

**THE PROBLEM OF THE DEFECTS IN THE PROCESS OF EXCITON
LUMINESCENCE OF MOLECULAR CRYSTALS**

V. M. AGRANOVICH

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IN the interpretation of experimental data on the luminescence spectra of crystals, the concept of the exciton is being used more and more often; this concept was first introduced by Ya. I. Frenkel¹ and has subsequently been developed in the papers of many authors.²

In these studies, the fundamental problem has been the search for the lowest elementary excitation states corresponding to the Hamiltonian of the electrons and nuclei of the crystal. However, in writing out this Hamiltonian, we ordinarily do not take into account the retardation interaction between the electrons of the crystal. Such a treatment is equivalent to the description of the electric interaction between charges in terms of Coulomb forces. Since actually the forces between the charges do not act instantaneously, but propagate with the finite velocity of light, the results of a theory taking into account only an instantaneous Coulomb interaction are only approximate.

The neglect of the interaction of the electrons with the field of virtual transverse photons, the exchange of which creates the retardation interaction between the charges, leads to a situation in which the lowest elementary excitation states in the crystal turn out to be the excitons and the transverse photons.

At low values of the quasi-momentum q , the energy $E(q)$ of an exciton may be written as follows:

$$E_{\text{exc}}(q) = E_0 \left(\frac{q}{|q|} \right) + \alpha_i \left(\frac{q}{|q|} \right) q_i + \beta_{ik} \left(\frac{q}{|q|} \right) q_i q_k + \dots \quad (1)$$

[we note that the terms linear in q_i may be present in Eq. (1) only in crystals showing natural optical activity].

Since the spectrum of the transverse photons is determined by the expression

$$E_{\text{phot}}(q) = \hbar |q| c, \quad (2)$$

where c is the velocity of light in vacuum, the energy branches of excitons and transverse photons in quasi-momentum space intersect. Then, taking into account even the weak interaction of the electrons with the transverse photons leads to a substantial change in the form of the spectra of the elementary excitations in the long-wave region. Thus, for example, in cubic crystals (see Fig. 1), the transverse exciton waves (retardation being neglected) "mix" with the radiation (light) waves, just as the transverse vibrations of an ionic lattice do. Thus the observed optical waves are formed.

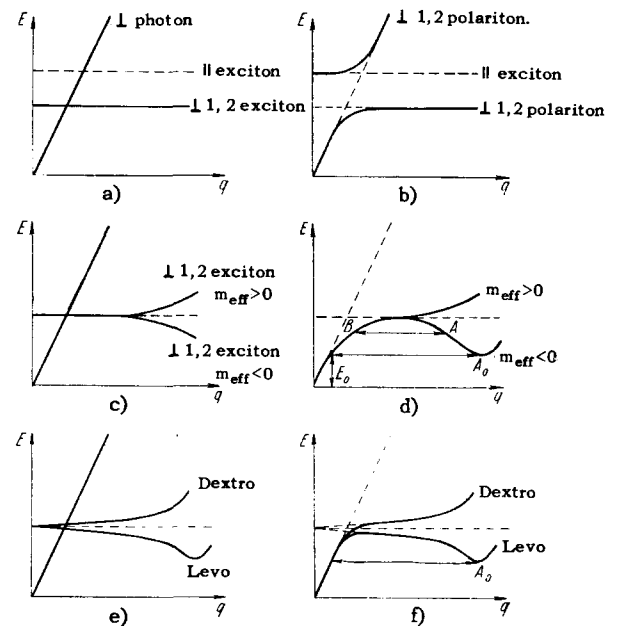


FIG. 1. The energy dispersion of elementary excitation states in crystals of cubic symmetry. a) Relation of the energies to elementary excitation states neglecting retardation and spatial dispersion; b) The same, but with retardation taken into account; c) Relation of the energies of elementary excitation states, neglecting retardation, but taking spatial dispersion into account; d) The same, but taking retardation into account. Figures 1a, b, c, and d correspond to optically-inactive cubic crystals. The symbols \parallel and \perp indicate longitudinal and transverse polarization of the excitons. Taking retardation into account has no effect on longitudinal excitons. e) Relation of the energies of elementary excitations in an optically-active crystal of cubic symmetry neglecting retardation, but taking into account spatial dispersion; f) The same, but taking retardation into account.

The situation described above is well known, and has been carefully studied in the classical theory of dispersion of light in crystals developed by M. Born and his students.³ It was shown in the papers of the cited authors that the ordinary electrostatic method is not suitable for calculating the frequencies of those transverse oscillations which possess a dipole moment, and whose phase velocity is greater than that of light in the medium. This conclusion, as applied to electronic excitations, implies that it may be essential to take retardation into account in the case of excitons corresponding to long wavelengths. As is known, it is these long-wave excitons which are responsible for the optical properties of crystals (see reference 2).

