

LIGHT WAVES IN CRYSTALS IN THE EXCITON ABSORPTION REGION AND THE IMPURITY PHOTOEFFECT

I. M. DYKMAN and S. I. PEKAR

Institute of Physics, Academy of Sciences, Ukrainian S.S.R.

Submitted to JETP editor March 10, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 510-521 (August, 1959)

We have used a new theory of electromagnetic waves in a crystal^{1,2} to evaluate, in the exciton light absorption region, the amplitudes of the waves occurring in a crystal for a given amplitude of the wave incident from the vacuum. We have considered the case of cubic crystals. We show that in the frequency region where the refractive index is much less than unity the amplitudes of the normal and the longitudinal waves in the crystal are appreciably larger (by factors of the order of several hundred) than the amplitude of the incident wave. The photoionization of impurities is therefore much more intensive in this frequency range than in the neighboring regions. This explains the frequently-observed sharp maximum of the external and internal photoeffects in the frequency range corresponding to exciton absorption. We show that there can occur in the crystal waves with an amplitude which increases linearly with the penetration depth into the crystal.

ONE of the authors has shown in previous papers¹⁻⁴ that if a monochromatic light wave, with a frequency which lies within the exciton absorption range, is incident upon a crystal from the vacuum, several light waves appear in the crystal, among which strictly longitudinal waves are also possible. In particular, four transverse waves and one longitudinal wave appear in cubic crystals.² The amplitudes of the two anomalous transverse waves tend rapidly to zero when the frequency of the light moves out of the exciton absorption range on the red or the violet side. The remaining two transverse waves then go over into the usual waves known in optics. As far as the longitudinal wave is concerned, its amplitude remains appreciable (of the order of the amplitude of the wave incident from the vacuum) in a much wider range of frequencies and important changes must be introduced into the usual electromagnetic optics for this range.

In the present paper, as in reference 2, we restrict our considerations only to cubic crystals and only to those cases where the coefficients of the expansion of the exciton energy in powers of the absolute magnitude of its wave vector do not depend on the direction of that vector (isotropy). In particular, the effective mass of the exciton will not depend on the direction of the wave vector. We emphasize that for excitons with a longitudinal and a transverse polarization (called henceforth longitudinal and transverse excitons) these expansion coefficients will be different. We shall restrict

ourselves, as was done earlier,² to considering the case where the expansion of the exciton energy in powers of the absolute magnitude of the wave vector does not contain a linear term.

The aim of the present paper is to estimate the amplitudes of all five waves appearing in the crystal in relation to the amplitude of the incident wave. The equations obtained will be used to determine the intensity and the frequency dependence of the impurity photoeffect, which will be shown to possess a number of peculiarities in the exciton absorption region.

1. AMPLITUDES OF ELECTRICAL FIELD INTENSITY OF WAVES PRODUCED IN A CUBIC CRYSTAL ILLUMINATED BY MONOCHROMATIC LIGHT

The amplitudes of the transverse waves (E_+ , E_-) and of the longitudinal wave ($E_{||}$) which appear in a crystal, and also the amplitude of the wave reflected into the vacuum R can be expressed in terms of the amplitude of the wave incident from the vacuum A through Eqs. (23) — (29) of reference 2. For the purpose of interest to us, we can simplify these equations in some limiting cases. Below we consider two such cases (we retain the notation of reference 2).

A. The case where the indices of refraction of the transverse waves, n_+ and n_- , have absolute magnitudes appreciably larger than unity. Let the

subscript *s* denote the component of the amplitude of the wave in the direction perpendicular to the plane of incidence, and subscript *p* the component in the plane of incidence. If $|n_{\pm}| \gg 1$, Eqs. (23), (24), and (25) of reference 2 can be re-written in the following simplified manner:

s -components:

$$E_{\pm s} = u_{\pm} A_s, \quad R_s = (u_+ + u_- - 1) A_s, \quad (1)$$

$$u_+ = 2 \cos \varphi / (n_+ - qn_-), \quad u_- = 2 \cos \varphi / (n_- - n_+/q),$$

$$\dot{u}_- = -qu_+, \quad (2)$$

$$q \equiv (n_-^2 - \mu) / (n_+^2 - \mu), \quad \mu \equiv (2Mc^2 / \hbar \omega_0^2) (\omega - \omega_0). \quad (3)$$

Here φ is the angle of incidence of the light on the crystal, *M* the effective mass of the transverse exciton, *c* the velocity of light in vacuo, $\omega_0 = \mathcal{E}_0 / \hbar$ where \mathcal{E}_0 is the energy of a transverse exciton with a zero wave vector, and ω the light frequency.

