Longitudinal-optical-vibration-induced high transparency of nominally opaque thin films

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(Received 24 February 1989)

It has been theoretically demonstrated that a presence of a very thin cubic crystal film deposited on a substrate can substantially modify infrared optical properties of the structure. The effect is due to excitation of longitudinal-optical vibrations within the film.

An investigation of the optical properties of layered structures provides important information on the discontinuities in the dielectric properties of the materials involved. Such an indirect diagnostic is based on excitation of eigenmodes of the structure by an external pump and observation of a response in the form of radiation emitted by the eigenmodes. For example, in the case of a simplest structure—a metal-vacuum boundary—a surface wave can be excited by an obliquely incident *p*-polarized electromagnetic wave by using, for example, the so-called attenuated total-reflection technique[1] (ATR) to match the phase velocities (wave numbers) of the pump and the surface wave. In the resonant conditions, the energy of the pump is totally converted into the energy of the surface wave, which is then dissipated within the metal. The coefficient of reflectivity of the structure then vanishes[2] despite the fact that one has formally created conditions for total internal reflection. More complex structure can be designed[3] allowing for total absorption of a pump with arbitrary polarization. Such a structure contains three dielectric films, providing a wave guide for the *s*-polarized component, and a metallic surface, so that both surface and guided waves can be excited simultaneously (i.e., for the same angle of incidence). The energy losses due to the dissipation within the metal substrate (or the wave guide) necessary to achieve vanishing reflection can be substituted by losses in the form of reemission of the electromagnetic wave on the other side of the structure when a metallic film is used instead of a thick metal substrate. In such a situation, an anomalously high transparency of (nominally opaque) metallic films can be obtained[4] where coupled surface or guided modes on each side of the film are responsible for the energy transfer.

In this paper we theoretically investigate a formally similar but physically quite different situation. Instead of exciting surface or guided modes we consider a case when the eigenmodes responsible for the energy transfer are optical-vibrational modes. This, however, requires that one adds to a boundary a transition layer formed by a crystal with cubic symmetry with at least two atoms per cell. Since optical phonons are eigenmodes of the transition layer, one can excite these modes directly by linear conversion of the obliquely incident *p*-polarized electromagnetic wave (an analog of resonance absorption in a plasma[5]), i.e., without using the ATR technique or any of its equivalents. We demonstrate that a very thin ($b_1 \ll \lambda$, where b_1 is the film thickness, and λ the wavelength of the incident wave) transparent film of a material which allows for excitation of optical phonons and whose dielectric constant $1 > \epsilon = \epsilon_1(\lambda) > 0$ deposited on a bulk substrate with metallic properties, i.e., with $\epsilon = \epsilon_2(\lambda) < 0$ can, under certain conditions that are specified below, be responsible for total absorbtion of the incident wave. Further, we will show that a structure consisting of a nominally opaque film with $\epsilon = \epsilon_2(\lambda) < 0$ and thickness a sandwiched between two very thin ($b_1, b_2 \ll \lambda$) films with $\epsilon = \epsilon_1(\lambda) > 0$ reveals anomalously high transparency caused by coupling of optical phonons excited in each of the films.

For completeness we note that effects on the dispersion properties of surface waves of such transition layers have been investigated by many authors (see, e.g., Refs. 6–9). Generally speaking, if any of the frequencies ω_{LO}, ω_{TO} of the longitudinal- and transverse-optical phonon, respectively, lies within the spectrum of transverse-magnetic (TM) surface waves then the presence of the transition layer causes a gap to appear in that spectrum whose magnitude is proportional[6] (in the limit $a \to \infty$) to $(b_1/\lambda)^{1/2}$. Moreover, an *s*-polarized transverse-electric (TE) surface wave[7] [which is strictly speaking a highly localized ($b_1/\lambda \ll 1$) guided wave] can appear in the gap of the TM surface-wave spectrum at frequencies $\omega \approx \omega_{TO}$. However, these effects differ from those investigated here where only optical-vibrational modes are involved, although a comparison is made between the phenomena induced by the presence of either surface waves or optical vibrations.

