FACULTÉ DES SCIENCES DE PARIS

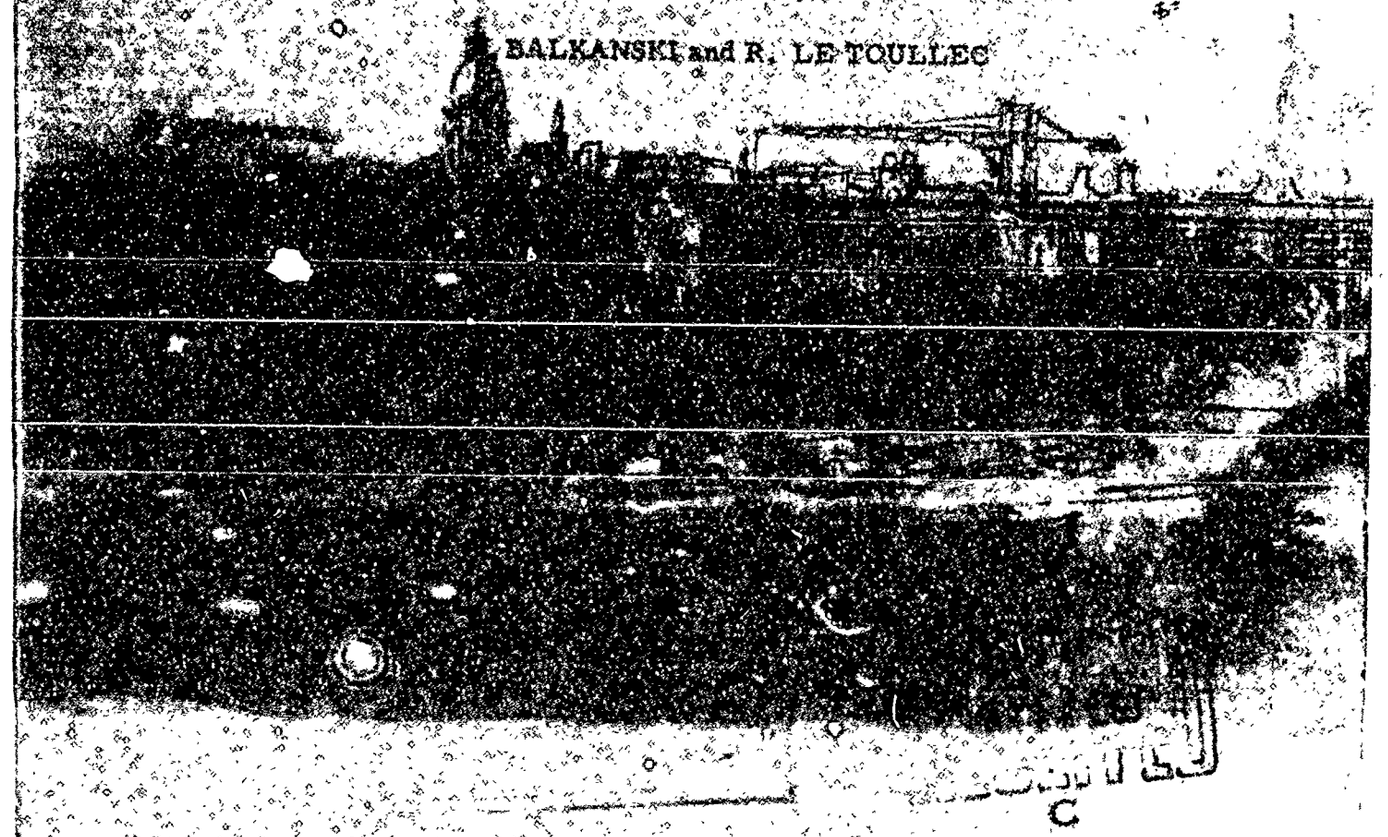
LABORATOIRE DE PHYSIQUE DES SOLIDES

Groupe de Recherche Associé au C.N.R.S. : OPTIQUE DES SEMICONDUCTEURS

SCIENTIFIC REPORT No 2

PHOTON-PHONON INTERACTION IN THIN FILMS

M. BALKANSKI and R. LE TOULLEC



THIS RESEARCH IS SPONSORED IN PART BY THE

EUROPEAN RESEARCH OFFICE

OF THE U.S. ARMY (THROUGH ITS EUROPEAN RESEARCH OFFICE)

CONTRACT DA-ERAR-68-0016

GRANT N° EOOAR-68-0016

SCIENTIFIC REPORT N° 2

PHOTON-PHONON INTERACTION IN THIN FILMS

M.BALKANSKI and R. LE TOULLEC

Laboratoire de Physique des Solides de la Faculté des Sciences de Paris
Equipe de Recherche Associée au C.N.R.S. : Optique des Semiconducteurs
9, Quai Saint-Bernard - Paris 5ème

This research has been sponsored in part by the
AEROSPACE RESEARCH LABORATORIES
Through the European Office of Aerospace Research, OAR,
United States Air Force under grant number EOOAR-68-0016

PHOTON-PHONON INTERACTION IN THIN FILMS

M. BALKANSKI and R. LE TOULLEC

Laboratoire de Physique des Solides
de la Faculté des Sciences de Paris, France,
Equipe de Recherche associée au C.N.R.S.

1. INTRODUCTION.

The normal modes of vibrations in a perfect crystal lattice resulting into net electric dipole moment with electric vector perpendicular to the propagation vector are strongly coupled with the radiation field. The resulting optical absorption is very strong at the frequencies of the transverse optical modes. Direct absorption studies can therefore be conducted only on thin films. Transmission measurements under normal incidence show an intense band centered at ω_{TO} .

The use of lineary polarized light under oblic incidence with $\vec{E}$ parallel to the plane of incidence leads to a strong band centered at ω_{TO} and a band less intense centered at ω_{LO} . For a polarized beam with $\vec{E}$ perpendicular to the plane of incidence only a strong band is observed centered at ω_{TO} . The treatment given by Berreman [1] accounts for the observation in the neighborhood of ω_{LO} but fails to explain the situation for frequencies near ω_{TO} . A detailed investigation on the optical modes of vibrations considering the effects due to the shape of the crystals have recently being developed by Fuchs and Kliewer [2]. It has been demonstrated that the optical properties of a thin crystal are determined by the existence of "virtual modes" whose frequencies and life time depend strongly on the boundary conditions : thickness of the crystal and on the angle of incidence.

Generally the optical transitions due to the interaction of the phonon field with the radiation field are determined by three factors : electric dipole moment, anharmonicity (higher order dipole moments) and the boundary conditions which may induce transitions not allowed in the bulk.

We shall examine here the particular case of thin films where the photon-phonon interaction can be treated in the frame of the collision theory for two types of particles, as a two-step process : first the strong coupling of the radiation field with the phonon field in terms of polaritons and the consequent polariton decay as a second step. The polariton decay is considered in terms of photon emission in which case the phenomenon is an elastic diffusion of the photon, or in terms of phonon emission which life time is limited by their coupling to the phonon field through the anharmonic potential.

The optical absorption at the normal mode frequencies is calculated in terms of band width related respectively to the polariton life time, to the phonon life time and to the elastic diffusion of photons.

