

MODERN STATUS OF THE THEORY OF LIGHT REFLECTION

Devoted to the memory of Grigorii Samuilovich Landsberg

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UNTIL recently, the optical characteristics needed to explain the properties and the structure of matter were determined essentially from the parameters of transmitted light. Yet the light reflected from matter contains no less information concerning its properties. This information is not identical to that obtained "by looking through" and frequently supplements it successfully. Therefore interest in the investigation of processes of reflection and the connection between the parameters of reflected light with the structure of matter is rapidly increasing. Metal optics has long been based on the study of reflection, as is the recent optics of semiconductors; recently these methods are more frequently employed for crystalline and amorphous dielectrics. Many results of the theory of interest both for optics and radiophysics of plasma. At the same time, certain unique difficulties are encountered here. All this calls for a detailed knowledge of the theory of the process of reflection from media having different physical natures.

The possibility of obtaining unprecedented powerful light fluxes makes it possible to measure many optical effects, for example nonlinear ones, which hitherto could not be observed. This raises interest in the development of a number of branches of theoretical optics which hitherto appeared to be completely exhausted and trivial, particularly the theory of reflection.

The field of reflected light is only part of the entire electromagnetic light field, which is formed in media on both sides of the interface, and the formation of the reflected beam is difficult to analyze separately from an examination of the entire process as a whole. However, the experimental specific features of the question makes it nevertheless necessary to separate the consideration of reflection phenomena as a distinct branch of physical optics.

The law of light reflection is regarded as the oldest and simplest of all the laws of optics. Whereas there is no doubt of the former, the simplicity of the law is only apparent; a more serious analysis reveals many complicated problems, which have not yet been resolved to this very day. This is precisely why a review of this question is continuing, and has recently yielded new results.

1. PRINCIPLES OF THE MACROSCOPIC THEORY

The customarily employed formulas describing the reflection of light are obtained in the classical macroscopic linear electrodynamics for the case of reflection of an unbounded plane monochromatic wave from a plane* immobile interface between two semi-infinite homogeneous media, with the radiation condition satisfied^[1], under the assumption of local connections between the field intensities and the inductions.

If the incident wave is specified by means of an expression of the form

$$\mathbf{E} = \mathbf{E}_0 e^{-i\omega \left(t - \frac{m\mathbf{r}}{c}\right)}; \quad \mathbf{m} = \frac{c}{\omega} \mathbf{k}, \quad (1)$$

where \mathbf{E}_0 is a complex vector that does not depend on r and t , \mathbf{m} is the refraction vector (generally speaking, complex), and \mathbf{k} is the wave vector (the expression for \mathbf{H} is similar), and if it is assumed that the reflected and refracted fields can also be represented as a result of a superposition of plane waves of the same type, then the reflection law can be written as follows:

$$\omega = \omega_{r_1} = \dots = \omega_{r_i} = \omega_{d_1} \dots = \omega_{d_i}, \quad (2a)$$

$$[\mathbf{m}\mathbf{N}] = [\mathbf{m}_{r_1}\mathbf{N}] = \dots [\mathbf{m}_{r_i}\mathbf{N}] = [\mathbf{m}_{d_1}\mathbf{N}] = \dots [\mathbf{m}_{d_i}\mathbf{N}]. \quad (2b)^\dagger$$

The index r pertains here to the reflected waves, and d to the refracted ones; \mathbf{N} is the normal to the interface in the direction of the transmitted light. Formula (2b) shows that the plane of incidence and the reflection planes are parallel. The phase of the reflected light is determined accurate to the sign (i.e., to the factor $e^{\pm i\pi}$ in (1)), which must be determined separately^[4-7]. The physical meaning of this fact is that definite limitations must be imposed on the boundary conditions^[7,8] to ensure that the amplitude decrease upon propagation.

*We consider in this paper only reflection from smooth surfaces (roughnesses very small compared with the wavelength). Reflection from rough surfaces is investigated, for example, in [2,3].

† $[\mathbf{m}\mathbf{H}] \equiv \mathbf{m} \times \mathbf{H}$.

By resolving, for example, the vectors \mathbf{E} into components parallel and perpendicular to the plane of incidence, we can obtain for the corresponding amplitudes

$$E_{r\perp} = E_{0\perp} \left(\frac{m_d N}{\mu_2} - \frac{mN}{\mu_1} \right) \left(\frac{m_r N}{\mu_1} - \frac{m_d N}{\mu_2} \right)^{-1}, \quad (3a)$$

$$E_{r\parallel} = E_{0\parallel} \left(\frac{n_2}{n_1 \mu_2} mN - \frac{n_1}{n_2 \mu_1} m_d N \right) \left(\frac{n_1}{n_2 \mu_1} m_d N - \frac{n_2}{n_1 \mu_2} m_r N \right)^{-1}. \quad (3b)$$

Here μ_1 and μ_2 are the magnetic permeabilities, and n_1 and n_2 the refractive indices; the subscript 1 pertains to the medium from which the light arrives. We have confined ourselves here to the case of isotropic media.*

For nonmagnetic media, denoting by φ and ψ respectively the angles of incidence and refraction ($\sin \psi = n_1/n_2 \sin \varphi$), we obtain the well-known Fresnel formulas

$$E_{r\perp} = -E_{0\perp} \frac{\sin(\varphi - \psi)}{\sin(\varphi + \psi)}, \quad (4a)$$

$$E_{r\parallel} = E_{0\perp} \frac{\text{tg}(\varphi - \psi)}{\text{tg}(\varphi + \psi)}. \quad (4b)$$

Unless otherwise stipulated, we shall henceforth assume that medium 1 is vacuum and use the term "medium" for the second medium, putting $n_2 = n$.

In the case when the medium absorbs, as is well known, the refraction vector is complex:

$$\mathbf{m}_d = n \mathbf{n}_{\text{wave}} + i \kappa \mathbf{n}_{\text{ampl}}$$

(and, in accordance with (2b), $\mathbf{n}_{\text{ampl}} \times \mathbf{N} = 0$). Here κ usually is called the absorption index (not quite correctly, better "attenuation index"), \mathbf{n}_{wave} and \mathbf{n}_{ampl} are respectively the wave and amplitude normals ($n_{\text{wave}}^2 = n_{\text{ampl}}^2 = 1$).

However, in such a notation, n and κ depend on φ and on the polarization of the incident light. If we introduce the complex refractive index† $\nu = n_0 + i\kappa_0$ (where n_0 and κ_0 are the values of n and κ when $\varphi = 0$) and the complex refraction angle χ , then ν will be a constant of the matter and Fresnel's formula with ν and χ replacing n and ψ will retain the same form (4a, b). If both media are absorbing, similar symbols are introduced for both media (ν_1 and ν_2 , χ_1 and χ_2). It is seen from formulas (4a, b)

*For anisotropic media the formulas become much more complicated. They become especially complicated for media with low structure symmetry, where the principal axes of the tensors ϵ , μ , and σ do not coincide. It turns out that 44 types of crystals of different optical properties can exist. For the general formulas see [8,9]. Formulas for uniaxial transparent crystals are given in [10], and for absorbing ones in [11].

†From the theoretical point of view [12] it is simpler to use complex ϵ and μ ; for an experimenter, however, it is more convenient to use the complex refractive index as a characteristic. To describe reflection from absorbing media (especially from metals in the presence of the anomalous skin effect [13]; (see Sec. 15) it is convenient to use the concept of surface impedance. This question was considered in Usp. Fiz. Nauk [14], as well as other special problems of reflection from metals.

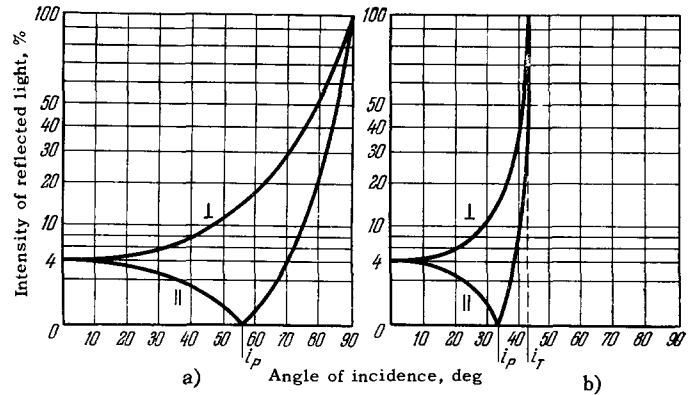


FIG. 1. $E_{r\perp}(\varphi)$ and $E_{r\parallel}(\varphi)$ for a transparent dielectric: a) $n_1 < n_2$, b) $n_1 > n_2$. The ordinates represent the reflection coefficients R_{\perp} and R_{\parallel} .

that in an absorbing medium the waves have a longitudinal component. Fresnel's formulas and their general consequences are discussed in many monographs, and will not be treated here in detail (see, for example, [15-18]). Figure 1 shows plots of $E_{r\perp}$ and $E_{r\parallel}$ against φ for nonabsorbing media 1, and Fig. 2 shows the same plots for the reflection coefficients for differently absorbing media 2 (see also Fig. 6). Tables of numerical data calculated from Fresnel's formulas for different values of n and κ are given, for example, in [19,20,21].

2. REGION OF APPLICABILITY OF THE THEORY

We must note first that the assumption on which the derivation of (2a)-(4b) is based, namely that the field at the surface can be resolved into incident, reflected, and refracted waves, and that these waves have the form (1), is not always correct.

A. For isotropic homogeneous media one can indicate cases [22,23] when Maxwell's equations are satis-

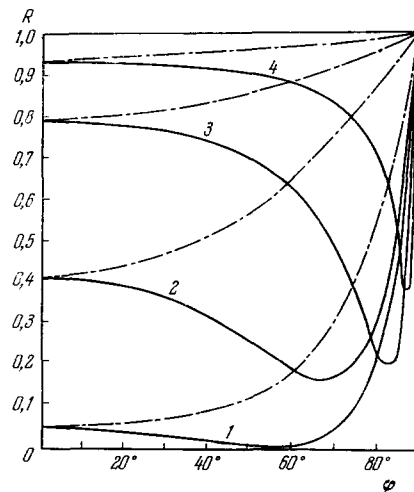


FIG. 2. $R(\varphi)$ (---) and $R(\varphi)$ (—) for reflection in vacuum from an absorbing medium: 1 - $n = 1.52$, $\kappa = 0.0$; 2 - $n = 1.52$, $\kappa = 1.0$; 3 - $n = 11$, $\kappa = 6$; 4 - $n = 44$, $\kappa = 43$.

fied only by solutions of the type

$$E = (E_0' e^{i \frac{mr}{c}} + E_0'' \frac{mr}{c} e^{i \frac{mr}{c}}) e^{-i\omega t}, \quad (5)$$

for which there are special propagation laws, and particularly reflection laws. Such waves have not yet been observed experimentally, nor were they investigated. They obviously can take place only in the immediate vicinity of the interface.

B. In the case of strong inhomogeneity of at least one of the contiguous media, the resolution of the field into incident and reflected waves is generally impossible [4,24], or, in the case of simpler cases of smooth variation of the parameters of the media, quite difficult [25]*. A complete solution of the problem in the case of a jumplike change in the properties is possible, although it is quite complicated physically and mathematically, only in the case of inhomogeneity in one dimension, namely in layered media, where the layers are parallel to the interface [4,26].

Reflection from inhomogeneous media is a special and separate branch of the theory and is beyond the scope of our review; we shall consider only the simplest case—reflection in the presence of a surface layer (Secs. 13–16).

C. An analysis of the reflection of bounded beams reveals also that the resolution of the field into incident and reflected waves becomes impossible in the region of large values of φ , close to glancing angles, owing to diffraction phenomena. In [29] there were obtained general formulas which include both the reflection law and the diffraction law, and which go over (practically) into Fresnel's formulas at not too large values of φ .

We emphasize once more the limitation stipulated by us: as indicated, formulas (4a) and (4b) were obtained for an immobile interface. An analysis of the processes of reflection from a moving surface is complicated; it was reviewed anew recently in an extensive and prolonged debate arising in connection with a discussion of [30] and of the dependence of the velocity of light on the motion of the source (see, for example, [31]). Reflection of light from a moving mirror was considered in detail in [31,32]. This question is also discussed in [33,34].

3. ENERGY BALANCE

We note that in the case homogeneous and isotropic media, to which we confine ourselves in the present review, Fresnel's formulas, which are the solution of the corresponding boundary-value problem, say nothing concerning the interaction between the waves after reflection, namely concerning their possible interference and formation of standing waves

(the latter, in particular, should influence the energy balance). An analysis [15] shows that upon reflection from the boundary between a transparent and an absorbing medium, the energy flux in the latter has a component $S_{\perp} \neq 0$. For a more detailed analysis of the energy balance it is necessary to consider bounded beams. The most consistent analysis is given in [35] for the most general case—reflection of a bounded beam from the interface between two absorbing media. The conditions for the flux components are given in the form [35]

$$\begin{aligned} (S_{\perp} + S_{r\perp} + S_{i\perp}) (\cos \chi_1)^* &= S_{d\perp} (\cos \chi_2)^*, \\ (S_{\parallel} + S_{r\parallel} + S_{i\parallel}) (\cos \chi_1) &= S_{d\parallel} (\cos \chi_2), \end{aligned} \quad (6)$$

where S , S_r , and S_d are the usual expressions for the energy fluxes of the corresponding rays, and

$$S_i = \frac{c}{4\pi} \{ [E_r H^*] + [E H_r^*] \} \quad (7)$$

is the "interference term." Only under such a choice of conditions is the energy balance satisfied.