Let us consider a *p*-polarized electromagnetic wave (i.e., the wave with the electric vector in the plane of incidence yz) that is obliquely (at an angle θ) incident onto a structure vacuum/(dielectric 1)/(dielectric 2)/dielectric1/vacuum which can be described by the following spatial distribution of the dielectric constant: $\epsilon = 1$ for $z < -b_1$ and $z > a + b_2$, $\epsilon = \epsilon_1$ for $-b_1 < z < 0$ and $a < z < b_2$, $\epsilon = \epsilon_2$ for $0 < z < a$. The coefficient of reflectivity of such a structure reads

$$R=-\frac{\alpha(1-\alpha_0^2)(\beta_1+\beta_2)+[1-\alpha^2\alpha_0^2+(\alpha^2-\alpha_0^2)\beta_1\beta_2+\alpha_0(1-\alpha^2)(\beta_1-\beta_2)]\tanh(\kappa_2 a)}{\alpha[(1+\alpha_0^2)(\beta_1+\beta_2)-2\alpha_0(1+\beta_1\beta_2)]+[1+\alpha^2\alpha_0^2+(\alpha^2+\alpha_0^2)\beta_1\beta_2-\alpha_0(1+\alpha^2)(\beta_1+\beta_2)]\tanh(\kappa_2 a)}\ , \tag{1}$$

where

$$\alpha=\frac{\epsilon_2\kappa_1}{\kappa_2\epsilon_1},\quad \alpha_0=i\frac{\epsilon_1}{\kappa_1}k_0,\quad k_0=\frac{\omega}{c}\cos\theta,\quad \kappa_{1,2}=\frac{\omega}{c}(\sin^2\theta-\epsilon_{1,2})^{1/2},\quad \beta_{1,2}=\tanh(\kappa_1 b_{1,2})\ ,$$

ω is the frequency of the incident wave, and c is the speed of light. We now assume that in the frequency range of our interest the intermediate film behaves like a metal, i.e., that $\epsilon_2<0$ and $-\epsilon_2\gg 1$. We will investigate conditions when $R=0$ assuming that $0<\epsilon_1<1$. Equation (1) has been analyzed in Refs. 3 and 4 for such layered media and such angles of incidence which allowed for excitation of guided $(b_1/\epsilon_1^{1/2}\lambda\cong N/2;\ N=1,2,\ldots)$ or surface $(\alpha\cong 1)$ modes.

In the simplest case when $a\to\infty$ and $\epsilon_2\to-\infty$ the requirement $R=0$ means that

$$\alpha_0^2-\beta_1^2=0,\quad \text{i.e.,}\ k_0^2\epsilon_1^2=-\kappa_1^2\tanh^2(\kappa_1 b_1)\ . \tag{2}$$

In what follows, we will show that the relationship (2) can be satisfied when neither surface wave $(\alpha\gg 1)$ nor guided wave $(2b_1/\epsilon_1^{1/2}\lambda<1)$ can be excited. We will consider simple cubic crystals with two atoms per cell, i.e., with a single transverse ω_{TO} and longitudinal ω_{LO} optical frequency limit at long wavelength. In this limit one approximates the dielectric constant of the cubic crystal film by $\epsilon_1(\omega)=\epsilon'+i\epsilon''$ with (see, e.g., Refs. 7 and 8)

$$\epsilon'(\omega)=\epsilon_\infty\frac{\omega^2-\omega_{\mathrm{LO}}^2}{\omega^2-\omega_{\mathrm{TO}}^2}\ , \tag{3}$$

where ϵ'' represents dissipation, and ϵ_∞ is that part of the dielectric constant that takes into account contributions of all excitations whose frequencies are far from the investigated resonance. In this sense the approximation (3) can be used even for cubic crystals with more than two atoms per cell which have more than one transverse and one longitudinal-optical vibrational mode (the number of such pairs of frequencies is given by the symmetry of the crystal).

