figure shows the incident radiation strikes the film from below, the discussion in the text considers in addition the case where the incident radiation strikes the film incident from the vacuum.

considered below we suppose $\mathrm{Re}(\epsilon_2(\Omega))>0$.

The calculation of the scattered fields will proceed along lines very similar to discussions presented elsewhere.[7,9,11,12] As a consequence, the initial discussion here will be schematic in nature.

If we wish to examine the scattering of the incident radiation by fluctuations within the film illustrated in Fig. 1, then if the incident radiation "sees" the fluctuations through their effect on the dielectric tensor of the film, we solve Maxwell's equations in the presence of the dielectric function

$$\epsilon_{\mu\nu}(\vec{x}, t) = \delta_{\mu\nu}\epsilon(z) + \delta\epsilon_{\mu\nu}(\vec{x}, t) , \tag{2.1}$$

where $\epsilon(z)$ is the dielectric function of the structure in the absence of fluctuations, and $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ is nonzero only within the film. In general, the fluctuation will lower the symmetry of the film, so $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ is a tensor quantity. As remarked in Sec. I, in this paper, we presume the incident electromagnetic wave couples to the fluctuations only when it is within the film. The method used here may be extended to a more general description of the scattering process. In another paper, we have presented a discussion of the case where the film is a Raman-inactive medium, and the interaction responsible for the Raman scattering takes place within the substrate.[11]

For $\epsilon(z)$, from Fig. 1 we have

$$\epsilon(z) = \begin{cases} 1 & d<z<\infty , \\ \epsilon_1 & 0<z<d , \\ \epsilon_2 & -\infty<z<0 . \end{cases} \tag{2.2}$$

To calculate the scattered fields that contribute to the first-order Raman spectrum, one solves Maxwell's equations to first order in $\delta\epsilon_{\mu\nu}(\vec{x}, t)$, under the presumption that when $\delta\epsilon_{\mu\nu}(\vec{x}, t)$ vanishes the solution is just the incident field $\vec{E}^{(0)}(\vec{x}, t)$. The procedure is quite analogous to the first Born approximation of quantum-mechanical scattering theory.

To derive the form of the scattered fields, as explained in the earlier works cited above, one introduces a Green's function $D_{\mu\nu}(\vec{x}\vec{x}'; t-t')$ of Maxwell's equations and its Fourier transform

$$D_{\mu\nu}(\vec{x}\vec{x}'; t-t') = \int \frac{d\omega}{2\pi} D_{\mu\nu}(\vec{x}\vec{x}'; \omega)\, e^{-i\omega(t-t')} , \tag{2.3}$$

where $D_{\mu\nu}(\vec{x}, \vec{x}'; \omega)$ satisfies

$$\sum_\lambda \left(\frac{\omega^2}{c^2}\epsilon(z, \omega)\delta_{\mu\lambda} - \frac{\partial^2}{\partial x_\mu \partial x_\lambda} + \delta_{\mu\lambda}\nabla^2 \right) D_{\lambda\nu}(\mathrm{x}\mathrm{x}'; \omega) = 4\pi\delta_{\mu\nu}\delta(\vec{\mathrm{x}} - \vec{\mathrm{x}}') . \tag{2.4}$$

In Eq. (2.4), the frequency dependence of $\epsilon(z)$ has been explicitly indicated. These differential equations are to be solved subject to the outgoing wave boundary conditions of scattering theory. For the geometry under consideration, the explicit form of $D_{\mu\nu}(\vec{x}\vec{x}'; \omega)$ has been derived in an earlier paper.[8] We quote the results in Appendix A of the present paper.

With the Green's functions introduced above, the expression for the scattered electric field becomes[8,12,13]

$$E_\alpha^{(s)}(\mathrm{x}, t) = \left(\frac{\omega_0}{c}\right)^2 \sum_{\beta\gamma} \int \frac{d^3x'\, dt'}{4\pi} D_{\alpha\beta}(\vec{x}\vec{x}'; t-t')\delta\epsilon_{\beta\gamma}(\vec{x}', t')E_\gamma^{(0)}(\vec{x}'t') . \tag{2.5}$$

In Eq. (2.5), $E_\gamma^{(0)}(\vec{x}'t')$ is the γth Cartesian component of the electric field of the incident radiation, the integration over z' ranges from 0 to d, and ω_0 is the frequency of the incident radiation.[14]

We require the intensity of the scattered radiation. The intensity of the scattered radiation (i.e., the Poynting vector) is readily calculated once the square $|\vec{E}^{(s)}(\vec{x}t)|^2$ is known either in the vacuum above the film, or within the substrate. The calculation of the square of the scattered field is straightforward, and follows readily from Eq. (2.5). The quantity we require is $\langle|\vec{E}^{(s)}(\vec{x}, t)|^2\rangle$, where the angular brackets denote a statistical average over the fluctuations in the dielectric tensor. We write the Green's function in the form

$$D_{\mu\nu}(\vec{x}\vec{x}'; t-t') = \int \frac{d^2k_\parallel\, d\omega_s}{(2\pi)^3} e^{i\vec{k}_\parallel\cdot(\vec{x}_\parallel - \vec{x}_\parallel')} e^{-i\omega_s(t-t')} \times d_{\mu\nu}(\vec{k}_\parallel\omega_s | zz') \tag{2.6}$$

and we note that after the statistical average is performed, the correlation function

$$\langle \delta\epsilon_{\beta'\gamma'}(\vec{x}'t')\delta\epsilon_{\beta\gamma}(\vec{x}t)\rangle \tag{2.7}$$

is necessarily a function only of $t-t'$, and $\vec{x}_\parallel - \vec{x}_\parallel'$, although it depends on z and z' separately. Furthermore, we let $\vec{k}_\parallel^{(0)}$ be the projection of the wave vector of the incident radiation on the plane parallel to the film surface, and write

$$E_\gamma^{(0)}(\vec{x}t) = e^{i(\vec{k}_\parallel^{(0)}\cdot\vec{x}_\parallel - \omega_0 t)} E_\gamma^{(0)}(\vec{k}_\parallel^{(0)}\omega_0 | z') . \tag{2.8}$$

It is then a straightforward matter to show that

$$\langle|\vec{E}^{(s)}(\vec{x}t)|^2\rangle = \left(\frac{\omega_0}{c}\right)^4 \sum_\alpha \sum_{\beta\beta'} \sum_{\gamma\gamma'} \int_0^d \frac{dz'\, dz''}{16\pi^2} E_\gamma^{(0)}(k_\parallel^{(0)}\omega_0 | z')E_\gamma^{(0)}(k_\parallel^{(0)} | z'')^* \int d^2k_\parallel\, d\omega_s\, d_{\alpha\beta'}^*(\vec{k}_\parallel\omega_s | zz'')\, d_{\alpha\beta}(\vec{k}_\parallel\omega_s | zz') \times \int \frac{d^2x_\parallel'\, dt''}{(2\pi)^3} e^{i\Omega t''} e^{-i\vec{Q}_\parallel\cdot\vec{x}_\parallel'} \langle \delta\epsilon_{\beta'\gamma'}(x_\parallel'z'', t'')\delta\epsilon_{\beta\gamma}(0z', 0)\rangle . \tag{2.9}$$

In Eq. (2.9) we have defined

$$\vec{Q}_{\parallel} = \vec{k}_{\parallel}^{(0)} - \vec{k}_{\parallel} \tag{2.10a}$$

and

$$\Omega = \omega_0 - \omega_s \, . \tag{2.10b}$$

The quantity Ω will be the frequency shift of the scattered radiation, and $\vec{Q}_{\parallel}$ the change in wave vector projected onto the xy plane. Our task is now to reduce the expression in Eq. (2.9) to manageable form. To proceed, we require the form of the correlation function which involves $\delta\epsilon_{\beta\gamma}(\vec{x}, t)$.

If we let $u_\alpha(\vec{x}, t)$ be the relative displacement of the ions in the unit cell and $\mathcal{E}_\alpha(\vec{x}, t)$ the electric field set up by the ion motion, then we write

$$\delta\epsilon_{\beta\gamma}(\vec{x}\,t) = \sum_\delta b_{\beta\gamma\delta}\mathcal{E}_\delta(\vec{x}, t) + \sum_\delta a_{\beta\gamma\delta}u_\delta(\vec{x}, t) \, , \tag{2.11}$$

where $b_{\beta\gamma\delta}$ is the electro-optic coefficient of the film, and the term proportional to $u_\delta(\vec{x}, t)$ describes the modulation of the dielectric tensor by atomic displacements of optical character. In Eq. (2.11), we can eliminate $u_\delta(\vec{x}, t)$ in favor of $\mathcal{E}_\delta(\vec{x}, t)$. If $\vec{P}_L(\vec{x}, \Omega)$ is the lattice contribution to the dipole moment per unit volume with frequency Ω, then

$$\vec{P}_L(\vec{x}, \Omega) = ne^*\vec{u}(\vec{x}, \Omega) \, , \tag{2.12}$$

where n is the number of unit cells/unit volume and e^* the transverse effective charge. If ϵ_1^∞ is the high-frequency dielectric constant of the film, we have also

$$\vec{P}_L(\vec{x}, \Omega) = (1/4\pi)[\epsilon_1(\Omega) - \epsilon_1^\infty]\vec{\mathcal{E}}(\vec{x}, \Omega) \, , \tag{2.13a}$$

so we may write

$$\vec{u}_L(\vec{x}, \Omega) = (1/4\pi ne^*)[\epsilon_1(\Omega) - \epsilon_1^\infty]\vec{\mathcal{E}}\,(\vec{x}, \Omega) \, . \tag{2.13b}$$

If we then define an effective electro-optic coefficient which contains a lattice contribution

$$\tilde{b}_{\beta\gamma\delta}(\Omega) = b_{\beta\gamma\delta} + \left(\frac{\epsilon_1(\Omega) - \epsilon_1^\infty}{4\pi ne^*}\right)a_{\beta\gamma\delta} \, , \tag{2.14}$$

one has the identity

$$\int \frac{dt'\, e^{i\Omega t'}}{2\pi}\langle\delta\epsilon_{\beta'\gamma'}(\vec{x}'t')\delta\epsilon_{\beta\gamma}(\vec{x}, 0)\rangle = \sum_{\delta\delta'}\tilde{b}^*_{\beta'\gamma'\delta'}(\Omega)b_{\beta\gamma\delta}(\Omega) \times \int \frac{dt'}{2\pi}\langle\mathcal{E}_{\delta'}(\vec{x}'t')\mathcal{E}_\delta(\vec{x}0)\rangle\, e^{i\Omega t'} . \tag{2.15}$$

We now define a spectral density function for electric field fluctuations in the film via the relation

$$[1 + n(\Omega)]\mathfrak{D}_{\delta'\delta}(\vec{Q}_{\parallel}\Omega; z''z') = \int d^2x_{\parallel}\, dt\, e^{i\Omega t}\, e^{-i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}} \times\langle\mathcal{E}_{\delta'}(\vec{x}_{\parallel}z'', t)\mathcal{E}_\delta(0z', 0)\rangle \, , \tag{2.16}$$

where $n(\Omega) = [\exp(\hbar\Omega/k_BT) - 1]^{-1}$ is the Bose-Einstein function, to write the intensity of the scattered field in the form

$$\langle|\vec{E}^{(s)}(\vec{x}, t)|^2\rangle = \left(\frac{\omega_0}{c}\right)^4\sum_\alpha\sum_{\substack{\beta\beta'\\\gamma\gamma'}}\sum_{\delta\delta'}\int_0^d \frac{dz'\, dz''}{16\pi^2}E_\gamma^{(0)}(k_{\parallel}^{(0)}\omega_0|\, z')E_{\gamma'}^{(0)}(k_{\parallel}^{(0)}\omega_0|\, z'')^* \times\int\frac{d^2k_{\parallel}\, d\omega_s}{(2\pi)^3}d^*_{\alpha\beta'}(\vec{k}_{\parallel}\omega_s|\, zz'')\, d_{\alpha\beta}(\vec{k}_{\parallel}\omega_s|\, zz')\tilde{b}^*_{\beta'\gamma'\delta'}(\Omega)\tilde{b}_{\beta\gamma\delta}(\Omega)[1 + n(\Omega)]\mathfrak{D}_{\delta'\delta}(\vec{Q}_{\parallel}\Omega; zz') \, . \tag{2.17}$$

To conclude the general discussion, we require a prescription which enables us to construct the spectral density function which appears in Eq. (2.17). We discuss the method by which this may be done in Appendix B. In fact, the spectral density function is readily related to precisely the same Green's function $d_{\alpha\beta}(\vec{k}_{\parallel}\omega|\, zz')$ that entered our scattering theory, as Abrikosov, Gor'kov, and Dzaloshinskii have shown.[15] The prescription that emerges is remarkably simple:

$$\mathfrak{D}_{\delta'\delta}(\vec{Q}_{\parallel}\Omega; zz') = (\Omega^2/ic^2)[d_{\delta'\delta}(\vec{Q}_{\parallel}, \Omega - i\eta|\, zz') - d_{\delta'\delta}(\vec{Q}_{\parallel}, \Omega + i\eta|\, zz')] \, . \tag{2.18}$$

Thus, once we are given the Green's functions tabulated in Appendix A, the spectral density functions which enter Eq. (2.17) are readily constructed. We prove Eq. (2.18) in Appendix B, and we call the readers attention to the useful relation displayed in Eq. (C8) of Appendix C.

