SOVIET PHYSICS JETP VOLUME 11, NUMBER 1 JULY, 1960

ON AN EXPERIMENTAL DEMONSTRATION OF THE EXISTENCE OF ADDITIONAL ANOMALOUS LIGHT WAVES IN A CRYSTAL IN THE EXCITON ABSORPTION REGION

M. S. BRODIN and S. I. PEKAR

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

Submitted to JETP editor July 29, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **38**, 74-81 (January, 1960)

We consider one possible experimental demonstration of the existence of additional waves in a crystal, predicted theoretically in references 1 — 3, in the exciton region of light absorption. We have used the experimental data[4] on the absorption of light in an anthracene single crystal at a temperature of 20° K, which show deviations from the Lambert-Burger law. We give an interpretation of the observed non-exponential dependence of the absorption of light in a crystal plate on its thickness. We show the existence of two identically polarized waves with different refractive indices and absorption coefficients in an anthracene crystal.

1. THEORY

IT has been shown earlier[1-3] that a monochromatic wave incident on a crystal from the vacuum can produce in the exciton absorption region several waves (usually two), which propagate with different velocities. These waves possess the same polarization and we are, therefore, not dealing with double refraction. One of these waves has properties which approximate those of the light wave occurring in normal crystal optics, but the others are essentially anomalous and their amplitudes tend to zero as one moves in the spectrum away either on the red or on the violet side from the exciton absorption region. One must therefore look experimentally for anomalous waves near the exciton absorption region. In the papers mentioned it was also noted that the anomalous waves appear more pronouncedly when the crystal is at a low temperature.

We suggested in reference 2 a number of methods of observing experimentally the existence of the anomalous waves. In the present paper we shall suggest still one more method, which enables us to use already existing experimental data to determine the parameters of both waves ocurring in the crystal. This method reduces to an investigation of the dependence of the intensity of the light transmitted through a plane parallel crystal plate on the plate thickness. One assumes usually that the intensity should decrease exponentially with the plate thickness. If, however, a more complicated dependence is observed in the case of small thicknesses, it is explained by the interference of waves which are multiply reflected from both surfaces of the plate. Such an interference undoubtedly occurs in many cases. In the following, however, we shall be dealing only with cases of strong absorption of the light in the plate, when we can neglect the intensity of the beam that is twice reflected and which passes thrice through the plate as compared with the intensity of the beam that passes once through the plate. In those cases the usual crystal optics predicts a simple exponential decrease in the intensity with thickness and cannot explain the more complicated dependence observed experimentally by Brodin and Prikhot'ko.[4] It will be shown in the following that this more complicated dependence is naturally explained by the generalized crystal optics developed in references 1 — 3.

We shall assume that a monochromatic wave of frequency ω is normally incident from the vacuum onto the plate and that this wave gives rise to two waves in the plate, with complex wave vectors $k_+ = k_+^0 + ik_+'$ and $k_- = k_-^0 + ik_-'$, respectively. One can then show that both waves will move in the plate and will emerge into the vacuum also normally, while the electrical field strength when they emerge from the plate into the vacuum can be written in the form

$$\mathbf{E}e^{-i\omega t} = [\mathbf{a}_+ e^{ik_+^0 l - k_+' l} + \mathbf{a}_- e^{ik_-^0 l - k_-' l}]\, e^{-i\omega t}, \qquad (1)$$

where l is the plate thickness. Different components of the vector $\mathbf{E}$ can, of course, have different complex arguments so that (1) can also describe an elliptically polarized wave. We have assumed that the amplitudes of the waves $\mathbf{a}_+$ and $\mathbf{a}_-$ take into account the reflection of the light from the entrance and exit surfaces (multiple reflections of the waves are neglected). The light intensity J when emerging from the plate will then be proportional to $|\mathbf{E}|^2$ so that

$$J \sim |\mathbf{E}|^2 = |\mathbf{a}_+|^2 e^{-2k'_+ l} + |\mathbf{a}_-|^2 e^{-2k'_- l} + 2|(\mathbf{a}_+, \mathbf{a}_-^*)| e^{-(k'_+ + k'_-) l} \cos[(k_+^0 - k_-^0) l + \alpha_0]. \tag{2}$$

We have introduced here the notation $(\mathbf{a}_+, \mathbf{a}_-^*) = |(\mathbf{a}_+, \mathbf{a}_-^*)| e^{i\alpha_0}$.

