

Vibrational states of thin crystalline films of polar semiconductors

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It is demonstrated experimentally and theoretically that in thin flat films there exist surface states that manifest themselves in the IR absorption spectra and in the optical Raman-scattering spectra in the form of a band near the frequency of the longitudinal optical oscillations of a bulky single crystal. A gradual redistribution of the intensities of the *LO*-phonon replicas is observed in the spectra of the secondary emission of the thin films, depending on the film thickness (from 1 to 0.1 μm), when excited by a laser high into the conduction band. These changes in the spectra offer evidence of a cascade scattering of electron-hole pairs by *LO*-phonons and of radiative recombination of the pairs during different stages of their thermalization.

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1. INTRODUCTION

Thin crystalline layers of semiconducting compounds are extensively used in various branches of technology: optoelectronics, microelectronics, energetics, etc. Numerous investigations indicate that many physical properties of thin films differ from the corresponding properties of the single crystals.¹ This pertains primarily to the phonon and electron elementary excitations. In 1963, Berriman² has shown that thin films of LiF have an additional infrared (IR) absorption band at the frequencies of the longitudinal optical phonons, whereas the absorption of light by longitudinal optical phonons in bulky single crystals is forbidden by the selection rules.³ Englman and Ruppin⁴ have shown that the optical properties of crystals depend strongly on their dimensions and shapes.

Investigations of thermostimulated IR emission of the polaritons of the films⁵ have shown that the IR emission (absorption) band in a film at a frequency coinciding with the *LO* phonon of the single crystal is due to a transverse dipole oscillation of the atoms, with an amplitude perpendicular to the plane of the film. The latter was confirmed by investigations of the influence of the conductivity of the substrate on the spectra of the thermostimulated radiation of the polaritons of the film.⁶ Nevertheless, until recently the nature of this additional absorption band in thin films remained unclear. Thus, in a number of papers^{2,4,7} this band is attributed to a longitudinal volume phonon of the layer (film), while others^{5,6,8} regard it as a transverse oscillation.

The purpose of the present study was to ascertain the nature of the thin-film vibrational states that appear in the spectra of IR absorption and of Raman scattering of light (RSL). To this end, experimental and theoretical investigations were made of the spectra of the thermostimulated emission and RSL of ZnSe films of various thicknesses on aluminum substrates. In addition, the same films were investigated by the method of resonant RSL, which yields additional information on the elementary excitations, since the cross section of resonant RSL are different for longitudinal and transverse phonons.⁹⁻¹¹

The choice of ZnSe films on aluminum substrates for the investigations was governed by a number of factors: 1) the technology of preparation of the crystalline film is well developed, 2) this is the simplest-structure compound with 2 atoms per unit cell and with spatial symmetry group T_d^2 , 3) the phonon spectra of single-crystal ZnSe have been well investigated (see, e.g., Ref. 12), 4) this is a relatively wide-band semiconductor suitable for investigations by the experimental procedures developed by us.

2. EXPERIMENTAL RESULTS

ZnSe films of various thicknesses were prepared by vacuum sputtering on hot substrates. After prolonged recrystallizing annealing, the amorphous films became polycrystalline, of uniform thickness, with approximate grain diameter 10 μm , solid, and with mosaic structure. The degree of their crystallinity was monitored against the spectra of the thermostimulated IR radiation.¹³ The experimental results discussed in the present paper were obtained with films whose amorphism did not exceed 1-5%.

The RSL spectra were excited by various lines of krypton, argon, and helium-cadmium lasers and were recorded with a DES-24 double monochromator. The spectra were excited in a "reflection" geometry at various incidence angles of the laser beam on the film and at various observation angles of the scattered light, so that the wave vector of the excited phonon had different components k_x along the film plane. It should be noted straight off that neither measurements of the angular dependence of the intensities of the RSL bands nor polarization measurements can separate unambiguously the longitudinal and transverse phonons. The primary reason is the difference in the orientations of the crystallographic axes of the individual grains (crystallites) of the film.

The RSL spectra at $\hbar\omega_L < E_g$ ($E_g = 2.61$ eV) and the spectra of the thermostimulated IR emission practically coincide—see Fig. 1. As seen from this figure, there are two bands with frequencies $\omega_1 = \omega_{TO} = 205$ cm^{-1} and $\omega_2 = \omega_{LO} = 252$ cm^{-1} (ω_{TO} and ω_{LO} are the frequencies of the transverse and longitudinal phonons of the single crystal). Some difference is observed between the rel-

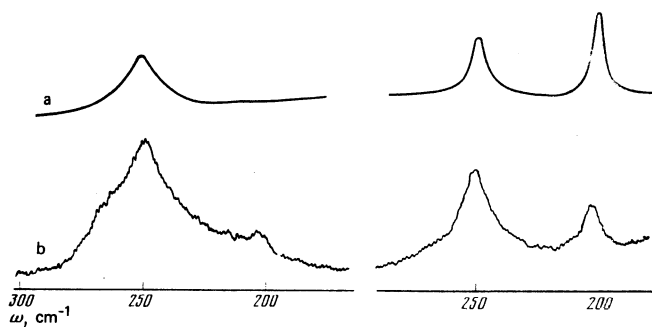


FIG. 1. Spectra: b) of Raman scattering of light from ZnSe films on an aluminum mirror, and a) of IR emission of the same films; left-hand spectra— $d = 0.1 \mu\text{m}$, right-hand spectra— $d = 1 \text{ mm}$.

ative intensities of the ω_1 and ω_2 bands in the IR radiation spectra and the RSL spectra, as a result of the difference between the values of k_x . Owing to the small RSL cross sections of thin films, the solid angle in which the scattered radiation was gathered is quite large, of the order of $\pi/3$, and this resulted in averaging of the values of k_x over a wide range.

It follows from the spectra of the thermostimulated IR emission of the films (Fig. 2) that the intensity of the band ω_1 depends very little on the emission angle θ , and consequently also on the value of $k_x \propto \sin\theta$. On the other hand, the intensity of the emission band ω_2 , which is observed only in p -polarized light, is proportional to $\sin^2\theta$.

The RSL spectra reveal also a dependence of the intensities of the RSL bands on the excitation and scattering angles, but this dependence is more complicated and less amenable to analysis. When the average values of k_x in the IR and RSL spectra of relatively thick films ($\sim 1 \mu\text{m}$) are equal, a qualitative agreement is observed also between the relative intensities of the IR emission and RSL bands. It is nonetheless worthy of attention that under equal experimental conditions the relative intensities of the bands ω_1 and ω_2 in the RSL spectra depend on the film thickness. By way of example, Fig. 3

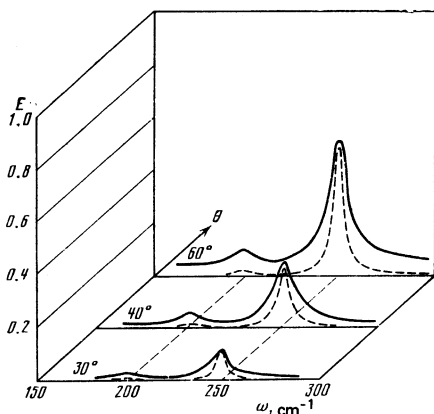


FIG. 2. Emissivity of ZnSe films of thickness $0.4 \mu\text{m}$ on an aluminum mirror in p -polarized light at various emission angles θ : solid lines—experiment, dashed—result of calculation⁶ using tabulated optical constants of single-crystal zinc selenide.