Fano⁴ was the first to take into account systematically, within the framework of the quantum theory, the effect of the interaction of elementary excitation states of the exciton type with the transverse photons. Thus, without bringing in the macroscopic Maxwell equations, he derived an expression for the refractive index in isotropic media. In Fano's study, the method of Tomonaga⁵ was used for separating the collective exciton-photon degrees of freedom.

In reference 6, in which the mathematical framework is taken from the paper of Fano, an analogous problem is solved for cubic crystals with one molecule in the unit cell. The suggestion was made in this paper to designate as "polaritons" the elementary excitation states which exist as "mixtures" of excitons and transverse photons, and which appear when the retardation interaction is taken into account in the zero-order approximation.

In reference 7, the author has discussed the elementary excitation states, taking into account retardation and the dispersion of light in optically inactive crystals of arbitrary symmetry.* In distinction from references 4 and 6 mentioned above, reference 7 used the method of considering the Hamiltonian in the form of a second quantization, as developed by Bogolyubov and Tyablikov (see reference 8).

We must note that the general formulas for the dispersion of light in molecular crystals derived in reference 7 may be reconciled with the results of the earlier reference of Pekar,¹⁰ who used a semi-classical method.

In connection with the problems touched upon above, we shall consider the situation occurring in the theory of light absorption in crystals.

In the language of polaritons, the process of light absorption in a crystal consists in the following. A monochromatic light wave impinging on the crystal from outside excites polaritons in the crystal. The magnitude of the quasi-momentum of the polaritons is determined by the condition $\hbar\omega = E_{\text{pol}}(\mathbf{q})$, where ω is the frequency of the impinging light. Since thus the energy in the crystal is transmitted by polaritons, the observed attenuation of the light on passing through the crystal is due to the interaction of the polaritons with the lattice vibrations.¹¹ In the one-phonon approximation, this interaction is determined by the following law of conservation of energy and quasi-momentum:

$$\hbar\omega = E_{\text{pol}}(\mathbf{q} \pm \mathbf{k}) \mp \varepsilon(\mathbf{k} + \mathbf{b}), \quad (3)$$

where \mathbf{q} is the quasi-momentum of the polariton before collision with the phonon, \mathbf{k} is the quasi-momentum of the phonon, $\varepsilon(\mathbf{k})$ is the energy of the phonon, and \mathbf{b} is an integral reciprocal-lattice vector. In

calculations of the light absorption in a crystal in which retardation is not taken into account in calculating the energies of the elementary excitation states, the expression analogous to Eq. (3) has the following form:

$$\hbar\omega = E_{\text{exc}}(\mathbf{Q} \pm \mathbf{k}) \mp \varepsilon(\mathbf{k} + \mathbf{b}), \quad (4)$$

where \mathbf{Q} is the quasi-momentum of the transverse photon ($|\mathbf{Q}| = \omega/c$).

Hence, when Eq. (3) is used, the absorption coefficient turns out to be somewhat different from the value obtained from Eq. (4). This difference becomes the more significant, the greater the oscillator strength of the transition characterizing the force of interaction between the electrons and the transverse photons.

Thus, for example, the use of Eq. (3) with either sign for the effective mass of the exciton leads, even at low temperatures, to the appearance of absorption in a frequency interval of width of the order of ω_0 . This interval is situated below the limiting frequency $E_{\text{exc}}(0)/\hbar$ [ω_0 is the dispersion frequency entering into the dispersion relation $n^2(\omega) = 1 - \omega_0^2 / (E_{\text{exc}}^2(0)/\hbar^2 - \omega^2)$]. This low-frequency absorption [$\omega \leq E_{\text{exc}}(0)/\hbar$], which in certain cases may be highly polarized, is due entirely to the taking into account of retardation. The reason for this is that only in this case are the elementary excitation states in the crystal with energy $< E_{\text{exc}}(0)$ anything but pure transverse photons. Here they are, rather, a "mixture" of excitons and transverse photons, and thus able to interact directly with the lattice vibrations (see Fig. 1).

We note that the effect indicated above may be essential in determining the form of the long-wave edge of exciton absorption bands which correspond to large oscillator strengths. In this case, we must introduce some necessary corrections into the theory of long-wave exciton absorption neglecting retardation.¹²

We shall proceed now to our fundamental theme, the study of possible mechanisms of exciton luminescence of molecular crystals. Along the way, we shall attempt to elucidate where and to what degree effects associated with the consideration of retardation might be substantial.