The physical meaning of (7) becomes clearest if we consider the case when $\chi_1 = \chi_2 = 0$ in (6), and the reflection is close to 100% (κ_2 is very large). In this case standing waves are produced in medium 1 as a result of interference between the incident and reflected waves. In the nodes of these waves, the energy is close to zero, and in the antinodes it is maximum. The term (7) represents the energy flux that causes the indicated redistribution of energy upon formation of standing waves (see also [36]) and maintains these waves.

If we introduce the symbols R , I , and D for the experimentally measured reflection and transmission coefficients respectively

$$1 - R = 1 + \frac{S_r}{S}; \quad I = \frac{S_i}{S}; \quad D = \frac{S_d \cdot \cos \chi_2}{S \cdot \cos \chi_1}, \quad (8)$$

then

$$1 - R + I = D.$$

The quantity I is pure imaginary and

$$\text{Re}(1 - R) = 1 - R = \text{Re } D.$$

On the other hand, if we assume, as is frequently done [37], that the experimentally measured quantities are

$$1 - R' = 1 + \frac{\text{Re}(S_r \cos \chi_1)}{\text{Re}(S \cos \chi_1)}; \quad I' = \frac{\text{Re}(S_i \cos \chi_1)}{\text{Re}(S \cos \chi_1)}; \quad D' = \frac{\text{Re}(S_d \cos \chi_2)}{\text{Re}(S \cos \chi_1)},$$

Then $\text{Re } I' \neq 0$ and it is necessary to introduce in formulas (4a) and (4b) the "Fresnel" and "energy" amplitudes [37]. The measurements of [35] also favor the notation (8), but the question still needs to be examined [38] (see also the discussion in [37–40]).

Connected to some degree with the question of the energy balance is also the question of the group velocity. L. I. Mandel'shtam [41] indicated that in deriving Fresnel's formulas it is implicitly assumed that the group velocity is positive in both media. Yet

*Some problems involving reflection from disperse or turbid media are considered in [27,28].

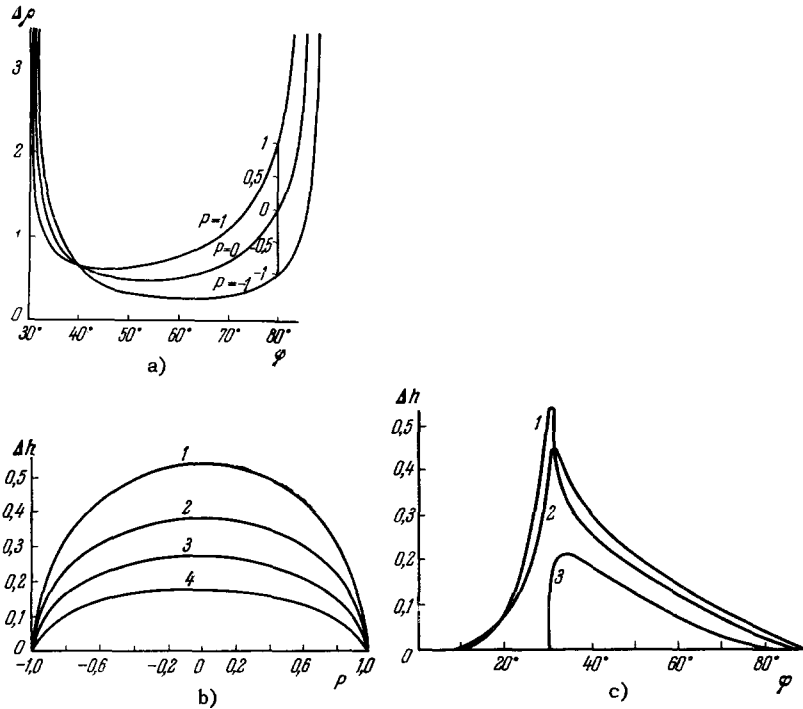


FIG. 3. a) Displacement of the reflected ray in the plane of incidence, $\Delta\rho(\varphi)$, for different values of the polarization of the incident ray; b) displacement of the reflected ray perpendicular to the plane of incidence $\Delta h(\varphi)$ for different values of the polarization of the incident ray, at a phase difference between E_{\parallel} and E_{\perp} in the incident ray (δ) and in the reflected ray (γ): 1 - $\delta = 90^\circ$, $\gamma = 90^\circ$; 2 - $\delta = 45^\circ$, $\gamma = 45^\circ$; 3 - $\delta = 0^\circ$, $\gamma = 90^\circ$; 4 - $\delta = 0^\circ$, $\gamma = 45^\circ$; c) $\Delta h(\varphi)$ for $n_1/n_2 = 2$. The incident ray is polarized: 1 - circularly, 2 - elliptically, 3 - linearly.

this is not always the case (in particular, for example, in the case of strong spatial dispersion $\langle \mathbf{m} \cdot \mathbf{v}_{gr} \rangle$ can be also larger than $\pi/2$) (see [41a]).

This is connected also with the problem of the character of reflection from a boundary between two media, one of which has positive anomalous dispersion and the other negative. Such a situation can arise on the boundary of a plasma or a medium with inverted level population. This question was not considered in detail for light waves; we point only to [42], which contains certain considerations of this question. Amplification of light is possible; when light is reflected from a medium with negative dispersion we can have $|\mathbf{E}_r|^2 > |\mathbf{E}|^2$, nonlinear interaction of waves, and other phenomena.

4. DIRECTION OF MOTION OF ENERGY

Using the languages of ray optics, we can state that the frequently made assumption that a reflected ray is produced at the same point of the surface at which the incident ray arrives cannot be proved. As already mentioned, during reflection the energy flux in the second medium has, generally speaking, a component $S_{\perp} \neq 0$. This takes place in the case of an absorbing medium and in the case of total internal reflection [15].

For an analysis of the direction of motion of the energy it is necessary to consider bounded beams. In the most general form, this was done for the boundary between two absorbing media in [42a] (see also the historical review [42b] and the references therein). It was shown that the point of emergence of the reflected ray is shifted relative to the point of

incidence of the arriving ray both in the plane of incidence (forward in the direction of the ray) and in the perpendicular direction (the displacements are respectively $\Delta\rho$ and Δh). The planes of incidence and reflection are parallel, as required by (2b), but they do not coincide. The displacements depend on the polarization of the incident ray, on φ , n , and κ ; some examples are shown in Fig. 3. Displacements take place also in the case of nonabsorbing media. When $n_1 < n_2$ we have $\Delta\rho = 0$ but $\Delta h \neq 0$ in the general case of elliptic polarization; when $n_1 > n_2$, generally speaking, $\Delta\rho \neq 0$ and $\Delta h \neq 0$. Experimental measurements of the phase differences arising in the latter case were made in [43].

The unique configuration of the field in the second medium in total internal reflection (t.i.r.) and the direction of motion of the energy in it were analyzed in greater detail in [44]. The energy flux in the second medium moves along a surface that assumes the role of a unique waveguide [45] and emergence to the first medium, with redistribution of the energy over the cross section of the beam.

Experimental measurements of $\Delta\rho$ were made in [46, 47] (see the review [42b]), and the results agree well with theory. Apparently no measurements were made of Δh . Measurements of the depth of penetration l of the field in the second, less dense medium were made with a photon counter [48]. l reaches a value on the order of $\sim 10\lambda$; it is largest at the critical angle and decreases with increasing φ (differently for E_{\perp} and E_{\parallel}).

We note that the presence of negligible absorption in a second (less dense) medium greatly changes the configuration of the entire field (Fig. 4). The total

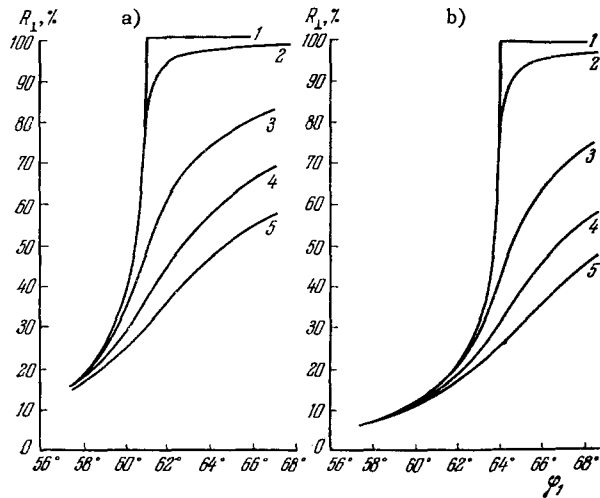


FIG. 4. Coefficient of reflection R_{\perp} upon reflection in a non-absorbing dielectric from a weakly-absorbing medium. 1 - $\kappa = 0$; 2 - $\kappa = 0.001$; 3 - $\kappa = 0.01$; 4 - $\kappa = 0.02$; 5 - $\kappa = 0.03$ for: a) $n_2/n_1 = 0.8733$ and b) $n_2/n_1 = 0.8998$.

internal reflection practically disappears; this is evidence of a strong dependence of the dimensions and shape of the region of formation of the reflected wave on the environment and on the properties of the medium.

The dependence of the field intensity at the interface on the angle of incidence was calculated in [50] (Fig. 5) and agrees with the measurements of [48], namely, the field intensity decreases rapidly with increasing φ .

5. EXPERIMENTAL VERIFICATION

Optics has returned to an experimental verification of Fresnel's formulas (4a) and (4b) many times; the history of the problem includes such names as Jamin, Rayleigh, Drude, Wood, Raman, and Mandel'shtam (for a bibliography see [51, 52]). It was shown that there are certain deviations from these formulas:

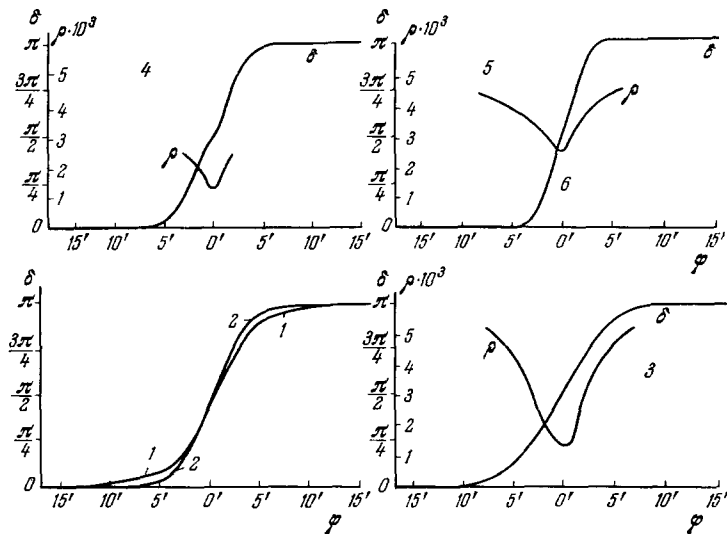
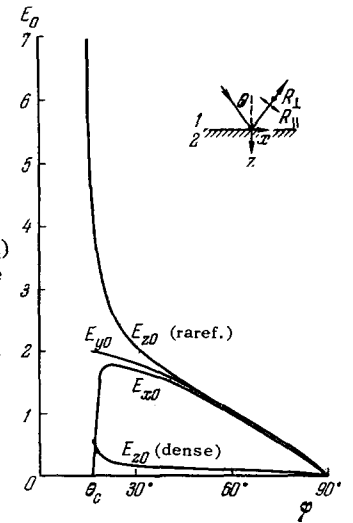


FIG. 6. Dependence of the phase difference δ between $E_{R\parallel}$ and $E_{R\perp}$ and of the ratio $\rho = |E_{R\parallel}|^2 / |E_{R\perp}|^2$ of the axes of the polarization ellipse on φ near φ_{Br} . The Brewster angle is assumed to be zero. 1 - CCl_4 , 2 - bromoform, 3 - xylol, 4 - chlorobenzene, 5 - hydrobromic acid, 6 - cyclohexanol.

FIG. 5. Field intensity at the surface in total reflection ($n_1 > n_2$) as a function of φ : E_{x0} - from the side of the medium 2, E_{y0} - from the side of the medium 2, E_{z0} - from the side of medium 2 - upper curve, E_{z0} - from the side of medium 1 - lower curve.



a) According to (4b) $E_{R\parallel}$ should vanish at $\varphi = \varphi_{Br}$ (Brewster angle), where $\tan \varphi_{Br} = n$, and the phase difference δ between $E_{R\perp}$ and $E_{R\parallel}$ should then change jumpwise from π to zero. Experiment shows that $E_{R\parallel}$ does not vanish and has larger values (compared with those predicted by the formulas) in the interval $\varphi_{Br} \sim 1-2^\circ$. The variations of $\delta(\varphi)$ and $\rho = |E_{R\parallel}|^2 / |E_{R\perp}|^2$ are shown in Fig. 6 [52].

The author and his co-workers [52-54] have shown (using as an example liquids, where mechanical finishing of the surface is impossible), that even when the medium is fully purified by all modern methods, the effect decreases but does not vanish, and remains also in the case of a surface that is under vacuum. In other words, there is no doubt that there is a residual effect which is not caused by contamination.

b) There should be no reflection when $n_1 = n_2$; yet it was observed. L. I. Mandel'shtam [35] pointed out a number of possible causes of these deviations. His considerations were developed in [51, 56], where it was shown that the only possible cause of the appearance

of the effect may be the presence at the surface layer of a special molecular structure, different from the structure deep in the matter (see Sec. 14). The effect b) was considered in less detail than a), but it can be stated that here, too, the cause is the presence of adsorption layers at the interface.

To clarify the causes of these deviations it is necessary to consider the microscopic theory.

6. MICROSCOPIC THEORY

In the case when the medium has a discrete structure (we consider only the microscopic molecular structure of a homogeneous medium), the reflection law becomes more complicated.

