

EXCITONS AND THEIR MOTION IN CRYSTAL LATTICES

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IN 1931^[1] Jacob Il'ich Frenkel first proposed the hypothesis of a possible excitation of a crystal lattice which is not associated with the appearance of electrical conductivity in the crystal. This excited state can arise under the influence of absorption of a light quantum by the lattice. The "electrically inactive" absorption of light, in contrast to the "electrically active" absorption, does not, as Frenkel proposed, lead to photoelectric phenomena. Such an optical excitation in a crystal, according to the notion of Frenkel,^[2] "may be transferred from the initially excited atom to another of its neighbors, and will thus move through the crystal." This excited state which is capable of migrating through the crystal may be regarded as a kind of quasiparticle, which Frenkel called an "exciton."^{*}

These ideas concerning the exciton quickly found further development in theoretical papers by Peierls,^[5] Slater and Shockley,^[6] Wannier,^[7] Mott,^[8] Seitz,^[9] Franck and Teller,^[10] etc. Later on, both theorists[†] and experimenters turned to the exciton hypothesis in connection with attempts to explain various phenomena. Thus, for example, the well-known broad bands (of the order of tenths of an eV) in the absorption spectra of alkali-halide crystals[‡] have sometimes been associated with the excitation by light of excitons in these crystals (cf. the survey of Ueta^[14]). However, the large width of these bands raises doubt as to their exciton origin. A concept close to the exciton was also invoked in connection with the migration of energy in luminescence processes by Fano^[15] and Terenin.^[16] A concept which is essentially similar to that of the exciton (the phenomenon of "inductive" resonance, leading to migration of energy) was

used by Vavilov^[17] for explaining certain luminescence phenomena in liquids. The role of the exciton as an energy carrier was considered in explaining the phenomena of external and internal photoeffects.

In very interesting and important investigations, Apker and his coworkers^[18] showed that many peculiarities in the phenomenon of photoemission in alkali-halide crystals become understandable if we assume the participation of an exciton in these phenomena. As a result of a whole series of studies of photoconductivity in Cu₂O crystals, Zhuze and Ryvkin^[19] came to the conclusion that there was an exciton mechanism for photoconductivity and that excitons played a fundamental role in this phenomenon.

However, the question whether such a quasiparticle actually exists in crystals remained open. A confirmation of the actual existence of such a particle in crystals was obtained later from a different aspect, from the point of view of optical phenomena, where a complex structure consisting of narrow, sharp absorption lines, was discovered in the spectra of many materials near the edge of the fundamental absorption band in agreement with the predictions of J. I. Frenkel.

Starting from the results of Zhuze and Ryvkin on photoconductivity,^[19] the author of this report in 1950, in the Physico-technical Institute of the U.S.S.R. Academy of Sciences, set up a study of optical absorption at low temperatures in crystals of copper oxide (Cu₂O). These investigations led in 1951 to the discovery of a hydrogen-like series of narrow lines at the absorption edge of this crystal^[20,21] (Figs. 1a and 1b). This series of lines which regularly converges to a limit, as do atomic spectra, showed the formation in the crystal of a particle with energy levels determined by an interaction according to Coulomb's law. This was clear evidence that this particle is an exciton and that the series of lines is the optical excitation spectrum of the exciton in Cu₂O.

On the basis of the exciton picture, an interpretation was made of the constants of the hydrogen-like series in Cu₂O^[21] and their connection with the reduced effective mass of the exciton (the effective masses of electron and hole) was shown, and furthermore their relation to the Rydberg and the index of refraction of the crystal was demonstrated on the one hand, and with the energy of photodissociation of the exciton on the other. Further experiments,^[22] both electro-optical^[23]* and magneto-optical,^[23] on the spectrum of Cu₂O are in agreement with the exciton interpretation.

*See the survey in UFN 63, 576 (1957).

*In a footnote to paper^[2] concerning the origin of the term "exciton," Frenkel writes: "The term 'quantum' would lead to confusion with the concept of a light quantum or a photon, at whose expense the exciton is produced." It is interesting to note that in the new theories devoted to excitons^[3,4] there is an attempt to consider them now as some sort of synthesis of photons and excitons; (for example, the "light excitons" of S. I. Pekar^[3]).

†A summary of the theoretical papers about excitons is not the purpose of the present paper. Questions of exciton theory are considered in the survey by Haken^[11].

‡The content of this paper is restricted to crystals of ionic compounds. The domain of molecular crystals and exciton states in them is not treated here. A whole series of very important and extremely interesting experimental efforts in this field are due to I. V. Obreimov and his school^[12]. The papers of A. S. Davydov^[13] are of prime importance for the theory of excitons in molecular crystals.

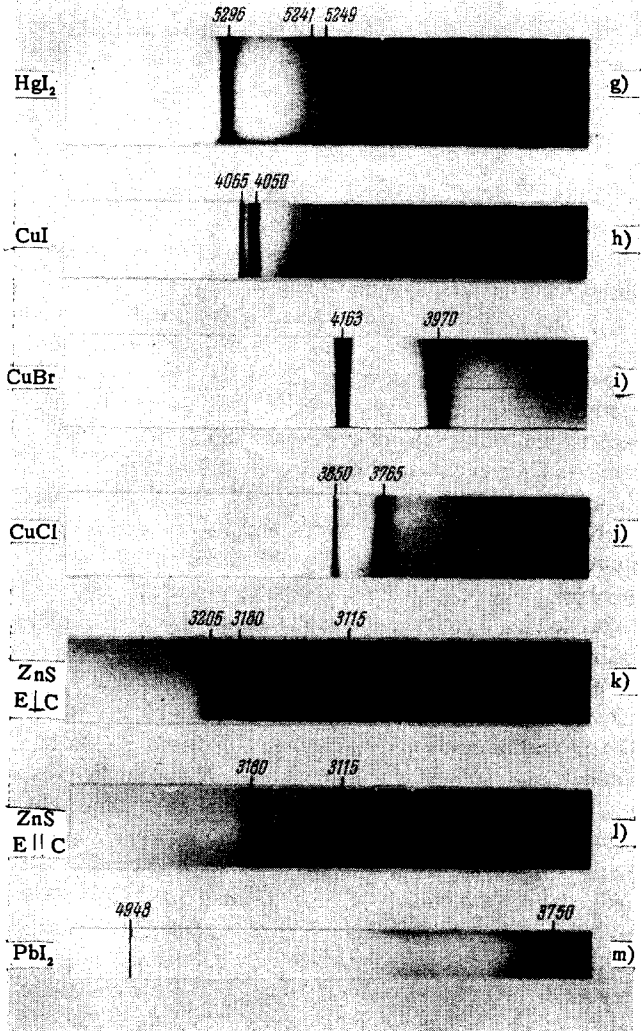
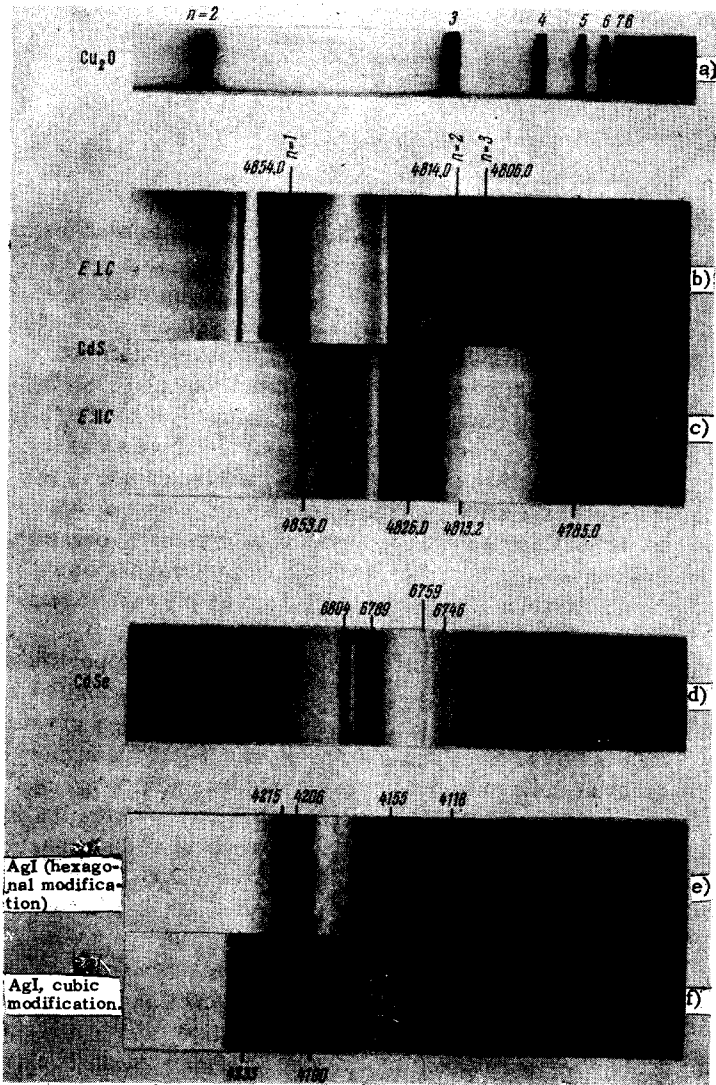


FIG. 1a. Exciton spectrum at the fundamental absorption edge of various crystals for $T = 4.2^\circ\text{K}$ (wave-lengths in Å). a) Cu_2O ^[1]; b) CdS ^[2], polarized light $E \perp c$; c) CdS ^[2], polarized light $E \parallel c$; d) CdSe ^[3]; e) AgI ^[4], hexagonal modification; f) AgI ^[4], cubic modification.

FIG. 1b. Exciton spectrum at the fundamental absorption edge of various crystals for $T = 4.2^\circ\text{K}$ (wave lengths in Å). g) HgI_2 ^[5]; h) CuI ^[6]; i) CuBr ^[6]; j) CuCl ^[6]; k) ZnS ^[7], polarized light $E \perp c$; l) ZnS ^[7], polarized light $E \parallel c$; m) PbI_2 ^[6]

The existence of hydrogen-like series at the absorption edge in Cu_2O was also discovered independently in Japan in the experiments of Hayashi.^{[25]*} Two years later, in 1954, our experiments with Cu_2O were repeated and confirmed in France by Nikitin.^[29]

*However, in this paper^[25] Hayashi does not relate the hydrogen-like series in Cu_2O with the exciton and does not give an interpretation of the coefficients. After the publication of our investigation of the exciton spectrum,^[21] Hayashi and Katsuku in a succeeding communication^[26] go over to our interpretation of the hydrogen-like spectrum of Cu_2O only for the green series. The yellow series of Cu_2O they associate with the polaron, and Hayashi stays with this interpretation in a publication of 1959.^[27] We cannot agree with the Japanese authors' polaron interpretation of the yellow series since their explanation contradicts the experimental facts.^[28]

1. THE ZEEMAN EFFECT IN THE EXCITON SPECTRUM OF Cu_2O

The fact that the optical spectrum of the exciton is well represented by a hydrogen-like series of absorption lines shows that in the copper oxide crystal the exciton, at least for highly excited states, can be described approximately by the Mott model; i.e., we can treat the exciton as a system of electron and hole interacting according to the Coulomb law, in a medium with a dielectric permeability ϵ_0 , and moving around their common center of gravity. A consequence of this is the increase in radius of the exciton orbit by a factor of $\epsilon_0 = n_0^2$ as compared to the orbit in an isolated hydrogen atom, so that

$$r_{\text{exc}} = \epsilon_0 \frac{\hbar^2}{\mu e^2} n^2. \tag{1}$$

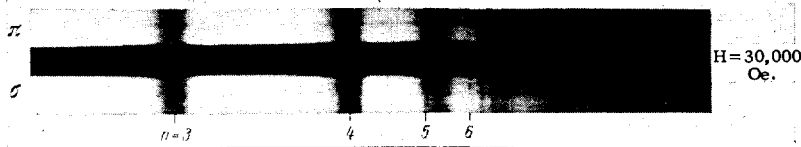


FIG. 2. Zeeman effect of lines of the yellow exciton series in Cu_2O in polarized light, for $T = 4.2^\circ\text{K}$, π and σ components.

Here μ is the effective reduced mass of the exciton, and n is the quantum number.

From formula (1) it follows that the orbit diameters of the exciton for large quantum numbers are enormous and reach values of several hundreds of angstroms. Determining μ from the exciton series ($\mu \cong 0.25 m$), we obtain from formula (1) for the smallest and largest values of n observed in an experiment the following values of the diameters of excitons:

$$\begin{aligned} n = 2 & \quad d_{\text{exc}} \cong 100 \text{ \AA}, \\ n = 10 & \quad d_{\text{exc}} \cong 2500 \text{ \AA}. \end{aligned}$$

Thus an exciton in Cu_2O is an enormous formation in the crystal, occupying many hundreds and thousands of unit cells, which in the form of a hydrogen-like quasiatom moves as a whole through the crystal.

As a consequence of the large dimensions of the excitons, it was possible to observe the Stark effect on lines of the exciton spectrum at fairly low fields (of the order of hundreds of volts) applied to the crystal as well as the phenomenon of pulling out of an electron (ionization of the exciton) by electrical fields with voltages in the kilovolt range, a phenomenon which in hydrogen atoms is observed only for fields of the order of 1,000 kV/cm.^[30]

In studying the effects of magnetic fields on the exciton spectrum, we discovered in solids a diamagnetic Zeeman effect which is quadratic in the field and can be observed because of the large orbits of the exciton.^[24]

The use of very low temperatures, like 1.3°K , and spectral apparatus of high dispersion made it possible to observe the Zeeman splitting not only of the narrow first line of the series $n = 1$, but also of other higher terms in the series. The first term of the yellow series of the exciton, $n = 1$, as shown by recent experiments of Kaplyanskiĭ and the author,^[31] is polarized, and its polarization is characteristic for quadrupole transitions in a cubic crystal (cf. below). The investigation of the Zeeman effect of this absorption line was carried out by Zhilich, Zakharchenya, Varfolomeev, and the author^[32] on single crystal foils* of Cu_2O in polarized light for different orientations of the axes c_2, c_3, c_4 of the crystal relative to the magnetic field H . The observed cases of magnetic splittings (doublets and triplets) were in complete agreement with the conclusions of the theory for the Zeeman splitting of a quadrupole line.