As one can see, Eq. (2) has a solution only if $\epsilon''\neq 0$ and, in particular,

$$\epsilon'\cong\left[\frac{\omega}{c}b_1\right]^2\tan^2\theta:\quad \epsilon''\cong\frac{\omega}{c}b_1\frac{\sin^2\theta}{\cos\theta}\ . \tag{4}$$

Since $\omega b_1/c\ll 1$ then $R=0$ for $\omega\cong\omega_{\mathrm{LO}}$ and $\epsilon''\gg\epsilon'$. This type of solution has been found by Kotov[10] for a thin layer of transparent $(\epsilon>0)$ plasma adjacent to a perfect conductor where the role of longitudinal-optical phonons was played by electron plasma oscillations (with $k\cong 0$). Notice that the presence of the substrate with $|\epsilon_2|\to\infty$ makes it impossible to achieve the same effect for an s-polarized incident wave via excitation of transverse-optical vibrational modes, for no electric field can exist adjacent and parallel to such a substrate.

For finite values of a and ϵ_2, however, such that $|\alpha|\gg 1$, and for the special case when $b_1=b_2=b$, the requirement $R=0$ implies

$$\alpha_0^2\cong\beta^2+\frac{2\beta}{\alpha\tanh(\kappa_2 a)}\quad \text{i.e.,}\ k_0^2\epsilon_1^2\cong-\kappa_1^2\tanh^2(\kappa_1 b)-2\kappa_1\frac{\kappa_2\epsilon_1}{\epsilon_2}\frac{\tanh(\kappa_1 b)}{\tanh(\kappa_2 a)}\ , \tag{5}$$

where $\beta=\beta_1=\beta_2$. While it was impossible to satisfy (2) for $\epsilon''=0$, it is possible to satisfy Eq. (5) even for real ϵ_1. The reason is that finite values of a and ϵ_2 now allow for reemission of the energy of optical vibrations in the form of outcoming electromagnetic waves on the other side of the sandwich structure. The energy losses in this form thus replace the dissipation necessary to obtain $R=0$.

For a finite thickness of the "metallic" film the real part of (5) becomes $D_1D_2=0$, where $D_{1,2}$ represent the dispersion functions of two new eigenmodes of the system as a whole, as discussed later. In the limit of a thick "metallic" film when $a\to\infty$ these two solutions degenerate into the bulk optical vibrations, i.e., $D_1=D_2\cong 0$, and the vibrations on each side of the film are decoupled.

We will now demonstrate the effect of vanishing reflectivity and anomalously high transparency on example of a Al_2O_3 film overcoated from both sides by a LiF crystal film. The choice of LiF is given by the fact that its frequency (in the long-wavelength limit) of longitudinal-optical phonons, $\nu_{1\mathrm{LO}}\cong 670\ \mathrm{cm}^{-1}$, (in fact, $\nu_{1\mathrm{LO}}\cong 670\ \mathrm{cm}^{-1}$ for bulk LiF crystal,[11] however, spectral measurements[12] indicate that in the case of thin LiF films $\nu_{1\mathrm{LO}}$ is closer to $650\ \mathrm{cm}^{-1}$) fits into the frequency region $570\ \mathrm{cm}^{-1}\cong\nu_{2\mathrm{TO}}<\nu_{1\mathrm{LO}}<\nu_{2\mathrm{LO}}\cong 900\ \mathrm{cm}^{-1}$, where the dielectric constant of the Al_2O_3 film ϵ_2 is negative.[12] Approximating the dielectric constant of Al_2O_3 by formally the same expression as (3) with[12] $\epsilon_{2\infty}\cong 3.2$ one obtains $\epsilon_2(\nu_{1\mathrm{LO}})\cong-12.8$. The coefficient of reflectivity of a structure consisting of a thin LiF crystal film deposited on a Al_2O_3 substrate as a function of the film thickness b_1/λ is shown in Fig. 1. The example corresponds to the frequency of the incident wave $\nu=664\ \mathrm{cm}^{-1}$ (which, for[13] $\epsilon_{1\infty}=1.9$, is equivalent to $\epsilon_1'\cong 0.1$), with $\epsilon_1''=0.01$ (see Ref. 14); the angle of incidence is a parameter; (a) $\theta=84°$, (b) $\theta=87.9°$, (c) $\theta=89°$. As can be seen, the coefficient of reflectivity reaches its absolute minimum $R=0$ for $\theta\cong 88°$