A calculation made within the framework of the classical theory for the case of reflection of light from the surface of an ideal cubic lattice consisting of immobile pointlike isotropic harmonic oscillators (see^[57,51]) leads to the following conclusion: The reflection occurs as if the medium were continuous, but on its surface there is a transition layer whose parameters are determined by the properties of the lattice.* The reflection laws are different in this case (see below), although numerically the deviations from Fresnel's formulas are small.

Let us consider this question in greater detail for the case of a transparent dielectric. When molecular optics was developed, reflection laws were also obtained with the aid of the developed calculation procedures in the classical papers^[58-60] and in a number of others (for a detailed bibliography see^[61,62]). The reasoning in all the papers reduces to the following:

The calculation was carried out by the methods of classical linear electrodynamics for the steady-state process. The medium is represented as an aggregate of immobile elementary isotropic centers (for example, molecules) distributed in space (in vacuum) in accordance with a definite law. This law was taken to be either "ideal disorder"—completely equal probability of all arrangements—or else arrangement in the sites of a cubic lattice. The incident wave is of the form (1). Under the influence of the wave field that is produced in the medium, an alternating electric dipole moment is induced in the molecules—a "polarization wave" is produced (with wave velocity c/n). As a result these molecules emit secondary coherent radiation (the variation of the frequency in the radiating center is disregarded) propagating with a velocity c in vacuum; the radiators are assumed to be undamped, and their natural frequencies remote from ω .

The summary effective field is represented in the form

$$E(r, t)_{\text{eff}} = E(r, t) + \int_{v'(\sigma)} \text{rot rot} \sum_{N_1} \frac{p(r', t - \frac{R}{c})}{R} dv', \quad (9)$$

$$R = |r - r'|, \quad p = \beta E_{\text{eff}}(r', t - \frac{R}{c}), \quad (9a)$$

where r' is the coordinate of the molecule under consideration, β its polarizability, and N_1 is the number of molecules in 1 cm^3 . The integration is carried out over the entire volume of the substance, with the exclusion of the "sphere of molecular action" (surface σ with radius a) surrounding this dipole, for which E_{eff} is calculated; the summation is over all the molecules except the one considered. The intermolecular forces and the effects of "coupling of the oscillators" are disregarded.

Further, the conditions are obtained under which a plane (refracted) light wave is produced as a result of the interference, described by (9), between the primary and all the secondary waves, and has in general different values of m and n than the incident wave, and the latter is extinguished as a result of the interference in the medium (hence the name—"extinction theorem"). There should obviously be two such conditions—one is the refraction law (the condition for ψ) and the other is the condition for n , from which one determines that value of n at which the sought wave field is established. Calculation of the field outside the medium, with the foregoing conditions observed, gives the reflected wave. In other words, the interference field contains two types of waves. Some of them propagate with velocity c , and the others with velocity c/n . The former make up the reflected wave and extinguish the primary wave in the medium, the latter form the refracted wave in the medium. The choice of the expression for the effective field is not free of objections (since the field E becomes deformed on penetrating into the medium), and is being disputed to this very day. Referring the reader to^[63,64] for details, we note only that, in accordance with the well-taken remark^[64] "the buried molecule does not see the field E " (we shall return later to the question of the size of the region in which the reflected wave is formed).

In the first investigations, the condition derived for n was the Lorenz-Lorentz formula

$$\frac{n^2 + 2}{n^2 - 1} = A, \quad A = \frac{3}{4\pi N_1 \beta}. \quad (10)$$

The limited applicability of this formula for real media indicates that the assumptions made during its derivation have limited validity (this, however, does not limit the applicability of the extinction theorem).*

In more correct calculations^[60] the condition obtained for n is somewhat more complicated:

$$\frac{n^2 + 2}{n^2 - 1} - \frac{n^2 + 10}{10} \left(\frac{2\pi a}{\lambda} \right)^2 + \frac{2}{3} i \left(\frac{2\pi a}{\lambda} \right)^3 = A. \quad (11)$$

*Generally speaking, this conclusion is valid also under more general assumptions concerning the nature of the oscillators.

*From (9a) - (10) it follows that $E_{\text{eff}} = E(n^2 + 2)/3$ (10a).

In all the cited papers, the Fresnel formulas were obtained as first terms of certain expansions in powers of a/λ , i.e., were not quite exact and, strictly speaking, were applicable only at distances much larger than a from the surface. The latest and most rigorous derivation, based on the smallest number of assumptions, was given in ^[61,62]; the condition obtained for n is

$$3e^{-ia} \left\{ \left(\cos an - \frac{\sin an}{an} \right) \times \left(\frac{1}{n^2-1} - \frac{1}{(an)^2} - \frac{i}{(an)^2} \right) + \frac{1+ia \sin an}{n^2-1} \frac{1}{an} \right\} = A. \quad (12)$$

Confining ourselves to terms up to the third order in a we get

$$\frac{n^2+2}{n^2-1} + \frac{n^2+10}{10} a^2 + \frac{i}{3} a^3 = A. \quad (13)$$

The calculation procedure used in ^[51,57] is close to that in ^[58,59]; the Fresnel formulas were obtained in the form

$$E_{r\perp} = -E_{0\perp} \frac{\sin(\varphi-\psi)}{\sin(\varphi+\psi)} \left\{ 1 + i \frac{4\pi d}{\lambda} \gamma_y \cos \varphi \right\}, \quad (14a)$$

$$E_{r\parallel} = E_{0\parallel} \frac{\operatorname{tg}(\varphi-\psi)}{\operatorname{tg}(\varphi+\psi)} \left\{ 1 + i \frac{4\pi d}{\lambda} \frac{\gamma_x \cos^2 \psi - \gamma_z \sin^2 \varphi}{\cos^2 \psi - \sin^2 \varphi} \cos \varphi \right\}. \quad (14b)$$

(the z axis is directed into the medium normal to the surface, the x axis is the line of intersection of the incidence plane and the surface). γ_x , γ_y , and γ_z are certain real lattice parameters which depend on the choice of the expression for n , and d is the lattice constant.

It should be noted that all the refinements introduced by later authors pertained to the calculation procedure and not to the initial physical premises concerning the character of the internal field, the arrangement and structure of the radiators, etc.

The appearance of complex terms in (11)–(14) means that in the case of incidence of linearly polarized light the reflected light will be elliptically polarized. On the other hand, the complex nature of n and m in (11)–(13) indicates that energy flows away from that form of the field which is considered in the problem* (there should be no absorption within the framework of these theories, since the oscillators are assumed to be undamped). In other words, besides the “interference maxima of reflection and refraction” there occurs also a certain scattering. A special investigation is necessary to explain its causes. We shall merely note here that failure to take the damping into account is an unjustified idealization, which leads to errors in the analysis of the energy balance. In addition, no account is taken in the derivation of the influence of the surface on the radiation from the closely-lying particles. As is well known, no scattering of light takes place in a homogeneous medium. However, the situation changes in

the presence of an inhomogeneity in the form of an interface, L. I. Mandel'shtam has shown ^[65] that for radiators located at a distance comparable with λ from the surface, the regular reflection and refraction give way to scattering; yet in our problem the radiators closest to the surface are precisely under such conditions.

Figure 7 shows the results of the calculation ^[65] of the amplitude $E_{d\parallel}$ of the light oscillations arriving at point B from source A for $z \gg \lambda$ and a comparable with λ . We see that when $a/\lambda \gg 1$ the boundary between the light and the shadow is sharp, but as $a/\lambda \rightarrow 0$ the amplitude decreases only continuously, i.e., strong scattering exists. In ^[66], the calculation was made also for the case when $z \approx \lambda$. The reversibility of the rays is demonstrated in ^[65].

The fact that Fresnel's formulas in ^[60] turn out to be approximate is valid only at a certain distance from the surface has caused the author to advance the proposition (which, to be sure, is not flawless) that the extinction theorem is valid not rigorously and only in the optical region; this statement is repeated also in some later paper ^[63].

However, it was shown in ^[62] that the proof of the theorem is more rigorous, and not only for ordinary but also for total internal reflection ^[61] as well as for optically active and anisotropic media ^[67-68]; we shall show that it is valid also for nonlinear media. A rigorous derivation by means of a simpler procedure is given in ^[69].

The problem of light reflection was solved in ^[70] in an entirely different manner—by a macroscopic calculation using the green's function method. This yielded integral equations that express the extinction theorem in general form; in other words, this theorem turned out to be simply a consequence of Maxwell's equations and not unique to the optical region* or for the microscopic treatment.

No microscopic treatment for absorbing media and for conductors, similar to the extinction theorem, has ever been proposed, in so far as we know, with the exception of a paper ^[68] in which a classical model of a metal is considered for $\lambda \rightarrow 1$ cm. A universal treatment of the problem is hardly possible here, owing to the great variety of the microprocesses. A semiphenomenological calculation of the reflection from an anisotropic metal was presented in ^[71] with allowance for the form of the Fermi surface (in somewhat primitive fashion, taking this surface to be an ellipsoid).

7. QUANTUM MECHANICAL CALCULATION

The problem was not solved by rigorous methods of quantum electrodynamics.

*For a detailed analysis of the energy balance it is necessary to consider bounded beams, and not unbounded plane waves.

*Moreover, it was generalized in ^[26] to include also acoustical processes.

In [72] are presented calculations where the scattering centers are assumed to be quantum systems—hydrogenlike single-electron atoms (with the spin disregarded), and account is taken of the electric and magnetic dipole and electric quadrupole moments. Their interaction with the electromagnetic field is calculated in accordance with the classical theory. The general calculation scheme described above is fully retained; the extinction theorem is employed. The calculation of the interaction with the field is confined to linear electrodynamics.

For electric-dipole radiation, as expected, the author obtains the Fresnel formulas and condition (10), where, however, the formally introduced polarizability parameter is replaced by the usual expression

$$\frac{e^2}{m_0 \omega^2} \left(\sum_s \frac{\omega_{sn}^2}{\omega_{sn}^2 - \omega^2} f_{sn} - 1 \right). \quad (15)$$

Here f_{sn} is the oscillator strength for the corresponding electric-dipole transitions.

For electric-quadrupole radiation (these radiators have no magnetic-dipole radiation) the expressions obtained are

$$E_{r\perp} = E_{0\perp} \frac{\sin(\varphi - \psi) \cos(\varphi + \psi)}{\sin 2\varphi} B (C - |\bar{m}|^2 D), \quad (16a)$$

$$E_{r\parallel} = E_{0\parallel} \left\{ \frac{\sin(\varphi - \psi) [\cos(\varphi + \psi) - \sin(\varphi + \psi)]}{\sin 2\varphi} BC - \frac{\sin(\varphi - \psi) \cos(\varphi + \psi)}{\sin 2\varphi} BD \frac{m_0 \omega^2}{e^2} \right\}, \quad (16b)$$

where

$$B = \frac{4\pi}{n^2 - 1} N_1,$$

$$C = \frac{e^2}{m_0 \omega^2} \sum_s \frac{\omega_{sn}^2}{\omega_{sn}^2 - \omega^2} q_{sn}, \quad D = \frac{e^2}{m_0 c^2} \int_0^\infty r^4 R_{nl}(r) R_{n'l'}(r) dr.$$

Here q_{sn} is the oscillator strength of the electric-quadrupole transition and R_{nl} is the radial part of the wave function.

We see that these formulas differ noticeably from (4a) and (4b), having different angular dependences and different densities, no Brewster angle, and

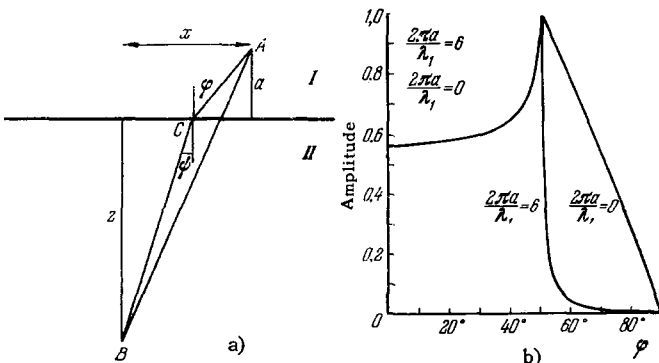


FIG. 7. a) A – source, B – point of observation. The oscillations are perpendicular to the plane of the figure. b) Results of calculation for $n = n_2/n_1 = \sin \varphi / \sin \psi = 1.33$. The amplitude is in relative units. The case $\sin \psi < n$ is considered.

elliptic polarization upon reflection. It is obvious that these circumstances can be used to determine the nature of the radiators.

The expression obtained in lieu of (10) is

$$B \{(2n^2 + 3)c - (n^2 + 4)n^2 D\} = 5.$$

The influence of the spin was taken into account in [73]. In so far as we know, these results have never been checked experimentally.

8. INFLUENCE OF THERMAL MOTION OF PARTICLES

In the arguments presented in Sec. 6 it was assumed that the particles are immobile and are uniformly distributed in space.

L. I. Mandel'shtam has shown that particle motion itself does not violate the coherence and does not change the character of the process (does not lead to scattering). The latter occurs only when fluctuations take place in the density or in other parameters (the question of ordered collective processes will be touched upon later), when the regularity of the interference is violated. Such a scattering differs from that discussed in Sec. 6 in that both the scattering and the fluctuations producing it are incoherent with the reflected light (the extinction theorem is nevertheless valid here). G. S. Landsberg has shown [74] that in regular reflection there is likewise no Doppler effect. Besides the reflection, there can take place on the interface itself additional scattering due both to fluctuations of the shape of the surface and the fluctuations of the parameters of the medium, to capillary waves, etc.