*The first experiments on the Zeeman effect of the $n = 1$ line were carried out on polycrystalline samples of Cu_2O , and therefore gave some averaged results for the splitting of the line in a magnetic field (triplet).

We succeeded in demonstrating the effect of the magnetic field on terms of the yellow series, $n = 3, 4, 5$, and 6 .^[24] In a magnetic field, the lines $n = 3, 4, 5$ are split into doublets. Polarization studies showed that these doublets are observed in π and in σ components, where the lines of the doublets are the same in both components, i.e., the appearance of the splitting in the π and σ components is apparently almost identical (Fig. 2). However, the possibility is not excluded that the splittings in the π and σ components are not completely the same. The separation $\Delta\lambda$ between the components of the doublets, within the limits of error of the measurements, is constant for all three terms of the series and equal to 0.84 \AA for a magnetic field of $H = 28,000 \text{ Oe}$. In sufficiently high fields one observes, for the term $n = 6$, a more complicated splitting. The doublet splitting is made more complicated because of the appearance of two weaker components, one on the short-wave side and the other on the long-wave side of the doublet. The picture of the splitting of the line $n = 6$ is also almost the same in the π and σ components. The separation between the lines of the doublet is the same as for the other terms of the series, and is equal to 0.84 \AA at $H = 28,000 \text{ Oe}$. The long-wave component is 0.8 \AA distant from the nearest component of the doublet, while the short-wave component is at a distance of 0.7 \AA .

In addition to Zeeman splittings, we observed still another interesting phenomenon.^[24] Terms of the series, when split in a magnetic field, are shifted toward the short-wavelength side from their original position in the absence of the field. This shift is the greater the greater the quantum number n of the corresponding series term, which is very evident in the spectrogram (Fig. 3). The magnitude of the shift, for example for the line $n = 5$ of the series, is found to be of the order 0.6 \AA for $H = 28,000 \text{ Oe}$.

Measurements of the magnitude of the shift of the "center of gravity" of the Zeeman components (doublets) in fields of various sizes showed that the shift increases like H^2 , i.e., is proportional to the square of the field (Fig. 5). This shows that in addition to the usual Zeeman splitting, one sees in the exciton spectrum a quadratic Zeeman effect, which, as is known, is associated with diamagnetism. From the theory of the quadratic diamagnetic effect^[33] it follows that the magnitude of the diamagnetic shift is proportional to the square of the radius r of the electron orbit, and consequently to the fourth power of the quantum number n^4 . In fact, the change in magnetic energy as a result of diamagnetism of the atom is equal to

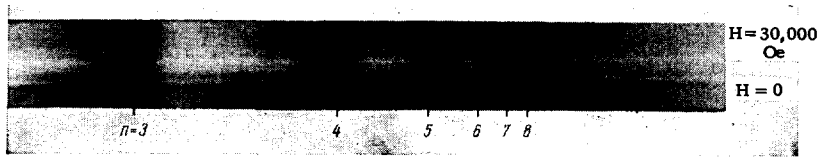


FIG. 3. Diamagnetic Zeeman effect on lines of the yellow exciton series in Cu_2O , for $T = 4.2^\circ\text{K}$ in unpolarized light. The diamagnetic shift of the split terms of the series in a field H relative to their position for $H = 0$.

$$\Delta W = \frac{e^2}{8mc^2} r^2 H^2. \quad (2)$$

If the phenomena observed by us are actually due to diamagnetism of the exciton, the observed magnitude of the shift should vary as n^4 . As Fig. 6 shows, the magnitude of the shift of the Zeeman components in the exciton spectrum is actually proportional to n^4 for a given field.

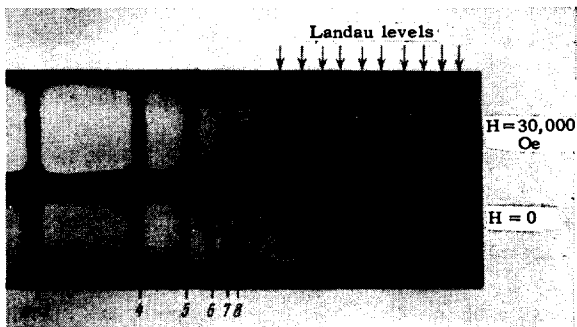


FIG. 4. Effect of magnetic-optic oscillations in the Cu_2O crystal at $T = 4.2^\circ\text{K}$. Absorption maxima on the continuous background beyond the edge of the yellow exciton series are produced by Landau levels.

From the foregoing it follows that the diamagnetic shift in the Zeeman effect of the exciton is very large, since one already observes it in series terms with quantum number $n = 3$, whereas in atomic spectra this shift, as shown by the experiments of Jenkins and Segre and Harting and Klinkenberg,^[34] is only observed for very high terms of the series. A noticeable shift for lines of the sodium spectrum was observed at approximately $n = 20$. This shows that the diamagnetism of the exciton is very large because of its large orbits.

The diamagnetic shift in the spectrum of the exciton gives us the possibility of determining the exciton radius. From our experiments it follows that the diamagnetic displacement of the center of gravity of Zeeman components of a term of the yellow exciton series with quantum number $n = 5$ is equal to 1.8 cm^{-1} for $H = 28,000 \text{ Oe}$. Substituting these numerical values in formula (2), we found that the value of the exciton radius for the series term $n = 5$ is $r_{\text{exc}} = 200 \text{ \AA}$. The value of the radius for the same excited state of the exciton, calculated from formula (1) which follows from the Mott model, was $r_{\text{exc}} = 280 \text{ \AA}$, which is in good agreement with that calculated from the diamagnetic shift, if we consider the approximate nature of the computation.

Investigations of the Zeeman effect in exciton spectra in very strong pulsed magnetic fields of several

hundred thousand oersted, developed in our laboratory by B. P. Zakharchenya, will undoubtedly give valuable information concerning excitons and bands in crystals.

II. EFFECT OF MAGNETO-OPTICAL OSCILLATIONS IN Cu_2O

The study of the effect of a magnetic field on the spectrum of the exciton in Cu_2O was carried out by Zakharchenya and the author and led to the observation of a very interesting phenomenon.^[35] We found that near the edge of the yellow exciton series, where the diamagnetic shift is comparable to the separation between neighboring terms of the series, one observes a spectrum consisting of almost equidistant lines. In addition, beyond the edge of the exciton series where, in the absence of magnetic field, one observes a continuous spectrum corresponding to ionization (dissociation) of the exciton, in a magnetic field on the background of the continuous spectrum there appear almost equidistant diffuse absorption maxima (Fig. 4). These maxima are also visible on photographs of the Zeeman effect in the exciton spectrum given in^[24] (Fig. 2a). In a field of $H = 30,000 \text{ Oe}$, the separation between maxima is about 7 cm^{-1} . In these maxima there are crowded together, so that they are difficult to resolve, a number of lines in the form of a fine structure. Further toward the short-wave side from the position of the edge of the series for $H = 0$, the intensity of the maxima decreases, and they fuse into the continuous background. At $H = 30,000 \text{ Oe}$ we could observe several tens of such maxima.

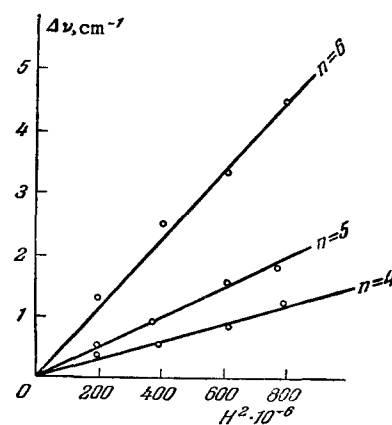


FIG. 5. Diamagnetic shift of "centers of gravity" of Zeeman components of terms of the yellow exciton series as a function of the square of the magnetic field H .

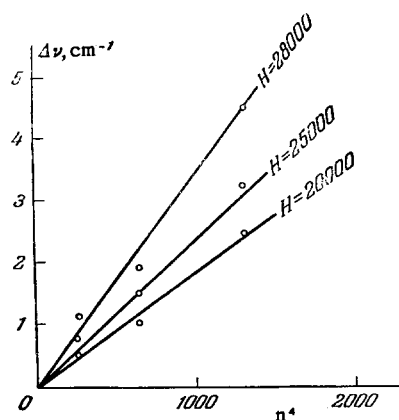


FIG. 6. Diamagnetic shift of "centers of gravity" of Zeeman components of terms of the yellow exciton series as a function of the fourth power of the quantum number n .

This picture of the exciton spectrum in a magnetic field beyond the series edge cannot be interpreted as a diamagnetic Zeeman effect with a strong diamagnetic shift of the higher terms of the series. The approximate equidistance of the absorption maxima beyond the series edge does not agree with the H^2 law for the diamagnetic shift. The separation between the maxima is proportional to magnetic field H . This fact leads us to the conclusion that we are dealing with a special phenomenon. The appearance of diamagnetic levels observed in the exciton spectrum is similar in character to the phenomenon in solids, where diamagnetic levels appear as the result of motion of free charge carriers in a magnetic field in accordance with Landau's theory.^[36] Experimentally, the Landau levels are observed in experiments on cyclotron resonance. The whole picture of a continuous spectrum with diffuse absorption maxima beyond the edge of the exciton series is well explained by the scheme of Landau levels.

These considerations are confirmed by theoretical investigations of the energy spectrum of the exciton in a magnetic field carried out by Pavinskii.^[35] Analysis of the phenomenon shows that the energy separation ΔE between absorption maxima beyond the series edge is equal to $\Delta E = \hbar\Omega$, where $\Omega = eH/\mu^*c$ is the cyclotron frequency corresponding to magnetic field H , and μ^* is the reduced effective mass of the exciton. The frequency Ω determined from the spectrum of magneto-optical oscillations beyond the edge of the exciton series spectrum is equal to the sum of the cyclotron frequencies Ω_e and Ω_h of the electron and hole forming the exciton:

$$\Omega = (\Omega_e + \Omega_h), \text{ where } \Omega_e = \frac{eH}{\mu_e^*c}, \quad \Omega_h = \frac{eH}{\mu_h^*c};$$

Ω may be called the cyclotron frequency of the exciton.

The phenomenon discovered by us in the exciton spectrum of Cu_2O in a magnetic field is similar in nature to the oscillatory magneto-absorption effect observed independently of us by Zwerdling and Lax^[38] in germanium and Burstein and Picus in InSb .^[37]

III. EXCITATION SPECTRA OF EXCITONS IN OTHER CRYSTALS

In further investigations in our laboratory and in other countries, there was discovered a complex structure of the absorption edge in several crystals of other chemical compounds besides Cu_2O . In Fig. 1 are shown the spectra of some crystals in the region of the fundamental absorption edge. As one sees from the spectrograms, they are characterized by narrow, sharp lines, sometimes reminding us very much of the lines in atomic spectra and located on the long-wave side of the fundamental absorption edge. In many crystals the width of these lines is of the order of thousandths of an eV, while in some cases (for example, CdS) they go down to 10^{-4} eV. The complex line structure at the fundamental absorption edge is characteristic for all the crystals. This phenomenon, which is observed with especial clarity for the example of Cu_2O , is a common property of crystal lattices.

The characteristic features of this phenomenon were already pictured thirty years ago by J. I. Frenkel. He noted then that in the spectrum of the exciton one should observe narrow lines. He understood that this was caused by the difference in selection rules for "electrically active absorption of light" (i.e., the case where the electron is transferred by light from the valence band to the conduction band) and for the "electrically inactive absorption" (i.e., for excitation of exciton levels of the crystal), a difference which is related to the energy and momentum conservation laws. He knew, of course, that in the case of "electrically active absorption of light" one should observe broad absorption bands in the spectrum. On the other hand, Frenkel writes concerning absorption of light:^[2] "In the case of electrically inactive absorption of light by a dielectric crystal, we deal with a condition which is completely analogous to that responsible for the optical excitation of an individual atom. Although the interaction between atoms leads to a splitting of the upper (excited) state into a broad band of states, corresponding to the n possible values of the momentum hp of the exciton (where n is the total number of atoms), in the present case this broadening does not lead to a broadening of the absorption line, in accordance with the equation

$$hp = hq \quad (3)$$

[where hq , according to Frenkel, is the photon momentum—E.G.], which, in accord with the equations for conservation of energy, permits only absorption of light of a definite frequency (shifted somewhat with respect to the frequency of excitation of the isolated atom). A true broadening of the absorption line corresponding to electrically inactive light should thus be caused by the accompanying change in the nature of

the motion of the atoms in the lattice, which were assumed to be at rest in the derivation of Eq. (3)."

As we have seen, experiment is in good agreement with these considerations, and the width of exciton absorption lines is of the order of 10^{-3} – 10^{-4} eV, while the width of absorption bands corresponding to zones in the crystal ("electrically active absorption" in Frenkel's terminology) reaches the order of several eV and more.

The location of exciton lines in the spectrum also agrees with Frenkel's arguments. Since, according to Frenkel, the electrically inactive absorption of light is associated with the expenditure of less energy than electrically active absorption, from his arguments it follows that the excitation spectrum of the exciton should lie on the long-wave side of the fundamental absorption edge.

As we see from all the spectrograms of Fig. 1, this is also confirmed by experiment.

Thus there is every reason for considering the line spectrum of crystals at the fundamental absorption edge as the excitation spectrum of excitons in the crystals.