In the case where the + and − waves correspond to the normal double refraction, the amplitudes $\mathbf{a}_+$ and $\mathbf{a}_-$ must be strictly mutually perpendicular, i.e., $(\mathbf{a}_+ \cdot \mathbf{a}_-^*) = 0$. The last term in (2) drops out in that case and the dependence of the intensity of the outgoing light on the plate thickness l must be strictly monotonic. It is represented by the dotted lines in Fig. 1. If, however, the + and − waves are of a different nature, so that $\mathbf{a}_+$ and $\mathbf{a}_-$ are not necessarily perpendicular, the intensity J may, owing to the third term in (2), depend on the thickness l in an oscillatory manner, represented by the full curves of Fig. 1. If the wave with the smaller absorption coefficient has an appreciably larger amplitude, it will dominate over the second wave for all l. One can then in general neglect the latter and obtain in all cases a simple exponential dependence of the intensity on l. The more interesting case is the other one, when the wave with the larger amplitude has the larger absorption amplitude. We have thus depicted in Fig. 1 the case $|\mathbf{a}_-| > |\mathbf{a}_+|$, $k'_- > k'_+$. In that case the − wave dominates for small l; the dependence of ln J on l is described by a straight line of slope $2k'_-$. In the limiting case of large l, on the other hand, the + wave dominates; the dependence of ln J on l is also described by a straight line, but with a smaller slope, which is equal to $2k'_+$. It is thus convenient to determine the absorption coefficients of the two waves in the limiting cases of small and large thicknesses l.

In the region of intermediate thicknesses both terms on the right hand side of (1) may be approximately equal, and the third term in (2) will then also be of the same order as the first two. A sinusoidal oscillation must then take place in the dependence of J on l. The cases when the amplitude of these oscillations is a maximum are depicted in Fig. 1; this takes place when the vectors $\mathbf{a}_+$ and $\mathbf{a}_-$ are parallel (or antiparallel). The maximum possible deviation of the peaks of the oscillations from the dotted curve is equal to ln 2 above and infinite below the curve. Such deviations are, however, realized only if the cosine takes on the values +1 and −1 respectively just for those l for which the absolute magnitudes of the two terms on the right hand side of (1) are exactly equal.

We have plotted Fig. 1 not in l and $\ln|\mathbf{E}|^2$, but in dimensionless relative magnitudes, so as to reduce the number of parameters of the family of curves.

One can determine the change in the phase of the wave when it passes through a plane parallel plate, as a function of l, using a normal interference method. For the limiting cases of small and large l this function must be linear, as can be seen from Eq. (1). The slopes of these lines enable us to determine k_-^0 and k_+^0. We can determine $k_+^0 - k_-^0$ also from the period of the oscillations in the dependence of J on l. The oscilla-