We can write down similarly Eqs. (26) – (29) of reference 2 in simplified form.

p -components:

$$E_{\pm p} = v_{\pm} A_p, \quad R_p = (v_+ n_+ + v_- n_- - 1) A_p, \quad (4)$$

$$v_+ = 2 / (n_+ - qn_-), \quad v_- = 2 / (n_- - n_+/q),$$

$$v_- = -qv_+, \quad (5)$$

$$E_{\parallel} = -(2 \sin \varphi / \varepsilon) A_p. \quad (6)$$

We have assumed that the other absorption bands are sufficiently far away from the one considered (or have low intensities), and thus the refractive index of the normal transverse waves tends asymptotically to a constant value $\sqrt{\varepsilon}$, when the light frequency moves away from the exciton absorption region under consideration. The refractive indices of the transverse waves are determined in that case by the formulae¹

$$n_{\pm}^2 = (\mu + \varepsilon) / 2 \pm \sqrt{(\mu - \varepsilon)^2 / 4 + b}, \quad (7)$$

$$b = 8\pi M c^2 a / \hbar^2 \omega_0^3, \quad (8)$$

where *a* is a constant proportional to the oscillator strength of the phototransition of the crystal in the exciton state; its exact meaning is explained in reference 1.

If the oscillator strength of the transition referred to an elementary cell of the crystal is of the order of 0.1, and if we assume that *M* is of the order of the free electron mass, *b* turns out to be of the order of several times ten thousand, as shown in reference 2. Correspondingly, $|n_{\pm}|$ turns out, from Eq. (7), to be of the order of 10 or larger. Such a large dispersion does, however, not yet mean an intensive absorption. The popular point of view, according to which a large dispersion is always combined with an intensive absorption, is in general incorrect, as shown in references 2 and 4.

The refractive index for the longitudinal waves is equal to²

$$n_{\parallel}^2 = (2M'c^2 / \hbar \omega_0^2) (\omega - \omega'_0), \quad (9)$$

where *M'* is the effective mass of a longitudinal exciton, $\omega'_0 = \mathcal{E}'_0 / \hbar$, and \mathcal{E}'_0 is the energy of a longitudinal exciton with zero wave vector. The connection between \mathcal{E}'_0 and \mathcal{E}_0 is given in Eq. (8) of reference 3 and Eq. (35) of reference 4. This connection can be written in the form

$$\mathcal{E}'_0 - \mathcal{E}_0 = b \hbar^2 \omega_0^2 / 2\varepsilon M c^2. \quad (10)$$

using the notation of the present paper. If μ is evaluated at the frequency $\omega = \omega'_0$ using Eq. (3), we get

$$\mu(\omega = \omega'_0) = b / \varepsilon. \quad (11)$$

From this it follows that ω'_0 is just the frequency for which, according to Eq. (7), the refractive index of one of the transverse waves (the normal wave) is equal to zero. At the frequency ω'_0 the macroscopic dielectric constant of the crystal is equal to zero.

We now proceed to estimate the relative magnitude of the amplitudes of the waves occurring in the crystal. In the case *M* > 0 the denominators in the expressions for v_{\pm} and u_{\pm} will, according to (7), not have a small absolute magnitude in the region $|n_{\pm}| \gg 1$. Hence, $|v_{\pm}| \ll 1$ and $|u_{\pm}| \ll 1$, i.e., the amplitudes of both transverse waves are appreciably less than the amplitude of the incident wave. As far as the longitudinal wave is concerned its amplitude is, according to (6), of the order of magnitude of the amplitude of the incident wave for not too small φ . The longitudinal wave is thus intense and dominates over the transverse waves. When *M* < 0, the longitudinal wave is determined in the region $|n_{\pm}| \gg 1$ by the same Eq. (6), and has the same amplitude as in the previous case. u_{\pm} and v_{\pm} are also small, except in the frequency region where $n_+ \approx n_-$, i.e., where the denominator of u_{\pm} or v_{\pm} tends to zero. u_{\pm} and v_{\pm} become then infinite. This anomaly deserves a special detailed consideration which shall be given in the following section.

In Figs. 1 – 4 are shown the frequency dependences of $|u_{\pm}|$, $|v_{\pm}|$, and $|E_{\parallel} / A_p|$ in the region $\omega \approx \omega_0$ evaluated by the exact formulae of reference 2. The following values of the parameters were used: $\hbar \omega_0 = 2$ eV, $\varepsilon = 2$, $M' = M$, lattice constant equal to 10 Bohr radii of the hydrogen atom, and an oscillator strength of the transition equal to 0.1 (referred to the elementary cell of the crystal).

B. The case $\omega \approx \omega'_0$, when the refractive in-

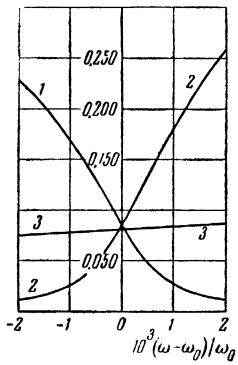


FIG. 1. Frequency dependence curves: 1) $|u_+| \approx |v_+|$; 2) $|u_-| \approx |v_-|$; 3) $|E_{||}/A_p|$. $M = m$ (m is the mass of a free electron), $b = 58400$, $\varphi = 5^\circ$.

dex of the normal transverse wave is much less than unity. In this frequency range we get $|q| \ll 1$, for $M > 0$ and $|q| \gg 1$ for $M < 0$. On the basis of these inequalities we can show that, according to Eqs. (23) – (29) of reference 2, the amplitude of one of the transverse waves (the anomalous wave) becomes negligibly small and all the properties of the second transverse wave (the normal one) approach the properties that follow from the usual electromagnetic crystal optics. The refractive index and the amplitude of the normal wave will henceforth be denoted by n and E , without the subscript \pm . On the basis of the above-mentioned inequalities, Eqs. (23) – (29) of reference 2 can be simplified and written in the following form:

s -components:

$$E_s = uA_s, \quad u = 2/[1 + \sqrt{n^2 - \sin^2 \varphi} / \cos \varphi], \quad (12)$$

$$\sin \psi = n^{-1} \sin \varphi, \quad \cos \psi = \sqrt{1 - n^{-2} \sin^2 \varphi}. \quad (13)$$

