Optical properties of an ionic-crystal slab

R. Ruppin
Soreq Nuclear Research Centre, Yavne, Israel
(Received 4 May 1973)

The macroscopic theory for the optical properties of an ionic-crystal slab is extended so as to allow for the possibility of exciting longitudinal-optical phonons. The resulting semimacroscopic method correctly reproduces the complex absorption structure which previous microscopic calculations have predicted to occur in the frequency range between ω_T and ω_L, the frequencies of the long-wavelength transverse- and longitudinal-optical phonons. Calculated spectra for the case of extremely thin LiF films are presented and the influence of various physical parameters on the absorptance is discussed.

I. INTRODUCTION

Two approaches have been employed in the past in the study of the vibrational modes and the optical properties of an ionic crystal slab. In the continuum method, which has been expounded in detail by Fuchs and Kliewer,[1] only the long-wavelength optical modes are treated. The relative displacement of the positive and the negative ions is written as a continuous function of the spatial coordinates, and its equation of motion is solved together with Maxwell's equations to yield the normal polariton modes of the slab. The contribution of the individual polaritons to the absorption peaks appearing in the spectrum can be identified, and the absorption spectrum can thus be completely understood from the properties of the polariton modes.[2] In this paper we will treat the case of very thin slabs, by which we mean that d, the thickness, is small in comparison with the characteristic wavelength c/ω_T, where ω_T is the frequency of the long-wavelength transverse-optical phonons. In this size range, the macroscopic theory predicts that in the absorption spectrum of obliquely incident P-polarized radiation two peaks will occur, one at ω_T and the other at ω_L, the frequency of the long-wavelength longitudinal-optical phonons. A typical calculated spectrum is shown in Fig. 1. Berreman[3] was the first to suggest this optical experiment as a simple and accurate method for obtaining the values of both ω_T and ω_L. Within the framework of the macroscopic theory, the optical properties of the slab are independent of the orientation of the crystal axes, provided that the crystal is of cubic symmetry.

The lattice-dynamical method has been employed by Tong and Maradudin,[4] by Chen *et al.*[5] and by Jones and Fuchs.[6] In this approach, the microscopic normal vibrational modes of a slab containing a small number of layers ($N = 15$ has been used most often) are obtained by direct diagonalization of the $6N \times 6N$ dynamical matrix. By adding an external field to the equations of motion, which were based on Kellerman's rigid-ion model, Jones and Fuchs[6] have also calculated the optical properties of the slab. They have presented the absorptance for P-polarized light incident at an angle of 75° on a 15-layer NaCl slab oriented so that the small dimension is along a [001] direction. In addition to the absorption peaks at ω_T and ω_L, which also the continuum method predicts, they obtained a series of absorption maxima in the frequency region between ω_T and ω_L. These were shown by them to arise from longitudinal-optical bulk phonons which have odd parity with respect to the midplane of the slab. Their calculation also predicted a surface-mode absorption peak just below ω_T. Analogous peaks in the imaginary part of the dielectric response tensor were obtained in the calculation of Tong and Maradudin,[4] who have also used the rigid-ion model for a 15-layer NaCl slab. Since the continuum theory predicts no absorption structure for thin films, other than the peaks at ω_T and ω_L, it seems that this theory becomes valueless for slabs that approach microscopic thickness. The present work is intended to show that it is possible to extend the macroscopic method in a simple way, so as to be of

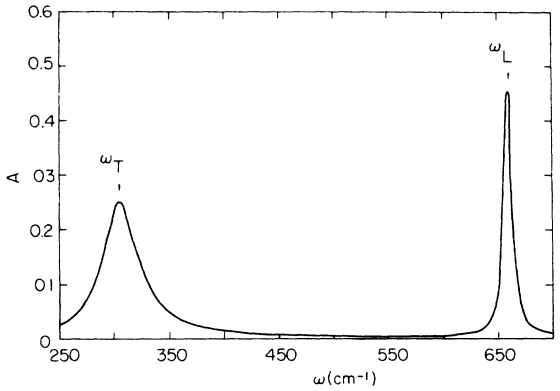

FIG. 1. Absorptance of a LiF slab of thickness 0.2 μm as calculated from macroscopic theory. The P-polarized beam is incident at an angle of 30°.

value even for extremely thin slabs. The semi-macroscopic method employed in this paper provides a bridging link between the macroscopic and the microscopic approaches. Our treatment is based on the work of Melnyk and Harrison,[7] who have extended the classical electromagnetic theory of reflection and transmission, so as to make it applicable to materials in which propagating longitudinal polarization waves exist. They have discussed in detail the optical properties of thin metal films, in which case the longitudinal polarization waves are electron plasma waves. They have also suggested the application of their theory to the case of ionic-crystal films, where the longitudinal-optical phonons play the role of the longitudinal polarization waves. After this paper had been initially submitted, a recent paper by Fuchs[8] came to our attention, which also treats the optical properties of an ionic-crystal slab by a semi-macroscopic method. The main conclusions are similar to ours, and the differences which do, however, exist will be noted in Sec. IV.