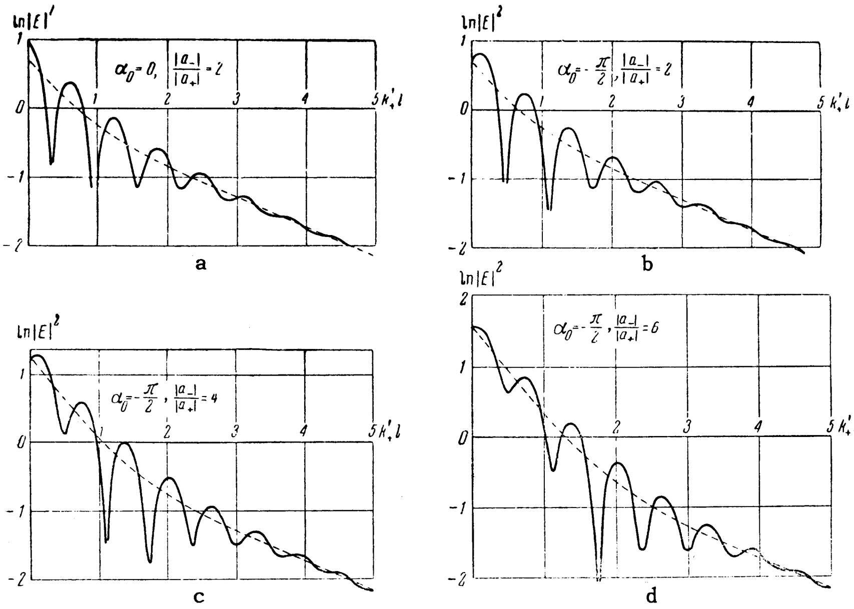

FIG. 1. The dependence of the absolute square of the amplitude of the electrical field of the transmitted wave on the crystal plate thickness; $(k_+^0 - k_-^0)/k'_+ = 10$; $k'_-/k'_+ = 3$.

tions themselves are convincing proof of the fact that the two waves under consideration do not represent double refraction.

The results and conclusions enumerated in the foregoing can be obtained merely from the dependence of the transparency of the plane parallel plate and of the phase shift on the plate thickness. One can obtain additional information about the nature of the two waves from the frequency dependence of the parameters of these waves. If the above-mentioned waves are identical with the ones predicted, in references 1 — 3, the frequency dependence of their parameters considered in reference 2 must be valid. We shall not repeat here the dispersion of the refractive index, which was evaluated there, but only introduce the frequency dependence of the amplitudes $\mathbf{a}_+$ and $\mathbf{a}_-$. The results following below are only valid in the case when there is an isolated exciton absorption band.

Reference 2 was devoted on the whole to an isotropically polarized medium and was applicable to cubic crystals, since we considered waves the wavelength of which was appreciably larger than the crystal constant. The results of that paper are, however, also applicable to some crystals of different symmetry, but only for selected directions of propagation and polarization of the light waves. The expressions for the refractive indices of the + and − waves and the formulae for the transparency of a plane parallel plate [Eqs. (60) and (61)] can, for instance, be obtained for a wider class of crystals. These results and all conclusions derived from them remain valid if the electrical field strength vector of the wave is parallel to one of the principal axes of the tensor a determined by Eq. (14) of reference 1. In those cases where this direction is defined by the symmetry of the crystal itself (as, for instance, for rhombic, tetragonal, or cubic crystals) it is frequency independent. The fact that the electrical field strength is parallel to the principal axis of the tensor a means that the latter can be replaced by a constant factor and after that the calculations take on the same form as in the case of an isotropic medium. We shall restrict ourselves to just such cases in the following.

The transparency of a plane parallel plate is determined by Eqs. (60) and (61) of reference 1. These formulae take automatically into account multiple reflection from both surfaces of the plate. We shall simplify these formulae using the above assumptions about the large absorption of the light in the plate and the possibility to neglect multiple reflection. From this assumption it follows that

$$|e^{2ik_\pm l}| \ll 1, \quad \cot k_\pm l \approx -i, \quad \sin k_\pm l \approx (i/2)e^{-ik_\pm l}. \tag{3}$$

As a result of this Eq. (60) of reference 1 takes the form of Eq. (1) of the present paper with

$$\mathbf{a}_+ = \frac{4\mathbf{A}n_+/(1-q)}{\left(1+\frac{n_+}{1-q}+\frac{n_-}{1-(1/q)}\right)^2}, \quad \mathbf{a}_- = \frac{4\mathbf{A}n_-/[1-(1/q)]}{\left(1+\frac{n_+}{1-q}+\frac{n_-}{1-(1/q)}\right)^2}. \tag{4}$$