Here ψ is the angle of refraction of the normal wave.

p -components:

$$E_p = vA_p, \quad v = 2 \cos \varphi / [\sqrt{1 - n^{-2} \sin^2 \varphi} + n \cos \varphi + \sin^2 \varphi / n \sqrt{\alpha^2 n^2 - \sin^2 \varphi}], \quad (14)$$

$$E_{||} = E_p \sin \varphi / n \sqrt{1 - \sin^2 \varphi / \alpha^2 n^2}. \quad (15)$$

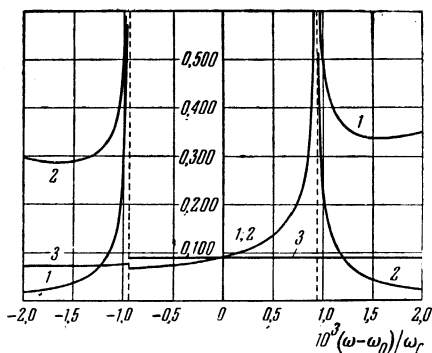


FIG. 3. Frequency dependence curves: 1) $|u_+| \approx |v_+|$; 2) $|u_-| \approx |v_-|$; 3) $|E_{||}/A_p|$. $M = -m$, $b = -58400$, $\varphi = 5^\circ$. The region of complex values of n^2 lies between the dotted straight lines.

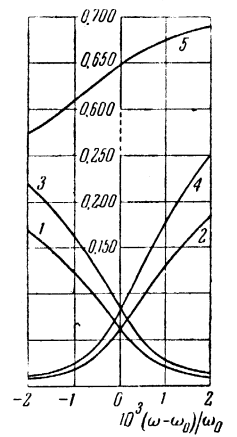


FIG. 2. Frequency dependence curves: 1) $|u_+|$; 2) $|u_-|$; 3) $|v_+|$; 4) $|v_-|$; 5) $|E_{||}/A_p|$. $M = m$, $b = 58400$, $\varphi = 45^\circ$.

Here

$$\alpha^2 \equiv n_{||}^2 / n^2 = (M' \omega_0^2 / M \omega_0'^2) b / \varepsilon^2. \quad (16)$$

To obtain the right hand side of Eqs. (16), we expanded $n_{||}^2$ and n^2 in a power series in $\omega - \omega_0'$ and limited ourselves to the first terms of the expansion, since we were considering the region $\omega \approx \omega_0'$.

In Eq. (14) we can always neglect $\sin^2 \varphi$ compared to $\alpha^2 n^2$ in $\sqrt{\alpha^2 n^2 - \sin^2 \varphi}$ since α is a very large quantity; we have, for instance $\alpha^2 \sim b/\varepsilon^2$ in the case when $M' \omega_0^2 / M \omega_0'^2 \sim 1$. In the numerical example considered above, α^2 was of the order of several thousands. Thus, even when the real part of n^2 goes through zero, $|\alpha^2 n^2|$ will in practice always be larger than $\sin^2 \varphi$, since the imaginary part of n^2 is then different from zero. The second of Eqs. (14) can therefore be simplified to

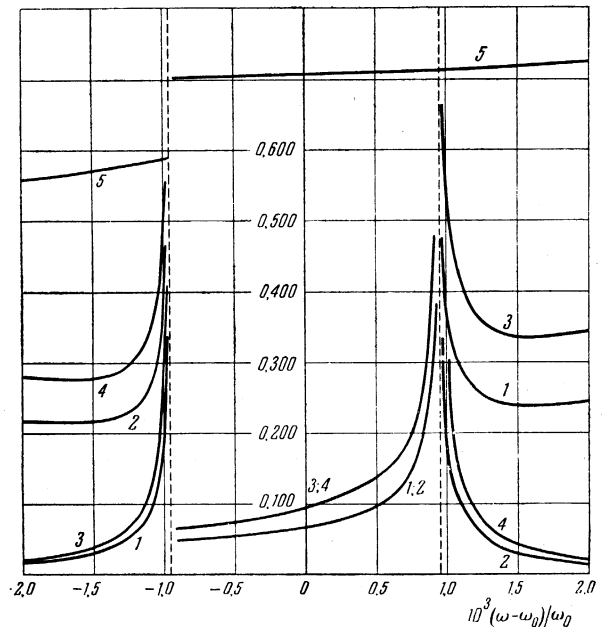


FIG. 4. Frequency dependence curves: 1) $|u_+|$; 2) $|u_-|$; 3) $|v_+|$; 4) $|v_-|$; 5) $|E_{||}/A_p|$. $M = -m$, $b = -58400$, $\varphi = 45^\circ$.

$$v = 2 \cos \varphi / [\sqrt{1 - n^{-2} \sin^2 \varphi} + n \cos \varphi + \sin^2 \varphi / n^2 \alpha]. \quad (17)$$

