

- ¹Since the stabilization of the temperature is disturbed in the region of strong energy dissipation, because of the large heat release, we investigated 2–3 (with a maximum of 5) MSCS.
- ²The normalization of $J_c(T)$ to $J_c(0)$ and of T to T_c yields a universal function $J_c(T)$ for films having different geometrical parameters and made of different materials.
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Resonance between dipole oscillations of atoms and interference modes in crystalline films

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Investigation of the optical properties of $\text{CdS}_{1-x}\text{Se}_x$ films in the long-wave IR region of the spectrum has revealed resonance between the gap oscillations of selenium atoms and the interference modes of the films. This resonance leads to a sharp increase of the absorption at the frequencies of the gap oscillations. The experimental results agree well with the theoretical calculations. It is also shown that this resonance should always take place when the interference mode coincides with the weakly absorbing IR active oscillations, including those on the low-frequency wing of the dipole oscillation in the region of the anomalous dispersions of the dielectric constant of the layer.

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1. INTRODUCTION

The use of optical properties of thin crystalline films makes it possible, as is well known, to obtain by a rather easy direct method information on the dynamics of crystal lattices, to determine the frequencies and the damping constants of transverse and longitudinal optical phonons. What are investigated in the main are

pure materials with low impurity concentrations.

Thin films of II-VI compounds were investigated by methods of long-wave IR spectroscopy in Refs. 1–5. The theory of the optical properties of thin crystalline films of compounds with fractions of ionic bond between the atoms was developed in Ref. 6, and it follows from it that these films contain, besides phonons, a rather

large set of interference modes. The interference modes, which correspond in transmission and reflection spectra to the interference minima well known for transparent films, lie in the frequency regions $\omega < \omega_{TO}$ and $\omega > \omega_{LO}$, and their position in the frequency scale depends on the dispersion of the dielectric constant of the film material and on the film thickness.⁶ It is therefore easy to vary the frequencies of the poles of the interference modes by varying the film thickness. It is of interest to trace the influence of these modes on the optical properties of films when these modes coincide with the frequencies of weakly absorbing dipole oscillations of the crystal-atoms (phonons with small oscillator strengths).

To our knowledge, the question of resonant interaction of IR-active oscillations with interference modes of a crystalline layer have heretofore not been discussed. We report here an investigation of the optical properties of films of solid solutions of $\text{CdS}_{1-x}\text{Se}_x$ at low x using long-wave IR spectroscopy methods.

2. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The object of the investigation were films of solid solutions $\text{CdS}_{1-x}\text{Se}_x$, since the optical phonons in single-crystal samples of these compounds were investigated many times.⁷⁻⁹ According to the published data, this system belongs to the "two-mode" type of restructuring of the optical phonons when x ranges from 0 to 1. As $x \rightarrow 0$ the oscillations of the selenium atom land in a gap with zero phonon-state density between the acoustic and optical branches. The frequency of such a dipole gap oscillation of the selenium atoms is $\Omega = 180 \text{ cm}^{-1}$ and lies in the region of the anomalous dispersion of the refractive index of the solvent matrix CdS ($\Omega < \omega_{TO}$ CdS). The oscillator strength of the gap oscillation is proportional to the concentration of the selenium atoms (x) and can be easily varied with changing composition of the solid solution.

To our knowledge, the optical properties of the films of solid solutions with two-mode behavior, and in particular of $\text{CdS}_{1-x}\text{Se}_x$ films, have heretofore not been studied.

The $\text{CdS}_{1-x}\text{Se}_x$ films were prepared by vacuum sputtering on hot substrates in the form of aluminum or silver mirrors on pyroceram. After the sputtering, the films were subjected to a prolonged recrystallizing annealing, during the course of which the films acquired a single-phase hexagonal structure. The hexagonal axis (the C axis) was parallel to the substrate. The single-crystal grains of the films, 0.5 to 10 μm thick, were close-packed in the plane of the film, their X axes were randomly directed, and their diameters reached 100 μm .