The experimental data are chosen among a complet set of results on the lattice dynamics of the II-VI compounds [3], in order to substantiate some of the main physical feathers.

2. THEORY.

2.1. General Photon-Phonon Interaction.

In a perfect crystal the normal modes frequencies are solutions of the secular equation representing the dynamical behaviour of the lattice.

In the harmonic approximation where the potential energy of the crystal is expanded in power of the displacement of the atoms from their equilibrium positions and the expansion is broken off at the quadratic terms, the equation

of motion of the atom k with mass m_k in the unit cell l subject to the displacement u_α with $\alpha = x, y, z$, is given by

$$m_k \ddot{u}_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) + \sum_{l'k'} \sum_{\beta} \Phi_{\alpha\beta}\left(\begin{smallmatrix} ll' \\ kk' \end{smallmatrix}\right) u_\beta\left(\begin{smallmatrix} l' \\ k' \end{smallmatrix}\right) = 0 \qquad (2.1)$$

where Φ is the force constant matrix depending only on the distance between cells $\vec{r}(l)-\vec{r}(l')$ due to the periodic symmetry of the lattice.

The normal modes and their frequencies are solutions of the set of equations for all unit cells of the crystal. Because of the periodic symmetry the modes have wave like phase variation from cell to cell and specific relative motion in the cell.

The dynamical matrix being of the form

$$C_{\alpha\beta}\left(\begin{smallmatrix} q \\ k\,k' \end{smallmatrix}\right) = \sum_{l} \frac{\Phi_{\alpha\beta}\left(\begin{smallmatrix} l \\ k\,k' \end{smallmatrix}\right)}{(m_k m_{k'})^{1/2}} \exp[-i\vec{q}.\vec{r}(l)] \quad . \qquad (2.2)$$

The system of 3n linear and homogenous equations has non-vanishing solutions only if the determinant

$$\| C_{\alpha\beta}\left(\begin{smallmatrix} q \\ k\,k' \end{smallmatrix}\right) - \omega^2 \delta_{kk'} \delta_{\alpha\beta} \| = 0 \qquad (2.3)$$

vanishes.

This "characteristic" equation gives the characteristic frequencies $\omega(\vec{q})$ whose graphic representations are the dispersion curves of the crystal.

The interaction with the radiation field results into strong absorption band on the optically active frequencies. The optical constants in the frequency region where the photon-phonon interaction occurs are deduced as solution of the simultaneous set of the Maxwell equations, the mechanical and the polarization equations.

The electromagnetic field is given by Maxwell's equations :

$$\begin{aligned} \overrightarrow{\text{rot}}\ \vec{H} &= \frac{1}{c}\dot{\vec{D}} \quad , \\ \overrightarrow{\text{rot}}\ \vec{E}_{int} &= -\frac{1}{c}\dot{\vec{H}} \quad , \\ \text{div}\ \vec{D} &= 0 \quad , \\ \text{div}\ \vec{H} &= 0 \quad , \end{aligned} \tag{2.4}$$

and $$\vec{D} = \vec{E}_{int} + 4\pi \vec{P} \quad . \tag{2.5}$$

The phonon field is described by the induced polarization due to the displacement in opposite directions of the two sublattices formed by charged ions and the internal electric field $\vec{E}_{int}$ equal to the macroscopic electric field in the crystal,

$$\vec{P} = Ne_T\vec{u} + \frac{\varepsilon_\infty - 1}{4\pi}\vec{E}_{int} \tag{2.6}$$

and also by the equation of motion

$$M\ddot{\vec{u}} + (M\omega_o^2 - \frac{4\pi Ne_s e_T}{3})\vec{u} = e_T\vec{E}_{int} \quad . \tag{2.7}$$

The solutions of the coupled system of equations representing the radiation field and the photon field give the infrared dispersion of the crystal.

2.2. Light propagation and dispersion relations in thin films.

The perfect crystal thin layers to be considered here have thickness larger than the interatomic distance so that the long wave approximation is applicable and one can define a macroscopic polarization $\vec{P}(\vec{r},t)$ and a macroscopic electric field $\vec{E}_{int}$.

The crystal plate is in the xOy plane limited in the z direction by $z = \pm d/2$.

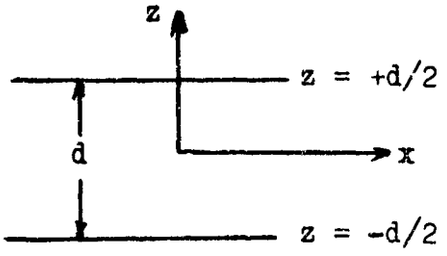


Fig.1

The infrared dispersion relations are deduced as shown in the previous chapiter but now using the boundary conditions and the continuity at the crystal surface.

In the incidence plane zOx, the electric field is taken as

$$\vec{E}_{int} = \vec{E}(z)\ \exp(ik_x x - i\omega t) \qquad (2.8)$$

for $\vec{E}$ parallel to the plane of incidence $E_y(z) = 0$ and the two of other components are given by

$$\frac{dE_z(z)}{dz} = -i\ k_x\ E_x(z) \qquad (2.9)$$

and

$$\frac{d^2E_x(z)}{dz^2} - \alpha^2\ E_x(z) = 0 \qquad (2.10)$$

with

$$\alpha^2 = k_x^2 - \frac{\omega^2}{c^2}\ \varepsilon \quad , \qquad (2.11)$$

$\varepsilon = 1$ outside the crystal giving α_o

and

$$\varepsilon = \varepsilon_\infty + \frac{(\varepsilon_o - \varepsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\Gamma_a\omega} \quad \text{inside the crystal} \ , \qquad (2.12)$$

