#### **REVIEWS OF TOPICAL PROBLEMS**

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## Semiconductor microcavity polaritons

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## Contents

1.	Introduction	1213
2.	Experimental techniques of phonon polariton research	1216
3.	Light emission by the plasmons of an ATR prism-above-metal structure	1220
4.	Light emission by the plasmons of a dielectric film-on-metal structure	1222
5.	Light emission by the polaritons of a semiconductor film-on-metal structure	1225
	5.1 Thin films; 5.2 Thick films; 5.3 Resonance of dipole vibrations of impurity atoms with crystal layer polaritons	
6.	Radiative polariton lifetime	1239
7.	Luminescence and resonance Raman scattering by interference polaritons	1240
8.	Femtosecond dynamics of semiconductor microcavity polaritons	1242
	8.1 Experiment; 8.2 Discussion of results	
9.	Conclusions	1247
	References	1248

<u>Abstract.</u> The optical properties of wide-gap semiconductor films on metal substrates were investigated experimentally by infrared spectroscopy, Raman scattering, and femtosecond spectroscopy techniques as well as theoretically in the framework of linear crystal optics. The optical spectra of such planar structures (microresonators) were shown to bear information on electromagnetic excitations of both the surface and the volume of the structure. The optical spectra are determined by the interaction of all dipole-active excitations of the component materials with the electromagnetic modes of the microresonator, which in turn are determined by the permittivities of each component material, microcavity (microresonator) thickness, and the experimental conditions.

### 1. Introduction

Optical properties of crystals have been the object of interest for several centuries. In recent years, traditional techniques of their investigation (absorption and reflection spectroscopy, luminescence, Raman scattering) were supplemented by relatively new ones: reflection – absorption spectroscopy, attenuated total internal reflection, and thermally induced emission. All of them are employed to study the interrelation between the crystal structure and its physical properties, i.e., for the determination of electronic and vibrational atomic (ion) energy levels, the nature and constants of interatomic

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Received 29 January 2002; revised 4 June 2002 Uspekhi Fizicheskikh Nauk **172** (12) 1371–1410 (2002) Translated by E N Ragozin; edited by S N Gorin binding forces, oscillator strengths, the parameters of anharmonicity of vibrations, etc. In this case, one of the prime objectives of optical spectroscopy is to find out which exactly specific vibrations of atoms and electrons are responsible for each peak in the spectrum (determination of normal coordinates and their frequencies). This problem can relatively easily be solved theoretically for an infinite crystal, with the understanding that the crystal structure (atomic coordinates, the space group of symmetry) and the nature of interatomic binding forces are known.

In experiments, crystals have finite dimensions and the crystal boundaries violate translational symmetry. The atoms on the crystal surface differ from the atoms in the crystal volume in the forces that bind them to the neighboring atoms, and therefore the bulk and surface crystal properties diverge. The basic notions of bulk properties of crystals have formed by the early 1970s (see, for instance, Refs [1, 2]). It became clear that the optical properties of crystals are determined by the interaction of an external electromagnetic field with dipole-active (possessing dipole moments) states of the crystal volume and crystal structure defects.<sup>1</sup> This interaction gives rise to the coupled state of the electromagnetic field and the vibrational motion of charged particles (dipoles) [1, 2]. Hopfield termed these states polaritons [3].

It is well known that any periodic motion of charged particles (including the thermal motion of electrons and ions) is accompanied by the production of an electromagnetic field [4]. This signifies that polaritons exist in a crystal without an external electromagnetic field either. In other words, the inextricably entwined charge motion and related fields are precisely the polaritons — electromagnetic waves in crystals [5].

The dependence of the frequency  $\omega$  on the wave vector **k** of an electromagnetic wave in a crystal is determined by a dispersion relation. For an infinite isotropic crystal, the

<sup>1</sup> In this case, the crystal surface is treated as a planar defect.

dispersion law for long-wavelength ( $\mathbf{k} \approx 0$ ) dipole-active vibrational crystal states is written as [1]

$$\frac{k^2 c^2}{\omega^2} = \varepsilon(\omega) \,. \tag{1}$$

Here, c is the velocity of light in vacuum and  $\mathbf{k}$  is the wave vector of the electromagnetic wave with a frequency  $\omega$  in a crystal with a dielectric function  $\varepsilon(\omega)$ .

For a diatomic isotropic crystal with an ion-covalent type of the interatomic bond (of the cubic ZnS type), the  $\varepsilon(\omega)$ function in a harmonic approximation is written as [1]

$$\varepsilon(\omega) = \varepsilon_{\infty} + (\varepsilon_0 - \varepsilon_{\infty}) \frac{\omega_{\rm TO}^2}{\omega_{\rm TO}^2 - \omega^2}, \qquad (2)$$

where  $\omega_{TO}$  is the frequency of transverse optical phonons (the optical vibrations of harmonic dipoles),  $\varepsilon_{\infty}$  and  $\varepsilon_0$  are the permittivities at frequencies much higher and much lower than the  $\omega_{\rm TO}$  frequency. Figure 1 shows the dispersion of phonon polaritons  $\omega = \omega(k)$  of an infinite crystal corresponding to Eqns (1) and (2). The horizontal straight line  $\omega_{\rm LO}$  in the plot corresponds to the longitudinal optical phonon near the center of the Brillouin zone, whose frequency is defined by the solution of the equation  $\varepsilon(\omega) = 0$ .

The dispersion of polaritons in crystals was studied by Raman scattering techniques. The results of these investigations [6, 7] were found to be in complete agreement with the theoretical predictions [1-3]. Much worse is the situation with the interpretation of absorption and reflection IR crystal spectra, especially when they are measured with a high photometric precision and a high spectral resolution, which became possible in the last few decades.

In the mid-1970s, the active study of the optical properties of solid surfaces started (the accomplishments of the first stage of this research are summarized in a collective monograph [5]). The surface atomic vibrations were shown to decay at depths of several hundred nanometers and to be accompanied by the appearance of a variable dipole moment and a macroscopic electric field. These vibrations are fairly well described in the context of macroscopic electrodynamics the Maxwell equations with the well-known boundary conditions for the tangential and normal components of electric and magnetic fields [8, 9].

It was also found that the bulk and surface crystal properties are described by the common frequency-dependent dielectric function  $\varepsilon(\omega)$ . Furthermore, the electronic and vibrational states of the atoms at the crystal surface are accompanied by surface electromagnetic waves, which decay

b

 $\omega_{\rm LO}$ 

 $\omega_{\rm sp}$ 

 $\omega_{\rm TO}$ 

### k $k_x$ Figure 1. Dispersion of the phonon polaritons (bold curves) of (a) infinite

 $\omega_{\rm LO}$ 

 $\omega_{\rm TC}$ 

[1] and (b) semiinfinite [2] crystals ( $n_0 = \sqrt{\epsilon_0}$ ).

exponentially on either side of the interface and propagate in the conventional wavelike manner along the interface. These so-called surface polaritons are different from the well-known transverse electromagnetic waves, which propagate through the crystal volume and through the vacuum [5, 8-11].

Electromagnetic waves in the form of plane waves with a conventional joining at the crystal-vacuum interface satisfy the Maxwell equations for a semiinfinite crystal. In addition to bulk polaritons, there emerge surface polaritons, which obey the dispersion relation [5-17]

$$\frac{k_x^2 c^2}{\omega^2} = \frac{\varepsilon_1(\omega) \varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)} \,. \tag{3}$$

Here,  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  are the dielectric functions of the first and second media, and  $\mathbf{k}_x$  is the wave vector of the surface polariton propagating along the interface.

Surface polaritons exist in the frequency range where the crystal permittivity is negative or, more precisely, where  $\varepsilon_1(\omega) < -|\varepsilon_2(\omega)|$  [9–11]. Strictly speaking, the electromagnetic wave of a surface polariton is not transverse: when the surface wave travels along the interface, its electric vector E 'rotates' in the plane perpendicular to the interface and has a component parallel to the wave vector  $\mathbf{k}_{x}$  of the surface wave. The magnetic field of the surface wave remains perpendicular to the vectors **E** and  $\mathbf{k}_x$  for all time [5–11].

It follows from Eqns (1) – (3) that the dispersion equations for bulk and surface excitations can be written in terms of the permittivities of the crystal and the medium in contact with it [8-17]. The specificity of the excitations (phonons, excitons, plasmons, etc.) manifests itself only in the concrete form in which the permittivity is written, so that the problem of determining the dispersion curves for specific polaritons (excitonic, phonon, plasmon, etc.) reduces to the substitution of the requisite  $\varepsilon(\omega)$  function into Eqns (1)–(3) and solving them for  $\omega$ . The experimenter's task is to distinguish surface vibrational states in the spectrum from the bulk ones (this can be done from the form of dispersion curves derived from experimental data) and reconstruct the  $\varepsilon(\omega)$  function from them.

Referring to Fig. 1b, the dispersion curve of a surface phonon polariton localized near the interface is located in the gap between transverse and longitudinal optical phonons. It is precisely in this range that the  $\varepsilon(\omega)$  function of an ionic crystal is negative [1, 2]. The dielectric function of metals  $\varepsilon_{\rm m}(\omega)$  is negative in a very broad spectral range (from zero to the plasmon frequency  $\omega_p$ , which lies in the vacuum ultraviolet range for highly conducting metals). The light straight line, which represents the light dispersion in vacuum  $\omega = k_0 c$  in Fig. 1, divides the  $\omega - k_x$  plane into the radiative and nonradiative domains [12-17]. The radiative domain (to the left of the light straight line) harbors the elementary excitations capable of absorbing and emitting electromagnetic waves, i.e., transient (virtual [12-17]) excitations.

In the nonradiative domain (to the right of the light straight line), there reside crystal excitations that are stationary in the harmonic approximation, because their wave vector  $k_x$  is greater than the wave vector of light in vacuum,  $k_0 = \omega/c$  [5–17]. These excitations do not absorb or emit electromagnetic waves (under ordinary conditions), because this would violate momentum conservation. This is the reason why ionic crystals in the  $\omega_{TO} < \omega < \omega_{LO}$ frequency range and metals in the  $\omega < \omega_p$  frequency range do not absorb or emit electromagnetic waves, but reflect them

ω

well, being good mirrors, with the understanding, of course, that their surface is plane and smooth and is not covered with oxides or some adsorbed molecules, i.e., is free from irregularities and contamination.

In the early 1980s, it also became clear that the boundaries of a crystal of finite size make up cavities (resonators) for electromagnetic waves and that the cavity modes (resonator modes) can play a fundamental role in determining the optical properties of the crystal. The cavity modes reveal themselves most strongly in a crystal microcavity with an optical thickness  $nd \approx \lambda/2$ , where  $n(\omega) = \sqrt{\varepsilon(\omega)}$  is the refractive index of the crystal layer with a thickness d, and  $\lambda$  is the wavelength of the electromagnetic field in vacuum at the vibration frequency under consideration [18-23]. The interaction of the electromagnetic modes of a cavity with the dipole-active states of the cavity material has long been the object of active research in laser physics and quantum optics [20]. The simplest and most interesting objects of this research are planar thin-film structures of the Fabry-Perot resonator type.

Of particular interest are microcavities with a semiconductor (or dielectric) film-on-metal structure. On the one hand, the study of these structures is of purely practical interest stemming from the need to efficiently control laser radiation and develop high-speed photodetectors based on the Schottky barrier, i.e., a radically new elemental base of optoelectronics [19–21]. On the other hand, the above systems provide a substantial, content-rich nonlinear optical model: planar microcavities are an example of the simplest physical model, which leaves room to consistently include the boundaries when employing a resonance medium of finite thickness.

Furthermore, the use of femtosecond laser pulses makes it possible to manipulate the boundary conditions in a microcavity and modify the temporal, spectral, and spatial characteristics of the nanostructures [22]. This opens up new avenues for the development of microresonator devices and the technology of optical processing of information and images [19–21]. Lastly, the systems of this type are promising in studying quantum electrodynamic effects in a microresonator (see Ref. [23] and references therein).

The optical properties of polar dielectric and semiconductor films were studied in an enormous number of publications (see, for instance, Refs [5-40]), since optical investigative techniques furnish a wealth of information on the electronic (excitonic, plasmon) and vibrational (phonon) excitations in the bulk and at the surface of a crystal layer. During the last three decades, new important results have been obtained, which enriched our notions of the interaction of electromagnetic radiation with the condensed state of matter. Several of them deserve mention:

• development of techniques for the investigation of surface electromagnetic waves of the visible and IR ranges, which are capable of traveling macroscopic distances (up to several centimeters) along the surface, and employing these waves for the investigation of surface properties [5, 29-31];

• observation of absorption spectra [5, 27, 28, 32-35], thermally induced emission [32-34, 38], luminescence [33-35], and Raman scattering [35-37] at the frequencies of interference modes of the film;

• discovery of a strong resonance interaction between the local vibrations of impurity atoms and interference modes of the film [38] and the interaction of dipole-active excitations of the contacting media (film and substrate) [5, 33, 39–47];

• discovery of a sharp lowering of the lasing threshold with a shortening of the resonator length to half the laser wavelength [48-50].

Highly significant for the understanding of the optical properties of metals as well as dielectric and semiconductor crystals and films are the experimental data on the direct measurement of dispersion of plasmon and phonon polaritons by IR spectroscopy [29-34] and Raman scattering techniques [35-37, 46, 47]. Also significant are the notions of electromagnetic field modes in a microcavity [20, 48-53] and the resonator modes in laser physics [53-55]. When discussing the experimental data on polariton research, one should take into account that the vibrations of the atoms (ions) of a crystal lattice are accompanied by the emergence of an electromagnetic field inside the crystal and that the energy of this field can partly escape from the crystal through the media interface [33, 56-60].

The polaritons in Fig. 1a and the surface polaritons in Fig. 1b are stationary states of the electromagnetic field of a crystal. The bulk polaritons in Fig. 1b (the same as in Fig. 1a) are, in principle, transient states owing to the possibility that they can experience a radiative decay. However, for a real value of  $\omega$ , Eqn (1) does not take into account this decay. The thermal motion of electrons and ions in the volume and at the surface of the crystal also generate an electromagnetic field. The field with a wave vector  $k_x < k_0$  is radiative, i.e., is radiated into the vacuum, and the field with a wave vector  $k_x > k_0$  is nonradiative. For bulk vibrations inside the crystal, the nonradiative field experiences total internal reflection from the surface, and for surface vibrations it remains bound to the interface [8–17, 29, 33].

The nonradiative surface polaritons with a two-dimensional wave vector  $q > k_0$  that are produced by the ion and electron thermal motion in the crystal region near the surface can become radiative if an attenuated total internal reflection (ATR) prism is placed above the crystal [5, 29]. In this case, the initially nonradiative surface polaritons of the planar crystal boundary prove to be capable of absorbing and emitting light. An ATR prism placed at the crystal surface as well as periodic grooves on the crystal surface transform the nonradiative vibrational states of the crystal – vacuum interface with  $q > k_0$  into states that absorb and emit light [8, 9].

The presence of an ATR prism above the crystal surface results in a perturbation of the surface polariton, with the consequential change of its characteristics, primarily its dispersion and lifetime [5, 31, 67]. The radiative decay of surface polaritons, i.e., their conversion to light, can be experimentally recorded as the radiation of a sample with an ATR prism above it. Therefore, in addition to the commonly considered anharmonic decay of crystal excitations, there exists another decay channel — radiative — which in some cases becomes dominant.

The interaction of polaritons with an external electromagnetic field is possible due to precisely their radiative instability. The absorption, reflection, and emission of light by the excitations of crystals and films are adequately described by the solutions of macroscopic Maxwell equations with conventional boundary conditions and material equations for the media in contact, i.e., employing the macroscopic dielectric functions of the media. As a rule, experimental results are in good agreement with the calculated light absorption, reflection, and emission spectra [5, 27–34].

One can see from Fig. 1b that semiinfinite crystals can absorb and emit light in the vacuum only at frequencies near

the frequency of a longitudinal optical phonon. For longitudinal ion vibrations, the electric field and the polarization of the medium (crystal) are parallel to the wave vector **k** and the magnetic field is identically equal to zero [1, 60]. This signifies that longitudinal phonons are purely electric ion vibrations, i.e., are not electromagnetic [1]. That is why longitudinal optical phonons in a crystal cannot absorb and emit light in single-event processes of the 'photon-producesphonon' type in any experimental geometry [33, 34, 60]. Berreman [24] discovered that an oblique incidence of *p*-polarized light on a film is accompanied by the occurrence of an absorption peak at the longitudinal optical phonon frequency of the film material. This contradicts selection rules, but is nevertheless employed in several papers [24-29,61-66] to determine the characteristics of optical phonons in crystals.

The optical properties of a crystal film were first studied theoretically by Fuchs and Kliewer [12–16]. They found that the dispersions of bulk and surface polaritons of a three-layer vacuum – dielectric film – substrate structure infinite in the x and y directions are of the form [5, 17]

$$\operatorname{coth}\left(\beta_{2}d\right) = \mathrm{i}\frac{\beta_{2}^{2}\varepsilon_{1}\varepsilon_{2} + \beta_{1}\beta_{3}\varepsilon_{2}^{2}}{\beta_{2}\varepsilon_{2}(\beta_{1}\varepsilon_{3} + \beta_{3}\varepsilon_{1})} \tag{4}$$

for the *p* polarization (TM polaritons) and

$$\coth(\beta_2 d) = i \frac{\beta_2^2 + \beta_1 \beta_3}{\beta_2 (\beta_1 + \beta_3)}$$
(5)

for the s polarization (TE polaritons). Here,

$$\beta_j = \left(\varepsilon_j \frac{\omega^2}{c^2} - \varepsilon_1 q^2\right)^{1/2}, \quad j = 1, 2, 3, \quad \mathbf{i} = \sqrt{-1};$$

**q** is the two-dimensional wave vector in the plane of the film; and  $\varepsilon_2$ ,  $\varepsilon_3$ , and  $\varepsilon_1$  are the permittivities of the film material (with a thickness *d*), the substrate, and the vacuum, respectively.

Equations (4) and (5) each describes three families of polariton branches (the  $\omega(q)$  relationships): one for a real value and two others for an imaginary value of  $\beta_1$ . The first family resides in the radiative domain of the  $\omega - q$  diagram and corresponds to the interference modes of a plane-parallel layer. The second and third families reside in the nonradiative domain of the  $\omega - q$  diagram and correspond to waveguide and surface (interfacial) modes of the structure.

The spectra of light absorption  $A(\omega)$  and thermal emission  $E(\omega)$  by all these modes (including the measurements of initially nonradiative modes in the ATR regime) are adequately described by the formula [5, 31–34]

$$A = E = 1 - \left| \frac{(\delta_1 - \delta_2) P + (\delta_1 + \delta_2) Q}{(\delta_1 + \delta_2) P + (\delta_1 - \delta_2) Q} \right|^2,$$
(6)  
$$P = (\delta_2 + \delta_3)(\delta_3 + \delta_4)$$

$$\begin{aligned} &+ (\delta_2 - \delta_3)(\delta_3 - \delta_4) \exp\left(-2\varkappa_3 \frac{l\omega}{c}\right), \\ &\mathcal{Q} = \left[ (\delta_2 - \delta_3)(\delta_3 + \delta_4) \right. \\ &+ (\delta_2 + \delta_3)(\delta_3 - \delta_4) \exp\left(-2\varkappa_3 \frac{l\omega}{c}\right) \right] \\ &\times \exp\left(-2\varkappa_2 \frac{d\omega}{c}\right), \\ &\varkappa_j = \left[\varepsilon_1(\omega) \sin^2 \varphi - \varepsilon_j(\omega)\right]^{1/2}, \ j = 1, 2, 3, 4. \end{aligned}$$

Here,  $\delta_j = \varepsilon_j / \varkappa_j$  for *p*-polarized light and  $\delta_j = \varkappa_j$  for *s*-polarized light;  $\varepsilon_1(\omega)$ ,  $\varepsilon_2(\omega)$ ,  $\varepsilon_3(\omega)$ , and  $\varepsilon_4(\omega)$  are the dielectric functions of the materials of the ATR prism, the gap, the film, and the substrate, respectively; *l* and *d* are the gap and dielectric (semiconductor) film thicknesses, respectively; and  $\varphi$  is the radiation angle inside the medium with a permittivity  $\varepsilon_1$ . In the quasi-harmonic approximation, the dielectric function of the film material is commonly written as

$$\varepsilon_{3}(\omega) = \varepsilon_{\infty} + (\varepsilon_{0} - \varepsilon_{\infty}) \frac{\omega_{\text{TO}}^{2}}{\omega_{\text{TO}}^{2} - \omega^{2} - i\gamma\omega}$$
(7)

( $\gamma$  is the damping factor of a phonon with a frequency  $\omega_{TO}$ ). The dielectric function of the metal substrate is defined by the Drude formula:

$$\varepsilon_4(\omega) = \varepsilon_{\rm m}(\omega) = 1 - \frac{\omega_{\rm p}^2}{\omega^2 - i\gamma_{\rm p}\omega}, \qquad (8)$$

where  $\omega_p$  is the plasma oscillation frequency in the metal substrate and  $\gamma_p$  is the electron collision frequency in the plasma.

In this review, an attempt is made to provide a consistent interpretation of the aggregate body of experimental data known to the author which concern the vibrational spectra of bulk and surface excitations of polar semiconductor films (ZnS, ZnSe, CdS, ZnTe, etc.) of different thicknesses (from ultrathin ones to bulk single crystals). The data were obtained by reflection – absorption spectroscopy, thermally induced emission, attenuated total internal reflection, and Raman scattering. This discussion concerns only those experimental data that were obtained with single crystals and films contacting a thick metal substrate.

Prior to describing the polaritons of the vacuum-filmmetal substrate structure, we briefly consider the technique of thermally induced polariton emission and then the polaritons of the simplest structure — of 'an ATR prism above the surface of a thick metal' type. In the final part of the review we discuss the results of the investigation of the excitation and relaxation dynamics of radiative (interference) polaritons of a semiconductor film on a metal obtained by the femtosecond laser pumping-broadband probing spectroscopic technique.

## 2. Experimental techniques of phonon polariton research

The frequencies of bulk and surface crystal phonons reside in the IR spectral range, and therefore the principal techniques used to investigate them are IR spectroscopy and Raman scattering (RS) spectroscopy. The optical density at optical phonon frequencies in crystals with an ion-covalent type interatomic bonding type is very high (3-5), which requires measuring the reflection spectra by IR spectroscopy in as broad a spectral range as possible or measuring the transmission spectra of thin films [68–70].

The investigation of optical properties of solids involves measurements of the spectral intensities of light emerging from a sample. This can be either the transmitted, reflected, or scattered light of an external source, or the light produced by some excitation (in particular, by the thermal motion of electrons and ions) inside the object of research. An optical experiment thereby investigates the result of a radiative polariton decay. It is precisely the polariton that we are dealing with in any optical experiments, even though the electromagnetic constituent of the polariton may sometimes be rather small.

As already noted, the polaritons in a crystal of finite size are divided into bulk and surface polaritons. Recourse to special tricks is to be made to experimentally separate them in the spectrum of light outgoing from a sample, especially so in the investigation of microcrystals.<sup>2</sup> Ruppin and Englman [17] were the first to show that the optical properties of microcrystals depend heavily on the shape and dimensions of the crystallites and on the matrix that contains them.

Much simpler is the case with the measurements and interpretation of the spectra of films, especially of films on a metal substrate — 'sandwich'-type structures. In this case, the transmission coefficient of light  $T(\omega)$  by a sandwich is zero and, from the energy conservation for light

$$T(\omega) + R(\omega) + A(\omega) = 1, \qquad (9)$$

where  $R(\omega)$  and  $A(\omega)$  are the reflection and absorption coefficients (we neglect scattering), it follows that

$$R(\omega) = 1 - A(\omega). \tag{10}$$

This signifies that the reflection spectrum of a sandwich-type sample is unambiguously determined by its absorption spectrum. The sandwich spectra in which  $T(\omega) = 0$  are referred to as reflection-absorption (RA) spectra. To find the  $A(\omega)$  spectrum in this case requires measuring only one spectrum— $R(\omega)$ — rather than two [ $R(\omega)$  and  $T(\omega)$  when  $T(\omega) \neq 0$ ].

The same applies to a bulk single crystal in the spectral ranges where it is opaque. For a normal incidence of light on a bulk crystal with a complex refractive index N = n + ik, the light reflection coefficient *R* is commonly written in the form [1]

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \,. \tag{11}$$

Relation (11) applies to a semiinfinite crystal which has a plane boundary with the vacuum. Experimentally, this relation corresponds to a situation where no light reflection from the rear crystal face does occur. This situation is extremely hard to realize with high precision, especially when the rear crystal face is a metal mirror.