A detailed analysis of the theory of the scattering and of its experimental investigation are found in [75]. The Doppler effect should also take place for this scattering [74], but the obtained change in frequency is too small to be observed.

9. DIMENSION OF THE REGION OF FORMATION OF THE REFLECTED BEAM

An analysis of the microscopic mechanism of the reflection raises a number of questions which are not answered by the derived formulas. The dimensions of the region in which the reflected wave is formed, the duration of the wave formation, and the coherence properties of the reflected light remain unclear. The question of the dimensions of the region in which the reflected wave is formed breaks up in turn into two: a) at what distance from the reflected surface can the reflected wave be separated from the total field, b) what is the practical depth of this layer of the reflecting medium, which determines the properties of the reflected wave? As applied to absorbing media, this question can be formulated (not quite equivalently to the first formulation) also as follows: What depth of penetration is sufficient, for example, in order for

the reflected wave to acquire the symmetry of the reflecting medium?

For simplicity, we consider below the case when medium 1 is vacuum. The calculations presented in Sec. 6 determine the field at distances from the surface which are appreciable compared with the microscopic dimension that is characteristic of the medium—the dimension of the molecules or the distance between them; the former distances, generally speaking, depend on the angle of incidence of the beam and on the field configuration (Sec. 4). The following can be stated with respect to the formation region. For transparent media, the upper limit of this region is determined by the coherence length, i.e., by the distance within which the secondary (scattered) particle radiation arriving at the surface is still coherent with the incident wave. In the approximation considered above, where the particles were assumed to be noninteracting and the radiation field weak, the coherence length is determined by the properties of the incident light (in this approximation, even multiple scattering is coherent^[76]); for interacting particles this is not the case; see, for example^[77-79]).

We note that it follows from the foregoing data on total internal reflection (Sec. 4) that a layer of thickness of the order of 10λ already forms the reflected ray fully. On the other hand, data on surface layers (Sec. 13) indicate that differences in the properties of the first few molecular layers change the character of the reflection only slightly, i.e., the entire forming layer is much thicker.

For absorbing media, the upper limit is determined by the depth of penetration, i.e., (for a metal) it amounts to fractions of λ . Here, however, we must bear in mind two considerations. On the one hand, in the presence of nonlocal couplings (spatial dispersion) and anomalous skin effect (which frequently takes place for the most strongly absorbing media, such as metals; see Sec. 14), the dimension of the layer influencing the formation of the reflected light will be larger than the depth of penetration, owing to transport phenomena. On the other hand, in considering reflection from absorbing media, it is no longer possible to neglect the interaction of the absorbing centers (regardless of the absorption mechanism). This interaction can greatly change the coherence length in the given medium, making it quite small.

By way of one example of the phenomena occurring upon reflection from an absorbing medium, we describe here experiments which make it possible to approach the reflection process from a different aspect, and trace the process of "formation of the reflecting surface." Referring the reader to^[80] for details, we shall describe the experimental setup (Fig. 8). A solution of a strongly absorbing and luminescent dye in a colorless solvent, with $n_{\text{solution}} \approx n_{\text{glass}}$, is poured into a cell. At low concentration, the reflection from the interface between

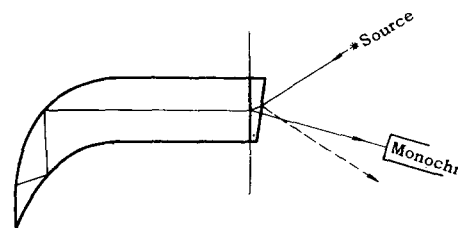


FIG. 8. Diagram of experiment for the observation of selective reflection.

the glass and the solvent is very weak. The beam penetrates to a large depth and produces luminescence on its path. When the concentration is increased, the depth of penetration decreases, and the luminescence is weakened by concentration quenching; the intensity of the reflected light increases, reflection from the glass-dye interface appears, and when the depth of penetration is $\sim (1-2)\lambda$ the reflection becomes fully "metallic" (with all its attributes—selectivity, ellipticity, etc.). Similar experiments with vapors of alkali and other metals were performed in^[81,82]. A general quantum-mechanical analysis of the phenomena is given in^[83,84].

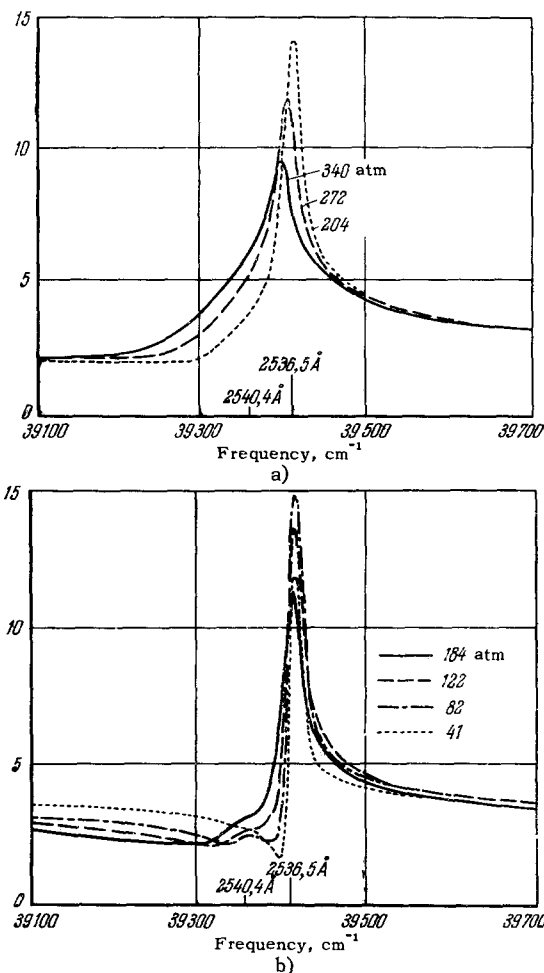


FIG. 9. Variation of mercury-vapor reflection line shape with pressure (in accordance with the scheme of Fig. 8).

Thus, it is possible to trace in similar experiments the gradual development (with decreasing distance) of the particle interaction and the occurrence of reflection from the surface produced by them gradually, and also the replacement of incoherent radiation by coherent scattering. The connection between the intensity of the selective reflection, the depth of penetration, and the character of the interaction become clearly manifest in this case.

It is explained in^[80], for example, that luminescence quenching sets in at intermolecular distances $\sim 50\text{--}150 \text{ \AA}$ (the gaskinetic diameter of the molecules is $\sim 5 \text{ \AA}$), selective regular reflection sets in at much shorter distances, and finally, interaction that changes the forces of the absorption oscillators occurs at still smaller distances, $\sim 10\text{--}30 \text{ \AA}$. A hypothesis was advanced in^[81,82] that coherent resonance fluorescence is present (see^[85]) and that the attenuation has a special mechanism. Figure 9 shows the change in the reflection line shape, and consequently in the absorption line and in the character of the dispersion when the particles come closer together (for Hg atoms). It is obvious that both the depth of penetration and the coherence length change here, and that they change differently for different λ .

The details of the treatment of the phenomena in^[80-82] may be debatable, but the very possibility of observing the gradual development of the interaction is subject to no doubt.

10. TIME OF ESTABLISHMENT OF THE FIELD IN REFLECTION

In all the preceding arguments we considered only stationary processes; the buildup of these processes was not considered.

The propagation of the front of a monochromatic wave in a dispersive medium, as is well known, was studied in detail by Sommerfeld, Brillouin, and Leontovich^[86,87,88]. However, they presented no quantitative estimates for the case of light waves, made no experimental measurements, and did not consider at all the particular question of the buildup time of the field during reflection (some qualitative considerations are found in^[89], but only in connection with a two-dimensional object, which greatly changes the situation).

An attempt to obtain a very crude estimate of the lower limit of this time was made in a note^[90] in which a figure 10^{-10} sec is cited for a metallic mirror, on the basis of a primitive calculation in the spirit of elementary classical electron theory; a reflection delay time Δt of this order of magnitude can explain the discrepancies in results of measurements of the velocity of light in installations using single and multiple reflections. The results of this calculation should not be overestimated; what is important is the indication that an experimental estimate is possible.

An attempt at experimental separation of (selective) reflected light and luminescence with respect to a duration parameter was made in^[91]. However, owing to the insufficient time resolution of the apparatus, only an upper limit was estimated, $\tau_{\text{ref}} < 40\tau_{\text{lum}}$. A rigorous analysis in^[91] yielded $\Delta t < 5 \times 10^{-14}$ sec for the visible region and $\Delta t < 6 \times 10^{-17}$ sec for ultraviolet. It was only possible to establish experimentally that $\Delta t < 10^{-12}$ sec.

The approach to the analysis of the problem should undoubtedly follow the way indicated by L. I. Mandel'shtam in^[89], with consideration of a three-dimensional object.

11. CHANGE OF COHERENCE UPON REFLECTION

The change of coherence upon reflection was considered in^[93,94]. If a wave of type (1) is incident, i.e., fully coherent light, the reflected light is also coherent (the analysis was made for transparent media). If the incident light is partially coherent, the picture changes. Coherence is essentially a characteristic of the microstructure of the light but, as is well known (see, for example,^[85,79,95]), the concept of coherence and its numerical measure—the degree of coherence—are introduced formally also in the macroscopic approach, as was indeed done in^[93]. The coherence of a beam is changed by reflection if $\varphi \neq 0$, and is variable along the beam.

12. REFLECTION FROM MEDIA HAVING SPATIAL DISPERSION

The optics of media having spatial dispersion (s.d.) was considered in detail in^[12,91,97], and we shall therefore confine ourselves only to a few remarks as applied to our case.

If we confine ourselves to relatively weak s.d., then for the majority of "usual" optical media (with the exception of plasma) it is sufficient to have in a homogeneous nonconducting medium

$$D_i(\omega, \mathbf{m}) = \epsilon_{ij}(\omega) E_j + i\gamma_{ijk}(\omega) \nabla_j E_k + \alpha_{ijkl}(\omega) \nabla_j \nabla_k E_l. \quad (23)$$

The first term on the right describes the frequency dispersion, the second the s.d. of first order (gyrotropic or optical activity), and the third s.d. of second order, etc.

Similar expressions should be written generally speaking, for $B_i(\omega, \mathbf{m})$; we confine ourselves to cases where μ_{ij} is a function of ω (but γ_{ikm} can also be different from zero).

The properties of the tensors $\hat{\gamma}$ and $\hat{\alpha}$ depend on the symmetry of the crystal and on the type of the exciton transition (or, on other physical properties causing the effect); an analysis of these properties is given in^[12].

The main consequences of the s.d. of first order in^[12] is the elliptic birefringence and, in some directions, the rotation of the plane of polarization. Fur-

ther, near the resonant frequency there can exist for a given direction three waves with different velocities; for the new, third wave, $n^{(3)}$ increases rapidly on approaching ω_{res} from the long-waves side, starting with distances on the order of $100\text{--}200 \text{ \AA}$, becoming much larger than $n^{(1)}$ and $n^{(2)}$.

The character of light propagation in media with s.d. (for the first order) as a function of the symmetry of the crystal is considered also in^[98]. It should be noted that we have used here an expression for the field energy different from that used in^[12,97]. The conclusions are somewhat different: there is no third wave in cubic crystals, and the third wave arises in some other crystals only when $\gamma_{ijk\text{magn}} \neq 0$. In cubic crystals it appears only when the coupling equation is chosen in the form

$$H_i(\omega, \mathbf{m}) = \mu_{ij}^{-1}(\omega) B_j + i\gamma'_{ijk\text{magn}} \nabla_j B_k.$$

To solve boundary-value problems for media with s.d., the number of boundary conditions must be larger than in the derivation of formulas (4a) and (4b). Indeed, if the "new wave" arises, the number of boundary conditions should also increase. This question is considered in^[12] (account must also be taken of surface states, which may cause the polarizability of the layer to become gyrotropic^[99]). General formulas for E_R and $R(\omega, \varphi, \theta)$ in first-order s.d. turn out to be quite cumbersome and not very instructive, and we shall therefore consider separately the dependences on ω , φ , and θ (where θ is the angle between \mathbf{E} and the plane of incidence).

The $R(\omega)$ was analyzed in^[12] for the case of normal incidence of a wave of type (1) on the surface of an isotropic gyrotropic medium. The most interesting conclusion is that, owing to the appearance of the new wave, for which $n^{(3)}$ is very large, in the region $\omega < \omega_{\text{res}}$, the maximum of $R(\omega)$ (Fig. 10), which lies in the region $\omega > \omega_{\text{res}}$ in the absence of s.d., may turn out to be shifted in this region and probably become strongly deformed. The reflected light will have elliptic polarization, and its intensity should oscillate with variation of the crystal thickness and depend on the polarization of the incident light.

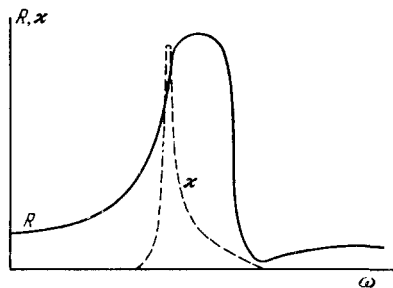


FIG. 10. $R(\omega)$ and $\kappa(\omega)$ for a medium consisting of strongly damped harmonic dipole oscillators in accordance with classical dispersion theory and Fresnel's formulas.