The expression in Eq. (2.17) may be used to calculate the intensity of the scattered field in the vacuum above the film, within the film itself, or in the substrate below the film, for an incident field of general angle of incidence and polarization. We confine our attention here to the radiation scattered into the vacuum above the film. For $z > d$, after consulting Appendix A we have

$$d_{\alpha\beta}(\vec{k}_{\parallel}\omega_s|\, zz') = 4\pi\, e^{ik_{0z}z}\epsilon^<_{\alpha\beta}(\vec{k}_{\parallel}\omega_s|\, z') \, , \tag{2.19}$$

where

$$\epsilon^<_{\alpha\beta}(\vec{k}_{\parallel}\omega_s|\, z') = \sum_{\mu\nu}S_{\alpha\mu}(\vec{k}_{\parallel})S_{\beta\nu}(\vec{k}_{\parallel})\Gamma_{\mu\nu}(\vec{k}_{\parallel}\omega_s)E^<_\nu(\vec{k}_{\parallel}\omega_s|\, z') \, , \tag{2.20}$$

with the matrix $\Gamma_{\mu\nu}(\vec{k}_{\parallel}\omega_s)$ defined by

$$\Gamma_{\mu\nu}(\vec{k}_{\parallel}\omega)=\begin{pmatrix} -\dfrac{k_0}{k_{\parallel}W_{\parallel}(k_{\parallel}\omega)} & 0 & +\dfrac{k_0}{k_{\parallel}W_{\parallel}(k_{\parallel}\omega)} \\ 0 & \dfrac{1}{W_{\perp}(k_{\parallel}\omega)} & 0 \\ \dfrac{1}{W_{\parallel}(k_{\parallel}\omega)} & 0 & -\dfrac{1}{W_{\parallel}(k_{\parallel}\omega)} \end{pmatrix}. \tag{2.21}$$

We may now form an expression for the frequency and angular distribution of the power radiated into the vacuum above the film. The time average of the total scattered power at a point in space is

$$\langle P^{(s)}\rangle=(c/8\pi)\langle|E^{(s)}|^2\rangle, \tag{2.22}$$

and from Eq. (2.17) the contribution to $\langle P^{(s)}\rangle$ from scattered radiation in the frequency interval between ω_s and $\omega_s+d\omega_s$, and with scattered wave vectors $\vec{k}_s$ which have a projection onto the xy plane in the phase-space element $d^2k_{\parallel}$ is given by

$$\frac{d^2P^{(s)}}{d\omega_s d^2k_{\parallel}}=\frac{\omega_0^4}{8\pi(2\pi)^3c^3}[1+n(\Omega)]\sum_{\alpha}\sum_{\substack{\beta\beta'\\ \gamma\gamma'}}\sum_{\delta\delta'}\bar{b}_{\beta\gamma\delta}(\Omega)\bar{b}^{*}_{\beta'\gamma'\delta'}(\Omega)$$
$$\times\int_0^d dz'\,dz''\,E_{\gamma}^{(0)}(\vec{k}_{\parallel}^{(0)}\omega_0|z')\epsilon^{<}_{\alpha\beta}(\vec{k}_{\parallel}\omega_s|z')E_{\gamma'}^{(0)}(\vec{k}_{\parallel}^{(0)}\omega_0|z'')^{*}\epsilon^{<}_{\alpha\beta'}(\vec{k}_{\parallel}\omega_s|z'')^{*}\mathfrak{D}_{\delta'\delta}(\vec{Q}_{\parallel}\Omega;z''z'). \tag{2.23}$$

We may calculate the distribution of scattered radiation directed into the solid angle $d\Omega(\hat{k}_s)$ by multiplying Eq. (2.22) by the ratio[7]

$$\frac{d^2k_{\parallel}}{d\Omega(\hat{k}_s)}=\left(\frac{\omega_0}{c}\right)^2\cos\theta_s. \tag{2.24}$$

Thus, our final expression for the distribution in angle and frequency of the scattered radiation is

$$\frac{d^2P^{(s)}}{d\omega_s d\Omega(\hat{k}_s)}=\frac{\omega_0^6\cos\theta}{64\pi^4c^5}[1+n(\Omega)]\sum_{\alpha}\sum_{\substack{\beta\beta'\\ \gamma\gamma'}}\sum_{\delta\delta'}\bar{b}_{\beta\gamma\delta}(\Omega)\bar{b}_{\beta'\gamma'\delta'}(\Omega)^{*}$$
$$\times\int_0^d dz'\,dz''\,E_{\gamma}^{(0)}(\vec{k}_{\parallel}^{(0)}\omega_0|z')\epsilon^{<}_{\alpha\beta}(\vec{k}_{\parallel}\omega_0|z')E_{\gamma'}^{(0)}(\vec{k}_{\parallel}^{(0)}\omega_0|z'')^{*}\epsilon^{<}_{\alpha\beta'}(\vec{k}_{\parallel}\omega_s|z'')^{*}\mathfrak{D}_{\delta'\delta}(\vec{Q}_{\parallel}\Omega;z''z'). \tag{2.25}$$

This expression gives the distribution in frequency and angle of the radiation scattered above the film, for an incident field of arbitrary direction and polarization. Thus, this one expression may be used to calculate both the forward and the back scattering intensities; in the former case (the configuration used by Ushioda and co-workers) the radiation is incident on the film through the substrate, and in the latter case the radiation strikes the film incident from the vacuum. In both cases, the Raman radiation is detected and studied in the vacuum above the film.

The expression in Eq. (2.24) may be converted into a scattering efficiency by dividing the expression by the power per unit area incident on the film. For the case of back scattering, the power per unit area incident on the film is

$$P_B^{(0)}=(c/8\pi)|E^{(0)}|^2\cos\theta_0, \tag{2.26}$$

where $E^{(0)}$ is the amplitude of the incident field and θ_0 the angle of incidence. For forward scattering, with the substrate presumed transparent at the incident frequency,

$$P_F^{(0)}=(c/8\pi)[\epsilon_2(\omega_0)]^{1/2}|E^{(0)}|^2\cos\theta_0, \tag{2.27}$$

where $E^{(0)}$ is the amplitude of the incident field, measured in the substrate.

The result in Eq. (2.25) is the principal result of the present general discussion. While the expression on the right-hand side is compact in appearance and its application straightforward, one is lead quickly to extremely lengthy and complicated expressions when this is done. As a consequence, we confine our attention in the remainder of the paper to application of Eq. (2.25) to a simple special case. This will lead us to appreciate the physical content of the general expression. We turn to the more quantitative applications in Sec. IV.

III. APPLICATION OF GENERAL RESULTS TO SPECIAL CASE

We now apply the result in Eq. (2.24) to a particular special case. We examine the following scattering configuration:

(i) We suppose the incident field is plane polarized in the $\hat{y}$ direction, and is normally incident on the film. Then

$$E_{\gamma}^{(0)}(k_{\parallel}^{(0)}\omega_0|z')=\delta_{\gamma y}E^{(0)}(\omega_0|z'), \tag{3.1}$$

where for normal incidence, $\vec{k}_{\parallel}^{(0)}=0$ and $\vec{k}_{\parallel}\equiv\vec{Q}_{\parallel}$.

(ii) We presume the film to be a crystalline film of zinc-blende structure material, with (100)

surfaces. Then for this case, we have

$$\alpha_{\beta\gamma\delta} = \alpha |\epsilon_{\beta\gamma\delta}| , \tag{3.2}$$

$$b_{\beta\gamma\delta} = b |\epsilon_{\beta\gamma\delta}| , \tag{3.3}$$

and as a consequence

$$\tilde{b}_{\beta\gamma\delta}(\Omega) = \tilde{b}(\Omega) |\epsilon_{\beta\gamma\delta}| , \tag{3.4}$$

where in these expressions, $|\epsilon_{\beta\gamma\delta}|$ is the absolute magnitude of the Levi-Civita tensor, i.e., $|\epsilon_{\beta\gamma\delta}|$ vanishes if any two incidences are equal, and assumes the value $+1$ when $\beta \neq \gamma \neq \delta$.

(iii) We confine our attention to the scattered radiation which emerges very close to the normal to the film. For forward scattering, this means we examine the region of small-angle scattering, and for back scattering, we examine the scattered radiation which emerges very near the specular direction. The extension to the case of large angle scattering is straightforward, but this assumption greatly simplifies the exposition of the present section.

For incidence radiation polarized along $\hat{y}$, and scattered radiation emerging very near the normal to the film, the nature of the Raman tensor and electro-optic coefficient requires the scattered radiation to be polarized along $\hat{x}$, and only electric field fluctuations in the film parallel to the normal are able to produce scattered fields. Thus, assumption (iii) when combined with (i) and (ii) enable us to replace Eq. (2.24) by the much simpler expression

$$\frac{d^2P^{(s)}}{d\omega_s d\Omega(\hat{k}_s)} = \frac{\omega_0^6 \cos\theta_s (1+n(\Omega))}{64\pi^4 c^5} |\tilde{b}(\Omega)|^2 \int_0^d dz'\, dz''\, E^{(0)}(\omega_0 | z') E^{(0)}(\omega_0 | z'')^* \times \left(\sum_\alpha \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z') \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z'')^* \right) \mathcal{D}_{zz}(\vec{Q}_\parallel \Omega, z'' z') , \tag{3.5}$$

where for incident radiation at normal incidence, one has $\vec{k}_\parallel = \vec{Q}_\parallel$.

After some algebra, with

$$\frac{Q_x}{Q_\parallel} = \cos\varphi_s \quad \text{and} \quad \frac{Q_y}{Q_\parallel} = \sin\varphi_s ,$$

one finds

$$\sum_\alpha \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z') \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z'')^* = \frac{\omega_s^2 \sin^2\varphi_s}{c^2 Q_\parallel^2 |W_\parallel(Q_\parallel, \omega_s)|^2} E^<_x(\vec{Q}_\parallel \omega_s | z') E^<_x(\vec{Q}_\parallel \omega_s | z'')^* + \frac{\cos^2\varphi_s}{|W_\perp(Q_\parallel, \omega_s)|^2} E^<_y(\vec{Q}_\parallel \omega_s | z') E^<_y(\vec{Q}_\parallel \omega_s | z'')^* . \tag{3.6}$$

As long as we examine scattered radiation which emerges close to the film normal, then to a good approximation we may set $\vec{Q}_\parallel$ to zero in $W_\parallel$ and $W_\perp$ that appears in Eq. (3.6). Then one has

$$|W_\perp(0, \omega_s)|^2 = (\omega_s^2/c^2) |d_\perp(\omega_s)|^2 , \tag{3.7a}$$

and for small $Q_\parallel$,

$$|W_\parallel(0, \omega_s)|^2 = \frac{\omega_s^6 |\epsilon_2|}{c^6 Q_\parallel^4} |d_\perp(\omega_s)|^2 , \tag{3.7b}$$

where

$$d_\perp(\omega_s) = (1+\sqrt{\epsilon_2}) \cos\left(\frac{\omega_s}{c}\sqrt{\epsilon_1}\, d\right) - i\left(\frac{\sqrt{\epsilon_2}}{\sqrt{\epsilon_1}} + \sqrt{\epsilon_1}\right) \sin\left(\frac{\omega_s}{c}\sqrt{\epsilon_1}\, d\right) . \tag{3.8}$$

In the same spirit, we may also let $\vec{Q}_\parallel \to 0$ in the factors $C_+^{(\perp)}$, $C_-^{(\perp)}$, $C_+^{(\parallel)}$, $C_-^{(\parallel)}$ which appear in $E^<_x$ and $E^>_x$. When this is done, then we find

$$\sum_\alpha \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z') \epsilon^<_{\alpha x}(\vec{Q}_\parallel \omega_s | z'')^* \cong \frac{c^2}{\omega_s^2} \frac{E^<(\omega_s | z') E^<(\omega_s | z'')^*}{|d_\perp(\omega_s)|^2} , \tag{3.9}$$

where

$$E^<(\omega_s | z) = \frac{1}{2}\left(1 + \frac{\sqrt{\epsilon_2}}{\sqrt{\epsilon_1}}\right) e^{ik_1^{(s)} z} + \frac{1}{2}\left(1 - \frac{\sqrt{\epsilon_2}}{\sqrt{\epsilon_1}}\right) e^{-ik_1^{(s)} z} , \tag{3.10}$$

where $k_1^{(s)}$ is the z component of scattered radiation in the film, chosen such that $\mathrm{Im}(k_1^{(s)}) < 0$, as described in Appendix A.

If we ignore the difference between ω_0 and ω_s in the prefactor of the expression for the scattered power as we have before, then Eq. (3.5) becomes

$$\frac{d^2P^{(s)}}{d\omega_s d\Omega(\hat{k}_s)} = \frac{\omega_0^4 \cos\theta_s (1+n(\Omega))}{64\pi^4 c^3} \frac{|\tilde{b}(\Omega)|^2}{|d_\perp(\omega_s)|^2} \times \int_0^d dz\, dz'\, E^{(0)}(\omega_0|\, z') E^{(0)}(\omega_0|\, z'')^* E^<(\omega_s|\, z') E^<(\omega_s|\, z'')^* \mathcal{D}_{zz}(\vec{Q}_\parallel \Omega, z'' z') \,. \tag{3.11}$$

There is one more simplification of Eq. (3.11) that is useful. The relation between $\mathcal{D}_{zz}(\vec{Q}_\parallel \Omega; zz')$ and $d_{zz}(\vec{Q}_\parallel \Omega \pm i\eta|\, zz')$ is stated in Eq. (2.18). Furthermore, from Eq. (C8) of Appendix C, we have

$$d_{zz}(\vec{Q}_\parallel, \Omega - i\eta|\, zz') = d^*_{zz}(\vec{Q}_\parallel, \Omega + i\eta|\, z'z) \,. \tag{3.12}$$

When Eq. (3.12) is combined with the observation that $d_{zz}(\vec{Q}_\parallel, \Omega - i\eta|\, zz')$ is left unchanged upon interchanging z and z', then Eq. (3.11) becomes

$$\frac{d^2P^{(s)}}{d\omega_s d\Omega(\hat{k}_s)} = \frac{\omega_0^4 \cos\theta_s (1+n(\Omega))}{16\pi^3 c^3} \frac{|\tilde{b}(\Omega)|^2}{|d_\perp(\omega_s)|^2} \frac{1}{i} \times \mathrm{Im}\left(\int_0^d dz\, dz'\, E^{(0)}(\omega_0|\, z) E^<(\omega_s|\, z) E^{(0)}(\omega_0|\, z')^* E^<(\omega_s|\, z')^* A_{zz}(Q_\parallel, \Omega + i\eta, zz') \right) , \tag{3.13}$$

where we have introduced

$$A_{zz}(\vec{Q}_\parallel, \Omega, zz') = \frac{\delta(z-z')}{\epsilon_1(\Omega)} - \frac{\Omega^2}{c^2 W_\parallel(Q_\parallel, \Omega)} [E^>_x(Q_\parallel \Omega|\, z) E^<_x(Q_\parallel \Omega|\, z') \theta(z-z') + E^<_x(Q_\parallel \Omega|\, z) E^>_x(Q_\parallel \Omega|\, z') \theta(z'-z)] \,. \tag{3.14}$$

While the expression in Eq. (3.13) is very much simpler than the general form in Eq. (2.24), nonetheless it retains all of the essential features of the general result. Note that we can apply Eq. (3.13) to either the analysis of forward or backward scattering, within the framework of assumptions (i) through (iii) stated at the beginning of the present section. The two cases differ only by the incident field that is to be inserted into Eq. (3.13).

