SOVIET PHYSICS JETP VOLUME 36 (9), NUMBER 1 JULY, 1959

ELECTRICAL, OPTICAL, AND ELASTIC PROPERTIES OF CRYSTALS OF THE DIAMOND TYPE. III. DISPERSION AND ABSORPTION OF LIGHT

V. S. MASHKEVICH

Kiev Polytechnic Institute

Submitted to JETP editor May 16, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 108-115 (January, 1959)

The dispersion, double refraction, and single-phonon absorption of light due to lattice vibrations are investigated in the infrared region. The parameters of the theory are determined and the numerical calculation of the effects mentioned above is performed.

IT is customarily assumed that the lattice vibrations of a homopolar crystal do not affect its optical properties in the harmonic approximation, since its atoms are electrically neutral. In reference 1 (which henceforth will be referred to as II) it is shown, however, that this is true only in the zero approximation with respect to d/λ (d is the lattice constant and λ the wavelength). A finite λ already leads to a coupling between the dipole moments of the atoms, which arise upon the passage of a light wave, and the displacements of the atoms and thus causes the lattice vibrations to affect the optical properties of the crystal. In particular, vibrations of a homopolar lattice cause dispersion and single-phonon absorption of light, effects hitherto not investigated (Lax and Burstein[2] have investigated qualitatively two-phonon absorption). In this paper we present a quantitative theory of the above phenomenon.

1. DISPERSION AND BIREFRINGENCE AWAY FROM THE SINGULARITY

The dependence of the index of refraction of the light wave on the frequency and on the direction of propagation away from the singularity (point of intersection of the light and optical branches of the zeroth approximation in d/λ; the coordinates of the singular point are Ω_{lim}, the limiting frequency of the optical vibrations, and n_0, the index of refraction of the extreme long waves; for more details see II) is determined by (26.II), from which we get

$$n_j = n_0 + \mu^2\Omega^2 \{g_1 + [Q/(\Omega_{\text{lim}}^2 - \Omega^2) - g_2]\, r_j(\mathrm{s})\},$$

$$r_j(\mathrm{s}) = s_x^4 + s_y^4 + s_z^4 + (-1)^j [(s_x^4 + s_y^4 + s_z^4 - 1)^2 - 12 s_x^2 s_y^2 s_z^2]^{1/2},$$

$$g_1 = q\,[e_1^{(1)} + e_2^{(1)} + (e_1^{(3)} + e_2^{(3)})/2], \tag{1}$$

$$g_2 = q\,(e_1^{(3)} + e_2^{(3)} - 2S^2/A)/2.$$

Here n_j is the index of refraction of the polarization wave, $j = 1, 2$; Ω is the dimensionless frequency; $\mu \sim 10^{-5}$ is a small parameter in which an expansion equivalent to the expansion in d/λ is made; s is the unit wave vector; numerical values of S and $e_i^{(k)}$ and expressions for q and Q are given in II; A is one of the parameters of the theory. It will be shown below that the light oscillations corresponding to various polarizations are mutually orthogonal. (This is difficult to see directly from Eqs. (25, 23a.II) which determine the directions of the oscillations, since the above system of equations is not self-adjoint).

Formulas (1) are valid if $|\Omega - \Omega_{\text{lim}}| \gg \mu$. If, however, Ω is still not too far from Ω_{lim}, we obtain from (1) approximately

$$n_j = n_0 + \mu^2 Q \Omega^2 r_j(\mathrm{s}) / (\Omega_{\text{lim}}^2 - \Omega^2),$$

i.e., the usual dispersion formula away from the natural frequency. The value of n_j depends on the number of the polarization, so that birefringence takes place. The directions of the optical axes are determined from

$$(s_x^1 + s_y^4 + s_z^4 - 1)^2 - 12 s_x^2 s_y^2 s_z^2 = 0$$

and are directions of the [1 0 0] and [1 1 1] type, i.e., the edges and diagonals of a cubic lattice. Thus, a crystal of the diamond type has seven axes; optical isotropy takes place only in the zeroth approximation in d/λ, to which the customary analysis is confined. For both polarizations, n_j depends on s so that both rays are extraordinary.