Taking advantage of the integral Kramers-Krönig relations, the reflectance spectrum  $R(\omega)$  is employed to reconstruct the complex dielectric function  $\varepsilon(\omega)$ , which is used to derive the optical phonon frequencies  $\omega_{TO}$  of the center of the Brillouin zone ( $\mathbf{k} \approx 0$ ), their lifetimes, oscillator strengths, etc. A polariton is characterized by a  $\omega(\mathbf{k})$  dependence even without the inclusion of spatial dispersion effects. The reconstruction of the  $\omega(\mathbf{k})$  dependence requires measurements of reflection – absorption spectra for different angles of light incidence on the crystal.

The reflectivity  $R(\omega, \varphi)$  of a crystal slab of an arbitrary thickness *d* in a three-layer vacuum–dielectric film–metal substrate structure is of the form [26, 31]

$$R = \left| \frac{(\delta_1 - \delta_2)(\delta_2 + \delta_3) + (\delta_1 + \delta_2)(\delta_2 - \delta_3) \exp(-2\varkappa_2 d\omega/c)}{(\delta_1 + \delta_2)(\delta_2 + \delta_3) + (\delta_1 - \delta_2)(\delta_2 - \delta_3) \exp(-2\varkappa_2 d\omega/c)} \right|^2.$$
(12)

Here,  $\delta_j = \varepsilon_j / \varkappa_j$  for *p*-polarized radiation and  $\delta_j = \varkappa_j$  for *s*-polarized radiation;

$$\varkappa_j = \left[\varepsilon_1 \sin^2 \varphi - \varepsilon_j(\omega)\right]^{1/2}, \quad j = 1, 2, 3,$$

where  $\varepsilon_1$  is the permittivity of vacuum,  $\varepsilon_2 = \varepsilon_2(\omega)$  is the dielectric function (7) of the film of thickness *d*, and  $\varepsilon_3(\omega)$  is the dielectric function (8) of the metal substrate.

Figure 2 shows the experimental reflection–absorption spectra of a bulk ZnSe single crystal and ZnSe films of different thicknesses on an aluminum mirror for a fixed radiation angle  $\varphi = 16 \pm 12^{\circ}$ . Also shown in Fig. 2 are the spectra of ZnSe films calculated without employing any fitting parameters. The calculation was performed by formula<sup>3</sup> (12) using the numerical parameters  $\omega_{\text{TO}}$ ,  $\gamma$ ,  $\varepsilon_0$ , and  $\varepsilon_{\infty}$ [which enter into  $\varepsilon_2(\omega)$ ] and the parameters  $\omega_p$  and  $\gamma_p$  [which



**Figure 2.** (a) *p*-polarized reflection – absorption spectra of ZnSe films of different thicknesses *d* on an Al mirror: points, calculation without fitting parameters; solid curves, experiment [33, 34, 59]. (b) *p*-polarized reflectance spectrum of a ZnSe single crystal (d = 5 mm) on an Al mirror [34, 73]. (c) Raman-scattering (RS) spectrum of a ZnSe film ( $d = 1 \mu$ m) on an Al mirror [34, 110].  $v_{TO} = 200 \text{ cm}^{-1}$ ,  $v_{LO} = 250 \text{ cm}^{-1}$ .

<sup>3</sup> For l = 0, Eqn (6) passes into formula (12).

<sup>&</sup>lt;sup>2</sup> Until recently, one of the main techniques of determining the optical constants of phonon spectra of crystals involved measurements of the transmission spectra of specially prepared samples. These samples were crystals ground to a powder state using a mortar and pressed into a transparent matrix (polyethylene or KBr). This was a peculiar way of diluting the optical density. In microcrystals, the surface-to-volume ratio S/V is high enough and the contribution of surface excitations may prevail over the contribution of the bulk ones. Eventually observed in experiment are strongly inhomogeneous broad absorption bands resulting from the scatter in shape and dimension of the powder crystallites, making it hardly possible to extract analytical information of any value. Thousands of earlier papers based on this technique were actually 'dumped' in the 1990s.

enter into  $\varepsilon_3(\omega)$ ] available from the literature for bulk ZnSe single crystals and a freshly deposited aluminum mirror. Good accord between the calculation and experiments is indicative of not only the adequacy of the theoretical description by Eqn (12) of reflection–absorption spectra, but also of the high photometric quality of the spectroscopic instrument and the measurement technique <sup>4</sup> [70].

The radiative polaritons of crystals and films are studied primarily by measuring their reflection–absorption or thermal emission spectra. In the latter case, the polaritons are produced by the thermal motion of charged particles inside the material. The radiative decay of polaritons (i.e., their conversion to light) is recorded in experiments.

In the measurements of emission spectra, the sample is mounted in a thermostat in place of a regular IR radiation source, the radiation angle is easily varied by rotating the thermostat without spectrometer realignment. Measurements of the angular dependence of the radiation requires no rotatable and moving mirrors, i.e., polaritons are much easier to investigate by the method of recording thermal radiation than from reflection spectra. The spectroscopy of thermal radiation produced by the vibrational states of crystals has been repeatedly employed to determine the optical properties of different materials [56-58, 74], including thin LiF films on a metal [57, 58].

According to the Kirchhoff theory, the radiation flux from a film on a metal substrate (the transmittance of the structure is zero, the light scattering is neglected) is defined by the relationship [57, 76]

$$W_{s}(\omega, \varphi, T) = [1 - R_{s}(\omega, \varphi)] W_{b,b}(\omega, T)$$
$$= E_{s}(\omega, \varphi) W_{b,b}(\omega, T), \qquad (13)$$

where  $W_{\rm s}(\omega, \varphi, T)$  is the radiation flux from a sample at temperature *T*, frequency  $\omega$ , and angle  $\varphi$  from the normal to the sample surface, and  $W_{\rm bb}(\omega, T)$  is the blackbody radiation flux. The temperature dependence of the coefficient  $E_{\rm s}$  now is insignificant and can be neglected.

To a crude approximation, the operation of a spectral device in the regime of measuring the thermal sample radiation (the spectroradiometer mode) can be perceived as follows. When the temperatures of the sample and of all elements of the spectroradiometer are equal, the device is filled (as a blackbody cavity) with equilibrium thermal radiation determined by the temperature of the device. On heating the sample to a temperature  $T_s$ , its thermal radiation flux  $W_{\rm s}(\omega, \varphi, T_{\rm s})$  increases and, on passing through the monochromator, is absorbed by the detector of thermal radiation (a bolometer, an acoustooptical Golay cell, etc.), whose sensitive element produces an electric signal proportional to its temperature change. The radiation detector also produces a thermal radiation flux  $W_{\rm D}(\omega, T_{\rm D})$ , which is partly absorbed by the sample ( $E_s = A_s < 1$ ) on passing through the optical path of the spectroradiometer (now, from the detector to the sample).

In the approximation under consideration, the signal  $I_s$  taken from the radiation detector is proportional to the difference of the thermal radiation fluxes from the sample

and the detector:

$$I_{\rm s} \propto k T_{\lambda} \left[ W_{\rm s}(\lambda, T_{\rm s}) - W_{\rm D}(\lambda, T_{\rm D}) \right], \tag{14a}$$

where k is the coefficient of conversion of the light flux into the electric signal, and  $T_{\lambda}$  is the spectral-device transmittance at a wavelength  $\lambda$ . In the long-wavelength IR spectral range  $(\lambda > 20 \ \mu\text{m})$ , the radiation flux from a sample is proportional to its temperature, and therefore the signal  $I_s$  recovered from the detector is proportional to the temperature difference of the sample and the sensitive element of the detector. As the sample temperature increases, the signal  $I_s$  increases, but in this case anharmonicity strengthens substantially and there occur side (undesirable in this case) effects.

A quantitative investigation of the emission spectra of a sample is a rather complicated task when its temperature only slightly differs from the temperature of the spectral device. This is related to the fact that the IR radiations of the walls of a conventional spectrometer, the radiation detector, the optical modulator, and other elements of the device are comparable in intensity to the radiation of samples heated to 100-200 °C, which possess a relatively low optical density.

Furthermore, the spectral radiation intensities of the individual elements of the spectroradiometer are unknown; along with the sample radiation, they make additive contributions to the signal recovered from the IR radiation detector [71]:

$$I_{\rm s} \approx k T_{\lambda} \big[ W_{\rm s}(\lambda, T_{\rm s}) - W_{\rm ch}(\lambda, T_{\rm ch}) + \beta W_{\rm w}(\lambda, T_{\rm w}) - (1 - \beta) W_{\rm D}(\lambda, T_{\rm D}) + W_{\rm th}(\lambda, T_{\rm th}) \big] + I_{\rm noise} \,.$$
(14b)

Here, k is the light flux-to-electric signal conversion coefficient;  $T_{\lambda}$  is the spectral-device transmittance at a wavelength  $\lambda$ ;  $W_{\rm s}$ ,  $W_{\rm ch}$ ,  $W_{\rm w}$ ,  $W_{\rm D}$ , and  $W_{\rm th}$  are the thermal radiation fluxes from the sample, the modulator, the device walls, the IR radiation detector, and the walls of the thermostat of the sample, respectively;  $\beta < 1$  is the dimensionless coefficient determined by the optical ray paths in the spectral device and the reflectivity of the sample;  $T_j$  is the temperature (in kelvins); and  $I_{\rm noise}$  is the electric signal fluctuations. For a low emission of the sample, none of the terms appearing in the square brackets of Eqn (14b) can be neglected, like is usually done, see, e.g., Eqn (14a). In addition, the coefficients k and  $T_{\lambda}$  are unknown.

By positioning a blackbody in lieu of the sample, we obtain a similar equation for the blackbody radiation intensity  $I_{bb}$ , which differs, to a first approximation, from Eqn (14b) by only the term in brackets:  $W_{bb}$  instead of  $W_s$ . The  $I_s/I_{bb}$  ratio is independent of k and  $T_{\lambda}$  when the noise  $I_{noise}$  is averaged to zero. To obtain the  $W_s/W_{bb}$  ratio, the remaining components  $W_j$  in Eqn (14b) should be excluded from consideration. The sought-for ratio can be derived in several ways [34, 56–58, 71], but the simplest way involves measurements of the spectrum  $I_m$  by placing a metal mirror instead of the sample. An ideal mirror does not radiate, and in this case the first term in the square brackets of Eqn (14b) is  $W_s = W_m \approx 0$ .

When the sample, blackbody, and mirror temperatures are equal, the alignment of the device in which the sample is successively replaced with a blackbody and a mirror remains invariable, and the device is thermostatically controlled, the ratio

$$\frac{I_{\rm s} - I_{\rm m}}{I_{\rm b,b} - I_{\rm m}} = \frac{W_{\rm s}}{W_{\rm b,b}} = E_{\rm s} \tag{15}$$

<sup>&</sup>lt;sup>4</sup> It is common practice in IR spectroscopy to measure frequencies in cm<sup>-1</sup>, which are denoted by v, unlike frequencies  $\omega$ , which are measured in s<sup>-1</sup> ( $v = \omega/2\pi c$ ).

The validity of the above procedure for measuring the thermally induced emission of samples is borne out by the good agreement between the experimental and calculated emission spectra of ZnSe films on an aluminum mirror. The measurements of the emission of the samples were conducted at a thermostat temperature  $T_s$  equal to 450 or 80 K and an IR radiation detector  $T_D = 300$  K. The measurements at  $T_s = 80$  K were, thus, conducted in the negative light flux <sup>5</sup> [56, 73, 74].

Figure 3 shows the thermally induced emission spectra E of the same samples as in Fig. 2 [33, 34] and the schematic of the density of single-phonon states (for optical phonons) of a ZnSe single crystal [72]. Apart from the experimental spectra, calculated spectra derived without a single fitting parameter are also given. The emission spectra E were calculated by formulas (12) and (13). The experimental spectra  $E(\omega, \varphi)$  coincided with the  $1 - R(\omega, \varphi)$  spectra when the angles  $\varphi$  and the sample temperatures were equal, the emission and reflection spectra being measured accurate to a small background pedestal (within a few percent), which was almost frequency-independent.



**Figure 3.** *p*-Polarized thermally induced emission spectra of ZnSe films of different thickness *d* on an Al mirror: points stand for experimental data; solid curves, calculation without fitting parameters [33, 89]. In the bottom: optical phonon density of ZnSe [72].

<sup>5</sup> For  $W_{\rm s} > W_{\rm D}$ , the sensitive element of the radiation detector heats up, but for  $W_{\rm s} < W_{\rm D}$  ( $T_{\rm s} < T_{\rm D}$ ) the detector radiates more than it absorbs, and its sensor cools. This mode of measurements of radiation spectra is referred to as negative-flux spectroscopy [56, 74].

The experimental data given in Fig. 3 allow several unexpected conclusions (they are discussed in Section 5).

(1) In thin films, *p*-polarized light emission occurs not only at the frequency of a transverse optical phonon, but also at the frequency of a longitudinal optical phonon, which is forbidden by selection rules in a bulk crystal [31-33, 57-59].

(2) In a bulk single crystal, the absorption and emission of light takes place not in the range of single-phonon crystal states  $\omega_{\text{TO}} < \omega < \omega_{\text{LO}}$ , but in the  $\omega_{\text{ex}} > \omega > \omega_{\text{LO}}$  and  $\omega < \omega_{\text{TO}}$  frequency ranges, from which the single-phonon states are missing [33, 89].

(3) The emission *E* of a bulk crystal in the  $\omega_{ex} > \omega > \omega_{LO}$ and  $\omega < \omega_{TO}$  frequency ranges proves to be close to unity, i.e., to the emission of a blackbody, and is not equal to E = 1 - R, as follows from Kirchhoff's law (13).

The investigation of nonradiative surface polaritons by the techniques of optical spectroscopy is possible, in particular, with the use of an ATR prism, which matches the twodimensional wave vector of a surface polariton to the wave vector of a bulk electromagnetic (light) wave in the prism [5, 29, 31]. The wave vectors of an external electromagnetic wave and a surface polariton can also be matched by applying periodic grooves on the crystal surface [5, 8, 51]. Therefore, an ATR prism located near the crystal surface and the periodic grooves on the crystal surface transform the nonradiative surface vibrational states near the crystal – vacuum interface into the states that absorb light.

It is pertinent to note that merely equalizing the wave vector of the light wave in an ATR prism to that of a surface polariton will not suffice to excite surface polaritons because, as was noted above, the electromagnetic field **E** of a surface polariton is, strictly speaking, not transverse. This field decays rather fast with depth in the crystal and somewhat slower into the vacuum, i.e., is nonuniform (decaying in the direction of the *z* axis), and therefore  $k_z^2 < 0$  [46, 75]. A similar nonuniform (evanescent) electromagnetic wave with  $k_z^2 < 0$ , traveling along the interface in the incidence plane and decaying exponentially toward the optically less dense medium, emerges in the case of the total internal reflection in the prism. This wave is not purely transverse either, because the component of **E** in its traveling direction is nonzero [67, 75].

Therefore, a light wave incident on the plane boundary of a prism located some distance away from the crystal surface can excite a surface polariton in the crystal with a frequency  $\omega$ and a wave vector  $q = k_0 n \sin \varphi > k_0$ , i.e., for angles  $\varphi$  larger than the critical one, when there emerges total internal reflection in the prism (*n* is the refractive index of the prism material). The presence of the prism near the crystal surface perturbs the surface polariton, which manifests itself in a significant change of its dispersion law [8, 31, 67]. The dispersion of the surface polariton in a ZnSe single crystal for a relatively wide (weakly perturbing) and zero vacuum gaps between a silicon prism and a ZnSe crystal is plotted in Fig. 4c.

The excitation of surface polaritons by light using the Otto technique via an ATR prism above the crystal [5, 29] results in the light absorption by 'nonradiative surface polaritons.'<sup>6</sup> In accordance with Kirchhoff's law, a system

<sup>&</sup>lt;sup>6</sup> Since the ATR prism transforms nonradiative polaritons into the radiative ones, the term 'nonradiative polaritons' becomes incorrect. It can be used where polariton dispersion is involved, but we will use quotation marks when it comes to the intensity of radiation.



**Figure 4.** *p*-Polarized radiation spectrum of a 'Si prism–gap–ZnSe single crystal–Al mirror' system: (a) for fixed radiation angles and with frequency scanning; (b) for fixed frequencies and with radiation-angle scanning [30, 39]. (c) Dispersion of a surface phonon-polariton of a ZnSe single crystal: points, experimental frequency values of the emission peaks for two structurally different single crystals [33, 34]; solid curves, calculations for a prism–crystal gap l = 1 cm and l = 1 µm.

which has absorbed light can radiate it. When an ATR prism is away from the crystal surface, the emission of light is not observed experimentally in the frequency range of existence of surface polaritons even when the sample is strongly heated. As the prism approaches the sample heated relative to the spectral device, emission arises. This emission is enhanced as the prism – sample distance shortens, to attain the emittance close to that of a blackbody.

The thermally induced emission by 'nonradiative surface polaritons' occurred when a prism (a semicylinder) of polycrystalline silicon or KRS-6 was brought close to a heated ZnSe crystal [30-34]. The radiation generated by 'nonradiative surface polaritons' was observed at radiation angles  $\varphi$  > arctan *n*, where *n* is the refractive index of the prism material. By measuring the emission spectra at different radiation angles it is possible to reconstruct from the experiment the surface-polariton dispersion of a bulk singlecrystal defined by relation (3). In our experiments, the ZnSe single-crystal sample and the silicon prism were fixed in the thermostat holder, the crystal-prism gap was specified by a Mylar film spacer. In the thermostat, measurements were successively made of the emission spectra of the sample $gap-prism(I_1)$ , mirror  $-gap-prism(I_2)$ , blackbody( $I_3$ ), and mirror  $(I_4)$  structures. The sought-for surface polariton emission spectrum at each radiation frequency was calculated employing the relation [30, 71]

$$\frac{I_1 - I_2}{I_3 - I_4} = \frac{E_{\rm p}}{E_{\rm bb}} \,. \tag{16}$$

In the course of measurements of the radiation spectra  $I_j$ (j = 1, 2, 3, 4), the thermostat temperature was maintained equal to  $150 \pm 0.5$  °C; the single-beam diffraction FIS-21 (Hitachi) IR spectrometer or the FS-720 (Beckman, RIIC) Fourier spectrometer were kept at room temperature. The thermostat was mounted in place of one of the regular radiation sources. The surface polariton emission spectra of a ZnSe single crystal for fixed angles of incidence in the frequency scanning mode are shown in Fig. 4a and for fixed frequencies in the radiation angle scanning mode are shown in Fig. 4b. The surface polaritons emitted *p*-polarized light. The positions of emission band peaks corresponded to points in the  $\omega - q$  space in the dispersion curve of the surface polariton. The solid curves in Fig. 4c were obtained by numerical calculations by Eqn (3) with  $\omega_{\rm TO}$ ,  $\gamma$ ,  $\varepsilon_0$ , and  $\varepsilon_{\infty}$ ZnSe permittivity parameter values reconstructed from the measurements of the reflectance spectrum of the same crystal for  $T = 150 \,^{\circ}\text{C}$  [34].

It is noteworthy that the radiation intensity of the sample-gap-prism structure depends strongly on the sample-prism gap thickness. As shown in Refs [31, 79, 83], the optimum gap thickness is on the order of the light wavelength. During each measurement, the widest possible gap for which the selective emission of the structure was still observable was optimized experimentally. Under these conditions, the frequency or angular position of the band peak in the emission spectra virtually corresponded to the unperturbed surface polariton.

#### 3. Light emission by the plasmons of an ATR prism-above-metal structure

In experiments, a dielectric prism in contact with a metal furnishes a good model of a semiinfinite dielectric medium [75, 77]. In this case, it is assumed that the prism is made of an ideal dielectric [Re  $\varepsilon_{\text{diel}}(\omega) = \text{const}$ , Im  $\varepsilon_{\text{diel}}(\omega) = 0$ ], i.e., that the prism material does not absorb electromagnetic waves in the frequency range of interest. The plasmon-polariton dispersion  $\omega(q)$  of the interface of two semiinfinite media, which corresponds to Eqn (4), is shown in Fig. 5a for two limiting cases: for a vacuum-metal interface and a metaldielectric interface (the permittivity of single-crystal ZnSe in the near-IR spectral range is  $\varepsilon_{diel} = 5.8$ ). Each of the surface (interfacial) plasmon polaritons is nonradiative, for their dispersion branches in the  $\omega - q$  diagram are located to the right of the light straight line in the vacuum and the light straight line in the dielectric medium. In the former case, their two-dimensional wave vector is  $q > k_0$ , and in the second case,  $q > k_0 \sqrt{\varepsilon_{\text{diel}}}$ . Therefore, Fig. 5a shows that the dispersion of surface plasmon polaritons changes strongly as the prism recedes from the metal surface to infinity. The electromagnetic fields of these plasmon polaritons decay exponentially on either side of the interface [9].

How does the plasmon-polariton dispersion of the prism-gap-metal structure change in relation to the prism-metal gap width *l*?

It is evident that, like in a conventional Fabry–Perot interferometer, there exist interference modes in the prism– metal gap, whose frequencies should depend on the wave vector q. We emphasize that the solution of dispersion equation (4) for real q is complex [ $\omega_N(q) = \omega_N^I(q) + i\omega_N^{II}(q)$ , where N is the interference-mode number], which signifies the existence of radiative decay of the states. The dispersion and the radiative half-width of the TM polaritons of the prism– gap–metal structure obtained by numerical calculation using Eqn (4) are shown in Figs 5b and 5c. Referring to Fig. 5b, a set



**Figure 5.** (a) Plasmon-polariton dispersion of a metal for (1) a vacuum– metal interface and (2) a metal–dielectric interface;  $\varepsilon_{diel} = 5.8$ . (b) TMpolariton dispersion of a prism–gap–metal structure;  $l = 1 \mu m$ ,  $\varepsilon_{diel} = 5.8$ ,  $v_p = 2 \times 10^4$  cm<sup>-1</sup>,  $\gamma_p = 10^3$  cm<sup>-1</sup>. (c) Radiative half-width of the TM polaritons of the structure;  $k_p = v_p$  [32, 89].

of radiative polariton branches appear for a fixed thickness *l* of the vacuum gap, which are located to the left of the light straight line in vacuum, the number of these branches being determined only by the gap thickness [32, 33, 79]. Note that the radiative half-width of interference polaritons depends both on the gap width and the polariton frequency. That is why we can speak of interference modes, so long as the spectral bandwidth of these modes is smaller than the distance between the neighboring modes, i.e., when  $\omega_N^{II} \ll |\omega_N^I - \omega_{N-1}^I|$ .

For small q values, far away from the plasmon-polariton frequency of the metal, the dispersion law for radiative polaritons is of the form [32]

$$\omega_N^{\rm I} = \frac{\pi N \omega_{\rm p}}{\omega_{\rm p} \, l/c + 1 - \varepsilon_1^{-1}} + q^2 c^2 \, \frac{\omega_{\rm p} \, l/c + 1 - \varepsilon_1^{-1}}{2\pi N \omega_{\rm p}} \,, \qquad (17a)$$

$$\omega_N^{\rm II} = \frac{c}{l} \operatorname{arctanh} \varepsilon_1^{-1/2} \,. \tag{17b}$$

It is also evident that the radiative domain of the  $\omega - q$  diagram for  $l \to \infty$  in the plane-wave approximation is completely filled with the electromagnetic field eigenstates of the structure under consideration.

The light absorption by radiative polaritons in a prismgap-metal structure is regularly observed in experiments on the investigation of surface plasmons in metals employing the ATR spectroscopy techniques [5, 31, 78, 79, 83] when the prism-sample gap width exceeds the wavelength of light in vacuum. Figure 6 shows the spectra of *p*-polarized thermally induced emission of a ZnSe prism – gap – metal structure. The gap width in the experiment was specified by a 20- $\mu$ m Mylar spacer and the role of a semiinfinite metal was played by metal mirrors, which were opaque in the visible range and were made up of chromium and aluminum layers (more than 500 nm thick) deposited on a quartz plate.

The thermally induced emission of the ZnSe prism – gap – aluminum structure was employed as a reference spectrum  $I_2$ [see formula (16)] obtained under the same conditions (the thermostat temperature T = 150 °C, the same radiation angle, the same spacer between the prism and the metal). Freshly evaporated aluminum makes one of the best mirrors in the IR spectral range (with a reflectivity of no less than 96%). The  $I_2$  radiation intensity amounted to about 40% of the blackbody radiation at the same temperature (150 °C), and the modulation of the  $I_2$  spectrum by the interference modes of the prism – aluminum gap was within 5% and could easily be smoothed out by averaging.