As we see, the experimental facts presented above do not contradict the concept of the exciton; however, some natural questions arise as to how well founded is the agreement of experimental facts and the attributing of the narrow lines in the absorption spectrum and the corresponding energy levels to the exciton, i.e., to quasiparticles which are "running around" in the crystal. Might they not actually be related to impurity centers and defects which are "fixed" in the crystal and which could have energy levels which are located in the forbidden band in the crystal? Since the lattices of real crystals always contain defects to one or another degree, one must always consider this possibility. These considerations arose with various investigators, and from time to time there have appeared suggestions and arguments concerning experimental tests which might solve this problem. I should like, for example, to recall the interesting arguments of Professor Kittel on this score* and also the considerations of Nikitin and Haken^[39] concerning the possibility of inducing a directed migration of excitons in a non-uniform magnetic field. To questions of this sort there have been devoted experimental attempts to observe the diffusion of excitons in phenomena of photoconductivity in CdS crystals, undertaken by Balkanskiĭ.^[40] However, these last experiments have been subject to contradiction and criticism.^[41]

One of the most fundamental properties of the exciton, following necessarily from the theoretical arguments and picture of J. I. Frenkel, is its motion in the crystal lattice. If experiment could give a proof of motion of the exciton, then one would obtain unquestionable evidence of its existence in the crystal.

One should remark that a direct observation of the movement of an exciton, say, from its place of creation to its place of annihilation, is hardly possible, and here one must agree with the remarks of Professor Seitz on this point.^[42] But one can refer to experiments which might give indirect proof of the motion of excitons.

IV. PHOTOELECTRIC PHENOMENA ASSOCIATED WITH EXCITONS

First we consider experiments on photoconductivity in crystals. Although according to the initial picture of J. I. Frenkel the exciton is not associated with electrically active absorption of light, and as an electrically inactive structure it should not produce photoconductivity, we shall see below that a complex line structure at the absorption edge is closely related to the photoelectric phenomena in crystals.

It was first noted^[43] that all crystals possessing a complicated structure of their absorption edge are good photoconductors; for example, Cu_2O , CdS, CdSe, ZnS, HgI_2 , PbI_2 , AgI, etc. All these substances at low temperatures show, near their absorption edge, narrow strong lines which should be associated with formation of excitons. In addition, one is struck by the fact that these groups of exciton lines are located at that place in the spectrum where one usually observes the maximum of photoconductivity.

In addition to crystals in which one observes clear exciton spectra with strong lines, there exist crystals which do not show a structure of the absorption edge, for example, MoO_3 , Bi_2O_3 , V_2O_5 , As_2S_3 , PbO (the yellow form), etc. It was pointed out that in such crystals photoconductivity is not observed or has a very low value.^[43]

The correlation between exciton lines and the photoeffect becomes especially evident in the case of the red and yellow modifications of HgI_2 .^[44] In the red modification there are exciton lines, and there is a strong photoeffect, while in the yellow modification exciton lines are absent, and the photoeffect is extremely weak. This fact is especially convincing since the correlation between exciton lines and the size of the photoeffect is observed here in one and the same material.

Of great importance for explaining the role of excitons in the phenomenon of photoconductivity would be a detailed study of the spectral photosensitivity of crystals, in the absorption spectrum of which one observes lines associated with excitation of excitons. The discovery of peaks of photosensitivity coinciding with exciton absorption lines would be direct evidence that formation of excitons by absorption of light leads to the production of current carriers.

The first experiments along this line were carried out by the author together with A. A. Kaplyanskiĭ and B. V. Novikov in 1955 on crystals of CdS and HgI_2 .^[45]

*Private communication

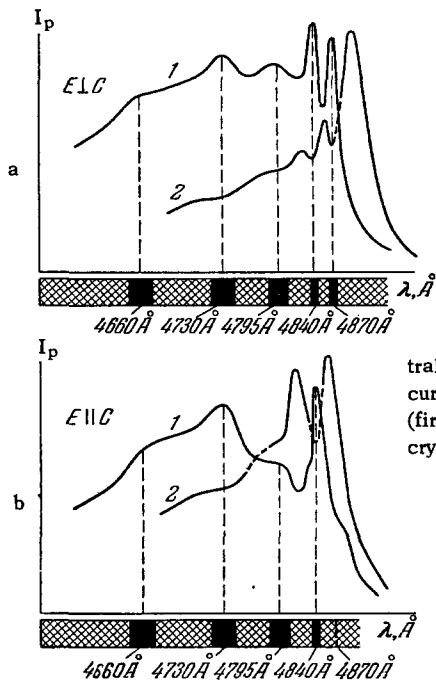


FIG. 7. Curves of spectral distribution of photocurrent for the two groups (first and second) of CdS crystals in polarized light.

Both these materials are good photoconductors and have a rich fine structure in absorption. An especially detailed study is being made at present of the spectrum of the absorption edge of CdS.^[46-49] The theoretical studies of Birman^[50] and Hopfield^[51] have made it possible to classify the intense exciton lines into three groups—A, B, C, each of which corresponds to a transition to the exciton levels from one of the lower bands.

Investigations of the spectral distribution of photocurrent in single crystals of CdS have been carried out at $T = 77^\circ\text{K}$ and 4°K in polarized light.^[52] The thickness of the CdS samples (and also of the other compounds investigated by us) was selected so that the light was completely absorbed by the crystal in the region of the exciton lines.

At low temperatures the spectral curves of the photocurrent of all the crystals investigated show clear maxima in the region of the exciton absorption lines. From the general appearance of the photocurrent curves and the nature of the correspondence between the absorption lines and the extreme values of photocurrent, it was possible to separate the large number of curves into two groups.

In some samples (we shall refer to these as the "first" group), there correspond to the absorption lines maxima of the photocurrent which are identical in position with them. In other samples (the "second" group), the spectral curve of photocurrent is markedly different from the curve for crystals of the first group: the absorption lines here coincide in position with minima in the photocurrent. The spectral curves of photocurrent for crystals of both groups depend essentially on the state of polarization of the light and the orientation of the crystal relative to the incident light beam.

In Fig. 7, as an example, we show characteristic spectral curves of photocurrent obtained by Novikov and the author on two samples belonging to different groups. The curves are taken with the sample illuminated by polarized light.

In the long-wave part of the curve for crystals of the first group (Fig. 7a,b, curves 1), there is a sequence of clear maxima. The first of these, $\lambda 4870 \text{ \AA}$, is polarized with the electric vector $E \perp c$. This maximum coincides in position and polarization with the longest wave intense absorption line in CdS crystals observed at $T = 77^\circ\text{K}$. To the other maxima of the photocurrent (some of them apparently partially polarized), to the narrow line at 4840 \AA and the broader lines located respectively near $\lambda 4795$, 4730 , and 4660 \AA , there also correspond intense absorption lines whose positions are shown schematically in Fig. 7. Both long-wave maxima of the photocurrent at $\lambda 4870$ and $\lambda 4840 \text{ \AA}$ are extremely narrow, their half-width being $6-8 \text{ \AA}$.

In crystals of the second group (Figs. 7a,b, curves 2) the steep rise of the photocurrent for both polarizations begins at considerably longer wavelengths than in the crystals of the first group described above. An essential difference is observed in crystals of the second group also in the behavior of the short-wave part of the curves. Crystals of the second group have a much steeper short-wave drop-off of the photocurrent curve, in which one can observe a definite structure consisting of narrow peaks and valleys. However, the essential point is that for crystals of this group the absorption lines correspond not to maxima, but to minima of the photocurrent curve. The narrow minima (with half-width $6-8 \text{ \AA}$) correspond to the absorption lines at $\lambda 4870$ and 4840 \AA ; the broader lines are located near $\lambda 4795$ and 4730 \AA . In individual samples one also sees a minimum near $\lambda 4660 \text{ \AA}$. Just as for crystals of the first group, the relative depth and sharpness of photocurrent minima may be different in different samples, and sometimes in different parts of one and the same crystal.

Polarization investigations show a strong dependence of the long-wave part of the photoconductivity curve on the polarization of the incident light. The drop in the photocurrent curve (Fig. 7a, curve 2) associated with the $\lambda 4870 \text{ \AA}$ line is present only in the component $E \perp c$, and is absent in the other one which is related to the strong polarization of this same absorption line with $E \perp c$. We note that to the strong maximum of the photocurrent near $\lambda 4890 \text{ \AA}$ on curve 2 (Fig. 7a) for the component $E \perp c$, as well as for the longer wave and more intense maximum for the component $E \parallel c$ (Fig. 7b, curve 2), there is no corresponding intense absorption line. There are no correspondences with absorption lines also for other maxima on the photocurrent curve of crystals of the second group (Fig. 7a,b, curve 2). These maxima whose positions, needless to say, vary greatly from sample to

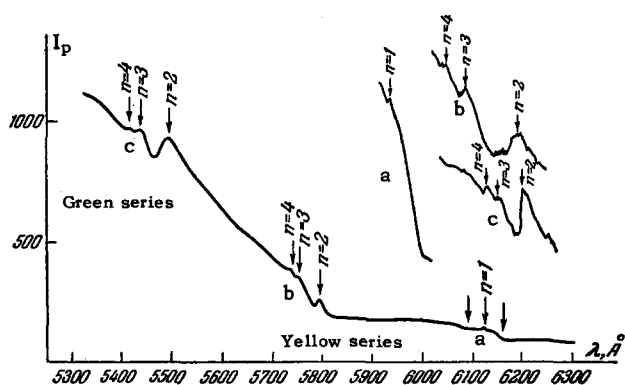


FIG. 8. Curves of spectral dependence of photocurrent in Cu_2O crystals. The applied electric field was $E = 750 \text{ V/cm}$, $T \approx 77^\circ\text{K}$. The original curves showing the fine structure of the spectral dependence of the photocurrent of Cu_2O . a—region of the first step and the line $n = 1$, $E = 1.5 \text{ kV/cm}$; b—region of the yellow exciton series, $E = 750 \text{ V/cm}$; c—region of the green exciton series, $E = 750 \text{ V/cm}$.

sample, are closely related to the depth of minima on the photocurrent curve of crystals of the second group. These maxima apparently are due to the outer edges of absorption lines whose central parts coincide with minima in the photocurrent curve. Thus the situation here is analogous to the phenomenon of self-inversion of spectral lines, where on the contour of a line in the radiation there appear two side maxima which change their position depending on the conditions of the experiment. In this sense, the maxima described above on the photocurrent curve of crystals of the second group must be regarded as some sort of "false" maxima which should not correspond to absorption peaks, and therefore no special physical significance should be ascribed to them.

A similar self-inversion of the maximum in a spectral curve of the external photoeffect with colored alkali-halide crystals has been observed under very specific conditions by Apker and Taft.^[18]

The question naturally arises whether the phenomena discovered by Novikov and the author and described above are common to all crystals with an exciton spectrum. A most interesting object from this point of view was copper oxide, where the exciton absorption spectrum was observed especially clearly. Actually, experiments carried out by Pastrnyak and the author^[53] and Apfel and Portis^[54] in the U.S.A. have shown that photocurrent maxima are observed on the photocurrent curve of Cu_2O in the yellow and green portions of the spectrum. They form two hydrogen-like series precisely corresponding to the yellow and green series for the exciton in Cu_2O (Fig. 8). The behavior of the photoconductivity curve reflects all the features of the structure of the absorption edge.

A similar correspondence between fine structures of absorption and photoconductivity have now been observed in a large number of crystals. Almost si-

multaneously with CdS, these phenomena were observed by us in crystals of the red modification of HgI_2 , and later by Novikov in crystals of PbI_2 , GaSe , AgI .

Thus the observations show that absorption lines are closely related to the structure of the spectral curves of photocurrent and may give rise to either an increase in photocurrent (in the case of maxima) or a decrease (in the case of minima). It would be of interest to investigate under what conditions the absorption lines appear in the spectral distribution of the photocurrent as maxima and under what conditions they appear as minima. Some of the experiments undertaken for this purpose were the heat treatment in air of CdS crystals with different annealing procedures (annealing and quenching).

It turned out that by means of quenching one can transfer crystals of the first group to the second group, and by annealing take crystals of the second group into the first group. The process of transferring crystals of CdS from one group to the other is completely reversible. One can transfer crystals of the first type by quenching to the second type, and then bring them back to the first type.

In addition to quenching and annealing, cold work of the surface (grinding and polishing) has a very strong influence on the structure of the photocurrent curve of crystals. Even for a very minor working of the surface, the maxima in the photocurrent are self-reversed and converted to minima.

As the experiments of Lider, Novikov, and the author show, cooling from 77°K to 4°K gives rise in some crystal samples to a significant change in the relation between the photocurrent curves and absorption lines. A crystal which at 77°K belonged to the second group (photocurrent minima coincide with absorption maxima) is transformed at 4°K to the first group (photocurrent maxima coincide with absorption lines).

The appearance of photopeaks in crystals, where light in the region of the fundamental absorption band is absorbed completely by the crystal, shows the existence of two mechanisms for producing a photocurrent. One of them is the usual one associated with direct formation of free electrons and holes. The second is related to the absorption of the light in lines. A definite assignment of the absorption lines to the exciton spectrum indicates that this second mechanism for producing free carriers has an intermediate stage in which a neutral particle, the exciton, is produced.

One can think of two fundamental processes for production of free charges via exciton states.

1. Dissociation of the exciton by thermal vibrations of the lattice. However, the relatively large binding energy of the exciton makes this process improbable. Furthermore, from this point of view it is very difficult to explain the experimentally observed phenomenon of transformation of photocurrent peaks into valleys when crystals of CdS are heat-treated. Be-

sides this process would have an exponential dependence on temperature, which is, however, not observed either in the peaks or in the background.*

2. Interaction of the exciton with impurity centers or defects, or with other excitons. This process visualizes a transfer of energy of the exciton to an electron of the impurity center or the defect as a result of a "collision of the second kind."

