Supplementary dispersion relations for optical characteristics of crystals in the exciton-resonance spectral region

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We consider the influence of interference effects connected with spatial dispersion in the exciton region of the spectrum on the validity of the Kramers-Kroning amplitude-phase relations for the reflection and transmission coefficients. The onset of supplementary terms in the classical relations is confirmed and analytic expressions are obtained for them. We investigate experimentally the supplementary relations for the exciton reflection spectra of CdSe and ZnSe crystals and for the transmission spectrum of the Cu_2O crystal (quadrupole transition).

INTRODUCTION

The Kramers-Kronig dispersion relations (DR) are by far not always applicable to crystal optics.[1,2] For the exciton region of the spectrum, in particular, the main hindrance to the applicability of the DR is due to the need for taking spatial dispersion (SD) into account. It is widely know [2–4] that the classical DR, which express the causality principle, are certainly valid for the dielectric tensor $\varepsilon_{ij}(\omega, \mathbf{k})$ only at $\mathbf{k} = 0$, i.e., in the absence of SD. However, since $\varepsilon_{ij}(\omega, \mathbf{k})$ are analytical functions of the complex wave vector, at each fixed value of $\mathbf{k}$ the same DR are effective for them in the case of weak SD ($\mathbf{k} \to 0$) as for $\mathbf{k} = 0$. Certain generalizations for the particular case of a $\mathbf{k}(\omega)$ dependence were made in Ref. 5.

Greatest interest attaches to DR between experimentally measured quantities, e.g., the refractive index and the extinction coefficient, or the amplitude and phase of reflected light. Experiments with molecular[6] and semiconducting[7] crystals have shown that violations of the DR between the refractive index and the absorption coefficient are substantial in the exciton branch of the spectrum at low temperatures, and vanish gradually with rising temperature, thus offering evidence in favor of the influence of the SD. An attempt[8] to measure the phase in low-temperature reflection spectra near exciton lines yielded results that did not correspond to the amplitude-phase DR.

In this paper we consider the relations between the optical characteristics of crystals on the basis of an investigation of the analytic properties of the complex reflection and transmission coefficients. In our opinion, this approach permits a most natural analysis of the singularities that lead to violation of the amplitude-phase DR, and verify experimentally the theoretical results.

I. THEORY

1. Analytic properties of reflection and transmission coefficients

In macroscopic solid-state theory, the SD represents the nonlocality of the connection between the quantities that describe electromagnetic processes in a medium.[3,4] Verification of the analytic properties of $\varepsilon_{ij}(\tilde{\omega}, \mathbf{k}(\tilde{\omega}))$ as functions of the complex variable $\tilde{\omega}$ is made complicated by the presence of additional integration over space in the linear relation between the electric induction $\mathbf{D}(r_0, t_0)$ and the electric field intensity $\mathbf{E}(r, t)$.[2] One can attempt, however, to get around this difficulty by choosing for the medium response functions that do not express explicitly the nonlocality of the interaction. Assume that an electromagnetic wave is incident from vacuum on a crystal plate and produces on the front face an intensity $E_0(t)$. We can then write for the respective intensities $E_1(t)$ and $E_2(t)$ of the reflected and transmitted waves

$$E_1(t) = \int_0^\infty \rho(t') E_0(t-t')\, dt',$$
$$E_2(t) = \int_0^\infty \tau(t') E_0\left(t-t'-\frac{z}{c}\right) dt', \tag{1}$$

where c is the speed of light in vacuum, z is the plate thickness, and the functions $\rho(t)$ and $\tau(t)$ are defined by the same token as the reflection and transmission coefficients of the crystal.[1)] Equations (1) relate quantities that describe the electromagnetic field in vacuum, and in the sense of the stationary problem are taken to be the boundary conditions; they describe therefore a local response of a linear medium.

It follows from expressions of type (1), written with account taken of the causality principle (see, e.g., Refs. 4, 5, and 9), that the Fourier transforms of the response functions, in this case $\rho(\omega)$ and $\tau'(\omega) \equiv \tau(\omega) \exp(-iz\omega/c)$, have unique analytic continuations into the upper half-plane of their variable, including an infinitely remote point. In addition, from the requirement that the response be real if $E_0(t)$ is real [a similar analysis was made, e.g., in Refs. 2 for $\varepsilon_{ij}(\tilde{\omega}, \mathbf{k})$] we can obtain that

$$\tau^*(\tilde{\omega}) = \tau(-\tilde{\omega}^*), \quad \rho^*(\tilde{\omega}) = \rho(-\tilde{\omega}^*). \tag{2}$$

The analyticity of the functions $\rho(\tilde{\omega})$ and $\tau(\tilde{\omega})$ in the upper half-plane of the complex variable $\tilde{\omega}$ [hereafter designated $I_+(\tilde{\omega})$] enables us to write down DR between their real and imaginary parts, while relation (2) permits the integration to be restricted to the region $\omega > 0$.