The spectra of the films of a number of solid solutions $\text{CdS}_{1-x}\text{Se}_x$ with $x \approx 0.15$ were registered with a long-wave vacuum IR diffraction spectrometer¹⁰ equipped with an automatic system for recording the spectra point by point.¹¹ The spectra were recorded in p - and s -polarized light at room temperature. Fig-

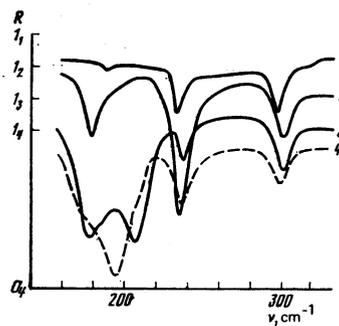


FIG. 1. Spectra of IR reflection of p -polarized light from $\text{CdS}_{1-x}\text{Se}_x$ ($x \approx 0.1$) films deposited on mirrors and having various thicknesses d : 1 - 0.8 μm , 2 - 2 μm , 3 - 3.5 μm , 4 - 6 μm .

ure 1 shows the reflection IR spectra in p -polarized light of films $\text{CdS}_{1-x}\text{Se}_x$ with $x = 0.1 \pm 0.05$ ¹⁾ of varying thickness.

It should be noted that the change of the film composition (of the value of x) by $\pm 5\%$ does not play a significant role, since the change of the phonon frequencies and of their longitudinal-transverse splitting does not exceed $\pm(1-10) \text{ cm}^{-1}$ in this case.⁷⁻⁹ The oscillations frequencies of the Cd-S dipoles when x is increased from 0 to 20% in single crystals change from $\omega_{TO}(x=0) = 237 \text{ cm}^{-1}$, $\omega_{LO}(x=0) = 298 \text{ cm}^{-1}$ to $\omega_{TO}(x=0.2) = 242 \text{ cm}^{-1}$, $\omega_{LO}(x=0.2) = 295 \text{ cm}^{-1}$, while the local oscillation in the same case also split into longitudinal and transverse components. The magnitude of the splitting $\Delta\Omega$ is proportional to x and increases from 0 to 8 cm^{-1} .

It is seen from Fig. 1, when the film thickness is increased a strong change takes place in the shape and intensity of the absorption bands near the frequency of the local oscillation. A similar picture is observed in s -polarized light. The only difference between p -polarized and s -polarized spectra is that the latter do not contain absorption bands at the frequency $\omega_{LO} \approx 290-300 \text{ cm}^{-1}$ at all film thicknesses used in the experiment (Fig. 2).

It follows from Fig. 1 that at a film thickness $d \leq 1 \mu\text{m}$ the intensities of the absorption bands ($A = 1 - R$) at the gap-oscillation frequencies $\Omega = 190 \text{ cm}^{-1}$ and $\omega_{TO}(\text{CdS}) = 235 \text{ cm}^{-1}$ are proportional to the composition of the solid solution, to x and $1 - x$, respectively. With increasing film thickness, the depth of the minima in the reflection spectrum also increases exponentially [$\exp(-\alpha d)$, where α is the absorption coefficient and is practically independent of the layer thickness d]. At a large film thickness and at the same impurity concentration, and consequently also at a constant absorption coefficient, a sharp increase of the effective absorption by the gap oscillation is observed (together with a splitting of this oscillation into two components at a

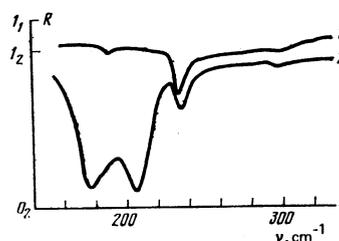


FIG. 2. IR reflection spectra of $\text{CdS}_{1-x}\text{Se}_x$ ($x \approx 0.1$) films in s -polarized light: 1 - $d = 0.8 \mu\text{m}$, 2 - $d = 3.5 \mu\text{m}$.

film thickness $3.5 \mu\text{m}$), and a decrease of the absorption by the transverse phonon of the solvent matrix CdS. With further increase of the layer thickness, one absorption band is again observed at the frequency of the impurity oscillation and with a smaller integral absorption than in the preceding case, and also an increase of the absorption at the frequency ω_{TO} of CdS.