II. EXTENSION OF THE MACROSCOPIC THEORY

In the macroscopic theory, only the polaritons, which are transverse modes, contribute to the optical properties of the slab. It is known, however, from the investigation of plasma waves in thin metal films[9] and in plasma columns,[10] that longitudinal modes can also be excited by an incident electromagnetic wave of appropriate polarization. In thin films this effect occurs only for obliquely incident P-polarized radiation; this is the case which we discuss here. The geometry is shown in Fig. 2. The P-polarized beam travels in a medium which has a dielectric constant ϵ_M. The medium on the other side of the thin slab has a dielectric constant ϵ_M'.

Since the excitation of longitudinal modes will be allowed, the usual boundary conditions, i.e., the continuity of tangential $\vec{E}$ and $\vec{H}$, have to be augmented by the additional condition that the normal component of the displacement current is continuous, as has been shown by Melnyk and Harrison.[7] Applying the continuity conditions at the boundaries leads to the following expressions for the reflectance, transmittance, and absorptance of the film[7]:

$$R = |X/Z|^2, \tag{1}$$

$$T = \frac{\epsilon_M' k_{Mx}'}{\epsilon_M k_{Mx}} \left| \frac{Y}{Z} \right|^2, \tag{2}$$

$$A = 1 - R - T, \tag{3}$$

where

$$X = (1-\phi_T\phi_L)(FD' - DF'\phi_T\phi_L) - (\phi_T - \phi_L)(CB'\phi_T - BC'\phi_L), \tag{4a}$$

$$Y = (F+D)[\phi_L(\phi_T^2 - 1)(F-B) + \phi_T(\phi_L^2 - 1)(F-C)], \tag{4b}$$

$$Z = (1-\phi_T\phi_L)(DD' - FF'\phi_T\phi_L) - (\phi_T - \phi_L)(BB'\phi_T - CC'\phi_L), \tag{4c}$$

and

$$\phi_T = e^{ik_{Tx}d} \tag{5a}$$

$$\phi_L = e^{ik_{Lx}d} \tag{5b}$$

$$B = (c/\omega)\left[\epsilon k_{Mx} - \epsilon_M k_{Tx} + k_z^2(\epsilon_M - \epsilon)/k_{Lx}\right], \tag{6a}$$

$$C = (c/\omega)\left[\epsilon k_{Mx} + \epsilon_M k_{Tx} - k_z^2(\epsilon_M - \epsilon)/k_{Lx}\right], \tag{6b}$$

$$D = (c/\omega)\left[\epsilon k_{Mx} + \epsilon_M k_{Tx} + k_z^2(\epsilon_M - \epsilon)/k_{Lx}\right], \tag{6c}$$

$$F = (c/\omega)\left[\epsilon k_{Mx} - \epsilon_M k_{Tx} - k_z^2(\epsilon_M - \epsilon)/k_{Lx}\right]. \tag{6d}$$

B', C', D', F' are obtained from B, C, D, F by replacing ϵ_M and k_M by ϵ_M' and k_M', respectively. The electromagnetic waves in the media ϵ_M and ϵ_M' have wave vectors $\vec{k}_M$ and $\vec{k}_M'$, and the transverse and the longitudinal modes inside the slab have wave vectors $\vec{k}_T$ and $\vec{k}_L$, respectively. The z components of all wave vectors, k_z, are equal because of the continuity conditions. ϵ denotes the dielectric constant of the crystal, for which we use the form

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - (\omega/\omega_T)^2 - i\gamma(\omega/\omega_T)}, \tag{7}$$

where ϵ_0 and ϵ_∞ are the static and the high-frequency dielectric constants and γ is the damping factor. The x components of the wave vectors inside the slab are determined from the appropriate dispersion relations. For the transverse polariton modes the dispersion law is

$$k_T^2 = \epsilon\omega^2/c^2. \tag{8}$$

For the longitudinal modes we use the dispersion relation $\vec{k}_L(\omega)$ of the longitudinal-optical branch.

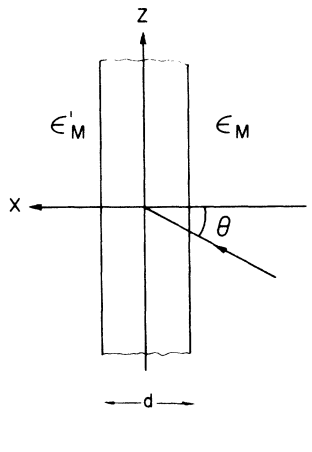

FIG. 2. Slab geometry.