We next turn to an anlysis of the structure of the right-hand side of Eq. (3.13). For definiteness, consider the case of near forward scattering of radiation incident on the film from below. Then the incident field has the form

$$E^{(0)}(\omega_0|\, z) = T^{(0)}_{21} [e^{-ik_1^{(0)}(z-d)} + R^{(0)}_{10} e^{+ik_1^{(0)} z}] \,, \tag{3.15}$$

where with our convention $\mathrm{Im}(k_1) < 0$, the first term describes the component of the incident wave in Eq. (3.15). We assume the incident field has unit amplitude [given by $\exp(-ik_2^{(0)} z)$] in the substrate below the film. Then in Eq. (3.15), $T^{(0)}_{21}$ is the transmission factor for transmission of the incident wave through the substrate-film interface while $R^{(0)}_{10}$ is the amplitude for reflection of the incident wave off the film-vacuum interface once it has been transmitted through to the film.

Crudely speaking, the integral in Eq. (3.13) has a form similar to the square of a matrix element which involves an effective interaction sandwiched between an incident state $E^{(0)}(\omega_0|\, z)$ and a final state $E^<(\omega_s|\, z)$. There are four terms in the product $E^{(0)}(\omega_0|\, z) E^<(\omega_s|\, z)$, and each term may be represented by a diagram, as illustrated in Fig. 2. Alongside each process is the phase factor which enters the contribution to the effective matrix element from the process. Each of the four processes "connects the same initial and final state," to

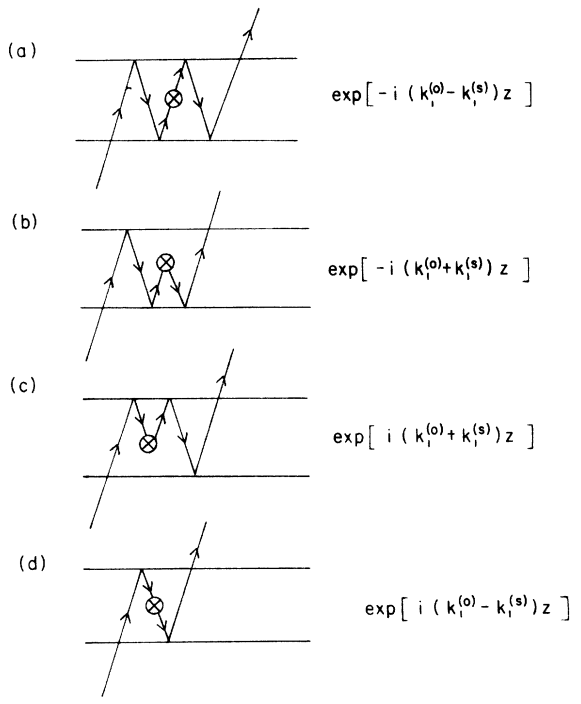

FIG. 2. Four fundamental scattering processes which contribute to the Raman cross section in the near forward direction. Alongside each figure is displayed the phase factors which enter the contribution to the effective matrix element from each processes. The scattering event takes place at the encircled cross.

use language appropriate to quantum-mechanical transition theory. The square of the matrix element contains a total of sixteen terms [the number of terms in $E^{(0)}(\omega_0|z)^*E^<(\omega_s|z)^*E^{(0)}(\omega_0|z')E^<(\omega_s|z')$] as a consequence. Thus, it is indeed a tedious task to evaluate even the greatly simplified expression in Eq. (3.13).

There is one important feature which enters the contribution of each term illustrated in Fig. 2. Two of the diagrams [(a) and (d)] of Fig. 2 describe a process in which the incident photon is *forward* scattered. The contribution to each of these two processes to the effective matrix elements involves an exponential which contains the *difference* between z components of the complex wave vector $k_1^{(0)}$ of the incident and that $k_1^{(s)}$ of the scattered radiation. The remaining two diagrams [(b) and (c)] involve *back scattering* of the radiation, and the effective matrix element involves an exponential with the *sum* of the same two wave vectors. When we discuss the theory of back scattering from the structure shortly, we shall see that the same rule holds there also.

As we have previously emphasized,[6,16] this is the origin of the large forward/back scattering asymmetry in the cross section for scattering from surface polaritons. This asymmetry is responsible for frustrating early attempts to observe surface polaritons in back scattering from thick (effectively semi-infinite) semiconducting samples, while the experiment of Evans, Ushioda, and McMullen in the forward scattering configuration was successful. If one computes $k_1^{(0)}$ and $k_1^{(s)}$ for typical semiconducting materials (GaAs, in particular) for frequencies in the visible, the real part of $k_1^{(0)}$ and $k_1^{(s)}$ is larger than the imaginary part by nearly an order of magnitude. Thus, the phase factor $\exp[i(k_1^{(0)}+k_1^{(s)})z]$ that enters the back scattering matrix element oscillates very rapidly with z, and reduces the back scattering matrix element strongly, compared to the forward scattering matrix element.[5,6] Our quantitative calculations show that for the configuration employed by Evans *et al.*, the intensity for back scattering from surface polaritons is smaller than that for forward scattering by nearly two orders of magnitude. We refer the reader to our earlier work for a quantitative discussion of this point.[6]

To calculate the intensity of back scattering from the structure, instead of the expression in Eq. (3.15), one inserts into the integral of Eq. (3.13) the result

$$E^{(0)}(\omega_0|z) = T_{01}^{(0)}(e^{+ik_1^{(0)}z} + R_{12}^{(0)}e^{-ik_1^{(0)}(z-d)}) . \quad (3.16)$$

The four fundamental scattering processes may be described in terms very similar to those which entered our discussion of the forward scattering case. The processes are illustrated in Fig. 3, along with the phase factors which enter the effective matrix element.

Evaluation of either the forward or the back-scattering intensity with the incident fields given in Eq. (3.15) or Eq. (3.16) leads to lengthy and unwieldy expressions for the scattered intensities. In the experimental studies of Ushioda and coworkers, the surface-active GaAs film has a thickness of roughly three absorption lengths of the incident or scattered radiation. If we confine our attention only to such thick films, then an adequate description that is much simpler may be obtained.

If we consider the case of forward scattering, then when the film is thick compared to the absorption length, the dominant contribution to the cross section comes from Fig. 2(a). The processes in Figs. 2(b) and 2(c) are small compared to the process in Fig. 2(a) because a back scattering event is involved in each case, while the process in Fig. 2(d) requires the radiation to pass through the film at least three times.

When we consider back scattering from a thick film in the sense just described, Fig. 3(a) is the dominant process. While Figs. 3(b) and 3(c) each involve a forward scattering, they each require two passes of the radiation through the film at least, while the scattering process in Fig. 3(a) may occur entirely within the optical skin depth

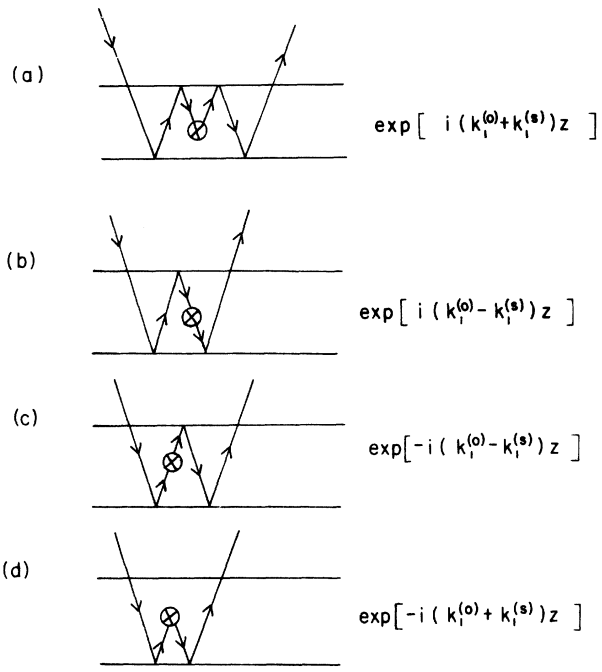

FIG. 3. Four fundamental scattering processes which contribute to the Raman cross section for back scattering. As in Fig. 2, alongside each figure we display the phase factors which control the contribution to the matrix element from each process.

of the upper interface.

In the thick film limit, the remarks above allow us to describe the spectrum by choosing for the incident fields the forms

$$E^{(0)}(\omega_0|z)=\begin{cases} T_{21}^{(0)}\exp(-ik_1^{(0)}z)\,(\text{forward scattering}), \\ T_{01}^{(0)}\exp[+ik_1^{(0)}(z-d)]\,(\text{back scattering}), \end{cases} \tag{3.17a}$$

while we may replace $E^{<}(\omega_s|z)$ by

$$E^{<}(\omega_s|z)=\frac{1}{2}\left(1+\frac{\sqrt{\epsilon_2}}{\sqrt{\epsilon_1}}\right)\exp(ik_1^{(s)}z)\ . \tag{3.17b}$$

In the work reported by Nkoma,[9] it has been assumed early in the discussion that the scattering processes illustrated in Figs. 2(a) and 3(a) play the dominant role. The results that follow may only be applied to analyze spectra from films thick compared to the absorption lengths of the incident and scattered radiation. Since this condition is not met either in thin films, or films transparent to the incident radiation, we have felt it worthwhile to construct explicit formulas that include all possible scattering processes, and may be applied readily to more general situations if desired.

When Eq. (3.17) is inserted into Eq. (3.13), we encounter the factor

$$\left|\frac{1+(\epsilon_2/\epsilon_1)^{1/2}}{\cdot d_\perp(\omega_s)}\right|^2 \equiv \left|\frac{2}{1+\sqrt{\epsilon_1}}\,\frac{1}{1-R_{10}R_{21}\exp[2i(\omega_s/c)\sqrt{\epsilon_1}\,d]}\right|^2 \times\exp\left(-2\,\frac{d}{l_s}\right), \tag{3.18}$$

where

$$R_{10}=(\sqrt{\epsilon_1}-1)/(\sqrt{\epsilon_1}-1) \tag{3.19a}$$

and

$$R_{12}=(\sqrt{\epsilon_1}-\sqrt{\epsilon_2})/(\sqrt{\epsilon_1}+\sqrt{\epsilon_2})\ . \tag{3.19b}$$

In Eq. (3.18), $l_s^{-1}=(\omega_s/c)\,\mathrm{Im}(\sqrt{\epsilon_1})$ is the absorption length of the scattered radiation, and the prefactor, which after here we write as $|T_{10}^{(s)}|^2$, is the amplitude transmitted through the film-vacuum interface of a field of unit strength and wave vector $k_1^{(s)}$ directed toward the interface.

The above ingredients, when combined with Eq. (3.13) and the remarks at the end of Sec. II, enable us to form an expression for the scattering efficiency/unit solid angle/unit frequency interval both back and forward scattering through our model film. We have, with l_0 the attenuation length of the incident beam

$$\frac{d^2S_F}{d\omega_s\,d\Omega\,(\hat{k}_s)}=\frac{\omega_0^4(1+n(\Omega))|\tilde{b}(\Omega)|^2}{8\pi^2c^4\sqrt{\epsilon_2(\omega_0)}}\,|T_{21}^{(0)}|^2|T_{10}^{(s)}|^2 \times\exp[-2(1/l_s+1/l_0)d](1/i)\,\mathrm{Im}[\mathbb{S}_{zz}(k_1^{(0)}-k_1^{(s)})] \tag{3.20a}$$

and[17]

$$\frac{d^2S_B}{d\omega_s\,d\Omega\,(\hat{k}_s)}=\frac{\omega_0^4(1+n(\Omega))|\tilde{b}(\Omega)|^2}{8\pi^2c^4}\,|T_{10}^{(0)}|^2|T_{10}^{(s)}|^2 \times\exp[-2(1/l_s+1/l_0)d](1/i)\,\mathrm{Im}[\mathbb{S}_{zz}(-k_1^{(0)}-k_1^{(s)})]\ , \tag{3.20b}$$

where

$$\mathbb{S}_{zz}(\Delta k)=\int_0^d dz\,dz'\,e^{-i\Delta k z+i\Delta k^* z'}A_{zz}(Q_\parallel,\Omega+i\eta;zz')\ . \tag{3.21}$$