Figures 6b-6d show the theoretical emission spectra of the prism-gap-metal structure calculated with the use of Eqn (6) for different light-emission angles in the prism  $\varphi$ . For  $q > k_0$  (i.e.,  $\varphi > \varphi_c = 24.54^\circ$  for a ZnSe prism), it is evident that there are no states that interact with light. For  $\varphi < \varphi_c$ (i.e.,  $q < k_0$ ), one can see light absorption bands due to radiative polaritons. Their frequencies are in perfect accord with the dispersion curves in Fig. 5b, and their half-widths, with the data in Fig. 5c. A comparison of Figs 6b and 6c suggests that the intensity of emission (absorption) spectra due to the radiative polaritons of the structure with chromium is significantly higher than that of the structure with aluminum. The spectral intensity is determined primarily by the magnitude of Im  $\varepsilon_{\rm m}(\omega)$ , i.e., by the metal conductivity (the electron collision frequency in the plasma of the metal). Good qualitative agreement between the theoretical (Fig. 6b) and experimental (Fig. 6a) spectra is evident.

A quantitative comparison of the experimental and theoretical spectra given in Fig. 6 is hampered by the inaccuracy of not only the determination of the gap thickness. If the gap thickness is used as the adjustment parameter, the frequencies of interference-mode bands and their halfwidths agree well with the theoretical ones, and the inaccuracy in the determination of emission-band intensities amounts to 50%. Experiments give higher intensities than the calculation. This may be due to the light absorption in the ATR prism, i.e., the existence of the imaginary part of the permittivity of the prism material. In conventional far-field experiments, the absorption in the prism results in a reduction of intensity. In our case, we are dealing with the near field: the evanescent field of the surface plasmon of the metal penetrates into the prism and is transformed by the gap into the far field recorded in the experiment.

As is shown in Ref. [80], the inclusion of the imaginary part of the permittivity of the ATR prism material in a prism – gap – metal structure results in a significant intensity increase of the emission by the interference polaritons of the structure; however, this effect has not been studied experimentally to date. The theoretical emission spectra of the ZnSe prism – gap – aluminum structure calculated with the inclusion of the complex permittivity of the prism material  $\varepsilon_{ZnSe} = 5.8 - 0.03i$  are given in Fig. 6d [89]. One can see that taking into account the small (frequency-independent) imaginary part of the permittivity of the prism material results in a significant change of the emission spectra (Figs 6c



Figure 6. (a) Experimental spectrum of *p*-polarized thermally induced radiation of the ZnSe prism – gap (20  $\mu$ m) – chromium structure for a radiation angle of 12 ± 3° inside the prism and (b)–(d) theoretical emission spectra of the ZnSe prism – gap – metal structure calculated for different light emission angles in the prism: (b) the metal is chromium,  $v_p = 5 \times 10^4$  cm<sup>-1</sup>,  $\gamma_p = 8 \times 10^3$  cm<sup>-1</sup> [33]; (c) the metal is aluminum,  $v_p = 1.2 \times 10^5$  cm<sup>-1</sup>,  $\gamma_p = 10^3$  cm<sup>-1</sup>; and (d) the same as (c), but  $\varepsilon_{ZnSe} = 5.8 - 0.03i$  [89].

and 6d). In this case, the experimental (Fig. 6a) and calculated (Fig. 6b) spectra coincide to within 10% in radiation intensity as well.

Therefore, the surface polaritons for a zero or infinitely large prism-metal gap are nonradiative, i.e., cannot absorb and emit light [32, 33, 40]. The radiative domain located to the left of the light straight line in the medium (Fig. 5a) is significantly larger than for the metal-vacuum interface, but both of them are empty, i.e., do not contain any states other than the vacuum ones. This signifies that the light with a frequency  $\omega < \omega_p$  incident on the metal in both media cannot be absorbed and should experience total reflection. When the gap has a finite thickness comparable with the depth of surface-polariton field penetration into the vacuum, there occurs field perturbation by the prism, which results in the occurrence of radiative modes in the gap (Fabry-Perot-type modes) [31-33]. The intensity of absorption (emission) bands arising from these modes depends on the imaginary parts of the permittivities of the metal and the prism material.

It is pertinent to note that the initial excitations of an ATR prism-vacuum gap-metal structure at room temperature are the surface plasmons of the metal. The emergence of radiative polaritons with the appearance of a prism-metal gap and the dependence of the intensity of the light absorption by these polaritons on the metal permittivity signify that the electromagnetic states of the plasmon polariton of the metal split due to their interaction with the dielectric prism. Part of the electromagnetic energy of the surface plasmon is radiated through the prism into the vacuum at the frequencies of the radiative states. The 'photons' produced in this way are not free photons traveling through the vacuum, for their dispersion at small q (Fig. 5b) differs greatly from the light dispersion in the vacuum (from the light straight line). These 'photons' (to be more precise, the radiative polaritons of the structure) are 'bound' in the vacuum gap between the metal and the prism, and they should be treated as the eigenstates of the electromagnetic field of the three-layer structure as a whole. For  $\operatorname{Im} \varepsilon_{\mathrm{m}}(\omega) = 0$  and  $R \equiv 1$  (E = A = 0), radiative polaritons are not observed experimentally even though they do exist in accord with Eqn (4).

A similar situation occurs when the dielectric medium above the metal surface is bounded (is finite in thickness).

## 4. Light emission by the plasmons of a dielectric film-on-metal structure

Let us consider an ideal dielectric film on a metal substrate. Like in the previous case, the initial excitations of this structure are surface metal plasmons and vacuum photons. Their interaction in the vacuum-dielectric film-metal structure results in the production of polaritons whose dispersion branches are described by Eqns (4) and (5).

The dispersion of TM polaritons of the vacuum– dielectric film (1 µm)–metal structure is given in Fig. 7 [32, 89]. Referring to Fig. 7, along with the nonradiative surface plasmon polariton  $\omega_{sp}$  of the metal–semiconductor interface this structure bears nonradiative (waveguide) polaritons located in the domain between the light straight line  $v = k_0/2\pi$  and the straight line  $k_0/2\pi n_0$  (where  $n_0 = \varepsilon_{diel}^{1/2}$  is the refractive index of the film material) as well as radiative (interference) polaritons to the left of the light straight line [32]. It is noteworthy that the number of interference and waveguide branches increases with increasing film thickness *d*. As  $d \to \infty$ , the number of modes in the plane-wave approximation tends to infinity. In this case, the modes fill out the waveguide and interference polariton bands completely.

The reflection – absorption spectra of a 1.25-µm-thick ZnSe film on an aluminum substrate for different angles of incidence of *p*-polarized light are shown in Fig. 8a and the reflection – absorption spectra at angles  $\varphi > \varphi_{Br}$  (where  $\varphi_{Br}$  is Brewster's angle) for *p*- and *s*-polarized light are shown in Fig. 8b [33, 35]. The plateau in the short-wavelength spectral region ( $\lambda < 460$  nm) arises from the fundamental band – band absorption of ZnSe (the energy-gap width is  $E_g = 2.7$  eV for T = 300 K).

Figure 9 shows the calculated absorption spectra of a real ZnSe film on a real metal (aluminum) [33, 89]. The calculation was made by Eqn (12) with the same dielectric function of the film  $\varepsilon_2(\omega)$  as for a bulk crystal. In this case, for  $\varepsilon_2(\omega)$  in the



**Figure 7.** Dispersion of TM polaritons of the vacuum–dielectric film  $(1 \ \mu\text{m})$ –metal structure for (a) an ideal dielectric film and (b) a ZnSe film [32, 89]. The domain of intersection of LO and TO phonons with the  $v = k_0/2\pi$  curve is considered in greater detail in Fig. 10;  $v_{sp}$  is the surface plasmon polariton of the metal–dielectric interface.



**Figure 8.** Reflection – absorption spectra of 1.25-µm-thick ZnSe film on an Al substrate: (a) for different angles of *p*-polarized light reflection; and (b) for  $\varphi = 75^{\circ} > \varphi_{Br}$  for *p*- and *s*-polarized light [33, 35].

frequency range  $\omega < \omega_{ex}$  advantage was taken of the expression

$$\varepsilon_{2}(\omega) = \varepsilon_{\infty} - \Delta_{\varepsilon} + \Delta_{\varepsilon} \frac{\omega_{ex}^{2}}{\omega_{ex}^{2} - \omega^{2} - i\gamma_{ex}\omega} + (\varepsilon_{0} - \varepsilon_{\infty}) \frac{\omega_{TO}^{2}}{\omega_{TO}^{2} - \omega^{2} - i\gamma\omega}, \qquad (18)$$

where  $\omega_{\rm ex} \approx E_{\rm g}/\hbar$  and  $\gamma_{\rm ex}$  are the frequency and the exciton damping constant ( $E_{\rm g}$  is the energy-gap width), respectively;  $\Delta_{\varepsilon}$  is the excitonic oscillator strength; and  $\omega_{\rm TO}$ ,  $\gamma$ , and  $\varepsilon_0 - \varepsilon_{\infty}$ are the frequency, damping constant, and oscillator strength of a transverse optical phonon, respectively.

Expression (18) provides a rather good description of the frequency dependence of ZnSe-film permittivity at frequencies  $\omega \ll \omega_{ex}$ , i.e., away from the frequencies of electron transitions from the valence to the conduction band [32, 33, 86]. The dielectric function of the metal  $\varepsilon_3(\omega)$  was taken in the form of Eqn (8). One can see good qualitative agreement between experimental and calculated spectra [32, 33, 86, 89]. The low-frequency ('phonon') part of the absorption spectrum in Fig. 9c is in very good accord with the experimental data in Figs 2 and 3 (see also Refs [59, 88]).

The frequency and the profile shape of the absorption band arising from the radiative polaritons of the structure under consideration are determined by the thickness and



**Figure 9.** Calculated *p*-polarized absorption spectra of a real 1-µm-thick ZnSe film ( $\Delta \varepsilon_{ex} = 0.05$ ,  $v_{ex} = 2 \times 10^4$  cm<sup>-1</sup>,  $\gamma_{ex} = 1.5 \times 10^3$  cm<sup>-1</sup>): (a) on an ideal metal substrate,  $v_p = 1.2 \times 10^5$  cm<sup>-1</sup>,  $\gamma_p = 0$ ; (b) on a real Al substrate,  $v_p = 1.2 \times 10^5$  cm<sup>-1</sup>,  $\gamma_p = 10^3$  cm<sup>-1</sup> [33, 89]; and (c) the 'phonon' absorption region is in good agreement with the data in Figs 2 and 3 [33].

permittivity of the dielectric film, and the absorption bands intensity is defined by the magnitude of  $\text{Im} \varepsilon_{\text{m}}(\omega)$ , i.e., the metal conductivity. The lower the metal substrate conductivity, the higher the intensities of emission (absorption) bands at the frequencies of the interference modes of the planeparallel dielectric layer on the metal.

It should be emphasized that the interference modes depend on the two-dimensional wave vector  $\mathbf{q}$ . For real and small q and at frequencies much lower than the metal plasmon frequency of the metal and the dielectric exciton frequency of the dielectric, the dispersion law for interference polaritons is of the form [32]

$$\omega_{N}^{\rm I} = \frac{\pi (2N+1)\omega_{\rm p} \varepsilon_{2}^{1/2}}{2(\omega_{\rm p} d/c + \varepsilon_{2} - 1)} + \frac{2q^{2}c^{2}(\omega_{\rm p} d/c + \varepsilon_{2} - 1)}{\pi (2N+1)\omega_{\rm p} \varepsilon_{2}^{1/2}} ,$$
(19a)

$$\omega_N^{\rm II} = \frac{c}{d\epsilon_2^{1/2}} \arctan \epsilon_2^{-1/2} \,. \tag{19b}$$

Formulas (19) rather well describe the positions of absorption band peaks in frequency  $\omega_N^{I}$  and their half-width  $\omega_N^{II}$  in the spectra in Figs 8 and 9 [32, 89].

Let the interference mode frequencies of a film on a metal substrate fall within the range of frequencies allowed by the selection rules for interband electron transitions in metals. As is shown in Refs [32, 33, 86], in this case there emerges a hybrid state of the electromagnetic field of the structure (interference cavity modes) with the electronic states of the substrate (cavity walls), and light is absorbed by a hybrid (mixed) polariton. In these experiments, measurements were made of the visible-range (400-700 nm) reflection-absorption spectra of 0.27-µm ZnSe films evaporated simultaneously (in one technological cycle) on substrates with thick (opaque) mirrors of aluminum, chromium, and copper. The position of the absorption band of the interference mode with N = 2, which is the only band in this spectral range, was found to strongly depend on the metal substrate (Fig. 23b). Unlike aluminum and chromium, the interband electron transitions allowed by selection rules substantially modify the dispersion of the surface plasmon polariton of copper [81]. When the interference mode frequency of a ZnSe film on copper coincides with the plasmon-polariton frequency, there occurs a resonance between them in the region of interband electron transitions, which results in the shift and broadening of the interference band in the reflection-absorption spectrum. This is most conspicuous in a thin film  $(nd \propto \lambda)$ : for a 0.27-µm ZnSe film on copper, the band shift to the lowfrequency spectral range was almost as large as 0.4 eV. The giant shift of the interference band in the film on copper and its large broadening in comparison with the same band in the films on aluminum and chromium testifies to the occurrence of a hybrid (mixed) polariton [86]. It is noteworthy that the hybrid polariton possesses an anomalously high integrated light absorption.

From the qualitative analysis performed above, it is clear that a film of ideal dielectric on a metal transforms the nonradiative (for zero and infinite film thicknesses) surface plasmon of the metal to a set of new plasmon states — to the interference and waveguide polaritons of the structure. We can put it differently: penetrating into the dielectric film, the electromagnetic field of the surface plasmon polariton of the metal is perturbed ('quantized') by the film boundaries, and in response to this size quantization, there arises interference and waveguide polaritons of the structure. The film in this structure can also be considered as a cavity (resonator) for the electromagnetic field (including that of the vacuum), and the interference and waveguide modes, as the cavity 'modes'<sup>7</sup> which interact with the plasmon of the metal wall of the cavity [23, 32, 84].

For a nonabsorbing film on an ideal metal (A = 0), it follows from relation (10) that R = 1 for any film thickness and angle of incidence. Under these conditions, there exist interference modes (cavity modes) in the sandwich, which obey dispersion laws (4) and (5), but cannot be experimentally observed in absorption, thermally induced emission, or reflection spectra. And it is only for A > 0 that the 'interference' spectra do show up in the reflection – absorption spectrum of the sandwich. This may be related to the tails of phonon or electronic state densities of bulk and surface film excitations, the density of multiphonon states, and crystal structure defects, as well as due to the damping of plasma oscillations in the metal substrate. All these states are renormalized due to the perturbation of the polariton electromagnetic field of the sandwich by the dielectric film.

Therefore, an initially nonradiative surface plasmon of a metal at the interface of semiinfinite media is partially transformed by the film on the metal into a radiative one. And even when the dielectric film material does not absorb light [ $\gamma_{ex} = \gamma = 0$  in formula (18)], the sandwich absorbs and radiates electromagnetic waves.

# 5. Light emission by the polaritons of a semiconductor film-on-metal structure

Now, we consider a film of a real dielectric (semiconductor) on a metal substrate. The inclusion of vibrational eigenstates of the film on a metal substrate leads to significant changes in the polariton dispersion of the structure and to specific changes of the optical properties of both the film and the metal substrate. The optical properties of thin dielectric and semiconductor films on metal surfaces were discussed in a plethora of papers (see, for instance, Refs [22–26, 31–35, 38-44, 57-59, 61-66, 79-92]. In doing this, some authors considered changes in the optical properties of substrate-free films arising from their contact with a metal, while others considered changes in the characteristics of metal-surface plasmons due to the film deposition on the metal.

Strictly speaking, the interaction of dipole-active excitations in a film on a metal with metal electronic states results in the modification of the excitations of both the film and the substrate. Experiments always yield the information on the structure as a whole (in our case, on the vacuum – film – metal structure). The polaritons in a sandwich-like structure are mixed polaritons with a unitary electromagnetic field for the structure as a whole. The electromagnetic field of a mixed polariton is defined by all elementary excitations of each medium in the structure [31-34].

#### 5.1 Thin films

To a first approximation, the dipole-active Coulomb vibrational states of a film (or of molecules adsorbed on the metal surface) with a frequency  $\omega_0$  are independent of the wave vector in the domain  $q \approx 0$ . For  $\omega_0 \ll \omega_p$ , a straight line parallel to  $k_x$  intersects the polariton branches (interference, waveguide, and plasmon mode branches) of the vacuum– film–metal structure. Their interaction should give rise to splitting of the branches in the neighborhood of their intersection points and to the formation of gaps in the spectrum of mixed polaritons (similarly to that discussed in Refs [40–44, 62, 87]).

We begin our analysis of real films on a metal surface with ultrathin films, because for them it is easier to find out which particular dipole-active states of the film on the metal interact with light and to elucidate the laws of this interaction. It is noteworthy that vibrational polaritons in crystals reside in the long-wavelength IR spectral range and the film can be treated as ultrathin if its optical thickness is much smaller than the wavelength of the excitation. From this viewpoint, a film approximately 1  $\mu$ m in thickness can be regarded as ultrathin (the wavelengths under our consideration are longer than 30  $\mu$ m). The concept of macroscopic permittivity applies to this film, since it contains several thousand atomic layers. This is attested by the good accord between experimental results and theoretical calculations in the framework of linear macroscopic crystal optics.

The absorption, reflection, and emission of light by the vibrational states of crystals and films (by optical phonons and plasmons) is adequately described by the Maxwell equations with the corresponding boundary conditions and the constitutive equations of the medium (the spatiotemporal relations between the electric induction and electric intensity vectors of the field inside the medium, for the effects of spatial dispersion can be neglected in the IR spectral range).

Indeed, when the permittivities of the crystal (film) and the ambient media are known, the solution of macroscopic Maxwell equations with conventional boundary conditions for the tangential and normal components of the electric and magnetic fields yields a correct answer. However, this approach does not make it possible to elucidate in detail into what the absorbed light energy converts and which particular vibrational state of the sample is responsible for one or other peak in the spectrum.

**5.1.1 Coulomb states of a dielectric film on a metal substrate.** We first consider the Coulomb normal modes of a vacuum–film–metal substrate structure, i.e., the states obtained with neglect of the interaction with transverse electromagnetic field, and then include this interaction [59, 88]. As is well known [2], the equations for these states are derived from the Maxwell equations when the velocity of light is formally let tending to infinity:

$$\operatorname{div} \mathbf{D} = 0, \qquad (20)$$

$$\operatorname{rot} \mathbf{E} = 0. \tag{21}$$

With neglect of spatial dispersion effects, the material relationship between the induction **D** and intensity **E** vectors of electric field is local:

$$\mathbf{D}(\omega, \mathbf{r}) = \varepsilon(\omega) \, \mathbf{E}(\omega, \mathbf{r}) \,, \tag{22}$$

which permits substituting in relationship (22) the dielectric function  $\varepsilon(\omega)$  known for a bulk single crystal [see Eqn (7)] [8].

The solution of the system of equations (20), (21) will be sought for in the form

$$\mathbf{E} = \mathbf{E}_q(z) \exp\left(\mathrm{i}qx\right).$$

The x axis will be taken parallel to the two-dimensional  $\mathbf{q}$  vector lying in the plane of the film, and the z axis will be taken

<sup>&</sup>lt;sup>7</sup> Cavity modes (electromagnetic waves) commonly considered in quantum optics are 'locked' inside the cavity. Their radiative decay probability is zero. From this viewpoint, the interference film modes are 'bad': they can be treated as modes with a finite lifetime. The interference modes are homogeneously broadened due to their radiative decay.

perpendicular to the film. The system of equations (20), (21) splits into two equations: for the  $E_x$  and  $E_z$  electric field components (the *p* polarization) and for the  $E_y$  field component (the *s* polarization).

*s-Polarized vibrations, transverse modes.* From Eqn (21), we obtain  $E_y = 0$  for *s*-polarized states, but the polarization in the medium  $\mathbf{P} = (\mathbf{D} - \mathbf{E})/4\pi$  may be nonzero. From the equality  $E_y = 0$ , it follows that  $P_y \neq 0$  when  $\varepsilon(\omega) \to \infty$ . This signifies that the frequency of the modes is  $\omega = \omega_{\text{TO}}$ . The  $P_y(z)$  function itself proves to be indefinite: for  $\omega = \omega_{\text{TO}}$ , any dependence  $P_y = P_y(z)$  in the interval -d < z < 0 is consistent with both the constraint  $E_y = 0$  and the boundary conditions (the normal component of the induction vector  $\mathbf{D}$  and the tangential component of the intensity vector  $\mathbf{E}$  of the electric field are everywhere zero for the vibrations under consideration).

In the -d < z < 0 interval, an arbitrary function  $P_y(z)$  can be represented as linear combinations of independent functions

$$P_{y}^{s}(z) = A_{n} \sin\left[\frac{\pi n}{d}(z+d)\right], \quad n = 1, 2, \dots,$$
 (23)

$$P_{y}^{c}(z) = B_{n} \cos\left[\frac{\pi n}{d} \left(z+d\right)\right], \quad n = 0, 1, \dots$$
 (24)

The system of these modes is multiply degenerate, i.e., the frequencies of all the modes are equal:

$$\omega_q^{\rm s} = \omega_q^{\rm c} = \omega_{\rm TO}$$

The atomic vibrations in the film are not accompanied by the emergence of a space charge ( $\rho = -\text{div } \mathbf{P} = 0$ ), nor are the transverse vibrations in bulk single crystals. Surface charges do not occur in this case either. By analogy with a bulk single crystal, modes (23) and (24) will be termed transverse film modes, being nevertheless aware that the unambiguous division of vibrations into longitudinal and transverse is possible only for uniform systems.

*p-Polarized vibrations, surface modes.* We first consider the modes for which  $\varepsilon(\omega) \neq 0$  and the electric intensity is not identically equal to zero. We cancel  $\varepsilon(\omega)$  in each of the media in Eqn (20) to obtain

$$\frac{\mathrm{d}E_z}{\mathrm{d}z} + \mathrm{i}qE_x = 0\,. \tag{25}$$

For a *p*-polarized field, Eqn (21) gives

$$\frac{\mathrm{d}E_x}{\mathrm{d}z} - \mathrm{i}qE_z = 0\,. \tag{26}$$

Considering that the field vanishes as  $|z| \rightarrow \infty$  and using conventional joining conditions at the vacuum-film and film-substrate interfaces, we obtain the field inside the film (-d < z < 0)

$$E_{x}(z) = E_{0} \left[ \cosh\left(qz\right) - \frac{1}{\varepsilon(\omega)} \sinh\left(qz\right) \right],$$
(27)

$$E_{z}(z) = iE_{0} \left[ \frac{1}{\varepsilon(\omega)} \cosh\left(qz\right) - \sinh\left(qz\right) \right], \tag{28}$$

and the dispersion equation for the mode frequency

$$\varepsilon^{2}(\omega) \tanh(qd) + \varepsilon(\omega)(1 + \varepsilon_{m}) + \varepsilon_{m} \tanh(qd) = 0.$$
 (29)

Equation (29) splits into two relations for  $\varepsilon(\omega)$ ; for  $|\varepsilon_{\rm m}| \ge 1$ , they are of the form

$$\varepsilon(\omega) = -\tanh\left(qd\right),\tag{30}$$

$$\varepsilon(\omega) = -\varepsilon_{\rm m} \coth\left(qd\right). \tag{31}$$

Let us consider the modes that correspond to these dispersion equations.