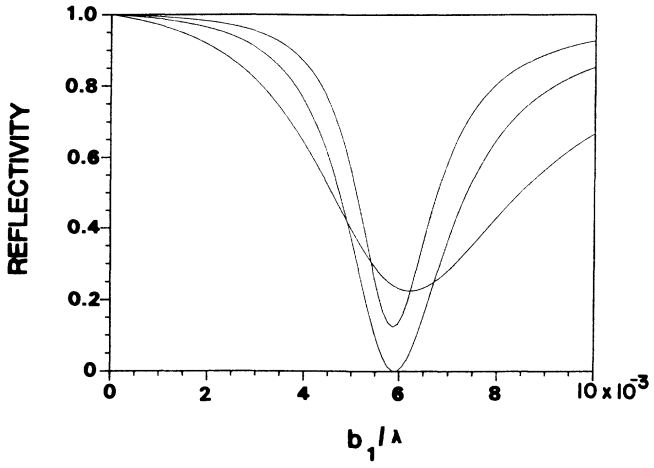

FIG. 1. The coefficient of reflectivity of a structure consisting of a thin LiF crystal film deposited on an Al_2O_3 substrate as a function of the film thickness b_1/λ for $\nu=664$ cm^{-1}, $\epsilon_1''=0.01$, and the angle of incidence: (a) $\theta=84°$, (b) $\theta=87.9°$, (c) $\theta=89°$.

and the film thickness $b_1/\lambda \simeq 5.86\times 10^{-3}$ when the energy balance is optimized, i.e., when the rate of energy input due to the incident wave equals the rate of dissipation of the longitudinal-optical phonon excited by linear conversion. The film thickness for which minimum reflectivity is obtained increases with decreasing angle of incidence.

When, instead, a structure consisting of an Al_2O_3 film overcoated on both sides by LiF crystal films is considered then, since $\epsilon_1' \ll 1$ and the normal component of the electrical inductance is preserved across the structure, the electric field within the film is very high (when compared of that of the incident wave) and allows, therefore, for efficient coupling to the field associated with the longitudinal-optical phonon on the other side of the film. The coefficient of transmissivity of such a structure as a function of the LiF film thickness $b_1/\lambda=b_2/\lambda$ is shown in Fig. 2. Here the frequency of the incident wave is

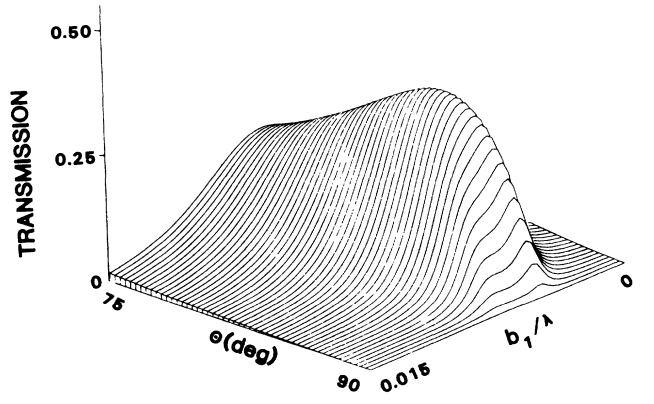

FIG. 2. The coefficient of transmission of LiF/Al_2O_3/LiF structure as the function of the LiF film thickness $b_1/\lambda=b_2/\lambda$ and the angle of incidence θ. Here the frequency of the incident wave is $\nu=664$ cm^{-1} and the thickness of the Al_2O_3 layer is $a/\lambda=0.1$.

again $\nu=664$ cm^{-1} and the thickness of the Al_2O_3 layer is $a/\lambda=0.1$. A maximum transmission $T\cong 44\%$ is obtained for $\theta\cong 85°$ and $b_1/\lambda\cong 0.006$ when the coefficient of reflectivity of the structure vanishes. A double-peak behavior corresponds to interference of the optical vibrations on each side of the structure. Obviously, the interference becomes important when the central film is thin enough. An increase in the angle of incidence means an increase in the longitudinal component of the incident wave which linearly couples to the longitudinal-optical vibrations. Consequently, the evanescent field within the central film increases relative to the amplitude of the incident wave, which is effectively equivalent to a reduction in the thickness of the central film. The interference of the optical vibrations excited in each of the two overcoating films results in a symmetric or antisymmetric spatial distribution of the electric field across the central film. The right peak (smaller b_1/λ) corresponds to the symmetric mode, while the left peak corresponds to the antisymmetric mode. We use this terminology in analogy with the coupled surface modes propagating along a very thin film.