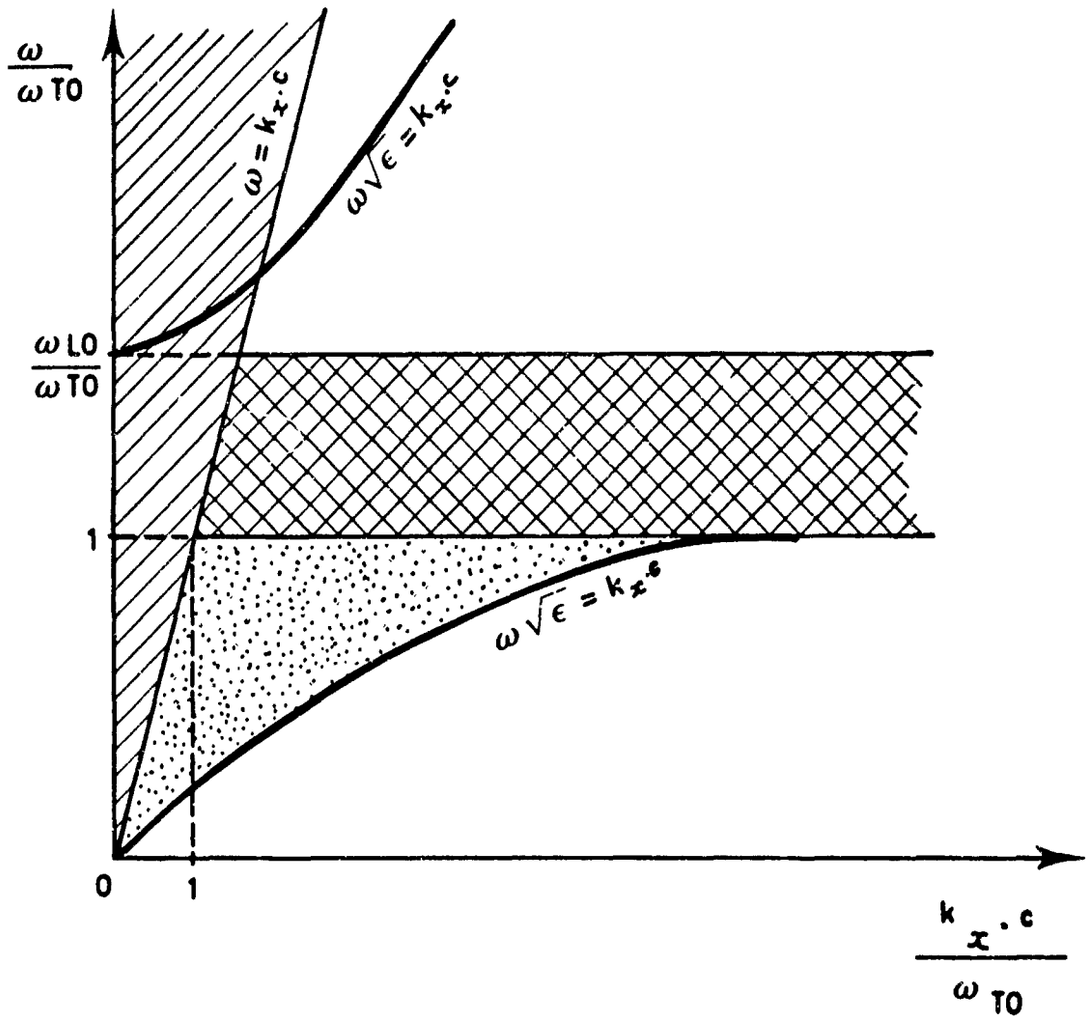
α^2 and α_o^2 can be positive or negative. Figure 2 gives the general feature of the dispersion.

On the right hand side of $\omega = k_x c$; α_o is real. The solutions are localized and referred to as "non-radiative". They are of two types :

- $\alpha^2 < 0$, left of $\omega\sqrt{\varepsilon} = k_x c$; $\alpha = ik_z$.

The sinusoidal solutions yield the "polaritons" correspond-

Figure 2



α_0 reel
α imaginaire
} polaritons

α_0 reel
α reel
} modes de surface

} modes non radiatifs

α_0 imaginaire
} modes radiatifs

ing to the dispersion relation of the transverse optical modes in the infinite crystal

$$\frac{\omega^2}{c^2}\,\varepsilon = k_x^2 + k_z^2 = |\vec{k}|^2 \quad . \qquad (2.13)$$

- $\alpha^2 > 0$. The electric field amplitude decays exponentially from the surface. For thick crystals : $\alpha(d/2) \gg 1$, the solutions are localized near the surface and yield the "surface mode" in the frequency region where $\varepsilon < 0$. This frequency region is situated between ω_{LO} and ω_{TO} .

On the left hand side of $\omega = k_x c$; α_o is imaginary. The solutions are sinusoidal outside the crystal and referred to as "radiative modes". These are the modes seen in the optical measurements.

2.3. Resonances in the thin films.

Considering all the solutions of the set of differential equations (2.2), (2.3), inside and outside the sample with the appropriate boundary conditions for the tangentiel and normal components of the electric field vector and the continuity at the surface, one can easily deduce the reflected R, transmitted T and absorbed A parts of the light beam :

$$R = \frac{\Gamma_v^2}{4(\omega-\omega_{TO})^2+(\Gamma_a+\Gamma_v)^2} \quad , \qquad (2.14)$$

$$T = \frac{4(\omega-\omega_{TO})^2 + \Gamma_a^2}{4(\omega-\omega_{TO})^2+(\Gamma_a+\Gamma_v)^2} \quad . \qquad (2.15)$$

$$A = \frac{2\,\Gamma_a\Gamma_v}{4(\omega-\omega_{TO})^2+(\Gamma_a+\Gamma_v)^2} \quad . \qquad (2.16)$$

The absorption A is given here by a formula of the type "Breit-Wigner" well-known in the theory of nuclear resonances. This is the absorption in the vicinity of a virtual mode de-

duced , under the assumption that the distance between two resonant modes is large enough to avoid interference.

The optical absorption of thin films has deduced here results from the strong photon-phonon interaction in the vicinity of resonant modes frequencies. The photon absorption takes place in two steps :

- First : the incident photons coupled with the phonons to give rise to quasi-stationary states the polaritons. For a very thin film the eigen-frequency of the polariton are ω_o : ω_{LO} , ω_{TO} and the breadth at half maximum is Γ_t .
- Second : after a characteristic time which is the life time of the polariton $\tau_t = \Gamma_t^{-1}$, the polaritons decay in emitting photons with the same incident frequency (elastic diffusion) and in exciting optical phonons whose further decay involve anharmonic processes. The polariton decay is consequently conducted through two channels : the first channel appears as a reflection of the photons in the two directions of propagation (2R) ; the second channel corresponds to the decay of the polaritons into optical phonons whose life time $\tau_a = 1/\Gamma_a(\omega)$ is determined by the anharmonic decay into other phonons.

First Channel : Optical reflectior in thin films.

The photons resulting from the polariton decay are "virtual modes". A system of polariton virtual modes is described by the assumption that there is no photon absorption inside the crystal hence

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon_\infty + \frac{(\varepsilon_o - \varepsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2} \qquad (2.17)$$

and that outside the crystal we have only emitted waves. The complex frequency for the virtual mode is

$$\omega_v = \omega_v' + i\omega_v'' \qquad (2.18)$$

with a line width $\Gamma_v = -2\omega_v''$.

For a polarized light beam with $\vec{E}$ parallel to the incidence plane the solutions of the differential equations to be retained introducing the appropriate boundary conditions and the characteristics of the virtual modes are

$$k_z \operatorname{cotg} k_z \frac{d}{2} = i \varepsilon k_z^o \quad , \tag{2.19}$$

$$k_z \operatorname{tg} k_z \frac{d}{2} = -i \varepsilon k_z^o \quad , \tag{2.20}$$

with

$$k_z = \left(\varepsilon \frac{\omega^2}{c^2} - k_x^2\right)^{1/2} = \frac{\omega}{c} \left(\varepsilon - \sin^2\theta\right)^{1/2}$$

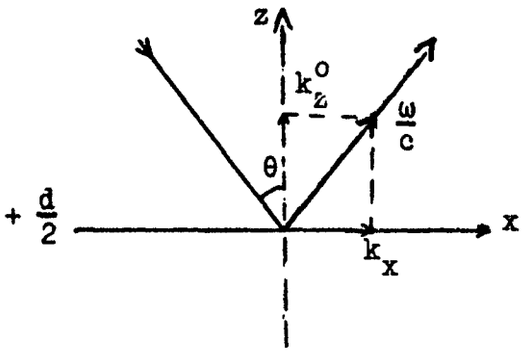


Figure 3

according to Figure 3 with

$$k_x = \frac{\omega}{c} \sin\theta \quad ,$$

$$k_z^o = \frac{\omega}{c} \cos\theta \quad .$$

We shall consider only thin films the thickness of which is less than the wavelength such as $k_z(d/2) \ll 1$ facing an incident light beam with an angle of incidence less than 90^o.