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$$\mathrm{Re}\,(\rho(\omega)-\rho_0)=\frac{2}{\pi}\int_0^\infty \frac{x\,\mathrm{Im}\,(\rho(x)-\rho_0)}{x^2-\omega^2}\,dx,$$

$$\mathrm{Im}\,(\rho(\omega)-\rho_0)=-\frac{2\omega}{\pi}\int_0^\infty \frac{\mathrm{Re}\,(\rho(x)-\rho_0)}{x^2-\omega^2}\,dx, \tag{3}$$

$$\mathrm{Re}\,(\tau'(\omega)-\tau_0)=\frac{2}{\pi}\int_0^\infty \frac{x\,\mathrm{Im}\,(\tau'(x)-\tau_0)}{x^2-\omega^2}\,dx$$

$$\mathrm{Im}\,(\tau'(\omega)-\tau_0)=-\frac{2\omega}{\pi}\int_0^\infty \frac{\mathrm{Re}\,(\tau'(x)-\tau_0)}{x^2-\omega^2}\,dx, \tag{4}$$

where ρ_0 and τ_0 are the limits of the functions $\rho(\tilde\omega)$ and $\tau'(\tilde\omega)$ as $|\tilde\omega|\to\infty$. Integration is meant everywhere in the sense of the principal value.

When an isolated exciton transition is considered, the contributions of the remaining resonances are usually taken into account by introducing the background dielectric constant over the entire spectrum. In this case the speed of light in (1) must be replaced by c/n_0, where $n_0=\sqrt{\varepsilon_0}$ is the background refractive index, and $\tau'(\tilde\omega)$ must be taken to mean

$$\tau'(\omega)\equiv\tau(\omega)\exp(-ik_0z),$$

where $k_0=n_0\omega/c$. In addition, in the isolated-resonance model the role of the imaginary coordinate in $I_+(\tilde\omega)$ is assumed by the damping γ (Ref. 10).

2. Amplitude-phase relations in transmission spectra

From the analyticity of the function

$$\rho(\tilde\omega)\equiv|\rho(\tilde\omega)|\exp i\delta(\tilde\omega)$$

it follows that its logarithm

$$\mathrm{Ln}\,\rho(\tilde\omega)=\ln|\rho(\tilde\omega)|+i\delta(\tilde\omega)$$

is also an analytic function in $I_+(\tilde\omega)$, except for the points at which $\rho(\tilde\omega)$ vanishes. According to Ref. 11 the coefficient of reflection from a crystal having nonzero absorption cannot vanish. Therefore in crystal optics without allowance for SD the classical DR between the amplitude and phase of the reflected light are valid.

An essential feature of SD is that the reflection coefficient can vanish in a crystal with finite damping (the analog of the Brewster effect in the exciton region 12).

Let $\tilde\omega_0=\omega_0+i\gamma_0$ be a first-order zero of the function $\rho(\tilde\omega)$ in $I_+(\tilde\omega)$. The measured amplitude and phase reflection functions correspond to values of $\rho(\tilde\omega)$ on a certain point shifted in $I_+(\tilde\omega)$ by the value of the damping $\gamma(\omega)$. If $\gamma_0<\gamma(\omega_0)$, the function $\mathrm{Ln}\,\rho(\tilde\omega)$ is analytic in the region of $I_+(\tilde\omega)$ bounded from below by the $\gamma(\omega)$ curve, and the classical DR between the measured quantities are valid. If $\gamma_0>\gamma(\omega_0)$ the logarithmic singularity of the function $\rho(\tilde\omega)$ turns out to be in the region of $I_+(\tilde\omega)$ that is vital for obtaining the integral relations, and the classical DR are violated. The contribution of the logarithmic singularity to the amplitude-phase DR is determined from an analysis of the integral[2)]

$$\int_C \frac{\mathrm{Ln}[\rho(\tilde x)/\rho_0]-ia}{\tilde x-\tilde\omega}\,d\tilde x=\oint_{\gamma(\omega)} \frac{\ln|\rho(\tilde x)/\rho_0|+i[\delta(\tilde x)-a]}{\tilde x-\tilde\omega}\,d\tilde x$$
$$+\int_G \frac{\ln|\rho(\tilde x)/\rho_0|+i[\delta(\tilde x)-a]}{\tilde x-\tilde\omega}$$
$$d\tilde x-i\pi\{\ln|\rho(\tilde\omega)/\rho_0|+i[\delta(\tilde\omega)-a]\}=0, \tag{5}$$

where the integration contour C differs from the usual one (Ref. 2, Fig. 3) that is closed at infinity with the pole singularity on the section $\gamma(\tilde\omega)$ bypassed because of the presence of the section G that bypasses the logarithmic singularity; $a=\delta_0$ at $\omega<\omega_0$ and $a=\delta_0+2\pi$ at $\omega>\omega_0$, where δ_0 is the phase of the coefficient ρ_0. Integrating[3)] along the contour G and recognizing that the integral of the measured quantities along the real axis is an integral with respect to $\gamma(\omega)$, we obtain the supplementary DR:

$$\delta(\omega)=\frac{\omega}{\pi}\int_0^\infty \frac{\ln[R_0/R(x)]}{x^2-\omega^2}\,dx+2\,\mathrm{arctg}\,\frac{\gamma_0-\gamma(\omega)}{\omega_0-\omega}+a, \tag{6}$$

$$\ln[R(\omega)/R_0]=\frac{4}{\pi}\int_0^\infty \frac{x(\delta(x)-a)}{x^2-\omega^2}\,dx\cdot$$
$$+2\ln\left[1+\left(\frac{\gamma_0-\gamma(\omega)}{\omega_0-\omega}\right)^2\right], \tag{7}$$

where $R(\omega)=\rho(\omega)\rho^*(\omega)$ and $R_0=\rho_0\rho$ are the energy reflection coefficients.