A formally macroscopic calculation for the same case is presented in^[100]. The region far from ω_{res} , isotropic media, or cubic crystals are considered without allowance for the third wave. The reflected light is elliptically polarized, and the ellipticity η depends strongly on φ . When $\mathbf{E} = \mathbf{E}_{\parallel}$ and $\varphi = 0$ we have $\eta = 0$; the ellipticity increases insignificantly with φ , and at a distance of several seconds of an angle from a certain value φ_I , which is close to φ_{BR} , it increases strongly, becoming circular, and drops to zero at $\varphi = \varphi_I$, and again increases to circular polarization of opposite direction at the same distance, and drops rapidly to a small value, vanishing at $\varphi = \pi/2$. In the case $\mathbf{E} = \mathbf{E}_{\perp}$ the ellipticity is very small and changes little, retaining the same sign. At intermediate orientations of \mathbf{E} , the value of η becomes smaller (unlike absorbing media without s.d., where $\eta = 0$ when $\mathbf{E} = \mathbf{E}_{\perp}$ and $\mathbf{E} = \mathbf{E}_{\parallel}$, and has a maximum at a certain intermediate orientation).

Reflection from gyroscopic media was considered in somewhat less detail in^[101]. In particular, the question of reflection from a ferrimagnetic medium was touched upon there. Questions of reflection from ferromagnetic and ferrimagnetic substances are considered also in^[8,17], where the appropriate phenomenological macroscopic calculations were made.

In the case when $\gamma_{ijk} = 0$, account must be taken of the spatial dispersion of second order. In some cases (when the exciton effective mass is negative) there can appear a third and fourth wave, but only at distances $10\text{--}20 \text{ \AA}$ from ω_{res} . In all cases, a cubic crystal, even of higher symmetry O_h , is anisotropic with respect to α . The s.d. effects of second order are much smaller than those of first order, and can be noticeable only when $\gamma = 0$.

Reflection from an isotropic medium was considered for this case, at normal incidence, in^[12]. Formulas similar to the Fresnel formulas are given also in^[102] for a crystal of class O_h and for arbitrary φ ; both the calculation procedure (microscopic) and the results differ somewhat from these of^[12], but the final conclusions are similar. The reflection is anisotropic with respect to the axes of the crystal, and its course depends on the polarization of the incident light. Reflection was also calculated in^[103], where it was shown that additional waves can influence the phase of the reflected light, shifting it by large angles (on the order of $5\text{--}20^\circ$). Reflection in the presence of surface excitons was considered in^[99]. Reflection from a medium with strong s.d.—plasma, including relativistic—was considered in^[97,104,105]. The effects of s.d.—nonlocal coupling between γ and \mathbf{E} , when anomalous skin effect take place—are appreciable in reflection from metals. The result for a low temperature plasma will be given below (Sec. 14) in the discussion of one particular case; this result has a wide range of applicability^[97].

Reflection from media with spatial dispersion of second order (CdS crystal) was investigated experimentally in [106,107], but the interpretation of the results is not unique. It should be noted that the only undisputed experimental proof of the existence of second-order effects is anisotropic absorption in the Cu₂O crystal [12,108] in the region of the quadrupole line. Reflection effects connected with excitons were observed in liquid and solid Xe [109]. Reflection from gyrotropic (nonmagnetic) media was investigated only in [110], but the effect was not observed there, in spite of the high precision of the measurements. The probable reason is the fact that the absorption oscillator strength in the investigated object (sodium uranyl acetate crystal) was too small.

13. REFLECTION IN THE PRESENCE OF A MACROSCOPIC SURFACE LAYER (COATING)

It is well known that no physical interface is ever a geometrical plane. Even if we assume complete absence of surface films, oxides, contaminations, or surface texture, caused by the inevitable finishing required in the optical region, and effects of the "stepwise structure" type on the surface of a crystal—this statement nevertheless remains in force, and the physical interface is always a transition layer of definite thickness.

In the presence of such a layer, the reflection laws become more complicated.

Macroscopic calculations of the course of reflection in the presence of thin transition dielectric layers were made recently in [111] (which contains a review of earlier works) and in [112]. It is assumed that the refractive index n_m of the transition layer of thickness l between the two media varies continuously from n_1 to n_2 . The solution of the problem is approximate and is given in the form of an expansion in powers of l/λ . If we choose the z axis perpendicular to the plane $n_m = \text{const}$ and direct it into the medium, then

$$E_{r\perp} = E_{0\perp} \left(\alpha + i \frac{\omega}{c} |\mathbf{m}| \rho + \frac{\omega^2}{c^2} |\mathbf{m}|^2 \tau \right), \quad (17a)$$

$$E_{r\parallel} = E_{0\parallel} \left(\alpha' + i \frac{\omega}{c} |\mathbf{m}| \rho' + \frac{\omega^2}{c^2} |\mathbf{m}|^2 \tau' \right), \quad (17b)$$

where α and α' are defined by formulas (4a) and (4b), and

$$\rho = 2n_1 \cos \varphi \frac{p - ln_2^2}{(n_1 \cos \varphi + n_2 \cos \psi)^2}; \quad p = \int_0^l n_c^2(z) dz;$$

$$\rho' = 2n_1 \cos \varphi \frac{ln_2^2 - p \cos^2 \psi - qn_1^2 n_2^2 \sin^2 \varphi}{(n_2 \cos \varphi + n_1 \cos \psi)^2}; \quad q = \int_0^l \frac{dz}{n_c^2(z)};$$

$$\begin{aligned} \tau &= 2n_1 n_2 \frac{h-f}{(n_1 \cos \varphi + n_2 \cos \psi)^2} \cos \varphi \cos \psi \\ &+ 2n_1 \cos \varphi \frac{p - l'n_2^2}{(n_1 \cos \varphi + n_2 \cos \psi)^3} (-p + ln_1^2 \sin^2 \varphi \\ &- ln_1 n_2 \cos \varphi \cos \psi); \end{aligned}$$

$$\begin{aligned} \tau' &= 2 \frac{(f-h) n_1 n_2 \cos \varphi \cos \psi}{(n_2 \cos \varphi + n_1 \cos \psi)^2} + 2 \frac{2(s-r) n_1^2 n_2 \sin^2 \varphi \cos \varphi \cos \psi}{(n_2 \cos \varphi + n_1 \cos \psi)^2} \\ &+ 2n_1 \cos \varphi \frac{ln_2^2 - p \cos^2 \psi - qn_1^2 n_2^2 \sin^2 \varphi}{(n_2 \cos \varphi + n_1 \cos \psi)^3} (-ln_1 n_2 - p \cos \varphi \cos \psi \\ &+ qn_1^2 n_2 \sin^2 \varphi); \\ f &= \int_0^l zn_c^2(z) dz; \quad h = \int_0^l p'(z) dz; \quad r = \int_0^l q'(z) n_c^2(z) dz; \\ s &= \int_0^l \frac{p'(z)}{n_c^2(z)} dz; \quad p'(z) = \int_0^z n_c^2(z) dz; \quad q'(z) = \int_0^z \frac{dz}{n_c^2(z)}. \end{aligned}$$

If $l = 0$, we obtain Fresnel's formulas; confining ourselves to terms of first order in $1/\lambda$, (i.e., putting $\tau = \tau' = 0$), we obtain the so-called Drude formulas, which coincide in form* with (14a) and (14b), but with values $\gamma_x = \gamma_y = (p - ln_2^2)/d(1 - n_2^2)$; $\gamma_z = (l - gb_2^2)/d(1 - n_2^2)$ if $n_1 = 1$. It is obvious that the calculations are valid only if $l \gg d$, where d is the microscopic characteristic dimension of the medium—the lattice constant or the dimension of the molecule; on the other hand, we should have (particularly if we confine ourselves to the first approximation $l \ll \lambda$, i.e., $5-10 \text{ \AA} \ll l \ll 5000 \text{ \AA}$). This indicates that the region of rigorous validity is not particularly large.† There are also other calculations, in which somewhat different assumptions and approximations are made. These are, for example, the formulas of [113], which in some case agree better with experiment [104]. A review of several papers of this kind is found in [28,115]. It must be assumed that for different objects it is necessary to choose different calculation procedures and to make different assumptions and approximations.‡

First-order macroscopic formulas for reflection with allowance for scattering in the surface layer, its dichroism, and birefringence are given in [118].

It follows from the first-order formulas that in the presence of a surface layer, $E_{r\parallel}$ does not vanish at $\varphi = \varphi_{Br}$, the phase δ varies smoothly, and the reflected light is elliptically polarized near φ_{Br} , i.e., all the phenomena described in Sec. 5 take place.

The second-order formulas give a more complicated picture. It turns out that the Brewster angle ($\tan \varphi_{Br} = n$), the "polarization angle" ($E_{r\parallel}$ is minimal), and the "principal angle" ($\delta = \pi/2$) do not coincide. This, as shown for example in [52,53] actually takes place, although the difference, in accordance with (17a) and (17b), does not exceed $1'$. The second-approximation calculation yields also reflection when $n_1 = n_2$.

*In (14a) and (14b) $n_1 = 1$ and $n_2 = n$.

†A more rigid upper limit is given in [112]: $l < 100 \text{ \AA}$ for the first approximation and $l < 1000 \text{ \AA}$ for the second approximation (in fact, the difference between these approximations is not so large).

‡It should be noted that the Drude formulas are applicable for all values of n also for thin films on metals [116]. For dielectrics, there are noticeable deviations already at -25 \AA [117].

For thicker layers, there are other calculation methods (reviewed, for example, in^[4,26,119,120]). These calculations play an important role in modern practical optics, and determine the parameters of non-reflective or reflective coatings, interference filters, etc.. Reviews of this special topic can be found in *Usp. Fiz. Nauk*^[121] and in a number of monographs^[4,26]. Reflection from a thin (~ 10 – 100 \AA) coating having characteristics different from those of the medium was considered in^[26] by starting from the notion that the particles of the layer ("two-dimensional colloid") are randomly distributed over the surface and are small that the Mie effect can be neglected.

14. REFLECTION IN THE PRESENCE OF A MICROSCOPIC LAYER. LIQUID SURFACE

Fewer studies have been devoted to the reflection from a surface on which the surface layer is produced not by a contamination coating or finishing, but by the special molecular structure of the material on the surface, due to anisotropy and asymmetry of the internal field in this region.

Thus, it is regarded as almost certain^[122,123] that there exists on the free surface of a liquid a mono- or bimolecular layer with specially ordered molecule orientation, and possibly with different intermolecular distances. On the surface of a solution there is likewise a layer (probably of the same order of thickness) where the concentration is different than in the volume, called the "Gibbs layer"^[124].

A microscopic calculation based on the physical premises of Sec. 6, but with an additional assumption concerning the special properties of the surface layers, was performed in^[51,56]. This yielded the formulas (14a) and (14b), but with different values of the parameters γ_x , γ_y , and γ_z . The calculation of these parameters requires, of course, the assumption of definite models of the surface layer. The calculations were made for a simple cubic lattice with primitive cell under the assumption that the molecules of the first layer are anisotropic and can be oriented in definite fashion, and that their polarizability $\hat{\beta}_0$ can be different than in the volume ($\hat{\beta}$); the distance from the first layer to the succeeding is $d_z \neq d$.

Starting from the described representation of the structure of the liquid surface, the calculation was subsequently extended, making certain assumption, to include the liquid under the assumption that its molecules are anisotropic; for the principal polarizabilities we can write

$$\beta_{0x} + \beta_{0y} + \beta_{0z} = \beta_1 + \beta_2 + \beta_3 = 3\beta.$$

(In the case when the orientations of the molecules are different, as is postulated for liquids, for example by the theory of^[115], it is possible to assume for

the β_{0i} values that are averaged over all the molecules of the layer.)

The following expressions were obtained (b^3 is the volume per liquid molecule)

$$\gamma_x = \gamma_y = \frac{1}{1 - (4\pi/3b^3)\beta_{0x}} \left\{ \frac{\beta - \beta_{0x}}{\beta} + \frac{B}{2b^3} \beta_{0x} \right\}, \quad (18a)$$

$$\gamma_z = \frac{1}{1 + (8\pi/3b^3)\beta_{0x}} \left\{ \frac{\beta - \beta_{0z}}{\beta} - \frac{B}{b^3} \beta_{0z} \right\}, \quad (18b)$$

$$B = 0,329 \exp \frac{2\pi(b-b_z)}{d}.$$

In spite of the fact that the theoretical calculations for the liquids are less well founded, owing to the insufficient development of the theory, an experimental verification can be made only in the case of liquids, for only in this case it is possible to obtain a reflecting surface of ideal quality without processing the surface.

In the latest papers^[54,126-129] (which also include a bibliography), the values of $\rho = |E_{R\parallel}|/|E_{R\perp}|$ and the phase differences δ between them were measured for many liquids, i.e., the ellipticity η of the reflected light. This ellipticity is the result of the presence of the factor i in formulas (14a) and (14b), and can serve as a measure of the difference between the structure of the surface and the interior of the liquid; its values, as follows from (14) and (18) are noticeable only near φ_{BR} .

The results of the experiment agree in order of magnitude* with the theory, although they yield somewhat undervalued ρ for anisotropic molecules and over-valued ones for isotropic molecules. This shows that the orientation factor is not the only one.

Attempts to improve the agreement by choosing for E_{eff} an expression that takes into account the anisotropy of the internal field that produces the ordered orientation^[128] were not fully successful.† Good agreement with experiment is obtained by taking into account the singularities of the distribution function on the surface^[211a]. The $\delta(\lambda)$ dependence agrees well with experiment^[53].

Experiment has shown that the properties of the layer vary with T , namely, ρ decreases, as expected, when an ordered orientation is assumed; the variation agrees with x-ray and electron-diffraction data and with the values of the parameters of the molecule orientation correlation^[125]; for anisotropic molecules the dependence on T is stronger, as expected. When T approaches the solidification temperature, the values of ρ , i.e., the differences of the surface layer, begin to increase rapidly and something in the nature of precrystallization is observed^[127-129] (Fig. 11).