Equation (2.19) shows that a "cotg" mode will account for the optical properties near the frequency ω_{TO} where ε is very large.

Equation (2.20) shows that a "tg" mode will account for the optical properties near ω_{LO} where ε is very small.

For the "cotg" virtual mode only the $E_x(z)$ component of the electric field vector is non-vanishing, consequently this mode corresponds to a uniform polarization parallel to the crystal surface.

Since $k_z(d/2) \ll 1$ equation (2.19) becomes

$$\frac{2\,c}{d\,\cos\theta} = i\varepsilon\omega \quad . \qquad (2.21)$$

Considering the relations (2.17) and (2.18) a straightforward manipulation of the real and imaginary parts of ε with the approximation $\omega_v''/\omega_v' \ll 1$ equivalent to $\varepsilon'/\varepsilon'' \ll 1$ leads to the breadth at half maximum for this virtual mode :

$$\Gamma_v = -2\omega_v'' = \pi\, d\, \cos\theta\, \omega_{TO}^2\, (\varepsilon_o - \varepsilon_\infty) \qquad (2.22)$$

(Γ_v and ω_{TO} are in cm^{-1}).

For the "tg" virtual mode the $E_z(z)$ component of the electric field vector is non-vanishing : this mode corresponds consequently to a uniform polarization normal to the crystal surface. The same type of considerations as in the case of the "cotg" mode leads now to

$$\omega_v' = \omega_{LO}$$

and

$$\Gamma_v = -2\omega_v'' = \frac{\pi d}{\cos\theta} \sin^2\theta\, \omega_{LO}^2\, \frac{\varepsilon_o - \varepsilon_\infty}{\varepsilon_o\, \varepsilon_\infty} \qquad (2.23)$$

(Γ_v and ω_{LO} are in cm^{-1}).

<u>Second Channel</u> : Optical absorption in thin films. In order to examine the optical absorption near the virtual mode "cotg" let us write

$$\frac{k_z}{\varepsilon\, k_z^{\,o}} \cot g\, k_z \frac{d}{2} = K = K' + iK'' \quad . \qquad (2.24)$$

One has then :

$$A = \frac{-2\,K''}{(K''-1)^2 + K'^2} \quad , \qquad (2.25)$$

$$R = \frac{1}{(1-K'')^2 + K'^2} \quad , \qquad (2.26)$$

$$T = \frac{K'^2 + K''^2}{(1-K'')^2 + K'^2} \quad . \qquad (2.27)$$

K is a function of the frequency and of the intrinsic damping Γ_a due to the coupling among phonons through the anharmonic potential.

The complex TO phonon frequency is

$$\Omega_{TO} = \omega_{TO} - i\Gamma_a/2 \quad . \qquad (2.28)$$

Near the resonance frequency it is possible to use the following linear approximation

$$K(\omega,\Gamma_a) = [\omega-(\omega_{TO}-i\Gamma_a/2)]a \quad , \qquad (2.29)$$

here a is a constant. Substituting this expression in the equation giving the virtual mode "cotg" we obtain

$$i\,K(\omega_v,0) = -1 \quad , \qquad (2.30)$$

hence

$$K' = 2\,\frac{\omega_{TO}-\omega}{\Gamma_v} \quad \text{and} \quad K'' = -\,\frac{\Gamma_a}{\Gamma_v} \quad . \qquad (2.31)$$

Substituting into equation (2.25) we obtain the expression (2.16) for the absorption, into equation (2.26) for the reflection (2.14), and into equation (2.27) for the transmission (2.15). Equation (2.25) shows that the absorption (A = 1-R-T) near the resonant mode frequency has a Lorentzian shape with a breadth at half maximum $\Gamma_t = \Gamma_a + \Gamma_v$. Substituting Γ_v by its value equation (2.23) one obtains

$$A_{TO} = 2\pi d\,(\varepsilon_o-\varepsilon_\infty)\,\omega_{TO}^2\,\Gamma_a(\omega_{TO})\,\cos\theta\,\frac{1}{4(\omega-\omega_{TO})^2+\Gamma_t^2} \qquad (2.32)$$

with

$$\Gamma_t = \pi d\,(\varepsilon_o-\varepsilon_\infty)\,\omega_{TO}^2\,\cos\theta + \Gamma_a(\omega_{TO}) \quad . \qquad (2.33)$$

The same arguments lead to the characteristics near the resonant mode "tg" at the frequency ω_{LO}

$$A_{LO} = 2\pi \frac{d}{\cos\theta} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_o}\right) \omega_{LO}^2 \, \Gamma_a(\omega_{LO}) \, \sin^2\theta \, \frac{1}{4(\omega-\omega_{LO})^2+\Gamma_t^2} \qquad (2.34)$$

with

$$\Gamma_t = \pi \frac{d}{\cos\theta} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_o}\right)\omega_{LO}^2 \sin^2\theta + \Gamma_a(\omega_{LO}) \qquad (2.35)$$

$\Gamma_a(\omega_{LO})$ is the intrinsic damping at the ω_{LO} frequency.

In summary : for each of the described processus a characteristic optical absorption has been deduced.

First step : the photon absorption a_p resulting into polaritons is

$$a_p = \frac{2\Gamma_v(\Gamma_v+\Gamma_a)}{4(\omega-\omega_o)^2+ (\Gamma_v+\Gamma_a)^2} \quad . \qquad (2.36)$$

Second step : Polariton decay into emitted virtual modes is characterized by

$$2\,R = a_p \frac{\Gamma_v}{\Gamma_v+\Gamma_a} \qquad (2.37)$$

where from

$$R = \frac{\Gamma_v^2}{4(\omega-\omega_o)^2+ (\Gamma_v+\Gamma_a)^2} \quad . \qquad (2.38)$$

Polariton decay into phonon annihilation is given by

$$A = a_p \frac{\Gamma_a(\omega)}{\Gamma_v+\Gamma_a} \qquad (2.39)$$

where from

$$A = \frac{2\,\Gamma_v\Gamma_a}{4(\omega-\omega_o)^2+ (\Gamma_a+\Gamma_v)^2} \quad . \qquad (2.40)$$

The transmission is $T = 1 - A - R$.

All these formulas are applicable only near the resonance frequency ω_o within the range $|\omega-\omega_o| < \omega_{LO}-\omega_{TO}$.

For polarized light with $\vec{E}$ parallel to the incident plane the transmission of a thin film gives two minima : one for $\omega = \omega_{LO}$ and the other for $\omega = \omega_{TO}$. The breadth at half maximum for these two Lorentzians is

$$\Gamma_t = \Gamma_a(\omega_o) + \Gamma_v \quad . \qquad (2.41)$$

For polarized light with $\vec{E}$ normal to the incident plane the only active virtual mode is TO at a frequency ω_{TO} and a breadth at half maximum

$$\Gamma_v = \pi \frac{d}{\cos\theta} (\varepsilon_o-\varepsilon_\infty) \omega_{TO}^2 \quad . \qquad (2.42)$$

3. EXPERIMENTAL RESULTS.

As examples for cases where these considerations can be applied we shall give few cases of transmission and reflectivity spectra where the measurements have been carried with plane polarized light for different incident angle and different film thickness.