Since the losses within the LiF films are $\propto \epsilon_1'' b_1 E_0^2/\epsilon_1^2$ the maximum transmission can, in fact, be obtained further from resonance. To demonstrate this we have plotted in Fig. 3 transmissivity as the function of b_1/λ and frequency ν. In this example $a/\lambda=0.15$ and $\theta=82°$, which corresponds to vanishing reflection for $\nu=730$ cm^{-1} and $b_1/\lambda\cong 0.07$ when $T\cong 75\%$. As usual, the curves broaden as one goes away from resonance. The two-peak structure is the signature of the presence of surface modes, as discussed in more detail later. Figure 4 illustrates the dependence of the transmission curves on the thickness of the central film. Here we have fixed the frequency of the incident wave $\nu=730$ cm^{-1} and the angle of incidence $\theta=82°$. The peaks due to excitation of symmetric and antisymmetric coupled modes are well separated for very thin films. The peaks coalesce as a/λ increases and approaches $\cong 0.15$. Further increase of a/λ then results in a drop in efficiency of the process because the field amplitude within the LiF film is not high enough to ensure efficient tunneling through the central film. For completeness, the dependence of the off-resonant case, $\nu=730$ cm^{-1}, on b_1/λ and the angle of incidence (with $a/\lambda=0.15$) is shown in Fig. 5, which is

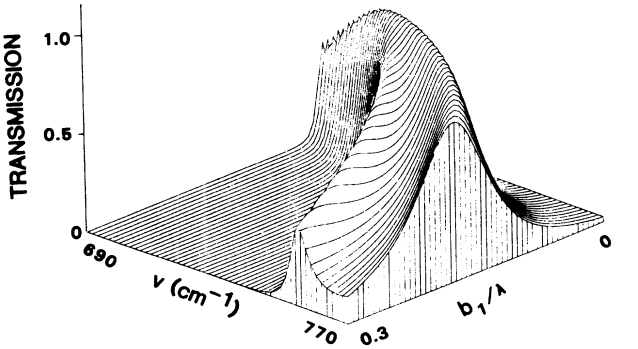

FIG. 3. Transmission versus $b_1/\lambda=b_2/\lambda$ and frequency of the incident wave for $a/\lambda=0.14$ and $\theta=82°$.

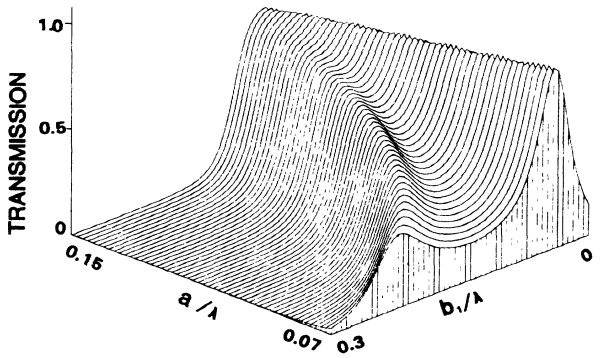

FIG. 4. The dependence of the shape of the transmission curves on the thickness of the central film for $\nu=730\ \mathrm{cm}^{-1}$ and the angle of incidence $\theta=82°$.

analogous to Fig. 2 (notice the difference in scale). Again, large angles of incidence lead to splitting of the peak, which is a signature of the presence of the symmetric and antisymmetric coupled longitudinal-optical vibrational modes.