We consider this mechanism for production of a photocurrent more probable as an explanation of the observed phenomena. The proposed mechanism also has the necessary feature of motion of the exciton. Therefore the existence of peaks on the photocurrent curve should be regarded as evidence in favor of migration of the exciton in the crystal lattice.

If we accept this mechanism for the production of photopeaks, it must also give an explanation of the appearance of minima in the spectral curve of photoconductivity. We suggest that here defects in the crystal lattice play an essential role. In fact, the defects should make more difficult the motion of the exciton and stimulate its "premature" nonphotoactive annihilation, hindering its migration to those centers where by interaction it gives rise to a photocurrent. It is natural to think that the number of such defects will be a maximum at the surface. This, it seems to us, can explain the specific form of the photoconductivity curves with their valleys.

The large absorption coefficient at the absorption maximum of exciton lines leads to the production of excitons preferentially in a thin, pre-surface layer of the crystal. For a large concentration of these defects, the annihilation of excitons will be a maximum for spectral regions with the largest absorption coefficients (centers of absorption lines).

Excitons formed at the outer edges of absorption lines will be produced at a great depth in the crystal where the concentration of defects is less than at the surface. This should lead to a self-shielding of the exciton peak of the photocurrent on the photoconductivity curve, which also gives rise to the production of minima in crystals of the second group and the appearance of false maxima. From this point of view the influence of quenching, of cold working, and annealing on the shape of the photocurrent curve is understandable.

Thus, the arguments presented above show that the exciton at the fundamental absorption edge of crystals is closely related to the peaks of the spectral curve of photoconductivity. We should here, however, note that this does not contradict J. I. Frenkel's picture of the exciton as a currentless state. When Frenkel developed the concept of the exciton, he undoubtedly considered only processes occurring in a lattice which contains no impurities.

*The possibility is not excluded that in individual cases this mechanism plays the decisive role in some of the phenomena investigated by us.

The primary act accompanying the electrically inactive absorption of light in such a lattice is the excitation of an exciton. The motion of the exciton in the crystal, according to Frenkel, does not lead to the appearance of an electrical current. In a lattice with impurities, the primary act of producing the exciton by light is also essentially not photo-active, in accordance with the ideas of J. I. Frenkel; but, as already pointed out and explained above, the secondary act, the motion of the exciton in the lattice and its interaction with impurities, produces photoconductivity. Without motion of the exciton there would be no peaks on the photoconductivity curve. The appearance of photopeaks coinciding with the exciton absorption line (lines of excitation of excitons) is a consequence of the motion of the exciton, and can serve as evidence in favor of its migration in the crystal.

It is interesting to note that, like photoconductivity, luminescence phenomena in crystals are also associated with exciton absorption of light.

V. LUMINESCENCE PHENOMENA ASSOCIATED WITH EXCITONS

If the line spectrum near the fundamental absorption edge is the spectrum for formation (creation) of excitons in a crystal lattice, a question arises about the inverse process, the disappearance (destruction) of excitons in a crystal. Does this process occur without radiation, or can the annihilation of the exciton proceed with radiation of light? Furthermore, it seems to the author that the recombination of a free electron and hole probably mainly occurs not directly, but via the intermediate formation of an exciton. If the process of annihilation of the exciton with radiation of light actually occurs, then in the luminescence spectra of crystals having exciton absorption lines one should observe lines of the radiation which are resonant with exciton lines.

After the discovery of the line spectra near absorption edges,^[21] in our laboratory and in the Leningrad Physico-technical Institute, experiments were set up on luminescence of crystals, for the purpose of observing annihilation of the exciton with radiation of light. In the experiments of A. A. Kaplyanskiĭ^[56] and M. A. Yakobson^[57] and the author, we observed in crystals of HgI₂ and CdS narrow lines in the luminescence, almost resonant with the exciton absorption lines of these same crystals. Later investigations^[58-61] confirmed our results and observed similar phenomena in other crystals: CdSe, ZnS, CuI, CuBr, and CuCl. In Fig. 9 we show the line spectra of luminescence at the absorption edges of several crystals. In Fig. 10 we give the spectrograms of the exciton absorption lines compared with the spectrograms of lines of luminescence for the following crystals: CdS (obtained by B. S. Razbirin), HgI₂, CdSe, CuCl, and CuI. From Fig. 10 one sees that the radiated lines are shifted

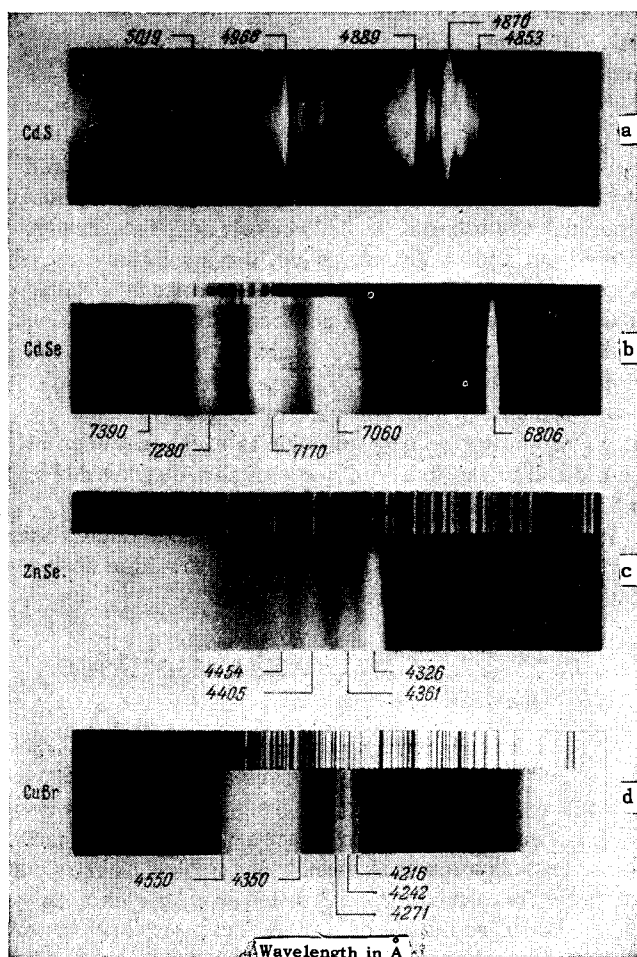


FIG. 9. Line spectra of luminescence at the fundamental absorption edge of crystals for $T = 4.2^\circ\text{K}$. a) $\text{CdS}^{[9]}$; b) $\text{CdSe}^{[10]}$; c) $\text{ZnSe}^{[11]}$; d) $\text{CuBr}^{[6]}$.

only slightly toward longer wavelengths relative to the exciton absorption lines. The slight shift (of the order of thousandths or tens of thousandths of an eV) of the annihilation lines of the excitons from resonant coincidence with the lines of excitation of excitons may easily be caused by familiar effects of polarization of the crystal lattice which should also occur in excitation of the exciton, effects which play a role in the phenomena of ordinary luminescence and give rise to a shift toward the red relative to the absorption spectrum. The role of these polarization effects in the case of a free, rapidly "moving" exciton is probably small, since the exciton is electrically neutral.

In the opinion of the author, it is not excluded that the red shift of exciton lines in emission relative to absorption lines is associated with effects of transfer of momentum and energy to photons in the formation and annihilation of the exciton. The energy transfer ΔE_{exc} , in the case where the system absorbing the light is an exciton in a crystal, is given by the relation

$$\Delta E_{\text{exc}} = \frac{E_{\text{exc}}^2 n^2}{2M_{\text{exc}}^* c^2},$$

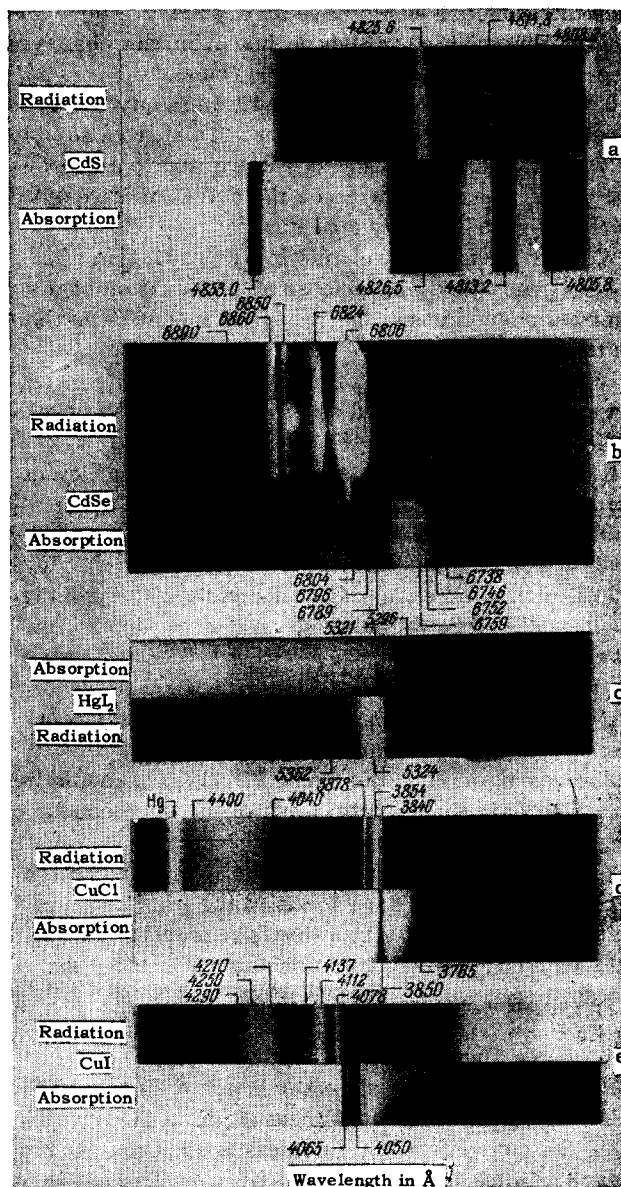


FIG. 10. Comparison of line spectra of luminescence and absorption at the fundamental absorption edge of crystals for $T = 4.2^\circ\text{K}$. a) $\text{CdS}^{[20]}$; b) $\text{CdSe}^{[3,12]}$; c) $\text{HgI}_2^{[5]}$; d) $\text{CuCl}^{[6]}$; e) $\text{CuI}^{[6]}$.

where E_{exc} is the energy of formation of the exciton, n is the index of refraction of the crystal, M_{exc}^* is the effective mass of the exciton, c is the velocity of light in vacuum. Since the exciton is a light particle, its effective mass M_{exc}^* may be 2,000 or more times smaller than the mass of the hydrogen atom M_{H} , while n in crystals may be fairly large (for example, $n \approx 2.5$ for CdS), the effect of the recoil ΔE , which is usually neglected in atomic and molecular optics, may become sizable, of the order of $\Delta E_{\text{exc}} \approx 10^{-4}$ eV and larger.

In addition to "resonance" radiation lines, i.e., exciton annihilation lines, in the luminescence spectra of crystals one sometimes observes (for example, in CdS) other lines which form groups of equidistant lines

located on the long-wave side of "resonant" lines, where the frequency of these lines ν_m is well represented by the relation

$$\nu_m = \nu_{exc} - m\omega, \quad m = 0, 1, 2, \dots,$$

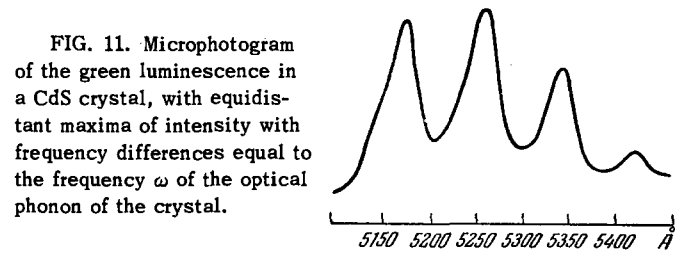
where ω is the frequency of an optical phonon of the crystal lattice. These groups of lines may possibly represent the process of annihilation of excitons with radiation of light and simultaneous exchange of energy with the lattice phonons.

It should be mentioned that Frenkel also concerned himself with processes of annihilation of excitons. Already in the Thirties he gave various interesting arguments concerning this point. Considering the question of the electrically inactive absorption of light and the transformation of light into heat, he wrote:^[2] "We should thus consider, in general, two different possible mechanisms for electrically inactive absorption of light in a dielectric. First, this absorption may lead to the production of a "free" exciton moving so fast through the lattice that the latter cannot deform near it. Absorption of light may also lead to the appearance of a "sticking" exciton, moving so slowly that it remains surrounded by a local distortion of the lattice, which does not permit it to move faster. In the former case light absorption may be accompanied by absorption or emission of, at most, one phonon, which leads to the formation of sharp absorption lines. In the latter case, the absorption may be accompanied by emission or absorption of large numbers of such phonons compatible with the conditions of conservation of energy and momentum and leading to the formation of a broad absorption band. It is also possible that a free exciton, changing to the "sticking" state, may be converted into heat (i.e., converted completely into phonons)."

Finally it is possible that an exciton, free or sticking, may convert to a photon, i.e., that the absorbed light will later be emitted in the form of (modified) resonant radiation. This secondary radiation can be neglected only in those cases where its probability is much lower than the probability of the processes considered above, which are not accompanied by radiation (and the corresponding processes of the "second kind" in the case of a gas).^[2]

As we have seen above, here too experiment essentially confirms the fundamental ideas of J. I. Frenkel on this point.

The role of excitons in luminescence of crystals is not restricted to the phenomena described above. In the luminescence spectra of crystals usually, not far from the fundamental absorption edge, one observes still another characteristic phenomenon: a group of equidistant, relatively narrow bands whose intensities drop off regularly toward the red end of the spectrum. The difference in frequencies of neighboring bands is equal to the frequency ω of the optical phonon of the crystal lattice. This phenomenon was first discovered



by Kröger^[63] in the green luminescence spectrum of CdS. In Fig. 11 is shown a microphotogram of this phenomenon. Further investigations detected similar phenomena in other crystals: ZnS, PbI₂, HgI₂, CuI, CuBr, AgI, and CdSe. In the literature this phenomenon is known under the name "edge emission." In most papers,^[64-67] the origin of this phenomenon is associated with impurities and defects in the crystal lattice. The edge emission is ascribed to recombination of a free electron and a hole captured by a defect, or conversely.