Here **A** is the electrical field strength amplitude of the incident wave in the vacuum, n_+ and n_- are the complex refractive indices of the + and − waves, and q has the same meaning as in reference 2:

$$q = \frac{n_-^2-\mu}{n_+^2-\mu} \equiv \frac{\text{э}-n_+^2}{\text{э}-n_-^2}, \qquad \mu = \frac{2Mc^2}{\hbar\omega}\left(1-\frac{\mathcal{E}_0}{\hbar\omega}\right), \tag{5}$$

where M is the effective mass of the "transversely polarized" exciton in the direction of propagation of the beam, $\mathcal{E}_0$ is the energy of exciting this exciton in the limit where its quasi-momentum tends to zero, and э the asymptotic value of the square of the refractive index when one goes away from the exciton absorption region either to the red or to the violet.

It follows from Eq. (4) that $\mathbf{a}_+$ and $\mathbf{a}_-$ are parallel. Then

$$\frac{\mathbf{a}_-}{\mathbf{a}_+} \equiv \left|\frac{\mathbf{a}_-}{\mathbf{a}_+}\right| e^{-i\alpha_0} = -q\frac{n_-}{n_+}. \tag{6}$$

If the lifetime of the exciton is sufficiently large and if we can neglect the small imaginary correction to $\mathcal{E}_0$ (see reference 3 for details) we can take the frequency dependence of n_+ and n_- approximately from reference 2. If $M > 0$ one can see from Fig. 1 of reference 2 that in the whole exciton absorption region n_+ is real and n_- purely imaginary and q real and negative. In Eq. (6) we have then $\alpha_0 = -\pi/2$. In the frequency region where $|n_\pm|^2 \gg \text{э}$ we get approximately $q \approx n_+^2/n_-^2$ and $g \equiv |\mathbf{a}_-/\mathbf{a}_+| \approx |n_+/n_-|$; g is a steeply increasing function of ω. The equality $g = 1$ occurs when $\omega \approx \omega_0 = \mathcal{E}_0/\hbar$. Hence $g > 1$ in the frequency region $\omega > \omega_0$ and just in that region one must expect a well defined oscillatory behavior of ln J vs. l, if $k_-' > k_+'$.

Let us now consider the case $M < 0$. The frequency dependence of n_+ and n_- is given in Fig. 2 of reference 2. Here one must consider separately three frequency regions. In the first (red) region n_+ and n_- are both real and positive, $q > 0$, and the right hand side of Eq. (6) is negative so that $\alpha_0 = \pi$. $g > 1$, but decreases with increasing frequency ω and becomes equal to 1 at the violet limit of this region when $n_+ = n_-$. In the first region the oscillations must thus appear distinctly when $k_-' > k_+'$. In the second region (intermediate frequencies) we have according to reference 2 $n_- = -n_+^*$. It follows from this that $|q| = 1$, $g = 1$. If we introduce the quantities k^0 and k' such that $k_+ = k^0 + ik'$, then $k_- = -k^0 + ik'$. Equation (2) then takes the form

$$|E|^2 = 4|a_+|^2 e^{-2k'l} \cos^2(k^0 l + \alpha_0/2). \quad (7)$$

In that case α_0 is a function of ω. The oscillations must thus be observable for all l, and on a plot such as Fig. 1 one will not observe the straight sections at large and small l. We must, however, note that the dependence (7) was obtained assuming the lifetime of the exciton to be infinite. Taking the finite lifetime into account leads to some deviations from Eq. (7).

In the third frequency region (violet) n_+ and n_- are purely imaginary and both must be taken with the plus sign. $q > 0$ so that the right hand side of Eq. (6) is real and negative. Thus $\alpha_0 = \pi$. Moreover, g is a decreasing function of the frequency. $g = 1$ at the red end of the third region, where $n_+ = n_-$. Thus $g < 1$ in the third region. Therefore $|a_-| < |a_+|$ and since k'_- is still greater than k'_+, the + wave will dominate over the − wave. The l-dependence of J must thus be expressed by a simple exponential formula with a damping coefficient k'_+.