*For liquids, the ratio of the axes of the oscillation ellipse lies in the range $1 : 30 \times 10^{-3} - 1 : 250 \times 10^{-3}$.

†Equally ineffective were the replacement, in the derivation of (18), of the Lorentz expression (9) for E_{eff} , used in^[56], by the Onsager formula or by the Buckingham formula.

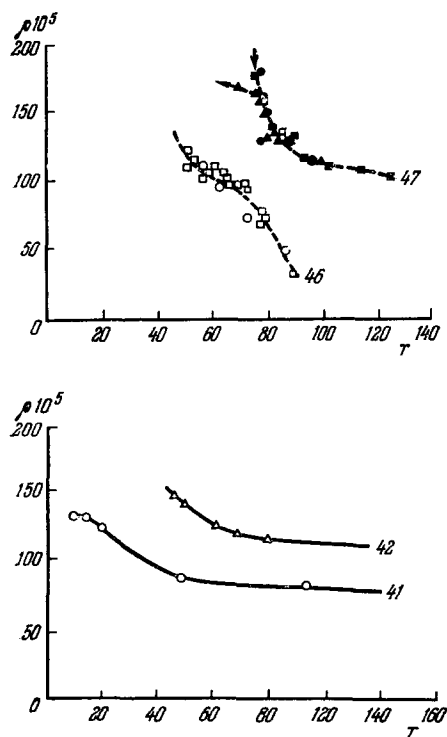


FIG. 11. Plot of $\rho(T)$ at $\varphi = \varphi_{Br}$ against the temperature. 41 — ethylene bromide, 42 — σ -nitrophenol ($T_{melt} = 44^\circ$), 46 — monochloroacetic acid ($T_{melt} = 61^\circ(\alpha)$, $56^\circ(n)$, $50^\circ(\gamma)$), 47 — acetamide ($T_{melt} = 82^\circ$). \blacktriangle — cooling, \bullet — heating.

From this example, which we examined in some detail, we see how many complicated molecular-optics problems can be investigated. We see also that these effects completely mask the effects predicted by (14a) and (14b), which are smaller by 1–2 orders of magnitude.

15. REFLECTION IN THE PRESENCE OF A MICROSCOPIC LAYER. SURFACES OF METALS AND SEMICONDUCTORS

Transition layers exist, naturally, not only in liquids. Thus, in a metal, even one with an ideal lattice, the density of the electron cloud at the surface drops to zero from its value inside the metal, not jumpwise but over a distance of $1\text{--}3 \text{ \AA}$. Further, on the equilibrium faces of metallic crystals, there are smeared out phase boundaries (i.e., “smeared-out lattices”) up to a depth of 5–10 atomic layers. In addition, the transition layer can be caused not only by the static structure, but also by kinetic processes, such as transport phenomena. Even if one neglects all the foregoing circumstances, the very fact that the electrons coming from the inside of the metal are reflected from the surface produces near the surface conditions that differ from those deep in the metal, i.e., a certain boundary layer is produced, whose thickness is approximately equal to the mean free path of the electron.

When light is reflected from the surface of a metal, this layer also introduces peculiarities in the course of the reflection, especially in the case of the anomalous skin effect, when the collective depth of penetration of the field in the metal is small compared with the mean free path of the electrons and with the mean distance covered by the electrons during one period of the field oscillation (spatial dispersion takes place). In this case another approach to the solution of the problem is appropriate.

Taking into account only the effect of electron reflection from the “geometric surface” of the metal, which is assumed to be ideal, and neglecting the other factors listed above, we can formally introduce certain surface currents and solve the problem macroscopically.

This yields^[130] the Fresnel formulas, but the refractive index in them depends on the polarization and on the angle of incidence:

$$n_{\perp}^2(\varphi, \omega) = \varepsilon(\omega) + \frac{8\pi\sigma_n(\omega)}{c} \sqrt{\varepsilon(\omega) - \sin^2\varphi} + \left(\frac{4\pi\sigma_n(\omega)}{c}\right)^2, \quad (19a)$$

$$n_{\parallel}^2(\varphi, \omega) = \varepsilon(\omega) + \frac{8\pi\sigma_n(\omega)}{c} \sqrt{\varepsilon(\omega) - \sin^2\varphi} + \left(\frac{4\pi\sigma_n(\omega)}{c}\right)^2 + \frac{4\pi\sigma_n(\omega)}{c} \frac{\sin^2\varphi}{\sqrt{\varepsilon(\omega) - \sin^2\varphi}}, \quad (19b)$$

where $\sigma_n(\omega)$ is the “surface conductivity,” which characterizes the course of the microscopic processes on the surface. An experimental verification of (19a) and (19b) would be of great interest, would make it possible to establish the existence of the anomalous skin effect, etc.

One more example is reflection from the surface of a semiconductor (InSb)^[131] having a thin surface layer with increased carrier density. Close to the plasma frequencies, the reflection coefficient R changes and it becomes possible to determine the density and the effective mass of the carriers. Such a method was used to control the surface cleanliness of InSb^[132,133]; the existence of a surface layer was proved also for GaAs crystals^[134]. These examples demonstrate the wide capabilities of the applications of the theory.

16. SURFACE STATES

It was assumed in the preceding arguments that the molecules or other elementary radiators can have a distinct arrangement and orientation. However, the properties of these radiators was usually assumed to be unaltered; in other words, it was assumed that the structure of the energy levels on the surface was the same as within the substance.

Yet it is known that distinct surface state, produced either by lattice defects, atoms in excess of stoichiometry, etc. or, even in the case of an ideal lattice, by differences in the intermolecular interactions, symmetry of the internal field (such as “Tamm

levels" in semiconductors; see also^[128]), always exist near the surface.

The question of surface levels, the surface excitations corresponding to them, and their displacements is the subject of an extensive literature; it deals both with the occurrence of singular surface excitons and with the influence of the boundaries on the behavior of volume excitons (see^[12]). Without entering into the details of these theories, we emphasize only the great variety of the possible states. The depth of the layer in which these phenomena should be observed depends on the type of state. Thus, for example, the estimates suggested for the depth of the surface-exciton band range from several Å for Frenkel excitons to ~ 100 Å for Wannier-Mott excitons (see, for example,^[12], p. 257).

As follows from the foregoing, all these phenomena should, generally speaking, influence the course of the reflection. The question of the influence of the surface excitons is considered in Sec. 12; we present here by way of an example a schematic but illustrative calculation^[135] made for the "Tamm levels." Introducing the concept of the "surface band" made up of these levels, the author considers the motion of the electrons (holes) in it. These electrons should be concentrated in the boundary region—a layer whose thickness is estimated by the author to be of the order of 10^{-8} cm, and their motion can therefore be regarded as a surface current. Introducing the corresponding surface conductivity σ_s , the author obtains, say for the case when $\mathbf{E} = \mathbf{E}_\perp$,

$$E_{r\perp} = E_{0\perp} \frac{\cos \varphi - \sqrt{\xi^2 - \sin^2 \varphi} - \xi}{\cos \varphi + \sqrt{\xi^2 - \sin^2 \varphi} + \xi}. \quad (20)$$

Here

$$\xi = \frac{|\mathbf{m}|}{|\mathbf{m}_d|}, \quad \alpha \xi = \frac{4\pi\sigma_n(\omega)}{c|\mathbf{m}_d|}.$$

In the particular case when $\mathbf{m} = \mathbf{m}_d$, i.e., when the reflection does not take place in the absence of surface levels, we get from (20)

$$E_{r\perp} = -E_{0\perp} \frac{\xi}{2 \cos \varphi + \xi}. \quad (21)$$

Figure 12 shows the obtained dependences of the components of \mathbf{E}_r on the angle of incidence. These plots are shown, for comparison, in the case when there is volume conductivity and for the case of a surface layer with $n = 1.05n_1$, calculated in accordance with Drude's formulas. For the surface conductivity, the plot for the $E_{r\parallel}$ component is entirely different; this can be used to observe this conductivity. The numerical estimates^[135] indicate that the effect can be observed in principle in semiconductors. Thus, far from the absorption band, with the band half-filled ($N_{\text{sur}} \sim 10^{15} \text{ cm}^{-2}$) we have $n_2^2 = 2$, $\xi = 1$, and $\varphi = 60$. The reflection coefficients R_\perp and R_\parallel are respectively equal to 40 and 4%, and in the absence of surface states the respective values are 15 and 0.3%. It must be noted, however, that the effect

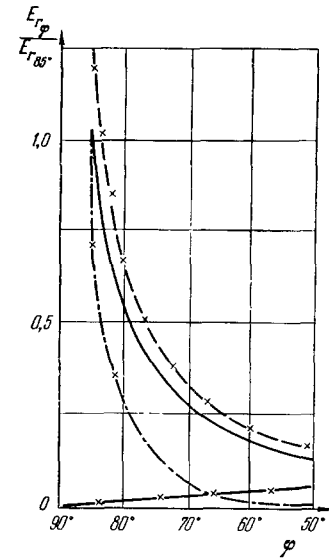


FIG. 12. Plots of $E_{r\perp}(\varphi)$ (—) and $E_r(\varphi)$ (*-.-.-*) in the presence of surface states, of E_r (*- - - -*) in the presence of volume conductivity and (*-*-**) in the presence of a surface layer with $n = 1.05n_1$ after Drude.

is probably masked by the much more noticeable influences of the surface dislocations and the micro-relief of the surface, if the latter is not finished, and of the texture, in the case of a finished surface, so that the appropriate object for an experimental verification is a liquid semiconductor. We must note, incidentally, that there are few reliable direct experimental observations of surface states^[136]. A general review of the optical properties of thin film is presented in^[137].

17. REFLECTION FROM NONLINEAR MEDIA

The question of the limits of applicability of the linear approximation for the analysis of the propagation of electromagnetic waves is considered, for example, in^[139]. It was shown that besides a plasma, which is nonlinear already in weak fields, nonlinearity effects can be observed also in other media at presently attainable field intensities. The linearity limits for metals were also investigated in^[140 151].*

Quantum optics is usually confined to the examination of two-photon scattering processes—second-order effects (i.e., in the second approximation of perturbation theory), and makes use of the Kramers-Heisenberg formula, which is obtained in this approximation (see, e.g.,^[142]). When nonlinear media (n.l.m.) are considered, it is necessary to take into account also "three-photon processes"; the dispersion formulas which take this (third) approximation into account

*We do not consider here ferromagnetic and ferrimagnetic media (for which macroscopic calculations are given, for example, in^[8,17] or ferroelectrics.

were first derived, apparently, in ^[143](see also ^[144]); detailed and more modern calculations for the scattering of light by atoms are given in ^[145-147].

The interaction of electromagnetic waves with matter was considered in this approximation in ^[145] and in a number of other papers (see, e.g., the reviews ^[148-150]). It has been shown that the phenomena can be treated macroscopically by introducing the nonlinear polarizability tensor (which itself must be calculated from the microscopic theory*). It is this treatment which we shall consider. We note only by way of an introduction, that the nonlinear effects can be caused not only by the nonlinearity of the polarizability of the individual molecules.

A light beam passing through a medium consisting of anisotropic molecules will exert an orienting action on these molecules. This effect makes the medium nonlinear. This circumstance was apparently first noted in ^[152,153], where it was indicated that the energy density necessary to obtain a noticeable effect in a non-absorbing dielectric is of the order of 10^5 W/cm² (i.e., attainable at present). A detailed theory was recently presented in ^[154]. In absorbing substances, an orientational photodichroism also takes place; this phenomenon was observed and investigated ^[156,157]. Nonlinearity can also result from spatial dispersion of nonlocalized excitations ^[158]. We do not concern ourselves here with "parametric effects" such as the change of non-optical parameters under the influence of light.

As shown in Secs. 13 and 14, the appearance of ordered orientation of molecules in even one or two surface layers is manifest in a measurable manner in reflection. Whereas the orientation introduced by the light field is insignificant, the dimensions of the region encompassed by this orientation greatly exceed the dimensions of those monomolecular or bimolecular layers whose action was discussed above, and the observation of effects connected with reflection is undoubtedly possible.

Inasmuch as the intensities of the light field are still much smaller than the intramolecular intensities, even for lasers, we can, in the case of the acting field (1), represent the polarizability (far from the natural frequencies) in the form

$$\begin{aligned} P_{i0}(t, \omega) &= \beta_{ij} E_j + \chi_{ijk} E_j E_k = P_{i \text{ lin}} + P_{i \text{ quad}} \\ &= \int_{-\infty}^0 \sum_j \beta_{ij}(t', \omega) E_j(t-t') dt' \\ &+ \int_{-\infty}^0 dt' \int_{-\infty}^0 dt'' \sum_j \sum_k \chi_{ijk}(t', t'', \omega) E_j(t-t') E_k(t-t'-t''), \end{aligned} \quad (22)$$

where the response functions $\hat{\beta}(t', \omega)$ and $\hat{\chi}(t', t'', \omega)$ of the system are determined by the dispersion formulas of the microscopic theory. An analysis of the symmetry properties of the tensor χ

is given in ^[147,159]; it has nonzero components for media that have no symmetry center (it is similar to the piezoelectric-effect tensor).