CdS has been chosen for its possibility to be studied under different crystallographic orientation and to be prepared in thin film of different thickness with c axis parallel or perpendicular to the plane of the layer. CdS crystallizes in wurtzite structure with two molecules in the unit cell. Twelve normal modes are to be expected out of which nine are optical modes. Symmetry considerations give the degeneracy of the different modes and selection rules indicate that for a direction of propagation three modes are optically active out of which two TO and one LO. Referred to the mutual orientation of the propagation vector $\vec{q}$ and the

crystal axis $\vec{c}$ one distinguishes between $\omega_{LO//}$, $\omega_{LO\perp}$, $\omega_{TO//}$ and $\omega_{TO\perp}$. Investigations on thin films allows to determine the frequency of $\omega_{LO//}$, $\omega_{LO\perp}$ and $\omega_{TO\perp}$.

A transmission spectrum at room temperature for a CdS thin film of thickness 0.7 μ on Si substrate with $\vec{c}$ normal to the substrate is given in Figure 4 for polarized light beam with E parallel to the incident plane and E perpendicular to the incident plane. The shape of the transmission band is what is generally obtained in this type of measurements and checks two essential features of equation (2.15) giving the transmission for the "cotg" virtual mode.

The breadth at half maximum Γ_t is much larger than the intrinsic damping Γ_a due to the anharmonicity. From our measurements $\Gamma_t \simeq 32\ cm^{-1}$ whereas $\Gamma_a \simeq 5\ cm^{-1}$.

The transmission minimum is very small. The experimental value is high also because the measurements are taken on a substrate. The theoretically calculated transmission minimum is

$$\Gamma_{min} = (\Gamma_a/\Gamma_t)^2 \simeq 0.030 \quad .$$

When oblic indicence is used for the transmission measurements according to the theory two minima should be observed : one broad and intense centered at the TO frequency and the other as indicated by equation (2.34) centered at the LO frequency. In Figure 5 is given the transmission spectrum for the same CdS layer with light beam at angle $\theta = 45^{\circ}$ in both polarizations. The intensity of the peak centered at ω_{LO} is much lower and the breadth at half maximum is also smaller. The infrared active modes in this particular geometry are $\omega_{TO\perp}$ and $\omega_{LO//}$ The frequency calculated by Kramers-Krönig inversion for a thick crystal are

Figure 4

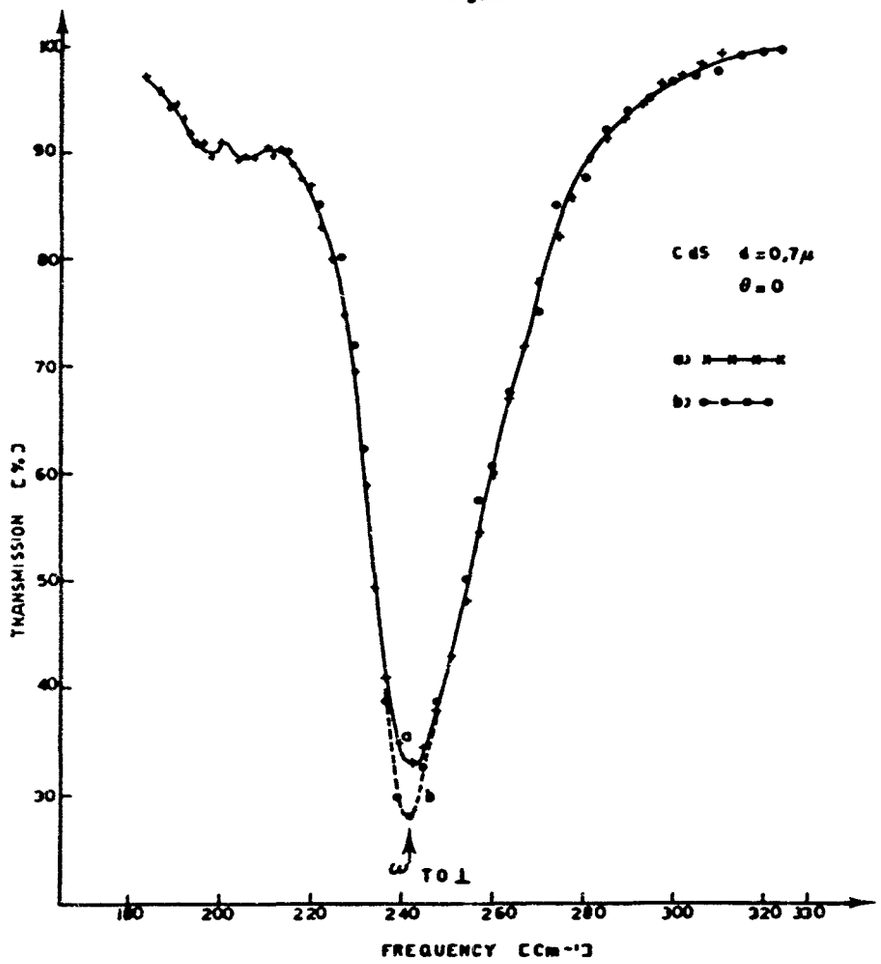
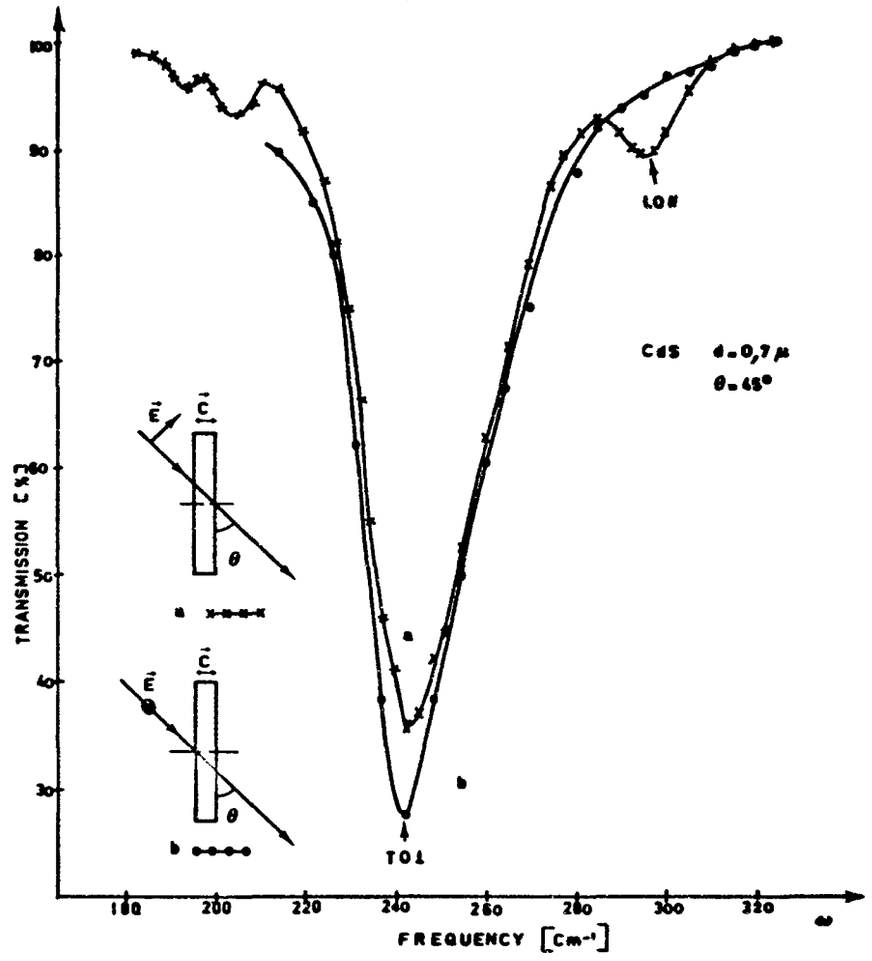