It is a straightforward matter to evaluate $\mathbb{S}(\Delta k)$. Before we display the result, a comment on the notation we shall use will be helpful. In Appendix A, we have defined certain quantities k_0, k_1, and k_2. These quantities are defined in Eq. (A5) and Eq. (A6). When these objects have been evaluated at the frequency and wave vector of the incident or scattered light, these quantities are the z component of the wave vector of the incident or scattered light in the vacuum above the film, within the film, and within the substrate, respectively. We have designated the resulting wave vectors by the symbols of the form $k_1^{(0)}$ or $k_1^{(s)}$, respectively. In the function A_{zz} that appears in Eq. (3.21), we encounter k_0, k_1, and k_2 evaluated at the frequency *transfer* Ω and wave vector *transfer* $\tilde{Q}_\parallel$ parallel to the surface suffered by the radiation. These values of k_0, k_1, and k_2 we denote below by κ_0, κ_1, and κ_2, i.e.,

$$\kappa_0\equiv k_0(Q_\parallel,\Omega+i\eta)\ , \tag{3.22}$$

$$\kappa_{1,2}=k_{1,2}(Q_\parallel,\Omega+i\eta)\ . \tag{3.23}$$

After $\mathbb{S}_{zz}(\Delta k)$ is evaluated, it is convenient to divide it into two parts whose physical interpretation shall become clear shortly:

$$\mathbb{S}_{zz}(\Delta k)=\mathbb{S}_{zz}^{(\infty)}(\Delta k)+\delta\mathbb{S}_{zz}(\Delta k)\ , \tag{3.24}$$

where we have

$$\mathbb{S}_{zz}^{(\infty)}(\Delta k)=\left(\frac{(\Delta k^*)^2}{Q_\parallel^2+(\Delta k^*)^2}\,\frac{1}{\epsilon_1(\Omega)}+\frac{Q_\parallel^2}{Q_\parallel^2+(\Delta k^*)^2}\,\frac{1}{\epsilon_1(\Omega)-(c^2/\Omega^2)[Q_\parallel^2+(\Delta k^*)^2]}\right)\left(\frac{\exp(id[\Delta k^*-\Delta k])-1}{i[\Delta k^*-\Delta k]}\right). \tag{3.25}$$

The expression for $\delta\mathbb{S}_{zz}(\Delta k)$ is more complex. Before we write it down, we define

$$f(Q)=(e^{iQd}-1)/Q\ . \tag{3.26}$$

Then we have in terms of the coefficients $A_\sigma^{(\mathrm{II})}$ and $C_\sigma^{(\mathrm{II})}$ defined in Appendix A

$$\delta S_{zz}(\Delta k) = \frac{\Omega^2}{c^2 W_{\parallel}(Q_{\parallel},\Omega)}\Big[C_{+}^{(\parallel)}A_{+}^{(\parallel)} f(\kappa_1 + \Delta k^*) f(\kappa_1 - \Delta k)$$
$$+ C_{+}^{(\parallel)}A_{-}^{(\parallel)}\left(f(\kappa_1 - \Delta k)\frac{\exp[i(\Delta k^* - \kappa_1)d]}{\Delta k^* - \kappa_1} - f(-\kappa_1 - \Delta k)\frac{1}{\Delta k^* + \kappa_1}\right)$$
$$+ A_{+}^{(\parallel)}C_{-}^{(\parallel)}\left(f(-\kappa_1 - \Delta k)\frac{\exp[i(\Delta k^* + \kappa_1)d]}{\Delta k^* + \kappa_1} - f(\kappa_1 - \Delta k)\frac{1}{\Delta k^* - \kappa_1}\right)$$
$$+ A_{-}^{(\parallel)}C_{-}^{(\parallel)} f(-\kappa_1 + \Delta k^*) f(-\kappa_1 - \Delta k)\Big]. \qquad (3.27)$$

The physical content of $S^{(\infty)}(\Delta k)$ is clear, since its form is quite elementary. It contains a portion which describes scattering from volume LO phonons [the part proportional to $1/\epsilon_1(\Omega)$], and a part that describes the scattering from volume transverse polaritons {the part proportional to $[\epsilon_1(\Omega) - (c^2/\Omega^2)(Q_{\parallel}^2 + (\Delta k^*)^2)]^{-1}$}. The quantity $\Delta k_T^2 = Q_{\parallel}^2 + (\Delta k_R)^2$, where Δk_R is the real part of Δk, is the change in wave vector of the scattered radiation in the film. The second term in Eq. (3.25) thus contributes a peak in the spectrum of scattered radiation whenever

$$(c^2/\Omega^2)(\Delta k_T)^2 = \epsilon_1(\Omega)\,, \qquad (3.28)$$

i.e., when the frequency and wave-vector change suffered by the scattered radiation equals the frequency and wave vector of a volume TO polariton.

The width of the LO phonon peak is controlled by the damping felt by the LO phonon in the medium, i.e., it is controlled by $\mathrm{Im}(\epsilon_1(\Omega))$. There are two distinct contributions to the linewidth of the bulk TO polariton. The first has its origin in the damping of the polariton itself [from the imaginary part of $\epsilon_1(\Omega)$], and the second from the combined effect of the curvature in the volume TO polariton dispersion relation, and the effect of attenuation of the incident and scattered radiation in the medium. Wave-vector components normal to the surface are then not strictly conserved, and in any measurement, a finite region of the bulk dispersion curve is sampled, even if the intrinsic linewidth of the bulk TO polariton is very small. Mathematically this effect enters through the complex part of $(\Delta k^*)^2$ in Eq. (3.23), which gives a finite width to the bulk TO polariton line even when $\epsilon_1(\Omega)$ is purely real. This feature is absent from the bulk LO phonon line simply because (in the present theory) no dispersion is present in the bulk LO phonon dispersion relation.

In the geometry assumed here, when the scattered light emerges right along the $\hat{z}$ direction ($\vec{Q}_{\parallel} = 0$), the selection rules allow the LO phonon line, while the TO polariton line is forbidden. One sees this feature in Eq. (3.25).

The coherence length or effective scattering length that determines the scattering intensity in the infinitely extended medium is controlled by the imaginary part of Δk. When this coherence length is long compared to the film thickness [$id(\Delta k^* - \Delta k)$ small compared to unity], the effective coherence length becomes the film thickness, and the scattering efficiency is proportional to the film thickness. In the opposite limit, coherence length is small compared to the film thickness, $S^{(\infty)}(\Delta k)$ becomes proportional to the coherence length $l_c = 2/(\Delta k - \Delta k^*)$.

Thus, the contribution $S_{zz}^{(\infty)}(\Delta k)$ to $S_{zz}(\Delta k)$ describes a contribution of the volume excitations (LO phonons and volume TO polaritons) to the Raman spectrum. The contributions $\delta S_{zz}(\Delta k)$ displayed in Eq. (3.27) may not be reduced to a simple transparent form in general. This contribution to $S_{zz}(\Delta k)$ contains two pieces of information: it describes the contribution to the Raman spectrum from the surface polaritons associated with the structure, and in addition it contains corrections to the intensities and shape of the volume LO phonon and volume TO polariton features. We next turn our attention to these features.

Since it is not possible to reduce $\delta S_{zz}(\Delta k)$ to a transparent form, in general, we consider a special limit that will allow us to explore pieces of the function. We suppose that the damping in the material is small enough that the volume LO phonon, volume TO polariton and surface polariton features in the spectrum are narrow, well defined and distinct features in the spectrum. In practice, this is a marginal assumption,[4,18] but with this assumption we can extract simple information from $\delta S_{zz}(\Delta k)$. We examine two features of the spectrum in this limit: the surface polariton lines, and size-dependent corrections to the volume LO phonon line.

A. Contribution to Raman spectrum from surface polaritons

In the frequency regime where the real part of the dielectric constant $\epsilon_1(\Omega)$ of the substrate is negative, while that of the substrate is positive, there are two surface polariton branches associated with the structure analyzed here.[5] In the limit as the film thickness d approaches infinity, one branch becomes localized at the vacuum-film in-

terface, and one becomes localized at the substrate-film interface. In the Raman studies reported to date, the film thickness is sufficiently thin that for both branches, the electric fields and atomic displacements associated with both branches extend throughout the film.

If we consider the function $W_{\parallel}(\vec{Q}_{\parallel}, \Omega)$ as a function of frequency for fixed real values of $\vec{Q}_{\parallel}$, then in the absence of damping [$\epsilon_1(\Omega)$ and $\epsilon_2(\Omega)$ presumed real], $W_{\parallel}(Q_{\parallel}, \Omega)$ has zeros when $\Omega = \Omega_+(Q_{\parallel})$ and $\Omega = \Omega_-(Q_{\parallel})$, where $\Omega_+(Q_{\parallel})$ and $\Omega_-(Q_{\parallel})$ are the surface polariton dispersion relations for the structure. We shall shortly cast $W_{\parallel}(Q_{\parallel}, \Omega)$ in a form where it may be directly compared with the implicit dispersion relation given by Maradudin and Mills.[5] When damping is present, and weak enough so the surface polariton remains a well defined excitation, the surface polariton poles lie close to the real Ω axis in the complex Ω plane. In some of the manipulations below, we presume these poles lie close enough to the real axis for the prefactors of $W_{\parallel}(Q_{\parallel}, \Omega)$ to be evaluated at the pole, with little error.

After some algebraic rearrangement, $\delta S_{zz}(\Delta k)$ may be broken into parts:

$$\delta S_{zz}(\Delta k) = \delta S_{zz}^{(a)}(\Delta k) + \delta S_{zz}^{(b)}(\Delta k) , \tag{3.29}$$

where

$$\delta S_{zz}^{(a)}(\Delta k) = -\frac{\Omega^2}{c^2 W_{\parallel}(Q_{\parallel}, \Omega)} \times\left(\sum_{\sigma} \frac{C_{\sigma}^{(\parallel)}}{(\Delta k^* + \sigma\kappa_1)}\left(1 - e^{i(\Delta k^* + \sigma\kappa_1)d}\right)\right) \times\left(\sum_{\sigma'} \frac{A_{\sigma'}^{(\parallel)}}{(\Delta k - \sigma'\kappa_1)}\left(1 - e^{-i(\Delta k - \sigma'\kappa_1)}\right)\right) \tag{3.30}$$

and

$$\delta S_{zz}^{(b)}(\Delta k) = \frac{Q_{\parallel}^2}{2\kappa_1\epsilon_1}\left(\frac{(e^{i(\Delta k^* - \kappa_1)d} - e^{i(\Delta k^* - \Delta k)d})}{(\Delta k^* - \kappa_1)(\Delta k - \kappa_1)} - \frac{(e^{i(\Delta k^* + \kappa_1)d} - e^{i(\Delta k^* - \Delta k)d})}{(\Delta k^* + \kappa_1)(\Delta k + \kappa_1)}\right) . \tag{3.31}$$

In Eq. (3.30), σ ranges over the values $+1$ and -1. To derive these results, we have employed an identity that will prove useful later:

$$C_+A_- - C_-A_+ = \frac{c^2 Q_{\parallel}^2}{\Omega^2}\,\frac{W_{\parallel}}{2i\kappa_1\epsilon_1} . \tag{3.32}$$

In particular, note that near the zero of $W_{\parallel}$ (the surface polariton poles of the response functions) we have

$$C_+A_- \cong C_-A_+ . \tag{3.33}$$

This relation will also prove useful.

Quite clearly, only the contribution $\delta S_{zz}^{(a)}(\Delta k)$ contains information about the surface polariton peak, since $\delta S_{zz}^{(b)}(\Delta k)$ does not contain the factor $W_{\parallel}(Q_{\parallel}, \Omega)$ that gives rise to the surface polariton poles in the response function. Thus, in what follows, we discard the piece $\delta S_{zz}^{(b)}(\Delta k)$, since it only contributes a small background to the spectrum near the surface mode poles.

In the absence of damping, the constants κ_0, κ_1, and κ_2 become pure imaginary at the surface polariton pole. In the presence of a small amount of damping they acquire a real part which will be small. We relable these constants, with the convention $\mathrm{Im}(\kappa_0) > 0$, $\mathrm{Im}(\kappa_{1,2}) < 0$ in mind:

$$\kappa_0 = +i\alpha_0 , \tag{3.34a}$$

$$\kappa_{1,2} = -i\alpha_{1,2} . \tag{3.34b}$$

We also introduce the quantities

$$a_\sigma = (1/\epsilon_1 - \sigma\alpha_0/\alpha_1) , \tag{3.35a}$$

$$b_\sigma = (\epsilon_2/\epsilon_1 + \sigma\alpha_2/\alpha_1) , \tag{3.35b}$$

so we have

$$A_\sigma^{(\parallel)} = 2a_\sigma \exp[-(\alpha_0 + \sigma\alpha_1)d] , \tag{3.36a}$$

$$C_\sigma^{(\parallel)} = 2b_\sigma . \tag{3.36b}$$

We may then write

$$W_{\parallel}(Q_{\parallel}, \Omega) = \frac{\alpha_1\epsilon_1\Omega^2}{4c^2Q_{\parallel}^2}\exp[(\alpha_1 - \alpha_0)d]\,d(Q_{\parallel}, \Omega) , \tag{3.37}$$

where

$$d(Q_{\parallel}, \Omega) = b_+a_- - b_-a_+\exp(-2\alpha_1 d) \tag{3.38a}$$

$$= \left(\frac{\epsilon_2}{\epsilon_1} + \frac{\alpha_2}{\alpha_1}\right)\left(\frac{1}{\epsilon_1} + \frac{\alpha_0}{\alpha_1}\right) - \left(\frac{\epsilon_2}{\epsilon_1} - \frac{\alpha_0}{\alpha_1}\right)\left(\frac{1}{\epsilon_1} - \frac{\alpha_0}{\alpha_1}\right)\exp(-2\alpha_1 d) . \tag{3.38b}$$

The statement $d(Q_{\parallel}, \Omega) = 0$ may be recognized as the implicit dispersion relation of the surface polaritons associated with the structure.[19] For this structure, as remarked above, there are two branches to the dispersion relation. As the film thickness $d \to \infty$, the two dispersion relations become

$$\epsilon_2/\epsilon_1 + \alpha_2/\alpha_1 = 0 , \tag{3.39a}$$

and

$$1/\epsilon_1 + \alpha_0/\alpha_1 = 0 . \tag{3.39b}$$

These may be recognized as the implicit dispersion relations of the surface polariton associated with the film-substrate interface, and that associated with the vacuum-film interface, respectively.