We can accordingly write down the Lorenz-Lorentz formula

$$\mathbf{E}_{\text{eff}} = \mathbf{E} + \frac{4\pi}{3} \mathbf{P}_{\text{lin}} + \frac{4\pi}{3} \mathbf{P}_{\text{quad}}. \quad (23)$$

It follows from the third approximation of the theory that a moment of frequency 2ω is induced when a monochromatic wave propagates in a n.l.m. It is directed along the wave vector of the fundamental wave; therefore no radiation is produced in the direction of this vector, and the transmitted waves of frequency ω do not produce second harmonics in an ideally homogeneous isotropic medium ^[145,160]. In the presence of an inhomogeneity in the form of an interface, a second harmonic will be produced. These considerations are somewhat oversimplified; in particular, they pertain to a relatively weakly dispersive medium (where c_ω and $c_{2\omega}$ differ little).* Reflection processes with the second medium nonlinear were considered in ^[160,162,163].

Calculations performed in ^[160,162] for the simplest case of reflection of unbounded plane monochromatic waves from the interface between a linear medium and an optically isotropic nonlinear one lead to the following picture. Besides the usual reflected and refracted waves at the fundamental frequency (respective angles φ and ψ), there is produced in n.l.m., in accord with (22) and (23), a nonlinear-polarization wave of frequency 2ω , in analogy with the linear-polarization wave (Sec. 6), traveling at an angle $\psi_{\text{polar}, 2\omega} = \psi$; this wave has a longitudinal component.† It produces a reflected ray, traveling at an angle $\varphi_{2\omega}$, and a refracted one at an angle $\psi_{2\omega}$. Here

$$\sin \varphi_{2\omega} = \frac{n_1(\omega)}{n_1(2\omega)} \sin \varphi, \quad (24)$$

where $n_1(\omega)$ and $n_2(2\omega)$ are the refractive indices for the linear approximation. For these waves, too, using a microscopic approach similar to that of Sec. 6, it is possible to prove the extinction theorem ^[162], making this theorem very general.

The following expressions were obtained in ^[147,162] for the amplitudes (for an optically isotropic medium):

$$\begin{aligned} E_{r\perp}(2\omega) &= -4\pi P_{\text{quad}\perp}(2\omega) \{n_2(2\omega) \cos \psi_{2\omega} + n_1(2\omega) \cos \varphi_{2\omega}\}^{-1} \\ &\quad \times \{n_2(2\omega) \cos \psi_{2\omega} + n_2(\omega) \cos \psi_\omega\}, \end{aligned} \quad (25a)$$

$$\begin{aligned} E_{r\parallel}(2\omega) &= 4\pi P_{\text{quad}\parallel}(2\omega) [\sin \alpha \{n_1(2\omega) \cos \psi_{2\omega} + n_2(2\omega) \cos \varphi_{2\omega}\}^{-1} \\ &\quad \times \{1 - [n_2^2(\omega) + n_2^2(2\omega)] n_1^2(2\omega) \sin^2 \varphi_{2\omega}\} \\ &\quad + \cos \alpha \sin \psi \{n_2(2\omega) n_2(\omega) \cos \psi_{2\omega} + n_2(2\omega) \cos \varphi_{2\omega}\}^{-1}]. \end{aligned} \quad (25b)$$

*If the medium has a strong dispersion, especially near its natural frequencies, the phenomena become more complicated ^[145,161]; they become even more complicated in the case when the wave is quasimonochromatic. In an anisotropic medium, where the number of rays is larger (different anisotropies of β and χ) and interference can occur between them ^[162], the course of the reflection will depend on the depth of penetration.

†We recall that we are considering electrically nonlinear media.

*See also ^[151].

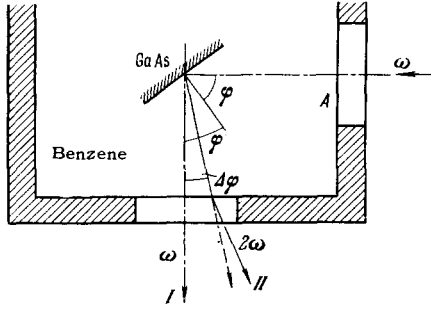


FIG. 13. Ray pattern in a cell with a crystal immersed in benzene.

Here α is the angle between $\vec{P}_{\text{quadr}\parallel}(2\omega)$ and $\vec{m}_d(\omega)$, and $\hat{n} = \sqrt{\epsilon_{\parallel\text{in}}}$. We recall that the anisotropy of the tensor $\hat{\chi}$ differs from that of $\hat{\epsilon}$. The intensity of the reflected wave can be approximately estimated by means of the formula^[150] $R \sim (\chi E_0)^2$.

For a KPD crystal, χ is on the order of 3×10^{-9} cgs esu, and in a field 10^5 V/cm we obtain a harmonic having an intensity of 10^{-12} of the fundamental wave. For the semiconductor GaAs, χ is on the order of 2.6×10^{-6} and the intensity of the reflected harmonic is on the order of 10^{-6} , which can certainly be measured. Values of the same order can be expected for InSb and Te.

The theory predicts further^[147,162] that when two waves of frequency $\omega_1 = \omega_2$ are incident on a surface of a n.l.m. at angles φ_1 and φ_2 , there are produced in the radiation field (besides the usual reflected waves of frequency ω) three reflected waves of frequency 2ω with the following reflection angles (for the case when m_1 and m_2 lie in the same plane:

$$\left. \begin{aligned} \sin \varphi_{11}(2\omega) &= \frac{2 \{m_1(\omega) i\}}{|m_r(2\omega)|}, \\ \sin \varphi_{12}(2\omega) &= \frac{\{m_1(\omega) i\} + \{m_2(\omega) i\}}{|m_r(2\omega)|}, \\ \sin \varphi_{22}(2\omega) &= \frac{2 \{m_2(\omega) i\}}{|m_r(2\omega)|}. \end{aligned} \right\} \quad (26)$$

Here i is a unit vector in the direction of the line of intersection of the plane of incidence and the sur-

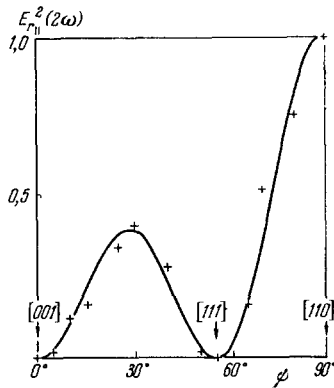


FIG. 14. Plot of $E_{r\perp}^2(2\omega)$ against the azimuth ψ of the plane of incidence relative to the $[001]$ axis for GaAs (E is relative units), with φ kept constant.

face (x axis). If ω_1 and ω_2 are different, then the frequency of the wave is

$$\omega_3 = \omega_1 + \omega_2.$$

An experimental verification of the theory was made for single-crystal GaAs in^[164-165]. Particular attention was paid (for reasons given below) to the procedure used in polishing the crystal; the depth of the layer deformed by the finishing process did not exceed $\sim 250 \text{ \AA}$. The crystal surface was then etched, but only to an extent that no roughness was produced. Relation (24) was verified in^[164] with the crystal immersed in benzene; $\Delta\varphi = \varphi - \varphi_{2\omega} = 2^\circ 10'$, in agreement with the theory; the reflection was from the face $(1\bar{1}0)$ (Fig. 13).

The same single crystal was used to investigate the dependence of $E_{r\perp}(2\omega)$ and $E_{r\parallel}(2\omega)$ on the orientation of the plane of incidence relative to the crystallographic axes (Fig. 14). The result agrees with the predictions of the theory.

The dependence of $E_{r\perp}(2\omega)$ and $E_{r\parallel}(2\omega)$ on φ was investigated in^[165] for reflections from the (110) plane (Figs. 15a, b) and the (001) plane (Fig. 15c). The obtained values

$$\epsilon(\omega) = 12.0 - i \cdot 0.2 \quad \text{and} \quad \epsilon(2\omega) = 19.5 - i \cdot 2.5 \quad (\lambda_{\text{exc}} = 1.06 \mu)$$

agree well with the data of^[166].

It follows also from the theory that the ratio of the intensities of the reflected and transmitted second-harmonic light does not depend on $\hat{\chi}$. This ratio was measured in^[164] for $\lambda_{\text{exc}} = 1.06 \mu$, and the result agreed well with the theory.

Experiments with InSb and Te also produced agreement with the theory^[164].

18. REFLECTION FROM MEDIA HAVING A SYMMETRY CENTER

Investigations were also made of nonlinear reflection from Ge and Si^[167] and from Au and Ag^[168]. Two circumstances come into play here. As already indicated, the χ_{ijkl} are different from zero only for a medium that has no symmetry center. This is valid, however, only in the dipole approximation; in the electric-quadrupole and magnetic-dipole approximations, the situation is reversed. Experimental measurements for metals were made in^[168] (this was preceded by a short paper^[169]). Reflection of giant Q-switched ruby-laser pulses from metal were investigated in^[171]. The second-harmonic power was 10^{-15} of the incident power (see also^[171]). It was shown that, for example for Ag (symmetry class O_h), for $\varphi = 45^\circ$ the second-harmonic reflection is equal to zero when $\mathbf{E} = \mathbf{E}_\perp$, and is maximal when $\mathbf{E} = \mathbf{E}_\parallel$, and that $|E_r| \sim \cos^4 \theta$ in the intermediate cases (θ —angle between \mathbf{E} and the plane of incidence). In the theoretical calculation it was assumed that

$$P_{\text{nonlin}} \approx (EVE). \quad (27)$$

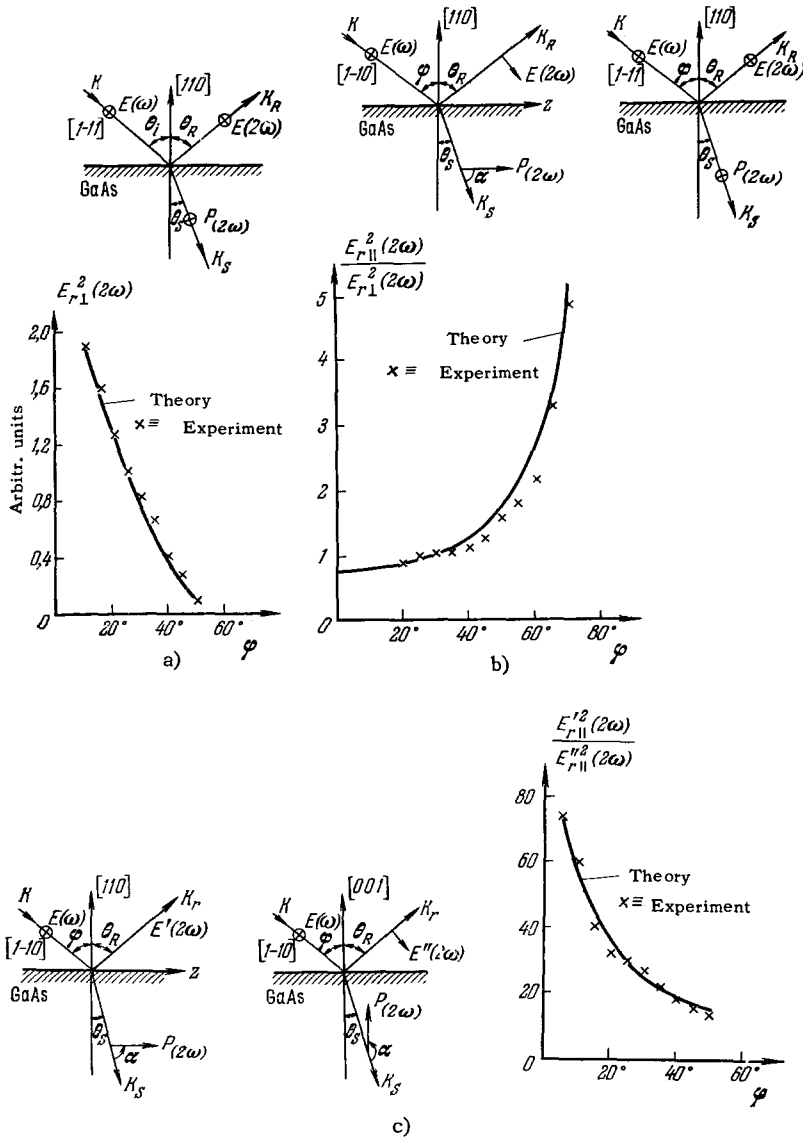


FIG. 15. a) $E_{r||}^2(2\omega)$ for the second harmonic for reflection from the (110) face of GaAs; b) the same intensity ratio for reflection from the (110) face and at different orientations of the plane of incidence; c) the same intensity ratio for reflection from faces (110) and (001) for the second harmonic (plane of incidence coincides with the (110) plane for GaAs).

The agreement with the theory was satisfactory.

It was indicated in [170] that a second term proportional to $\mathbf{E} \times \partial \mathbf{H} / \partial t$, should be added to (27) to improve the agreement with experiment.

However, the conclusion drawn in [170], are the results of [173], where the contributions of the plasma conduction electrons and of the closed shells of the atoms are considered in greatest detail; the role of these shells in the quadrupole nonlinear polarizability turns out to be appreciable, approximately the same as that of the plasma.

19. REGION OF FORMATION AND COHERENCE FOR THE CASE OF NONLINEAR MEDIA

This question is much more complicated; whereas the arguments of Secs. 9–11 remain in force for the linear components, the picture is changed for the nonlinear ones. Generally speaking, the phases $\epsilon(\omega)$ and $\epsilon(2\omega)$ do not agree and the phase velocities of

the waves are not the same, $\{2m(\omega) \neq m(2\omega)\}$ [147]. The linear and nonlinear processes turn out to be incoherent (or not fully coherent); however, two nonlinear processes of like order are coherent with each other if they are the result of the action of two coherent waves of fundamental frequency [165]. As a result, the reflected second-harmonic ray is formed practically in a layer not larger than λ even in a transparent medium, such as KDP,* while the remaining regions make practically no contribution.