We now go over to an estimate of the relative magnitude of the amplitudes of the waves occurring in the crystal. According to Eq. (12), u attains its largest absolute magnitude, $u = 2$, at the frequency for which $n = \sin \varphi$. In that point E_S is twice the amplitude of the incident wave A_S (assuming that $\varphi \neq \frac{1}{2}\pi$). From (17) it follows, for the p -components, that if $n > \sin \varphi$ we can neglect the last term in the denominator of expression (17), after which it is clear that v is a monotonically decreasing function of n and thus also of ω . v attains its largest value at the frequency for which $n = \sin \varphi$. This value is

$$[v]_{n=\sin \varphi} = 2 \cos \varphi / (\sin \varphi \cos \varphi + 1/\alpha). \quad (18)$$

We have retained here also the third term in the denominator of Eq. (17), since $\sin \varphi$ can be very small. The quantity (18) has a very sharp maximum as a function of φ at the point $\varphi = 0$: when $\varphi = 0$, $[v]_{n=\sin \varphi} = 2\alpha$, i.e., it can take on a value of the order of 10^2 . This means that the amplitude of the normal transverse wave in a crystal can be larger than the amplitude of the incident wave by a factor of the order of a hundred. When φ is of the order of 5 or 6 degrees, the magnitude of $[v]_{n=\sin \varphi}$ falls to 20 and varies further as $2/\sin \varphi$ with increasing φ (one must bear in mind that following a change in φ one must change here the frequency, to keep the condition $n = \sin \varphi$ satisfied).

In the region $\omega < \omega'_0$, when $n^2 < 0$, $|v|$ goes through a maximum at a frequency determined by the condition $\tan \varphi = -n^2$. The maximum value of $|v|$ is then equal to $2 \cos \varphi / \sqrt{1 + 2 \sin \varphi \cos \varphi}$, i.e., it does not exceed two. The amplitude of the transverse wave in the crystal can thus not exceed appreciably the amplitude of the incident wave in this frequency range.

Figure 5 shows the frequency dependences of the absolute magnitudes of the coefficients u (curve 1) and v (curve 2) for angles of incidence $\varphi = 5^\circ$ and $\varphi = 45^\circ$, evaluated by the exact formulae of reference 2 [the values of the parameters are the same as for Figs. 1 - 4 (see case A)].

The amplitude of the longitudinal wave in the frequency range $\omega \approx \omega'_0$ can be estimated using Eq. (15), which can be written in simplified form:

$$E_{||} = n^{-1} E_p \sin \varphi. \quad (19)$$

From this it is clear that if $|n| \sim \sin \varphi$ the amplitude of the longitudinal wave is of the same order of magnitude as the amplitude of the transverse wave considered above, i.e., it can exceed by a

factor of the order of a hundred the amplitude of the incident wave. But if $|n| < \sin \varphi$, the amplitude of the longitudinal wave is larger than the normal transverse wave. Figure 5 (curve 3) shows the frequency dependence of $|E_{||}/A_p|$. As is clear from the figure the peaks of the curves for $|E_{||}/A_p|$ and $|v|$ coincide approximately both in height and in their position along the frequency scale.

We must emphasize that the estimates given are made assuming that the absorption is so small that we can neglect the imaginary part of n^2 . In selected frequency intervals, however, it turns out that even a small imaginary part of n^2 plays an essential role. The condition $n = \sin \varphi$, for instance, used above, cannot even approximately be satisfied in the case $\varphi \rightarrow 0$ if n possesses an imaginary part. (The fact is that the imaginary part of n^2 does, generally speaking, not vanish at the fre-

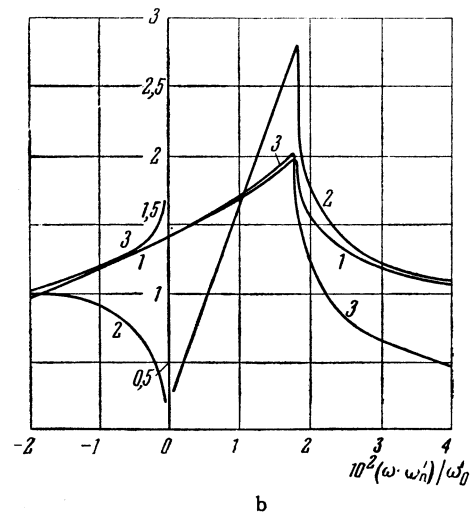
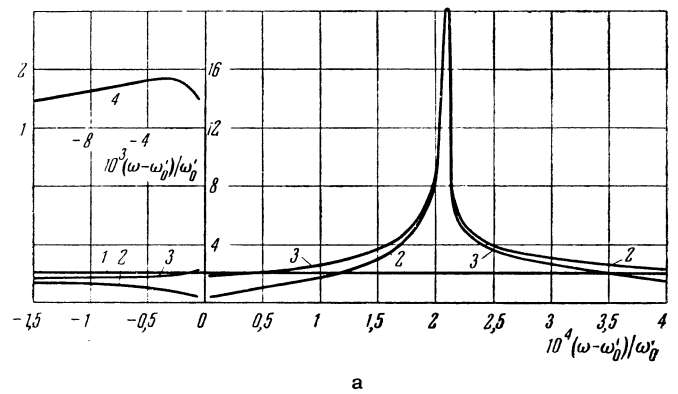