One may imagine,^[68] however, that edge emission may also be excited by excitons with participation of impurity centers or defects. In this case one should expect a relation of the edge luminescence with exciton absorption lines of the crystal. The primary act should be the excitation of the exciton by light. Then, by virtue of migration of the exciton, a collision occurs between it and a center or a defect, and their interaction leads to radiation of edge luminescence with simultaneous interaction with the phonons of the lattice. Actually the existence of a correlation between edge emission and exciton structure of the absorption edge is observed experimentally.^[68] Those crystals in which there is an exciton structure also give edge luminescence. Crystals where there is no exciton structure give no edge luminescence.

A still more convincing proof of the role of excitons in the phenomenon of edge luminescence is given by a study of the excitation spectra. The investigations of Dutton^[69] of the excitation spectrum of the green luminescence of CdS in polarized light at low

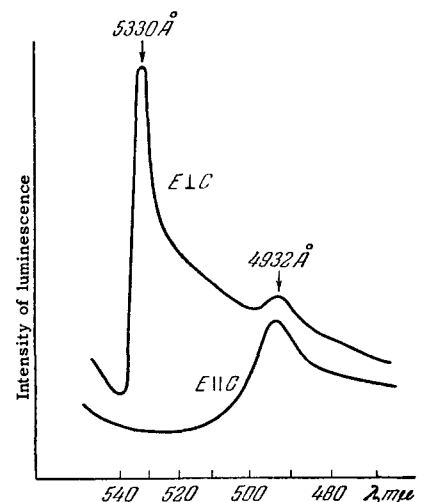


FIG. 12. Curves of spectral dependence of intensity of red luminescence of HgI₂ on wave length of exciting light, $T = 77^\circ\text{K}$. Below — exciting light polarized with $E \perp c$; above — exciting light polarized with $E \parallel c$.

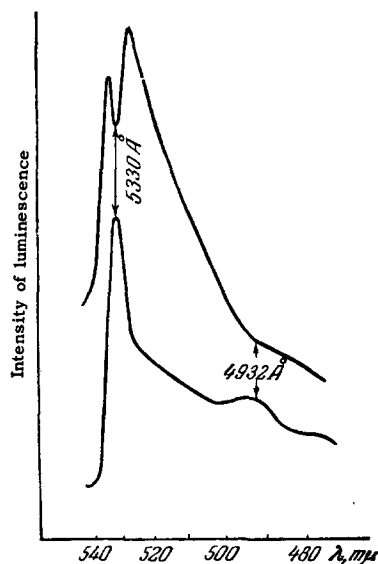


FIG. 13. Curves of spectral dependence of intensity of luminescence of crystals of HgI_2 on wave length of exciting light, $T = 77^\circ\text{K}$. Below - curve of excitation of red luminescence; above - curve of excitation of yellow-green luminescence.

temperature, and a comparison with the spectrum of the absorption edge, showed two maxima coinciding with the exciton absorption lines of the CdS crystal at $\lambda 4874$ and 4844 \AA . More thorough studies, carried out by Shekhmamet'ev, Razbirin, and the author, [70,71] showed that the coincidence of peaks on the spectral curves of excitation of luminescence and exciton lines at the fundamental absorption edge is a general phenomenon. They were also observed and investigated in crystals of CdS , HgI_2 , PbI_2 . In the course of these investigations a correlation was established between the structure of the luminescence excitation spectrum and the exciton absorption spectrum of these crystals.

In Fig. 12 is shown the spectrum of excitation of the red luminescence band of HgI_2 , when excited by polarized light with $E \parallel c$ (lower curve) and $E \perp c$ (upper curve); one sees excitation peaks whose locations and polarizations precisely correspond to the lines $\lambda 5330$ and 4932 \AA of the exciton absorption of the same crystal. In Fig. 13 is shown the dependence of the intensity of the red (lower curve) and yellow-green (upper curve) luminescence on wavelength of the exciting (unpolarized) light. Whereas for the red luminescence one observes maxima on the spectral excitation curve, for the yellow-green luminescence there correspond to the exciton lines not maxima, but minima on the excitation curve. The maxima at $\lambda 5360$ and 5280 \AA on the upper curve in Fig. 13 do not correspond to absorption lines. The spectral location of these maxima changes by $20\text{--}30 \text{ \AA}$ from crystal to crystal. These maxima are "false" and result from minima coinciding with the absorption lines. As we have seen earlier, such "false" maxima are observed on curves of the spectral distribution of photoconductivity of HgI_2 and PbI_2 crystals.

These phenomena are observed even more clearly in the green luminescence of CdS crystals. From the investigations of Razbirin, Shekhmamet'ev, and the author [71] it is established that, just as in the case of the photoeffect, crystals of CdS can be divided essentially into two groups according to the appearance of their luminescence excitation curves.

In CdS crystals of the first group, the maxima in the spectral excitation curve for the green luminescence coincide with the absorption lines. In Fig. 14 are shown spectra of excitation of the green lumines-

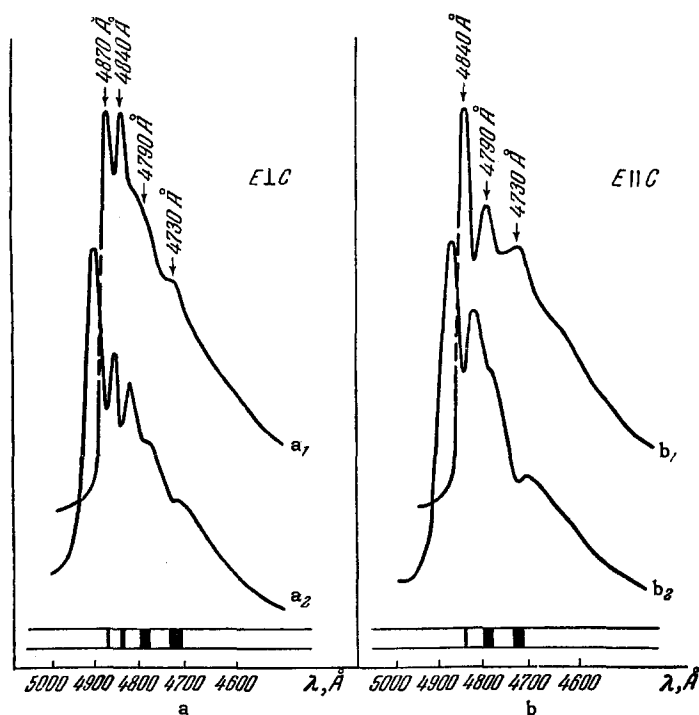
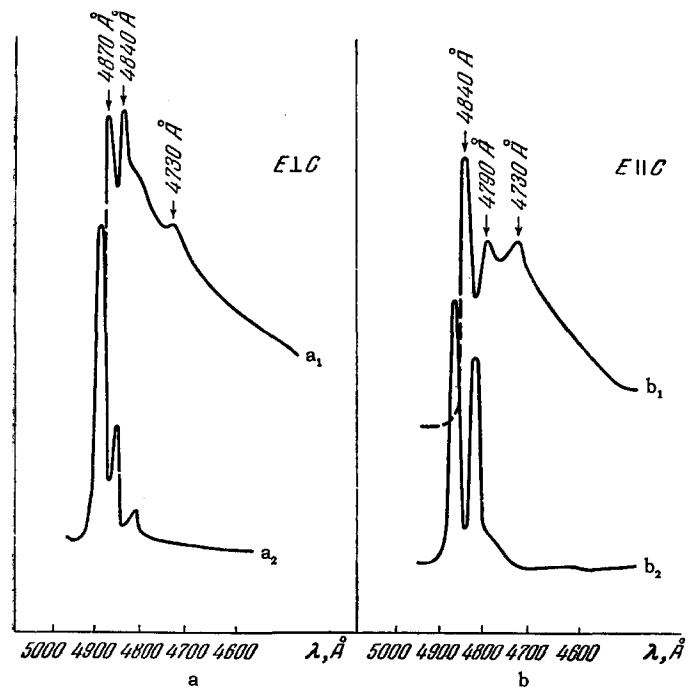


FIG. 14. Excitation spectra of green luminescence from CdS crystals at $T = 77^\circ\text{K}$ (under the spectra, above the abscissa axis, we indicate the position of the exciton absorption lines). a) The exciting light is polarized with $E \perp c$; b) $E \parallel c$; a_1 and b_1 are the excitation curves of the luminescence from crystals of the first group, a_2 and b_2 - from crystals of the second group.

FIG. 15. Spectra of excitation of green luminescence of CdS crystals at $T = 77^\circ\text{K}$. a, b are the same as in Fig. 14; a_1, b_1 are excitation curves for the luminescence before heat treatment of the crystal; a_2, b_2 —curves of excitation of luminescence after heat treatment of the crystal.



cence of CdS crystals (in arbitrary units for each curve) in polarized light with $E \perp c$ (a) and $E \parallel c$ (b). On curve a_1 (polarization $E \perp c$), one sees two narrow maxima at $\lambda 4870$ and 4840 \AA and a broader one at $\lambda 4730 \text{ \AA}$, coinciding with absorption lines of the CdS crystal at $T = 77^\circ\text{K}$. With polarization $E \parallel c$ there are observed maxima at $\lambda 4840, 4790,$ and 4730 \AA (curve b_1). The two last maxima are observed more clearly than in polarization $E \perp c$. The maximum at $\lambda 4870 \text{ \AA}$ does not appear in this polarization ($E \parallel c$), since the corresponding absorption line is polarized with $E \perp c$.

In crystals of the second group the minima on the curve of spectral excitation of luminescence (Fig. 14, curves a_2, b_2) coincide with the absorption lines. On the curves (a_2 and b_2) there are also clearly visible maxima; these maxima are "false" (corresponding to no lines in the absorption spectrum). Such "false" maxima are observed on curves of the spectral distribution of photoconductivity of crystals of CdS of the second group, and were described in detail earlier.

Thus here we have the same situation as in the case of photoconductivity phenomena. The question arises whether in luminescence there is a relation between the phenomena in crystals of the first and second groups, as there is in the case of the photoeffect. We have succeeded in establishing that such a connection actually does exist. By means of suitable heat treatment of a crystal of the first group, it can be brought over into the second group. For this purpose one must heat the crystal to a temperature around 250°C and then cool it rapidly by plunging it into liquid nitrogen (quenching). After such quenching, the spectral excitation curve for the luminescence is changed in a drastic fashion. As we see from Fig. 15, to the absorption lines before the quenching there corresponded maxima

on the excitation curve (curves a_1 and b_1), while after quenching there correspond to them minima (curves a_2 and b_2 ; curves are obtained on one and the same crystal). From these curves a_2 and b_2 (Fig. 15) one sees that the structure corresponding to the short-wave absorption lines at $\lambda 4790$ and 4730 \AA does not appear in the excitation spectrum. This apparently is related to the fact that after quenching of the crystals, the short-wave part of the excitation curve for the luminescence is greatly reduced.

We have attempted to transform crystals of the second group into the first group by annealing. Clear results have not yet been obtained. The minima were not changed to maxima; however, during the annealing there was significant reduction in the depth of the minima, and in certain cases it was reduced so much that the minima on the curve became barely noticeable. At the same time, the short-wave part of the luminescence excitation curve was greatly enhanced.

A striking feature is the explicit analogy between the phenomena of photoconductivity and the luminescence phenomena described here. It seems natural to us to look for a common origin of these phenomena and to assume that the luminescence, like the photoconductivity, to a considerable extent is produced by excitons. The appearance of maxima or minima on the curves of excitation of luminescence and their behavior during heat treatment of the crystal must then be associated with the annihilation (recombination) of excitons, as was done in detail for the case of photoconductivity.

The existence of exciton peaks on the spectral curve of excitation of luminescence of crystals, where the luminescence is undoubtedly associated with impurity centers and lattice defects, is a convincing fact, as in the case of photoconductivity, that there is mo-

tion of the exciton in crystals and that it migrates from its point of origin to the impurity center of luminescence.

VI. EXCITON ABSORPTION AND PHENOMENA ASSOCIATED WITH SPATIAL DISPERSION

I should like, furthermore, to call attention to the fact that one can give an indirect proof of the motion of the exciton also by specifically optical phenomena which, according to the theoretical studies in recent years, should be observed in the immediate vicinity of exciton absorption lines. These studies are due mainly to Pekar,^[72] partially to his predecessors Heller and Marcus,^[73] and recently to Ginzburg^[74] and Hopfield.^[4]

The work of Pekar shows that ordinary crystal optics becomes invalid when one studies light waves whose frequencies fall in the region of exciton absorption of light in a crystal, or near to it. In this case one can no longer assume that the dielectric constant ϵ is a function only of ω . One cannot neglect spatial dispersion, i.e., the dependence of ϵ on wavelength λ , or in other words on the wave vector $\mathbf{k} = (\omega/c)n\mathbf{s}$ where ω is the frequency, c the velocity of light in vacuum, n the index of refraction, \mathbf{s} a unit vector along the normal to the light wave. The magnitude of spatial dispersion is usually characterized by the parameter $(a/\lambda)^2 = (an/\lambda_0)^2$, where a is the lattice constant, λ_0 the wavelength in vacuum, and n the index of refraction. As Pekar remarks, this quantity characterizes the effect of spatial dispersion for a "fixed" excitation (for example, in an isolated impurity center in a crystal). The magnitude of the effect of spatial dispersion for a "moving" excitation like the exciton, according to Pekar, is determined by the expression $(an/\lambda_0)^2 \omega_0 / (\omega - \omega_0)$, where ω_0 is the frequency of the exciton absorption line. From this it follows that effects of spatial dispersion can become very large near exciton absorption lines because of the marked increase of n as ω approaches ω_0 . As a consequence of this, in the neighborhood of exciton absorption lines there should be observed qualitatively new phenomena unknown in ordinary crystal optics.