These spectrum singularities observed with changing film thickness can be qualitatively explained in the following manner.

In the region of normal dispersion of the transverse phonon of CdS at $\omega < \omega_{TO}$, the refractive index of the crystal has a maximum and therefore, starting with a certain layered thickness, conditions for the appearance of an interference fringe can occur in this narrow frequency interval. The frequency and half-width of this interference minimum are determined by the dispersion of the refractive index and by the thickness of the layer. With increasing layered thickness, this initially single interference fringe shifts smoothly into the high-frequency region of the spectrum, and crosses in its path the gap-oscillation level. The film (plane-parallel plate) can be regarded as a Fabry-Perot interferometer. If there is no absorption in the frequency band of interest to us, then we should observe the ordinary interference pattern distorted by the dispersion of the refractive index (since the spectrum region of interest to us lies near the frequency of the transverse phonon of the plate). On the other hand if absorption is introduced inside the interferometer, at a frequency that coincides with an interferometer mode, then, as a result of multiple passage inside the interferometer, the optical path increases greatly and as a result the intensity of the absorption peak increases.

The interference (virtual) modes are the natural modes of a plane-parallel plate (film). The frequencies of these modes are determined from the equation⁶

$$\alpha \operatorname{tg}(\alpha d) = i\epsilon(\omega)\alpha_0, \quad (1)$$

where

$$\alpha = \frac{\omega}{c} [\epsilon(\omega) - \sin^2 \theta]^{1/2}, \quad \alpha_0 = \frac{\omega}{c} \cos \theta,$$

θ is the angle of incidence of the light on a film of thickness d , $\epsilon(\omega)$ is the dielectric constant of the film material. A polariton with frequency ω_{TO} is a solution of this equation when $\alpha d \approx \pi/2$. If $\alpha d = m\pi/2$ (where $m = 2, 3, 4, \dots$) we have the frequencies of the minima in the interference pattern or the poles of the interference modes. Thus, starting with a certain thickness d , the first interference-mode pole lands in the spectral region of interest to us $\omega < \omega_{TO}$, followed by the second, etc. In each case, the frequency of the interference mode coincides with the frequency of the impurity oscillation, i.e., a resonance of the Fermi type in molecular crystals sets in.¹²

Solving Maxwell's equations with the corresponding boundary conditions for a three-layer medium consisting of a vacuum (ϵ_1), the film $\text{CdS}_{1-x}\text{Se}_x$ (ϵ_2), and the metal (ϵ_3) we easily obtain an expression for the light reflection coefficient in the form (see also Ref. 13)

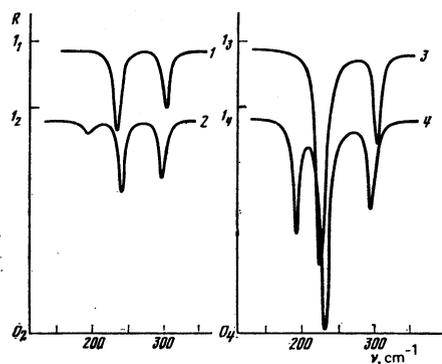


FIG. 3. A calculated reflectivities of CdS and $\text{CdS}_{0.9}\text{Se}_{0.1}$ films on aluminum mirrors in p -polarized light at an angle $\theta = 25^\circ$: 1 - $d = 1 \mu\text{m}$ (CdS), 2 - $d = 1 \mu\text{m}$ ($\text{CdS}_{0.9}\text{Se}_{0.1}$), 3 - $d = 2 \mu\text{m}$ (CdS), 4 - $d = 2 \mu\text{m}$ ($\text{CdS}_{0.9}\text{Se}_{0.1}$).