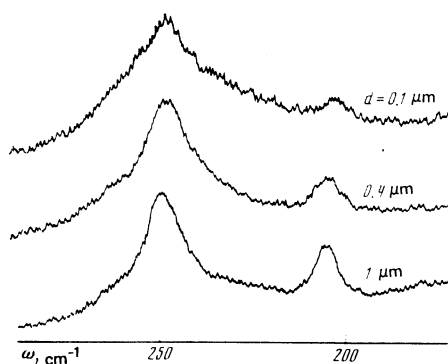


FIG. 3. RSL spectra of ZnSe films of various thicknesses excited by the laser emission line 514.5 nm ($\hbar\omega < E_g$).

shows the RSL spectra of ZnSe films of various thicknesses, obtained in identical scattering geometry at room temperature. The intensity of the ω_2 band in these spectra depends nonlinearly on the film thickness, while in the IR emission spectra the intensity of this band is proportional to the film thickness. In addition, the ω_2 band in the IR emission spectra is symmetrical and has a Lorentz shape, whereas in the RSL spectra this band has a complicated shape.¹⁾ (Fig. 3).

With increasing energy of the exciting laser quantum, the RSL spectra turn into the resonant RSL spectra when $\hbar\omega_L > E_g$. Figure 4 shows the spectra of first-order resonant RSL spectra of ZnSe films $0.1 \mu\text{m}$ thick excited by various laser lines. Attention is called to the fact that when the exciting-quantum energy increases, the half-width of the high-frequency band ω_2 decreases considerably, whereas the half-width of the ω_1 band (205 cm^{-1}) remains practically unchanged. In addition, the ω_2 band becomes symmetrical. This decrease of the half-width of the ω_2 band is accompanied by an increase of its intensity. The increase of the intensity of the ω_2 band precedes that of the ω_1 band. The change of the intensities of the ω_1 and ω_2 bands in the spectra of the resonant RSL spectra with changing laser quantum energy in the films is in agreement with the changes of the intensities of the resonant RSL bands in

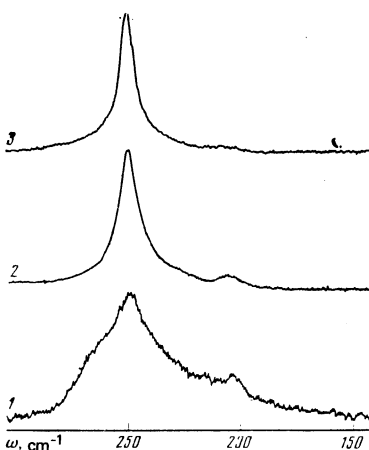


FIG. 4. Resonant RSL spectra of ZnSe films $0.1 \mu\text{m}$ thick on an aluminum mirror excited by various laser lines: 1— 514.5 nm , 2— 472.7 nm , 3— 454.5 nm . The intensities of the bands at 252 cm^{-1} are related as $30I_1 \approx 3I_2 \approx I_3$.

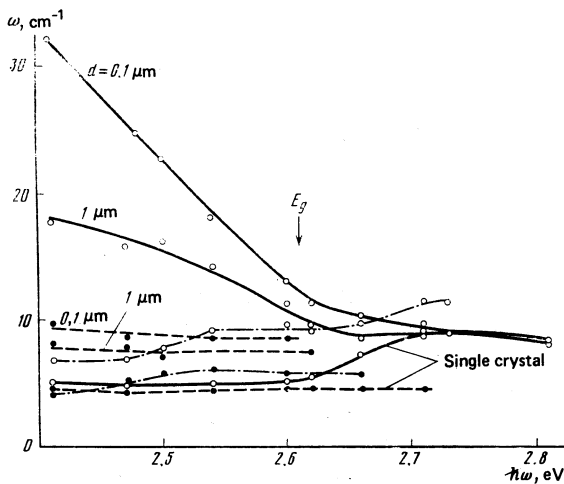


FIG. 5. Half-width of RS bands as a function of the exciting photon energy: solid lines—for band half-width 252 cm^{-1} , dashed—for 205 cm^{-1} , dash-dot—for both bands in the spectra of ZnSe powder. Points: \circ —LO band, \bullet —TO band.

the single crystals.¹⁴

Figure 5 shows the dependence of the half-width of the RSL films of various thicknesses, of finely dispersed powder, and of ZnSe single crystals on the energy of the exciting quantum. In spontaneous RSL ($\hbar\omega_L < E_g$) the difference in the half-widths of the ω_2 bands of the single crystal and of the films increases with decreasing film thickness. When resonant excitation conditions are approached, this difference decreases, and at $\hbar\omega_L > 2.7 \text{ eV} > E_g$ (at room temperature) the half-widths of the bands ω_2 coincide for all the thicknesses of the films and of the single crystal. In finely dispersed powder, the dependence of the half-widths of ω_1 and ω_2 on $\hbar\omega_L$ is qualitatively the same as for the single crystal.

A similar picture is observed also for thin ZnSe films immersed in liquid nitrogen. The shape of the band contour in the spectra of the RSL does not change, and the band becomes drastically narrower and its intensity increases simultaneously on going to the resonant RSL. The observable initial decrease of the half-width with temperature amounts to 25–30% and agrees percentage-wise with the decrease of the half-widths of the bands of a single crystal subjected to the same cooling.

The agreement between the shapes of the contours and their relative intensities in the IR emission and spontaneous RSL spectra in a wide temperature interval indicates that the spectra 1–4 of Fig. 5 receive no contribution from absorption or scattering of higher orders (multiphonon processes). In addition, the frequencies of the edge of the Brillouin zone are well known¹² and the broadening of the ω_2 band cannot be attributed to a contribution from any combination of the phonons of the critical points of the Brillouin zone for second-order processes.

The results indicate that at the frequency ω_{LO} (or near it) one observes in the spectra of the spontaneous RSL of thin films scattering by atom vibrations of transverse character and manifesting themselves in the IR absorption (emission) spectra. Against this broad background, however, in the spectra of the resonant

RSL form, a band of scattering by longitudinal phonons, with an intensity and a half width that are the same in the film as in the single crystal.

For a more accurate interpretation of the results, we consider the natural modes of the three-layer “vacuum–semiconducting film–metal” system investigated in the present study.

3. PROPER NORMAL STATES OF A DIELECTRIC FILM ON A METALLIC SUBSTRATE

We consider first the Coulomb normal modes of the system, i.e., states obtained neglecting the interaction with the transverse electromagnetic field. It is known¹⁵ that the equations for these states are obtained from Maxwell’s equations by letting the speed of light go formally to infinity:

$$\text{div } \mathbf{D} = 0, \quad (1)$$

$$\text{rot } \mathbf{E} = 0. \quad (2)$$

The material relation between the induction vector \mathbf{D} and the electric field \mathbf{E} , neglecting spatial-dispersion effects, is local:

$$\mathbf{D}(\omega) = \epsilon(\omega) \mathbf{E}(\omega), \quad (3)$$

and the locality makes it possible to substitute into this relation the quantity $\epsilon(\omega)$, which is known for the bulky single crystal:

$$\epsilon(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty) \omega_{T0}^2}{\omega_{T0}^2 - \omega^2}. \quad (4)$$

The validity of this substitution is confirmed by the agreement between the calculated and experimental IR spectra of the system^{6,8} (see also Fig. 2).