FIG. 5. Frequency dependence of $|u|$ (curve 1), $|v|$ (curve 2), and $|E_{||}/A_p|$ (curve 3) in the region $\omega \approx \omega'_0$: a for $\varphi = 5^\circ$, and b for $\varphi = 45^\circ$. In the point $\omega = \omega'_0$ the quantities $|v|$ and $|E_{||}/A_p|$ tend to infinity; it is difficult to depict the corresponding delta-function curves in the figures and they are therefore not given. Curve 4 in Fig. 5a is the function $|v|$ in the neighborhood of the additional maximum at $n^2 = -\tan \varphi$ (different scale).

quency at which the real part of n^2 vanishes.) This causes in fact a deformation of the curves of Fig. 5: the peaks are lowered and their position along the frequency scale is determined approximately by the condition that $|1 - n^{-2} \sin^2 \varphi|$ be a minimum. Moreover, in the region $\omega = \omega'_0$ the condition $n = 0$ will be violated if account is taken of the fact that the imaginary part of n is different from zero. In that point $|v|$ does therefore not attain, strictly speaking, an infinite value. One can take these changes explicitly into account only if the frequency dependence of the absorption coefficients of the normal and the longitudinal waves are known.

In case A, when the amplitudes of the four transverse waves have the same order of magnitude, the results obtained above differ appreciably from the results of the usual crystal optics. In case B, however, it turns out that the normal transverse wave possesses almost the same properties as follow from the usual crystal optics, since the amplitude of the anomalous transverse wave is very small. Equation (12) is thus, for instance, exactly the same as the corresponding usual Fresnel equation, and Eq. (17) goes over into the usual Fresnel equation if we neglect the last term in the denominator. The amplitude of the transverse wave in the crystal has thus, as in the usual crystal optics, a sharp maximum as function of the frequency at the frequency for which the condition $n = \sin \varphi$ is satisfied. One can easily understand this by considering that under the condition mentioned the angle of refraction is equal to 90° , i.e., the refracted light goes along the crystal surface. The ratio of the cross section of the light beam in the crystal to the cross section of the corresponding light beam in vacuo is then equal to zero. Hence, even though E_p is large, the energy flux in the crystal, integrated over the cross section, may anyhow be small. All the same, however, such a wave propagating under the crystal surface itself, and possessing a large amplitude, can cause an intensive external photoeffect and also a surface internal photoeffect.

As to longitudinal waves in crystals, they do not arise, generally speaking, in the usual crystal optics, and are the consequence of the new boundary conditions formulated in references 1 and 2. We must emphasize that these boundary conditions do not go over into the boundary conditions of the usual crystal optics, not even in the limiting case of very long waves, when one may neglect the effects of the spatial dispersion in the volume equations. Under the condition $n = \sin \varphi$ the ampli-

tude of the longitudinal wave has also a steep maximum as a function of the frequency and can exceed the amplitude of the incident wave by a factor of the order of a hundred. But the angle of refraction $\psi_{||}$ is smaller by the same factor:

$$\sin \psi_{||} = \sin \varphi / n_{||} = \sin \varphi / \alpha n = 1 / \alpha.$$

The cross section of the light beam in the crystal is therefore not small; there is no energy flux into the crystal because there is no magnetic field in the longitudinal wave.^{1,4} This wave is, however, able to cause an intensive internal or external photoeffect.

A non-zero energy flux into the crystal, due to the expenditure of energy on photoionization can be obtained in the next approximation, by introducing a weak absorption of the waves in the crystal.

2. THE CASE OF TWO WAVES OF THE SAME POLARIZATION WITH THE SAME REFRACTIVE INDEX

In the following we consider the case where the dispersion follows the curve of Fig. 6, i.e., where ω has an extremum as a function of n^2 . Equations (20) – (22) which follow refer not only to crystals, but also to any dielectric medium with a dispersion of the kind shown in Fig. 6 (for instance, to a plasma in a magnetic field). Such a dispersion occurs, for instance, when the refractive index is expressed by Eq. (7) with negative b . In particular, if we are dealing with excitons, this case corresponds to $M < 0$. At the point B (Fig. 6) we have $n_+^2 = n_-^2$. The two solutions, which have the form of plane waves with refractive indices n_+ and n_- and which are usually linearly independent, are thus identical at the point B and are, therefore, only one solution. The second linearly independent solution is obtained in that case, as is well known, by differentiating the first solution with respect to the parameter n . If we write the first solution in the form $\exp \{ i(\omega/c)n(\mathbf{s}, \mathbf{r}) \}$ and take it into account that at the boundary between the medium under consideration and the

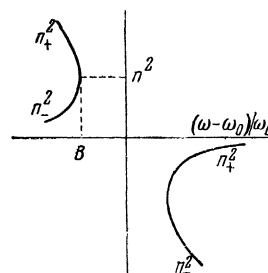


FIG. 6

vacuum (the plane $z = 0$) the relations

$$nS_x = S_{0x}, \quad nS_y = S_{0y} \quad (20)$$

must be satisfied by virtue of the usual boundary conditions (\mathbf{s}_0 is a unit vector in the direction of the propagation of the incident wave in the vacuum, which is independent of n), the second linearly-independent solution is of the form

$$z \exp \left\{ i \frac{\omega}{c} n(\mathbf{s}, \mathbf{r}) \right\}. \quad (21)$$

The solution (21) is thus a wave whose amplitude increases linearly with the distance z from the surface of the medium.