$$R = \left| \frac{(\beta_1 - \beta_2)(\beta_2 + \beta_3) + (\beta_1 + \beta_2)(\beta_3 - \beta_2)\exp(-2\kappa_2\omega d/c)}{(\beta_1 + \beta_2)(\beta_2 + \beta_3) + (\beta_1 - \beta_2)(\beta_3 - \beta_2)\exp(-2\kappa_2\omega d/c)} \right|^2, \quad (2)$$

where $\beta_i = \epsilon_i/\kappa_i$, $\kappa_i = (\epsilon_1 \sin^2 \theta - \epsilon_i)^{1/2}$, θ is the angle of incidence of the light in vacuum, and $i = 1, 2, 3$.

To use (2) for the calculations we must know the analytic expression for $\epsilon_2(\omega)$ of the solid solution $\text{CdS}_{1-x}\text{Se}_x$ at the given x . To obtain the analytic expression for $\epsilon_2(\omega)$, we use the refraction additivity principle,¹⁴ which yields for solutions of the type A_xB_{1-x}

$$\frac{\epsilon_2 - 1}{\epsilon_2 + 2} = x \frac{\epsilon_A - 1}{\epsilon_A + 2} + (1 - x) \frac{\epsilon_B - 1}{\epsilon_B + 2}. \quad (3)$$

Here $\epsilon_A(\omega)$ is the dielectric constant of CdSe, $\epsilon_B(\omega)$ is the dielectric constant of CdS.²⁾ The dielectric constant of the substrate $\epsilon_3(\omega)$ is given by¹⁵

$$\epsilon_3(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\omega\gamma} \quad (4)$$

with $\omega_p = 122,000 \text{ cm}^{-1}$ and $\gamma = 700 \text{ cm}^{-1}$ for aluminum.

Calculation by formula (2), with account taken of (3) and (4), was carried out with an electronic computer. The results of the calculation of the reflection spectrum in p -polarized light for films of several thickness are shown in Figs. 3 and 4 for pure CdS and $\text{CdS}_{0.9}\text{Se}_{0.1}$. It is seen that the experimental reflection spectra (Fig. 1)

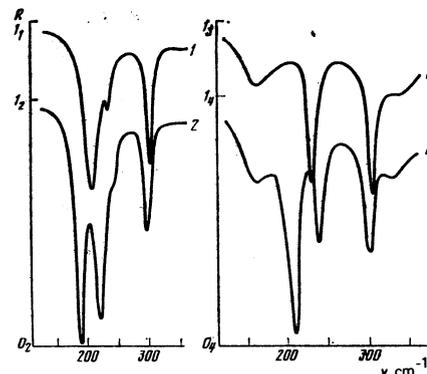


FIG. 4. Calculated reflectivity of films Cd and $\text{CdS}_{0.9}\text{Se}_{0.1}$ on aluminum mirrors in p -polarized light: 1 - $d = 3 \mu\text{m}$ (CdS), 2 - $d = 3 \mu\text{m}$ ($\text{CdS}_{0.9}\text{Se}_{0.1}$), 3 - $d = 5 \mu\text{m}$ (CdS), 4 - $d = 5 \mu\text{m}$ ($\text{CdS}_{0.9}\text{Se}_{0.1}$).

and those calculated (Figs. 3 and 4) are in qualitatively good agreement.

A comparison of the calculated reflection spectra shown in Figs. 3 and 4 makes it possible to estimate the increase of the defective optical density of the sample at the frequency of the gap oscillation under resonance conditions. It turns out that the optical density, equal to $-\ln(1-R)$, increases by 20–30 times even if the resonance conditions are not exactly fulfilled. This increase of the optical density corresponds effectively to up to 30 passes in the film. By varying the oscillator strength of the gap oscillations and calculating the optical density, we can see that the number of effective passes of the light in the film at the oscillation frequency of the selenium atoms decreases in inverse proportion to the optical density when their concentration increases (in the region of small x).