Figure 5



$$\omega_{TO\perp} = 240 \text{ cm}^{-1} ,$$

$$\omega_{LO//} = 298 \text{ cm}^{-1} .$$

The values obtained for the thin film from the results shown in Figure 5 are :

$$\omega_{TO\perp} = 242 \text{ cm}^{-1} ,$$

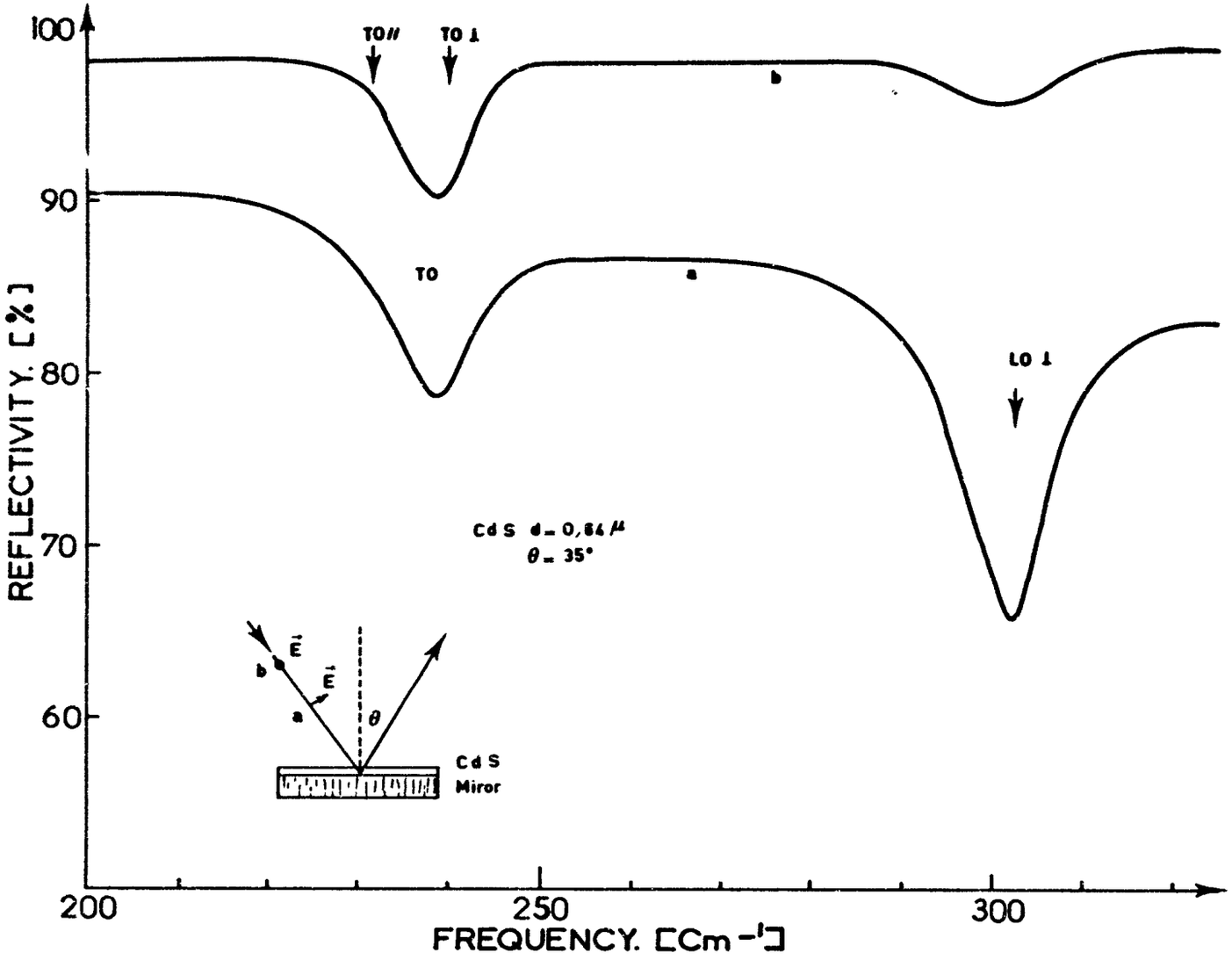
$$\omega_{LO//} = 296 \text{ cm}^{-1} .$$

This agreement shows that studies on thin films can be extremely useful in determining the normal mode frequencies.

If the thin film is evaporated on a metallic substrate the electric field vector parallel to the metal surface being vanishing no TO mode should be observed for polarized light with $\vec{E}$ parallel to the incident plane. The reflectivity spectra shown in Figure 6 for a CdS thin film of thickness $d = 0.64\ \mu$ evaporated on an aluminium mirror exibit two minima, the one corresponding to $LO_{\perp}$ expected for polarized light with $\vec{E}$ parallel to the plane of incidence, the other centered at ω_{TO} which should not have been observed if we were working with very thin films. The only reason for observing the TO mode in these conditions is not the thickness because as it can be seen from Figure 8, the intensity of the peak is not proportional to the thickness of the layer but it is clear that the TO is not observed for very thin films.

From the reflectivity minima given in Figure 6 one can deduce $\omega_{TO} = 238 \text{ cm}^{-1}$ and $\omega_{LO} = 301.5 \text{ cm}^{-1}$. According to the theoretical previsions for CdS with $\vec{c}$ in the plane of the substrate one should observe $\omega_{LO\perp} = 302 \text{ cm}^{-1}$ which is in very good agreement with the experiments and the observed TO frequency should be situated between $\omega_{TO\perp} = 240 \text{ cm}^{-1}$ and

Figure 6


100
90
80
70
60
REFLECTIVITY. [%]
TO//
TO ⊥
TO
LO ⊥
b
a
CdS d= 0,84 μ
θ= 35°
E
E
b
a
θ
CdS
Miror
200
250
300
FREQUENCY. [Cm⁻¹]

$\omega_{TO//} = 232\ cm^{-1}$ the observed frequency $238\ cm^{-1}$ is well between these two values.

In Figure 7 are given the reflectivity spectra for different values of angle of incidence. This demonstrates according to the theory that $1-R = 2A$ vanishes and consequently the mode "tg" tends to zero when the incidence approaches the normal. This again is in agreement with the theory.