We note in conclusion that Eqs. (3) to (6) are applicable for an exciton absorption band isolated in a wide frequency interval, while the qualitative analysis given in the foregoing is valid only for $|n_\pm|^2 \gg \epsilon$, i.e., in a narrow frequency interval near the maximum of the band and only for large exciton lifetimes (which are, for instance, realized at low temperatures).

2. EXPERIMENTAL RESULTS

We chose for the object of our experimental investigation an anthracene crystal at 20° K. The long-wave band of light absorption in the electronic phototransition region was studied. The maximum of this band lies approximately at 25300 cm^{-1}. This absorption is real, since it is very intensive in very pure crystals. The polarization of the absorption and the corresponding luminescence along the crystal axes[5] are some arguments in favor of the idea that this band corresponds to the excitation of a fast moving exciton (with a small effective mass).

Single-crystal layers of anthracene were grown by the method of sublimation from a pure preparation. The most perfect among them, plane parallel and with smooth surfaces, were chosen for the measurements. They were put in optical contact on plane parallel plates of quartz. Because of the strong absorption we chose thin crystals (0.1 − 0.4μ). The crystal was placed in a cryostat filled with liquid hydrogen for cooling.

The surfaces of the crystal coincided with the crystallographic (a, b) plane. The light was perpendicularly incident upon this surface and the electric field strength vector was parallel to the monoclinic b axis. The direction of b was the second-order crystal axis and coincided therefore with a principal axis of the polarization (and also with a principal axis of the a tensor, mentioned in the first section of this paper). The directions of the incidence of the light and of the polarization were thus just such that the equations of reference 2 were applicable. It is of particular importance to stress that the normal double refraction cannot occur in this case.

Brodin and Prikhot'ko[6] measured the dispersion and absorption in an anthracene plate of well defined thickness. The results of their measurements were evaluated using the formulae of the normal crystal optics. Similar investigations were performed on stilbene toluene, and 1,2-benzene-anthracene. In all four crystals essential deviations were noted from the general Kramers-Kronig dispersion relations[7] between the refractive index and the absorption coefficient.[8] These deviations increased when the crystals were cooled, but in anthracene they were already observed at room temperatures. They could not be explained in the framework of the usual crystal optics.

A little later[4] the absorption of light in an anthracene crystal was measured in more detail and in that case crystals of different thicknesses were used. The results were again evaluated by the usual method. The imaginary part of the refractive index was evaluated using the equation

$$\varkappa = \ln(J_0/J)/2\omega l. \quad (8)$$

The values for κ obtained from crystals of different thicknesses are not reproducible. The Lambert-Bouguer law is this violated. It is impossible to explain this violation by interference phenomena, since one can neglect multiple reflection because of the strong absorption. Indeed, within the absorption band, even away from the maximum and for very thin plates, the intensity of the beam that passes thrice through the plate is some tenths of a per cent of the intensity of the beam passing once through the plate (see the third section of this paper).

The authors decided to evaluate the experimentally obtained results on the absorption, using the generalized theory of exciton absorption,[1-3] as explained in the first section of the present paper. It was first necessary to consider the dependence upon the plate thickness l of the intensity of the light J which had passed through the crystal. The observed dependence of $\log(J/J_0)$ on l for the frequencies $1/\lambda = 25100$ and $25425\ \mathrm{cm}^{-1}$ is given in Fig. 2. The points on the curves are given with their probable experimental errors in the ordinate and abscissa directions. An analysis of the errors is given in the third section of the paper. The magnitude of J_0 was measured experimentally in relative units, which means the presence of an unknown constant term in the quantity $\log(J/J_0)$; the curves in Fig. 2 may thus possibly be shifted vertically, retaining their form. The accuracy and the number of points is for the time being still insufficiently large. The curves in the figure are therefore tentative. All the same, it seems to us that one can reach the following conclusions from these curves:

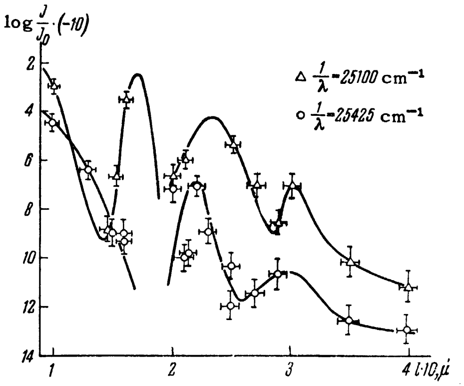

FIG. 2. The dependence of the optical thickness of anthracene crystals on thickness at T = 20°K (the electrical field is parallel to the b axis).

a) The Lambert-Bouguer law is violated since it is impossible to fit all the points on one straight line. It is impossible to reduce this violation to a consequence of interference, or to a consequence of the spatial inhomogeneity of the crystal (if the crystal is deformed in an inhomogeneous manner, the dependence on l of $\ln(J/J_0)$ must remain monotonic). It is therefore not clear that this violation can be explained in the framework of the usual theory.

b) The position of the points indicates an oscillatory dependence rather than a scatter. This follows from the fact that the amplitudes of the oscillations here and there exceed by far the errors of the measurements. Apart from this, the oscillations show a systematic character which may be observed in both curves. We have thus obtained qualitatively and approximately an l-dependence such as was predicted theoretically (see Fig. 1) and there is evidence of the existence of two waves in the crystal with different refractive indices and absorption coefficients. The oscillations show that these waves are not double refraction. Double refraction is also excluded by the above mentioned choice of the polarization of the incident wave.

c) According to the first section, the amplitudes of the two waves must be parallel and then the amplitude of the deviation of the curve from the average behavior (see the dotted curve in Fig. 1) on the positive side cannot exceed log 2. It can be seen from Fig. 2 that this is approximately observed. The deviations from the average behavior on the negative side can according to the theory have any value.

The experimental data confirm thus qualitatively the generalized theory of exciton absorption.[1-3] We shall perform shortly more extensive measurements for a larger number of thicknesses. We hope that they will enable us to determine quantitatively the parameters of both waves and their frequency dependence.

3. DESCRIPTION OF THE EXPERIMENTAL SET-UP AND ANALYSIS OF THE ACCURACY OF THE MEASUREMENTS

To measure the optical thickness of crystals we used photoelectric apparatus together with a spectrometer of average dispersion. A block diagram of the optical part of the apparatus is shown in Fig. 3.

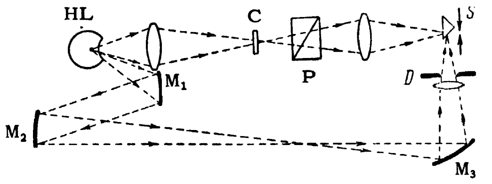

FIG. 3. Block diagram of the optical part of the photoelectric set-up for measuring optical thicknesses.

Two light beams, a direct beam and a comparison beam, emerge from the light source, a hydrogen lamp (H.L.). The first of these is incident upon the crystal C after which it passes through a polarizer P and is focused upon a slit S. The comparison beam is also led to the slit by means of the mirrors M_1, M_2, and M_3 and reflection from a prism. The triangular reflecting prism vibrates with a frequency of 70 cps, letting the direct and comparison beams pass alternately on to the spectrometer slit. A photomultiplier serves as receiver for the light. The intensity of the direct beam was measured by a null method, by comparing it with the intensity of the comparison beam. To compare the intensities we used a variableaperture diaphragm D placed along the path of the comparison beam.

There was no need to measure the intensity of the light reflected from the crystal, since the theoretical formulae [in particular, (2) and (4)] express the intensity of the transmitted light, but with account of the reflection of the light from the crystal. The experimental curves of Fig. 2 represent therefore only the intensity of the transmitted light for a comparison with the theory.