(i) We substitute relation (30) into expressions (27) and (28) to obtain the field in the film:

$$E_x(z) = E \sinh\left[q(z+d)\right],\tag{32}$$

$$E_z(z) = -iE\cosh\left[q(z+d)\right].$$
(33)

Hence, it follows that the field in the mode is, for a large film thickness  $(qd \ge 1)$ , concentrated near the vacuum – film interface and decays exponentially with depth in the film. For  $qd \rightarrow \infty$ , dispersion equation (30) passes into the well-known [8, 9, 17] equation for a surface phonon at the semiinfinite medium – vacuum interface (with neglect of retardation):

$$\varepsilon(\omega) = -1. \tag{34}$$

Taking this into account for the dielectric function (7), we obtain the surface-phonon frequency  $\omega_{\rm S}$  when  $d \to \infty$ :

$$\omega_{\rm S} = \omega_{\rm TO} \left( \frac{\varepsilon_0 + 1}{\varepsilon_\infty + 1} \right)^{1/2}.$$
 (35)

For a film of arbitrary thickness d, the solution of Eqn (30) with the dielectric function (7) is of the form

$$\omega_{\rm S+}(q,d) = \omega_{\rm TO} \left( \frac{\varepsilon_0 + \tanh\left(qd\right)}{\varepsilon_\infty + \tanh\left(qd\right)} \right)^{1/2}.$$
(36)

The type of vibrations under consideration is not related to bulk charges (since div  $\mathbf{E} = 0$  for -d < z < 0), but is accompanied by the occurrence of surface charges at the film boundaries:

$$\rho_{S+} = iE \frac{\varepsilon(\omega) - 1}{4\pi} \cosh\left(qd\right), \quad z = 0, \qquad (37)$$

$$\rho_{\mathbf{S}+} = -\mathbf{i}E \,\frac{\varepsilon(\omega) - 1}{4\pi} \,, \quad z = -d \,. \tag{38}$$

These vibrations will be referred to as surface modes [16, 33, 59, 88]. As is shown in Section 5.1.4, the surface modes with  $q < \omega/c$  interact with the transverse electromagnetic field and are transient (radiative).

We highlight the following fact, which is of great significance for the interpretation of experimental data: according to relation (30), for  $qd \rightarrow 0$  the permittivity  $\varepsilon(\omega) \rightarrow 0$  and the frequency of the surface mode of the vacuum-film interface is defined by the relation

$$\omega_{\mathrm{S}+}(qd) \to \omega_{\mathrm{LO}} = \omega_{\mathrm{TO}} \left(\frac{\varepsilon_0}{\varepsilon_{\infty}}\right)^{1/2},$$

where  $\omega_{\text{LO}}$  is the frequency of a longitudinal optical phonon in a bulk crystal. Furthermore, the electric field of a surface mode in a thin film ( $qd \ll 1$ ) is directed almost perpendicular to the film surface and is almost uniform in depth [24, 25, 33]. (ii) We consider the mode that corresponds to dispersion equation (31). The permittivity of a metal substrate appears explicitly in this equation. To an ideally conducting substrate there corresponds a limit  $|\varepsilon_m| = \infty$ ; in this case, it follows from Eqn (31) that  $\varepsilon(\omega) = \infty$ , and from expression (7) we obtain that

$$\omega_{\mathbf{S}-}(qd) = \omega_{\mathbf{TO}}$$
.

We are also interested in the field distribution in the mode involved. It follows from the finiteness of the induction vector  $\mathbf{D} = \varepsilon(\omega) \mathbf{E}$  that the electric field in the film tends to zero when  $|\varepsilon_{\rm m}| \to \infty$ , but the magnitude of polarization  $\mathbf{P} = (\varepsilon(\omega) - 1) \mathbf{E}/4\pi$  remains finite in the medium. With the aid of expressions (27) and (28), we find the field for a finite  $|\varepsilon_{\rm m}|$  value and pass to the limit  $|\varepsilon_{\rm m}| \to \infty$  to obtain the polarization of this mode:

$$P_x(z) = P\cosh\left(qz\right),\tag{39}$$

$$P_z(z) = -iP\sinh\left(qz\right). \tag{40}$$

For a large film thickness  $(qd \ge 1)$ , the vibrational mode is thus seen to be concentrated in the domain of greatest possible |z| values in the film, i.e., at the boundary with the metal (z = -d), and decays exponentially with distance from this boundary.

Therefore, we are dealing here with the second type of surface modes of the vacuum-film-substrate structure. Note that the polarization **P** of this mode in a thin film  $(qd \ll 1)$  is directed almost parallel to the film surface and is almost constant throughout the whole depth of the film.

The finite conductivity of the metal substrate has the effect that the surface-mode frequency may be somewhat different from  $\omega_{TO}$  and there is a weak dependence of the frequency from the wave vector **q** and the film thickness *d*. For  $|\varepsilon_m| \ge 1$ , from Eqn (31) we obtain

$$\omega_{\rm S-}(q,d) = \omega_{\rm TO} \left[ 1 + \frac{\varepsilon_0 - \varepsilon_\infty}{2\varepsilon_{\rm m}} \tanh\left(qd\right) \right]. \tag{41}$$

Hence, it explicitly follows for a thin film that the frequency shift, which is proportional to  $\operatorname{Re} \varepsilon_{\mathrm{m}}^{-1}$ , and the mode damping, which is proportional to  $\operatorname{Im} \varepsilon_{\mathrm{m}}^{-1}$ , prove to be linearly dependent on *d* and *q* [39, 40, 90].

*p*-*Polarized vibrations, longitudinal modes.* Now, let us consider *p*-polarized modes, which correspond to the condition

$$\varepsilon(\omega) = 0. \tag{42}$$

From Eqn (21) we obtain Eqn (26), which is valid both in the vacuum and in the film. Equation (20) subject to condition (42) is identically fulfilled inside the film.

From the boundary condition  $E_z(0 + \delta) = \varepsilon(\omega) E_z(0 - \delta)$ and Eqns (25) and (26) we deduce that the field in the vacuum is identically equal to zero. That is why the boundary condition for the field in the film is  $E_x(0 - \delta) = 0$ . This condition combined with the relation  $E_x(-d) = 0$  determines the type of eigenmodes in the film:

$$E_x^{(n)}(z) = C_n \sin\left[\frac{\pi n}{d}(z+d)\right],\tag{43}$$

$$E_z^{(n)}(z) = -\mathrm{i}C_n \frac{\pi n}{d} \cos\left[\frac{\pi n}{d}(z+d)\right],\tag{44}$$

where *n* = 1, 2, ...

We make use of condition (42) and expression (7) to find the frequency of the modes that correspond to Eqns (43) and (44):

$$\omega = \omega_{\rm TO} \left(\frac{\varepsilon_0}{\varepsilon_\infty}\right)^{1/2} \equiv \omega_{\rm LO} \,. \label{eq:mass_eq}$$

These vibrations are accompanied by the appearance of bulk and surface charges:

$$\rho(q) = -i \frac{C_n}{4\pi} \left( q + \frac{\pi^2 n^2}{q d^2} \right) \sin\left[\frac{\pi n}{d} (z+d)\right],\tag{45}$$

$$\rho_{\rm S}(q) = {\rm i} \, \frac{C_n \, n}{4qd} \begin{cases} (-1)^n, & z = 0, \\ 1, & z = -d. \end{cases}$$
(46)

The properties of modes (45) and (46) are close to those of the longitudinal modes (phonons) of a single crystal, while their frequencies are just equal. These modes will be referred to as longitudinal film modes.

*p-Polarized vibrations, transverse modes.* Finally, we consider *p*-polarized film modes, for which the electric field **E** is identically zero (we discuss the Coulomb modes, i.e., without the inclusion of retardation). The medium polarization **P** and the induction vector **D** can be nonzero. From the condition  $\mathbf{D} = \varepsilon(\omega) \mathbf{E} \neq 0$  with  $\mathbf{E} \equiv 0$ , it follows that  $\varepsilon(\omega) = \infty$ . The frequencies of the modes under investigation coincide with the frequency of transverse phonons in a single crystal:

 $\omega = \omega_{\rm TO}$ .

From Eqn (20), we obtain for the polarization P

$$iqP_x(z) + \frac{dP_z(z)}{dz} = 0.$$
(47)

Equation (21) is evidently an identity for the modes under consideration. From the continuity condition on the tangential component of the electric field  $\mathbf{E}$  at the vacuum-film interface, it follows that the components  $E_x$  and therefore  $E_z$ are zero in the vacuum. From the equality  $E_z = 0$  in the vacuum and the continuity condition for the normal component of the induction vector  $\mathbf{D}$ , we have the boundary condition  $P_z(0) = 0$ . For a finite value of the permittivity  $\varepsilon_m$ of the metal substrate, it is possible to obtain, in a similar way, the second boundary condition for  $P_z$ :  $P_z(-d) = 0$ , which retains its form in the passage to the case of an ideally conducting substrate ( $|\varepsilon_m| \to \infty$ ).

Equation (47) and both boundary conditions determine the form of the function P(z):

$$P_{x}(z) = \sum_{n} C_{n,q} \cos\left[\frac{\pi n}{d}(z+d)\right],$$
(48)

$$P_z(z) = -i \frac{qd}{\pi} \sum_n \frac{C_{n,q}}{n} \sin\left[\frac{\pi n}{d}(z+d)\right].$$
(49)

The  $\mathbf{P}(z)$  function is thus seen to be a linear superposition of independent modes. As shown above, the frequency of each of modes (48) and (49) is equal to  $\omega_{\text{TO}}$ . These vibrations are not accompanied by the occurrence of either a surface charge [since  $P_z(0) = P_z(-d) = 0$ ], or a bulk charge on the strength of Eqn (47). It would appear natural that these modes would be termed transverse.

The interaction of the Coulomb modes obtained above with a transverse electromagnetic field results in the production of surface and bulk polaritons of the vacuum-filmmetal substrate structure, which are eigenstates of the structure. The states with  $q < \omega/c$  prove to be radiative and possess a finite radiative lifetime [15, 16], and the states with  $q > \omega/c$  prove to be nonradiative [13, 16]. The interaction of transverse Coulomb modes with the electromagnetic field entails a variation of their dispersion law. As for the longitudinal modes (longitudinal phonons), they do not interact with the electromagnetic field, and the inclusion of retardation does not change their dispersion law (their state) [12–17, 33].

**5.1.2.** Dispersion of surface polaritons. In the case of a film on a metal substrate, it is possible to observe either a surface polariton  $\omega_{S+}$  related to the Coulomb mode (36) of the vacuum-film interface or (in addition to it) a surface polariton  $\omega_{S-}$  near the film-metal interface related to Coulomb mode (41), depending on the substrate conductivity.

As is shown below, the feasibility of observing the  $\omega_{S-}$ polariton arises from the finite substrate conductivity. In accord with expression (41), the surface-polariton frequency  $\omega_{S-}$  for an ideally conducting metal substrate proves to be equal to the frequency  $\omega_{TO}$  of transverse optical film phonons. As a consequence, it is impossible to find out without additional analysis from which states this peak in the emission spectrum arises: from the emission of a surface polariton of the film-metal interface or the emission of transverse film modes, which were considered in Section 5.1.1.

To derive the dispersion equation for surface polaritons with the inclusion of retardation, we take advantage of the system of Maxwell equations supplemented in each of the three media (including the vacuum above the film) by a material relation  $D(\omega) = \varepsilon(\omega) E(\omega)$  with the corresponding permittivity values in the three media. We will seek for the solution of the extended system of equations for a *p*-polarized electromagnetic field in the form

$$E(\mathbf{r}) = E(z) \exp\left(\mathrm{i}qx\right),$$

and in doing this we impose the requirement that the field should tend to zero when  $z \to \infty$ .

We join the fields at the z = -0 and z = -d interfaces to obtain the dispersion equation for surface polaritons [39, 90]:

$$\varepsilon(\omega) = \frac{\varkappa}{2} \coth\left(\varkappa d\right) \left(\frac{1}{\varkappa_0} + \frac{\varepsilon_m}{\varkappa_m}\right) \times \left[-1 \pm \left(1 - \frac{4\varepsilon_m \tanh^2(\varkappa d)}{\varkappa_0 \varkappa_m (1/\varkappa_0 + \varepsilon_m/\varkappa_m)^2}\right)^{1/2}\right], \quad (50)$$

where  $\varepsilon(\omega)$  and  $\varepsilon_m$  are the film and substrate dielectric functions,

$$\begin{split} &\varkappa = \sqrt{q^2 - k_0^2 \varepsilon(\omega)} , \quad \varkappa_0 = \sqrt{q^2 - k_0^2} , \\ &\varkappa_{\mathrm{m}} = \sqrt{q^2 - k_0^2 \varepsilon_{\mathrm{m}}} , \quad \operatorname{Re} \varkappa > 0 , \quad \operatorname{Re} \varkappa_{\mathrm{m}} > 0 \, . \end{split}$$

We note that Eqn (50) coincides with Eqn (4), and both of them coincide with Eqn (30) when the velocity of light in expressions (50) and (4) tends to infinity. Therefore, Eqn (50) describes the polaritons which correspond to Coulomb modes

with dispersion relation (30). The inclusion of retardation changes not only the polariton dispersion, but also the characteristics of the field associated with these modes in the film. The surface-polariton field in the film with the inclusion of retardation is written as

$$E_x \propto i \frac{\varkappa}{q} \left[ \frac{1}{\varepsilon(\omega)} \sinh(\varkappa z) - \frac{\varkappa_0}{\varkappa} \cosh(\varkappa z) \right], \tag{51}$$

$$E_z \propto \frac{1}{\varepsilon(\omega)} \cosh(\varkappa z) - \frac{\varkappa_0}{\varkappa} \sinh(\varkappa z); \qquad (52)$$

in this case, the corresponding solution of Eqn (50) should be substituted in lieu of  $\varepsilon(\omega)$  in expressions (51) and (52) for the fields.

In the IR spectral range, the magnitude of  $|\varepsilon_m|$  for a medium with a metallic conduction is high  $(|\varepsilon_m| \ge |\varkappa_m| \ge 1)$  and, for surface waves, the second term in the square brackets in Eqn (50) is small in comparison with unity. We therefore expand the square root in Eqn (50) to obtain the following equations for surface-polariton frequencies  $\omega_{S+}$  and  $\omega_{S-}$ :

$$\varepsilon(\omega_{S+}) \approx -\frac{\varkappa}{\varkappa_0} \tanh\left(\varkappa d\right) \left[ 1 - \frac{\varkappa_m}{\varepsilon_m \varkappa_0} \left( 1 + \frac{\tanh^2(\varkappa d)}{4} \right) \right], (53)$$

$$\varepsilon(\omega_{\mathrm{S}-}) \approx -\frac{\varepsilon_{\mathrm{m}}\varkappa}{\varkappa_{\mathrm{m}}} \coth(\varkappa d).$$
 (54)

In the derivation of Eqn (53), we have retained a small (to the first order) term which takes into account the finite substrate conductivity (the second term in square brackets). It follows from Eqn (53) that the dielectric function for a thin film  $\varepsilon(\omega_{S+}) \sim qd$  is small and the  $\omega_{S+}(q)$  frequency is close to the  $\omega_{LO}$  frequency for  $q > \omega/c$ . We neglect the second term in the parentheses in Eqn (53) and consider only the wavelengths of surface polaritons for which  $qd \ll 1$  to obtain a simplified dispersion equation for  $\omega_{S+}$ :

$$\varepsilon(\omega_{\rm S+}) \approx \frac{q^2 d}{\sqrt{q^2 - k_0^2 - k_0^2 d}} \,.$$
(55)

We substitute the value of  $\varepsilon(\omega_{S+})$  from Eqn (53) into Eqns (51) and (52) to find the field in the film that corresponds to mode (55):

$$E_x(z) \propto \mathrm{i} \, \frac{\varkappa_0}{q} \, \mathrm{sinh} \big[ \varkappa(z+d) \big],$$
 (56a)

$$E_z(z) \propto -\frac{\varkappa_0}{\varkappa} \cosh\left[\varkappa(z+d)\right].$$
 (56b)

Hence, it follows that the field of this mode is strongest at the vacuum-film interface and decays exponentially with depth in the film.

In a thin film  $(qd \leq 1)$ , the depth nonuniformity of the field is very weak, the electric component of the field is directed nearly perpendicular to the film, because  $|E_z| \gg |E_x|$ . The dissipative processes in the metal are taken into account by the imaginary part of  $\varepsilon_m$ , and therefore the term with  $\varkappa_m/\varepsilon_m$  in Eqn (53) allows determining the metal quenching of the surface polariton [39, 40]. The corresponding increase in the line half-width  $\gamma_m$  arising from the metal quenching is a quantity of the order of

$$|\omega_{\mathrm{S}+} - \omega_{\mathrm{LO}}| \operatorname{Im} \frac{\varkappa_{\mathrm{m}}}{\varepsilon_{\mathrm{m}}}$$

Since Im  $(\varkappa_m / \varepsilon_m) \ll 1$ , for a 'good' metal the  $\gamma_m$  value for the  $\omega_{S+}$  polariton is negligible.

Unlike Eqn (53), the solution of Eqn (54) gives the dispersion law of the surface polariton of a film–substrate interface  $\omega_{\rm S-}(q)$  that is strongly affected by substrate properties. For an ideally conducting metal substrate ( $\varepsilon_{\rm m} \rightarrow \infty$ ), it follows from Eqn (54) that  $\omega_{\rm S-}(q) = \omega_{\rm TO}$ . With impairment of 'metallic' properties of the substrate, the difference  $|\omega_{\rm S-}(q) - \omega_{\rm TO}|$  increases. The field distribution in the film associated with this mode is obtained when the dielectric function defined by Eqn (54) is substituted in relation (56). For  $|\varepsilon_{\rm m}| \ge 1$ , we have

$$E = \left(\cosh \varkappa z, \ 0, \ -i \frac{q}{\varkappa} \sinh \left(\varkappa z\right)\right). \tag{57}$$

As is evident from Eqn (57), for these atomic vibrations the field in the film attains a maximum value at the film-substrate interface, i.e., for z = -d.

The dispersion of the Coulomb film modes considered in Section 5.1.1 and the surface metal polariton without the inclusion of their interaction are shown in Fig. 10a. The inclusion of this interaction results in the splitting of the surface metal polariton. The resultant polariton dispersion curves of a vacuum-film-metal structure are shown in Fig. 10b. The polariton branches falling within the radiative domain of the  $\omega - q$  diagram, i.e., the states with  $q < k_0$ , are considered in Section 5.1.4. The dispersion of nonradiative surface polaritons for  $q > k_0$  can rather easily be reconstructed from experiments (see Fig. 4c for bulk single crystals and Fig. 13 for films).



**Figure 10.** Dispersion relations for the vibrational states of a ZnSe film on a metal [32, 33]: (a) dispersion of the Coulomb modes  $v_{S+}$  and  $v_{S-}$  and the surface metal plasmon polariton  $v_{pp}(q)$  neglecting their interaction; (b) interaction between the Coulomb film modes and the substrate polariton is included; and (c) dispersion curves in the neighborhood of the resonance gap  $\Delta_2$ .

The polariton dispersion curves for  $q \approx k_0$  are much harder to reconstruct, because the polariton of the structure is strongly perturbed by the ATR prism in this range of wave vector values [31, 79, 83]. This perturbation arises from the occurrence of radiative decay of 'nonradiative' polaritons of the film on a substrate due to the prism above the film and is determined by the prism – film gap thickness. Figure 11 shows the absorption spectra of the thermally induced emission of a silicon prism – gap – 1-µm ZnSe film – aluminum substrate structure calculated by formula (6) for different radiation angles for a gap thickness of 3, 40, and 60 µm. One can see how the surface polaritons that are 'nonradiative' at  $\varphi > \varphi_c = 17^\circ$ , transform into radiative surface polaritons at  $\varphi < \varphi_c$ .

The spectra in Fig. 11a correspond to weakly perturbed surface polaritons for  $\varphi > 30^\circ$ , and the absorption band for



Figure 11. Absorption spectra of thermally induced emission of a Si prism-gap-ZnSe film  $(1 \mu m)$ -aluminum substrate structure for different gap thicknesses *l* [33].

 $\varphi \approx 17^{\circ}$  parallel to the frequency axis corresponds to the light absorption by the surface metal plasmon. When this band intersects the Coulomb modes  $\omega_{S-}$  and  $\omega_{S+}$  (Fig. 10a), they are seen to experience resonance interaction with an increase in absorption intensity, and the occurrence of a weakly pronounced gap near  $\omega_{S+}$  is observed. The spectra in Fig. 11b correspond to weakly perturbed surface polaritons for  $\varphi > 20^{\circ}$ . The polariton branches that are formed in the vicinity of the gaps  $\Delta_1$  and  $\Delta_2$  correspond to Fig. 10b. The spectra in Fig. 11c may be regarded as weakly perturbed 'nonradiative' polaritons for  $q \approx k_0$ , i.e., for  $\varphi \ge 17^{\circ}$ .

For  $\varphi < 17^{\circ}$ , clearly seen in Figs 11b and 11c is a specific behavior of radiative polariton branches (see Sections 5.1.3 and 5.1.4) as well as the occurrence of the  $\Delta_1$  and  $\Delta_2$  gaps in the surface-polariton spectra. The frequency-angular dependence of absorption band peaks in Fig. 11c corresponds to the dispersion curves in Figs 10b and 10c in the vicinity of the resonance between the surface Coulomb modes of the film on a metal substrate and the surface plasmon polariton of the substrate. When the gap between the prism and the semiconductor film on the metal is greater than the wavelength, as is the case in Fig. 11c, in the radiative range ( $\phi < 17^{\circ}$ ) there emerge absorption bands due to the interference modes of the prism-film gap. The relatively weak absorption bands for  $\varphi \approx 15^{\circ}$  and  $\varphi \approx 16^{\circ}$  in the high-frequency region of the spectrum in Fig. 11c have the same nature as the absorption bands in Fig. 6.

5.1.3 Nonradiative polaritons. The experimental thermally induced emission spectra of a ZnSe film of different metal substrates were obtained in the same way as those of the surface polaritons of a bulk single crystal, i.e., employing a semicylindrical silicon ATR prism [33, 39, 83, 90]. Figures 12a and 12b show the experimental and calculated p-polarized radiation spectra of the surface polaritons of a 1-µm ZnSe film on an aluminum mirror for radiation angles  $\varphi = 18^{\circ}$  and  $\varphi = 30^{\circ}$ . Figure 12c gives the thermally induced emission spectra of a silicon prism-gap-ZnSe film-aluminum mirror structure for a radiation angle  $\varphi = 20^{\circ}$ , which is greater than the critical one ( $\varphi_c = 17^\circ$ ), for different film – prism gap thicknesses specified by the thickness of a Mylar film. The thickness of the ZnSe film and the aluminum mirror was about 1 µm, the aluminum mirror being much thicker than the skin layer in the frequency range of interest.

The emission spectra of the structure with a prism was numerically calculated by formula (6). The parameters appearing in formulas (7) and (8) were borrowed from the independent measurements of the emission spectra of a ZnSe film on an aluminum mirror (without a prism) [73]. The calculated emission spectra normalized to the blackbody radiation measured in similar conditions are in good qualitative agreement with the experimental data. Some nonfundamental difference in the calculation from the experiment arises from the following inherent experimental errors.

(i) The material of the semicylindrical silicon prism possessed a relatively high intrinsic nonselective emissive capacity: the radiation intensity of a prism-gap-mirror structure amounted to about 80% of the radiation intensity of a prism-gap-film-mirror structure.

(ii) The illumination optical scheme of a FIS-21 spectrometer employed in the experiments had not been intended for the investigations of this kind: owing to large aberrations in the scheme (coma, astigmatism), there was no way of ensuring the parallelism of the light beam in the ATR prism to better



**Figure 12.** *p*-Polarized radiation spectra of the 'nonradiative surface polaritons' of a ZnSe film (1µm) on an Al mirror: (a), (b) for radiation angles 18° and 30°, respectively (solid curves, experiment; dotted curves, calculation) [88]; (c) for  $\varphi = 20 \pm 2^{\circ}$  and different gap thicknesses *l* (dashed curve, film emission without the prism) [39, 90].

than  $\pm 2^{\circ}$ . The uncertainty in the determination of the radiation angle  $\varphi$  led to the uncertainty in the determination of the wave vector  $q = k_0 n_{\rm Si} \sin \varphi$  ( $n_{\rm Si}$  is the refractive index of the prism), which brought about the broadening of the emission band, especially so for radiation angles  $\varphi \approx \varphi_{\rm c} = 17^{\circ}$ , when  $q \approx k_0$ .

(iii) The gap thickness was not measured, but was assumed to be equal to the Mylar film thickness.

The best agreement between the calculation and the experiment (Figs 12a and 12b) was reached when the gap thickness *l* was used as the fitting parameter. The departure of the *l* value from that preset in the experiment amounted to as much as 50%. This is not surprising, for it is precisely the gap thickness that is not easily verifiable under the conditions of a thermostat in the vacuum. Furthermore, a small correction of the zero curve was made in the experimental spectra (to the background level of the calculated spectra). The dispersion curves reconstructed from the experimental data for surface polaritons of a ZnSe film sputtered onto a metal substrate as well as the data calculated numerically by formulas (53) and (54) are given in Fig. 13. One can see good agreement between the calculation and the experiment, particularly for the dispersion curves.