4. DISCUSSION.

The experimental results presented here demonstrate the general qualitative features of the theory and suggest that detailed studies of the optical properties of thin films may be of great interest for the knowledge of the fundamental mechanism of optical transitions due to the interaction of the radiation field with the phonon field.

A particular case of same practical importance is this of very thin film. This is practically the only one which has been previously studied [1,4]. For this case in our notations we shall have $\Gamma_v \ll \Gamma_a$ which can be realized in choosing the thickness very small. It should be also remained that $\Gamma_v(TO) \simeq \varepsilon_\infty^2\, \Gamma_v(LO)$. The condition $\Gamma_v \ll \Gamma_a$ will then be obtained at ω_{LO} for a thickness much larger than at ω_{TO} . Let us take as an example a crystal with $\varepsilon_\infty = 5$, $\varepsilon_o = 9$ for $\theta = \pi/4$, $\omega_{TO} = 250\ cm^{-1}$, $\omega_{LO} = 335\ cm^{-1}$ and $\Gamma_a = 10\ cm^{-1}$, the virtual mode damping will then be $\Gamma_v(LO) = 1\ cm^{-1}$ for a thickness $d = 4500$ Å whereas for the TO we shall have the same $\Gamma_v(TO) = 1\ cm^{-1}$ for a thickness $d = 180$ Å . The line width and even the possibility of observing a given mode under oblic incidence are therefrom strongly dependent on the thickness of the crystal plate.

Figure 7

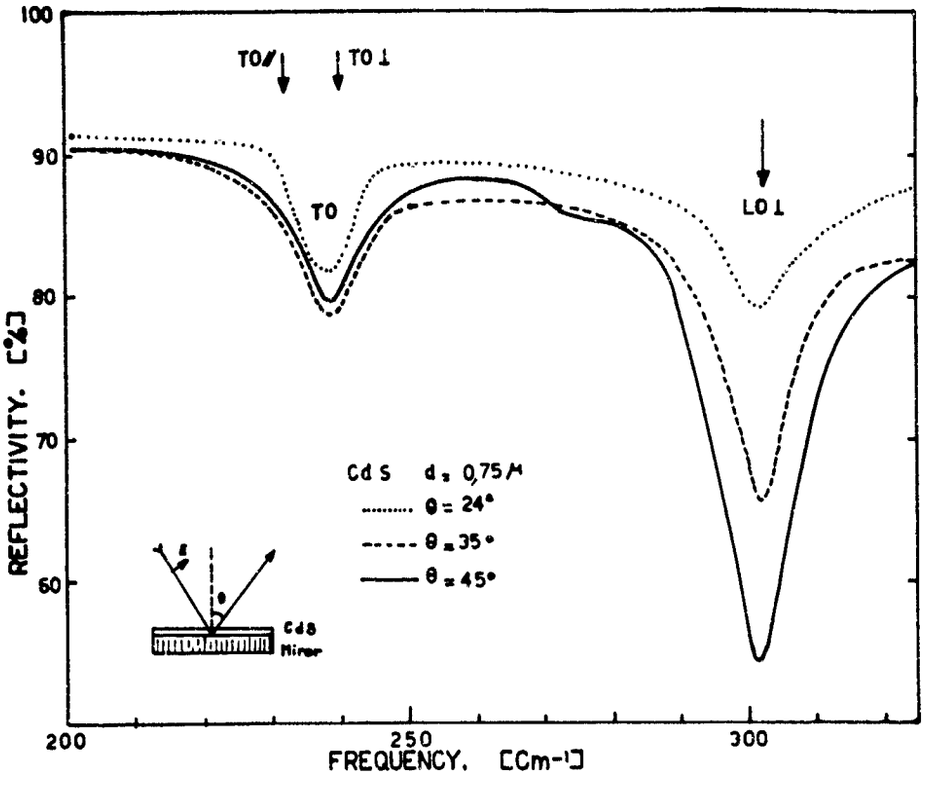
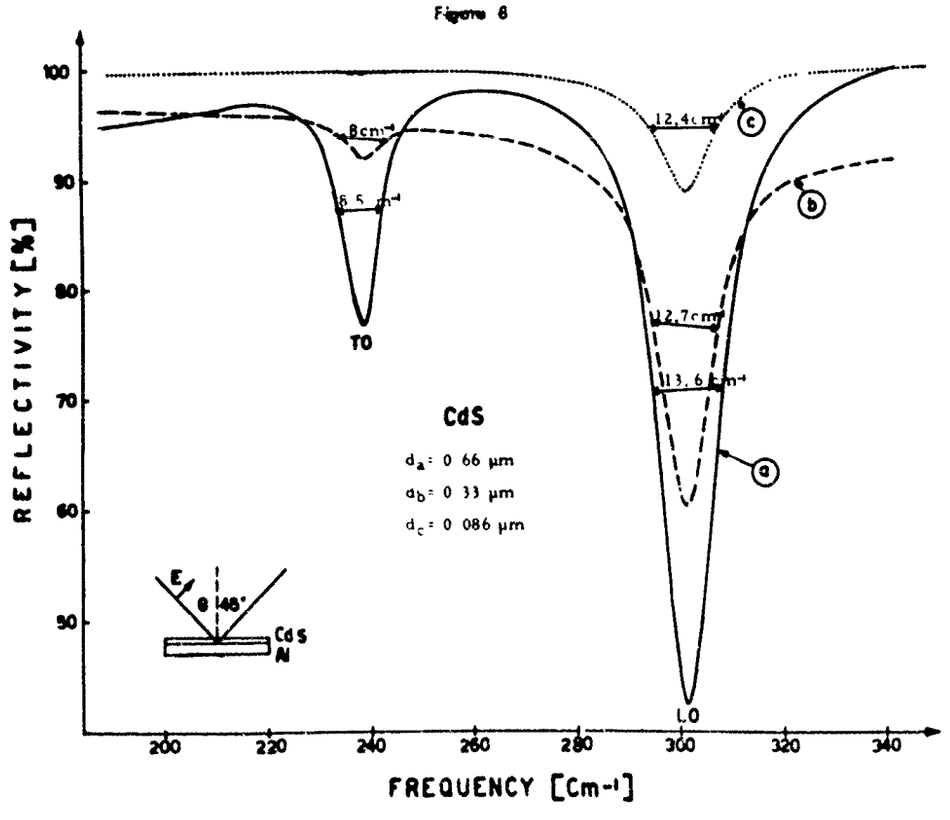


Figure 8



For the condition $\Gamma_v \ll \Gamma_a$ we have $\Gamma_t \simeq \Gamma_a$ and therefore the absorption coefficient is

$$A \simeq \frac{2\,\Gamma_v \Gamma_a}{4(\omega-\omega_o)^2+\Gamma_a^{\,2}} \qquad (4.1)$$

where from

$$A_{max} \simeq \frac{2\,\Gamma_v}{\Gamma_a} \ll 1 \quad . \qquad (4.2)$$

Hence this particular case is the one of weak photon-phonon interaction. The photon absorption in this case is weak and the reflection which is proportional to $(\Gamma_v)^2$ can be neglected.