We seek a solution of Eq. (1) and (2) in the form $E = E(z)e^{iqx}$ (the x axis is chosen along the two-dimensional wave vector q that lies in the plane of the film, and the z axis is perpendicular to the film). The system (1) and (2) breaks up into equations that connect the E_x and E_z components of the field (p polarization) and equations for the E_y component (s polarization).

1. s -polarization. We have from (2)

$$E_y = 0. \quad (5)$$

However, the polarization in the medium $\mathbf{P} = (\mathbf{D} - \mathbf{E})/4\pi$ can still differ from zero in this case. It follows from (5) that $P_y(z) \neq 0$ if $\epsilon(\omega) \rightarrow \infty$. From the latter we obtain the frequency of the modes with nonzero P_y : $\omega = \omega_{TO}$. These modes are multiply degenerate, since any equation for $P_y(z)$ agrees at $-d < z < 0$ both with Eq. (5) and with the boundary conditions. The arbitrary function $P_y(z)$ in the interval $-d < z < 0$ can be represented as a linear combination of the following linearly independent functions:

$$P_y^s(z) = \sum_n A_n \sin \frac{\pi n(z+d)}{d}, \quad n=1, 2, \dots \quad (5a)$$

$$P_y^c(z) = \sum_n B_n \cos \frac{\pi n(z+d)}{d}, \quad n=0, 1, \dots \quad (5b)$$

The system of these modes is multiply degenerate—the frequencies of all the modes are equal: $\omega_q^c = \omega_q^s = \omega_{TO}$. Just as the transverse oscillations in a single crystal, the oscillations of the films are not accompanied by the appearance of space charge: $\rho = -\text{div } \mathbf{P} = 0$. Nor is

surface charge produced in this case. We shall call these, for brevity, the transverse modes of the film, recognizing, however, that a strict distinction between longitudinal and transverse oscillations is possible only for homogeneous systems.

2. *p*-polarized oscillations. We consider here only modes for which $\epsilon(\omega) \neq 0$ and the electric field E does not vanish identically. We introduce here the dielectric constant of the metallic substrate ϵ_M . Cancelling out $\epsilon \neq 0$ in (1) we have in each of the media

$$dE_x/dz + iqE_x = 0. \quad (6)$$

Equation (2) takes for the *p*-polarized field the form

$$dE_x/dz - iqE_x = 0. \quad (7)$$

Recognizing that the field vanishes as $|z| \rightarrow \infty$, and using the usual continuity conditions on the boundaries between the vacuum and the film and between the film and the substrate, we obtain the field inside the film ($-d < z < 0$):

$$\begin{aligned} E_x(z) &= E^0 \left[\operatorname{ch} qz - \frac{1}{\epsilon(\omega)} \operatorname{sh} qz \right], \\ E_z(z) &= iE^0 \left[\frac{1}{\epsilon(\omega)} \operatorname{ch} qz - \operatorname{sh} qz \right] \end{aligned} \quad (8)$$

and the dispersion equation for the frequency of the mode:

$$\epsilon^2(\omega) \operatorname{th} qd + \epsilon(\omega) (1 + \epsilon_M) + \epsilon_M \operatorname{th} qd = 0. \quad (9)$$

The last equation breaks up into two relations for $\epsilon(\omega)$, which take at $|\epsilon_M| \gg 1$ the form

$$\epsilon(\omega) = -\operatorname{th} qd, \quad (10a)$$

$$\epsilon(\omega) = -\epsilon_M \operatorname{cth} qd. \quad (10b)$$

We now describe the corresponding modes.

a) Substituting (10a) in (8) we obtain for the field in the film

$$E_x(z) = E \operatorname{sh} q(z+d), \quad E_z(z) = -iE \operatorname{ch} q(z+d). \quad (11)$$

It is seen from (11) that at large film thickness, i.e., at $qd \gg 1$, the field in this mode is concentrated near the boundary between the vacuum and the film and weakens exponentially in the interior of the film. As $qd \rightarrow \infty$ the dispersion equation (10a) goes over into the well known^{4,15,16} equation (obtained neglecting retardation) for the surface phonon on the boundary between an infinite medium and a vacuum:

$$\epsilon(\omega) = -1. \quad (12)$$

From (12) we obtain, for the given form (4) of the dielectric constant, the frequency ω_s of this surface phonon as $d \rightarrow \infty$:

$$\omega_s = \omega_{ro} \left(\frac{\epsilon_0 + 1}{\epsilon_\infty + 1} \right)^{1/2}.$$

For arbitrary d , the solution of Eq. (10a) with allowance for (4) is

$$\omega_s(q, d) = \omega_{ro} \left(\frac{\epsilon_0 + \operatorname{th} qd}{\epsilon_\infty + \operatorname{th} qd} \right)^{1/2}. \quad (13)$$

The considered type of oscillations is not connected with the space charge ($\operatorname{div} \mathbf{E} = 0$ at $-d < z < 0$), but is accompanied by the appearance of a surface charge on the film boundaries:

$$\begin{aligned} \rho_s &= iE \frac{\epsilon(\omega) - 1}{4\pi} \operatorname{ch} qd \quad \text{at } z=0, \\ \rho_s &= -iE \frac{\epsilon(\omega) - 1}{4\pi} \quad \text{at } z=-d. \end{aligned} \quad (14)$$

We shall name this oscillation the surface mode. As will be shown in Sec. 4, interaction with a transverse electromagnetic field makes states with $q < \omega/c$ non-stationary (radiative). We note a fact of great importance for a subsequent interpretation of the experimental data, namely that as $qd \rightarrow 0$ the value of $\epsilon(\omega)$ tends to zero in accordance with (10a), while the frequency

$$\omega_s(q, d) \rightarrow \omega_{LO} = \omega_{ro} (\epsilon_0/\epsilon_\infty)^{1/2},$$

where ω_{LO} is the frequency of the longitudinal phonons in the bulky single crystal. We note also that in a thin film ($qd \ll 1$) the electric field of the considered mode is almost perpendicular to the surface of the film and is practically uniform in thickness.

(b) We consider now the mode that corresponds to the dispersion relation (10b). This equation contains explicitly the dielectric constant of the metallic substrate. An ideally conducting substrate corresponds to $|\epsilon_M| = \infty$, in which case it follows from (10b) and (4) that $\epsilon(\omega) = \infty$ and

$$\omega_s(q, d) = \omega_{ro}. \quad (15)$$

We are interested also in the field distribution in this mode. However, since the induction vector $\mathbf{D} = \epsilon(\omega) \mathbf{E}$ in the film is finite, it follows that as $|\epsilon_M| \rightarrow \infty$ the electric field in the film tends without limit to zero. However, the vector of the specific polarization of the medium

$$\mathbf{P} = \frac{\epsilon(\omega) - 1}{4\pi} \mathbf{E}$$

still remains finite. Finding this value of P with the aid of Eqs. (8) at a finite value of $|\epsilon_M|$ and then going to the limit as $|\epsilon_M| \rightarrow \infty$ we obtain for \mathbf{P} in the given mode

$$P_x(z) = P \operatorname{ch} qz, \quad P_z(z) = -iP \operatorname{sh} qz. \quad (16)$$

As seen from (16), at large film thickness ($qd > 1$) the oscillation in question is concentrated in the region of the maximum $|z|$ possible in the film, i.e., at the boundary with the metal ($z = -d$), and attenuates exponentially with increasing distance from this boundary. We are thus dealing with the second surface mode of the vacuum-film-metal system.