Only one band is observed in *s*-polarized radiation: in the vicinity of the  $\omega_{TO}$  single-crystal frequency [31, 92]. In the



**Figure 13.** Dispersion of surface TM polaritons of a ZnSe film (1  $\mu$ m) on a metal substrate for  $q > k_0$ : (1) and (2)  $v_{S+}$  and  $v_{S-}$  branches for a ZnSe film on aluminum, respectively; (3) and (4)  $v_{S+}$  and  $v_{S-}$  branches for a ZnSe film on chromium, respectively; (5)  $v_{S-}$  branch for a ZnSe film on a thin (less than 0.1  $\mu$ m) Al mirror [39]; solid curves, calculation; points, experiment [39, 90]. Branch 2 coincides with the  $v_{TO}$  frequency.

thermally induced *p*-polarized surface-polariton radiation of a 1-µm-thick ZnSe film on a chromium substrate, the highfrequency peak remains the same as in the emission spectra of the same ZnSe film on an aluminum substrate [33, 39, 88–90]. This peak corresponds to the surface polariton of a vacuum – film interface and its frequency, as follows from experiments and theory, depends only slightly on the substrate permittivity. Indeed, for a thin film ( $qd \ll 1$ ) at  $q > k_0$  and  $|\varepsilon_m| \ge 1$  it follows from Eqn (53) [39, 90] that

$$\omega_{\rm S+} = \omega_{\rm LO} \left( 1 - qd \, \frac{\varepsilon_0 - \varepsilon_\infty}{2\varepsilon_0 \varepsilon_\infty} \, \operatorname{Re} \frac{\varepsilon_{\rm m}(\omega)}{1 + \varepsilon_{\rm m}(\omega)} \right). \tag{58}$$

The low-frequency peak in the *p*-polarized radiation spectra of a ZnSe film on chromium for  $q > k_0$  corresponds to the surface polariton of a film – metal interface, i.e., to the interfacial polariton. Its dispersion depends strongly on the substrate conductivity. The frequency of this polariton for a thin ZnSe film on chromium for  $q > k_0$  splits off from  $\omega_{TO}$  to coincide with  $\omega_{TO}$  for a ZnSe film on aluminum (Fig. 13) [39, 88, 90].

As was noted above, the splitting  $|\omega_{S-} - \omega_{TO}|$  is determined by the substrate conductivity and the dependence on *d* and *q*. Employing  $\varepsilon(\omega)$  for ZnSe in the form of Eqn (7), we have for  $q > k_0$  and  $|\varepsilon_m| \ge 1$  from Eqn (54) [90]

$$\omega_{\rm S-} = \omega_{\rm TO} \left[ 1 + \frac{\varepsilon_0 - \varepsilon_\infty}{2} \operatorname{Re} \frac{\tan(qd)}{\varepsilon_{\rm m}} \right], \tag{59}$$

which is consistent with expression (41) obtained neglecting retardation for any q value. For a thin film on a metal substrate, the frequency shift of an interfacial polariton  $|\omega_{\rm S-} - \omega_{\rm TO}|$  and its damping, which is proportional to  ${\rm Im} \, \varepsilon_{\rm m}^{-1}(\omega)$ , thus prove to be linearly dependent on d and q.

A similar linear dependence of the frequency difference  $|\omega_{\text{LO}} - \omega_{\text{S}+}|$  on q and d follows from Eqn (58) and the experiment for the upper surface-polariton branch. The surface-polariton dispersions of the vacuum–ZnSe film–

chromium structure for  $q > k_0$  reconstructed from experiments [39, 88, 90] are shown in Fig. 13 along with dispersion curves calculated numerically by formula (50). Good accord between the calculated and the experimental data is evident.

The negative slope of both surface-polariton dispersion branches of the vacuum – film – chromium structure signifies the following: for a specific frequency  $\omega$  in the negative-slope domain of the dispersion branch there exist two surface waves with different  $q = 2\pi/\lambda$ , which correspond to different  $\lambda$ . In this case, for one surface wave with a given frequency  $\omega$  [for each of the branches  $\omega_{S+}(\omega)$  or  $\omega_{S-}(\omega)$ ], the wave vector  $q_1 \approx k_0 [1 + \text{Re}(1/2\varepsilon_m(\omega))]$  is slightly different from  $k_0$ , while for the other one with the same frequency the wave vector  $q_2 \gg k_0$ .

The surface waves with a wave vector  $q_1$  are conventional surface polaritons, and those with a wave vector  $q_2$  are additional surface polaritons, whose existence was predicted by Agranovich (see, for instance, reviews [9, 40]).

Additional surface polaritons arise from the resonance interaction of a dipole-active vibrational mode with a frequency  $\omega_0$  in a thin film with a surface plasmon polariton in a metal. This resonance is responsible for the splitting of the branch of a conventional metal surface polariton, i.e., for the occurrence of a gap at the  $\omega_0$  frequency in its spectrum, whose width is proportional to  $\sqrt{d/\lambda}$  [5, 9, 40, 62]. For a thin ZnSe film on a metal, the width of this gap for the upper surfacepolariton branch with  $\omega_0 = \omega_{S+} \approx \omega_{LO}$  is determined by the expression [32, 40]

$$\Delta_{1} = \omega_{\rm LO} \left( 2d \operatorname{Re} \frac{\omega_{\rm LO} \varepsilon_{\rm m}(\omega) (\varepsilon_{0} - \varepsilon_{\infty})}{c \varepsilon_{0} \varepsilon_{\infty} (1 + \varepsilon_{\rm m}(\omega))} \right)^{1/2}.$$
 (60)

One can see from expressions (58) and (60) that the gap width  $\Delta_1$  is hardly dependent on the permittivity of a metal substrate. For a 1-µm ZnSe film on aluminum, the gap width is  $\Delta_1 \approx 13 \text{ cm}^{-1}$ .

For the lower surface-polariton branch with  $\omega_0 = \omega_{S-} \approx \omega_{TO}$ , the gap width is [32, 40]

$$\Delta_2 = \omega_{\rm TO} \left( 2d \operatorname{Re} \frac{\omega_{\rm TO}(\varepsilon_0 - \varepsilon_\infty)}{c(1 + \varepsilon_{\rm m}(\omega))} \right)^{1/2}.$$
 (61)

The gap width  $\Delta_2$  is seen to depend on  $\varepsilon_{\rm m}(\omega)$ ; it is  $\Delta_2 \approx 2 \text{ cm}^{-1}$  for a 1-µm ZnSe film on aluminum and  $\Delta_2 \approx 10 \text{ cm}^{-1}$  for that on chromium. The  $\Delta_1$  and  $\Delta_2$  values calculated by formulas (60) and (61) agree well with the experiments.

Note that the gaps in the polariton spectra of the structure under consideration are produced only for *p*-polarized (TM) surface polaritons. For *s*-polarized (TE) surface polaritons of the structure, similar gaps are missing from their spectra [92].

Consider a vacuum – ZnSe film – metal film on a dielectric substrate structure wherein the metal film is much thinner than the skin layer. As follows from the emission spectra of this structure in the inverted ATR mode, the interfacial polariton  $\omega_{S-}$  splits off from  $\omega_{TO}$  toward the high-frequency domain [39, 88, 90]. This signifies that the effective permittivity of a thin metal film is positive (rather than negative, as is usually the case) in the spectral range under investigation and is no longer described by the Drude formula.

With the use of formula (59), from the magnitude and sign of the departure of the interfacial polariton  $\omega_{S-}$  from  $\omega_{TO}$ (derived from experimental data) it is possible to estimate the magnitude and sign of Re  $\varepsilon_m(\omega)$  of a thin aluminum film located between the plate of fused quartz and the ZnSe film. In our case, the quantity Re  $\varepsilon_{\rm m}(\omega)$  proved to be positive and almost 200 times as small as that for a freshly evaporated aluminum film [39]. This change in the permittivity of a thin aluminum film (approximately 50-nm thick) comes as a surprise, since the high positive permittivity of metal films results when the films exhibit a granular structure with a very weak percolation conduction [92].

Such properties are normally observable in films several nanometers thick prepared by thermal evaporation from a melt. For a radio-frequency magnetron sputtering of metals employed in our case, uniform continuous films with a metallic conduction, whose thickness is on the order of a nanometer, are usually formed [93]. When the structure is annealed, there supposedly occurs a continuous-to-island film transformation of the thin aluminum film.

Experiments and theory suggest that the  $|\omega_{TO} - \omega_{S-}|$  splitting increases with a decrease in the  $|\text{Re} \epsilon_m(\omega)|$ , i.e., with impairment of metallic substrate properties. If a degenerate semiconductor with  $\omega_p$  greater than  $\omega_{TO}$  of the film is used as a substrate, the  $|\omega_{TO} - \omega_{S-}|$  splitting should be much greater than in the above cases of a film on a metal. In experiments with a vacuum–ZnSe film–degenerate InSb structure performed in Ref. [42], three ordinary coupled plasmon-phonon polaritons were observed: the first one in the domain  $\omega_I > \omega_{LO}$ , the second in the domain  $\omega_{TO} > \omega_{II} > \omega_{LO}$ , and the third in the domain  $\omega_{III} < \omega_{TO}$ . In this case, no additional surface polaritons were observed.

The picture is somewhat more complicated for a film on a dielectric substrate with  $\varepsilon_m > 1$ , since part of the dispersion branches of surface and interfacial film polaritons fall within the existence domain of bulk (waveguide) substrate polaritons. The interaction of these two families of excitations of adjacent media has the effect that four branches (in lieu of two) of mixed surface polaritons are formed in the frequency range  $\omega_{TO} < \omega < \omega_{LO}$  (see, for instance, Refs [47, 94]).

Therefore, experimental data confirm theoretical calculations and are indicative of a strong influence of substrate conductivity on the characteristics of p-polarized surface polaritons in multilayer structures. As follows from Ref. [92], s-polarized polaritons emerge where  $|\operatorname{Re}\varepsilon_{m}(\omega)|$  is not too large. Furthermore, the experimental data given in Fig. 13 suggest that the transverse Coulomb modes considered in Section 5.1.1 do not show up for  $q > k_0$  in experiments. In the vicinity of  $\omega_{TO}$ , there is only an emission peak belonging to the interfacial  $\omega_{S-}$  polariton, and no clearly defined peaks are observable at the frequency of transverse Coulomb  $\omega_{TO}$  modes. This conclusion may be drawn by recognizing the fact that the interfacial polariton frequency  $\omega_{S-}$  depends on the substrate permittivity and that the frequencies of transverse Coulomb modes (as bulk film states) are independent of it. Their absence from the spectra is supposedly due to a strong metal quenching of radiation [40].

**5.1.4 Radiative polaritons.** In Section 5.1.1, we found normal Coulomb modes of a vacuum–film–metal structure, i.e., states obtained neglecting the interaction with a transverse electromagnetic field. The Hamiltonian of this interaction is written as [59]

$$H_{\rm int} = -\int \widehat{P}\widehat{E}^{\perp} \,\mathrm{d}V, \qquad (62)$$

where **P** is the polarization corresponding to the Coulomb modes of the structure and  $\mathbf{E}^{\perp}$  is the transverse electromagnetic field of free photons.

Interaction (62) results, generally speaking, in a radical change in film eigenmodes due to their mixing with the transverse field (the polariton effect). In the problem of the absorption of an incident transverse electromagnetic wave, the inclusion of multiple reabsorption processes, described by Hamiltonian (62), is also of significance. It leads, in particular, to a renormalization of the incident-wave field inside the film in accordance with Fresnel formulas. However, as the film thickness decreases, the role of higher-order processes in interaction (62) diminishes. In a film with an optical thickness small in comparison with the wavelength of the transverse field, it is possible to restrict oneself to the inclusion of interaction (62) in the lowest order.

We investigate light absorption by a thin film in a vacuum-film-metal structure, namely, determine the relative contribution of each Coulomb mode found in Section 5.1.1 to the light absorption and derive the dependence of absorption by each Coulomb mode on the film thickness and the angle of light incidence.

Naturally, the absorption and emission of light by a film on a substrate can be determined in a simpler way: employing Kirchhoff's law and the Fresnel equations (without a prior derivation of Coulomb modes). However, having obtained in this fashion the formulas that describe the absorption of light by the structure, we would fail to elucidate in detail what the absorbed energy goes to and which specific vibrational states of the structure are responsible for one or other peak in the spectrum [33, 59].

The interaction of Coulomb modes of a thin film on a metal with the electromagnetic field of free photons is described by Hamiltonian (62). In the absorption of a photon with the excitation of a Coulomb mode, the energy and the wave vector parallel to the plane of the film should be conserved:

$$\omega(q) = \omega \,, \tag{63}$$

$$q = \frac{\omega(q)}{c} \sin \varphi \,. \tag{64}$$

Here,  $\omega$  and  $\omega(q)$  are the frequencies of the incident light and of the Coulomb mode, respectively, and  $\varphi$  is the angle of light incidence. Relations (63) and (64) lead to the inequality

$$q < \frac{\omega(q)}{c} \,, \tag{65}$$

which limits the set of modes capable of absorbing or emitting light in one-photon processes. Therefore, the modes with  $q > \omega(q)/c$  do not participate in the linear absorption or emission of light.

When conditions (63) and (64) are fulfilled, the probability of absorbing a photon (the integrated absorption of the corresponding band in the spectrum), according to the 'golden' Fermi rule, is, accurate to a normalizing factor independent of the film thickness *d* and the angle of incidence  $\varphi$ , quadratic in the matrix element of the interaction Hamiltonian:

$$A \propto \frac{\left|\int P_q^*(z) E_q^{\perp}(z) dz\right|^2}{\int \left|P_q(z)\right|^2 dz}.$$
(66)

The  $P_q(z)$  functions in expression (66) correspond to the Coulomb modes under investigation, which were derived in Section 5.1.1. The functions  $E_q^{\perp}(z)$  describe the transverse electromagnetic field with neglect of the interaction with the film but with the inclusion of the reflection from the metal

$$E_q^{\perp} \propto (0, \sin\left[k_z(z+d)\right], \ 0) \tag{67}$$

for the *s* polarization and

$$E_q^{\perp} \propto \left( i \cos \varphi \sin \left[ k_z(z+d) \right], \, 0, \, \sin \varphi \cos \left[ k_z(z+d) \right] \right), \tag{68}$$

for the *p* polarization, where

 $k_z = \frac{\omega}{c} \cos \varphi \,.$ 

We investigate the absorption of light by different Coulomb modes in the same order in which they were considered in Section 5.1.1.

*s-Polarized vibrations, transverse modes* ( $\omega = \omega_{TO}$ ). Clearly, these modes interact only with *s*-polarized light. Substituting expression (67) for the amplitude of the incident wave and formulas (23) and (24) for the polarization of sinusoidal and cosine modes into expression (66), for  $k_0 d \ll 1$  we obtain

$$A \propto (k_0 d)^3 n^{-2} \cos^2 \varphi$$
,  $n = 1, 2, ...$  (69)

for sinusoidal modes and

$$A \propto \begin{cases} (k_0 d)^3 \cos^2 \varphi, & n = 0, \\ (k_0 d)^7 n^{-4} \cos^6 \varphi, & n = 2, 4, \dots, \\ (k_0 d)^3 n^{-4} \cos^2 \varphi, & n = 1, 3, \dots \end{cases}$$
(70)

for cosine modes.

The light absorption by all *s*-polarized transverse modes results in the appearance of a peak in the thin-film absorption spectrum at a frequency  $\omega_{\text{TO}}$ . One can see from expressions (69) and (70) that the main contribution to the absorption peak at small  $k_0d$  is made by the sinusoidal and cosine modes with n = 0 and n = 1, 3, ... We sum up the contributions of these modes to find the integrated absorption for *s*-polarized light at the  $\omega_{\text{TO}}$  frequency:

$$A \propto (k_0 d)^3 \cos^2 \varphi \,. \tag{71}$$

*p-Polarized vibrations, surface modes.* The interaction of a *p*-polarized electromagnetic field with the first surface mode results in the appearance of an absorption peak near the  $\omega_{LO}$  frequency [according to formula (36), for  $qd \ll 1$ ]. We employ formulas (32), (33), (66), and (68) to obtain the integrated absorption

$$A\left(\omega_{\rm S+}\approx\omega_{\rm LO}\right)\propto k_0d\sin^2\varphi\,.\tag{72}$$

The interaction with the second surface mode is responsible for an absorption peak near the  $\omega_{TO}$  frequency. Using formulas (39) and (40), we find the integrated absorption

$$A\left(\omega_{\rm S-}\approx\omega_{\rm TO}\right)\propto \left(k_0d\right)^3.\tag{73}$$

*p-Polarized vibrations, longitudinal modes* ( $\omega = \omega_{LO}$ ). We employ formulas (43), (44), and (68) and perform integration

in expression (66) to obtain that the matrix element is

$$\left|\int P^* E^\perp \,\mathrm{d} z\right|^2 = 0\,.$$

Accordingly, we have

$$A\left(\omega_{\rm LO}\right) \equiv 0\,.\tag{74}$$

Therefore, the modes with the  $\omega_{LO}$  frequency investigated in Section 5.1.1 do not interact with the free electromagnetic field in one-photon processes at all (like the longitudinal modes of a bulk crystal). This justifies the name 'longitudinal modes' given to them.

*p-Polarized vibrations, transverse modes* ( $\omega = \omega_{TO}$ ). We employ Eqns (48) and (49) to find the absorption by each mode with the  $\omega_{TO}$  frequency:

$$A(\omega_{\rm TO}) \propto \begin{cases} (k_0 d)^3 n^{-4}, & n = 1, 3, \dots \\ (k_0 d)^7 n^{-4} \cos^4 \varphi, & n = 2, 4, \dots \end{cases}$$
(75)

The total contribution of all transverse modes to absorption will be

$$A\left(\omega_{\rm TO}\right) \propto \left(k_0 d\right)^3. \tag{76}$$

Making an interim summary of the investigations outlined in this Section, we note that the interaction of light with the Coulomb modes of a vacuum – thin film – metal structure results in the appearance of absorption peaks at the frequencies of these modes.

In *s*-polarized light, there occurs only one peak at a frequency  $\omega_{\text{TO}}$  related to the absorption of light by the TE film modes. For an 'ideal' metal, the vibrational modes of the film are accompanied by neither bulk nor surface charges, the light absorption being proportional to  $(k_0d)^3$ . For  $d \to \infty$ , they pass into conventional transverse optical phonons.

Broadly speaking, in *p*-polarized light there are three absorption peaks. One of them is located near the  $\omega_{LO}$ frequency of the film and arises from the light absorption by the radiative surface vibration of atoms near the film– vacuum interface, which is accompanied by surface charges (bulk charges are equal to zero). The light absorption at the frequency of this vibration is independent of the metal substrate conductivity and is proportional to  $k_0 d \sin^2 \varphi$ . For a thin film at large  $\varphi$ , this is the strongest absorption peak.

We emphasize that the absorption peak near the  $\omega_{LO}$  frequency, which was first observed by Berreman [24], was erroneously interpreted as the peak of absorption by longitudinal optical phonons in many subsequent papers (including our early papers) [16, 17, 61–67]. As suggested by the above analysis, the longitudinal optical phonons (modes) do not interact with the transverse electromagnetic field at all.

Two other peaks of light absorption by *p*-polarized modes reside near the  $\omega_{TO}$  frequency and exhibit almost similar dependences of intensity on the film thickness and the wave vector: the light absorption is proportional to  $(k_0d)^3$ . One of them is related to transverse vibrational modes of the film, which are not accompanied by the appearance of either bulk or surface charges. The frequency of atomic vibrations in the transverse modes is independent of the substrate material. For  $d \to \infty$ , these modes are the well-known transverse optical phonons of the crystal. The other peak arises from the radiative surface (interfacial) polaritons of the film – substrate interface, which are accompanied by the appearance of surface charges. The frequency of atomic vibrations in them depends on the conductivity of the metal substrate and is proportional to a small quantity  $k_0 d/\epsilon_m$ .

The theoretical relationships considered above are in good agreement with the experimental data [31-34, 59, 83-90]. In order to verify the theoretical relationships given in Table 1, series of measurements of film emission spectra similar to those shown in Fig. 3 were used to obtain the dependences of radiation intensity at the frequencies  $\omega_1 \approx \omega_{TO}$  and  $\omega_2 \approx \omega_{LO}$  on the film thickness and radiation angle. The experimental and theoretical intensities of the emission peak (for the *p* polarization) for ZnSe films on aluminum as functions of the film thickness for fixed radiation angles are given in Figs 14a and 14b and as functions of the radiation angle for fixed film thicknesses in Figs 14c and 14d [39, 88, 90]. One can see that the calculations are in good accord with the experiment.

Table 1. Optical vibrational modes of a thin film on a metal substrate

Polarization	Frequency	Absorption	Charge	$d \to \infty$
s (TE) p (TM) p (TM) p (TM) p (TM)	$\omega \equiv \omega_{\text{TO}}$ $\omega \equiv \omega_{\text{TO}}$ $\omega \equiv \omega_{\text{LO}}$ $\omega \approx \omega_{\text{TO}}$ $\omega \approx \omega_{\text{LO}}$	$(k_0d)^3 \cos^2 \varphi$ $(k_0d)^3$ $0$ $(k_0d)^3$ $k_0d \sin^2 \varphi$	$\begin{array}{c} 0 \\ 0 \\ \rho_{\rm S}, \rho_{\rm V} \\ \rho_{\rm S} \\ \rho_{\rm S} \end{array}$	TO TO LO S_ S_+



**Figure 14.** Emission intensity of ZnSe films on aluminum (a, b) against the film thickness for different radiation angles and (c, d) against the radiation angle for different film thicknesses: points, experiment; solid curves, calculation;  $v_2 \approx v_{LO} = 250 \text{ cm}^{-1}$ ,  $v_1 \approx v_{TO} = 200 \text{ cm}^{-1}$  [59, 88].

The above data suggest that the emission peak at a frequency  $\omega_2 \approx \omega_{\rm LO}$  belongs to the radiative surface polariton localized at the film-vacuum interface. The series of experiments presented above do not permit one to determine which vibrational mode refers to the emission peak at the frequency  $\omega_1 \approx \omega_{\rm TO}$  (the bulk one or the surface one at the film-metal interface).



**Figure 15.** *p*-Polarized radiation spectra of 0.6-µm ZnSe films on aluminum, chromium, and titanium: points, experiment; solid curves, calculation [43].

Theoretical calculations suggest that an unambiguous reference of the emission peak at the frequency  $\omega_1$  to the transverse vibrational states of the film volume or the interfacial surface polariton is possible only judging from the difference in the action on them of the electronic subsystem of the metal substrate. The thermally induced emission spectra of the vacuum–ZnSe film–metal structure with thick layers of aluminum, chromium, and titanium, which differ in the magnitude of Im  $\varepsilon_m(\omega)$ , are shown in Fig. 15. The ZnSe films were simultaneously deposited on all these metal substrates by thermal evaporation in a vacuum.

As a rule, films produced under thermal evaporation are partially amorphous with a high density of stacking faults in a strongly stressed crystal lattice (in microcrystal grains clusters). To improve the crystal-structure quality of the films, the samples were subjected to a long-term recrystallization annealing [95] in an argon atmosphere in a common quartz ampule in a single technological cycle. This gives promise that the thickness and crystal structure of the ZnSe films and, hence, the bulk vibrational properties of the samples produced are virtually the same.

One can see from Fig. 15 that the high-frequency *p*-polarized radiation band  $\omega_2$  virtually remains invariable. This is experimental evidence that the crystal structures of all three ZnSe films are of the same quality. The last statement is also borne out by the form of the RS spectra of these samples, in which the longitudinal optical phonons of the film volume manifest themselves. The coincidence of the RS bands (arising from longitudinal and transverse optical phonons) of the samples signifies that the bulk properties of the ZnSe films are similar<sup>8</sup> and are independent of the substrate conductivity [59, 110].

The low-frequency band of *p*-polarized radiation  $\omega_1$  broadens and shifts to the low-frequency spectral region as the conductivity of the metal substrate decreases. Taken

<sup>&</sup>lt;sup>8</sup> It is noteworthy that electron diffraction and X-ray diffraction analyses of the crystal structure are most sensitive to short-range disturbances of atomic arrangement, while vibrational and excitonic spectroscopy techniques are sensitive to long-range disturbances as well. That is why the degree of crystallinity (amorphism) of a sample, i.e., the long-range order quality, is most conveniently studied by optical techniques where possible [82, 95].

together, this implies that the  $\omega_1$  band in *p*-polarized thermally induced radiation of the vacuum–ZnSe film– metal structure is related to the radiative surface (interfacial) polariton of the film–metal interface rather than with the transverse vibrational states of the film volume.