It must be noted that a similar resonance between a weakly absorbing dipole transition and an interference mode should take place in all cases. Thus, when the weakly absorbing dipole oscillations land in the region of the anomalous dispersion due to the transverse optical phonon, this effect can lead to a distortion of the band corresponding to ω_{TO} . In fact, at frequencies $\omega < \omega_{TO}$ the absorption coefficient decreases rapidly into the interference mode can amplify the absorption at the low-frequency wing of the band, thereby altering the shape of the band. This is easily demonstrated with a pure CdS film (without Se impurity) as an example. Figure 5 shows the calculated reflection spectra of CdS films of various thicknesses.

As seen from this figure, the intensity of the band of absorption by a transverse optical phonon depends strongly on the film thickness. At small thicknesses the film intensity increases exponentially with thickness until the first interference mode begins to be formed in the low-frequency region of the absorption band (the first reflection-spectrum interference minimum in the region of the sharp increase of the refractive index). The fact that the interference mode ω_1 is on the low-frequency wing of the absorption band of the transverse phonon (ω_{TO}) leads to a strong redistribution of the intensities of the absorption peaks at the frequencies ω_{TO} and ω_1 . With further increase of the film thickness, ω_1 shifts towards the low-frequency region of the spectrum and moves away from the ω_{TO} band wing. This causes an increase in the intensity of the absorption band at the frequency ω_{TO} and to a decrease of the intensity of the ω_1 band. All this proceeds as in the case of Fermi resonance of two quantum states (transfer of intensities of dipole transitions). At small film thicknesses, a shift of the ω_{TO} band towards lower frequencies is observed before the first interference mode has appeared in the region of the anomalous dispersion.⁵

The nonmonotonic character of the increase of the intensity of the ω_{TO} band with increasing thickness, and the dependence of the position of this band on the thickness, both due to interference, make it difficult to use the absorbed spectra of thin films to determine the parameters of the absorption bands. The resonance with interference modes can be neglected only if there is no

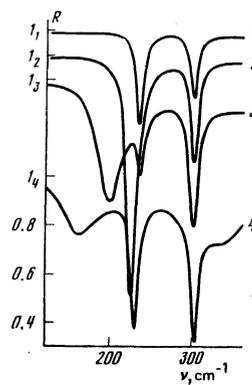


FIG. 5. Calculated reflection spectra of CdS films of various thicknesses (p polarization): 1 - $d=1 \mu\text{m}$, 2 - $d=2 \mu\text{m}$, 3 - $d=3.5 \mu\text{m}$, 4 - $d=5 \mu\text{m}$.

interference, at a very small film thickness ($d \ll \lambda/n_{\text{max}}, n_{\text{max}} \geq 10$).

Our investigations have shown that the spectra of the elementary excitations of the thin crystalline layers can differ substantially from the spectra of elementary excitations in a single crystal. The results also offer evidence that by choosing the film thickness such that one of the interference minima coincides with the frequency of the weakly absorbing IR active oscillation (state) can increase substantially (by several dozen times) the sensitivity of the IR spectroscopy method for the detection of states with small optical density (small amounts of impurities). This circumstance must be borne in mind also when protective and anti-reflection coatings are produced for optical elements, and also in the investigation of the optical samples in the submillimeter region of the spectrum where, as a rule, the sample thicknesses are comparable with the wavelength.

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- ¹The composition of the films (the quantity x) was monitored against the position of the exciton level accurate to $\pm 5\%$.
- ²The method of calculating the optical properties of solutions with the aid of additivity of the refraction does not take into account the specifics of the interaction between the atoms inside the crystal lattice, but it makes it easy to obtain the basic semiquantitative relations in the case of a "two-mode" restructuring of the phonon spectrum with change of the composition of the solid solutions.

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