The relations obtained explain not only the violation of the classical amplitude-phase DR in exciton reflection spectra at low temperatures, but also the "nonclassical" behavior of the reflected-light phase, wherein the long- and short-wave limits of $\delta(\omega)$ differ by 2π.[13-17] Therefore the quantity γ_0 has the same meaning as the limiting damping constant,[14,17] which is the upper limit of the damping values[4)] at which the phase in the spectrum can change by 2π.

It is easily seen that at low values of $\gamma_0-\gamma(\omega)$ the contributions from the logarithmic singularity may turn out to be dominant only in the vicinity of ω_0. We can therefore with good accuracy replace $\gamma(\omega)$ in (6) and (7) by $\gamma(\omega_0)$.

§ 3. Amplitude-phase relations in transmission spectra

For analogy with classical crystal optics, it is convenient, when considering the amplitude-phase spectra, to introduce the concept of effective refractive index $\tilde n(\omega)=n(\omega)+i(\varkappa\omega)$. It can be specified by writing down the expression for the coefficient of transmission through a layer of thickness z in a semi-infinite crystal[18] in the form

$$\tau'(\omega)=[1+\rho(\omega)]\exp[i(\omega/c)\Delta\tilde n(\omega)z], \tag{8}$$

where $\Delta\tilde n(\omega)=\tilde n(\omega)-n_0$. The interference of the opto-exciton waves leads to a dependence of the so-defined effective refractive index on the crystal thickness.

In accordance with the maximum-modulus principle, we can state that in $I_+(\tilde\omega)$ we have $|\rho(\omega)|<1$. Therefore the function

$$\Theta(\tilde\omega)=\tau'(\tilde\omega)/[1+\rho(\tilde\omega)]$$

is analytic in $I_+(\tilde\omega)$. The proof given in Ref. 9 that the function $\Theta(\tilde\omega)$ has no zeros is not valid in our case, since it is based

on a fact obvious for classical crystal optics, that the refractive index is independent of the crystal thickness. To obtain the DR between the refractive index and the extinction coefficient with allowance for interference of the opto-exciton waves it is therefore necessary to use an analysis similar to that given in the preceding section.

In this case, if $\tilde{\omega}_{0j} = \omega_{0j} + i\gamma_{0j}$ are zeros of the function $\Theta(\tilde{\omega})$ in $I_+(\tilde{\omega})$, the supplementary DR are of the form

$$\Delta n(\omega) = \frac{2}{\pi}\int_0^\infty \frac{x\varkappa(x)}{x^2-\omega^2}dx + \frac{2c}{\omega z}\sum_j \operatorname{arctg}\frac{\gamma_{0j}-\gamma}{\omega_{0j}-\omega}, \tag{9}$$

$$\varkappa(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\Delta n(x)}{x^2-\omega^2}dx - \frac{c}{\omega z}\sum_j \ln\left[1+\left(\frac{\gamma_{0j}-\gamma}{\omega_{0j}-\omega}\right)^2\right]. \tag{10}$$

The phase terms corresponding to a in Eq. (6) are left out here to preserve the analogy with classical crystal optics, where the refractive index is uniquely determined from the connection between the vector **k** of the transverse waves and the dielectric constant. The latter is incorrect when account is taken of the SD, and it is therefore not surprising that the function $\Delta n(\omega)$, defined only in terms of the phase of the transmitted light, becomes non-single-valued.

§ 4. Possibilities of using the supplementary DR

The newly obtained relations cannot be used directly to calculate the phase spectra from the known amplitude spectra, and vice versa. This calls for knowledge of the coordinate of the singularities of $I_+(\tilde{\omega})$ and of the damping constant. Amplitude and phase measurements in the exciton region of the spectrum are thus mutually complementary, as was already noted in Ref. 13.

The problem of determining the positions of the zeros of $\rho(\tilde{\omega})$ and $\Theta(\tilde{\omega})$ in $I_+(\tilde{\omega})$, which are due to interference of the opto-exciton waves, presupposed the use of supplementary boundary conditions (SBC) in some form of another (otherwise the ratio of the amplitudes of the interfering waves is not defined). This adds to the unknown parameters of the exciton transition one other that characterizes the effect of the surface on the dielectric constant of an infinite crystal.[20] On the other hand the values, determined from joint amplitude-phase measurements, of the additional terms (the contributions of the logarithmic singularities) in (6), (7), (9), and (10) yield new information that allows us to check whether the SBC and the values of the parameters were correctly chosen.