Figure 15 also shows the calculated emission spectra of the sandwiches. Since the plasmon frequencies and the electron-collision frequencies were not known for chromium and titanium, the calculations made use of the Hagen–Rubens relation [96], which relates the conductivity of a metal substrate to its reflectivity:

$$R_{\rm m}(\omega) \approx 1 - \left(\frac{2\omega}{\pi\sigma}\right)^{1/2}.$$
 (77)

Here,  $\sigma = \sigma(\omega)$  is the substrate conductivity, which can be determined from the reflection spectra  $R_{\rm m}(\omega)$  of the pure metal surface prior to the deposition of the ZnSe film.

The Hagen – Rubens relation (77) provides a rather good description of the reflection by metals in the frequency range  $\omega \ll \omega_p$  [96]. The aluminum plasmon parameters and, hence, its permittivity are well known. That is why the emission spectrum of a ZnSe film on an aluminum mirror was used to verify the correctness of employing the expression Im  $\varepsilon_m(\omega) = 4\pi\sigma/\omega$  with the value of the substrate conductivity  $\sigma$  obtained from the experimental value of  $R_m(\omega)$  and Eqn (77) when calculating emission spectra.

The ZnSe permittivity parameters ( $\omega_{\rm TO}$ ,  $\gamma$ ,  $\varepsilon_0$ ,  $\varepsilon_{\infty}$ ) were determined from the emission spectrum of a ZnSe film on aluminum. These parameters were used to calculate the emission spectra of the ZnSe film on chromium and titanium. For them, the substrate conductivity was the only fitting parameter. The best agreement between the experimental and calculated spectra was attained for the values  $\sigma_{\rm Al} = 8000 \ \Omega^{-1} \ {\rm cm^{-1}}$  $(R_{\rm Al} = 0.94), \sigma_{\rm Cr} = 500 \ \Omega^{-1} \ {\rm cm^{-1}} (R_{\rm Cr} = 0.76)$ , and  $\sigma_{\rm Ti} =$  $250 \ \Omega^{-1} \ {\rm cm^{-1}} (R_{\rm Ti} = 0.67)$ .

Referring to Fig. 15, the experimental data agree well with the theoretical calculations. A minor (and nonfundamental) discordance between them in the  $v > 260 \text{ cm}^{-1}$  frequency range for ZnSe films on chromium and titanium is supposedly due to the fact that the conductivity of the substrates involved is not quite adequately described by the Hagen–Rubens formula at high frequencies. In this spectral range, the frequency dependence of the chromium and titanium conductivities corresponds to a 'bad' metal. The values of substrate conductivities in sandwiches derived in this way are only 10-25% below the values obtained from independent reflection measurements of the pure metal surfaces (prior to ZnSe film deposition on them and the subsequent longduration annealing).

The investigations conducted show that it is the radiative surface states (the film-vacuum and film-substrate interfacial polaritons) rather than the bulk vibrational states of the film that are responsible for the absorption of light by thin films of wide-gap semiconductors. The dipole moments of transverse optical phonons supposedly experience a strong metal quenching, because for thin films the total dipole moment of a transverse phonon parallel to the plane of the film together with its image in the metal is close to zero [40]. The image forces of the dipole moments in the metal, which are responsible for transverse bulk vibrational states of the film, can be reduced by separating the film from the metal or, more precisely, by producing a dielectric interlayer between the metal and the ZnSe film.



**Figure 16.** *p*-Polarized radiation spectrum of the vacuum–ZnSe film  $(0.6 \ \mu\text{m})$ –Si interlayer–Al substrate structure for different silicon interlayer thicknesses: points, experiments; solid curves, calculation. The experimental points are shifted downward by 0.06 for the spectra for d = 0 and  $d = 1 \ \mu\text{m}$  and by 0.13 for the spectrum for  $d = 3 \ m$  (reduction to allow for the background radiation) [44].

Figure 16 gives the thermally induced emission spectra of a vacuum – ZnSe film – Si interlayer – Al substrate structure [44]. Silicon has no dipole-active vibrational states in the IR spectral domain, and therefore its emission is very weak and nonselective. The spectra calculated by formula (6) (if it is assumed that  $\varepsilon_1$  is the permittivity of the vacuum,  $\varepsilon_2$  is the permittivity of the ZnSe film of thickness l,  $\varepsilon_3$  the permittivity of the silicon interlayer of thickness d, and  $\varepsilon_4$  the permittivity of the aluminum substrate) agree very well with the experimental ones. One can see that the radiation intensity and the half-width of the low-frequency band rise steeply with interlayer thickness; also evident is a small shift of this band toward the low-frequency spectral region. In this case, the intensity, half-width, and peak frequency of the highfrequency band remain invariable.

It follows from Fig. 16 and the theoretical analysis that the metal quenching of absorption is characteristic of only the states with dipole moments parallel to the plane of the substrate [they are described by formulas (70) and (75)]. The states with dipole moments perpendicular to the substrate do not, according to formula (72), interact with conduction electrons of the metal substrate. It is likely that at a frequency  $\omega_1 \approx \omega_{TO}$  for a small silicon interlayer thickness, we are dealing both with the interfacial polariton and with strongly weakened transverse bulk vibrational states of the ZnSe film, while for a large silicon interlayer thickness, practically only with transverse bulk vibrational states.

Strictly speaking, the above states are not transverse bulk optical phonons of the film, as was earlier recognized, since the half-width  $\Gamma$  of the bands of absorption by these states significantly depends on the interlayer thickness and the film thickness. For a thick interlayer, the half-width of absorption bands  $\Gamma$  is several times the half-width of the imaginary part of permittivity  $\gamma$  of a bulk ZnSe single crystal. This discordance is due to the radiative decay channel of the states, whose probability  $\gamma_r$  in thin films is additive with the anharmonic decay probability  $\gamma$ , i.e.,  $\Gamma \approx \gamma + \gamma_r$  [16, 25].

Similar results were earlier obtained in the investigation of reflection – absorption and thermal radiation spectra of LiF

films [24, 57, 58] and reflection – absorption spectra of CdS films [25, 65, 69] evaporated on metal and dielectric substrates. They also exhibited a large increase in intensity of absorption bands at the  $\omega_1$  frequency and in their half-width when the metal substrates were replaced with dielectric ones.

Therefore, the investigations conducted suggest that only the surface polaritons of the film–vacuum and the film– substrate interfaces absorb and emit light in thin ( $\beta_2 d \leq 1$ ) wide-gap semiconductor films on metal substrates. Bulk vibrational states of the film (longitudinal and transverse optical phonons) do not absorb or emit *p*-polarized light, but they are well observable in RS spectra [6, 7, 36, 59]. The transverse optical phonons of the film can manifest themselves in absorption and thermal radiation spectra when a dielectric interlayer separates the film from the metal substrate [33, 44, 85].

#### 5.2 Thick films

The results of investigations of radiative vibrational polaritons of a thin (about 1  $\mu$ m) dielectric (semiconductor) film on a metal substrate were outlined in Section 5.1. Let us trace the evolution of vibrational absorption spectra of films on a metal with increasing film thickness from several microns to several millimeters, when the film can be safely taken as a bulk single crystal.

In films whose optical thickness exceeds the wavelength of elementary excitations, there exist, according to the theoretical data of Refs [12–17], a set of additional (in comparison with a thin film) normal states whose frequencies and halfwidths depend on the crystal-layer thickness. These states are the interference modes of a plane-parallel slab (the Fabry – Perot modes). The equations that describe these states [15, 16] pass into the usual equations for interference modes in those frequency regions where the imaginary part of the permittivity of the layer material vanishes.

Interference film modes were repeatedly used for the measurements of *n* and *k* in weakly absorbing media [27, 91, 97]. Nevertheless, there is good reason to consider once again the formation conditions for the interference modes in a relatively thin film. The first and the only 'interference mode' (for  $2nd \approx \lambda$ ) emerges in the spectral region where the index of refraction  $n(\lambda)$  is maximum, i.e., in the region where the normal dispersion of the refractive index passes into anomalous dispersion. This spectral region is adjacent to the transverse optical phonon frequency of the crystal  $\omega_{\text{TO}}$  on the low-frequency side [68], where the crystal possesses large Re  $\varepsilon(\omega)$  and Im  $\varepsilon(\omega)$ . For a film on an ideal metal ( $\varepsilon_{\text{m}} \to \infty$ ), Eqn (4), which describes the dispersion of TM polaritons, passes into the equation

$$\beta_1 \cot\left(\beta_2 d\right) = \mathbf{i}\beta_2 \,\varepsilon(\omega) \,. \tag{78}$$

For  $\beta_2 d \ll 1$ , Eqn (78) earlier gave us the dispersion of *p*-polarized surface polaritons  $\omega_1(q)$  and  $\omega_2(q)$  of the film–substrate and film–vacuum interfaces. For  $\beta_2 d \approx N\pi/2$  (N = 1, 3, ...), this equation gives the frequencies of additional (in comparison with a thin film) states of the film, which are the interference modes of a Fabry–Perot mirror interferometer for real  $\varepsilon(\omega)$  values [91]. So, in going over from  $\beta_2 d \ll 1$  (i.e., N = 0) to  $\beta_2 d \approx \pi/2$  (N = 1), the radiative interfacial polariton passes smoothly into the first interference mode. Further increase in film thickness should bring about the following modes: N = 3, 5, ...

Figures 2 and 3 show the *p*-polarized reflection – absorption and thermally induced emission spectra of vacuum –

ZnSe film-metal structures with ZnSe films of different thicknesses: from 1 µm to 5 mm. Also shown in these figures are the calculated reflection-absorption and thermally induced emission spectra of these structures with ZnSe films of different thicknesses. The reflection-absorption spectra were recorded in *p*-polarized light for an angle of reflection  $\varphi = 16^{\circ} \pm 12^{\circ}$ , the calculated spectra were averaged over the same range of angles  $\varphi$ . The *p*-polarized radiation spectra were recorded for a radiation angle  $\varphi = 30^{\circ} \pm 10^{\circ}$ , the calculated spectra were approach and the spectra were averaged over the same range of angles  $\varphi$ . The *p*-polarized radiation spectra were recorded for a radiation angle  $\varphi = 30^{\circ} \pm 10^{\circ}$ , the calculated spectra were also averaged over this aperture angle.

A small discordance between the calculated and the experimental reflection-absorption and emission spectra of the films is related to the uncertainty of measurements of their thickness. The discordance between the experimental and calculated emission spectra of a 5-mm ZnSe single crystal (Fig. 3) far exceeds the experimental error and is of fundamental significance. The point is that the emission spectrum of the crystal is calculated via its reflectance spectrum with neglect of radiation trapping (reabsorption).

It is well known [77] that the reflectance spectrum is formed at a small depth from the crystal surface  $(L < \lambda)$ . The domain of radiation trapping in the crystal depends on its absorption coefficient  $\alpha(\omega) = 2\pi k/\lambda$ . According to the Bouguer-Lambert-Beer law, an electromagnetic wave emitted by an element of crystal volume at a depth *L* from its surface escapes from the crystal being attenuated by a factor of exp  $(-\alpha L)$ . Therefore, only the near-surface crystal layer shines in the range of high  $\alpha$  values, while the entire crystal volume can shine in the range of small  $\alpha$  values. That is why thick crystal layers radiate as a blackbody in those spectral domains where they are opaque. By virtue of this fact, Kirchhoff's law  $E(\omega) = A(\omega) = 1 - R(\omega)$  should be applied to such crystals with caution.

Referring to Figs 2 and 3, as the ZnSe film thickness increases, additional bands appear in absorption and thermally induced emission spectra in the frequency ranges  $\omega < \omega_{TO}$  and  $\omega > \omega_{LO}$ , i.e., where single-particle states are nonexistent in the film. In thick films (thin crystal slabs) there occurs smoothing (averaging) of reflection – absorption spectra at the frequencies of interference modes by the instrument function, because the spectral distance between the interference modes of the thick film is smaller than the width of the instrument function of the crystal layer as a Fabry–Perot interferometer, i.e., smaller than its resolving power.

As the ZnSe film thickness increases from 1 to 2 µm, the  $\omega_1$  absorption (emission) band shifts smoothly to the low-frequency spectral range (from 200 to 190 cm<sup>-1</sup>) with a simultaneous rise in its intensity in proportion to  $d^3$ . For  $\beta_2 d \approx \pi/2$  and  $\epsilon_m \to \infty$ , Eqn (78) gives the dependence of the frequency of the first interference polariton  $\omega_{N=1}$  on the film thickness d [33] as follows:

$$\omega_{N=1} \approx \omega_{\rm TO} \left[ 1 - \frac{\pi d\gamma}{4} \left( \varepsilon_0 - \varepsilon_\infty \right) \cos \varphi \right]. \tag{79}$$

From Eqn (79) it follows that the difference between the frequency of the interference mode with N = 1 and the transverse optical phonon is proportional to d and  $\gamma$ . As the ZnSe film thickness increases further up to 3 µm, on the high-frequency wing of the absorption band (190 cm<sup>-1</sup>) there appears a new, initially very weak, absorption band at a frequency of 200 cm<sup>-1</sup>. With an increase in the film thickness, this band also shifts to the low-frequency spectral region with

a simultaneous rise in intensity. With an increase in the film thickness, the former absorption band continues to shift to progressively lower frequencies, broadens, and lowers in peak intensity.

Therefore, increasing the film thickness brings about more and more new absorption bands at the  $\omega_{TO}$  frequency, which pass into interference modes with  $N = 3, 5, \ldots$  Each new absorption (emission) band emerging at the  $\omega_{TO}$ frequency rises steeply in intensity, attains its maximum, and then falls off slowly with a strong broadening [32–34]. The film thickness at which the *N*th band attains its maximum coincides with the instant of appearance of the (N + 1)th band. When the film thickness exceeds 2 µm, it is no longer possible to unambiguously ascribe the absorption bands to surface or bulk polaritons. These bands are radiative states of the film which pertain to the corresponding polariton branches of the sandwich.

The number *N* of radiative polariton branches in the film and their dispersion, which is described by Eqns (4) and (5), depends both on the thickness of the film and on its permittivity  $\varepsilon(\omega)$ . One can see from the above results that the number of interference polariton branches in the film increases with its thickness. For  $\beta_2 d \rightarrow \infty$ , the number of these branches also tends to infinity, <sup>9</sup> to completely fill the bands in which they can exist. Therefore, in a semiinfinite crystal the radiative domain of the  $\omega - q$  diagram is not void, as in Fig. 1b, but is completely filled with polariton states in the plane-wave approximation [33].

We emphasize that the interference modes can actually participate in different processes involving the absorption and emission of light when the light can really (at least twice) travel through the film without total absorption in it. For a semiinfinite crystal, a backward (returning back to the crystal surface) wave cannot emerge even for an infinitely small value of Im  $\varepsilon(\omega)$ ; moreover, the length of the incident-wave train should be infinite to interfere with the backward wave. Several infinities devoid of physical significance are superimposed in this case. In this sense, the concepts of empty and completely filled radiative bands are identical for a semiinfinite crystal.

One can see from the *p*-polarized reflection – absorption spectra of single-crystal ZnTe films shown in Fig. 17a that the frequencies of absorption bands and their intensities in reflectance spectra depend on the film thickness (like the ZnSe film spectra in Figs 2 and 3). Similar dependences of reflection – absorption spectra on the thickness of a thin film were observed in the thin films of CdS, ZnS, and CdTe on metal substrates [64–66].

Good accord between the theoretically calculated absorption spectra of films on a metal substrate and the experimental data (Figs 2, 3, and 17a) permits one to numerically analyze the behavior of absorption spectra in relation to the film thickness and permittivity [32, 33]. The theoretical film-thickness dependences of the absorption spectra of a ZnSe film on aluminum in Fig. 17b show how the absorption band at a frequency  $v_1 \le v_{TO}$  smoothly transforms into the first interference mode and new bands (with N = 2, 3, ...) appear at the  $v_{TO}$  frequency with increasing film thickness. One can also see that the light absorption by the films does not obey the Bouguer-Lambert-Beer law, according to which it increases exponentially with film thickness.



**Figure 17.** (a) *p*-Polarized reflection – absorption spectra of ZnTe films on aluminum for  $\varphi = 20^{\circ}$  and different film thicknesses: points, experiment; solid curves, calculation [38]. (b) *p*-Polarized absorption of ZnTe films on aluminum against film thickness calculated for  $\varphi = 20^{\circ}$  [33].

It is commonly recognized that a photon, which belongs to the spectral region being considered, incident on a crystal from the vacuum produces in the crystal one phonon near the center of the Brillouin zone, since the light wave vector  $k_0 = \omega/c = 2\pi/\lambda$  is much smaller than the wave vector of a phonon at the edge of the Brillouin zone  $Q = \pi/a$  (*a* is the lattice constant and  $\lambda$  is the wavelength of light in the vacuum). Without the inclusion of multiple-beam interference in the crystal layer, the light absorption is proportional to the imaginary part of permittivity

$$\operatorname{Im}\varepsilon(\omega) = \frac{(\varepsilon_0 - \varepsilon_\infty) \,\gamma \omega_{\mathrm{TO}}^2 \,\omega}{(\omega_{\mathrm{TO}}^2 - \omega^2)^2 + \gamma^2 \omega^2} \,. \tag{80}$$

The spectrum of  $\text{Im} \varepsilon(\omega)$  and, hence, the absorption spectrum have a Lorentzian profile with a peak at the  $\omega_{\text{TO}}$ frequency and a rapidly decaying intensity of the profile wings. Experiments yield a series of light absorption (and emission) bands at frequencies  $\omega < \omega_{\text{TO}}$  (and  $\omega > \omega_{\text{LO}}$ ), where single-phonon states of the film material are nonexistent, and a nonmonotonic dependence of absorption at the  $\omega_{\text{TO}}$  frequency on the film thickness over a very wide range of thicknesses.

<sup>&</sup>lt;sup>9</sup> For a ZnSe film on a metal, two sets of interference bands appear as  $N \to \infty$ : the first one with frequencies ranging from zero to  $\omega_N \to \omega_{\text{TO}}$ , and the second one from  $\omega_{\text{LO}}$  to  $\omega_N \to \omega_{\text{ex}}$ .

It is evident from expression (80) that light absorption would occur only when the probability of the anharmonic phonon decay is nonzero, i.e., when  $\gamma > 0$ . One optical phonon in a dielectric crystal can decay only into several other phonons in a single event (into 2, 3, ... phonons), i.e., into multiphonon states, because the energy and the momentum should be conserved during phonon decay. Despite the fact that expression (80) implies the anharmonic decay of only one crystal phonon with a probability  $\gamma$ , the real light absorption in the  $\omega > \omega_{\rm LO}$  and  $\omega < \omega_{\rm TO}$  frequency ranges is supposedly determined by the density of multiphonon states: the introduction of nonzero decay probability of a singlephonon state ( $\gamma > 0$ ) implies a finite density of multiphonon states.

Furthermore, in a crystal of finite dimensions there arises a polariton decay channel related to the 'quantization' of the electromagnetic field of a bulk crystal polariton by crystal boundaries and related emergence of waveguide and interference modes. The electromagnetic field produced by thermal dipole vibrations can escape from the crystal via the interference modes of the structure.

A bulk polariton split into interference and waveguide modes is an eigenstate of a crystal of finite dimensions. Any transient process in a real material is always thermodynamically irreversible. This signifies that  $\text{Im }\varepsilon(\omega) \neq 0$  for all  $\omega > 0$ . The change in dispersion of a bulk polariton in going from an infinite crystal to a crystal of finite dimensions results in a significant increase in the density of polariton states in the radiative domain, which is responsible for an enhancement of light absorption by interference polaritons at the frequencies  $\omega > \omega_{\text{LO}}$  and  $\omega < \omega_{\text{TO}}$ .

The notions that a photon incident on a crystal from the vacuum produces a phonon (a bulk vibrational crystal excitation) prove to be in contradiction with the aggregate results under discussion. In the  $\omega_{TO} < \omega < \omega_{LO}$  frequency range, where the density of single-phonon states (see Fig. 3) is nonzero, there is no light absorption in the experimental spectra. Nevertheless, it is pertinent to note that the optical properties of crystals and films in a wide spectral range are adequately described with the aid of macroscopic permittivity determined by crystal phonons (excitons).

## 5.3 Resonance of dipole vibrations of impurity atoms with crystal layer polaritons

The existence of crystal structure defects may change the density of phonon states in the frequency ranges  $\omega > \omega_{LO}$  and  $\omega < \omega_{TO}$ . For low densities of defects (impurity atoms), the changes in the density of phonon states and crystal permittivity are small [98–101]. However, the introduction of even a low density of impurity atoms, which make up local vibrations, into the crystal film may result in very strong changes in optical properties.

This change shows up most amply in the interaction of local vibrations of impurity atoms of the crystal lattice with interference modes, which was observed in reflection– absorption spectra of films of  $CdS_{1-x}Se_x$  and  $Zn_{1-x}Cd_xTe$  solid solutions [38]. The optical phonons of these solid solutions exhibit a so-called 'two-modal behavior' [98]. For small *x*, the optical vibrations of Se and Cd atoms split off from the corresponding CdS and ZnTe bands of single-phonon states, and their frequencies  $\omega_g < \omega_{TO}$  fall into the gap region between acoustic and optical phonons [98–101].

By varying the  $CdS_{1-x}Se_x$  and  $Zn_{1-x}Cd_xTe$  film thicknesses for the same impurity densities, the interference mode

frequencies can be made coinciding with the frequencies of gap vibrations of impurity atoms. (We note that the frequencies of the local vibrations of impurity atoms, being bulk vibrational states of the film, are independent of substrate properties.) Each time as the local vibration frequencies of impurity atoms coincided with the interference modes, a resonance increase in the integrated light absorption at the frequency of gap vibrations of impurity atoms (up to a factor of 10<sup>5</sup> for the first resonance) was observed [33, 34, 38]. Figure 18 shows the reflection – absorption spectra of singlecrystal films of the Zn<sub>0.95</sub>Cd<sub>0.05</sub>Te solid solution of different thicknesses on an aluminum mirror. Comparing Figs 18 and 17 reveals that a low admixture of CdTe to ZnTe is responsible for dramatic changes in the absorption spectrum depending on the thickness of the solid-solution film. For small and large film thicknesses, the relative intensity of the absorption band arising from the gap vibrations of impurity atoms is proportional to the impurity concentration in the solid solution [98-101]. The integrated light absorption coefficient of the film depends strongly on the order number of the interference mode that coincides in frequency with the gap vibration. The



**Figure 18.** (a) *p*-Polarized reflection – absorption spectra of  $Zn_{0.95}Cd_{0.05}Te$  films on an Al mirror for  $\varphi = 20^{\circ}$  and different film thicknesses: points, experiment; solid curves, calculation [38]. (b) Calculated *p*-polarized absorption of  $Zn_{0.95}Cd_{0.05}Te$  films versus film thickness for  $\varphi = 20^{\circ}$  [33].

absorption enhancement at resonance is greatest for N = 1and decreases with increasing N. No resonance exists for very large N, i.e., in thick crystals ( $d \approx 1$  mm).

Along with the enhancement of absorption at the frequencies of the gap vibrations of impurity atoms, there occurs a significant decrease in light absorption at the  $\omega_{TO}$  frequencies of matrix (solvent) vibrations [38]. A similar absorption intensity redistribution depending on the film thickness was discussed in Section 5.2. In thin films on a metal substrate, it will be recalled, the vibrational mode at the  $\omega_{TO}$  frequency is a radiative surface (interfacial) polariton of the film – substrate boundary [33, 59], and it is an interference polariton of the structure for  $d \approx \pi c / (\omega_{TO} \sqrt{\epsilon(\omega)})$ .

The number of polariton branches in the film and their dispersion depend on the film thickness and the  $\varepsilon(\omega)$  function of the film material, which changes only slightly on addition of small amounts of dopant [98–101]. The reflection– absorption spectra of  $(ZnTe)_{1-x}(CdTe)_x$  films on an aluminum mirror (Fig. 18b) were calculated by formula (12). For small *x*, the permittivity of the  $(ZnTe)_{1-x}(CdTe)_x$  solid-solution film was approximated by the relation [38]

$$\varepsilon(\omega) = (1-x)\,\varepsilon_{\text{ZnTe}}(\omega) + x\,\frac{(\varepsilon_0 - \varepsilon_\infty)_{\text{CdTe}}\omega_g^2}{\omega_g^2 - \omega^2 - i\gamma_g\omega}\,,\tag{81}$$

where  $\omega_g$  and  $\gamma_g$  are, respectively, the frequency and damping factor of the gap vibrations of Cd atoms, which replace Zn atoms in the ZnTe lattice. The values of  $\omega_g$  and  $\gamma_g$  for the calculations were borrowed from the experimental data on the reflectance spectra of bulk solid-solution crystals [99, 100]. Expression (81) is a rather crude approximation for the permittivity of a solid solution, but nevertheless it yields good agreement with the experiment.