We assume a sodium chloride structure and take the x axis to be along the [001] direction. The z component of $\vec{k}_L$ is equal to the corresponding component $k_M \sin\theta$ of the external field. For waves in the infrared region, $k_M \ll \pi/r_0$, where r_0 is the lattice constant. Thus, on the Brillouin-zone scale k_z is negligible, and we can use for the longitudinal modes the dispersion law of the [001] direction.

III. OPTICAL PROPERTIES

We have performed calculations of the optical properties of thin LiF films. For the longitudinal-optical branch the dispersion relation determined by Dolling *et al.*[11] by inelastic neutron scattering experiments has been used. LiF is convenient for our purpose, since it has a smooth longitudinal-optical branch which extends over a wide frequency range of 300 cm^{-1}, starting from 457 cm^{-1}, which is the frequency at the edge of the Brillouin zone. Only this frequency range will be shown in the calculated spectra, since outside it the theory reduces to the usual macroscopic treatment. For the optical constants appearing in Eq. (7) the following experimental values[12] have been used:
$\omega_T = 305\ cm^{-1}$, $\epsilon_0 = 9.02$, $\epsilon_\infty = 1.93$. For the damping factor γ the value 0.02 has been assumed, as in previous calculations of the optical properties.[2,6] With the inclusion of the damping factor in the dielectric constant (7) the transverse modes acquire a finite lifetime, which makes the process of absorption by these modes possible. A corresponding damping of the longitudinal modes has to be included as well. This will be done by allowing their wave vector to be complex, $\vec{k}_L = \vec{k}' + i\vec{k}''$. Assuming for the longitudinal modes a damping frequency Γ, we write the dispersion relation of the longitudinal-optical branch in the form

$$\omega^2(\vec{k}' + i\vec{k}'') = \omega^2 + i\Gamma\omega . \tag{9}$$

Expanding for $k'' < k'$ we find that

$$k'' = \Gamma/2\left(\frac{\partial\omega}{\partial k}\right) \tag{10}$$

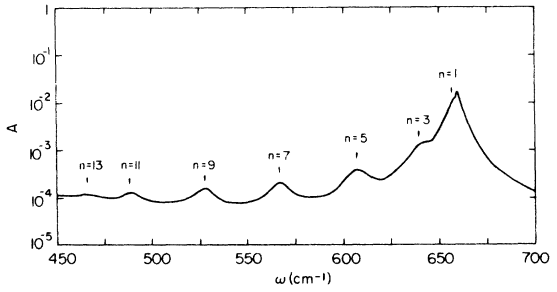

FIG. 3. Calculated absorptance of P-polarized light incident at an angle of 30° on a LiF slab of thickness 30 Å.

where, with the assumed crystal orientation, the derivative is taken along the [001] direction. We note that the last relation holds even at critical points, in which case the group velocity appearing in the denominator vanishes. We then have from Eq. (10) that k'' becomes infinite, which simply expresses the fact that the wave cannot propagate energy. In the calculation we have used for Γ/ω_L the value 0.02, as for the transverse modes. The group velocity along the [001] direction was obtained from the experimental dispersion curve of the longitudinal-optical branch.[11]

In Fig. 3 the calculated absorptance for P-polarized light incident at an angle of 30° on a 30-Å-thick LiF slab in air ($\epsilon_M = \epsilon_M' = 1$) is shown. A film of this thickness contains 15 atomic layers. In addition to the absorption peak at ω_L, which is due to a polariton mode of essentially uniform polarization,[1,2] there appears a series of subsidiary maxima, which are due to longitudinal bulk phonons. These absorption maxima appear whenever an odd number of half-wavelengths of the longitudinal wave fits into the film thickness, i.e., when

$$k_{Lx}d = n\pi , \quad n = 1, 3, 5, \ldots . \tag{11}$$

The values of n corresponding to the different peaks in the spectrum are given in Fig. 3. By calculating the polarization fields associated with the absorbing longitudinal modes given by Eq. (11), it is found that they have odd parity with respect to the midplane of the slab, in complete agreement with the result of the microscopic calculation.[6]

Within the semimacroscopic approach adopted here, it is very easy to investigate the dependence of the absorption spectrum on various parameters, such as the dielectric constants of the surrounding media, or the slab thickness. In the microscopic approach this would be a formidable task, since a change in one of the parameters usually requires the solution of a new huge system of equations. We have found that the absorption peaks become sharper and reach a higher maximum, without changing their location, when the angle of incidence is increased. As an example, the case of $\theta = 60°$, with all other parameters as before, is shown in Fig. 4(a). A further sharpening of the spectrum is attained by decreasing the damping factor γ, which can be achieved experimentally by cooling the specimen. The calculated absorptance for $\theta = 60°$ and γ reduced to 0.01 is shown in Fig. 4(b). We have also calculated the absorptance for various values of the dielectric constants ϵ_M and ϵ_M'. No significant changes in the spectrum were found to occur. We have also investigated the dependence of the spectrum on the slab thickness. As the thickness increases, the number of the absorption peaks due to longitudinal modes increases, but their intensity decreases. For d larger than 100 Å (and with