We note that in a thin ($qd \ll 1$) film the specific-polarization vector \mathbf{P} of the medium in this mode is almost parallel to the surface of the film, and its magnitude is practically constant over the film thickness.

3. *p*-polarized modes corresponding to the relation

$$\epsilon(\omega) = 0. \quad (17)$$

From (2) follows the equation (7) which is valid both in vacuum and in the film, while Eq. (1) is satisfied identically inside the film if the condition (17) holds. From the boundary condition $E_x(0 + \delta) = \epsilon(\omega) E_x(0 - \delta)$ and from Eqs. (6) and (7) it follows that the field in the vacuum is equal to zero identically and therefore the boundary condition for the field in the film yields $E_x(0 - \delta) = 0$. The last condition together with the relation $E_x(-d) = 0$ determines the form of the natural modes in the film:

$$E_x^{(n)}(z) = C_n \sin \frac{\pi n(z+d)}{d}. \quad (18)$$

$$E_z^{(n)}(z) = -iC_n \frac{\pi n}{qd} \cos \frac{\pi n(z+d)}{d}, \quad (19)$$

where $n = 1, 2, 3, \dots$. From (14) and (4) we obtain the frequency of these modes:

$$\omega = \omega_{TO} (\epsilon_0/\epsilon_\infty)^{1/2} = \omega_{LO}. \quad (20)$$

The considered oscillations are accompanied by the appearance of both space charge

$$\rho_{(q)}^{(n)} = \frac{i}{4\pi} \left[q + \left(\frac{\pi n}{d} \right)^2 \frac{1}{q} \right] \sin \frac{\pi n(z+d)}{d}, \quad (21)$$

and surface charge

$$\rho_s^{(n)}(q) = \frac{1}{4\pi} C_n \frac{\pi n}{qd} \begin{cases} (-1)^n & \text{for } z=0 \\ 1 & \text{for } z=-d \end{cases}. \quad (22)$$

The properties of these modes (we shall call them the longitudinal modes of the film or, for brevity, longitudinal) are close to the properties of the longitudinal mode of the single crystal, and their frequencies coincide.

4. *p-polarized film modes in which the electric field E vanishes identically.* (We have in mind Coulomb modes without allowance for retardation.) The polarization \mathbf{P} of the medium and the induction vector \mathbf{D} can still be different from zero in this case. From the condition $\mathbf{D} = \epsilon(\omega) \mathbf{E} \neq 0$ at $\mathbf{E} = 0$ it follows that $\epsilon(\omega) = \infty$, and the frequency of the investigated modes coincides with the frequency of the transverse phonons of the single crystal: $\omega = \omega_{TO}$. From Eq. (1) we obtain for the polarization \mathbf{P} the equation

$$iqP_x(z) + \frac{dP_x(z)}{dz} = 0. \quad (23)$$

Equation (2) for the modes in question is obviously an identity. From the condition of continuity of the tangential component of the electric field \mathbf{E} on the vacuum—film boundary it follows that the values of E_x and hence of E_z in vacuum are equal to zero. From the vanishing of E_x in vacuum and from the condition of continuity of the normal component of the induction vector \mathbf{D} we get the boundary condition $P_x(0) = 0$.

At a finite value of the dielectric constant ϵ_M of the metallic substrate we can analogously obtain also for $P_x(0) = P_x(-d) = 0$ a second boundary condition that retains its form also on going to the case of an ideally conducting substrate ($|\epsilon_M| \rightarrow \infty$). Equation (23) and the two boundary conditions determine the form of the function $P(z)$:

$$P_x(z) = \sum_n C_{n,q} \cos \left[\frac{\pi n}{d} (z+d) \right],$$

$$P_z(z) = -\frac{iqd}{\pi} \sum_n \frac{1}{n} C_{n,q} \sin \left[\frac{\pi n}{d} (z+d) \right], \quad n=1, 2, \dots \quad (24)$$

The function $P(z)$, as seen from this, is a linear superposition of independent modes. The frequency of each of these modes, as shown above is ω_{TO} . These oscillations are not accompanied by the appearance of either surface [since $P_x(0) = P_x(-d) = 0$] or volume [by virtue of (23)] charges. It is natural to call these film modes transverse. Just as the *s*-polarized transverse film modes, the presently considered *p*-polarized transverse modes can interact with the electromagnetic field, and this leads to a finite radiative width of the modes with $q < \omega_{TO}/c$.

4. INTERACTION WITH THE TRANSVERSE FIELD (ALLOWANCE FOR RETARDATION). IR ABSORPTION

The Coulomb film modes obtained above can interact with the transverse electromagnetic field E^\perp of the free photons. The Hamiltonian of this interaction is

$$H_{int} = - \int P E^\perp dV, \quad (25)$$

where P is the polarization corresponding to the Coulomb modes of the films. The interaction (25) leads, generally speaking, to a radical change in the natural modes of the film on account of their mixing with the transverse field (the polariton effect). In the problem of absorption of an incident transverse wave, the allowance, described by the Hamiltonian (25), for the multiple reabsorption processes is also important, and leads, in particular, to a renormalization of the field of the incident wave inside the film in accordance with the Fresnel formulas. However, when the film thickness decreases, the role of the higher-order processes in the interaction (25) decreases. In a film whose optical thickness is small compared with the wavelength of the transverse field, we can confine ourselves to allowance for the interaction (25) in the lowest order.

In this section we investigate the absorption of light by such a film, determine the relative contribution made to the absorption of light by each of the modes obtained in the preceding section, and in addition, obtain the dependence of the absorption on the film thickness and on the light incidence angle. Of course, light absorption by a film on a substrate can be obtained by a simpler method, by using Kirchhoff's law and the Fresnel formulas^{4,6,8} without first finding the Coulomb modes of the system. However, the formulas obtained in this way do not enable us to determine the form taken by the absorbed energy, or to identify the system oscillations responsible for any particular peak in the spectrum.