A comparison of the data given in Figs 17 and 18 suggests that a small amount of a dopant changes not only the intensity of film absorption spectra, but the dispersion of the lower polariton branch of the nonradiative bulk polariton of ZnTe, and is therefore responsible for the emergence of a gap in it in the vicinity of the frequency of vibrations of Cd-Te impurity dipoles. The absorption intensity transfer from one spectral range to another that can be seen in the spectra of Fig. 18 is indicative of the occurrence of an additional mechanism of interaction between the dipole vibrations of impurity atoms and the polariton states of the film. The filmboundary-induced transformation (perturbation) of the lower branch of the bulk polariton of a bulk crystal, which is responsible for the splitting off of interference and waveguide modes from it, supposedly is just the additional channel of polariton-state density transfer from one spectral region to another, i.e., from the nonradiative bulk polariton of the matrix or interfacial polaritons of the sandwich to radiative polariton branches that coincide in frequency with the gap vibrations of impurity atoms in the film.

Therefore, the seemingly correct division of optical phonons in solid solutions into matrix phonons and local impurity vibrations for bulk single crystals [99] becomes invalid for films, because the gap vibrations are no longer local but in some sense are resonant due to the effects discussed in the preceding paragraphs.

A similar resonance interaction of 'local vibrations' should most likely be observable with waveguide polaritons as well, which exist in the nonradiative domain. The literature on the physics and technology of waveguide modes is quite voluminous, with monographs also being available (see, for example, Refs [102, 103]). Waveguide modes possess an oscillating electromagnetic field inside and an exponentially decaying field outside of the slab (film) [102, 103].

In other words, the waveguide modes experience total internal reflection from the slab boundaries to remain 'confined' within the slab. Their two-dimensional wave vector is  $q > k_0$ . In particular, the waveguide modes in optical experiments can be excited in the same way as nonradiative surface polaritons - with the aid of an ATR prism [102, 103]. The dispersion of TM waveguide modes is described by Eqn (4), and the dispersion of TE waveguide modes, by Eqn (5) for imaginary  $\beta_1$ . The waveguide modes fill the domains of the  $\omega - q$  diagram between the dispersion curve of the bulk polariton of an infinite crystal and the light straight line in the vacuum. The intersection of the domains of existence of waveguide modes by the straight line corresponding to a specific angle in the ATR prism (i.e., to the energy and momentum conservation condition in the excitation of waveguide modes) defines the frequencies of the waveguide modes with a given wave vector q and the spectral range of their excitation when the distance between them is smaller than their half-width.

Formula (6) describes the spectra of energy losses in a light wave due to the waveguide-mode excitation with the aid of an ATR prism above a crystal layer – metal substrate structure [33]. A comparison of theory with experiment shows that theory adequately describes the dispersion curves of the waveguide polaritons in planar structures. Direct measurements of the dispersion of the waveguide polaritons of crystal layers and the bulk polaritons of crystals are also afforded by small-angle RS and hyper-RS techniques [7, 36, 37, 47].

#### 6. Radiative polariton lifetime

As was repeatedly emphasized above, in crystals of finite dimensions there exists a radiative channel due to polariton decay, which has the effect that the dielectric function  $\varepsilon(\omega)$  is a complex function even in the harmonic approximation. As is shown in Refs [12–17], the radiative polariton decay can be taken into account by replacing the real current frequency  $\omega$  in Eqn (1) with the complex one:  $\omega = \omega' + i\omega''$ . By definition, the radiative decay probability of a polariton with a frequency  $\omega' = \omega_v$  is  $\gamma_r = 2|\omega''| = \tau_r^{-1}$ , where  $\tau_r$  is the radiative lifetime of the polariton, which was termed virtual in these papers.

The radiative lifetime of polaritons in plane-parallel slabs of substrate-free ionic crystals was theoretically investigated in Refs [12–16]. In Refs [25, 33, 34, 57, 58, 64–66, 69], an experimental study was made of the films on substrates, but only for one thin-film polariton branch with a frequency  $\omega_2$ (the OTH mode in the notation of Refs [25, 57, 58, 65, 69]) related to the radiative surface polariton at the film – vacuum interface.

The dispersion laws for a radiative surface polariton with a frequency  $\omega_2 = \omega_v \approx \omega_{LO}$  of a free-standing film and a film on a metal substrate coincide, being virtually independent of the substrate. That is why the radiative broadening of this polariton can be studied experimentally and theoretically in the pure state. For a thin film ( $\beta d \ll 1$ ), the calculations of Refs [25, 58, 65, 69] yield the following expression for the probability of the radiative decay of a surface polariton:

$$\gamma_{\rm r} = -2\omega'' = 2\pi d \left(\varepsilon_{\infty}^{-1} - \varepsilon_0^{-1}\right) \omega_{\rm v}^2 \frac{1}{\cos\varphi} \sin^2\varphi \,. \tag{82}$$

Semiconductor film	<i>d</i> , μm	$v_1$ , cm <sup>-1</sup>	$\gamma(v_1), \mathrm{cm}^{-1}$	$v_2,  {\rm cm}^{-1}$	$\gamma(v_2),  \mathrm{cm}^{-1}$	$\gamma_r(v_2), cm^{-1}$ (experiment)	$\gamma_r(v_2), cM^{-1}$ (theory)
ZnSe	0.5	205	5.0	252	6.5	0.16	0.18
ZnSe	1.6	202	5.5	252	7.5	0.45	0.56
ZnS	1.0	270	18	352	10	0.6	0.87
CdS	0.6	237	8.0	302	12	0.7	0.45
CdTe	0.5	140	5.5	167	6.0	0.045	0.047
CdTe	0.9	139	6.5	167	6.0	0.09	0.087
CdTe	2.4	137	5.5	167	5.0	0.22	0.23

Table 2. Optical constants of thin semiconductor films on an aluminum mirror

Instead of formula (12), the reflectivity of the sandwich in this case is of the form [25, 33]

$$R(\omega, \varphi) = 1 - \frac{4\gamma\gamma_{\rm r}}{4\left(\omega_{\rm v} - \omega\right)^2 + \left(\gamma + \gamma_{\rm r}\right)^2} - \frac{1}{\cos\varphi} \sqrt{\frac{2\omega}{\pi\sigma}},$$
(83)

where  $\sigma$  is the conductivity of the metal substrate at a frequency  $\omega$ . Assuming the substrate to be an ideal metal, i.e., putting  $\sigma \to \infty$ , it is possible to obtain from expression (83), as was shown in Refs [25, 64–66], the relation

$$\frac{A}{R} = \frac{1-R}{R} = \frac{4\gamma\gamma_{\rm r}}{4\left(\omega_{\rm v} - \omega\right)^2 + \left(\gamma - \gamma_{\rm r}\right)^2} \,. \tag{84}$$

The functions (83) and (84) have Lorentzian profiles with half-widths  $\gamma + \gamma_r$  and  $\gamma - \gamma_r$ , respectively. This permits reconstructing  $\gamma$  and  $\gamma_r$  from the experimental data and comparing the latter with the theoretically predicted value (Table 2). For the radiative surface polariton under discussion, its radiative decay probability  $\gamma_r$  proves to be less than 1 cm<sup>-1</sup>, which is approximately ten times smaller than the anharmonic decay probability  $\gamma$ .

Note that the absorption and emission of light by the vibrational states of the sandwich at a frequency  $\omega_v$  is only possible, according to formulas (83) and (84), when  $\gamma$  and  $\gamma_r$  are nonzero.

Referring to Table 2, the experimental values for  $\gamma_r(\nu_2)$  agree very well with the theoretical calculations based on formula (82) [34, 64–66], particularly for ZnSe and CdTe semiconductor compounds with a cubic crystal symmetry, which are optically isotropic.

The radiative lifetime of the interference modes of freestanding films was estimated theoretically in Refs [15, 32, 86]. As suggested by these papers, the interference modes with  $\omega_N \ll \omega_{\text{TO}}$  and  $\omega_N \gg \omega_{\text{LO}}$  have a half-width  $\gamma_r \gg \gamma$ , i.e., the spectral width of the interference modes is defined by their radiative decay. For not-too-thick films ( $\beta d \approx 1$ ), the calculations yield  $\gamma_r \propto \omega_N/4\pi$ ; furthermore, the half-width  $\gamma_r$ depends strongly on *q* to attain a maximum value for Brewster's angle for *p*-polarized light [15]. Similar results for  $\omega_N \ll \omega_{\text{TO}}$  for films on an ideal metal substrate were theoretically obtained in Refs [65, 69].

Good agreement between the experimental data and the calculated absorption spectra at the frequencies of interference modes (including the values of frequencies and halfwidths, the band profiles in the absorption and emission spectra of the interference modes and their intensities) testifies to the fact that the interference-mode bands in the spectra are homogeneously broadened. Their width is defined primarily by the radiative decay probability  $\gamma_r$ , i.e., by the time  $\tau_r$  of

multiple light passage through the film in the sandwich structure.

A crude estimation of the time  $\tau_r$  can be obtained from the simple relation  $\tau_r = 2dnN_{\text{eff}}/c$ , where  $N_{\text{eff}}$  is the effective number of light passages through the film. From the theory of a reflection Fabry–Perot interferometer [91, 104], it is possible to determine the  $N_{\text{eff}}$  value and compare the lifetime  $\tau_r$  with the  $\Gamma^{-1} = (\gamma_a + \gamma_r)^{-1}$  value obtained from the measurements of the spectral half-widths of the interference bands in reflection–absorption spectra (here,  $\gamma_a$  is the nonradiative anharmonic decay probability of a polariton at the interference-mode frequencies). For the interference modes with frequencies  $\omega_N \ll \omega_{\text{TO}}$  and  $\omega_N \gg \omega_{\text{LO}}$ , the estimations give  $\Gamma \approx \gamma_r$ , i.e.,  $\gamma_r \gg \gamma_a$  for all the samples investigated in our work.

Therefore, the lifetime of radiative sandwich polaritons with  $\omega_N \ll \omega_{\text{TO}}$  and  $\omega_N \gg \omega_{\text{LO}}$  can be determined from the measurements of the spectral width of absorption or emission bands. In the case of thin films, the radiative lifetime can be very short for the first interference modes (N = 1, 3, ...). For the absorption bands displayed in Figs 6, 8, 17, and 18, it is in the range of only several hundreds of femtoseconds, and for the absorption bands in Fig. 23b, in the range of only several tens of femtoseconds [32, 86]. A substantial increase in the radiative-decay rate for the excitonic polaritons of thin films on metal substrates was predicted by Agranovich and Mukamel [105].<sup>10</sup>

### 7. Luminescence and resonance Raman scattering by interference polaritons

It was shown in the previous sections that the interference modes of a sandwich absorb and emit light in the IR spectral range. The reflection – absorption spectra of thin ZnSe films on a metal in the visible spectral range were shown in Figs 8 and 9. In this Section we consider how the radiative polaritons (interference modes) of the sandwich show up in luminescence and Raman scattering (RS) spectra. These effects will be investigated by the example of 1.25-µm ZnSe films deposited on aluminum, chromium, and titanium substrates in one technological run.

The secondary emission (luminescence and RS) spectra were excited in the sandwiches by different lines of a cw argon laser with  $\hbar\omega_{\rm L} < E_{\rm g}$  (Fig. 19b) for different angles of incidence of the laser beam on the sample and observed

<sup>&</sup>lt;sup>10</sup> Unfortunately, no papers devoted to direct measurements of the radiative lifetime for radiative film polaritons by pico- and femtosecond spectroscopy techniques have been reported to date. However, it is known to strongly depend on the crystal layer thickness [109] and the configuration of the electromagnetic field inside a multilayer thin-film structure (in particular, in superlattices with quantum wells) [45, 49, 53].



**Figure 19.** (a) *p*-Polarized absorption spectra of a 1.25-µm ZnSe film on aluminum. (b) Secondary emission spectra for exciting laser lines  $\lambda_{\rm L} = 488$  nm and  $\lambda_{\rm L} = 514.5$  nm. (c) Secondary emission spectra for different scattering angles and  $\lambda_{\rm L} = 488$  nm. (d) RS spectra of a ZnSe film on aluminum for *s*- and *p*-polarized exciting radiation with  $\lambda_{\rm L} = 496.5$  nm incident on the film at an angle greater than Brewster's angle. *T* = 300 K [33, 35].

(Fig. 19c) at different emission (scattering) angles [33, 35, 59]. Along with ordinary bands at the frequencies of transverse and longitudinal optical phonons and surface polaritons [35, 59, 110], the spectra of spontaneous RS in ZnSe films exhibited broad bands in the longer-wavelength spectral region [33, 35].

Referring to Figs 19a and 19b, the location of the broad bands is independent of the wavelength of exciting radiation and the angle of radiation incidence. Furthermore, when the excitation and emission angles are equal, the band parameters (the frequencies, the half-widths, and the profiles) correspond to the reflection-absorption spectra of the interference modes [33, 35, 59]. All this suggests that what was observed in these experiments was the luminescence from interference polaritons [35].

The low luminescence intensity, comparable with the intensity of RS by phonons, can be qualitatively interpreted by the fact that the ZnSe film has a low absorption for laser radiation for  $\hbar\omega_{\rm L} < \hbar\omega_{\rm ex} \approx E_{\rm g}$ . The light is absorbed and emitted by different states in the forbidden band of ZnSe and the interfacial states of the film-substrate structure. As suggested by Fig. 9, the largest contribution to absorption comes from substrate plasmons, but only at the frequencies of radiative polariton branches — at the interference modes [33, 34].

It also turns out that the intensity of luminescence and spontaneous RS by phonons increases when the wavelength of exciting radiation coincides with the peaks of light absorption by the interference modes. The resonance enhancement of spontaneous RS for fixed excitation wavelengths can be achieved in two ways.

First, by taking advantage of the angular dependence of interference-mode frequencies in accord with their dispersion law  $\omega_N(q)$  (see Figs 7 and 8a), the interference-mode frequency can be made to coincide with the excitation frequency by increasing the angle of light incidence on the sample, thereby making the interference-mode frequency to 'crawl over' the excitation frequency. Away from the resonance angle, the angular dependence of the intensity peak of the longitudinal optical phonon is very weak. In going over to the resonance angle, the cross section for scattering by optical phonon increases by at least a factor of three [33, 35, 59].

Second, it follows from Fig. 8b that the absorption minimum of the interference mode for *s*-polarized light for angles  $\varphi > \varphi_{Br}$  coincides with the absorption peak for *p*-polarized light. When the exciting laser wavelength (the arrow on the abscissa axis in Fig. 8b) coincides with the absorption band for *p*-polarized light, by changing the polarization of the exciting radiation (under the same geometry of experiment), it is possible to change the intensity of the electromagnetic field in the film and hence the RS cross section, the absorption of exciting radiation, and the luminescence intensity. It is precisely this case that is illustrated in Fig. 19d, which shows the resonance enhancement of spontaneous RS by interference modes at the frequency of exciting radiation [33, 35, 59].

A similar effect was earlier observed in Refs [106, 107], in which a transparent dielectric layer was deposited on top of a thin film to increase the light-scattering cross section. The layer thickness was such that the total sandwich thickness was a multiple of  $\lambda/2$  of the exciting radiation. In this case, there occurred a 'standing wave' (in terms of Refs [106, 107]) at the interference-mode frequency and the electric intensity of the light-wave field strengthened by about a factor of  $N_{\rm eff}$  — the number of light passages (multiple reflections) in the film. It is precisely this value of enhancement  $N_{\rm eff}$  (ranging from 5 to 15 from sample to sample) that was observed in our experiment [33, 35, 59] and in Refs [106, 107].

It is well known from numerous investigations of resonance RS that resonance enhancement is also observed when the frequency of scattered light coincides with some real electronic level (exciton) [108]. To verify the existence of such a resonance in our case, i.e., to verify whether the cross section for light scattering by phonons depends on the coincidence of the scattered light wavelength with the peak of light absorption by the interference mode, we studied the dependence of the position of interference-mode bands in luminescence spectra on the angle of secondary emission [33, 35, 59]. The dependence observed in the above investigations corresponds to the interference-mode dispersion law  $\omega_N = \omega_N(q)$ ; in this case, the RS by phonons was seen to become stronger when the TO and/or LO band coincided with some interference mode.

In such measurements, the enhancement of the RS is usually hard to estimate quantitatively. That is why the RS spectra were normalized employing measurements of the band intensity ratio between the first- and second-order RS at different scattering angles [33, 35, 59]. Owing to a relatively large frequency difference between the longitudinal optical phonon (250 cm<sup>-1</sup>) and its overtone (2LO phonon separated by 500 cm<sup>-1</sup> from the excitation line), they coincide with the interference modes for different scattering angles. This formulation of experiment made it possible to estimate the dependence of the intensity of the RS spectrum on the scattering angle without measuring the absolute spectral intensities.

The investigations in Refs [33, 35, 59] showed that there occurs a resonance rise in RS intensity when the wavelength of radiation scattered by longitudinal optical phonons coincides with the wavelength of some interference mode. This rise in RS and luminescence intensity is moderate (only several-fold) and is much smaller than in the case of excitation high into the band  $\hbar\omega_L > E_g$  [59, 110].

# 8. Femtosecond dynamics of semiconductor microcavity polaritons

We consider the interaction of ultrashort laser pulses with semiconductor-metal microcavities (microresonator structures). The investigation of the excitation and relaxation of the eigenstates of these structures by the femtosecond laser excitation-broadband probing spectroscopic technique [111, 112] showed that the interference polaritons of ZnSe and ZnS films on different metal substrates are highly sensitive to ultrafast photo-induced processes in the semiconductor-metal structure.

#### 8.1 Experiment

As planar microresonator structures, various structures were used, e.g., 400- and 820-nm ZnSe films on a thick (opaque in the visible spectral range) chromium film, a 285-nm ZnSe film on a semitransparent copper layer, and ZnS films of different thicknesses ( $0.29-1.17 \mu m$ ) on a thick nickel layer. The structures under investigation were grown on 500-µm quartz substrates. The excitation was accomplished by optical pulses with a pumping duration  $\tau \approx 50$  fs ( $\hbar \omega_{pu1} = 2.34 \text{ eV}$  and  $\hbar \omega_{pu2} = 2.75 \text{ eV}$ ) and  $\tau \approx 70$  fs ( $\hbar \omega_{pu3} = 5.5 \text{ eV}$ ). The energy of pumping pulses was varied in the  $0.4-2 \mu J$  range. The diameter of the pulsed-excitation spot was  $150-250 \mu m$ .

Measurements were made of reflection – absorption spectra for a broadband probe pulse of the same duration as the excitation pulse. The spot diameter of the probe pulse was about 100  $\mu$ m. The broadband probing pulse (1.6–3.2 eV) was dispersed with a polychromator with a resolution of 1 nm, the spectrum of this pulse was recorded with a 512-pixel photodiode matrix.

The optical density of the microcavity  $D_R(\hbar\omega) = \log R(\hbar\omega)$  for different time delays  $t_d$  was determined from the reflection – absorption spectra of a probing pulse. With the use of an optical delay line, the probe pulses were delayed by times ranging from –0.2 to 2.5 ps relative to the pumping pulse. The pumping – probing cross-correlation time for the  $\hbar\omega_{pu1}$  and  $\hbar\omega_{pu2}$  pump was  $\tau_{cc} \approx 70$  fs (full width at halfmaximum) and for the  $\hbar\omega_{pu3}$  pump the value  $\tau_{cc} \approx 90$  fs for all probe wavelengths. Difference spectra  $\Delta D_R(\hbar\omega) =$  $-\Delta \log R(\hbar\omega)$  of the optical density for excited and unexcited samples were analyzed. For a time delay  $t_d = -0.2$  ps, the probe pulse did not overlap with the excitation pulse, and the spectrum of an unexcited sample was recorded.

The dynamics of the photo-induced reflection  $\Delta D_R(\hbar\omega)$ was determined by varying the time delay between the excitation and probe pulses with an increment of 7 fs. The signal was averaged over eight measurements recorded with a repetition rate of 2 Hz. The spectra under measurement were corrected in time [111, 112] to take into account the chirp of a probe pulse. The uncertainty of temporal correlation was  $\pm 10$  fs. The investigations were conducted at room temperature. The sample quality was monitored in the course of the experiments. No irreversible changes in the sample arising from its exposure to relatively intense femtosecond pulses were discovered after conducting the series of experiments.

To make the temporal correction of the experimental difference spectra and determine the characteristic relaxation rates, the signal  $\Delta D_R(\omega, t)$  was approximated as follows:

$$\Delta D_{\rm fit}(\omega, t) = \int_{-\infty}^{\infty} S(t - t') F(t') \,\mathrm{d}t' \,. \tag{85}$$

Here,

$$S(t) = \exp\left[-\left(1.665 \frac{t}{\tau_{\rm cc}}\right)^2\right]$$

is the pumping-probing cross-correlation function, and

$$F(t) = \theta(t - t_0) \left[ C_1 \exp\left(-\gamma_1(t - t_0)\right) + C_2 \exp\left(-\gamma_2(t - t_0)\right) \right].$$

The first term in the square brackets of the last expression describes the fast relaxation process with a characteristic rate  $\gamma_1(\omega)$ , and the second term corresponds to a slower process, which occurs at a rate  $\gamma_2(\omega)$ . The  $\gamma_1(\omega)$  and  $\gamma_2(\omega)$  parameters and the original time delay  $t_0(\omega)$  were varied to best approximate the experimental signal  $\Delta D_R(\omega, t)$ .

Figure 20a shows the spectra of difference response  $\Delta D_R(\hbar\omega)$  for different time delays of the probe pulse relative to the excitation pulse for a ZnSe film (400 nm) on chromium and the results of approximation of these spectra using exponential response functions [116]. One can see the good quality of the fit with the use of procedure (85). We emphasize that the greatest intensity change in the spectrum  $\Delta D_R(\hbar\omega)$  occurs at the frequencies of interference modes of the film — the electromagnetic cavity modes (Fig. 20b).

From the characteristic kinetics  $\Delta D_R(\hbar\omega)$  of the ZnSe film (400 nm) on chromium for different probing frequencies and  $\Delta D_{\rm fit}(\hbar\omega)$  (solid curves in Fig. 21), the existence of two characteristic time stages can be deduced: a fast stage with a characteristic time of the order of the excitation pulse duration and a slow one with a characteristic time of the



**Figure 20.** (a) Temporal evolution of the spectrum of the difference response of a ZnSe film (400 nm) on chromium for an excitation photon energy of  $\hbar\omega_{pu1} = 2.34$  eV: points, experiment; solid curves, approximation with the use of a two-exponent response function [116]. (b) Absorption spectrum of a ZnSe film (400 nm) on chromium.



**Figure 21.** Temporal evolution of the photo-induced difference response of a ZnSe film (400 nm) on chromium for different probing frequencies: points, experiment; solid curves, fitting using procedure (85) [116].

order of 1 ps. The oscillatory residual  $\Delta D_R(\hbar\omega) - \Delta D_{\text{fit}}(\hbar\omega)$ in Fig. 21 is due to coherent phonon generation [122–124].

Fourier analysis of the time dependence of the oscillatory residual revealed that vibrations with frequencies of 200 and 250 cm<sup>-1</sup> are excited in the ZnSe/Cr sample, which correspond to transverse and longitudinal optical phonons of the center of the Brillouin zone of the ZnSe single crystal. The coherent phonons are excited throughout the probed frequency range (1.6–3.2 eV). The coherent-phonon intensity distribution depends on the probing wavelength and agrees qualitatively with the spectral dependence of the linear response (the linear reflection – absorption spectrum) [114–116].

Note that different mechanisms of coherent phonon production are possible in the sample under investigation. One of them may be associated with the excitation of coherent vibrations at frequencies  $\omega \leq \tau^{-1}$  (where  $\tau$  is the excitation pulse duration) due to the parametric pumping of microcavity modes [23]. Another likely mechanism may be due to the excitation of electrons in the metal and the pulsed injection of nonequilibrium carriers into the semiconductor via a Schottky barrier [115, 116].