In the reduction of the experimental results we used the supplementary DR (6) and (9), which express the phase characteristics in terms of the amplitude characteristics, and the Pekar SBC.[19,21,22] The supplementary parameter in this case was the thickness l of the "dead" layer.[23] We note that the effect of the dead layer as a clearing film[11] can lead to violation of the DR in the absence of SD.[5)]

To indicate another possibility of employing the foregoing results, we rewrite (3) and (4) in terms of the amplitude and the phase

$$\cos\delta(\omega) = \frac{2|\rho_0|}{\pi|\rho(\omega)|}\left\{\frac{\pi}{2} + \int_0^\infty \frac{x|\rho(x)/\rho_0|\sin\delta(x)}{x^2-\omega^2}dx\right\}, \tag{11}$$

$$\sin\delta(\omega) = -\frac{2\omega|\rho_0|}{\pi|\rho(\omega)|}\int_0^\infty \frac{|\rho(x)/\rho_0|\cos\delta(x)-1}{x^2-\omega^2}dx;$$

$$\cos b(\omega) = \frac{2\exp d(\omega)}{\pi}\left\{\frac{\pi}{2} + \int_0^\infty \frac{x\exp(-d(x))\sin b(x)}{x^2-\omega^2}dx\right\}, \tag{12}$$

$$\sin b(\omega) = -\frac{2\omega\exp d(\omega)}{\pi}\int_0^\infty \frac{\exp(-d(x))\cos b(x)-1}{x^2-\omega^2}dx,$$

where $b(\omega) + id(\omega) \equiv (\omega/c)z\Delta\tilde{n}(\omega)$. The relations obtained, which are valid both in ordinary crystal optics and when SD is taken into account, represent weaker restrictions on the changes of the amplitude and phase of the reflected (and transmitted) light than the classical DR. There are systems of linear integral equations in the functions $|\rho(\omega)/\rho_0|\cos\delta(\omega) - 1$ and $|\rho(\omega)/\rho_0|\sin(\omega)$ (11) as well as $\exp(-d(\omega))\cos b(\omega) - 1$ and $\exp(-d(\omega))\sin b(\omega)$ (12). Given the amplitude spectra, the phase solutions (11) and (12) are not unique. It can be shown that besides the true phase functions $\delta(\omega)$ and $b(\omega)$ determined in the general case by the supplementary DR, relations (11) and (12) are also satisfied by the functions $\delta_k(\omega)$ and $(\omega/c)z\Delta n_k(\omega)$, which correspond to the first terms in the right-hand sides of (6) and (9). Nonetheless, a search for the true phase solutions is possible in certain cases if the supplementary DR (6) and (9) are used. After determining the first term in the right-hand side and knowing the analytic expression for the second term, approximate satisfaction of (11) and (12) can be achieved by varying the parameters ω_{0j} and $\gamma_{0j} - \gamma$. The result of such an analysis is a reconstruction of the phase spectrum from the known amplitude spectrum. This is done, however, by a more complicated and less reliable method than the use of DR in ordinary crystal optics.

§ 5. Analysis of transmission spectrum on the basis of supplementary DR

The dependence of the zero-reflection coordinates for p- and s-polarization on the dead-layer thickness and on the light incidence angle in the SBC method[23] was considered in Ref. 24. Our calculations of $\Theta(\tilde{\omega})$ by using the SBS from Ref. 19 (dipole transitions) and Ref. 21 (quadrupole transitions) have shown that all the transmission zeros in $I_+(\tilde{\omega})$ lie in the band $\gamma < \gamma_{cr}$, where γ_{cr} is the imaginary coordinate of the branch point of the dispersion-equation solution in the effective-mass approximation: $\tilde{\omega}_{cr} = \omega_{res} + i\gamma_{cr}$. At $\gamma > \gamma_{cr}$ the classical DR between $\Delta n(\omega)$ and $\varkappa(\omega)$ are thus satisfied; this corresponds to the conclusion that the SD has a negligibly small effect.[10,25,26] In the case $\gamma < \gamma_{cr}$, the number of zeros of $\Theta(\tilde{\omega})$ in the vital region of $I_+(\tilde{\omega})$ increases with increasing crystal thickness, and each individual zero point moves in such a way that $\tilde{\omega}_{0j}(z) \to \tilde{\omega}_{cr}$, and the larger z the closer the trajectory $\tilde{\omega}_{0j}(z)$ to the curve corresponding to equality of the extinction coefficient of opto-exciton waves of various types.[10]

Taking into account this behavior of the singularities of the function $\Delta\tilde{n}(\tilde{\omega})$, we can describe on the basis of the supplementary DR the interference thickness dependence of the optical quantities in the exciton-resonance region (e.g., the integral absorption—see Ref. 18, Fig. 2). It can be also be shown that $\Delta\tilde{n}(\tilde{\omega})$ (8) coincides at $z=0$ with the effective refractive index, used in many papers, for reflection at normal incidence of light

$$n(\tilde{\omega})=[1-\rho(\tilde{\omega})]/[1+\rho(\tilde{\omega})], \qquad (13)$$

which can be easily seen to be a function analytic in $I_+(\tilde{\omega})$. Therefore the usual DR are valid at $z=0$, and the integral absorption reaches its classical value. At small crystal thicknesses, the appearance of each new transmission zero and its displacement in $I_+(\tilde{\omega})$ causes large "perturbations" of $\Delta\tilde{n}(\tilde{\omega})$. An increase of the thickness causes the zeros to condense in the region of $\tilde{\omega}_{cr}$, and their combined influence exceeds considerably the influence of the individual zeros in the region $\gamma<\gamma_{cr}$. At large z one can approximately conceive, at the point $\tilde{\omega}_{cr}$, of one transmission zero whose multiplicity increases linearly with thickness ($\Delta n(\omega)$ and $\varkappa(\omega)$ cease to depend on the thickness). This treatment, in addition to the usual notions concerning damped thickness-governed oscillations, explains also the increase of the integral absorption as $z\to 0$.