To conclude, we firstly note that Berreman[15] was probably the first to investigate infrared absorption at longitudinal-optical frequency in cubic crystal films. His theoretical analysis and experimental data showed dips in the reflection spectrum of thin LiF films deposited on bulk silver substrate. The dips were interpreted as due to excitation of longitudinal-optical phonons within the film. However, Berreman did not realize that, as reported for the first time (to our knowledge) in this paper, the conditions can be found when total (100%) absorption occurs. Moreover, we have found that this effect can be considered as the first stage of a process leading to anomalously high transparency of nominally opaque films overcoated from both sides by very thin (relative to the wavelength of the incident wave) cubic crystal films which support longitudinal optical modes. There is no need for ATR-type techniques to be used to couple the incident wave to the optical vibrations because the longitudinal-optical phonons can be driven directly by a linear conversion of the pump. The cases of vanishing reflection (Fig. 1) and of an anomalously high transmission (in the absence of dissipation one would, obviously, obtain 100% transmission) represent physically very interesting situations. Namely, a substantial modification of the optical properties of nominally highly reflecting and opaque (within the considered frequency range) material has been achieved by overcoating the material by a very thin $b_1/\lambda \ll 1$ film of a transparent material. For comparison, the surface-wave-induced vanishing reflection or high transparency occurs for $\sin^2\theta_{SW} \cong \epsilon_1'\epsilon_2'/(\epsilon_1'+\epsilon_2')$, which for $|\epsilon_2| \gg 1$ means $\sin^2\theta_{SW} \approx \epsilon_1'$. Therefore, for the frequencies of the incident wave considered here $20° < \theta_{SW} < 70°$.

Physically, the difference between the cases of surface-wave- and optical-vibration-induced phenomena becomes obvious when one analyzes the spatial distribution of the electromagnetic field within the structure. In the case of surface waves the magnetic component $B = B_x$ and the longitudinal component $E_z \propto B_x$ have a peak at the boundaries between the central film and the coatings, while E_y is more or less uniform across the overcoating films. This is in contrast to the case considered here when E_y peaks at the boundaries, while E_z, B_x are nearly uniform across the cubic crystal films as a signature of excitation of long-wavelength longitudinal-optical vibrations. In both cases the modes excited on each side of the structure can, for a very thin central film, interfere to form a new mode of the structure as a whole which is either symmetric or antisymmetric. As a result, the transmission peak splits in two. In the case of surface waves the antisymmetric mode has a lower damping rate due to the fact that it carries less energy within the central film which is typically more lossy than overcoating films. Since the optical vibrations are the eigenmodes of the overcoating cubic crystal films, they carry and dissipate their energy within the crystal and, consequently, in contrast to the previous case, the symmetric mode has the lower damping rate (see, e.g., Fig. 5) because it occurs for smaller thickness of the overcoat. In fact, the most interesting feature, reported for the first time here, is the possibility of a continuous transition from one effect to the other, which ob-

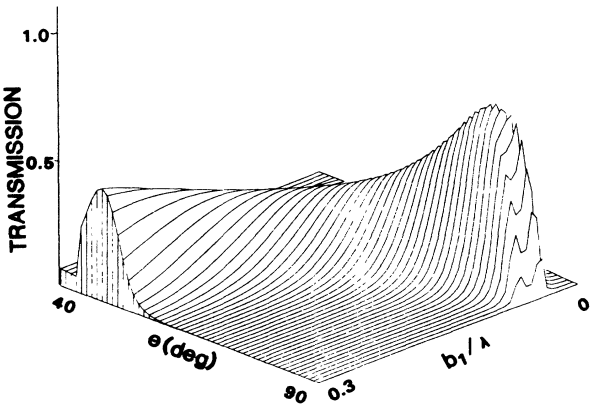

FIG. 5. The illustration of the existence of hybrid modes, i.e., of the continuous transition from the effect of high transparency induced by the excitation of longitudinal-optical phonon modes to that induced by the presence of surface waves. The parameters are $\nu=730\ \mathrm{cm}^{-1}$ and $a/\lambda=0.15$.