Pekar's theory predicts the existence in a crystal of several waves of a given frequency with the same polarization, but with different indices of refraction, i.e., a special kind of double refraction. This phenomenon of the existence in a crystal of additional anomalous waves in the region of exciton absorption of light is different from ordinary double refraction and should occur even in isotropically polarizing cubic crystals. Furthermore, the theory predicts the existence of longitudinal electric waves in the region of exciton absorption and other unusual phenomena.

As Pekar remarks, these phenomena can occur if the excitation moves through the crystal, i.e., for any

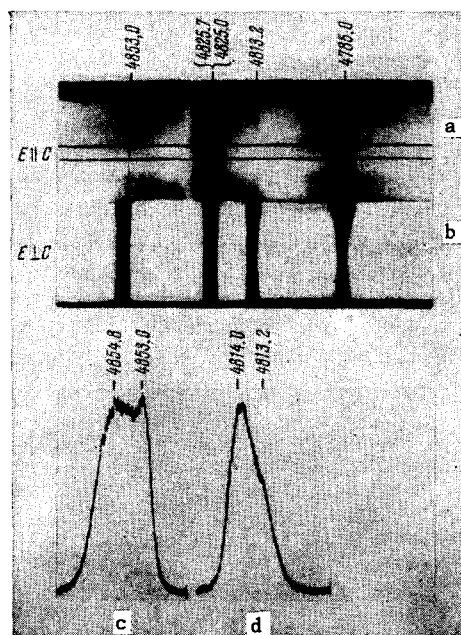


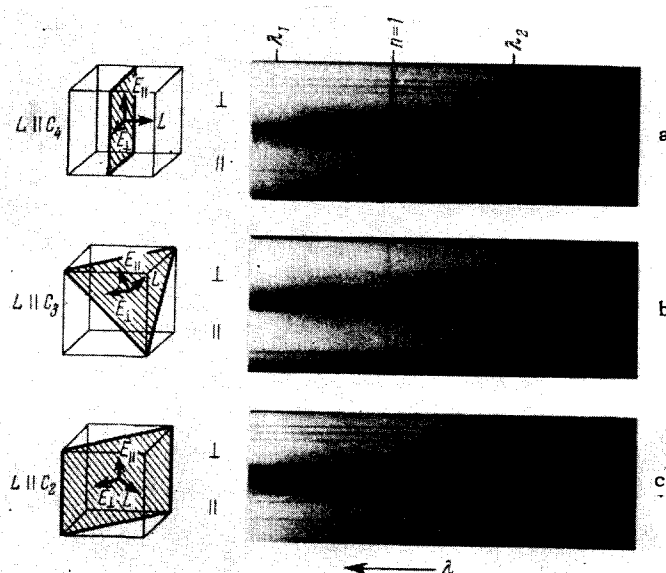
FIG. 16. Fine structure of absorption lines of the series $\Gamma_9 - \Gamma_7$ ($\lambda 4853$ and 4813) in a CdS crystal at $T = 4.2^\circ\text{K}$. a) Spectrum of CdS in the component $E \parallel c$; b) spectrum of CdS in the component $E \perp c$; c) microphotogram of absorption curve in the region of the first line of the series $\Gamma_9 - \Gamma_7$ ($\lambda 4853 \text{ \AA}$) for linearly polarized light incident perpendicular to the crystal ($\varphi = 0$); the angle between the electric vector of the incident light and the optic axis c of the crystal is 80° ; d) microphotogram of the absorption curve in the region of the second line of the series $\Gamma_9 - \Gamma_7$ ($\lambda 4813 \text{ \AA}$), $\varphi = 0$, $E \perp c$.

kind of exciton. These phenomena should not be observed for excited states which do not move through the lattice and are "localized" (for example, excitation of impurity centers whose concentration in the lattice is low). Therefore it is of interest and very attractive to study phenomena associated with spatial dispersion, which are interesting in themselves, and to use them as a proof of the existence of motion of excitons. But are these phenomena actually observed? Let us turn to the experimental facts.

VII. OPTICAL ANISOTROPY OF CUBIC CRYSTALS

In studying light absorption in Cu_2O crystals, Kaplyanskiĭ and the author^[75] discovered a phenomenon, unusual for cubic crystals, of anisotropic absorption of light in the line $n = 1$ ($\lambda 6125 \text{ \AA}$) of the yellow exciton series. It appeared that the degree of polarization of the line and its integral intensity depend on the orientation of the light ray L relative to the crystallographic axes of the sheet of Cu_2O . In Fig. 17 are shown spectrograms of absorption lines $n = 1$ for passage of polarized light along fourfold, threefold and twofold symmetry axes. If the light goes through a sheet of single crystal Cu_2O along a fourfold axis ($L \parallel c_4$), the light absorption is relatively intense and not polarized. Along a threefold axis ($L \parallel c_3$), the

FIG. 17. Optical anisotropy of cubic crystals. A spectrogram of the absorption line $n = 1$ ($\lambda 6125 \text{ \AA}$) of the yellow exciton series in Cu_2O for passage of polarized light along the direction L through single-crystal sheets cut along different crystal planes (cross-hatched) perpendicular to fourfold, threefold, and twofold symmetry axes (C_4 , C_3 , and C_2). $\lambda_1 6164$ and $\lambda_2 6086 \text{ \AA}$ are the long-wave edges of the steps in the continuous absorption.



line is again unpolarized, but its intensity is lower than for $L \parallel c_4$. Along the twofold axis ($L \parallel c_2$), the line is intense and completely polarized with the electric vector \mathbf{E} perpendicular to the plane of the cube in which the axis c_2 lies, which is the direction of observation. In intermediate directions the line $n = 1$ is partially polarized. Thus a cubic crystal has seven optic axes ($3c_4$ and $4c_3$), along which the absorption is isotropic.

The observed optical anisotropy of a cubic crystal of Cu_2O should occur if there is motion of the exciton excitation, according to the theory of Pekar (Pekar and Tsekvava^[76]). It also should be observed according to Ginzburg's^[77] theory.

The observed dependence of intensity and polarization of the line on the direction of the light ray in the lattice corresponds to an electric quadrupole, and was treated some years ago by Hellwege.^[78] The quadrupole character of the absorption line $n = 1$ is confirmed by theoretical and experimental studies of the Zeeman effect of this line carried out in our laboratory by Zakharchenya, Zhilich, Varfolomeev, and the author.^[32] It was also confirmed by the quantitative measurements of Kaplyanskiĭ and the author^[79] of the absorption coefficient for the $n = 1$ line in the direction along the threefold and fourfold axes ($L \parallel c_3$ and $L \parallel c_4$). The theoretical coefficient for quadrupole absorption $K(c_4)$ along c_4 should be greater than the coefficient $K(c_3)$ along c_3 , where the ratio of the coefficients should be $K(c_4)/K(c_3) = 3$. This result was actually found experimentally. The quadrupole absorp-

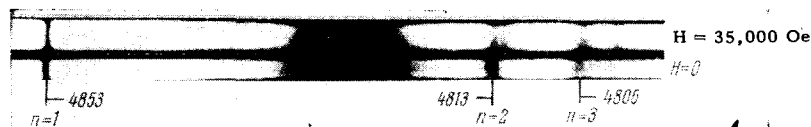
tion in the $n = 1$ line also corresponds to conclusions of Elliott's theory^[80] on the forbiddenness of dipole transitions to the ground state of the exciton in Cu_2O . Recently, the $n = 1$ quadrupole line in the Cu_2O crystal was treated in a theoretical paper of Elliott^[81] which also gave a new explanation of the phenomena right at the absorption edge of Cu_2O ("steps"). The theory of quadrupole transitions has also been worked out by Cherepanov and Galishev,^[82] who also studied theoretically the influence of electric fields on quadrupole lines. Anisotropy of absorption in other terms of the yellow series ($n \geq 2$) has not been observed.

It is interesting to note that, at the end of the preceding century, Lorentz^[83] in working out the theory of dispersion in the quadrupole approximation (essentially introducing the treatment of spatial dispersion) obtained an optical anisotropy for cubic crystals. Academician A. F. Ioffe has told me that Lorentz was so interested in the experimental proof of this phenomenon that he asked A. F. Ioffe, who was then working on elastic properties of rock salt, to set up experiments for detecting it.

VIII. TRANSVERSE AND LONGITUDINAL EXCITONS

Another experimental fact which is of interest for the problem of motion of the exciton is observed, as has been shown by Hopfield and Thomas,^[4] in crystals of zinc oxide; the author and Razbirin observed it in the spectrum of cadmium sulfide.^[84] At the time when the exciton spectrum was first detected in cadmium

FIG. 18. Paramagnetic and diamagnetic Zeeman effect in the lines $n = 1$, $n = 2$, and $n = 3$ of the hydrogen-like exciton series in CdS . The diamagnetic shift of the Zeeman splittings of lines $n = 2$ and $n = 3$.



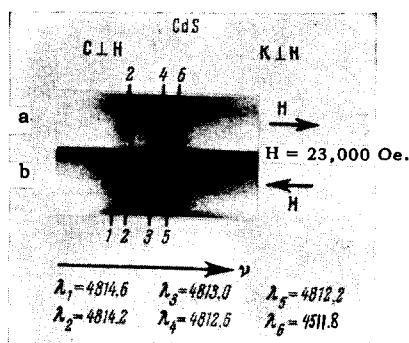


FIG. 19. Effect of reversal of magnetic field on the exciton absorption line λ_{4813} Å in the spectrum of CdS. The shift by 0.4 Å at $H = 23,000$ Oe and the change in intensity of Zeeman components when the direction of the magnetic field is changed from H to $-H$ (a and b); $\lambda_1 = 4814.6$, $\lambda_2 = 4814.2$, $\lambda_3 = 4813.0$, $\lambda_4 = 4812.5$, $\lambda_5 = 4812.2$, $\lambda_6 = 4511.8$ Å.

sulfide several years ago by Yakobson and the author,^[46] they noted that certain lines in the spectrum of a sheet of CdS with planes parallel to the optic axis c are observed in the extraordinary ray if one merely tilts the crystal through some angle to the ray of light around the direction perpendicular to the c axis, i.e., only when the electric vector E is not parallel to c . For strictly perpendicular incidence on the plate of light polarized parallel to the axis c of the crystal, this line is very weak and is practically absent. We then explained this phenomenon as the excitation of a plane vibrator perpendicular to the optic axis of the crystal.

The theoretical work of Pekar encouraged Razbirin and the author to study the cadmium sulfide spectrum more carefully, and we found^[84] that for CdS the exciton lines have a fine structure and are narrow doublets with components which are polarized at right angles to one another (Fig. 16). Only one of these components, the long-wave component, could be associated with a plane vibrator perpendicular to the axis,* since it alone is observed for arbitrary direction of polarization on a plate, which is cleaved perpendicular to the c axis of the crystal, when one observes along the c axis. The short-wave component is then absent. It cannot be assigned to a vibrator parallel to the axis since it is then not excited by the electric vector of light directed along the crystal axis. Short-wave components of the CdS doublets and their behavior when the crystal is rotated are well explained on the basis of the theories of Pekar^[72] and Hopfield,^[4] if we assign these lines to longitudinal excitons. The long-wave components of the doublets must be assigned to "transverse" excitons. The difference in the frequencies of "transverse" and "longitudinal" excitons observed in experiment can occur, according to the exciton theory of Pekar,^[3,76] only when the exciton momentum $K \neq 0$, i.e., when the excitation in the form of

an exciton moves through the lattice, and cannot occur when the excitation is "fixed."

IX. OSCILLATION OF INTENSITY OF LIGHT PASSING THROUGH PLATES OF CRYSTALS OF VARIOUS THICKNESSES

Still another piece of evidence in favor of the new crystal optics and the motion of excitons was found by Brodin and Pekar.^[85] They set up an experiment to demonstrate the existence of the additional anomalous waves which should, according to Pekar's theory, propagate in crystals in the region of exciton absorption. In a crystal of anthracene, they obtained an oscillating curve for the light intensity passing through a plate of an anthracene crystal as a function of its thickness. The oscillating character of the observed curve shows the existence in the anthracene crystal of two identically polarized waves with different indices of refraction and absorption, and the interference between them. Similar experiments with Cu_2O were carried out recently by Gorban'.

X. EFFECT OF REVERSAL OF THE MAGNETIC FIELD ON THE EXCITON SPECTRUM

The most convincing experimental fact, which shows directly the motion of the exciton in a crystal, is given by a study of the Zeeman effect. These experiments were carried out by Zakharchenya, Razbirin, and the author^[87] on exciton lines in the CdS crystal, satisfying the hydrogen-like series law. In August, 1959, the author reported on these experiments at the semiconductor conference in Rochester,^[86] and in particular reported the discovery in the exciton lines of the CdS crystal, in addition to the usual paramagnetic effects, of a diamagnetic Zeeman effect similar to that which had previously been discovered in the exciton spectrum of Cu_2O ^[24] (cf. below). In Fig. 18 one sees the paramagnetic splitting of exciton lines of CdS and their diamagnetic shift which increases with quantum number n .

Continuing these studies, Zakharchenya, Konstantinov, and the author^[88] discovered in CdS crystals an interesting magneto-optic effect unknown for an isolated atom. It appeared that under certain conditions the nature of the splitting of exciton absorption lines depends on the direction of the magnetic field even for a fixed position of the crystal in the field. Changing the direction of the magnetic field H by 180° (from H to $-H$) causes a shift in the position of the Zeeman components and changes their intensity.