2. QUASI-NORMAL COORDINATES

It was shown in II that in the μ-vicinity of the singular point the normal oscillations connected with the propagation of the light wave are of mixed character: even in the zeroth approximation, neither the dipole moments of the cells nor the displacements of the atoms are zero. These oscillations therefore do not contain purely light oscillations, which have no displacements in the zeroth approximation, and their corresponding normal coordinates are not suitable for a direct description of the light waves. The latter are described by the so-called quasi-normal coordinates,[3] which, for the case considered here, are introduced in the following manner. The general solution of the equations of motion (1.II) is

$$\mathbf{u}_s^l = \sum_{\alpha\mathbf{K}} q^\alpha(\mathbf{K}, t)\,\mathbf{u}_s^\alpha(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}_s^l),$$

$$\mathbf{P}_s^l = \sum_{\alpha\mathbf{K}} q^\alpha(\mathbf{K}, t)\,\mathbf{P}_s^\alpha(\mathbf{K}) \exp(i\mathbf{K}\cdot\mathbf{r}_s^l),$$

where $\mathbf{u}_s^l$ and $\mathbf{P}_s^l$ are respectively the displacement and the dipole moment due to deformation of the electron shell of the s-th atom of the l-th elementary cell, α is the number of the branch of the spectrum of normal oscillations, **K** is the wave vector, $\mathbf{u}_s(\mathbf{K})$ and $\mathbf{P}_s(\mathbf{K})$ are the amplitudes, $q^\alpha(\mathbf{K}, t)$ are the normal coordinates and $\mathbf{r}_s^l$ are the coordinates of the lattice sites. The following orthogonality condition holds[4]

$$\begin{gathered} I_{\alpha\beta} = \sum_s m_s \mathbf{u}_s^\alpha(\mathbf{K})\cdot\mathbf{u}_s^\beta(-\mathbf{K}) + (4\pi/\Delta) K^2 c^2 [(\mathbf{P}^\alpha(\mathbf{K}), \mathbf{P}^\beta(-\mathbf{K})) \\ - (\mathbf{P}^\alpha(\mathbf{K}), \mathrm{S})(\mathbf{P}^\beta(-\mathbf{K}), \mathrm{s})] \\ \times \{[n_\alpha^2(\mathbf{K}) - 1][n_\beta^2(-\mathbf{K}) - 1]\,\omega_\alpha^2(\mathbf{K})\,\omega_\beta^2(-\mathbf{K})\}^{-1} = 0, \\ \alpha \neq \beta, \qquad (2) \\ \mathbf{P}^\alpha(\mathbf{K}) = \sum_s \mathbf{P}_s^\alpha(\mathbf{K}), \end{gathered}$$

which is a generalization of the orthogonality relation

$$\sum_s m_s \mathbf{u}_s^\alpha(\mathbf{K})\cdot\mathbf{u}_s^\beta(-\mathbf{K}) = 0, \quad \alpha \neq \beta,$$

which applies if the theory does not take into account the retardation of the electromagnetic interaction;[5] m_s is the mass of the atom, ω the frequency, Δ the volume of the elementary cell, and c the velocity of light in vacuo. Considering that, according to (23, 23a.II), $\mathbf{u}_s = 0$ and $(\mathbf{P}^\alpha \cdot \mathbf{s}) = 0$ in the zeroth approximation for light oscillations, we obtain from (2) the above-mentioned orthogonality of **P** for light waves of different polarizations.

If we impose the normalization condition

$$I_{\alpha\alpha} = N^{-1}, \qquad (3)$$

on the amplitudes, where N is the number of cells in the principal region, the energy of the crystal becomes[4]

$$E = \sum_{\alpha\mathbf{K}}{}' [\dot{q}^\alpha(\mathbf{K})\dot{q}^{*\alpha}(\mathbf{K}) + \omega_\alpha^2(\mathbf{K})\,q^\alpha(\mathbf{K})\,q^{*\alpha}(\mathbf{K})];$$

The prime indicates that the summation is in the half-space **K**. We introduce new generalized coordinates $Q^\alpha(\mathbf{K}, t)$:

$$q^\alpha(\mathbf{K}, t) = \sum_\beta c_{\alpha\beta}(\mathbf{K})\,Q^\beta(\mathbf{K}, t).$$