With the above rearrangements, the expression for $\delta S_{zz}^{(a)}(\Delta k)$ may be written

$$\delta S_{zz}(\Delta k) = -\frac{Q_{\parallel}^2}{\alpha_1 \epsilon_1} \frac{\exp(-2\alpha_1 d)}{d(Q_{\parallel}, \Omega)} \times \left(\sum_{\sigma} \frac{b_\sigma}{(\Delta k^* - i\sigma\alpha_1)} (1 - e^{i\Delta k^* d} e^{\sigma\alpha_1 d}) \right) \times \left(\sum_{\sigma'} \frac{a_\sigma}{(\Delta k + i\sigma\alpha_1)} (e^{-\sigma'\alpha_1 d} - e^{-i\Delta k d}) \right) . \quad (3.40)$$

So far, save for the neglect of $\delta S_{zz}^{(b)}(\Delta k)$, we have made no approximations. Near the zero of $d(Q_{\parallel}, \Omega)$, we have

$$b_- a_+ \cong b_+ a_- \exp(2\alpha_1 d) . \quad (3.41)$$

This becomes an equality in the limit of zero damping, right at the surface polariton poles. In the weak-damping limit, we make little error by presuming it to be an equality.

If we use Eq. (3.41) to rearrange the quantities in curly brackets, and we define

$$r = b_-/b_+ , \quad (3.42)$$

then in the "pole approximation" defined by treating Eq. (3.41) as an equality, and disregarding the imaginary part of r,

$$\delta S_{zz}(\Delta k) = \frac{Q_{\parallel}^2}{\alpha_1 \epsilon_1} e^{-2\alpha_1 d} \frac{b_+ a_+}{d(Q_{\parallel}, \Omega)} \times \left| \int_0^d dz\, e^{-i\Delta k z} (e^{+\alpha_1 z} + r e^{-\alpha_1 z}) \right|^2 . \quad (3.43)$$

When the form for $\delta S(\Delta k)$ displayed in Eq. (3.43) is inserted into the expressions for the scattering efficiencies given in Eqs. (3.20a) and (3.20b), then simple and workable expressions for the scattering efficiencies from the surface polaritons follow. It is straightforward to generate expressions for the scattering efficiencies for other film geometries [i.e., for a film with a (111) surface, for example]. It must be kept in mind that results such as these are valid in the weak damping limit, since it is only then that the surface polariton piece can be extracted from the total response function.

We conclude with some remarks about the approximate result for $\delta S_{zz}(\Delta k)$ displayed in Eq. (3.43).

In a language appropriate to quantum-mechanical perturbation theory, the factor

$$\left| \int_0^d dz\, e^{-i\Delta k z} (e^{+\alpha_1 z} + r e^{-\alpha_1 z}) \right|^2$$

is equivalent to the matrix element of the wave function of the excitation created in the scattering process (the surface polariton) between the initial and final photon states. Our formula is written with the surface polariton wave function normalized so that the piece proportional to $\exp(\alpha_1 z)$ has coefficient unity.

The only difference between the forward and back scattering intensities [other than the transmission factors in Eqs. (3.20)] occur in the effective matrix element just described. For forward scattering we have

$$\Delta k = k_1^{(0)} - k_1^{(s)} , \quad (3.44a)$$

while for back scattering

$$\Delta k = -k_1^{(0)} - k_1^{(s)} . \quad (3.44b)$$

As discussed above, and in quantitative detail in our earlier work,[6] for GaAs under the conditions relevant to the experiments of the Ushioda group, we have

$$\left| k_1^{(0)} + k_1^{(s)} \right| \gg \left| k_1^{(0)} - k_1^{(s)} \right| ,$$

with the result that the surface polariton intensity is very weak in back scattering.

Notice that in forward scattering, the imaginary part of Δk is the difference between the imaginary part of $k_1^{(0)}$ and that of $k_1^{(s)}$. This result, expected on physical grounds,[20] emerges naturally from the present approach.

The analogues of the phonon strength functions which enter the description of Raman scattering from bulk polaritons[21] are contained in the residue of the function $a_+ b_+/d(Q_{\parallel}\Omega)$ at the surface polariton poles. We could extract analytic expressions for these quantities from the approximate form for $\delta S_{zz}(\Delta k)$, but the resulting expressions are complex in form. Indeed, it is easiest to work directly with Eq. (3.43) rather than with the expressions valid in the no-damping limit.

We conclude this subsection with a comment on the behavior of $\delta S_{zz}(\Delta k)$ in the limit as the film thickness $\to \infty$, and the surface polaritons become well localized to the film-vacuum and film-substrate interfaces.

First, let the film thickness $d \to \infty$, and consider scattering from the surface polariton localized on the film-vacuum interface. We then have

$$b_+ a_+/d(Q_{\parallel}, \Omega) \to a_+/a_- ,$$

while the integral is dominated by the contribution from the term $e^{+\alpha_1 z}$. Then for the surface mode at the film-vacuum interface, as $d \to \infty$, we have[22]

$$\delta S_{zz}(\Delta k) = -\frac{Q_{\parallel}^2}{\alpha_1 \epsilon_1} \left(\frac{\alpha_1 - \alpha_0 \epsilon_1}{\alpha_1 + \alpha_0 \epsilon_1} \right) \frac{\exp[-id(\Delta k - \Delta k^*)]}{|\Delta k + i\alpha_1|^2} . \quad (3.45)$$

As $d \to \infty$, the dispersion relation of the film-substrate surface polariton becomes $b_+ = 0$ in the present notation. Then as $d \to \infty$, $r \to \infty$, and the contribution from the substrate-film surface polariton comes from the term in the wave function proportional to $r \exp(-\alpha_1 z)$. If we keep only this term and disregard the contribution from the upper limit as d becomes large, we find for large d the contribution from the surface polariton localized at the film-substate interface is

$$\delta S(\Delta k) = -\frac{Q_{\parallel}^2}{\alpha_1 \epsilon_1}\frac{a_+}{a_-} r^2 \exp(-2\alpha_1 d)\frac{1}{|\Delta k - i\alpha_1|^2}$$

$$\equiv -\frac{Q_{\parallel}^2}{\alpha_1 \epsilon_1}\frac{(\epsilon_2\alpha_1 - \epsilon_1\alpha_2)}{(\epsilon_2\alpha_1 + \epsilon_1\alpha_2)}\frac{1}{|\Delta k - i\alpha_1|^2} . \quad (3.46)$$

These remarks conclude our subsection of the contribution to the Raman spectrum from the surface polaritons, in the weak damping limit. We see that for large d, the spectrum consists of a line from the mode localized near the film-vacuum interface, and a second line from the mode localized near the film substrate interface.

B. Contribution to volume LO phonon peak from $\delta S_{zz}(\Delta k)$

As we remarked earlier, when the spectrum of scattered light from the film is examined, one finds not only the new features associated with the surface polariton, but in addition the intensities of the volume LO phonon and TO polariton lines are size dependent. The physical origin of these effects is the modification of the eigenfunctions associated with the bulk excitations by the electromagnetic boundary conditions at the interfaces. For example, in the case of LO phonons in an isotropic, lossless dielectric slab, it is simple to show[23] that these boundary conditions require the tangential component of the electric field set up by the mode to vanish at the interface, while the normal component approaches the interface with zero slope. Because of the influence of these boundary conditions, the contribution to the LO phonons to the electric field fluctuations are influenced by the boundaries, with the consequence that the intensity of the LO phonon Raman line becomes size dependent.

These size-dependent effects which arise from the influence of the boundary conditions are contained in the contribution $\delta S_{zz}(\Delta k)$ displayed in Eq. (3.27). In this subsection, we isolate the size dependent corrections to the LO phonon line intensity, in the spirit of the small-damping approximation used in Sec. III A.

When the damping is small, and the frequency transfer Ω lies near the LO phonon frequency of the film, then $\epsilon_1(\Omega)$ becomes very small, while all other quantities remain finite. Then with $\epsilon_1(\Omega)$ near zero, we have

$$\kappa_1 = -iQ_{\parallel} , \quad (3.47)$$

and furthermore we have

$$A_\sigma^{(\parallel)} \cong (1/2\epsilon_1)\exp(i\kappa_0 d - \sigma Q_{\parallel} d) , \quad (3.48a)$$

$$C_\sigma^{(\parallel)} \cong (1/2\epsilon_1)\epsilon_2/2\epsilon_1 , \quad (3.48b)$$

and also

$$W_{\parallel}(Q_{\parallel}, \Omega) \cong (\Omega^2\epsilon_2/c^2 Q_{\parallel}\epsilon_1) e^{i\kappa_0 d}\sinh(Q_{\parallel} d) . \quad (3.48c)$$

Even with these simplifications, the form assumed by $\delta S_{zz}(\Delta k)$ is reasonably complex. As a consequence, we present results for two limits where the results become simple:

1. *Limit $Q_{\parallel} d \gg 1$ (thick-film limit)*

Here we find

$$\delta S_{zz}(\Delta k) \cong -\frac{1}{\epsilon_1(\Omega)}\left(\frac{Q_{\parallel}\Delta k^*}{(\Delta k^* + iQ_{\parallel})(\Delta k^* - iQ_{\parallel})}\right) \times\left(\frac{1}{\Delta k - iQ_{\parallel}} + \frac{\exp[i(\Delta k^* - \Delta k)d]}{\Delta k + iQ_{\parallel}}\right) . \quad (3.49)$$

The first term in Eq. (3.49) has its origin in the modification of the LO phonon contribution to the electric field fluctuations near the film-substrate interface at $z=0$, and the second term comes from the film-vacuum interface at $z=d$.

If the film is perfectly transparent to the incident radiation (then $\Delta k = \Delta k^*$), the contribution to the LO phonon line intensity from Eq. (3.50) is independent of d, while that from $S_{zz}^{(\infty)}(\Delta k)$ increases linearly with d. In general, however, the correction from $\delta S_{zz}(\Delta k)$ is size dependent.

2. *Limit $Q_{\parallel} d \ll 1$ (thin-film limit)*

Here we find for Ω near the LO phonon frequency

$$\delta S_{zz}(\Delta k) = -\frac{d}{\epsilon_1(\Omega)}\frac{4|\Delta k|^4}{|Q_{\parallel}^2 + (\Delta k)^2|^2}\left|\frac{\sin(\frac{1}{2}\Delta k d)}{\Delta k d}\right|^2 . \quad (3.50)$$

Once again we have a size-dependent correction to the LO phonon intensity.

In this section, we have applied our general Green's-function theory of Raman scattering from films to a description of the spectrum for scattering from a particular film geometry, either near the forward direction, or very near the specular direction in back scattering. We have tried to illustrate the main effects that arise from the finite thickness of the film by examining selected features of the Raman spectrum in the limit of small damping. There are two effects that one encounters: new lines associated with scattering from surface polaritons arise in the spectrum, while the cross section for scattering from volume LO phonons and also from volume TO polaritons (we did not discuss this case here) become size dependent.

When $Q_{\parallel} d$ is comparable to unity, one encounters "guided volume modes" for the structure considered here, in frequency regions where the real part of $\epsilon_1(\Omega)$ is positive. These modes have fields which vary like a linear combination of $\cos(Q_z z)$ and $\sin(Q_z z)$, where the values assumed by Q_z are quantized, with adjacent values separated by $\Delta Q_z \sim \pi/d$. These guided modes also have fields localized to the near vicinity of the film, i.e., the fields in the vacuum decay to zero exponentially as

one moves away from the film, and into the substrate. These modes in principle may contribute structure to the Raman spectrum, and a description of this structure is contained in the present treatment. However, we reserve discussion of these modes to a future publication.

It is a straightforward matter to calculate the full expression for $S_{zz}(\Delta k)$ numerically, once the dielectric constant of the film and substrate, as well as the frequency of the incident radiation is known. One may then obtain calculated spectra with invoking the weak damping assumption used liberally here. In Sec. IV, we present examples of such calculations.

IV. NUMERICAL STUDIES OF SPECTRUM

In Sec. III, we examined the structure of $S_{zz}(\Delta k)$ by analytic methods, under the assumption that in the film the damping of the polaritons may be presumed sufficiently weak that the various contributions to the Raman spectrum stand free as distinct lines. As remarked earlier, in practice this assumption is marginal. For example, the frequency of upper surface polariton branch lies close to the frequency of the LO phonon in the structure examined by Ushioda and co-workers,[18] while as the scattering angle is decreased to zero, the line associated with the lower branch merges with that from the volume TO polariton.[4] Under these circumstances, one should calculate the spectrum from the full response function $S_{zz}(\Delta k)$. This is in fact a straightforward matter, since the full form of $S(\Delta k)$ is given by a simple algebraic expression. Indeed, it is no less complicated to study the full function $S_{zz}(\Delta k)$ than the various pieces pulled out of the full spectral density in the discussion of Sec. III. We also present calculations of $\mathrm{Im}\{S_{xx}(\Delta k)\}$, where

$$A_{xx}(\vec{Q}_{\parallel}\Omega, zz') = \frac{\Omega^2}{c^2 W_{\parallel}(Q_{\parallel}, \Omega)}\left[E_x^{>}(Q_{\parallel}\Omega \mid z)E_x^{<}(Q_{\parallel}\Omega \mid z') \times \theta(z-z') + E_x^{<}(Q_{\parallel}\Omega \mid z)E_x^{>}(Q_{\parallel}\Omega \mid z')\theta(z'-z)\right] . \quad (4.1)$$

From a physical point of view, $\mathrm{Im}\{S_{zz}(\Delta k)\}$ represents the contribution to the Raman spectrum from thermal fluctuations in the atomic displacements and the electric field fluctuations normal to the film surfaces, while $\mathrm{Im}\{S_{xx}(\Delta k)\}$ describes the contribution from fluctuations parallel to the film surfaces. The Raman spectrum from a perfect crystalline films will contain in addition contributions from cross-correlation functions $S_{xz}(\Delta k)$ and $S_{zx}(\Delta k)$.