We consider the interaction of the Coulomb modes in a thin film with the electromagnetic field of the free photon, as described by the Hamiltonian (25). When the photon interacts with a Coulomb-mode excitation, the energy and the wave vector parallel to the plane of the film should be conserved:

$$\omega(q) = \omega, \quad (26)$$

$$q = (\omega/c) \sin \theta. \quad (27)$$

Here ω and $\omega(q)$ are respectively the frequencies of the incident light and of the Coulomb mode, and θ is the angle of incidence of the light. Relations (26) and (27) lead to an inequality that limits the set of modes capable of absorbing or emitting light in single-quantum processes²⁾

$$q < \omega(q)/c. \quad (28)$$

When the conditions (26) and (27) are satisfied, the probability of photon absorption (the integral absorptivity of the system), accurate to normalization factor that does not depend on the film thickness d and on the incidence angle θ , is in accordance with the Fermi rule quadratic in the matrix element of the interaction Hamiltonian (25):

$$A \propto \left| \int P_q(z) E_q(z) dz \right|^2 / \int |P_q(z)|^2 dz. \quad (29)$$

The functions $P_q(z)$ corresponding to the investigated Coulomb modes were obtained in the preceding section. The functions $E_q(z)$ describe a transverse electromagnetic field without allowance for the interaction with the film but with allowance for the reflection from the metal:

$$E_q(z) \sim (0, \sin [k_z(z+d)], 0), \quad (30)$$

for s polarization and

$$E_q(z) \sim (i \cos \theta \sin [k_z(z+d)], 0, \sin \theta \cos [k_z(z+d)]) \quad (31)$$

for p -polarization, where $k_z = (\omega/c) \cos \theta$.

We investigate now the absorption of light by various Coulomb modes in the sequence used to obtain these modes in the preceding section.

1. *s-polarized transverse modes* $\omega = \omega_{TO}$. These modes interact, obviously, only with s -polarized light. Substituting in (29) the expression (30) for the amplitude of the incident wave and the formulas (5) for the polarizations of the sinusoidal and cosinusoidal modes, we obtain at $k_0 d \ll 1$ ($k_0 = \omega/c$) for the sinusoidal modes (5a)

$$A \propto \frac{(k_0 d)^3}{n^2} \cos^2 \theta, \quad n=1, 2, \dots \quad (32)$$

and for the cosinusoidal modes (5b)

$$A \propto \begin{cases} (k_0 d)^3 \cos^2 \theta, & n=0 \\ (k_0 d)^3 n^{-4} \cos^4 \theta, & n=2, 4, 6, \dots \\ (k_0 d)^3 n^{-4} \cos^2 \theta, & n=1, 3, 5, \dots \end{cases} \quad (33)$$

Absorption of light by all the s -polarized modes leads to a peak in the absorption spectrum of the thin film at the frequency ω_{TO} (we recall that all the modes considered here have a frequency ω_{TO}). The main contribution to this peak $k_0 d$ is made, as seen from (32) and (33), by the sinusoidal modes (5a) and by the cosinusoidal modes with $n=0$ and $n=1, 3, \dots$. Summing the contributions of these modes, we obtain the integral intensity A of the ω_{TO} peak of absorption of the s -polarized light:

$$A \propto (k_0 d)^3 \cos^2 \theta. \quad (34)$$

2. *p-polarized oscillations, surface modes*. The interaction of p -polarized light with the first surface modes (described in Sec. 3.1a) leads to the appearance of an absorption peak near the frequency ω_{LO} (in accordance with formula (13), at $qd \ll 1$). Using Eqs. (11) and (29), and (31), we obtain the integral value of the absorption:

$$A(\omega_s \sim \omega_{LO}) \propto k_0 d \sin^2 \theta. \quad (35)$$

The interaction with the second surface mode, described in Section 3.2b, leads to an absorption peak near the frequency ω_{TO} . We obtain its integrated value with the aid of (15):

$$A(\omega_s \sim \omega_{TO}) \propto (k_0 d)^3. \quad (36)$$

3. *p-polarized oscillations, longitudinal modes* $\omega \equiv \omega_{LO}$. Using (15), (16), and (31) and integrating in (29), we see that the matrix element $|\int P^* E dz|$ is equal to zero, and accordingly

$$A(\omega_{LO}) = 0. \quad (37)$$

Thus, the modes investigated in Sec. 3.3 with frequency ω_{LO} , just as the longitudinal modes of the bulky

single crystal, do not interact at all with the free electromagnetic field. This justifies our designating these film modes as "longitudinal."

4. *p-polarized oscillations, transverse modes* $\omega = \omega_{TO}$. Using (24), we obtain for the absorption intensity of each mode

$$A_n(\omega_{TO}) \propto \begin{cases} (k_0 d)^3 n^{-4}, & n=1, 3, \dots \\ (k_0 d)^3 n^{-4} \cos^4 \theta, & n=2, 4, \dots \end{cases} \quad (38)$$

the summary contribution of all these transverse modes to the absorption is consequently

$$A(\omega_{TO}) \propto (k_0 d)^3. \quad (39)$$

We now summarize the results of the present section. We see that interaction of light with the Coulomb modes of the system leads to the appearance of absorption peaks at the frequency of these modes. In s -polarized light, only one peak (34) is produced at the frequency ω_{TO} and is connected with absorption of light by the s -polarized transverse modes, in full agreement with the experimental results. In p -polarized light there are, generally speaking, three absorption peaks. One of them (35) lies near the frequency ω_{LO} and is connected with the absorption of the light by the surface oscillation described in Sec. 4a. This is a very intense peak, $1/(k_0 d)^2$ times larger than the remaining peaks.

We emphasize that the absorption peak near ω_{LO} (observed experimentally in Refs. 2, 5, 6, and 8) is connected just with the surface mode (11) and not with the absorption of light by the longitudinal mode, as was suggested in Refs. 2, 3, and 7. The longitudinal modes of the films, according to (37), do not interact at all with the transverse electromagnetic field.

In the absorption of p -polarized light there is also a peak (39) located at the frequency ω_{TO} and connected with the absorption of light by p -polarized transverse modes. In addition, near this frequency there is a peak (36) due to light absorption by the second surface mode (15). The frequency of this peak is quite close to ω_{TO} , and the dependence of the peak on the angle θ and on the thickness d is the same as for the ω_{TO} peak of absorption by transverse modes. Therefore both peaks merge into one slightly asymmetrical peak at the frequency ω_{TO} . The integral value of this peak in accordance with (36) and (39) is

$$A(\omega_{TO}) \propto (k_0 d)^3. \quad (40)$$

Thus, the theoretical relations obtained in the present section agree very well with the experimental results on IR emission of films.

In the RSL spectra, besides the modes active in IR absorption, there appear "longitudinal" film modes that are similar to the longitudinal phonons of the single crystal, especially modes with $n \gg 1$ [see expressions (15), (16), and (18)]. However, the cross section for scattering in films should differ from the cross section for scattering in single crystals, since the polarization fields for "longitudinal" oscillations in films with small n are strongly distorted by the boundaries.

5. RSL IN BOUNDED MEDIA

RSL in films was theoretically investigated in connection with RSL by surface polaritons.¹⁷⁻¹⁹ The presence

of the boundary leads to a change in the spectrum of the volume oscillations. The influence of the boundaries in the RSL spectrum near the frequency of the longitudinal phonon was investigated in Ref. 19, but no account was taken there of the fluctuation forces, which can be neglected only if dissipation processes are disregarded.

In RSL by polaritons,³⁾ the exciting radiation becomes mixed with the fluctuation polaritons and generates radiation at the difference and sum frequencies. The scattered-radiation intensity is then connected with the mean squared fluctuations of the amplitude of the oscillations, and can be estimated with the aid of the fluctuation-dissipation theorem.^{20,21} It is possible to take into account within the framework of this method the dissipation processes, and also the possibility of reflection and refraction of the high-frequency fields by boundaries between the media.