To these correspond new amplitudes

$$\tilde{\mathbf{u}}_s^\alpha(\mathbf{K}) = \sum_\beta{}' c_{\beta\alpha}(\mathbf{K})\,\mathbf{u}_s^\beta(\mathbf{K}), \quad \tilde{\mathbf{P}}_s^\alpha(\mathbf{K}) = \sum_\beta{}' c_{\beta\alpha}(\mathbf{K})\,\mathbf{P}_s^\beta(\mathbf{K}). \qquad (4)$$

If we subject the coefficients $c_{\alpha\beta}$ to the normalization and orthogonality conditions

$$\sum_\beta c_{\beta\gamma}^*(\mathbf{K})\,c_{\beta\alpha}(\mathbf{K}) = \delta_{\gamma\alpha}, \qquad (5)$$

which indicate the equivalence of normalization of the old and new amplitudes and the orthogonality of the transformation of the kinetic energy, the energy in Q coordinates becomes

$$\begin{gathered} E = E^0 + E', E^0 = \sum_{\alpha\mathbf{K}}{}' [\dot{Q}^\alpha(\mathbf{K})\,\dot{Q}^{*\alpha}(\mathbf{K}) \\ + \tilde{\omega}_\alpha^2(\mathbf{K})\,Q^\alpha(\mathbf{K})\,Q^{*\alpha}(\mathbf{K})], \\ E' = \sum_{\mathbf{K}}\sum_{\beta\alpha<\gamma} c_{\beta\gamma}^*(\mathbf{K})\,c_{\beta\alpha}(\mathbf{K})\,\omega_\beta^2(\mathbf{K})\,Q^{*\gamma}(\mathbf{K})\,Q^\alpha(\mathbf{K}) \\ + \text{compl. conj.}, \end{gathered} \qquad (6)$$

where

$$\tilde{\omega}_\alpha^2(\mathbf{K}) = \sum_\beta |c_{\beta\alpha}(\mathbf{K})|^2\,\omega_\beta^2(\mathbf{K}). \qquad (7)$$

The coefficients $c_{\alpha\beta}$ must be so chosen that the two Q coordinates described purely light-like oscillations. According to (23.II), there are no displacements of atoms in such oscillations, so that

$$\tilde{\mathbf{u}}_s^{0\alpha} = \sum_\beta c_{\beta\alpha}^0\,\mathbf{u}_s^{0\beta} = 0, \qquad (8)$$

where $\alpha = 1, 2$ corresponds to the light oscillations. When formulating expressions (4) for light oscillations in the vicinity of the singular point in the zeroth approximation, one must use only the mixed oscillations, since in all others the dipole moment of the cell is zero. The orthogonality of the mixed oscillations of different polarizations can be derived from (2) and (29a, 30, 30a.II). Therefore different polarizations can be considered independently. We denote the coefficient c in terms of $c_{\alpha\beta}^j$, where $\alpha = 1, 2$, pertains to the two old (mixed) branches of the polarization j and $\beta = 1, 2$ pertains to the two new ones. Let q^{1j} describe the light oscillations. Then, changing to dimensionless amplitudes (see II) and inserting (3.II) into (8), we get

$$c_{11}^{0j}(\mathbf{w}^{01j} \overset{+}{\times} \mathrm{s})/\rho^{1j} + c_{21}^{0j}(\mathbf{w}^{02j} \overset{+}{\times} \mathrm{s})/\rho^{2j} = 0, \quad \rho \equiv \Omega_1^2, \qquad (9)$$

where $\mathbf{w} = \mathbf{P}/ed$ (e is the absolute value of the electron charge), Ω_1^2 is the correction of first order to the square of frequency ($\Omega^2 = \Omega_{\text{lim}}^2 + \mu\Omega_1^2 + \ldots$). It follows from (29a, 30, 30a.II) that $\mathbf{w}^{02j}$ is parallel to $\mathbf{w}^{01j}$. Putting

$$\mathbf{w}^{02j} = D^j \mathbf{w}^{01j}, \tag{10}$$

we find from (3), in the zero approximation

$$\begin{gathered} |D^j|^2 = [\chi p_j(\mathbf{s}) / (\rho^{1j})^2 + 1]/[\chi p_j(\mathbf{s}) / (\rho^{2j})^2 + 1], \\ p_j(\mathbf{s}) = |\mathbf{w}^{01j} \underset{\times}{+} \mathbf{s}|^2 / |\mathbf{w}^{01j}|^2, \\ \chi = mQ_1^2 \Delta\omega_{\text{lim}}^4 (n_0^2 - 1)^2 / 2\pi K_0^2 c^2 e^2. \end{gathered} \tag{11}$$