Thus, even a qualitative analysis based on the supplementary DR helps describe a number of singularities of the spectral characteristics of crystals near exciton resonances.

II. EXPERIMENT

1. Procedure

The experimental setup was built around a DFS-12 spectrometer. For photography we used also the spectrographs DFS-8, DFS-4, and DAS-2. The amplitude spectra were measured by the usual procedure with modulation of the light beam and with synchronous detection. The results were referred to the values of the amplitude far from the resonances, inasmuch as for our purposes we need determine only the relative reflection coefficient $R(\omega)/R_0$ and the absorption coefficient in the region of an isolated resonance. The small dispersion of the refractive index in the vicinity of the quadrupole transition of Cu_2O (Ref. 27) allows us to neglect the spectral changes of the reflection and obviates the need for the appropriate correction to the absorption coefficient of a sufficiently thick crystal.

The phase spectra were measured both with a Bequerel interferometer (Ref. 13) and by modulating the phase difference between the signals in two mutually perpendicular polarizations, followed by synchronous detection at the modulation frequency. The phase difference was made periodic in time by vibrating a birefringent wedge (along the thickness-variation direction perpendicular to the spectrometer slit) placed between the crystal and the analyzer. By varying the average position of the wedge or by introducing a quarter-wave plate it was possible to obtain signals that were proportional in the case of reflection at oblique incidence of the light, e.g., $|\rho_s(\omega)\rho_p(\omega)|\cos\delta(\omega)$ and $|\rho_s(\omega)\rho_p(\omega)|\sin\delta(\omega)$, where $\delta(\omega)=\delta_p(\omega)-\delta_s(\omega)$, is the phase difference between the p- and s- polarizations of the reflected light. Synchronous detection preserves the information on the signs of the measured quantities, so that the phase is determined accurate to a term $\pm 2\pi$. A similar procedure is described in greater detail, e.g., in Ref. 16.

We note that analyticity of the functions $\rho_p(\tilde{\omega})\rho_s^*(\tilde{\omega})$ and $\tau_\parallel'(\tilde{\omega})\tau_\perp'^*(\tilde{\omega})$ (the symbols $\parallel$ and $\perp$ pertain to the orientation of the vector **E** of the corresponding wave relative to the direction of the variation of the wedge thickness) in $I_+(\tilde{\omega})$ can decrease the number of measurements in this procedure by one-half, owing to the use of relations of the type (11) and (12). The quantitative differences between the phase spectra obtained by the procedure of Ref. 13 and by modulating the phase difference do not exceed 5°.

§2. Results and their reduction

1. *Reflection from hexagonal* CdSe *crystals (T = 4.2 and 77 K)*

The CdSe crystals were mounted such that the hexagonal axis, which lies in the plane of the reflecting face, was perpendicular to the incidence plane. In this case the polarization of the leading line of the exciton spectrum $A_{n=1}$ coincides in the dipole approximation with the incidence plane, meaning that the spectral changes of the reflection coefficient and of the phase take place only in the p component.[13,14,16] Measurement of the amplitude-phase reflection spectra in a wide range of incidence angles has shown that at $\varphi\geqslant\varphi_{Br}$ ($\varphi_{Br}\approx 71°$) the DR are satisfied independently of temperature. At $\varphi<\varphi_{Br}$ the difference between the experimental phase spectra and those calculated with the usual DR increased with increasing incidence angle, and the deviation at lower temperature was larger (at $T=77$ K, and at small incidence angles, the experimental spectra satisified the DR). Thus, φ_{Br} (Refs. 17, 24) is the limiting incidence angle at which the reflection zero turns out to be in $I_+(\tilde{\omega})$. In Ref.

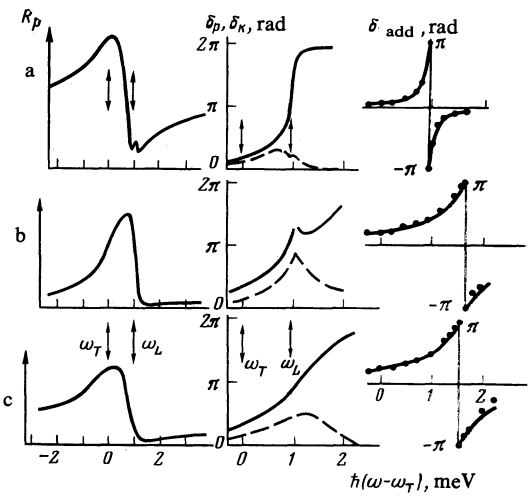

FIG. 1. Reflection energy and phase spectra in the region of the exciton transition $A_{n=1}$ of a CdSe crystal: a—$T=4.2$ K, $\varphi=45°$; b—$T=4.2$ K, $\varphi=65°$; c—$T=77$ K, $\varphi=65°$. The solid lines denote the experimental reflection and phase spectra and the calculated $\delta_{add}(\omega)$ with parameters obtained from experiment. The dashed lines show the spectra $\delta_\kappa(\omega)$ calculated using the usual DR from the energy spectra. Points—experimental values of the additional term; ω_L and ω_T are the longitudinal and transverse exciton frequencies.