All of the quantities which appear in the general expressions are readily computed from information available in the literature. Values for the complex index of refraction of GaAs at the 4880-Å line are quoted in the paper by Evans *et al.*,[6] and the parameters which enter the infrared dielectric constant have been given by McWhorter and Mooradian.[24] We have taken the dielectric constant of the sapphire substrate to be purely real, and equal to 10. We also require the magnitude and sign of the ratio $4\pi n e^* b/\epsilon_\infty a$ to compute the frequency dependence of the effective electro-optic coefficient $\tilde{b}(\Omega)$ defined in Eq. (3.4). We take this ratio to have the value -0.3, as in our previous work.[6]

Finally, we have the variables related to the kinematics of the scattering process. For example,

$$Q_{\parallel} = (\omega_s/c)\sin\theta \cong (\omega_0/c)\theta , \quad (4.2)$$

where θ is the angle made by the wave vector of the scattered radiation and the normal to the film surface, and the last statement is valid for small scattering angles, with incident radiation in the visible. Note that θ is the scattering angle measured *outside* the film. This seems to us the natural variable to use in describing the spectrum. In the papers by Ushioda and co-workers,[4,18] their angle ψ is the scattering angle inside the film, related to θ by Snell's law. When our computed spectra are compared to their data, one must realize that $\theta \cong 4.4\psi$.

For small-angle forward scattering through the film,

$$k_1^{(s)} = k_1^{(0)} + \Delta k , \quad (4.3)$$

where

$$\Delta k = \pm \frac{k_1^{(0)}}{\epsilon_1(\omega_0)}\left(\frac{\Omega}{\omega_0}\epsilon_1(\omega_0) + \Omega\frac{\partial\epsilon_1(\omega_0)}{\partial\omega} \mp \tfrac{1}{2}\theta^2\right), \quad (4.4)$$

where the upper sign is used for the anti-Stokes spectrum, and the lower sign for the Stokes side. All the calculations reported below are of the shape of the Stokes spectrum, and we have ignored the influence of the $(\partial\epsilon_1/\partial\omega)$ term of Eq. (4.4).

The quantities displayed in the figures discussed below are $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$, where

$$f_{xx}(\theta, \Omega) = \left|\frac{\tilde{b}(\Omega)}{b}\right|^2 \frac{1}{id}\mathrm{Im}\{S_{xx}(\Delta k)\} , \quad (4.5)$$

with a similar definition of $f_{zz}(\theta, \Omega)$.

In Fig. 4, we show f_{xx} and f_{zz} for the scattering angle $\theta = 30°$, for forward scattering. In both spectra, the bulk TO phonon and LO phonon peaks are clearly visible. In addition, in both spectra one sees a clear, well defined line from the lower surface polariton branch centered slightly above $1.04\omega_{TO}$. In addition, the contribution to f_{xx} near the LO phonon frequency ($\omega_{LO} \cong 1.085\omega_{TO}$) is distorted toward the low-frequency side. This comes about because the upper surface polariton branch lies close to, but just below ω_{LO}. The peak near $1.08\omega_{TO}$ contains contributions from both the bulk LO phonon, and the upper surface polariton branch,

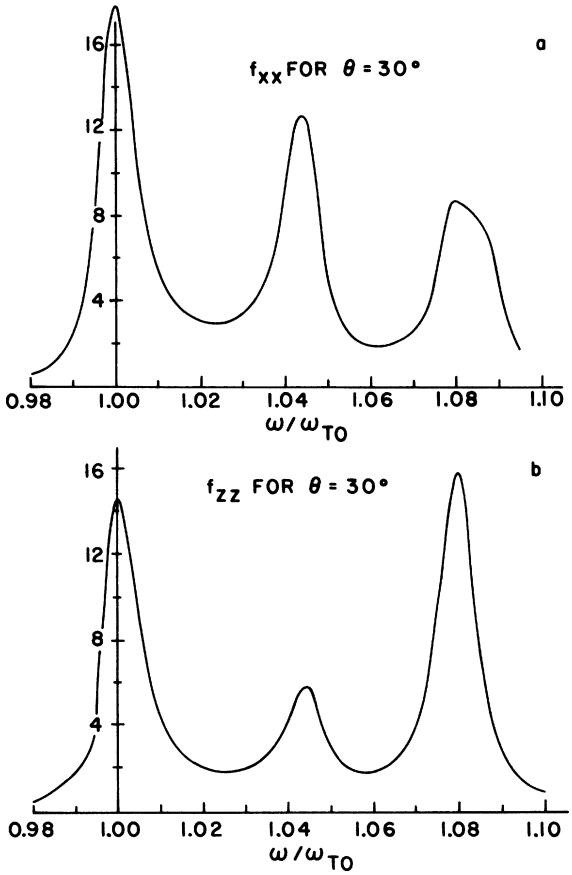

FIG. 4. Contributions for (a) f_{xx} and (b) f_{zz} to the Raman spectrum of 4880-Å radiation forward scattered through a 2500-Å film of GaAs placed on a sapphire substrate. The scattering angle has been taken to be 30°, and the film thickness 2500 Å.

and the two peaks overlap. Here one appreciates the use of the complete response function to generate the spectrum, since the two modes do not contribute distinct lines to the spectrum, but overlap strongly. We note that Prieur and Ushioda[18] have observed such distorted lines near the LO phonon frequency in their study of a GaAs film on a sapphire substrate. By comparing the forward and back scattering spectra, they were able to extract information about the frequency of the upper mode from the data.

As one moves to smaller scattering angles, the dominate contribution to the prominent peak in the spectrum from the lower surface polariton branch comes from $f_{xx}(\theta, \Omega)$. As the scattering angle decreases, the frequency of the lower branch approaches ω_{TO}, and the strength of $f_{xx}(\theta, \Omega)$ becomes concentrated around ω_{TO}. This is illustrated in Figs. 5(a) and 6(a), where $f_{xx}(\theta, \Omega)$ is plotted for $\theta = 10°$ and $\theta = 3.5°$. One clearly sees the lower branch decrease in intensity and merge with the TO phonon peak, while at the same time the contribution from $f_{xx}(\theta, \Omega)$ to the structure near ω_{LO} becomes very small.

In Figs. 5(b) and 6(b) we show the behavior of $f_{zz}(\theta, \Omega)$ for $\theta = 3.5°$ and $\theta = 10°$. One sees that as the scattering angle decreases, there is very little contribution to the intensity of the peak from the lower surface polariton branch from fluctuations normal to the surface. The strength of $f_{zz}(\theta, \Omega)$ is concentrated near ω_{TO} and ω_{LO} at these small angles.

As we remarked earlier, to compute the complete Raman spectrum of a crystalline film, we require additional spectral functions $f_{ij}(\theta, \Omega)$ for $i \neq j$, i.e., functions such as $f_{xz}(\theta, \Omega)$. These are readily constructed from the general Green's functions. The GaAs film employed in the experiments of Ushioda and co-workers, however, are surely polycrystalline in nature.[25] Thus, to form a complete expression for the Raman cross section, we would have to perform an average over the orienta-

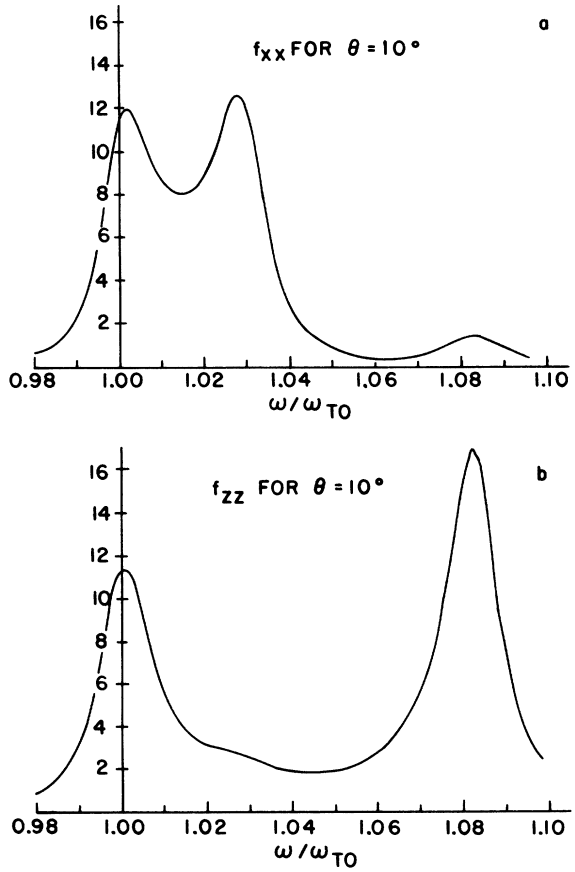

FIG. 5. Contributions from (a) f_{xx} and (b) f_{zz} to the Raman spectrum of 4880-Å radiation forward scattered through a 2500-Å film of GaAs placed on a sapphire substrate. The scattering angle is 20°, and the film thickness 2500 Å.

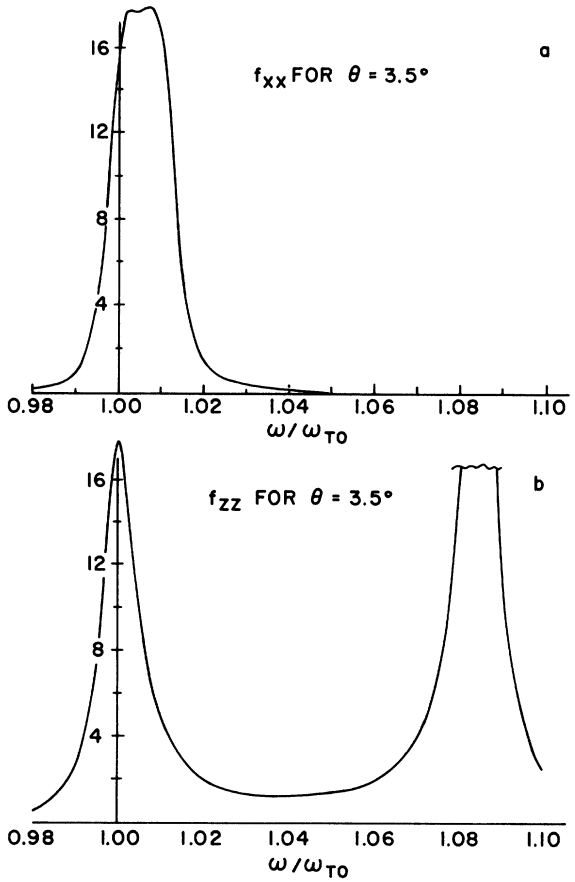

FIG. 6. Contribution from (a) f_{xx} and (b) f_{zz} to the Raman spectrum of 4880-Å radiation forward scattered through a 2500-a film of GaAs placed on a sapphire substrate. The scattering angle is 3.5° and the film thickness 2500 Å.

tion of the crystal axes. Since both $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$ are both positive definite functions, they will appear in the final expression for the cross section preceded by weight factors that depend on the nature of the film. The off-diagonal functions $f_{ij}(\theta, \Omega)$ can be both positive or negative, and describe scattering from correlations between the fluctuations parallel and normal to the film surface. It is not unreasonable to suppose that in a polycrystalline film, these contributions are less important than $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$. Thus, we shall make a crude representation of the forward scattering Raman spectrum by simply superimposing $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$. In fact, we get a reasonably good representation of the LO/TO ratio by simply adding together $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$ with equal weight.

In Fig. 7, again for near forward scattering, we show the Raman spectrum for the film generated by the procedure described in the preceding paragraphs. The results are strikingly similar to those displayed in Fig. 1 of the paper by Evans, Ushioda, and McMullen.[7] Such a simple procedure is not quantitatively correct. For example, in the figure, the theoretical ratio between the height of the bulk TO phonon peak and that produced by the lower surface polariton branch is about $\frac{1}{2}$, where the experimental value is about $\frac{1}{3}$. Our earlier paper[6] paid careful attention to the quantitative details, and provided calculated results in excellent accord with the data. Despite the oversimplified method of constructing the theoretical spectra displayed in Fig. 7, the correspondence with the data is very good. There is only one adjustable parameter in this calculation, and that is the ratio of the admixture of f_{xx} and f_{zz}.

In our previous paper, and in the discussion above, we showed the reason why the surface polariton peak was absent in the back scattering spectrum, while it is present as a strong and clear feature in a forward scattering measurement. To illustrate this point again, we present in Fig. 8 a calculation of the Raman spectrum of 4880 Å back scattered from our model slab. This spectrum was constructed by means of the approximate procedure employed to construct the spectra displayed in Fig. 7. There is no hint of structure from surface polaritons in the spectra, as our earlier argu-

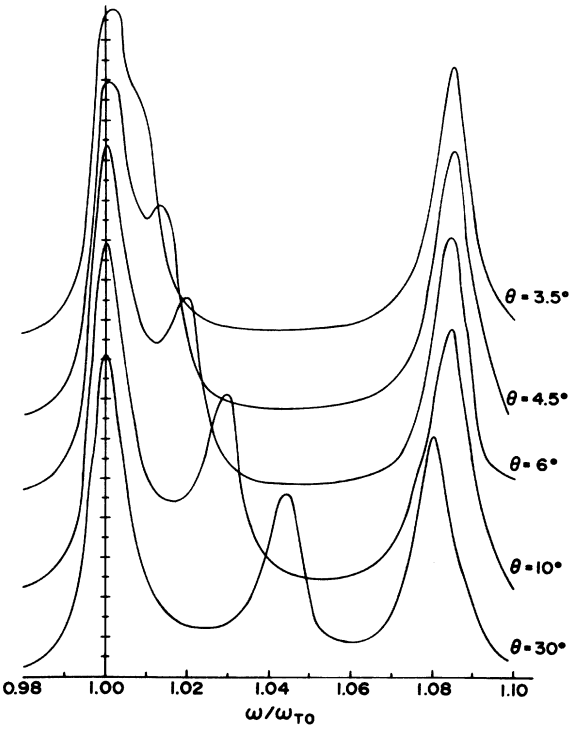

FIG. 7. Raman spectrum for a 2500-Å GaAs film on a sapphire substrate constructed from $f_{xx}(\theta, \Omega)$ and $f_{zz}(\theta, \Omega)$, as described in the text. Several scattering angles θ have been used.