Let us now go over to an analysis of the errors of the measurements.

1. The accuracy of the comparison of the intensities of the two beams. The equality of the intensities of the beams is determined by the zero position of the galvanometer pointer. The accuracy of the fixing of this position for a given level of noise depends on the absolute intensities of the beams. In the most unfavorable case of low intensities, the relative error in the measurement of $\log(J/J_0)$ does not exceed 6%, if we disregard the appreciable systematic error connected with the possible inequality of the time during which the basic beam and the comparison beam pass into the spectrograph slit. This systematic error may introduce a constant additive to $\log(J/J_0)$, independent of l, and leads thus to a vertical shift of the curves of Fig. 2 without changing their form. This systematic error will be eliminated in a following paper.

2. The influence of the apparatus function of the spectrometer. The half-width of the spectrometer apparatus function was approximately equal to 1 A. Its influence can therefore be only appreciable at the very steep fall at the red end at the left absorption maximum. As we have chosen points which are situated at least 10 A from the above mentioned red absorption edge for the construction of the l-dependence of $\log(J/J_0)$, we can neglect the influence of the apparatus function.

The crystal thicknesses were measured in two ways: by birefringence using a Berek compensator and a microscope, and by using a Jamin interferometer. The maximum error in the thickness measurement was less than 4%.

There remains the task of estimating the influence of the interference effect due to a possible multiple reflection of the light at the crystal surfaces. Its role changes along the spectrum and depends strongly on the reflection and attenuation coefficients. One can see from Fig. 2 that the majority of the experimental points correspond to values of $\log(J/J_0)$ equal to -0.6 or less. Let us therefore consider the case $\log(J/J_0) = -0.6$ which is far from being very favorable from the point of view of the possibility of neglecting multiple reflection. When the coefficient for reflection of light from the vacuum-anthracene surface is equal to 0.3 and the reflection coefficient from the anthracene-quartz surface equal to 0.1, it turns out that for a beam twice reflected and thrice passing through the crystal the intensity is 0.003 times the intensity of the beam passing once through. We can therefore neglect the multiply reflected beams.

The authors express their gratitude to A. F. Prikhot'ko for his assistance with this experiment and for discussing the results.

Note added in proof (December 14, 1959). A source of appreciable errors may be a break in the light polarized along the a axis of the crystal because of the imperfection of the polarizer and the inaccuracy of its adjustment relative to the crystal. When emerging from the crystal the amplitude of the a-component may turn out to be comparable to the amplitude of the b-component as the first is absorbed much less than the second. To exclude the influence of the a-component we have now introduced measurements with two parallel polarizers, placed before and after the crystal.

---

[1] S. I. Pekar, JETP **33**, 1022 (1957), Soviet Phys. JETP **6**, 785 (1958).

[2] S. I. Pekar, JETP **34**, 1176 (1958), Soviet Phys. JETP **7**, 813 (1958).

[3] S. I. Pekar, JETP **36**, 451 (1959), Soviet Phys. JETP **9**, 314 (1959).

[4] M. S. Brodin and A. F. Prikhot'ko, Оптика и спектроскопия, (Optics and Spectroscopy) **7**, 132 (1959).

[5] Zhevandrov, Gribkov, and Varfolomeeva, Izv. Akad. Naul SSSR, Ser. Fiz. **23**, 57 (1959), Columbia Tech. Transl., p. 59.

[6] M. S. Brodin and A. F. Prikhot'ko, Оптика и спектроскопия, (Optics and Spectroscopy) **2**, 448 (1957).

[7] Propagation of Short Radio Waves, Ed. D. E. Kerr, Sec. 8.1, New York, 1951.

[8] Brodin, Prikhot'ko, and Soskin, Оптика и спектроскопия, (Optics and Spectroscopy) **6**, 28 (1959).

Translated by D. ter Haar
14