17 it was shown by calculation that Γ_{lim} for an acutal crystal increases when the incidence angle is varied from zero to φ_{Br}. The latter, according to (6), leads to an increase, with increase of angle, of the additional phase term at each fixed point of the spectrum, and it is this which explains the described angular dependence of the amplitude-phase relations.

Figure 1 shows the energy and phase reflection spectra of the CdSe crystal at $T = 4.2$ and 77 K and at different incidence angles. They were reduced on the basis of (6) by separating and analyzing the additional phase term

$$\delta_{\text{add}}(\omega) = 2 \operatorname{arctg} \frac{\gamma_0 - \gamma(\omega_0)}{\omega_0 - \omega}.$$

It is easily seen that ω_0 corresponds to the point of the spectrum at which $\delta_{\text{add}}(\omega_0) = \pm\pi$. By measuring $\delta_{\text{add}}(\omega)$ at some other frequency not too different from ω_0, we can obtain the value of $\gamma_0 - \gamma(\omega_0)$. Next, solving with a computer the equation $\rho(\tilde{\omega}, \varphi, l) = 0$ (in the model with the SBC[19] and with a dead layer) at a fixed incidence angle, we established the relation

$$\tilde{\omega}_0(l) = \omega_0(l) + i\gamma_0(l),$$

which enabled us to determine the values of l and γ_0, and hence also the damping $\gamma(\omega_0)$. It suffices to determine the thickness l for one incidence angle. It can be shown that the best accuracy is reached at $\varphi \approx \varphi_{\text{Br}}$. The value obtained was used to plot $\omega_0(\varphi)$ and $\gamma_0(\varphi)$. The calculated values of $\omega_0(\varphi)$ are in good agreement with the experimental ones, thereby confirming the model employed. At incidence angles $45 < \varphi < \varphi_{\text{Br}}$ it is possible to record in experiment the variation of the frequency ω_0 in a quite sizable spectral range $\omega_0 > \omega_L$. This makes it possible, knowing $\gamma_0(\varphi)$, to track the frequency dependence of the damping in the given spectral region. Our measurements, however, revealed no substantial changes of $\gamma(\omega)$ in the indicated region at either liquid helium or nitrogen temperature. The results of the reduction of the spectra shown partially in Figs. 1a and 1b ($T = 4.2$ K) are:

φ	0°	25°	45°	65°
$\hbar(\omega_0 - \omega_T)$ (meV)	0.92	0.92	0.96	1.69
$\hbar(\gamma_0 - \gamma(\omega_0))$ (meV)	0.014	0.027	0.082	0.535
$\hbar\gamma_0$ (meV)	0.036	0.052	0.109	0.558
$\hbar\gamma(\omega_0)$ (meV)	0.022	0.025	0.027	0.023

The values of ω_0 correspond to a dead-layer thickness $l = 7.0 \pm 0.5$ nm.

It was indicated above that the usual amplitude-phase DR hold at liquid-nitrogen temperature and at small incidence angles. Violation of the DR comes into play in the phase spectra at $\varphi \approx 50°$, but already at $\varphi = 65°$ the additional phase term reaches approximately the same value as at $T = 4.2$ K (see Fig. 1c). This indicates that in a CdSe crystal a temperature rise, besides increasing the damping, changes also the $\gamma_0(\varphi)$ dependence. Calculation shows that this behavior of the anglular dependence is due to an increase of the dead-layer thickness. Reduction of the experimental spectra shown in Fig. 1c ($T = 77$ K, $\varphi = 65°$) leads to the following results:

$$\hbar(\omega_0 - \omega_T) = 1.53 \text{ meV}, \quad \hbar\gamma_0 = 0.8 \text{ meV},$$
$$\hbar\gamma(\omega_0) = 0.31 \pm 0.02 \text{ meV}, \quad l = 10.5 \pm 0.5 \text{ nm}$$

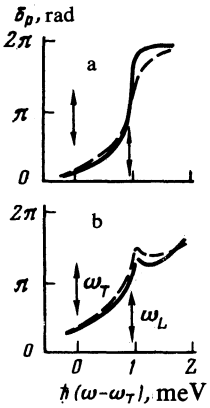

FIG. 2. Comparison of the reflection phase spectra of CdSe crystal ($A_{n=1}$), calculated from relations (6) and (11) (dashed lines), with experiment (solid lines): $T = 4.2$ K, $\varphi = 45°$ (a), $\varphi = 65°$ (b).