In an absorbing medium the formation region is determined by the depth of penetration, which is different for the fundamental frequency and for the harmonic, as can be seen from the figures given above for GaAs. This crystal is almost transparent at $\lambda_\omega = 1.06 \mu$ and absorbs strongly at $\lambda_{2\omega}$ for the second harmonic; the depth of the formation region

*However, the amplitude of the reflected wave does not depend on the matching of the velocities.

therefore does not exceed $\lambda/6$ (in contrast to the fundamental wave). This depth is apparently sufficient to impart to the reflected ray the symmetry properties of the medium. It must be borne in mind here, however, that in the first few molecular layers the symmetry can and should be lower than inside the volume (even if the precautions described above were taken during the surface finishing). This can also contribute in the case of reflection from media possessing a symmetry center in depth (Ge, Ag). In view of the smallness of the region in which the second harmonic is formed, the presence of total internal reflection at the fundamental has in general little effect on the second-harmonic amplitude, and changes noticeably only the phase; for details see [147,162]. For a KDP crystal illuminated by a ruby laser, the second-harmonic coherence length was estimated quite approximately in [174] to be 1 cm.

20. DETERMINATION OF THE OPTICAL PROPERTIES OF SUBSTANCES FROM THE PARAMETERS OF THE REFLECTED LIGHT

The practical applications of the reflection laws are boundless; in accordance with the scope of the present review, we shall consider only the applications dealing with the physical structure of matter. Certain possibilities were already indicated above; we shall consider here the most important problem, that of determining the main parameters of the absorption spectrum $\kappa(\lambda)$ and the dispersion $n(\lambda)$ from the reflection spectrum $R(\lambda)$. There are many various methods for such a determination.

I. Since two constants must be determined for a given λ , two independent measurements must be made. These may be, for example:

A. Measurements of the reflection coefficient R_{nat} (for natural light) in normal incidence from two different external media ("media 1"). This includes, for example, the method of Kravets [155].

B. Measurements of R following incidence from a given medium at different angles:

- 1) R_{nat} for two incidence angles,
 - 2) R_{\perp} or R_{\parallel} for two incidence angles,
 - 3) R_{\perp} and R_{\parallel} for one incidence angle.
- C. Measurements of the ratio R_{\perp}/R_{\parallel} :

- a) at two incidence angles,
- 2) at one angle of incidence with measurement of the phase difference between the components.

D. Measurements of the components and of the Brewster angle:

- 1) R_{\perp} or R_{\parallel} and the Brewster angle,
- 2) R_{\perp} or R_{\parallel} or R_{\perp}/R_{\parallel} for an arbitrary incidence angle and of the Brewster angle,
- 3) R_{\perp}/R_{\parallel} at φ_{Br} and the Brewster angle φ_{Br} .

E. Measurements of the three characteristic angles (Sec. 13)—the principal angle, the Brewster, angle, and the angle of largest polarization [175].

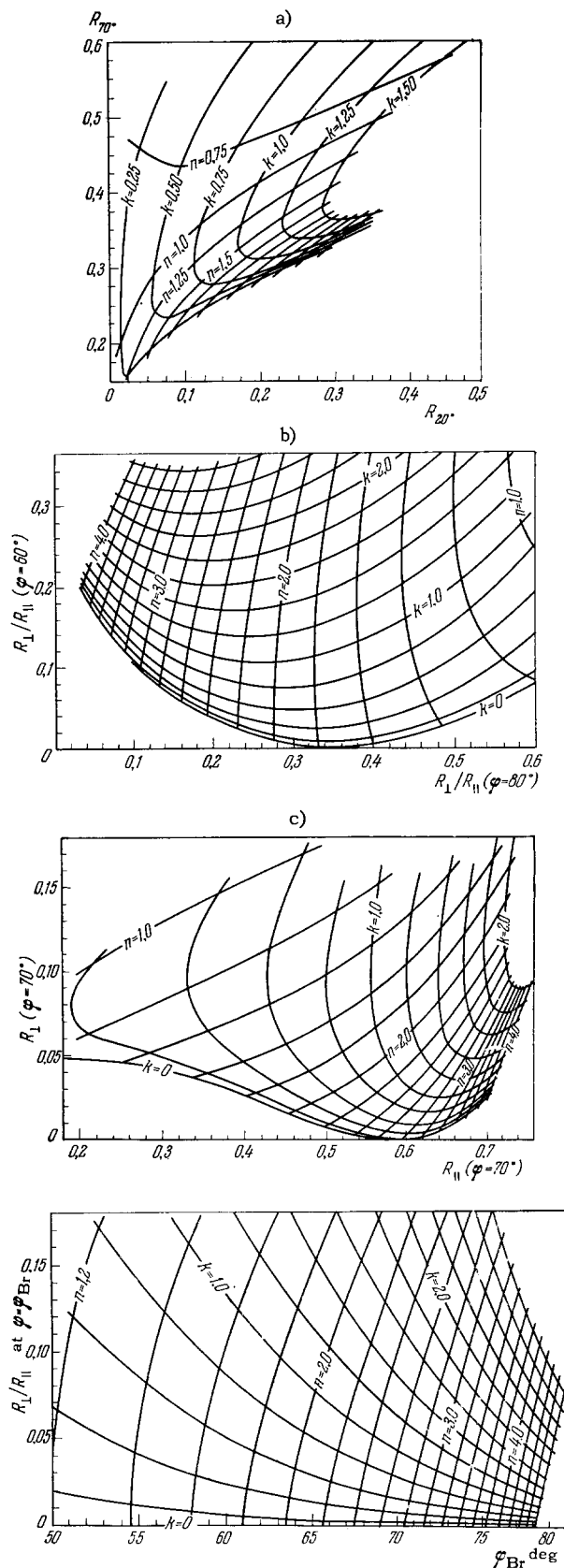


FIG. 16. a) Nomograms for n and κ for use with method B1; the angles are $\varphi_1 = 20^\circ$ and $\varphi_2 = 70^\circ$; b) the same for method C1 with $\varphi_1 = 60^\circ$ and $\varphi_2 = 80^\circ$; c) the same for method B3 with $\varphi = 70^\circ$; d) the same for method D3.

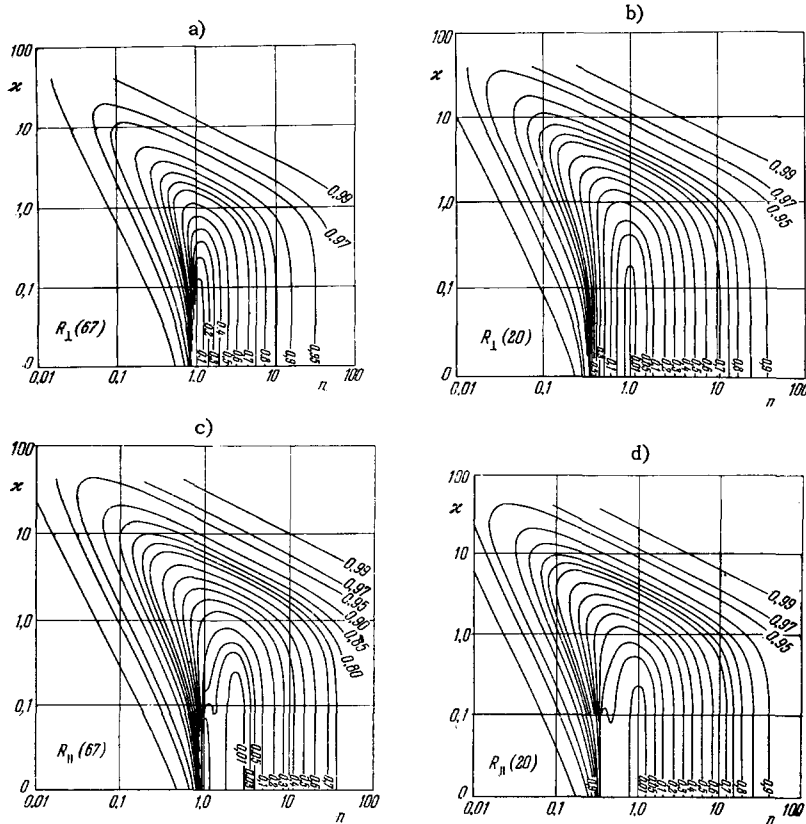


FIG. 17. Nomogram for the reflection coefficients R_{\perp} and R_{\parallel} at incidence angles 20 and 67°.

A large number of such parameter combinations can be proposed. Since the function $F(n, \varphi, R)$ is very complicated and nonmonotonic, the measurement accuracy depends strongly on the values of the parameters. A comparative analysis of the accuracy of these methods has been made by many authors^[19, 20, 176-185]. A number of graphic methods^[187] and monograms^[187] were also developed. For anisotropic media, the possibility of determining the location and dispersion of the axes was also demonstrated^[188].

We present here the results of calculations^[189] (Fig. 16) and the data of^[190] in a somewhat different form (Fig. 17). We see that the measurement accuracy, given the values of n and κ , is quite different in the different methods, and depends on the chosen values of φ . It should be noted that from the point of view of the experiment, the accuracy with which the absolute values of R are measured is much lower than that of R_{\perp}/R_{\parallel} or $E_{r\perp}/E_{r\parallel}$.

We see from the foregoing, further, that there is not optimal universal method of measuring n and κ , and that the procedure should depend on the values of these quantities. It seems therefore that a somewhat more universal method is that of the Stokes parameters, in which four quantities characterizing the intensity and the polarization are measured^[20, 19]. A different method of specifying the parameters of a light beam was recently proposed, and describes more fully the beam in general and its reflection in

particular^[192]. However, there is still no analysis of its use for the measurement of n and κ and of its potentialities in this respect. It is seen from Figs. 16 and 17, in particular, that measurements at small values of κ are particularly difficult.*

II. The method of "disturbed total internal reflection," which uses the effect shown in Fig. 6, has recently gained wide popularity. Referring the reader to^[194, 195, 210] for technical details we merely point out that this method is apparently particularly suitable for small κ ^[196].

III. Methods were proposed^[197] (particularly for the case of small κ ^[80]), whereby the reflection data were processed under definite assumptions concerning the dispersion law—the connection between n and κ ; as seen from the figures, if one of these quantities is inaccurately determined, the situation is usually reversed for the other.

IV. It is also possible, without making such assumptions, to use the connection established between n and κ by the Kramers-Kronig formulas, which have a very wide range of applicability^[201]. There are a number of methods for using these formulas^[184, 189-200]. The calculations are usually made in the following manner: $R(\omega)_{\varphi=0}$ is measured and then $r(\omega)$ —the amplitude reflection coefficient for normal incidence (medium 1 is vacuum)—is determined:

*It is noted in^[193] that in some method the accuracy drops also at very large values of n and κ .

$$r(\omega) e^{i\theta(\omega)} = -\frac{v(\omega)-1}{v(\omega)+1} \quad r(\omega) = \sqrt{R(\omega)}, \quad (28)$$

where $\theta(\omega)$ is determined from the formula

$$\theta(\omega) = \frac{\omega}{\pi} \int_0^\infty \ln \frac{R(\omega)}{R(\omega_0)} \frac{1}{\omega_0^2 - \omega^2} d\omega_0. \quad (29)$$

From (28) and (29) it is possible, further, to obtain

$$\begin{aligned} \kappa(\omega) &= \frac{2\sqrt{R(\omega)} \sin \theta(\omega)}{\{1 - \sqrt{R(\omega)}\}^2 + 4\sqrt{R(\omega)} \sin^2 \frac{\theta(\omega)}{2}}, \\ n(\omega) &= \frac{1 - R(\omega)}{\{1 - \sqrt{R(\omega)}\}^2 + 4\sqrt{R(\omega)} \sin^2 \frac{\theta(\omega)}{2}}. \end{aligned} \quad (30)$$

The main difficulty here is that the integration in (29) and in similar formulas must be carried out in the entire region in which $(n - 1)$ and κ are different from zero, whereas the real measurements are made in a very limited spectral interval, which usually does not include, for example, the strong absorption bands in the far ultraviolet ($\lambda < 2000 \text{ \AA}$). Therefore the main problem here is a reasonable extrapolation of the data beyond the region in which the measurements were made, with correct allowance for the resultant errors. The question of the extrapolation procedure is considered in [202, 203], and an estimate of the errors and the validity of the extrapolation is given in [204, 205], in many cases it is apparently possible to attain an accuracy 0.5–1%.

V. Figure 10 shows a plot of $R(\omega)$ calculated for a medium consisting of dipole oscillator with large damping, in accordance with the classical dispersion theory and Fresnel's formulas. We see that the "line width" of $R(\omega)$ is much larger than the width of $\kappa(\omega)$, i.e., the resolution will be much worse (a similar conclusion is reached with any other formula for the dispersion), and the determination of κ from R is sometimes difficult. The optimal conditions for such a determination as applied to a narrow line are indicated, for example, in [206], it turns out that the form of the isolated line depends on φ and on the polarization; the structure of the line is best revealed when $E_{r\parallel}$ is observed at the Brewster angle. (We note that certain estimates in [206] have caused objections [207].)

We see that the simple and ancient law of light reflection turns out to be, upon deep analysis, far from trivial, exhaustive, or completely explained. We were able to note and emphasize unsolved problems in any of the facets which we considered. This proves once more how useful it is to periodically review the basic premises of science, for this reveals to the researcher many new possibilities and confronts him with many new problems.

Note Added in Proof. 1) It is shown in [208] that the change in frequency upon reflection (formula (2a)) does not exceed 5×10^{-21} (for a metal). 2) A rigorous macroscopic derivation of the Fresnel formulas see, e.g., [209].

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