The experiment was carried out at a temperature of $1.3^\circ K$. The surfaces of the CdS sheets which were $1-3 \mu$ thick were parallel to the optic axis A of the crystal. One could place the sheet with either $A \perp H$ or $A \parallel H$. The observation of the absorption lines in magnetic field was done in polarized light with the electric vector E almost parallel to the crystal axis.

*It is not clear why it should not be increased when the crystal is rotated around an axis perpendicular to c .

The effect of reversal of the magnetic field was observed most markedly on the exciton line of CdS at $\lambda 4813 \text{ \AA}$ and its satellite at $\lambda 4814 \text{ \AA}$. These lines, in a magnetic field H perpendicular to the axis A of the crystal, $A \perp H$, are split into doublets (Fig. 19b), where the components of the $\lambda 4813 \text{ \AA}$ doublet are stronger than those of the $\lambda 4814 \text{ \AA}$ doublet. When we reverse the direction of the magnetic field, the picture of the splitting is changed fundamentally. The components of the doublet of the line $\lambda 4813-4813.0$ and 4812.2 are shifted for a magnetic field $H = 23,000$ Oe toward higher energies by $\Delta\lambda = 0.4 \text{ \AA}$ and change their intensities. For the doublet 4814 \AA , the change consists in the fact that the longer wave component, $\lambda 4814.6$, disappears, while the $\lambda 4814.2$ component increases in intensity (Fig. 19a). These changes can be regarded as a shift of the doublet $\lambda 4814$ by the same magnitude $\Delta\lambda = 0.4 \text{ \AA}$ toward higher energy with a marked change in intensity in which the short-wave component practically vanishes.*

Thus the change in spectrum on reversal of the field, which is observed for $E \parallel A$, when $H \perp A$, $k \perp H$, and $k \perp A$, consists in a shift of the Zeeman components and a change in their intensities. The same effect is observed if one leaves the field H unaltered and turns the crystal through 180° about the direction of the field H .

The fact that the absorption spectrum of the crystal changes when the magnetic field is reversed cannot be explained in terms of spectroscopy of an isolated atom. In the case of an isolated atom, such an effect contradicts the invariance of the Schrödinger equation with respect to time reversal. The theory of this phenomenon shows that the change in absorption spectrum of the crystal when the magnetic field is changed in sign can occur only if the following two conditions are simultaneously satisfied: 1) the wave vector k of the electromagnetic wave must be finite (spatial dispersion); 2) there must be no center of inversion in the medium absorbing the light.†

The following effect can result in an energy shift of the Zeeman components of the exciton splitting when the magnetic field is inverted. Obviously the exciton, excited by an electromagnetic wave, has a perfectly definite direction of propagation with velocity $v = \hbar k / \mu$, where k is the wave vector of the exciton, which is equal to the wave vector of the exciting electromagnetic wave; μ is the effective mass of the exciton. In the presence of a constant magnetic field, in a system of coordinates moving with the exciton,

there is produced an electric field*

$$E = \frac{\hbar}{c\mu} [k, H].^\ddagger$$

In a crystal which does not have a center of inversion, the state of the exciton should have a dipole moment d . Therefore there is an addition to the energy of the exciton in a magnetic field equal to $-(d \cdot E)$. Then the energy of the exciton transition $\hbar\omega_e$ is given by the expression

$$\hbar\omega_e = E_{mk} - \frac{\hbar}{c\mu} (d, [k, H]) - E_0,$$

where E_{mk} is the energy of excitation of the exciton state in the magnetic field, which does not change when the field is reversed; E_0 is the energy of the ground state when all the electrons are in the valence band. It is clear that in this expression there is a term with a dipole moment which changes sign and thus leads to a change in energy of the level when the magnetic field is reversed.

It should be remarked that in a uniaxial crystal, such as CdS, the dipole moment vector d may be directed along the optic axis A^\ddagger and then the energy determining the shift is $\Delta\epsilon \sim A \cdot k \times H$. From this it follows that $\Delta\epsilon = 0$ if any of these vectors are parallel. Actually the effect has not been observed for $A \parallel H$.

It should especially be noted that O. V. Konstantinov made a special study of the effect of changes in direction of magnetic field on the spectra of fixed impurities and defects. The theory shows that the position in the spectrum of absorption peaks associated with transitions between levels of a fixed impurity center or defect cannot change when the magnetic field is reversed.

Thus the change in location of absorption bands when the magnetic field is reversed is specific only to a moving exciton state, having an intrinsic dipole moment, in a crystal which has no center of inversion, and is therefore the most direct proof of motion of the exciton through the crystal.

*As already explained, in 1955 Samoïlovich and Korenblit treated the effect of such a field on an exciton, considering it in formulas (4) and (5) of their paper.^[90]

In the studies of magneto-optic oscillations in Cu_2O by Zakharchenya, Pavinskiĭ, and the author, we also considered the problem of the electric field associated with the motion of the center of gravity of the exciton in a magnetic field. This magnetic effect was then assumed to be weak and was not taken into account (^[35], page 2179).

It should be noted that $k = \omega \cdot n(\omega) / c$ where $n(\omega)$ is the index of refraction. In the cases in which we are interested, n should be taken at the resonance frequency and should therefore be large. It is just for this reason that the electric field has a very large value.

† $[k, H] = k \times H$

‡The optic axis of the CdS crystal can be regarded as a vector since there is no center of inversion in the crystal.

*Studies of the effect of reversing the magnetic field have also been carried out recently by American investigators,^[89] who believe that the change in the spectrum on reversing the field is expressed only in a redistribution of the line intensity without shift. The solution to this question requires further investigations.

†Actually this phenomenon has not been observed in Cu_2O which has a center of inversion.

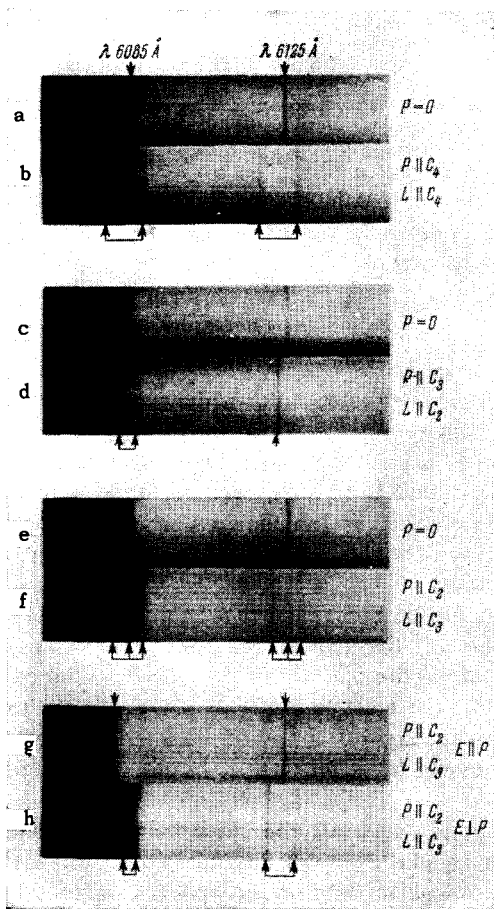


FIG. 20. Splitting of the first term $n = 1$ of the yellow exciton series and the edges of steps in the spectrum of Cu_2O for compression of the crystal along symmetry axes of fourth, third, and second order. The direction of observation L is perpendicular to the axis of compression. a), b), c) — free crystal ($P = 0$); d), e), f), g), h), — deformed crystal ($P \neq 0$); a) — f) unpolarized light; g), h) — polarized light.

XI. EXCITON SPECTRA AND THE BAND STRUCTURE OF CRYSTALS

I should now like to consider the importance of exciton states for the study of band structure of crystals. Because of the discreteness of the exciton spectrum and the narrowness of its lines, it opens great possi-

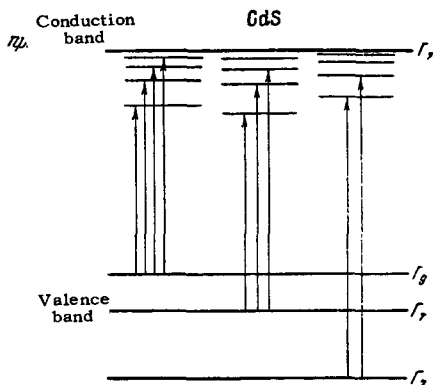


FIG. 21. Diagram of band structure of exciton levels and excitation of three groups of excitons in the CdS crystal.

Lines in the blue-green and blue regions of the reflection spectrum of Cu_2O crystals

Group	Quantum number n	Wave-length λ_n (Å)	Wave number ν_n (cm^{-1})	Half-width $\Delta\lambda_n$ (Å)	
				77.3°K	4.2°K
Blue-green	1	4796 *	20852	15	12
	2	4733	21128	—	4
Blue	1	4569 *	21887	35	25
	2	4505	22198	—	8

*The positions of the first bands of the blue-green and blue groups, $\lambda_{b.g.} = 4796 \text{ \AA}$ and $\lambda_b = 4569 \text{ \AA}$, obtained by us, differ from the positions of these same bands $\lambda_{b.g.} = 4880 \text{ \AA}$ and $\lambda_b = 4635 \text{ \AA}$, obtained by Pastrnyak.^[95]

bilities for spectroscopic investigation of the structure of complex zones. Each zone (of course, taking into account selection rules) can give an exciton spectrum, so that in the neighborhood of the fundamental absorption edge one should sometimes observe a complicated superposition of lines of exciton spectra of different bands, which is not always easy to unravel. However, recently one has gradually succeeded in unraveling these even in such complicated line spectra as that of cadmium sulfide at the edge of the fundamental absorption band.

Based on the theoretical investigations of Birman,^[50] who applied group theory for the analysis of band structures of crystals of the wurtzite type, Thomas and Hopfield^[49] treated the line spectrum of cadmium sulfide. In Fig. 21 we show a diagram of the bands of this crystal according to Birman. Each of the bands can give its own group of exciton levels near the conduction band. Starting from this band diagram, Thomas and Hopfield^[49] succeeded, by introducing some corrections to the initial interpretation of the CdS spectrum given by Razbirin and the author, in explaining the spectrum of strong lines of CdS , grouping them into three exciton series of three levels of the valence band of this crystal. One then obtains an explanation of the state of polarization of the lines in accordance with the symmetry properties of the different bands. Thus the analysis of the exciton spectrum of CdS made possible an experimental test of band theory.

Another example of a comparison of band structure with exciton spectra is given by the copper oxide crystal. The discovery in the spectrum of copper oxide of two exciton hydrogen-like series, yellow and green, brought forth the proposal^[91] that there exist two sub-bands of the valence band of Cu_2O . The theoretical basis for this assumption is contained in papers of Pavinskiĭ and Zhilich,^[92] Zhilich,^[93] Elliott^[80] and Moskalenko,^[94] who treated the band structure of copper oxide. Zhilich associates the valence band of Cu_2O with the $2p$ -levels of the ion O^{2-} , and the free band with the $4s$ -levels of Cu . The appearance of two series in the Cu_2O spectrum he associates with

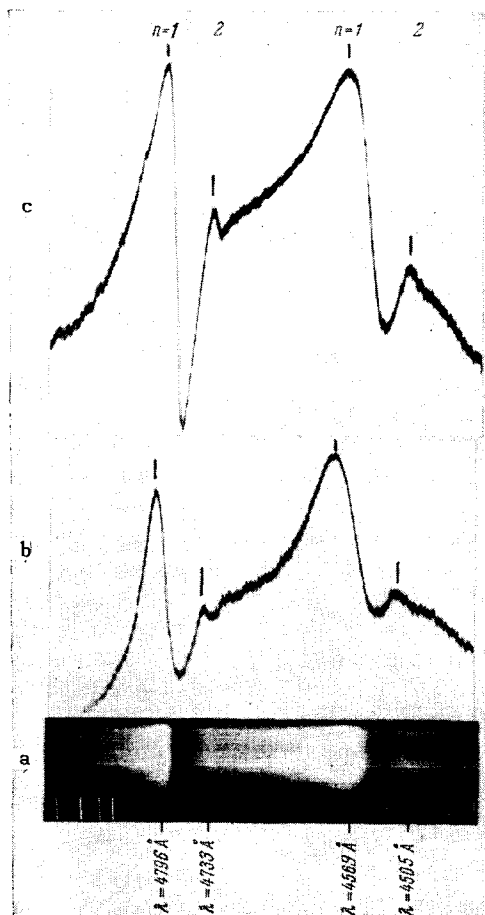


FIG. 22. Reflection spectrum from Cu_2O crystal in the blue-green and blue region. a) Spectrogram with groups of blue-green and blue lines; b) Microphotogram of the reflection spectrum of a Cu_2O crystal in the region of the blue-green and blue lines; c) microphotogram of the spectrum of reflection of another Cu_2O crystal in the region of the blue-green and blue lines.

the splitting by the crystalline field of the valence band of Cu_2O into two threefold degenerate sub-bands Γ_{25} and Γ_{15} (omitting spin-orbit interaction). The free band, in his opinion, is simple. Later Zhilich considered the band scheme of Cu_2O including spin-orbit coupling. Elliott relates the valence band with the $3d^{10}$ -levels of Cu^+ and the free band with the $4s$ -levels of Cu^+ . Elliott explains the appearance of two series by a splitting of the valence band of Cu_2O as a result of spin-orbit interaction.

From the work of Zhilich, Elliott, and Moskalenko it follows that the band structure of crystals of the type of copper oxide is complex, since both the valence band and the conduction band consist of several sub-bands. The yellow and green series exhibit only transitions between the upper valence sub-bands and the lower conduction sub-bands. The question naturally arises whether there is still some other experimental indication of the existence of other exciton states associated with other sub-bands of the complex band structure of Cu_2O . Actually such evidence was

obtained in our laboratory (L.F.T.I.) by Pastrnyak,^[95] who observed in reflections from the surface of a Cu_2O crystal a marked structure consisting of two discrete lines in the blue-green and blue region of the spectrum.