Here ω_{lim} and K_0 are the frequency and modulus of the wave vector of the singular point, and m is the mass of the atom. The expression for Q_1 is given in II. We obtain from (9), (10) and (5)

$$\begin{gathered} c_{11}^{0j} = -\rho^{1j} D^j / b^j, \quad c_{21}^{0j} = \rho^{2j} / b^j, \\ b^j = [(\rho^{2j})^2 + |D^j|^2 (\rho^{1j})^2]^{1/2}. \end{gathered} \tag{12}$$

Using (12), we get from (5)

$$c_{12}^{0j} = \rho^{2j} / b^j, \quad c_{22}^{0j} = \rho^{1j} D^{*j} / b^j. \tag{13}$$

According to II, we have in the μ-vicinity of the singular point

$$\omega^2 = \omega_{\text{lim}}^2 + \mu\Gamma^2\rho, \quad \Gamma^2 = e^2/md^3. \tag{14}$$

From (6), (14), and (5) it is seen that in the first approximation E' contains only $c_{\alpha\beta}^{0j}$. Taking this into account and inserting (12), (13), and (14) into (6) we get

$$E' = \mu\Gamma^2 \sum_{j\mathrm{K}} \{D^j \rho^{1j} \rho^{2j} (\rho^{2j} - \rho^{1j})/(b^j)^2\} Q^{*2j} Q^{1j} + \text{compl. conj.}$$

3. DISPERSION AND BIREFRINGENCE IN THE VICINITY OF THE SINGULAR POINT

Inserting (12) and (14) into (7) we find in the first approximation the squares of the frequencies of the light branches:

$$\widetilde{\omega}_{1j}^2 = \omega_{\text{lim}}^2 + \mu\Gamma^2 [(\rho^{2j})^3 + (\rho^{1j})^3 |D^j|^2]/(b^j)^2. \tag{15}$$

For the mixed branches we obtain from (30, 30aII)

$$\begin{gathered} \rho^{nj} = \{\varkappa_0\varkappa_1 + (-1)^n [\varkappa_0^2\varkappa_1^2 + 2n_0^2 r_j(\mathbf{s}) r]^{1/2}\} n_0^{-2}, \quad n = 1,\ 2, \\ \varkappa = Kd/2\mu, \quad \varkappa_0 = K_0 d/2\mu, \\ \varkappa_1 = (\varkappa - \varkappa_0)/\mu, \quad r = -Q_1 R_1 > 0, \end{gathered} \tag{16}$$

an expression for R_1 is given in II; (Eqs. (15), (16), and (27.II) give for the index of refraction

$$\begin{gathered} n_j = n_0 + \mu [\chi p_j(\mathbf{s}) - 2r_j(\mathbf{s}) r n_0^{-2}] \varkappa_1 / 2\Omega_{\text{lim}} [\varkappa p_j(\mathbf{s}) \\ + 2r_j(\mathbf{s}) r n_0^{-2} + 2\varkappa_0^2\varkappa_1^2 n_0^{-4}]. \end{gathered} \tag{17}$$

This expression describes the dispersion and the birefringence in the μ-vicinity of the singular point. The maximum departure of n_j from n_0 is

$$(\Delta n_j)_{\max} = \mu [n_0^2 \chi p_j(\mathbf{s}) - 2rr_j(\mathbf{s})]/4\sqrt{2}\Omega_{\text{lim}}^2 [n_0^2 \chi p_j(\mathbf{s}) + 2rr_j(\mathbf{s})]^{1/2}.$$

It follows from (30, 30a.II) that

$$w_x^{0j} \sim s_x [r_j(\mathbf{s}) + 1 - 2s_y^2][r_j(\mathbf{s}) + 1 - 2s_z^2];$$

on this basis, Eq. (17) leads to the foregoing seven optical axes. For the principal directions $\mathbf{s}$ (the directions of the diagonals of the faces of the lattice cube, II) $r_1(\mathbf{s})$ and $p_1(\mathbf{s})$ vanish and consequently $n_1 = n_0$. Here $\mathbf{w}^{01}$ and $\mathbf{s}$ are in the plane of the same face.