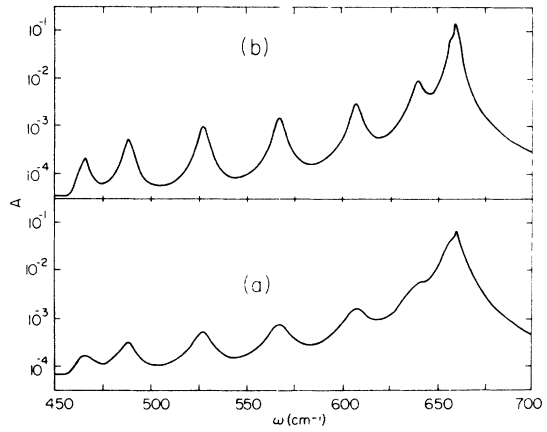

FIG. 4. Calculated absorptance for P-polarized light incident at an angle of 60° on a LiF slab of thickness 30 Å for two different damping factors: (a) $\gamma = 0.02$; (b) $\gamma = 0.01$.

$\gamma = 0.02$) they are not observable any more, and the spectrum assumes the simple two-peak structure of the macroscopic theory (Fig. 1).

IV. CONCLUSION

By introducing the dispersion of the longitudinal-optical phonons and including the possibility of their optical excitation, the macroscopic theory for the optical properties of an ionic crystal slab was extended so as to yield the correct shape of the absorption spectrum in the frequency range between ω_T and ω_L. The advantage of the present semimacroscopic method over the exact microscopic lattice-dynamical approach lies in its ready computational applicability to various physical situations. Thus, by using the formulas of Sec. II, the optical spectra can be easily calculated for different values of the parameters involved—i.e., the properties of the slab material, the dielectric constants of the media on both sides of the slab, the angle of incidence, and the slab thickness. Conversely, once experimental spectra become available, it should be possible, using the semimacroscopic theory, to extract from them information about the dispersion, as well as the damping, of the longitudinal-optical phonons.

We next discuss the simplifying assumptions that are implicit in the semimacroscopic approach used here. For the longitudinal-optical phonons the dispersion law of the appropriate phonon branch, as measured on bulk crystals, is used. This implies that we ignore any deviation of this branch in the thin film from the corresponding branch in large samples. Surface effects on the dispersion of bulk phonons (as distinguished from surface phonons) are small, so that this is a very satisfactory assumption. As regards surface modes, these have not given any contribution to the spectra calculated in the present work. The macroscopic theory predicts the existence of only two surface mode branches, which lie in the region between ω_T and ω_L. These are surface polaritons which do not interact with an incident electromagnetic wave in a simple optical experiment. This is due to the fact that they are nonradiative modes, which have only decaying (rather than oscillating) field components outside the slab, as discussed in detail by Kliewer and Fuchs.[1] Microscopic calculations have shown that, in addition to these Fuchs-Kliewer modes, there also exist other types of surface modes—which the macroscopic theory overlooks because they are modes that decay over a few atomic distances—unlike the Fuchs-Kliewer modes, which penetrate very deeply. Thus, any contributions of microscopic surface modes to the absorption will not be reproduced by the semimacroscopic method. Scrutiny of the spectra calculated from microscopic models[4,6,13] reveals that there appears only one surface-mode absorption peak, which is located just below ω_T. For a slab containing 15 layers this peak is almost as strong as the neighboring peak at ω_T. By extrapolating to the case of a 100-layer slab, Grimm *et al.*[13] have found that in the latter case the surface-mode absorption peak still exists, but its intensity is very small in comparison with that of the peak at ω_T. It can be concluded that, with the exception of one surface-mode absorption peak just below ω_T, the semimacroscopic method is adequate for calculating all the features of the absorption in thin films in the reststrahlen region. This conclusion has also been reached by Fuchs,[8] who has employed a slightly different semimacroscopic method. In Ref. 8 the optical properties were calculated from expressions for surface impedance derived for a metal in which the electrons have the special boundary condition of specular scattering at the surface. Such a boundary condition has little physical meaning for ionic crystals. We have employed the general macroscopic boundary conditions due to Melnyk and Harrison.[7] Also our results are potentially comparable to experimental measurements on LiF thin films, since we have used as input data the measured dispersion of the longitudinal-optical branch of LiF. In Ref. 8 the dispersion was calculated from the simplified rigid-ion model of NaCl. We have also investigated the dependence of the absorption on the phonon damping and on the film thickness.

ACKNOWLEDGMENT

We would like to thank Professor R. Englman for helpful discussions.

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