Chang Kuang-yin and the author subjected these reflection lines to a more careful study, improving the conditions for observation of the reflection spectra. Under these conditions we succeeded at liquid helium and nitrogen temperatures in observing^[96] new weak reflection lines on the short-wave side of each reflection line previously observed by Pastrnyak.

In Fig. 22a is shown the reflection spectrum of Cu_2O in the p-component obtained at $T = 4.2^\circ\text{K}$ for an angle of incidence of 72° . In Figs. 22b and c are shown the microphotograms of two other spectra of reflection of Cu_2O . The positions of the bands and their half-widths are given in the table. The whole collection of observed reflection lines can be divided into two groups—blue-green and blue, in each of which one clearly sees two lines. In the blue-green group on each of the photographs one can see a trace of a third line (cf. the microphotograms in Figs. 22b and c). Apparently these reflection lines form a blue-green hydrogen-like series of lines:

$$\text{blue-green series: } \nu_n = 21\,220 - \frac{368}{n^2} (\text{cm}^{-1}), \quad n = 1, 2, \dots;$$

where n is the quantum number and $\bar{\nu}_n$ the wave number.

Because of the great similarity of the blue-green and blue groups of lines, there is reason to assume that the two lines of the blue group are also the first terms in a hydrogen-like series of lines:*

$$\text{blue series: } \nu_n = 22\,302 - \frac{415}{n^2} (\text{cm}^{-1}), \quad n = 1, 2, \dots$$

One striking point is that the differences in wave numbers between the lines with the same n in the blue and blue-green series, as well as between their limits, $\nu_b - \nu_{b.g.} = 1055 \text{ cm}^{-1}$, within the limits of accuracy of the experiments agree well with the difference in wave numbers between the limits of the green and yellow exciton series of Cu_2O : $\nu_g - \nu_y = 1064 \text{ cm}^{-1}$.† Furthermore it should be pointed out that the lines of the blue series are considerably broader than those of the blue-green series. Possibly this results from a reduction in the lifetimes of these excitons as a result of autoionization into the conduction band.

From the fact that we can observe fairly strong reflection lines in the blue-green and blue regions of the spectrum, we can draw the conclusion that these lines must be very intense in absorption. Their absorption coefficients should be considerably greater than for

*In the microphotogram of Fig. 22b and c one can see a crude indication of a third line of this group.

†For the first line this was already pointed out by Pastrnyak.^[95]

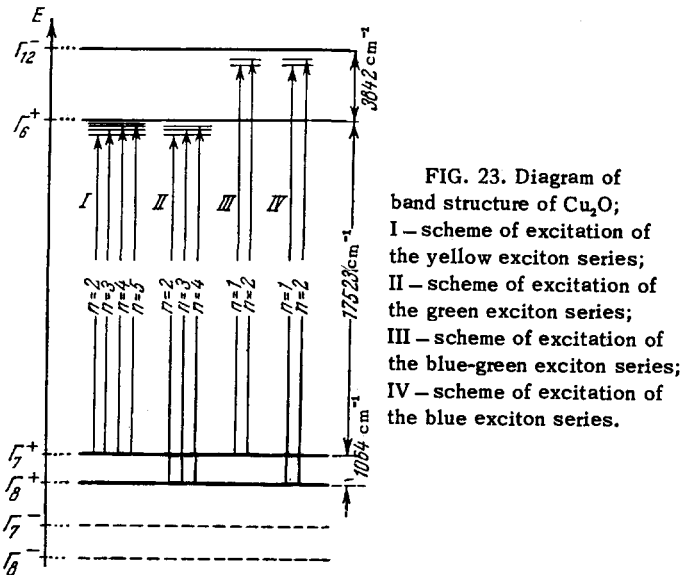


FIG. 23. Diagram of band structure of Cu₂O; I – scheme of excitation of the yellow exciton series; II – scheme of excitation of the green exciton series; III – scheme of excitation of the blue-green exciton series; IV – scheme of excitation of the blue exciton series.

the green and yellow series which, as we know, are not observed in reflection. In fact, in the blue-green and blue regions there are observed^[96] absorption lines whose positions are shifted relative to the reflection lines because of deformation of the Cu₂O plates as a result of their being glued to the backing. Furthermore, the extreme sensitivity of the blue-green and blue reflection lines to surface defects of the crystal indicates that these reflection lines are associated with properties of a perfect lattice and not with a disturbed crystal lattice. Therefore we feel that the existence of these intense lines can be explained only through excitons.

Let us compare our experimental data with the band structure model of Zhilich^[93] and Elliott^[80,97] for crystals of the copper oxide type. In Fig. 23 is shown a possible diagram of excitations of excitons. On the left in Fig. 23 are shown the positions of the energy levels of the parts of the valence sub-bands (Γ_7^+ , Γ_8^+ , Γ_7^- , Γ_8^-) and the conduction sub-bands* (Γ_6^+ , Γ_{12}^+). As a result of transitions of electrons from the valence sub-bands Γ_7^+ and Γ_8^+ to the corresponding exciton levels in the lowest-lying conduction sub-band Γ_6^+ , excitons of the yellow and green series are formed and when there are transitions of electrons from the valence sub-bands Γ_7^+ and Γ_8^+ to the corresponding exciton levels in the upper sub-bands of the conduction band Γ_{12}^+ , excitons of the blue-green and blue series are formed.

In a paper on the symmetry of excitons in Cu₂O, Elliott,^[97] starting from a picture which is somewhat different from that of Zhilich, gives a diagram of the band structure of the copper oxide crystal which is similar to Zhilich's scheme. The blue-green and

*As is shown by an analysis of the investigations of Kaplyanskiĭ, Agekyan, and the author concerning the influence of oriented elastic deformations on the first terms of the blue-green and blue series of Cu₂O, the upper conduction sub-band must have the symmetry Γ_{12}^+ .

blue series observed by us also fit readily into Elliott's scheme.*

The formation of excitons in the blue-green and blue regions of the spectrum can also be explained differently, as excitation of electrons from the lower valence sub-bands Γ_7^- and Γ_8^- to the corresponding exciton levels of the conduction sub-band Γ_6^+ . However, on the basis of the experimental facts cited above we regard the first diagram of excitation of excitons (shown in Fig. 23) as more probable.

A point of interest is that the Rydberg constants for the blue-green and blue series are less by a factor of two than the constants for the yellow and green series. This shows that the effective masses of electrons in the upper (Γ_{12}^+) and lower (Γ_6^+) exciton bands are different, and apparently less in the upper bands.

From these studies of Cu₂O it follows that exciton lines in a spectrum can be located not only on the long-wave side of the absorption edge (exciton levels in the forbidden bands below the conduction band), but also down deep in the continuous spectrum of the fundamental absorption of crystals (exciton levels near other upper conduction bands). The location of discrete exciton spectra depends on the relative position of the complex bands in the energy structure of the crystal. Optical studies of overlapping complex bands giving a continuous absorption spectrum would be an extremely difficult, if not a hopeless problem. The exciton line spectra associated with such bands, because of their discreteness, as we have seen in the example of Cu₂O, open great possibilities for spectroscopic study of the energy structure of crystals in the case of complex overlapping bands.

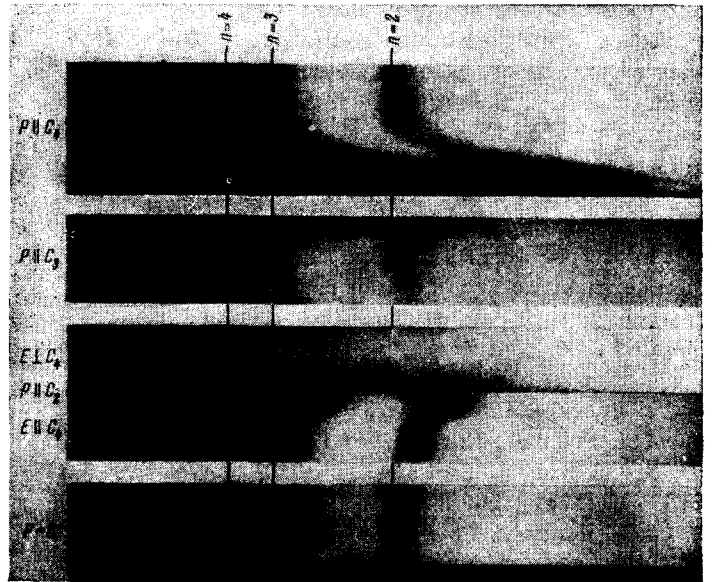
XII. EFFECT OF ORIENTED UNIAXIAL ELASTIC DEFORMATIONS ON EXCITON LEVELS OF CRYSTALS

A delicate method for studying exciton states is the study of directed elastic deformations in crystals, which has been developed in our laboratory by A. A. Kaplyanskiĭ. This method can give information concerning the symmetry of exciton states and the degree of their degeneracy. The degeneracy of different kinds of energy states in crystals is either completely or partially lifted when one applies an oriented elastic deformation. The effect of oriented elastic deformation is very clearly observed in the spectrum of excitons in copper oxide.

According to the theoretical studies of Elliott^[97] and Zhilich, an exciton state corresponding to the first term of the yellow series of the exciton $n = 1$, has the symmetry type Γ_{25}^+ and is threefold degenerate. This prediction of the theory is confirmed in the experiments of Kaplyanskiĭ and the author^[96] on the influ-

*The author is very grateful to Professor Elliott for acquainting him with this work before publication.

FIG. 24. Influence of uniaxially directed deformation P on terms $n = 2, 3, 4$ of the yellow exciton series. Direction of observation L coincides with direction of compression ($L \parallel P$) along fourth-, third-, and second-order axes (C_4, C_3 and C_2). Complete polarization of the series for $P \parallel C_2$ and $E \parallel C_4$. Disappearance of the series for $P \parallel C_2$ and $E \perp C_4$.



ence of directed elastic deformations on the $n = 1$ line in the Cu_2O spectrum.

The observations of absorption spectra of single crystals of Cu_2O , subjected to uniaxial compression at $T = 77^\circ\text{K}$, were carried out in a direction L perpendicular to the compression axis P ($L \perp P$). It was shown that for uniaxial compression of the crystals both steps and the line $n = 1$ show a splitting as a result of polarization. The picture of the splitting depends on the direction of compression relative to the symmetry axes of different order (C_4, C_3, C_2) of the crystal (Fig. 20). The two jumps, whose behavior in deformation is completely similar, are split for $P \parallel C_4$ and $P \parallel C_3$ into two jumps each, while for $P \parallel C_2$ they are split into three jumps each. The magnitude of the splitting is linearly dependent on the strength of the unidirectional compression for all directions of compression and amounts, for example, for $P \parallel C_4$, to approximately 1 \AA per kg/mm^2 . Observation in polarized light ($E \parallel P$ and $E \perp P$) showed that the split jump edges are markedly polarized, while for $P \parallel C_2$ the picture depends on the direction of observation. The multiplicity and the magnitude of the splitting of the $n = 1$ line are the same as the splitting of the steps, but the polarization of the components of the split line, whose absorption has quadrupole character and is anisotropic in the free crystal^[75] (cf. above) is more complex than for the steps. As an illustration, in Fig. 20 we show spectrograms of absorption of uniaxially stressed crystals of Cu_2O with $P \parallel C_4$, $P \parallel C_3$, and $P \parallel C_2$. In the spectrograms one sees the multiplicity of the splitting of the second step ($\lambda 6085 \text{ \AA}$) and the line $n = 1$ ($\lambda 6125 \text{ \AA}$) and their polarization for the case of $P \parallel C_2$.

The largest multiplicity of splitting of both the line $n = 1$ and of the step edges, as obtained in experiment, is three, in complete agreement with the results of the

theoretical study and the results of experimental investigations of the Zeeman effect of these lines^[32] (cf. above). The nature of the splitting of the step edges is in good agreement with the notions of Elliott^[97] concerning the origins of the steps as a result of indirect transitions to the first exciton $1s$ level.

The influence of uniaxial deformation on the higher terms of the yellow series ($n = 2, 3, 4$) has as yet been observed only qualitatively^[98] and only for observation along the direction of compression ($L \parallel P$), by compressing thin plates of Cu_2O between transparent quartz plates. It was established (Fig. 24) that with $P \parallel C_4$ and $P \parallel C_3$ there is a shift of the series toward the long-wave end of the spectrum. For $P \parallel C_2$, in addition to this long-wave shift of the series there is also an interesting polarization effect. Almost complete polarization of the series lines occurs so that in the series one observes only the component with vibrations $E \parallel C_4$ (in the plane of the rhombododecahedron). In the perpendicular direction the series disappears from the spectrum. For the lines of the series $n \geq 2$ we observed no splitting on deformation. These experimental results have still not received a satisfactory explanation.

The phenomena described above show that the study of the influence of oriented deformations on the optical spectra of crystals provides us with a new and very effective method for studying symmetry and degree of degeneracy of exciton states. It seems to the author that this method for studying energy states of solids is as effective as that using Zeeman and Stark effects. One may imagine that the development of this method and the further building up of the theory could give vital information concerning the structure, symmetry, and degeneracy of the crystal bands.

From all that we have said one can see how fruitful has been the idea of J. I. Frenkel concerning the ex-

citon. One can now scarcely doubt the reality of the existence of excitons in crystal lattices. The exciton does exist, and its optical spectrum is the spectrum of an excitation moving through the crystal. Exciton spectra give to the spectroscopy of solids wide possibilities for studying physical phenomena in solids, and they now form a whole branch of the physics of solids. One may hope that with the discovery of exciton spectra, spectroscopy of solids may give for the study of the energy structure of solids just what atomic spectroscopy gave for the study of the structure of the isolated free atom.*

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*The limited size of this paper allowed us only to present very briefly some of the questions arising in the study of excitons. The author has restricted himself principally to investigations in his own laboratory.

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