From the energy reflection spectra of the CdSe crystal at $T = 4.2$ K ($\varphi = 45$ and 65°) and $T = 77$ K ($\varphi = 65°$) we were able to obtain the phase spectrum with the aid of (11). To this end, expressions (11) were transformed so as the leave in the left-hand sides only the trigonometric functions of the additional phase term, whose spectral dependence was specified in the form

$$\delta_{\text{add}}(\omega) = 2 \operatorname{arctg} \frac{Q}{B - \omega},$$

where Q and B are fit parameters whose variation leads to the equality. When a concrete value of $\delta_{\text{add}}(\omega)$ is substituted in the newly obtained equation, the deviation from the equalities can be characterized by a function $F(Q, B)$. This reduces the problem to a search for the minimum of a function. The deviation from equalities [the sum of the absolute values of the differences of the right- and left-hand parts of two working equations, referred to $\delta_{\text{add}}(\omega)$] was averaged over a spectral interval made commensurate with Q. The comparison interval was chosen in the region of the most appreciable overlap of the functions $\delta_k(\omega)$ and $\delta_{\text{add}}(\omega)$. Variation of B changes the degree of the overlap and distorts strongly the result of the minimization of the deviation with respect to the parameter Q. However, the sought value of B is none other than the spectral coordinate of the zero of the function $\rho(\tilde{\omega})$ so that it is reasonable to multiply the deviation function by the energy reflection coefficient: $F(Q, B) = R(B)F_0(Q, B)$.

Some of the phase spectra obtained in this manner are compared with the experimental ones in Fig. 2. It can be seen that this method is suitable at any rate for a qualitative estimate of the phase spectra from the reflection spectra.

2. *Reflection of light from cubic* **ZnSe** *crystals (4.2* **K***)*

The dipole transition corresponding to the leading line of the exciton spectrum of the ZnSe spectrum is allowed for any polarization state. Therefore spectral (amplitude and phase) changes of the reflection coefficient always take place both in the p and in the s components of the reflected light. The phase spectra of cubic crystals were first measured in Ref. 17. The properties of the investigated ZnSe spectra turned out to differ more from ideal than the properties of

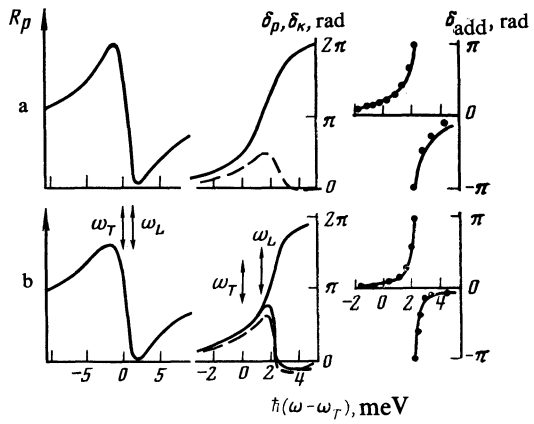

FIG. 3. Reflection energy and phase spectra of ZnSe crystals in the spectral region of the leading exciton-spectrum line. The notation is that of Fig. 2.

the CdSe crystal. Therefore deviations from the ususal DR (change of phase in the spectrum by 2π) could be obtained only for incidence angles close to φ_{Br} ($\varphi_{Br} \approx 71°$). Figure 3 shows the amplitude and phase spectra of the two ZnSe samples at an incidence angle $\varphi = 67°$. The quantity measured for cubic crystals is $\delta(\omega) = \delta_p(\omega) - \delta_s(\omega)$. In Ref. 17, however, a qualitative similarity was observed between the phase curves of cubic and hexagonal crystals in obliquely incident light. Calculation of the phase in the s component, using the DR for reflection spectra, yields a change $\delta_s(\omega)$ within 6° for both samples at $\varphi = 67°$, so that it can be assumed that $\delta(\omega) \approx \delta_p(\omega)$. The parameters obtained for the first sample (Fig. 3a) were

$$\hbar(\omega_0-\omega_T)=2.25\ \text{meV}, \quad \hbar\gamma_0=1.41\ \text{meV},$$
$$\hbar\gamma(\omega_0)=0.7\pm0.1\ \text{meV}, \quad l=7.1\pm0.5\ \text{nm}.$$

The phase spectrum of the second sample, obtained by using a Becquerel interferometer, has at $\omega > \omega_L$ a two-mode structure (Fig. 3b; see also Ref. 17). The lower branch is in good agreement with the usual DR, i.e., corresponds to the function $\delta_k(\omega)$. The upper branch is described by Eq. (6) with

$$\hbar(\omega_0-\omega_T)=2.2\ \text{meV}, \quad \hbar\gamma_0=1.42\ \text{meV},$$
$$\hbar\gamma(\omega_0)=1.2\pm0.1\ \text{meV},$$

corresponding to a dead-layer thickness $l = 7.3 \pm 0.5$ nm. The presence of a two-mode picture is evidence of a "mosaic" structure of the crystal surface relative to the damping,[17] whose scatter is estimated at ~ 0.3 meV. A remarkable fact is that the frequency ω_0 and an estimate of the dead-layer thickness can be deduced directly from the two-mode phase spectrum obtained with a Becquerel interferometer.