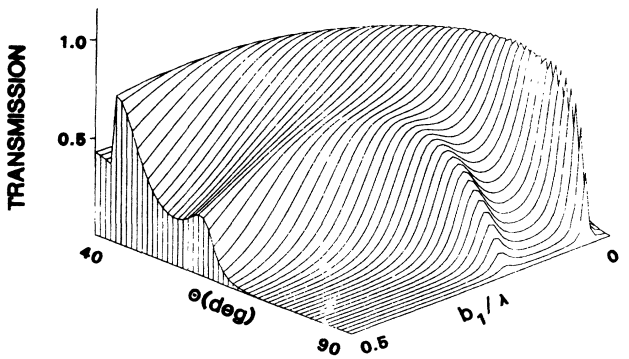

FIG. 6. Same as in Fig. 5, however, for a very thin central film with $a/\lambda=0.075$. The symmetric and antisymmetric modes in each of the limit cases swap their roles.

viously suggests the existence of hybrid modes which are neither purely surface waves nor purely longitudinal-optical vibrations. As seen from Fig. 5, the optical-vibration-assisted high transparency at large angles and thin overcoats is gradually replaced by the surface-wave-induced high transparency at relatively large thicknesses of the overcoating and moderate angles close to the limit for total internal reflection $\sin^2\theta=\epsilon_1'$. The depth of the dip linking the two phenomena increases as one gets closer to the resonance $\nu\rightarrow\nu_{1LO}$. In the case of a very thin central film, either of the modes splits into the symmetric and antisymmetric modes, as shown in Fig. 6, which corresponds to $a/\lambda=0.075$ and $\nu=730$ cm^{-1}. During the transition from one pure situation to the other, the symmetric and antisymmetric peaks swap the roles, i.e., while the peak corresponding to the symmetric mode of longitudinal-optical vibrations occurs for smaller thickness of the overcoating film, the symmetric surface-wave mode gives a rise to the transmission peak occurring at larger angle θ than the one which is due to the antisymmetric surface mode.

ACKNOWLEDGMENTS

The authors wish to acknowledge discussions with B. Luther-Davies.

[1]A. Otto, in *Optical Properties of Solids, New Development,* edited by B. O. Seraphin (North-Holland, Amsterdam, 1976).

[2]S. Vukovic and Z. Radovic, Opt. Commun. **24**, 217 (1978); W. Lukosz and H. Wahlen, Opt. Lett. **3**, 88 (1978).

[3]S. Vukovic, R. Dragila, and A. M. Smith, Opt. Lett. **13**, 164 (1988).

[4]R. Dragila, B. Luther-Davies, and S. Vukovic, Phys. Rev. Lett. **55**, 1117 (1985).

[5]N. G. Denisov, Zh. Eksp. Teor. Fiz. **31**, 609 (1956) [Sov. Phys.—JETP **4**, 544 (1957)].

[6]V. M. Agranovich and A. G. Mal'shukov, Opt. Commun. **11**, 169 (1974).

[7]V. E. Kravtsov, E. I. Firsov, V. A. Yakovlev, and G. N. Zhizhin, Solid State Commun. **50**, 741 (1984).

[8]V. M. Agranovich, V. E. Kravtsov, T. A. Leskova, A. G. Mal'shukov, G. Hernandez-Cocoletzi, and A. A. Maradudin, Phys. Rev. B **29**, 976 (1984).

[9]V. M. Agranovich and V. I. Ydson, Opt. Commun. **5**, 422 (1972); G. N. Zhizhin, M. A. Moskaleva, V. G. Nazin, and V. A. Yakovlev, Zh. Eksp. Teor. Fiz. **72**, 687 (1977) [Sov. Phys.—JETP **45**, 360 (1977)].

[10]A. K. Kotov, Fiz. Plazmy **11**, 629 (1985) [Sov. J. Plasma Phys. **11**, 368 (1985)].

[11]A. Kachare, G. Anderman, and L. B. Brantley, J. Phys. Chem. Solids **33**, 467 (1972).

[12]G. N. Zhizhin, M. A. Moskaleva, V. G. Nazin, and Y. A. Yakovlev, Zh. Eksp. Teor. Fiz. **72**, 687 (1977) [Sov. Phys.—JETP **45**, 360 (1977)].

[13]C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971), p. 190.

[14]H. Bilz, L. Genzel, and H. Happ, Z. Phys. **160**, 535 (1960).

[15]D. W. Berreman, Phys. Rev. **130**, 2193 (1963).