Two types of excitation of the samples under investigation were experimentally realized: (i) 'subgap' excitation, when the photon energy of the excitation pulse is smaller than the semiconductor energy gap  $E_g$ ; (ii) 'overgap' excitation, when the photon energy of the excitation pulse is higher than  $E_{\rm g}$ . The temporal evolution of photo-induced reflection spectra (difference optical density) for different delay times in the case of subgap excitation of ZnS/Ni, ZnSe/Cu, and ZnSe/Cr samples is shown in Figs 22a, 23a, and 24, respectively. The spectra in the case of overgap excitation of the ZnS/Ni and ZnSe/Cr samples are shown in Figs 22b and 25. For overgap excitation of the samples, the responses of all the structures under study proved to be qualitatively similar. For short delay times ( $t_d < 0.5 \text{ ps}$ ), a sign-alternating signal was observed. Its amplitude peaked for  $t_d \approx 0.1$  ps to subsequently relax to a signal with a constant sign in a characteristic time of the order of 1 ps.

The bipolar signal of the photo-induced difference response is similar in appearance to the first derivative of the absorption – reflection spectrum at the frequencies of interference modes — the linear spectrum of optical density of the structures (Fig. 20a). This testifies to the occurrence of a spectral shift of the interference bands upon the excitation of the structure by femtosecond laser pulses. The frequency shift of the interference mode of a plane-parallel dielectric layer on a metal is, in accord with formula (19a), possible primarily due to a change in the semiconductor film permittivity and, to a smaller degree, due to a change in the metal plasmon frequency. The time behavior of photo-induced spectra in the case of overgap-type excitation is different from that of subgap-type excitation spectra.

The temporal dynamics of photo-induced response in the case of subgap-type excitation depends on the metal used to make up the rear microresonator boundary. The photo-induced difference response of the ZnSe/Cr structure for positive time delays  $t_d = 0-0.5$  ps is similar to that for overgap-type excitation, i.e., is of alternating sign. The response for the ZnSe/Cu and ZnS/Ni structures is of constant sign (with the exception of the domain in the vicinity of the forbidden-band edge for the ZnSe/Cu structure) for all delays investigated [113–121]. Meanwhile, the ZnSe/Cr-structure response (Fig. 24) for small negative time



**Figure 22.**  $\Delta D_R(\hbar\omega)$  spectra of a ZnS film (293 nm) on an Ni substrate for different delay times: (a) the excitation photon energy  $\hbar\omega_{pu2} = 2.75$  eV, the excitation pulse energy is 1.6 µJ, and the spot diameter of the pumping pulse is 120 µm; (b) the excitation photon energy  $\hbar\omega_{pu3} = 5.5$  eV, the excitation pulse energy is 1.2 µJ, and the spot diameter of the pumping pulse is 250 µm [119–121].  $E_g$ (ZnS)  $\approx 3.7$  eV for T = 300 K.

delays  $t_d = -0.04$  ps is qualitatively similar to the response of the ZnS/Ni structure (Fig. 22a).

The difference spectrum of photo-induced response of constant sign is indicative of a change in light absorption intensity at the frequencies of interference modes. As shown in Sections 4 and 5.2, the intensity of the absorption spectrum of the structures under discussion at the interference-mode frequencies is determined by the imaginary part of metal permittivity. The absorption strengthens with increasing Im  $\varepsilon_{\rm m}(\omega)$ .

Two characteristic stages can be recognized for the ZnS/Ni structure: a fast stage (with a characteristic time equal to the pulse duration) and a slow stage (with a characteristic time  $t_d \approx 0.4$  ps). During the fast stage, the signal attains its maximum for a zero delay and then decreases to transform



**Figure 23.** (a)  $\Delta D_R(\hbar\omega)$  spectra of a ZnS film (285 nm) on a Cu substrate (22 nm) for different delay times. The excitation photon energy  $\hbar\omega_{pu1} = 2.34$  eV, the excitation pulse energy is 0.6 µJ, and the spot diameter of the pumping pulse is 150 µm.  $E_g(\text{ZnSe}) \approx 2.7$  eV for T = 300 K [118]. (b) *p*-Polarized reflection – absorption spectra of a thin (270 nm) ZnSe film on thick (over 500 nm) metal substrates [86].

into a growing signal (for  $t_d \approx 0.4$  ps), which subsequently dies away to zero for  $t_d > 1$  ps. The ZnSe/Cu-structure response in Fig. 23a is similar to the ZnS/Ni-structure response (except for the fast stage, which was not observed for the ZnSe/Cu structure) [114, 115, 118–120].

Note that all characteristic relaxation times exceeded the settling time of the microresonator modes  $t_{\rm rt} = \tau_{\rm r}$  (where  $\tau_{\rm r}$  is the radiative lifetime of the interference polariton), i.e., the total time  $N_{\rm eff}$  of the forward and backward light passages (the number of effective beams of multiple-beam interference) through the microresonator. For instance, for a 800-nm ZnSe film on a metal mirror ( $N_{\rm eff} \approx 8$ ,  $n \approx 2.5$ ), this time is  $t_{\rm rt} \approx 100$  fs. We also note that the fast stage of photo-induced response was observed in difference reflectance spectra in a time much shorter than the microresonator-mode settling time  $t_{\rm rt}$  [117, 119].

#### 8.2 Discussion of results

To analyze the processes that determine various contributions to the observed temporal behavior of difference photoinduced spectra, calculations were made of the optical density  $D_R(\hbar\omega) = -\log R(\hbar\omega)$  and its derivatives with respect to the metal and superconductor permittivities ( $\varepsilon_m$ and  $\varepsilon_s$ ):  $dD_R(\hbar\omega)/d\varepsilon_{m1,2}$  and  $dD_R(\hbar\omega)/d\varepsilon_{s1,2}$ , where  $\varepsilon_{m1}$ 



**Figure 24.**  $\Delta D_R(\hbar\omega)$  spectra of a ZnSe film (820 nm) on a Cr substrate for different delays. The excitation-photon energy is  $\hbar\omega_{pu1} = 2.34$  eV, the excitation-pulse energy is 1.5 µJ, and the spot diameter of the pumping pulse is 150 µm.  $E_g(\text{ZnSe}) \approx 2.7$  eV for T = 300 K [119, 120].

and  $\varepsilon_{s1}$  are the real parts of the permittivities and  $\varepsilon_{m2}$  and  $\varepsilon_{s2}$  are their imaginary parts, respectively. The difference optical density  $\Delta D_R(\hbar\omega)$  can be represented in the form [119, 120]

$$\Delta D_R(\hbar\omega) = \frac{\mathrm{d}D(\hbar\omega)}{\mathrm{d}\varepsilon_{\mathrm{s}1}} \,\Delta\varepsilon_{\mathrm{s}1} + \frac{\mathrm{d}D(\hbar\omega)}{\mathrm{d}\varepsilon_{\mathrm{s}2}} \,\Delta\varepsilon_{\mathrm{s}2} \\ + \frac{\mathrm{d}D(\hbar\omega)}{\mathrm{d}\varepsilon_{\mathrm{m}1}} \,\Delta\varepsilon_{\mathrm{m}1} + \frac{\mathrm{d}D(\hbar\omega)}{\mathrm{d}\varepsilon_{\mathrm{m}2}} \,\Delta\varepsilon_{\mathrm{m}2} \,. \tag{86}$$

The main contribution to the difference optical density  $\Delta D_R(\hbar\omega)$  of the semiconductor is determined by the change in the real part of the permittivity  $\varepsilon_{s1}$ , whereas the main contribution to  $\Delta D_R(\hbar\omega)$  of the metal comes from the imaginary part of the permittivity  $\varepsilon_{m2}$ . Calculating the  $dD_R(\hbar\omega)/d\varepsilon_{s1}$  and  $dD_R(\hbar\omega)/d\varepsilon_{m2}$  derivatives for semiconductor-metal structures shows that their spectral dependences are different. Variations in  $\varepsilon_{s1}$  result in the shifts of the resonator modes, and the  $dD_R(\hbar\omega)/d\varepsilon_{s1}$  derivative is, within a scale factor, close to the  $dD_R(\hbar\omega)/d\omega$  derivative. This response will be referred to as the semiconductor one. The  $dD_R(\hbar\omega)/d\varepsilon_{m2}$  derivative has a peaked structure with the peaks located near those of  $\Delta D_R(\hbar\omega)$ . This kind of photo-induced response will be termed as the metallic one.

The variation of metal permittivity can be written as

$$\Delta \varepsilon_{\rm m}(\hbar \omega) = \Delta \varepsilon_{\rm m}^{\rm inter}(\hbar \omega) + \Delta \varepsilon_{\rm m}^{\rm Drude}(\hbar \omega) \,. \tag{87}$$



**Figure 25.**  $\Delta D_R(\hbar\omega)$  spectra of a ZnSe film (820 nm) on a Cr substrate for different delays. The excitation-photon energy is  $\hbar\omega_{pu3} = 5.5$  eV, the excitation-pulse energy is 1.2 µJ, and the spot diameter of the pumping pulse is 250 µm [120, 121].

Here, the contribution of interband transitions is [125]

$$\Delta \varepsilon_{\rm m}^{\rm inter}(\hbar\omega) = \sum_{n} C_{{\rm m},n} \frac{1}{(\hbar\omega)^2} \\ \times \left[ \frac{E_{{\rm m},n}^4}{\left(E_{{\rm m},n}^2 - \hbar\omega(\hbar\omega + {\rm i}\gamma_{{\rm m},n})\right)^2} - 1 \right], \tag{88}$$

and the Drude contribution is

$$\Delta \varepsilon_{\rm m}^{\rm Drude}(\hbar\omega) = -\frac{(\hbar\omega_{\rm p} + \Delta\hbar\omega_{\rm p})^2}{\hbar\omega(\hbar\omega + i(\gamma_{\rm m} + \Delta\gamma_{\rm m}))} + \frac{\hbar\omega_{\rm p}^2}{\hbar\omega(\hbar\omega + i\gamma_{\rm m})}$$
(89)

The variation of the semiconductor permittivity can be represented as [125]

$$\Delta \varepsilon_{\rm s}(\hbar \omega) = \sum_{n} C_{{\rm s},n} \frac{1}{\left(\hbar \omega\right)^2} \left[ \frac{E_{{\rm s},n}^2}{E_{{\rm s},n}^2 - \hbar \omega (\hbar \omega + {\rm i} \gamma_{{\rm s},n})} - 1 \right]. \tag{90}$$

We will distinguish two excitation types for the structures under investigation: below and above the energy gap  $E_g$  of the semiconductor [120].

**8.2.1. First excitation type (subgap excitation).** For an excitation energy smaller than the semiconductor energy gap (subgap excitation), the laser pulse primarily excites electrons in a thin surface metal layer at the boundary with the semiconductor. The thickness of this layer can be estimated

as  $l_{ex} = 2/\alpha_m(\hbar\omega) \approx 20-30$  nm (for Ni and Cr). The nonequilibrium charge carriers of the metal penetrate above the Schottky barrier (and partly through it) into the semiconductor. As for direct semiconductor excitation, it can occur only due to two-photon absorption.

From difference optical density measurements, it follows that the ZnSe/Cr-structure response differs from those of the ZnSe/Cu and ZnS/Ni structures [118–121]. What is the cause of this difference? The physical processes peculiar to the subgap-type excitation and the corresponding hierarchy of time periods were considered in Ref. [120]. Note the principal ones among them:

(i) excitation of electrons in the metal, which results in changes in the boundary conditions for the microresonator eigenmodes;

(ii) tunneling of nonequilibrium charge carriers into the semiconductor;

(iii) two-photon absorption in the semiconductor layer;

(iv) heating of the structure.

The first two processes are directly related to the band structure of the metal, and therefore the photo-induced response is determined by the metal.

Two types of electronic transitions lead to changes in metal permittivity: one is associated with the absorption by free charge carriers [the Drude contribution to the permittivity (89)] and the other with interband transitions (88). The absorption by free charge carriers in the surface metal layer produces a nonequilibrium charge carrier distribution (electrons above the Fermi level and holes below the Fermi level) in a wide energy range  $E_{\rm F} \pm \hbar \omega_{\rm pu}$ .

The interband transitions perturb the charge carrier distribution in a narrow domain corresponding to the transition energy. In a time of the order of electron – electron collision times, the strongest changes in the electron distribution function take place near the Fermi level, which results in the greatest changes in metal permittivity. That is why the existence of interband transitions in (or from) the region of the Fermi level is extremely efficient from the viewpoint of observation of metal permittivity changes [126].

Part of the nonequilibrium metal charge carriers excited by an ultrashort pulse penetrates above the Schottky barrier (or through it) into the semiconductor. If the electron velocity at the Fermi surface of the metal is  $v_F \approx 10^8$  cm s<sup>-1</sup> and the thickness of excited metal layer is  $l_{ex} \approx 2/\alpha_m(\hbar\omega) = 20-30$  nm, the time of electron transit through the barrier can be estimated as  $\tau_b \approx 10$  fs. This estimate is in good agreement with the difference response (Fig. 24) observed for negative time delays ( $t_d \approx -0.04$  ps), when the response is determined by the change in chromium permittivity, though the response for a zero delay is determined by the change in semiconductor permittivity.

After a quasi-equilibrium in the electron subsystem of the metal and the semiconductor sets in, the Schottky barrier becomes impenetrable for the majority of quasi-equilibrium electrons. The holes injected into the semiconductor from the metal during the initial excitation stage 'float up' in the valence band to penetrate back into the metal. The density of electrons injected is proportional to the density of states in the metal at the height of the Schottky barrier. The Schottky-barrier height at the *n*-type semiconductor – metal interface is  $\Phi_b \leq E_g/2$ . The nonequilibrium carriers injected into the semiconductor change its permittivity. During the action of the excitation pulse, the electrons penetrate from the metal into the semiconductor to a depth of several tens of

nanometers to become distributed over the entire film volume in a time of the order of 1 ps. The injection time is limited by the electron–electron relaxation time [120].

The metals employed in microresonator structures belong to 3d transition metals. The band structure of transition metals is characterized by five narrow d bands, which intersect and hybridize with the wide band of nearly free electrons formed from s and p states. The distinctions in the electronic structure between different transition metals are related primarily to the relative position of sp and d bands, their width and occupancy, which determine the position of the Fermi level.

We analyze the distinctive features of the density of states and interband transitions related to different positions of the Fermi level relative to the *s* bands.

Chromium (3d transition metal). In Cr, broad d bands are approximately half-filled and overlap with the sp bands at the Fermi level. The density of states at the Fermi level is low and increases with increasing  $|E - E_F|$  [132]. Unlike Cu and Ni, in Cr there is no forbidden band for interband transitions. That is why the change in the permittivity in Cr can be described only employing the Drude contribution (89), where  $\Delta \hbar \omega_{\rm p}$  is the change in the plasma frequency ( $\hbar\omega_p = 6.27 \text{ eV} [125]$ ) and  $\Delta \gamma_m$  is the change in the electron relaxation rate  $(\gamma_m = 0.063 \text{ eV} [125])$ . The Schottky-barrier height for a ZnSe/Cr structure is not precisely known, but it is on the order of 1 eV. One would therefore expect the change of the permittivity of Cr after excitation to be hardly noticeable, because the contribution of interband transitions is nonexistent. Meanwhile, Cr will be an efficient injector of electrons and holes [133], because the density of states near the Schottky-barrier energy is high.

The change in the Cr permittivity was calculated in the context of the Drude model. It follows from the above analysis that the Drude contribution to the change in the Cr permittivity is small and can be neglected. This conclusion is borne out by the measurements of the difference optical density of a pure Cr film upon femtosecond pulse excitation, wherein the difference signal (to within experimental error) was not observed.

Nickel (3d transition metal). The d bands in Ni (with a width of 4 eV and a high density of states) are nearly filled and the Fermi level is located near the upper edge of the d band [127]. For energies above the Fermi level (by 1 eV), the density of states is low and is determined by the sp bands. There is a group of interband transitions from deep d bands in the neighborhood of the Fermi level. They reside near 2.3 eV and are observed as a weak structure in stationary experimental spectra. This is due to the fact that the initial and final states are the *d*-type states and the  $d \rightarrow d$  transition is forbidden. For Ni, the variation of the permittivity in relation to the temperature is small [128], although thermomodulation experiments [129] show that there exists a characteristic structure in  $\Delta \varepsilon_{m2}(\hbar \omega)$  near the Fermi level, which vanishes at 2.3 eV. For ZnS/Ni, the Schottky-barrier height is  $\Phi_{\rm b} \approx 1.7$  eV. The excitation of the metal would therefore be expected to only slightly change the optical density of the structure under investigation, since the contribution from interband transitions is small and the electron injection into the semiconductor is also small owing to the low density of states both below and above the Schottky-barrier energy.

**Copper (3d transition metal).** The d band in copper is completely filled and resides below the Fermi level [130]. Direct transitions from the d band to the neighborhood of the

Fermi level begin at 2.1 eV. These transitions produce a strong shift and broadening of the interference mode in the band reflection – absorption spectra of a thin ZnSe film on copper in comparison with similar spectra of ZnSe films on Cr and Al (Fig. 23b). Therefore, in Cu there are two types of transitions responsible for permittivity changes: the first ones are related to the absorption by free charge carriers [the Drude contribution to the permittivity (89)] and the second ones to interband transitions result in the population of the electronic states above the Fermi level by about 0.2 eV. For ZnSe/Cu, the Schottky barrier height is  $\Phi_b \approx 1.1$  eV.

One would therefore expect that the excitation of Cu strongly changes the optical density of the structure under investigation, because there is a strong contribution from the interband transitions. Meanwhile, the electron injection into the semiconductor is small for the same reason as for Ni: due to the low density of states near the Schottky-barrier energy.

The change in the Cu permittivity can be represented by Eqns (87)–(89), where  $\hbar\omega_p = 9.3$  eV is the plasma frequency and  $\gamma_m = 33$  meV is the electron relaxation rate [131]. Comparing the experimental spectra of the difference optical density with the line reflection–absorption spectra shows that the main contribution to photo-induced processes in the energy range of  $\hbar\omega < 2.5$  eV is related to the change in the Cu permittivity, while in the higher energy range, to the change in the ZnSe permittivity is small.

An analysis reveals that the excitation entails a lowering of the plasma frequency by a value of about 5 eV. The greatest increase in the relaxation rate  $\Delta \gamma_{\rm m}$  amounts to about 100 meV. A significant permittivity change ( $|\Delta \varepsilon_{\rm m2}| \sim 1$ ) due to the contribution of interband transitions is observed in the region of transitions to the neighborhood of the Fermi level, which is located at 2.15 eV. The imaginary part of the permittivity increases below the Fermi level and decreases above the Fermi level.

Therefore, the electron structure of metals determines the differences in the photo-induced responses of ZnS and ZnSe films on these metals. For the structures on Ni and Cu, the response for time delays  $t_d < 1$  is determined by the response of a thin metal layer. For the structures on Cr, the response is determined by the change in the semiconductor permittivity irrespective of the excitation type: above or below the semiconductor forbidden band. For ZnS and ZnSe films on Cu, this response should be more pronounced, which follows from the experimental data (cf. the amplitudes of difference responses in Figs 22a and 24 with the  $\Delta D_R(\hbar\omega)$  amplitudes in Fig. 23a [119–121]).

Another contribution (during a time period of the order of the pulse length) to the change in the difference optical density for zero time delays is associated with two-photon absorption in the semiconductor. Note that second harmonic generation at the metal – semiconductor interface is also possible, and the one-photon absorption of the second harmonic in the semiconductor should entail the same effects as the twophoton absorption. The spectral dependence of two-photon absorption is directly related to the microcavity eigenmodes and copies the profile of the line absorption spectrum of the sample. The two-photon absorption changes the real part of  $\varepsilon_{s1}(\hbar\omega)$  of the semiconductor. For subgap excitation this contribution is negative, which is in qualitative agreement with the experimental signal for the difference optical density for time delays in the vicinity of the zero value. Interestingly, the microcavity-mode settling time may be longer than the time of the observed evolution of the difference spectrum. This fact may be of significance for the observation of the nonstationary Casimir effect [23] and other effects of quantum electrodynamics.

The slow relaxation stage (for times of the order of 1 ps and longer) of the photo-induced change in the reflection spectra for the structures under investigation is due to electron – phonon interaction, which results in lattice heating by the electron subsystem. The permittivity change arising from these processes has the effect that the microcavity modes shift and adopt new spectral positions.

**8.2.2 Second excitation type (overgap excitation).** For an excitation energy greater than the semiconductor energy gap width, the laser pulse is absorbed in a thin semiconductor surface layer (for ZnS and the  $\hbar\omega_{pu3}$  pumping, the thickness of this layer is  $l_{ex} = 2/\alpha_{ZnS}(\hbar\omega_{pu3} \approx 40 \text{ nm})$  to produce a nonuniform distribution of hot carriers in the semiconductor. For overgap excitation, the physical processes responsible for the observed response of the structures under investigation and the typical time scales of these processes were considered in Ref. [118], in which one-photon absorption was shown to make the main contribution for times  $t_d < 1$  ps.

The appearance of nonequilibrium charge carriers in the semiconductor layer changes the semiconductor permittivity due to the occupation of states in the conduction band and the emptying of states in the valence band (and the screening of excitonic transitions as well). This results in a change in the permittivity near the absorption edge  $\hbar \omega \approx E_g$  and a negative change of the refractive index in the subgap energy range. In the range of  $\hbar \omega > E_g$ , the permittivity change is determined by free-carrier absorption and intraband absorption. The contribution of two-photon processes is small in comparison with the one-photon processes and can be neglected.

The nonequilibrium electrons in a thin semiconductor surface layer relax due to electron – electron and electron – phonon interactions and diffuse inward to gradually fill the entire volume of the semiconductor layer. The temporal evolution of the semiconductor permittivity is determined by these processes; in this case, as Figs 22–25 suggest, the relaxation time does not exceed 0.5 ps. Similar estimates of the relaxation time of nonequilibrium charge carriers in ZnSe films on aluminum were earlier obtained from the investigations of intensity redistribution of LO-phonon satellite peaks in hot luminescence (resonance RS) spectra under the variations of ZnSe film thicknesses [59, 109]. The nonequilibrium photoelectron – phonon relaxation time at room temperature also proved to be shorter than 1 ps.

### 9. Conclusions

Optical properties of crystals were investigated with recourse to the spectroscopic techniques of surface electromagnetic waves. The investigations showed that an initially nonradiative surface plasmon of the metal in structures of the ATR prism-gap-metal and semiconductor film-metal type transformed into a set of radiative states, whose electromagnetic field is determined by the dipole-active excitations of each material of the structure and depends on the real geometry of the experiment.

The results of the experimental and theoretical investigations of optical properties of crystals testify that the light absorption in crystals of finite size is effected not in a single step (a photon being absorbed produces a phonon). A photon is initially transformed into an intermediate state of electromagnetic field in the crystal — a radiative polariton, which  $\frac{1002}{2}$  7. next interacts with the entire set of dipole-active states of the sample. As a result of this interaction, the polariton transforms into a phonon or a multiphonon excitation, an exciton or a free electron (a hole), or a plasmon of the metal substrate. In this case, the light absorption is determined by the probabilities of radiative and anharmonic decay of polariton. The polariton of a thin-film multilayer structure is a 12 mixed state of different dipole-active excitations of each 13. material of the structure. doi>14.

The spectra of films clearly exhibit absorption, thermally **15**. induced emission, and luminescence at the frequencies of 16. interference modes, a sharp increase in light absorption at the <sup>doi>17.</sup> 18. frequencies of local vibrations of impurities of the crystal lattice of the film (when they coincide with an interference mode frequency), and a rise in the intensity of spontaneous 20. RS spectra when the frequency of incident and (or) scattered light coincides with an interference mode frequency. All this 21 suggests that interference modes are real states of electromagnetic field in thin-film structures. The interference modes are homogeneously broadened, and the half-width of their <sup>1012</sup>22. bands in the absorption, thermally induced emission, and luminescence spectra is determined primarily by the radiative lifetime. Under specific conditions, the radiative lifetime is 10224. unparalleled-short among all known oscillators: it may be as short as several tens of femtoseconds. The interference modes are the experimentally well-characterized analogues of cavity modes, which are treated in the problems of quantum electrodynamics.

Taking advantage of femtosecond pulses, it is possible to selectively manipulate the boundary conditions in a micro- dollar 28. resonator and control the interference modes and also to modify the temporal, spectral, and spatial characteristics of semiconductor-metal structures. This opens up new possibilities for the incorporation of these structures into the elemental base of optoelectronics.

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