In the presence of fluctuation fields, the nonlinear polarization at the frequency ω' of the scattered light can be represented²⁰ (we disregard effects of resonant RSL) in the form of a sum of two contributions:

$$P_i(\omega') = (a_{ij}u_k + b_{ij}E_k)E_j^2, \quad (41)$$

where the first term describes the dependence of the polarizability on the relative position of the ions [$\mathbf{u}(\mathbf{r}, t)$ is the displacement vector], while the second describes the dependences of the polarizability on the electric field of the polariton $\mathbf{E}(\mathbf{r}, t)$.

Knowledge of $P(\omega')$ makes it possible to solve Maxwell's equations with allowance for the usual boundary conditions for the field of the scattered radiation and, consequently, obtain the sought scattering cross sections

$$\sigma = \frac{\omega_L}{|E_L|^2} \sum_k \frac{S \cos \theta}{\omega'} \langle |E'|^2 \rangle, \quad (42)$$

where $S \cos \theta$ is the cross-section area of the beam of the scattered radiation. This is precisely the relation that we must average over the fluctuations of $\mathbf{u}(\mathbf{r}, t)$ and $\mathbf{E}(\mathbf{r}, t)$.

The amplitudes of the motion of the ions in the polariton field are determined by the simultaneous solution of the equations of motion and Maxwell's equations in the presence of the fluctuation forces.^{20,21} Leaving out the intermediate cumbersome manipulations, we present the final expression for the scattering cross section in a reflection-scattering geometry:

$$\frac{\partial^2 \sigma}{\partial \omega' \partial \Omega} = \frac{\hbar \omega_L \omega'^3}{2\pi c^4} S t_L^2 t'^2 [n(\omega) + 1] (I_1 + I_2 + I_3). \quad (43)$$

Here t_L and t' are the transmission coefficients of the exciting and scattered light, Ω is the solid angle in which the scattered light is gathered;

$$I_1 = \sum_{k_z} 4\pi d \left\{ \frac{\alpha^2 k_x^2 + k_z^2}{q^2} \left| a \left(q^2 - \varepsilon_\infty \frac{\omega^2}{c^2} \right) + b \frac{\omega^2}{c^2} \right|^2 \right. \\ \left. \times \operatorname{Im} \frac{1}{q^2 - \varepsilon \omega^2 / c^2} - \frac{\alpha^2 k_x^2 + k_z^2}{q^2} |a \varepsilon_\infty - b|^2 \operatorname{Im} \frac{1}{\varepsilon} \right\}, \quad (44)$$

$$k_z = (k_{Lz} - k_x) = v, \quad k_{Lz} + k_x = w, \quad q^2 = k_x^2 + k_z^2, \\ \alpha = \operatorname{tg} \varphi = k_{Lz} / k_{Lz};$$

$$I_2 = -4\pi \operatorname{Im} (a(\varepsilon - \varepsilon_\infty) + b) (a^*(\varepsilon - \varepsilon_\infty) + b^*) \frac{2}{D_s} \\ \times \frac{1}{e^{\omega' - e^{-\omega d}}} \{ \xi^2 (e^{\omega d} - e^{-\omega d})^2 + [2p - \eta (e^{\omega d} + e^{-\omega d})]^2 \\ - 2\xi (e^{\omega d} - e^{-\omega d}) [2p - \eta (e^{\omega d} + e^{-\omega d})] \}, \quad (45)$$

$$p = \frac{\alpha x + k_x w / \kappa}{\omega^2 + \kappa^2} - \frac{\alpha x + k_x v / \kappa}{v^2 + \kappa^2}, \\ \eta = \frac{\alpha x + k_x w / \kappa}{\omega^2 + \kappa^2} \cos \omega d - \frac{\alpha x + k_x v / \kappa}{v^2 + \kappa^2} \cos v d, \\ \xi = \frac{\alpha w - k_x}{\omega^2 + \kappa^2} \sin \omega d - \frac{\alpha v - k_x}{v^2 + \kappa^2} \sin v d, \\ D_s = \left(\frac{\varepsilon}{\kappa} + \frac{1}{\kappa_1} \right) e^{\omega d} - \left(\frac{1}{\kappa_1} - \frac{\varepsilon}{\kappa} \right) e^{-\omega d}; \\ I_3 = 8\pi \operatorname{Im} (a(\varepsilon - \varepsilon_\infty) + b) (a^*(\varepsilon - \varepsilon_\infty) + b^*) \frac{\kappa}{\varepsilon} \\ \times \{ (p^2 + \eta^2) (e^{\omega d} + e^{-\omega d}) - 4p\eta + 2\eta\xi (e^{\omega d} - e^{-\omega d}) \}. \quad (46)$$

In the derivation of (43)–(46) we have considered a film with a zincblende structure, neglected the damping of the high-frequency fields in the film, and regarded the substrate as an ideal metal. The scattering cross section (43) was represented in the form of a sum of three contributions: scattering by volume polaritons (I_1) and by surface polaritons (I_2), and one (I_3) with a nonlinear dependence on the thickness of the film and having poles at the frequencies of the volume polaritons.

The function I_1 describes scattering by volume polaritons and has an obvious meaning. The function I_3 , as seen from (46), has a maximum on the dispersion curves of the volume polaritons and is the result of the influence of the boundary on the fluctuating electric field of the volume excitations of the medium. It should be noted that in the limit as $d \rightarrow \infty$ and $\varepsilon'' \rightarrow 0$, we have $I_3 \rightarrow 0$. This additional contribution to the RSL has a nonlinear dependence on the film thickness. As seen from (46), the contribution from the function I_3 to the intensity of the RSL by the transverse phonon is negligibly small and can be disregarded completely.

The intensity of the RSL by surface polaritons is described by expression (45). However, just as in IR spectroscopy, in the case of very thin films and sufficiently small k_x , i.e., when $k_x d \ll 1$, $k_x > \varepsilon_1^{1/2} \omega / c$, the frequency of the surface polariton is determined by expression (13) and the maximum of the intensity of the RSL by the surface phonon also turns out to be close to the frequency of the longitudinal phonon. This effect can lead both to an increase in the intensity of the RSL at the frequency ω_{LO} and to a broadening of the RSL line.

Thus, in the case of thin films ($k_x d \ll 1$) the intensity of the RSL at the frequency of the longitudinal phonon is determined by three contributions: scattering by a longitudinal volume phonon not perturbed by the boundary, scattering by longitudinal oscillations due to the region next to the surface, where the field of the LO phonon is perturbed by the boundary (generally speaking, these oscillations are no longer longitudinal), and finally, scattering by a surface phonon. The total RSL cross section at the frequency ω_2 at small ε'' is given by

$$\frac{\partial^2 \sigma}{\partial \omega \partial \Omega} = -\frac{2\pi \hbar \omega_L \omega'^3}{c^4} S t_L^2 t'^2 [n(\omega) + 1] |a \varepsilon_\infty - b|^2 \\ \times \left\{ d \frac{\alpha k_x^2 + v^2}{v^2 + k_x^2} + d \frac{\alpha k_x^2 + w^2}{w^2 + k_x^2} + 4k_x \left(\frac{\alpha k_x + w}{w^2 + k_x^2} - \frac{\alpha k_x + v}{v^2 + k_x^2} \right) \right. \\ \left. \times \left(\frac{\alpha w - k_x}{w^2 + k_x^2} \sin \omega d - \frac{\alpha v - k_x}{v^2 + k_x^2} \sin v d \right) \right\} \operatorname{Im} \frac{1}{\varepsilon}. \quad (47)$$