4. ABSORPTION OF LIGHT

The energy of the crystal (6) corresponds to the Lagrangian

$$L = \sum_{\alpha\mathrm{K}}{}' [\dot{Q}^\alpha(\mathrm{K}) \dot{Q}^{*\alpha}(\mathrm{K}) - \widetilde{\omega}_\alpha^2(\mathrm{K}) Q^\alpha(\mathrm{K}) Q^{*\alpha}(\mathrm{K})] - E';$$

from which we find the generalized momenta

$$\begin{gathered} P^\alpha(\mathrm{K}) = \partial L/\partial\dot{Q}^\alpha(\mathrm{K}) = \dot{Q}^{*\alpha}(\mathrm{K}), \\ P^{*\alpha}(\mathrm{K}) = \partial L/\partial\dot{Q}^{*\alpha}(\mathrm{K}) = \dot{Q}^\alpha(\mathrm{K}) \end{gathered}$$

and the Hamiltonian

$$H = \sum_{\alpha\mathrm{K}}{}' [P^\alpha(\mathrm{K}) P^{*\alpha}(\mathrm{K}) + \widetilde{\omega}_\alpha^2(\mathrm{K}) Q^\alpha(\mathrm{K}) Q^{*\alpha}(\mathrm{K})] + E'.$$

In the vicinity of the singular point we have for the oscillations connected with the propagation of light

$$\begin{gathered} H = \sum_{\mathrm{K}}{}' \sum_{j=1,2} \sum_{n=1,2} [P^{nj}(\mathrm{K}) P^{*nj}(\mathrm{K}) + \widetilde{\omega}_{nj}^2(\mathrm{K}) Q^{nj}(\mathrm{K}) Q^{*nj}(\mathrm{K})] \\ + \Big\{\mu\Gamma^2 \sum_{\mathrm{K}} \sum_{j-1,2} [D^j \rho^{1j} \rho^{2j} (\rho^{2j} - \rho^{1j})/(b^j)^2] Q^{*2j}(\mathrm{K}) Q^{1j}(\mathrm{K}) \\ + \text{compl. conj.}\Big\}. \end{gathered} \tag{18}$$

In view of the small interaction energy ($\mu \sim 10^{-5}$), the absorption of light can be considered by the usual method of the theory of quantum transitions. Light oscillations of the polarization j are described by the coordinates $Q^{1j}(\mathbf{K})$. We shall call the corresponding quasi-particles, which appear as a result of quantization of (18), photophonons. The particles corresponding to $Q^{2j}(\mathbf{K})$ are ordinary phonons. The state of the unperturbed system (the perturbation is E') is characterized by the number of photons $n^j(\mathbf{K})$ and the number of photophonons $n_f^j(\mathbf{K})$. The probability of transition per unit time from the state $n^j(\mathbf{K})$, $n_f^j(\mathbf{K})$ into the state $n^j(\mathbf{K}) + \delta_{\mathbf{KK}'}$, $n_f^j(\mathbf{K}) - \delta_{\mathbf{KK}'}$ is

$$\begin{gathered} P_j(\mathrm{K}') = (2\pi/\hbar) |(n^j(\mathrm{K}) + \delta_{\mathrm{KK}'}, \\ n_f^j(\mathrm{K}) - \delta_{\mathrm{KK}'} | E' | n^j(\mathrm{K}),\ n_f^j(\mathrm{K}))|^2 \delta(E - E_0), \end{gathered}$$