In calculating the mean power absorbed per unit volume in a crystal under an external electric field [4] in terms of the response function of the dielectric constant one can deduce the absorption which is respectively :

$$A_{TO} = \frac{\omega}{c}\,\frac{d}{\cos\theta}\,\mathrm{Im}\,\varepsilon_{xx}^{\,2}\cos^2\theta \quad , \qquad (4.3)$$

$$A_{LO} = \frac{\omega}{c}\,\frac{d}{\cos\theta}\,\mathrm{Im}\,\varepsilon_{zz}^{\,2}\sin^2\theta \quad . \qquad (4.4)$$

In terms of normal dielectric constants for an isotropic crystal and in cm^{-1} this is :

$$A_{TO} = 2\pi\omega\,\frac{d}{\cos\theta}\,\mathrm{Im}\,\varepsilon\cos^2\theta \,, \qquad (4.5)$$

$$A_{LO} = 2\pi\omega\,\frac{d}{\cos\theta}\,\mathrm{Im}\left(-\frac{1}{\varepsilon}\right)\sin^2\theta \quad . \qquad (4.6)$$

Taking ε under the form of equation (2.12) in the harmonic approximation and developing near the poles one finally obtains :

$$\text{Im } \varepsilon \simeq \frac{(\varepsilon_o-\varepsilon_\infty)\ \Gamma_a\ \omega_{TO}}{4(\omega_{TO}-\omega)^2+\ \Gamma_a^{\ 2}} \quad , \qquad (4.7)$$

$$\text{Im } (-\frac{1}{\varepsilon}) \simeq \frac{(1/\varepsilon_\infty-1/\varepsilon_o)\Gamma_a\ \omega_{LO}}{4(\omega_{LO}-\omega)^2+\ \Gamma_a^{\ 2}} \qquad (4.8)$$

and consequently

$$A_{TO} \simeq 2\pi \frac{d}{\cos\theta} (\varepsilon_o-\varepsilon_\infty)\omega_{TO}^2\cos^2\theta\ \Gamma_a(\omega_{TO})\ \frac{1}{4(\omega_{TO}-\omega)^2+\Gamma_a^2(\omega_{TO})} \ , \qquad (4.9)$$

$$A_{LO} \simeq 2\pi \frac{d}{\cos\theta} (\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_o})\omega_{LO}^2\sin^2\theta\ \Gamma_a(\omega_{LO})\ \frac{1}{4(\omega_{LO}-\omega)^2+\Gamma_a^2(\omega_{LO})} \ . \qquad (4.10)$$

This is well the form forseen in equation (4.1). This result shows that $\Gamma_a(\omega_{TO})$ is well the breadth at half maximum of the function $\text{Im } \varepsilon = 2nk$ whereas $\Gamma_a(\omega_{LO})$ is the breadth at half maximum of the function $\text{Im}(-1/\varepsilon) = 2nk/(n^2+k^2)^2$. These formulas are therefore susceptible of direct verification. For very thin films the absorption can be deduced from the measurements of R for thin films evaporated on a mirror :

$$R = 1 - 2A$$

and equation (2.23) gives for CdS with $d = 0.72\ \mu$ using $\theta = 45^o \pm 8^o$:

$$\Gamma_v(\text{calculated}) = 1.05 \pm 0.54\ \text{cm}^{-1} \ ,$$

$$\Gamma_a = 10 \pm 0.5\ \text{cm}^{-1} \ .$$

Hence the calculated value is $\Gamma = 11.05 \pm 1.04\ \text{cm}^{-1}$ whereas experimentally one obtains $\Gamma = 13\ \text{cm}^{-1}$.

The maximum calculated absorption is $2A_{max} = 0.35 \pm 0.12$ and the experimental value is $2A_{max} = 0.37$.

All these results show that further experimental investigation and theoretical developments are the photon-phonon interaction in thin films will lead to progress in the related physical phenomena.

It may be of interest to mention that the same formalism may be used to study the plasmons which leads to the results of Ferrel and Stern [5]. The correspondence from phonons to plasmons may be reached by taking $\varepsilon_o = \infty$, the expression for A, R, and T, remains the same. The breadth at half high for photon emission is given by

$$\Gamma_v = \pi\, d\, \frac{\sin^2\theta}{\cos\theta}\, \omega_p^{\,2}$$

with

$$\omega_p^{\,2} = 4\pi N e^2/m\varepsilon_\infty \quad ,$$

ω_p being the plasma frequency.

ACKNOWLEDGEMENTS

The authors wish to express theirs acknowledgements to F. PROIX for having communicated experimental results summarized in Figure 8 prior to publication.

REFERENCES

1. D.W. BERREMAN, Phys. Rev. 130, 193 (1963).
2. R. FUCHS and K.L. KLIEWER, Phys. Rev. 140, A 2076 (1965).
   K.L. KLIEWER and R. FUCHS, Phys. Rev. 144, 495 (1966).
   K.L. KLIEWER and R. FUCHS, Phys. Rev. 150, 573 (1966).
   R. FUCHS, K.L. KLIEWER, and W.J. PARDEE, Phys. Rev. 150, 589 (1966).
3. R. LE TOULLEC, Thesis, Paris.
4. E. BURSTEIN, Dynamical Processes in Solid State Optics, p.1, (1967).
5. R.A. FERRELL, E.A. STERN, Am. J. Phys. 31, 810 (1962).

FIGURE CAPTIONS

Figure 1 -

Figure 2 - Infrared dispersion relations for four thin films. In the space on the left hand side of $\omega = k_x c$, α_o is imaginary, the dispersion concerns the "radiative modes". In the space on the right hand side α_o is real and the modes are "non radiative". On the left of $\omega \sqrt{\varepsilon} = k_x c$, $\alpha^2 < 0$: "polaritons", $\alpha^2 > 0$: modes of surface.

Figure 3 -

Figure 4 - Transmission spectra of CdS thin films, $d \simeq 0.7\ \mu$, $\vec{c} \perp$ Si substrate. At normal incidence,
a) x —— x —— x , E // plane of incidence,
b) o —— o —— o , E $\perp$ plane of incidence.

Figure 5 - Transmission spectra of CdS thin films, $d \simeq 0.7\ \mu$, $\vec{c} \perp$ Si substrate, angle of incidence $\theta = 45^\circ$,
a) x —— x —— x , E // plane of incidence,
b) o —— o —— o , E $\perp$ plane of incidence.

Figure 6 - Reflectivity spectra of CdS thin films, $d = 0.64\ \mu$, $\vec{c}$ parallel to the substrate which is an aluminium mirror for two polarizations of the incident light beam $\vec{E} \perp \vec{q}$ and $\vec{E} // \vec{q}$. The angle of incidence is $\theta = 35^\circ$.

Figure 7 - Reflectivity spectrum for CdS thin films, $d = 0.72\ \mu$, $\vec{c}$ // aluminium mirror substrate for different angles of incidence : a --- $\theta = 24^\circ$; b --- $\theta = 35^\circ$; —— $\theta = 45^\circ$.

Figure 8 - Reflectivity of CdS thin films evaporated onto aluminium for one reflection at 45° of incidence, with E // plane of incidence.
The thickness d and half-width Γ of the peak at ω_{LO} are as follows :

Sample a : d = 0.66 μ , Γ = 13.6 cm^{-1} .
Sample b : d = 0.33 μ , Γ = 12.7 cm^{-1} .
Sample c : d = 0.09 μ , Γ = 12.4 cm^{-1} .