The additional contribution to the RSL intensity at the

frequency of the longitudinal phonon can be easily separated from the main contribution because of its linear dependence on the thickness. Since the measurement of the absolute intensities in RSL spectra is difficult, quantitative information can be obtained by measuring the relative intensities of the RSL bands at the frequencies ω_1 and ω_2 . This ratio takes in the present case the form

$$\frac{I_{\omega_2}}{I_{\omega_1}} = \frac{|ae_{\omega} - b|^2}{\varepsilon''(\omega_2)\varepsilon''(\omega_1)|a|^2} \frac{w^2 + k_x^2}{\alpha^2 w^2 + k_x^2} \left\{ \frac{\alpha^2 k_x^2 + w^2}{w^2 + k_x^2} + \frac{\alpha^2 k_x^2 + v^2}{v^2 + k_x^2} + \frac{4k_x}{d} \left(\frac{\alpha k_x + w}{w^2 + k_x^2} - \frac{\alpha k_x + v}{v^2 + k_x^2} \right) \times \left(\frac{\alpha w - k_x}{w^2 + k_x^2} \sin wd - \frac{\alpha v - k_x}{v^2 + k_x^2} \sin vd \right) \right\}. \quad (48)$$

It should be noted that whereas in the measurement of IR absorption the wave vectors are always small, $k_x < \omega/c$, in the measurement of RSL spectra the wave vector q can be relatively large, $q \sim k_L$. Therefore qd can even become sufficiently large even if the condition $k_x d \ll 1$ is satisfied, and consequently (48) remains a function of the film thickness. This is precisely the situation realized in the discussed experimental scattering geometry.

Figure 6 shows plots of $I_{\omega_2}/I_{\omega_1}$ against the reciprocal relative thickness of the film $(k_x d)^{-1}$. It shows also the experimental plots of the relative intensities of the RSL bands, which agree well qualitatively⁴⁾ with that calculated from Eq. (48).

The asymmetrical contour of the RSL band ω_2 , observed in the RSL spectra (Fig. 3), is apparently due precisely to the additional contribution of the RSL by the surface phonon, whose frequency [see expression (13)] differs somewhat from the frequency ω_{LO} , and whose intensity (47) turns out to be of the order of the intensity (46).

Thus, the RSL spectra of thin films differ substantially from the RSL spectrum of the single crystal. Additional contributions to the RSL cross section appear at the frequency of the longitudinal phonon of the single crystal, due to the surface oscillations given by expression (13) at $k_x d \ll 1$, or by the surface oscillations with $k_x d > 1$, as well as to the surface-distorted longitudinal oscillations with small n in expressions (18), (19), (21), and (22). The longitudinal phonons accompanied by space charges (21) interact strongly with the electrons and holes (Froehlich interaction). As a result of this

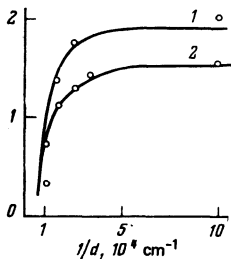


FIG. 6. Dependence of the relative intensities of the bands of spontaneous RSL at the frequencies ω_2 and ω_1 on the film thickness (θ is the incidence angle): 1— $\varphi = 0$, $\theta = 75^\circ$; 2— $\varphi = 15^\circ$, $\theta = 45^\circ$; points—experiment.

interaction, the cross section of the resonant RSL by longitudinal phonons greatly exceeds²² the cross section of resonant RSL by transverse phonons and by the quasitransverse surface mode of the film, for which there are no volume charges, the main contribution to the cross section being made by modes with $n \gg 1$.

Thus, a narrow band of resonant RSL by the longitudinal phonon ($n \gg 1$), with a width equal to that of single-crystal bulky samples, appears in the spectra of Fig. 4 on going from spontaneous to resonant RSL on top of the broad band of RSL by the "quasitransverse" surface mode.

6. LO-PHONON REPLICAS IN THE SPECTRA OF RESONANT RSL OF FILMS

The cross section of resonant RSL in polar semiconductors by longitudinal oscillations is known^{11,23} to be determined primarily by the constants of the Froehlich interaction between the electrons and the phonons, an interaction due to the electric fields of the polarization of the dipole oscillations of the ions. When the resonant RSL is excited high into the conduction band ($\hbar\omega_L > E_g$) one observes, as a rule, a high intensity of scattering of high orders, when bands separated from the excitations by $n\omega_{LO}$ with $n \geq 3$, the so-called LO-phonon replicas²⁴, are observed in the secondary-emission spectra. This phenomenon was interpreted in Refs. 25 and 26 as a cascade hot-luminescence process, although in other papers this is regarded as a multiphonon process.^{24,27}

The intensity of the hot luminescence depends explicitly on the states of the electron-hole pairs (excitons).²⁸ If we regard the band process as a cascade process, then the electrons excited high into the conduction band, becoming thermalized, emit LO phonons in succession. After each act of LO-phonon emission there is a certain probability of radiative recombination of the nonthermalized (hot) electron-hole pairs.⁵⁾ The probability of these recombination processes should depend on the distance from the electron-hole pairs to the surface of the crystalline layer, since the surface is, as is well known, an effective trap for electron-hole pairs (the rate of surface recombination greatly exceeds the rate of volume recombination of nonequilibrium carriers).³⁰ Therefore if the distance from the electron-hole pair to the surface is less than the mean free path of the pair, then the pair can recombine on the surface of the crystal before it has a chance to emit an LO phonon, i.e., without becoming thermalized. We can therefore expect the form of the hot luminescence spectrum (resonant RSL following excitation high into the band³¹) to depend on the film thickness.

Figure 7 shows the secondary-emission spectra of films of different thicknesses excited high into the conduction band by a helium-cadmium laser ($\hbar\omega_0 = 2.81$ eV). The spectra shown in Figure 7 were registered at an identical experimental geometry and at room temperature. The spectra of the LO-phonon replicas of the single crystal and of thick films practically coincide. When the film thickness is decreased, a smooth redistribution of the LO-phonon replica intensities

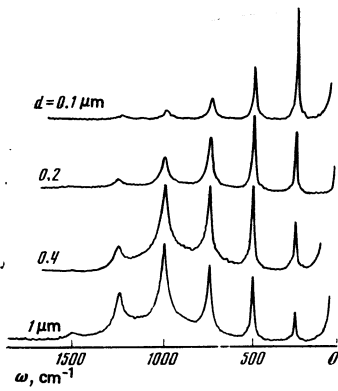


FIG. 7. Secondary emission spectra of ZnSe films of various thicknesses on an aluminum mirror, excited by helium-cadmium laser, $E_g = 2.81$ eV.

takes place. Thus, the maximum of the intensity of the secondary emission of a film $0.1 \mu\text{m}$ thick occurs not for the fourth LO phonon, as in thick films, but for the first. These changes in the spectra of resonant RSL might be interpreted as being due to an increase in the width of the forbidden band of the material of the films when their thickness is decreased. The increase of E_g in thin films might be attributed to the fact that ZnSe can crystallize at 300 K either into a sphalerite structure, $E_g = 2.67$ eV, or a wurtzite structure, $E_g = 2.73$ eV.³²

Investigations of the relative intensities of the bands of the resonant RSL of films of various thicknesses, as functions of the energy of the exciting photon, have shown that the width of the forbidden band does not depend on the film thickness. This follows from the fact that the positions of the maxima of the intensity of scattering by TO phonons as a function of the energy of the exciting photon (Fig. 8, see also Ref. 14), remain practically unchanged with changing film thickness.