where E and E_0 are the energies of the final and

Numerical values of certain quantities

	Diamond	Si	Ge
d **(cm)**	$3.6\cdot10^{-8}$	$5.4\cdot10^{-8}$	$5.6\cdot10^{-8}$
m **(g)**	$2.0\cdot10^{-23}$	$4.7\cdot10^{-23}$	$12\cdot10^{-23}$
n_0^2	5.8	12	16
c_{11} **(dyne/cm²)**	$9.5\cdot10^{12}$	$1.7\cdot10^{12}$	$1.3\cdot10^{12}$
c_{12} ,,	$3.9\cdot10^{12}$	$0.64\cdot10^{12}$	$0.48\cdot10^{12}$
c_{44} ,,	$4.3\cdot10^{12}$	$0.80\cdot10^{12}$	$0.67\cdot10^{12}$
$\omega_{1\mathrm{lim}}$ **(sec⁻¹)**	$2.5\cdot10^{14}$	$1.2\cdot10^{14}$	$0.65\cdot10^{14}$
$\mu=(4mc^2d/e^2)^{-1/2}$	$0.95\cdot10^{-5}$	$0.50\cdot10^{-5}$	$0.30\cdot10^{-5}$
A	53	43	40
D	$2.0\cdot10^{2}$	$1.7\cdot10^{2}$	$1.5\cdot10^{2}$
L	$2.8\cdot10^{2}$	$2.4\cdot10^{2}$	$2.2\cdot20^{2}$
$\|F\|$	59	23	20
C^{++}	53	29	27
C^{+-}	32	2.9	0.0
Q	$2.3\cdot10^{2}$	$7.9\cdot10^{2}$	$18\cdot10^{2}$
g_1	0.87	6.5	14
g_2	−0.14	−5.3	−14
χ	$1.2\cdot10^{7}$	$0.99\cdot10^{8}$	$1.4\cdot10^{8}$
a	60	0.62	0.063
r	$0.44\cdot10^{8}$	$5.5\cdot10^{8}$	$11\cdot10^{8}$
$a(\chi n_0^2+2r)n_0/c\approx S_j$	0.77	0.16	0.037
$(n_2-n_1)_{\max}$	$\sim10^{-4}$	$\sim10^{-4}$	$\sim10^{-4}$

initial states, respectively, so that

$$E-E_0=\hbar\omega^j(\mathbf{K}')-\hbar\omega_f^j(\mathbf{K}')\equiv\hbar\tilde{\omega}_{2j}(\mathbf{K}')-\hbar\tilde{\omega}_{1j}(\mathbf{K}').$$

The energy of light of polarization j, absorbed during the time dt, is

$$dE_j=dt\sum_{\mathbf{K}}\hbar\omega_f^j(\mathbf{K})P_j(\mathbf{K})=dtV(2\pi)^{-3}\int\hbar\omega_f^j(\mathbf{K})P_j(\mathbf{K})K^2dKd\Omega,$$

where V is the volume of the principal region and dΩ is the solid-angle element in K space. Taking into account the readily-shown fact that the phonon and photophonon branches intersect at the point $\kappa_1 = 0$, changing from integration over K to integration over $E - E_0$, and carrying out this integration, we get

$$dE_j=dtV(2\pi)^{-2}n_0aK_0^2\hbar\omega_{1\mathrm{lim}}\int u_j(\mathrm{s})\,[n_f^j(n^j+1)]_{\varkappa_1=0}d\Omega,$$

$$u_j(\mathrm{s})=\chi p_j(\mathrm{s})\,n_0^2+2rr_j(\mathrm{s}),\quad a=\mu^3\Gamma^2/4dn_0\varkappa_0\omega_{1\mathrm{lim}}. \qquad (19)$$

The spectral density of the energy of light in the reciprocal wavelength scale (in vacuo), referred to unit solid angle, is

$$I_j^0=n_0(2\pi)^{-2}\hbar\omega_f^jn_f^jK^2. \qquad (20)$$

Comparing (19) and (20) we obtain for the energy absorbed per unit volume

$$dE_j^0=dta\int u_j(\mathbf{s})\,[(n^j+1)\,I_j^0]_{\varkappa_1=0}\,d\Omega.$$

For light propagating in the direction **s**, this yields

$$dE_j^0=dtau_j(\mathrm{s})\,\{[n^j(\mathrm{s})+1]\,\varepsilon_j\}_{\varkappa_1=0},$$

where ϵ_j is the spectral density of the energy. From this we obtain approximately[6] for the area of the absorption line

$$S_j(\mathrm{s})=au_j(\mathrm{s})(\bar{n}+1)/v_j(\mathrm{s}), \qquad (21)$$

where v_j is the group velocity

$$\bar{n}=[\exp(\hbar\omega_{1\mathrm{lim}}/kT)-1]^{-1}.$$

To find the width of the line it is necessary to take into account the anharmonicity of the displacements of the atoms, since the interaction due to this anharmonicity greatly exceeds E′. This is indeed why one can assume $n^j = \bar{n}$ (the absorption of light does not disturb noticeably the thermal equilibrium) and disregard the transitions involving annihilation of phonons and creation of photophonons.

According to (21), the area of the absorption line depends on the polarization and on the direction of propagation of the light wave. The dependence on s is particularly pronounced for j = 1. From (19), (11), and (1) it follows that $S_1(\mathbf{s})$ vanishes for the singular directions of **s**. As indicated above, in this case $\mathbf{w}^0$ lies in the plane of the same face as s itself. Such light waves do not experience single-phonon absorption.