Both solutions are waves with a zero group velocity. This follows from the fact that $k = \omega n/c$ and the reciprocal of the group velocity is

$$\frac{1}{g} = \frac{dk}{d\omega} = \frac{n}{c} + \frac{\omega}{c} \frac{dn}{d\omega} = \infty, \quad (22)$$

since the derivative $dn/d\omega = \infty$ in the point B, because ω , as a function of n^2 , possesses an extremum at that point. The energy flux into the medium is therefore equal to zero.

The amplitudes of both waves mentioned above can be related to the amplitude of the wave incident from the vacuum if the appropriate boundary conditions are known. Turning from the general case to the case of light waves in a crystal near the exciton absorption band, we can again use Eqs. (23) to (29) of reference 2. From these equations we get $u_+ \rightarrow -u_- \rightarrow \infty$ and $v_+ \rightarrow -v_- \rightarrow \infty$ if $n_+ \rightarrow n_-$. If, however, we write down the total field of the +wave and the -wave, we get an indeterminate expression of the kind $\infty - \infty$. Writing it out explicitly under the assumption that $n_+ \rightarrow n_-$, and taking it into account that the quantities

$$n_+ S_{+x} = n_- S_{-x} = S_{0x}, \quad n_+ S_{+y} = n_- S_{-y} = S_{0y} \quad (23)$$

are independent of n_{\pm} , we get the following results:

For the s-components:

$$E_s(\mathbf{r}, t) = 2 \cos \varphi \frac{2n \cos \psi + (i\omega/c)(n^2 - \mu)z}{2n \cos \psi (\cos \varphi + n \cos \psi) + n^2 - \mu} \times A_s \exp \left\{ i\omega \left[\frac{n}{c} (\mathbf{s}, \mathbf{r}) - t \right] \right\},$$

$$\sin \psi = \sin \varphi / n; \quad (24)$$

where n is the value of the refractive index for the frequency for which n_+ and n_- are the same.

For the p-components:

$$E_{px}(\mathbf{r}, t) = 2A_p \frac{Q_x}{R} \exp \left\{ i \frac{\omega}{c} n(\mathbf{s}, \mathbf{r}) \right\},$$

$$E_{pz}(\mathbf{r}, t) = 2A_p \frac{O_z}{R} \exp \left\{ i \frac{\omega}{c} n(\mathbf{s}, \mathbf{r}) \right\}, \quad (25)$$

where

$$Q_x = \cos \psi \left[2n + \frac{n^2 - \mu}{n} \tan^2 \psi - \frac{n^2 - \mu}{n} \tan \psi \tan(\psi - \psi_{\parallel}) + \frac{i\omega z}{c \cos \psi} (n^2 - \mu) \right],$$

$$Q_z = -\sin \psi \left[2n - \frac{n^2 - \mu}{n} - \frac{n^2 - \mu}{n} \tan \psi \tan(\psi - \psi_{\parallel}) + \frac{i\omega z}{c \cos \psi} (n^2 - \mu) \right],$$

$$R = 2n \frac{\cos \psi}{\cos \varphi} + 3n^2 - \mu + \frac{b \sin \psi_{\parallel} \tan \psi}{\sin \cos \varphi \cos(\psi - \psi_{\parallel})} + \frac{n^2 - \mu \sin \psi \tan \psi}{\cos \varphi} - \frac{n^2 - \mu}{n} \left(\frac{\cos \psi}{\cos \varphi} + n \right) \tan \psi \tan(\psi - \psi_{\parallel}),$$

$$\sin \psi_{\parallel} \equiv \frac{\sin \varphi}{n_{\parallel}}. \quad (26)$$

The solution (25), (26) is the linear combination of the usual wave, of the type $\exp \{ i(\omega/c)n(\mathbf{s}, \mathbf{r}) \}$, with a wave (21) satisfying the boundary conditions formulated in references 1 and 2.

We must emphasize that the solution (25), (26) is a wave which is not transverse. All the same, we can verify that for this solution, too, $\text{div } \mathbf{E} = 0$, as should be the case in cubic crystals. Equations (24) - (26) can be simplified if $n^2 \gg 1$. We then get $\cos \psi \approx 1$, $\mu \approx 2n^2$ and Eq. (24) takes on the following form:

s-components:

$$E_s(\mathbf{r}, t) = 2 \cos \varphi \frac{2 - (i\omega/c)nz}{2 \cos \varphi + n} \times A_s \exp \left\{ i\omega \left[\frac{n}{c} (\mathbf{s}, \mathbf{r}) - t \right] \right\}. \quad (27)$$

Equations (25) reduce approximately to the following ones:

p-components:

$$E_{px}(\mathbf{r}, t) = 2 \cos \varphi \frac{2 - (i\omega n/c)z}{2 + n \cos \varphi} A_p \exp \left\{ i\omega \left[\frac{n}{c} (\mathbf{s}, \mathbf{r}) - t \right] \right\},$$

$$E_{pz}(\mathbf{r}, t) \approx 0. \quad (28)$$

These formulae show that (if $\cos \varphi$ is approximately of order unity) the amplitude of the wave in the crystal exceeds the amplitude of the incident wave by a factor $(4\pi/\lambda)z$, where λ is the wavelength of the light in the vacuum.