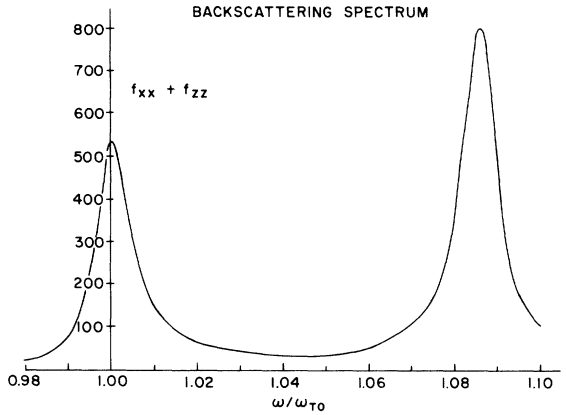

FIG. 8. A theoretical calculation of the back scattering spectrum from a thin film (2500 Å thick) of GaAs as a sapphire substrate.

ments predict. We have estimated that for both surface polariton branches, the integrated intensity of the surface polariton contributions to the back scattering spectrum should be smaller by roughly two orders of magnitude compared to their strength in the forward scattering spectrum. When it is realized that this small scattering intensity is spread over a frequency interval with width comparable to the surface polariton feature in Fig. 7, then one expects no perceptible structure from surface polaritons in the back scattering spectrum, as Fig. 8 shows.

Notice also that if the scales of the vertical axes in Fig. 7 are compared with that in Fig. 8, one sees the back scattering spectrum is much more intense than the forward scattering spectrum. The physical origin of this is simply absorption of the incident and scattered radiation. In back scattering, the interaction may take place entirely within the skin depth.

The calculations presented here offer considerable insight into the nature and frequency distribution of the fluctuations responsible for the spectra reported by Ushioda and co-workers. While our method of producing the Raman spectrum is a bit oversimplified, the calculations produce spectra quite close to the observed spectra, with only one adjustable parameter.

We wish to conclude with the remark that the numerical calculations required to generate the spectra displayed above are extremely easy to carry out. All that is involved is a computer evaluation of a straightforward, although somewhat lengthy algebraic expression. We hope the theoretical structure developed in this paper is complete enough to enable more information to be extracted in future experimental Raman studies of size effects and surface polaritons in planar geometries.

APPENDIX A: FORM OF ELECTROMAGNETIC GREEN'S FUNCTIONS $D_{\mu\nu}(\vec{x}\vec{x}';\omega)$ FOR PRESENT GEOMETRY

As remarked in the text, a derivation of the form of these Green's functions is presented in Ref. 8. Here we simply quote the results.

We write

$$D_{\mu\nu}(\vec{x}\vec{x}';\omega) = \int \frac{d^2k_{\parallel}}{(2\pi)^2} e^{i\vec{k}_{\parallel}\cdot(\vec{x}_{\parallel}-\vec{x}'_{\parallel})} d_{\mu\nu}(\vec{k}_{\parallel}\omega|zz'), \quad \text{(A1)}$$

where $\vec{x}_{\parallel}$ and $\vec{x}'_{\parallel}$ are projections of $\vec{x}$ and $\vec{x}'$ on the xy plane. We introduce a matrix $\underline{S}(\vec{k}_{\parallel})$ defined by

$$\underline{S}(\vec{k}_{\parallel}) = \frac{1}{k_{\parallel}} \begin{pmatrix} k_x & k_y & 0 \\ -k_y & k_x & 0 \\ 0 & 0 & k_{\parallel} \end{pmatrix}, \quad \text{(A2)}$$

and write

$$d_{\mu\nu}(\vec{k}_{\parallel}\omega|zz') = \sum_{\mu'\nu'} g_{\mu'\nu'}(k_{\parallel}\omega|zz') S_{\mu'\mu}(\vec{k}_{\parallel}) S_{\nu'\nu}(\vec{k}_{\parallel}) . \quad \text{(A3)}$$

This operation rotates the coordinate system, so $g_{\mu\nu}(k_{\parallel}\omega|zz')$ is the function $d_{\mu\nu}(\vec{k}_{\parallel}\omega|zz')$ calculated in a coordinate system with $\vec{k}_{\parallel}$ directed along the $\hat{x}$ axis.

We have

$$g_{\mu y}(k_{\parallel}\omega|zz') = g_{y\mu}(k_{\parallel}\omega|zz') \equiv 0 \quad \text{for } \mu = x \text{ or } z . \quad \text{(A4)}$$

The remaining five elements of $g_{\mu\nu}(k_{\parallel}\omega|zz')$ are expressed compactly in terms of two fields $\vec{E}^{>}(k_{\parallel}\omega|z)$ and $\vec{E}^{<}(k_{\parallel}\omega|z)$. To define these fields, we introduce the quantities

$$k_0 = [(\omega + i\eta)^2/c^2 - k_{\parallel}^2]^{1/2}, \quad \mathrm{Im}(k_0) > 0, \quad \text{(A5)}$$

$$k_{1,2} = [(\omega^2/c^2)\epsilon_{1,2} - k_{\parallel}^2]^{1/2}, \quad \mathrm{Im}(k_{1,2}) < 0 . \quad \text{(A6)}$$

In Eq. (A5), the limit $\eta \to 0+$ is implied. Careful attention must be paid to the sign conventions in Eq. (A5) and Eq. (A6) when the results below and in the text are utilized.

We now define the fields

$$E_y^{>}(k_{\parallel}\omega|z) = \begin{cases} e^{+ik_0 z}, & z > d, \\ A_+^{(\perp)} e^{ik_1 z} + A_-^{(\perp)} e^{-ik_1 z}, & 0 < z < d, \\ B_+^{(\perp)} e^{ik_2 z} + B_-^{(\perp)} e^{-ik_2 z}, & z < 0, \end{cases} \quad \text{(A7)}$$

$$E_y^{<}(k_{\parallel}\omega|z) = \begin{cases} D_+^{(\perp)} e^{ik_0 z} + D_-^{(\perp)} e^{-ik_0 z}, & z > d . \\ C_+^{(\perp)} e^{ik_1 z} + C_-^{(\perp)} e^{-ik_1 z}, & 0 > z > d, \\ e^{ik_2 z}, & z < 0, \end{cases} \quad \text{(A8)}$$

$$E_x^>(k_\parallel\omega\,|\,z) = \begin{cases} -(k_0/k_\parallel)\,e^{ik_{0z}} & z>d\,, \\ -(k_1/k_\parallel)(A_+^{(\parallel)}\,e^{ik_{1z}} - A_-^{(\parallel)}\,e^{-ik_{1z}}), & 0<z<d\,, \\ -(k_2/k_\parallel)(B_+^{(\parallel)}\,e^{ik_{2z}} - B_-^{(\parallel)}\,e^{-ik_{2z}}), & z<0\,, \end{cases} \tag{A9}$$

$$E_z^>(k_\parallel\omega\,|\,z) = \begin{cases} e^{ik_{0z}}, & z>d\,, \\ A_+^{(\parallel)}\,e^{ik_{1z}} + A_-^{(\parallel)}\,e^{-ik_{1z}}, & 0<z<d\,, \\ B_+^{(\parallel)}\,e^{ik_{2z}} + B_-^{(\parallel)}\,e^{-ik_{2z}}, & z<0\,. \end{cases} \tag{A10}$$

$$E_x^<(k_\parallel\omega\,|\,z) = \begin{cases} -(k_0/k_\parallel)(D_+^{(\parallel)}\,e^{ik_{0z}} - D_-^{(\parallel)}\,e^{-ik_{0z}}), & z>d\,, \\ -(k_1/k_\parallel)(C_+^{(\parallel)}\,e^{ik_{1z}} - C_-^{(\parallel)}\,e^{-ik_{1z}}), & 0<z<d\,, \\ -(k_2/k_\parallel)\,e^{ik_{2z}}, & z<0\,, \end{cases} \tag{A11}$$

and finally

$$E_z^<(k_\parallel\omega\,|\,z) = \begin{cases} D_+^{(\parallel)}\,e^{ik_{0z}} + D_-^{(\parallel)}\,e^{-ik_{0z}}, & z>d\,, \\ C_+^{(\parallel)}\,e^{ik_{1z}} + C_-^{(\parallel)}\,e^{-ik_{1z}}, & 0<z<d\,, \\ e^{ik_{2z}}, & z<0\,. \end{cases} \tag{A12}$$

In these expressions, with $\sigma = +$ or $-$, we have

$$A_\sigma^{(\perp)} = \tfrac{1}{2}\,e^{ik_{0d}}(1+\sigma k_0/k_1)\,e^{-i\sigma k_1 d}\,, \tag{A13}$$

$$A_\sigma^{(\parallel)} = \tfrac{1}{2}\,e^{ik_{0d}}(1/\epsilon_1+\sigma k_0/k_1)\,e^{-i\sigma k_1 d}\,, \tag{A14}$$

$$B_\sigma^{(\perp)} = \tfrac{1}{2}\,e^{ik_{0d}}[(1+\sigma k_0/k_1)\cos(k_1 d) - i(k_0/k_1+\sigma k_1/k_2)\sin(k_1 d)], \tag{A15}$$

$$B_\sigma^{(\parallel)} = \tfrac{1}{2}\,e^{ik_{0d}}[(1/\epsilon_2+\sigma k_0/k_2)\cos(k_1 d) - i(k_0\epsilon_1/k_1\epsilon_2+\sigma k_1/\epsilon_1 k_2)\sin(k_1 d)], \tag{A16}$$

$$C_\sigma^{(\perp)} = \tfrac{1}{2}(1+\sigma k_2/k_1)\,, \tag{A17}$$

$$C_\sigma^{(\parallel)} = \tfrac{1}{2}(\epsilon_2/\epsilon_1+\sigma k_2/k_1)\,,$$

$$D_\sigma^{(\perp)} = \tfrac{1}{2}\,e^{ik_{0d}}[(1+\sigma k_2/k_0)\cos(k_1 d) + i(k_2/k_1+\sigma k_1/k_0)\sin(k_1 d)], \tag{A18}$$

$$D_\sigma^{(\parallel)} = \tfrac{1}{2}\,e^{ik_{0d}}[(\epsilon_2+\sigma k_2/k_0)\cos(k_1 d) + i(\epsilon_1 k_2/k_1+\sigma k_1\epsilon_2/k_0\epsilon_1)\sin(k_1 d)]. \tag{A19}$$

We require two more quantities before we may write down expressions for the nonzero elements of $g_{\mu\nu}(k_\parallel\omega|\,zz')$:

$$W_\perp(k_\parallel\omega) = (e^{ik_{0d}}/k_1)[(k_1^2 - k_2 k_0)\sin(k_1 d) + i(k_0-k_2)k_1\cos(k_1 d)], \tag{A20}$$

$$W_\parallel(k_\parallel\omega) = (\omega^2 k_0/ic^2 k_\parallel^2)\,e^{ik_{0d}}[(\epsilon_2 - k_2/k_0)\cos(k_1 d) + i(\epsilon_1 k_2/k_1 - \epsilon_2 k_1/\epsilon_1 k_0)\sin(k_1 d)]. \tag{A21}$$

In term of the quantities define above, we have

$$g_{yy}(k_\parallel\omega\,|\,zz') = [4\pi/W_\perp(k_\parallel\omega)]\,[E_y^>(k_\parallel\omega\,|\,z)E_y^<(k_\parallel\omega\,|\,z') \times\theta(z-z') + E_y^<(k_\parallel\omega\,|\,z)E_y^>(k_\parallel\omega\,|\,z')\theta(z'-z)]\,, \tag{A22}$$

$$g_{xx}(k_\parallel\omega\,|\,zz') = [4\pi/W_\parallel(k_\parallel\omega)]\,[E_x^>(k_\parallel\omega\,|\,z)E_x^<(k_\parallel\omega\,|\,z') \times\theta(z-z') + E_x^<(k_\parallel\omega\,|\,z)E_x^>(k_\parallel\omega\,|\,z')\theta(z'-z)]\,, \tag{A23}$$

$$g_{zx}(k_\parallel\omega\,|\,zz') = [4\pi/W_\parallel(k_\parallel\omega)]\,[E_z^>(k_\parallel\omega\,|\,z)E_x^<(k_\parallel\omega\,|\,z') \times\theta(z-z') + E_z^<(k_\parallel\omega\,|\,z)E_x^>(k_\parallel\omega\,|\,z')\theta(z'-z)]\,, \tag{A24}$$

$$g_{xz}(k_\parallel\omega\,|\,zz') = -[4\pi/W_\parallel(k_\parallel\omega)]\,[E_x^>(k_\parallel\omega\,|\,z)E_z^<(k_\parallel\omega\,|\,z') \times\theta(z-z') + E_x^<(k_\parallel\omega\,|\,z)E_z^>(k_\parallel\omega\,|\,z')\theta(z'-z)]\,, \tag{A25}$$

$$g_{zz}(k_\parallel\omega\,|\,zz') = [4\pi c^2/\omega^2\epsilon(z,\omega)]\delta(z-z') - [4\pi/W_\parallel(k_\parallel,\omega)]\,[E_z^>(k_\parallel\omega\,|\,z)E_z^<(k_\parallel\omega\,|\,z') \times\theta(z-z') + E_z^<(k_\parallel\omega\,|\,z)E_z^>(k_\parallel\omega\,|\,z')\theta(z'-z)]\,. \tag{A26}$$

In Eq. (A26), $\epsilon(z,\omega)$ is the frequency-dependent dielectric constant of the three-layer structure, i.e., the coefficient of $\delta_{\mu\tau}$ in Eq. (2.1) of the text. As remarked earlier, the elements of $g_{\mu\nu}(k_\parallel\omega|zz')$ not displayed explicitly in Eqs. (A22)–(A26) vanish identically.