5. PARAMETERS OF THE THEORY. NUMERICAL RESULTS

The theory contains five parameters (see II)—A, D, L, F, and C. A is determined uniquely from (23.II):

$$A=32\pi(n_0^2+2)/3(n_0^2-1).$$

The values of D and L (also unique) are obtained from (13, 16.II):

$$D=2(d^4/e^2)(c_{11}+c_{12}),\quad L=4(d^4/e^2)c_{11}.$$

Eq. (19.II) yields two values for F

$$F=\pm[A(2L-\Omega_{1\mathrm{lim}}^2)]^{1/2}/2. \qquad (22)$$

When the value of F is fixed, Eqs. (13, 16.II) yield two values for C:

$$C = (2DF \pm \{4D^2F^2 - 2AL\,[D^2 - 2\Omega^2_{\mathrm{lim}}(d^4/e^2)\,(c_{11} - c_{44})]\}^{1/2})/2L, \tag{23}$$

which lead, according to (22), to the four values $C^{--} = C^{++}$, $C^{-+} = -C^{+-}$ [the first sign of C is from (22), the second from (23)]. The quantities that characterize the optical properties contain F and C only in the combination $(C - 4FS/A)^2$ (cf. II), and therefore the four different sets of parameters lead to two different variants.

The table lists the experimental[7,8,2] (first seven lines of the table) and calculated values of the parameters and quantities that characterize the optical properties, for $F = |F|$ and $C = C^{+-}$. In calculating the area of the absorption band, the group velocity is approximately replaced by the phase velocity, $\bar{n}$ is taken to be zero, and it is assumed that $r_j(s) = p_j(s) = 1$. This latter simplification is used also in the estimate of $(n_2 - n_1)_{\max}$, the maximum difference in the index of refraction.

The value obtained for $(n_2 - n_1)_{\max}$ is $\sim 10^{-4}$, so that an attempt can be made to observe experimentally the birefringence in the region of the frequency ω_{lim}. An experimental investigation of absorption in the infrared region was made by Collins and Fan,[8] but their results give only the total absorption. An investigation of the dependence of the absorption on the direction of propagation and polarization of light would make it possible to separate the single-phonon absorption and to compare the theory with experiment.

CONCLUSIONS

1. The theory predicts the presence of dispersion and birefringence due to oscillations of the crystal atoms. Both effects are maximal near the limiting frequency of the experimental oscillations, where the difference in the indices of refraction for the two polarizations reaches 10^{-4}.

2. A diamond-like crystal has seven axes, while the directions of the optical axes are along the edges and diagonals of the cubic lattice.

3. The theory leads to a single-phonon absorption of light with a frequency equal to the limiting frequency of the optical oscillations, and predicts a substantial dependence of the absorption on the direction of propagation and polarization of the light.

4. It is desirable to verify experimentally the predictions of the theory; this verification would permit a comparison between experiment and the part of the theory that concerns the optical properties.

The author thanks K. B. Tolpygo for an evaluation of the results of this work.

---

[1] V. S. Mashkevich, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 866 (1957), Soviet Phys. JETP **5**, 707 (1957).

[2] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[3] V. S. Mashkevich, Paper delivered to XI Conference on Spectroscopy (in press).

[4] V. S. Mashkevich, Dokl. Akad. Nauk SSSR **121**, 247 (1958), Soviet Phys. "Doklady" **3**, 768 (1958).

[5] M. Born and M. Goeppert Mayer, Theory of Solids (Russ. Transl.) ONTI, 1938.

[6] V. S. Mashkevich, Dissertation, Kiev, 1956.

[7] Bundy, Hall, Strong, and Wentorf, Nature, **176**, 51 (1955); W. C. Dunlap and R. L. Watters, Phys. Rev. **92**, 1396 (1953); S. Bhagavantan and J. Bhimasenacher, Proc. Roy. Soc. (London) **A187**, 381 (1946); H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953); P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1347 (1953); K. Kohlrausch, Raman Spectra (Russ. Transl.) IIL, 1952.

[8] R. J. Collins and H. J. Fan, Phys. Rev. **93**, 674 (1954).

Translated by J. G. Adashko
16