3. FREQUENCY DEPENDENCE OF THE IMPURITY PHOTOEFFECT IN THE EXCITON ABSORPTION REGION

It has been established in several experimental papers that both for the internal and for the external impurity photoeffect the frequency dependence of the photocurrent has a maximum in the frequency range corresponding to the exciton absorption of light in the crystal. In this way, for instance, Zhuze and Ryvkin⁵ were the first to discover in

cuprous oxide a maximum in the frequency dependence of the photoconductivity at the same frequencies at which Gross and collaborators⁶ detected exciton absorption in cuprous oxide. The frequency dependence of the external impurity photoeffect also often shows a maximum at the frequencies corresponding to the exciton absorption of light. This was shown experimentally by Apker and Taft⁷ for KI and RbI films in which F-centers played the role of impurities, and by Borzyak⁸ for a cesium-antimony photocathode. Later similar maxima were detected by Taft and Philipp⁹ in the spectral distribution of the external photoeffect in a number of other alkali halide films and in single crystals of KI, and also by Philipp¹⁰ in BaO. In all these cases the intensity of the photoeffect was proportional to the impurity concentration, indicating the impurity character of the photoeffect. In the experiments of Apker and Taft the proportionality of the photocurrent to the intensity of the incident light was also noted.

One usually explains the connection between the photoeffect and the exciton absorption of the light (position of the photoeffect maximum in the exciton absorption region) as follows. It is assumed that the direct influence of the light on the electrons of the impurity centers is not very great, because of the small impurity concentration. In the exciton absorption region, however, the light creates in the crystal, a large number of excitons, which diffuse and collide with and ionize the impurity centers. The energy of light spent on the ionization of the impurity centers is thus not determined by the impurity absorption, which is small, but by the intrinsic absorption.

The exciton photoeffect mechanism described here is perfectly feasible and is, perhaps, in some cases the dominant one. There is, however, another possible explanation of the photoeffect, to which we wish to call attention. This explanation assumes normal photoionization of the impurity centers directly by the electrical field of the light wave. It is well known that the probability of such an ionization, per unit intensity of the light incident from the vacuum, is equal to

$$\omega = C(\omega) |\mathbf{E}|^2 / |\mathbf{A}|^2, \quad (29)$$

where \mathbf{E} is the amplitude of the electrical field of the light wave in the crystal, and $C(\omega)$ a coefficient of proportionality independent of the field of the light wave and determined by the properties of the impurity center and the crystal. $C(\omega)$ is a smooth function of the light frequency ω . As far as $|\mathbf{E}|/|\mathbf{A}|$ is concerned, however, this ratio has a sharp maximum as a function of ω in the exci-

ton absorption region, as was shown in the preceding sections. In the frequency region $\omega \approx \omega'_0$, for instance, we thus have from Eqs. (17) – (19) that $|v|$ and $|E_{||}/A|$ can attain values of the order of one hundred (for small angles of incidence φ). The dependence of $|v|$ and $|E_{||}/A|$ on the frequency is shown in Fig. 5. For $\omega \approx \omega'_0$, the probability for photoionization can thus, according to (29), be larger by a factor 10^4 than in the neighboring frequency regions. A similar peak in the frequency dependence can also occur for the photoconductivity and the external photocurrent, since they are proportional to w while the coefficient of proportionality is like $C(\omega)$, a smooth function of ω .

We must emphasize that such a high photoeffect peak is obtained in the exciton absorption region precisely because $n^2 \approx 0$ in the region $\omega \approx \omega'_0$. This however, is not always realized, but only when the following conditions are fulfilled: a) The oscillator strength for the phototransition in the exciton state must not be very small, so as to make the constant b in Eq. (7) large. This insures the vanishing of n_+^2 or n_-^2 in the frequency range $\omega = \omega'_0$, which lies outside the region of strong absorption of light. b) The violet side of the band under consideration must have no intensive absorption bands, the presence of which can lead to such deviations from Eq. (7), that neither n_+^2 nor n_-^2 vanish. c) In the region $\omega \approx \omega'_0$ the light in the crystal must be absorbed only very weakly (at the same time, the absorption background must also be weak), so that n^2 is almost real. Otherwise the condition $n = \sin \varphi$, which is necessary in order that the quantity (17) take on the particularly large value (18), will not be satisfied even approximately. If these three conditions are not realized, the photoeffect peak will be appreciably lower.

We note that our explanation of the photoeffect peak in the region of the exciton absorption is essentially different from the explanation based upon the mechanism of a photocreation of excitons, their diffusion and the subsequent transfer of their energy to the electrons of the impurity centers. The present explanation requires neither the absorption of light in general nor the formation of real excitons. If the latter do appear, it is only as an accompanying phenomenon, which is not used for the explanation. The whole effect is caused only by a large dispersion (connected with the formation of virtual excitons) which causes n^2 to take on the value zero. It turns out in this case that even the boundary conditions at the surface of the crystal lead to such relations between the ampli-

tudes of the incident wave and the waves occurring in the crystal, as to cause $|E_p/A|$ and $|E_{||}/A|$ to have a steep maximum as functions of the frequency ω .