APPENDIX B: RELATION BETWEEN SPECTRAL DENSITY FUNCTION AND GREEN'S FUNCTIONS OF ELECTROMAGNETIC SCATTERING THEORY

The relationship between the spectral density associated with fluctuations of the electromagnetic field, and the Green's functions of the scattering theory of classical electromagnetic waves has been discussed and utilized in Chap. 6 of the well known text of Abrikosov, Gorkov, and Dzyaloshinskii.[14] As a consequence, the description we present here is somewhat schematic.

From Eq. (2.16) of the text we have

$$[1+n(\Omega)]\mathfrak{D}_{ij}(\vec{Q}_\parallel\Omega;\,zz') = \int d^2x_\parallel\,dt\,e^{i\Omega t\,-\,i\vec{Q}_\parallel\cdot\vec{x}_\parallel}\langle\mathcal{E}_{0'}(\vec{x}_\parallel z,\,t)\mathcal{E}_0(0z',\,0)\rangle\,. \tag{B1}$$

We regard $\vec{\mathcal{E}}(\vec{x},\,t)$ as the electric field operator in the Heisenberg representation, where the Hamiltonian describes the electromagnetic field and its interaction with matter. Then if Z is the partition function of the system at temperature T, with $\beta = 1/k_B T$ one may obtain the spectral representation

$$[1+n(\Omega)]\mathfrak{D}_{ij}(\vec{Q}_{\parallel}\Omega;\, zz') = \frac{2\pi}{Z}\sum_{nm} e^{-\beta E_n}\delta(\Omega+\omega_{nm}) \times \int d^2Q_{\parallel}\, e^{-i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}}\langle n|\, \mathcal{E}_i(\vec{x}_{\parallel}z)\,|m\rangle\langle m|\, \mathcal{E}_j(0z')\,|n\rangle \ . \tag{B2}$$

In this expression, $\vec{\mathcal{E}}(\vec{x})$ is $\vec{\mathcal{E}}(\vec{x},\, 0)$, the Heisenberg operator $\vec{\mathcal{E}}(\vec{x},\, t)$ evaluated at $t=0$, E_n is the energy of eigenstate $|n\rangle$, and $\omega_{nm}=E_n-E_m$. The electric field is related to the vector potential in the gauge where $\varphi=0$

$$\vec{\mathcal{E}} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}\ , \tag{B3}$$

so in terms of the vector potential one may write

$$[1+n(\Omega)]D_{ij}(\vec{Q}_{\parallel}\Omega;\, zz') = \frac{2\pi\Omega^2}{c^2Z}\sum_{nm} e^{-\beta E_n}\delta(\Omega+\omega_{nm}) \times \int d^2x_{\parallel}\, e^{-i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}}\langle n|\, A_i(\vec{x}_{\parallel}z)\,|m\rangle\langle m_{\parallel}\, A_j(0,\, z')\,|n\rangle \ . \tag{B4}$$

Now examine the retarded Green's function

$$D_{ij}^{(A)}(\vec{x}\vec{x}';\, t-t') = -i\Theta(t-t')\langle[A_i(\vec{x},\, t),\, A_j(\vec{x}'t')]\rangle \ . \tag{B5}$$

We introduce the Fourier transform with respect to time

$$D_{ij}^{(A)}(\vec{x}\vec{x}';\, t-t') = \int \frac{d\Omega}{2\pi} e^{-i\Omega(t-t')} D_{ij}^{(A)}(\vec{x}\vec{x}',\, \Omega) \tag{B6}$$

and then transform out the coordinate dependence parallel to the surface:

$$D_{ij}^{(A)}(\vec{Q}_{\parallel}\Omega;\, zz') = \int d^2x_{\parallel}\, e^{-i\vec{Q}_{\parallel}\cdot(\vec{x}_{\parallel}-\vec{x}'_{\parallel})} D_{ij}^{(A)}(\vec{x}\vec{x}';\, \Omega) \ . \tag{B7}$$

By comparing the spectral representation of $D_{ij}^{(A)}(\vec{Q}_{\parallel}\Omega;\, zz')$ with that of $D_{ij}(\vec{Q}_{\parallel}\Omega;\, zz')$ one may establish the identity

$$\mathfrak{D}_{ij}(\vec{Q}_{\parallel}\Omega;\, zz') = (\Omega^2/ic^2)[D_{ij}^{(A)}(\vec{Q}_{\parallel},\, \Omega-i\eta;\, zz') - D_{ij}^{(A)}(\vec{Q}_{\parallel}\Omega+i\eta;\, zz')] \ . \tag{B8}$$

In their discussion, Abrikosov, Gorkov, and Dzyaloshinskii demonstrate that $D_{ij}^{(A)}(\vec{x}\vec{x}';\, \Omega)$ obeys the differential equation (for a planar geometry)

$$\sum_k [-(\nabla\times\nabla\times)_{ik} + (\Omega^2/c^2)\epsilon(z,\, \Omega)\delta_{ik}] D_{kl}^{(A)}(\vec{x}\vec{x}';\, \Omega) = 4\pi\delta_{il}\delta(\vec{x}-\vec{x}') \ . \tag{B9}$$

This equation is identical to Eq. (2.4) of the text. Furthermore, $D_{ij}^{(A)}(\vec{x}\vec{x}';\, \Omega)$ obeys the same boundary condition as the Green's function of the classical scattering theory. Thus, the two functions are identical and Eqs. (B8) and (2.18) of the text are identical.

APPENDIX C: USEFUL RELATION BETWEEN $g_{ij}(Q_{\parallel},\Omega-i\eta|\, zz')$ AND $g_{ij}(\vec{Q}_{\parallel},\Omega+i\eta|\, zz')$

In the appendix of Ref. 8, the functions of $d_{ij}(\vec{Q}_{\parallel},\, \Omega;\, zz')$ are constructed as solutions to a certain set of differential equations. If we keep track of the frequency variable Ω, then when Ω lies just above the real axis, in these differential equations,

$$\epsilon_{1,2}(\Omega+i\eta) = \epsilon_{1,2}^{(r)} + i\epsilon_{1,2}^{(i)} \tag{C1}$$

and when Ω lies just below the real axis,

$$\epsilon_{1,2}(\Omega-i\eta) = \epsilon_{1,2}^{(r)} - i\epsilon_{1,2}^{(i)} \ , \tag{C2}$$

where $\epsilon_{1,2}^{(i)}>0$. Thus we have

$$\epsilon_{1,2}(\Omega-i\eta) = \epsilon^*(\Omega+i\eta) \ . \tag{C3}$$

Now the solution for $g_{ij}(\vec{Q}_{\parallel}\Omega+i\eta|\, zz')$ must have a form identical to the functions in Appendix A, and so must $g_{ij}(\vec{Q}_{\parallel}\Omega-i\eta|\, zz')$. In one case k_1 and k_2 are calculated with $\epsilon_1(\Omega+i\eta)$ and $\epsilon_2(\Omega+i\eta)$ and k_0 is given by Eq. (A5) with $\omega+i\eta$ replaced by $\Omega+i\eta$. In the second case, these same quantities are to be computed with $\Omega-i\eta$. In *both* cases, we are to choose

$$\mathrm{Im}(k_0)>0 \ , \tag{C4}$$

$$\mathrm{Im}(k_{1,2})<0 \ . \tag{C5}$$

By examining the position of the roots in the complex plane, one shows that the conditions in Eqs. (C4) and (C5) require

$$k_0(\Omega-i\eta) = -k_0^*(\Omega+i\eta) \ , \tag{C6}$$

$$k_{1,2}(\Omega-i\eta) = -k_{1,2}^*(\Omega+i\eta) \ . \tag{C7}$$

If these relations are used in the explicit forms for the Green's functions given in Appendix A, then one may establish the identity

$$g_{ij}(\vec{Q}_{\parallel},\, \Omega+i\eta|\, zz') = g_{ji}(Q_{\parallel},\, \Omega-i\eta|\, z'z)^* \ . \tag{C8}$$

This relation is extremely useful in constructing the spectral density $\mathfrak{D}_{ij}(\vec{Q}_{\parallel}\Omega;\, zz')$ defined in Eq. (2.18) of the text.

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*Supported by Grant No. AFOSR 76-2887 of the Air Force Office of Scientific Research, Office of Aerospace Research, U.S.A.F.

†Supported in part by the NSF Material Research Laboratory through Grant No. GH 33633 and by the Army Research Office-Durham under Contract No. DAHC-0181.

[1]See Sec. X of D. L. Mills and E. Burstein, Rep. Prog. Phys. 37, 817 (1974); and also the discussion by E. Burstein, A. Hartstein, J. Schoenwald, A. A. Maradudin, D. L. Mills, and R. F. Wallis, in *Proceedings of the First Taormina Research Conference on the Structure of Matter, Taormina, Italy*, 1972, edited by E. Burstein and F. de Martini (Pergamon, New York, 1974), p. 89.

[2]Andreas Otto, Festkörperprobleme XIV, 1 (1974).

[3]R. Ruppin and R. Englman, in *Proceedings of the International Conference on Light Scattering Spectra of*

Solids, *New York*, 1968 edited by G. B. Wright (Springer-Verlag, New York, 1969), p. 157.

[4]D. J. Evans, S. Ushioda, and J. D. McMullen, Phys. Rev. Lett. 31, 372 (1973).

[5]In the structure used by Evans *et al.* (Ref. 4), there are two surface polariton branches in the frequency region between the TO frequency and the LO phonon frequency of the GaAs film. See D. L. Mills and A. A. Maradudin, Phys. Rev. Lett. 31, 372 (1973). In Ref. 4, only the lower branch was observed. In subsequent work [J. Y. Prieur and S. Ushioda, Phys. Rev. Lett. 34, 1012 (1975)] observation of the upper branch by an indirect method was reported.

[6]Y. J. Chen, E. Burstein and D. L. Mills, Phys. Rev. Lett. 34, 1516 (1975).

[7]D. L. Mills, A. A. Maradudin, and E. Burstein, Ann. Phys. (N.Y.) 56, 504 (1970).

[8]D. L. Mills and A. A. Maradudin, Phys. Rev. B 8, 2943 (1975).

[9]J. S. Nkoma, Proceedings of the Third International Conference on Light Scattering in Solids, Campinas, Brazil, 1975 (unpublished); J. S. Nkoma and R. Loudon, J. Phys. C 8, 1950 (1975).

[10]In the theory of the scattering of light by bulk polaritons in infinitely extended crystals, the Green's-function method used by H. J. Benson and D. L. Mills [Phys. Rev. B 1, 4835 (1970)] has been compared with the response function analysis presented subsequently by A. S. Barker and R. Loudon [Rev. Mod. Phys. 44, 18 (1972)] and the two have been shown to be equivalent. See Appendix C of the article by D. L. Mills and E. Burstein cited in Ref. 1.

[11]Y. R. Chen, E. Burstein, and D. L. Mills, Proceedings of the Third Internatioanl Conference on Light Scattering, Campinas, Brazil, 1975 (unpublished).

[12]A. A. Maradudin and D. L. Mills, Phys. Rev. B 11, 1392 (1975).

[13]In a recent paper, Pine and Dresselhauss asserted that the Green's-function method employed here and in Ref. 7 omits a portion of the scattered fields in the medium within which the incident field couples to the fluctuations responsible for the scattering. [See A. S. Pine and G. Dresselhaus, Solid State Commun. 16, 1009 (1975).] Their assertion is incorrect. This may be seen by direct evaluation of the scattered field within the crystal field from Eq. (2.5).

[14]The Green's functions $D_{\mu\nu}$ defined here, in Refs. 8 and 12 differ by a factor of 4π from the functions $G_{\mu\nu}$ introduced in Ref. 7 for the semi-infinite geometry. Also, in the prefactor of Eq. (2.5), we have ignored the difference between the frequency of the incident and scattered radiation.

[15]A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

[16]Y. Chen, E. Burstein, D. L. Mills and S. Ushioda, Proceedings of the Fourth International Conference on Raman Spectroscopy, Brunswick, Maine, 25-29 August, 1975 (unpublished).

[17]The factor of $\exp[-2(l^{(s)}+l^{(0)})d]$ has its origin in our choice for the location of the outer surface of the film at $z=d$. In the case of back scattering from a semi-infinite material (the limit $d\to\infty$), this factor is cancelled by a factor of $\exp[+2(1/l_s+1/l_0)d]$ which emerges from $s_{zz}(-k_1^{(0)}-k_s^{(0)})$ as one allows d to approach infinity. The finite result (after $d\to\infty$) then becomes independent of d as physical cosiderations require.

[18]J. Y. Prieur and S. Ushioda, Phys. Rev. Lett. 34, 1012 (1975).

[19]In the earlier work of Mills and Maradudin (see the paper cited in Ref. 5), the anisotropic character of the substrate was taken into accout. To compare the statement $d(Q_{\parallel},\Omega)=0$ with this earlier dispersion relation, one must equate the dielectric constant parallel and perpendicular to the optic axis of the substrate.

[20]J. Y. Prieur (private communication).

[21]See Sec. III of the article by Mills and Burstein cited in Ref. 1.

[22]Note that for back scattering, $\exp[-id(\Delta k-\Delta k^*)]$ becomes $\exp[2d(1/l_s+1/l_0)]$, so the cross section for scattering from this mode becomes independent of d as $d\to\infty$, as it must, as we commented earlier in Ref. 17.

[23]For example, see the discussion in Sec. II of E. Evans and D. L. Mills, Phys. Rev. B 8, 4004 (1973).

[24]A. Mooradian and A. L. McWhorter, in *Proceedings of the International Conference on Light Scattering Spectra of Solids*, *New York*, 1968 edited by G. B. Wright (Springer-Verlag, New York, 1969), p. 297.

[25]J. Y. Prieur and S. Ushioda (private communication).