As seen from Fig. 8, the change of the width of the band in the film, compared with the single crystal, does not exceed $\Delta E_g \sim \omega_{LO} = 0.031$ eV. An attempt to explain the observed redistribution of the intensities of the LO replicas (Fig. 7) as being due to a change in the band width would require the band to change by an amount (3–4) ω_{LO} (~ 0.1) eV. An independent determination of

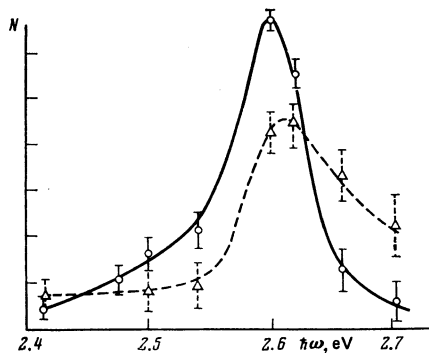


FIG. 8. Dependence of the intensity of light scattering at the frequency $\omega_1 = \omega_{TO}$ of ZnSe films ($d = 0.3 \mu\text{m}$ —dashed curve, single crystal—solid curve) on the energy of the exciting photon.

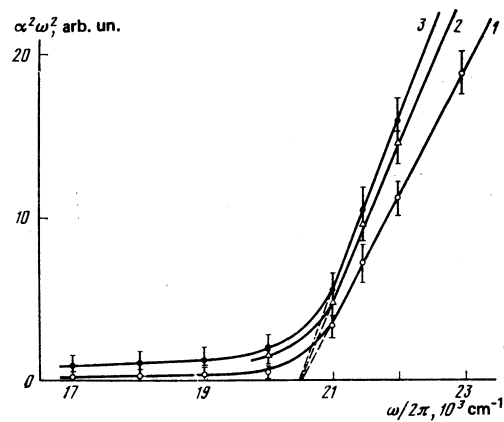


FIG. 9. Interband absorption edge of films of ZnSe: 1— $d = 0.1 \mu\text{m}$, 2— $d = 0.4 \mu\text{m}$, 3— $d = 1 \mu\text{m}$. The dashed lines satisfy the equation $(\alpha \hbar \omega)^2 \sim (\hbar \omega - 2.56 \text{ eV})$, where α is the absorption coefficient.

the forbidden band from the absorption spectra of the films yielded a somewhat underestimated value $E_g = 2.56 \pm 0.04$ eV at room temperature (Fig. 9) for all the investigated ZnSe films regardless of their thickness.⁶⁾

We note that the optical properties of thin films ($d \geq 0.1 \mu\text{m}$) are well described by the macroscopic dielectric constant $\epsilon(\omega)$ in the form (4) (Sec. 3).⁷⁾

The observed change in the intensities of the phonon replicas in the spectra of Fig. 7 can be easily explained from the point of view of a cascade process of phonon emission by hot electron-hole pairs and recombination radiation of these pairs during different stages of thermalization. In single crystals and thick films, the electron-hole pairs have time to become thermalized, and the maximum of the secondary emission (hot luminescence) coincides with the position of the edge of the conduction band; therefore the spectrum of the resonant RSL and the spectrum of the hot luminescence in analogous experiments are practically inseparable, if we disregard the previously observed¹⁴ broadening of the LO-phonon band with increasing energy of the exciting photon. On the other hand, in thin films whose thickness is comparable with the mean free paths of the electron-hole pairs, the latter recombine on the surface of the film. The pairs do not have time to become thermalized, so that the maximum of the intensity of the secondary emission is not connected with the position of the exciting line relative to the edge of the conduction band (we have in mind the case $\hbar \omega_L > E_g$). The spectrum of the thinnest film of Fig. 7 can be well explained by the fact that the thickness of the film amounts apparently to 4 or 5 exciton mean free paths. This corresponds to a mean free path $200 - 300 \text{ \AA}$ at room temperature. With this interpretation, the experimentally observed smooth shift of the maximum of the secondary emission from the fourth to the first LO phonon with decreasing film thickness to $0.1 \mu\text{m}$ becomes obvious.

CONCLUSION

Our investigations of the elementary excitations of thin films of polar semiconducting compounds lead to

the following conclusions:

1. Thin films have surface states that manifest themselves in the experimental IR absorption and RSL spectra in the form of a band near the frequency of the longitudinal phonon of the single crystal. These long-wave surface vibrational states of thin films produce in the volume of the film a polarization field that is quasi-homogeneous in thickness and is due to the surface charges.
2. The film vibrational states corresponding to the equation $\epsilon(\omega)=0$ ("longitudinal" phonons) do not interact with IR radiation. They appear in the RSL spectra and particularly strongly in the spectra of resonant RSL.
3. The spectrum of the *LO* phonon replicas of thin films points to a cascaded emission of *LO* phonons by electron-hole pairs and to radiative recombination of the pairs during different stages of their thermalization.

In conclusion, the authors thank professor V. M. Agranovich for valuable remarks in the discussion of the results of this work.

- ¹Broadening of the ω_2 band with decreasing film thickness is observed both in IR spectra and in RSL spectra. It is possible that this broadening is due to the polycrystalline character of the films (the "roughness" of the surface).
- ²The modes with $q > \omega(q)/c$ do not take part thus in the linear absorption or emission of light. Their interaction with electromagnetic fields leads only to a renormalization of the dispersion law—to formation of surface polaritons.
- ³In the RSL spectra, unlike in the IR emission spectra, the wave vector of the investigated elementary excitation can be sufficiently large ($kd \approx 1$), and allowance for polariton effects is essential here.
- ⁴The observed inessential difference between the experimental and theoretical curves of Fig. 6 is due to the error in the measurement of the film thickness. Thicknesses less than $0.5 \mu\text{m}$ were determined from independent measurements of the positions of the minima in the interference pattern recorded in the near-infrared region of the spectrum with an IKS-16 spectrophotometer. On the other hand, the thickness of films with $d < 0.5 \mu\text{m}$ was determined with a quartz sensor during the sputtering time. In the course of recrystallization annealing, the films are partially evaporated and their thickness decreases somewhat.
- ⁵In our qualitative analysis of the secondary emission of films we shall not distinguish between non-equilibrium electron-hole pairs and excitons, inasmuch as at $\hbar\omega > E_g$ the principal role is played by the states of the continuous spectrum of the excitons.²⁹ In addition, the experimental results were obtained at room temperature, when kT exceeds the ionization energy of the exciton in ZnSe.
- ⁶It should be noted that various disorders in the film, defects, and other imperfections of the crystal structure decrease as a rule the effective width of the forbidden band.
- ⁷In expression (4) for $\xi(\omega)$, owing to the radiative decay of the polaritons, the frequency ω becomes complex even in the harmonic approximation, i.e., the radiation leads to a broadening of the corresponding states.

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