The value $n^2 = 0$ as a result of a large dispersion can be realized not only near the exciton absorption band, but also near other bands, for instance, the impurity absorption band. In that case $|E_p/A|$ will also have a sharp maximum as a function of the frequency which leads to a corresponding peak in the photoeffect. The longitudinal wave, however, will not occur then, since its appearance is caused by the special boundary conditions^{1,2} ($P = 0$ at the crystal surface) which occur near the exciton absorption band, but not near the impurity absorption band.

The probability for the photoionization of an impurity center is determined by the total electrical field at the point where the center is situated. We must thus take \mathbf{E} in Eq. (29) to mean the amplitude of the vector sum of the electrical fields of all waves occurring in the crystal.

When $n = \sin \varphi$ the angle of refraction of the transverse wave $\psi = 90^\circ$. This wave does therefore not penetrate into the crystal but is propagated along its surface, causing an external photoeffect and an internal surface photoeffect. Photoionization inside the crystal, however, can be caused only by the longitudinal wave, the amplitude of which has a peak of the same height as the transverse wave and the angle of refraction of which, $\psi_{||}$, is determined by the condition $\sin \psi_{||} = \sin \varphi / \alpha n$. In the case $n_+^2 = n_-^2$ (this is possible only for a negative effective exciton mass and only for a well defined value of the frequency ω) a wave occurs with an amplitude which increases from the surface into the crystal according to Eqs. (24) – (26). If we assume that absorption is weak and that the complex refractive index is of the form $n = n' + i\kappa$, $\kappa \ll n'$, where n' and κ are real, the wave of Eq. (21) will have an amplitude that depends on z , its depth of penetration into the crystal, according to the law

$$z \exp \left\{ -\frac{\omega \kappa}{c} \frac{z}{\cos \psi} \right\}. \quad (30)$$

This amplitude has a maximum at $z = c \cos \psi / \omega \kappa$. The probability for ionization of an impurity will thus change with z as the square of the amplitude (30). Therefore, when a thin plane-parallel crystal plate is illuminated, the intensity of the external photoeffect will turn out to be less at the illuminated side of the plate than at the back side.

An experimental verification of the theory given here would be a quantitative agreement between the formulae obtained and experiment. In particular, the theory predicts the appearance of a peak in the photoeffect only then when the refractive index be-

comes much less than unity. Moreover, Eqs. (17) and (18) predict a definite dependence of the peak height on φ . The peak height must also depend essentially on the polarization of the incident light, since for p-components the ratio $|E_p/A_p|$ can be very large (of the order of a hundred), and a longitudinal wave with the same peak in amplitude occurs as well, while for the s-component $|E_s/A_s|$ does not exceed two and no longitudinal wave appears. For the s-component the peak in the photo-current can thus not be large in the exciton absorption region.

In conclusion we note that the present idea of the explanation of the photoeffect peak in the region of exciton absorption of light was first proposed by one of the authors at the First All-Union Conference on Photoelectrical and Optical Phenomena in Semiconductors (Kiev, 1957).¹¹

The authors express their gratitude to I. G. Zaslavskaya for performing the numerical calculations.

¹S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 1022 (1957), Soviet Phys. JETP **6**, 785 (1958).

²S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 1176 (1958), Soviet Phys. JETP **7**, 813 (1958).

³S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 522 (1958), Soviet Phys. JETP **8**, 360 (1959).

⁴S. I. Pekar, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 451 (1959), Soviet Phys. JETP **9**, 314 (1959).

⁵V. P. Zhuze and S. M. Ryvkin, Izv. Akad. Nauk SSSR, Ser. Fiz. **11**, 93 (1952).

⁶E. F. Gross and N. A. Karryev, Dokl. Akad. Nauk SSSR **84**, 261 471 (1952); E. F. Gross and B. P. Zakharchenya, Dokl. Akad. Nauk SSSR **90**, 745 (1953).

⁷L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951); E. Taft and L. Apker, J. Chem. Phys. **20**, 1648 (1952).

⁸P. G. Borzyak, Tr. Ин-та физики АН УССР (Proc. Inst. Phys. Acad. Sci. Ukr. S.S.R.) **4**, 28 (1952).

⁹H. R. Philipp and E. A. Taft, J. Phys. Chem. Solids **1**, 159 (1956); Phys. Rev. **106**, 671 (1957); E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids **3**, 1 (1957).

¹⁰H. R. Philipp, Phys. Rev. **107**, 687 (1957).

¹¹S. I. Pekar, Tr. 1-го Всесоюзн. совещания по фотоэлектрич. оптич. явлениям в полупроводн. (Proc. First All-Union Conference on Photoelectrical and Optical Phenomena in Semiconductors) Acad. Sci. Ukr. S.S.R., 1959; see also the survey by Rashba, Snitko, and Tolpygo, J. Tech. Phys. (U.S.S.R.) **28**, 2696 (1958) (p. 2699, Sec. II), Soviet Phys.—Tech. Phys. **3**, 2464 (1959).