3. *Transmission of cubic* Cu_2O *crystals in the quadrupole-transition region (T = 4.2* K*)*

Transition to the lowest exciton state of cuprous oxide is dipole-forbidden. In the quadrupole approximation, for light propagating along the C_2 crystal axis, the line in polarized; $\mathbf{E} \| C_4$ (Ref. 28). In Refs. 18 and 27 we observed the birefringence and investigated the influence of SD on the optical characteristics of Cu_2O crystals in the vicinity of a quadrupole transition. The experimental geometry corresponded to complete polarization of the exciton line and to maximum birefringence.

The spectral interval in which the opto-exciton waves E_+ and E_- are comparable in amplitude at $\gamma = 0$, and the critical damping connected with the quadrupole-transition oscillator strength,[29] are small quantities compared with the corresponding dipole-transition parameters. Nevertheless, in hydrothermal Cu_2O samples it was possible to observe experimentally the decrease, peculiar to SD, of the integral absorption as $T \to 0$ (Ref. 30). This means that at low temperatures the damping constant in the region of the quadrupole transition can be smaller than critical ($\hbar\gamma_{cr} = 4.1 \times 10^{-7}$ eV). In this case the interference of the opto-exciton waves should lead to the appearance of transmission zeros in the $I_+(\tilde{\omega})$ region bounded from below by the $\gamma(\omega)$ curve. The thickness of the Cu_2O crystal investigated by us (3 mm) was larger by about two orders than the period of the thickness-dependent oscillations of the integral absorption.[18] It can therefore be approximately assumed that all the transmission zeros are concentrated at the point $\tilde{\omega}_{cr}$. The additional term in (9) takes then the form

$$\Delta n_{add}(\omega) \approx \frac{2cN}{\omega_{res} z} \operatorname{arctg} \frac{Q}{\omega_{res} - \omega},$$

where N is the number of the transmission zeros in $I_+(\tilde{\omega})$ and $Q = \gamma_{cr} - \gamma(\omega_{res})$. By calculating the refractive indices $\tilde{n}_\pm(\omega)$ we can estimate the number of zeros, viz., $N \approx 120$ at $z = 3$ mm.

The experimental width of the quadrupole line in the case when a decrease of the integral absorption is observed[30] is noticeably larger than that calculated from the SD theory, so that the broadening must be taken into account. The broadened birefringence and absorption curves calculated[18] by the formulas of the SD theory using the additional boundary conditions[21] at $\hbar\gamma = 10^{-7}$ eV and a half-width of the instrumental function 0.6×10^{-4} eV (0.5 cm^{-1}) are in good agreement with experiment. For the additional phase term

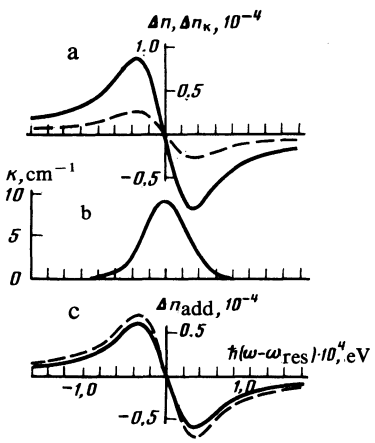

FIG. 4. Birefringence (a), absorption (b), and additional phase terms (c) in the region of the quadrupole absorption line of a cuprous-oxide crystal. Solid lines—experiment; dashed—birefringence calculated with the usual DR (a) and $\Delta n_{add}(\omega)$ calculated from Eq. (14) (c).

we can write, when account is taken of the broadening,

$$\Delta n_{\text{add}}(\omega)=\frac{2cN}{\omega_{\text{res}}z}\int_0^\infty A(\omega-x)\operatorname{arctg}\frac{Q}{\omega_{\text{res}}-x}\,dx. \qquad (14)$$

It is reasonable to use for $A(\omega-x)$ a Gaussian distribution. The integral in (14) can then be determined by asymptotic methods.

The experimental birefringence and absorption curves are shown in Fig. 4. The value of Δn_{add} calculated from Eq. (14) at $Q=3.1\times10^{-7}$ eV, half-width $A(\omega-x)=0.6\cdot10^{-4}$ eV, and $N=120$ (Fig. 4c) describes well the difference between the birefringence obtained with the usual DR from the absorption spectra and the experimental $\Delta n(\omega)$ curve.

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[1)]In real experiments the geometry is usually so chosen that the problems of reflection and transmission of the light become scalar. We can confine ourselves therefore to the use of scalar ρ and τ, assuming a more specific experimental geometry.

[2)]We disregard the conjugate singularity which occurs, according to (2) at the point $-\tilde{\omega}^*$, since it makes a vanishingly small contribution to the considered spectral region: $\Delta\omega\ll\omega$.

[3)]To obtain a single-valued result of integration over the section G is must be recognized that the functions $\ln|\rho(\omega)/\rho_0|$ and $(1/\pi)\int_{-\infty}^{\infty}[\ln|\rho(x)/\rho_0|/(x-\omega)]\,dx$ make up a Hilbert pair.

[4)]In Ref. 17 the term "damping" is used for the quantity $\Gamma=2\gamma$, therefore $\gamma_0=\Gamma_{\text{lim}}/2$.

[5)]The clearing action of the dead layer is considered in Ref. 24

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