Without taking into account retardation, which leads to the "mixing" of excitons and transverse photons, the appearance of exciton luminescence in a molecular crystal may be represented as follows.

Under the action of a transverse photon impinging on the crystal from outside, an exciton may be generated. Because of the conservation laws, the exciton will have an energy and quasi-momentum equal, respectively, to those of the photon.* The exciton which appears may in turn be transformed into a transverse photon, etc.

*The results of this paper were subsequently generalized to the case of optically active crystals, and as a result a dispersion formula was derived for the rotation of the plane of polarization.

*For the sake of simplicity, possible processes of change in the energy of the photon will not be considered.

Such a process of successive transformation of a photon into an exciton and back without loss of energy and quasi-momentum to the lattice generates an ordinary optical wave in the medium (a long-wave polariton). This wave is described by the macroscopic Maxwell equations, with the laws of refraction and reflection of light etc., resulting from these equations.

If, however, the exciton is able to exchange its energy or quasi-momentum due to interaction with the crystal lattice before it transforms into a transverse photon, then, even if a transverse photon appears later, the conditions for coherence of this photon with impinging photons will be violated. In such a case, a process takes place which is experimentally manifested as an absorption of light in the medium.

In an ideal crystal, the energy and quasi-momentum of excitons capable of transformation into transverse photons are determined, because of the conservation laws, by the point of intersection of the energy branches of excitons and transverse photons. Hence, for excitons which have already interacted with the lattice vibrations and have suffered a substantial change in their quasi-momentum,* transformation into transverse photons is no longer possible in the dipole approximation without further participation of the lattice vibrations. That is, exciton luminescence becomes impossible. This difficulty in exciton luminescence, which was pointed out by Davydov,¹³ and which was recently discussed in reference 14 in connection with new experimental data, becomes essential at low temperatures, and especially in cases in which the region of low quasi-momentum does not correspond to a stable minimum in the exciton energy.

In this case, as has already been pointed out,¹³ the occurrence of luminescence must be associated with violations of the ideal crystal structure, due to which the law of conservation of quasi-momentum may be violated. Thus the transformation of excitons into transverse photons becomes possible even in the case in which the quasi-momentum of the exciton does not lie on the "conservation" surface. However, we must note that defects in the crystal structure may play a double role here.

Above all, the presence of such defects leads in general to the appearance of local electronic excitation levels. At low defect concentrations, these levels may be represented relatively weakly in the absorption spectrum. However, they may play an essential role in luminescence, due to the possibility of transfer of energy of excitons to the electrons at the defect, with subsequent emission. Such a mechanism of luminescence with the participation of defects is com-

*In this case, we mean by "substantial change" of quasi-momentum a change such that the quasi-momentum of the exciton is outside the "conservation" surface in quasi-momentum space:

$$\hbar\mathbf{q}c = E_{\text{exc}}(\mathbf{q}).$$

pletely analogous to the mechanism occurring in impurity organoluminophores,¹⁵ in which absorption of light by the fundamental substance is followed by luminescence of the impurity. The existing experimental data on the spectra of molecular crystals at low temperatures¹⁴ give evidence that many crystals actually show weak long-wavelength absorption bands, which occur in resonance coincidence with the principal luminescence lines.*

The position, intensity, and polarization of these lines are subject to the influence of external factors.

Hence it is natural to seek an explanation for the origin of these lines in the assumption that these lines are due to transitions of electrons in defects in the crystal structure.

However, to create a basis for this viewpoint, we need careful polarization measurements of the absorption and luminescence spectra. Spectra due to local levels in general are determined by the symmetry in the vicinity of the defect, rather than by the space group of the crystal. Hence, the above explanation of the origin of the luminescence is hardly to be considered satisfactory in cases in which the absorption and luminescence of lines in resonance coincidence turn out to be strongly polarized along the crystallographic axes of the crystal (see, e.g., reference 17).

We shall give another curious example. In optically active crystals, Eq. (1) contains terms linear in q_1 . Hence, for example, in dextrorotatory crystals of cubic symmetry, the point $|\mathbf{q}| = 0$ corresponds to an energy maximum of an exciton for levo-polarized excitons ($E_{\text{lev}} = E_0 - |\gamma|q + \dots$) and a minimum for dextro-polarized excitons ($E_{\text{dex}} = E_0 + |\gamma|q + \dots$).

The "right-handed" and "left-handed" excitons which are generated by the light have quasi-momenta \mathbf{q} which are small in modulus ($|\mathbf{q}| \approx 0$). Hence, at low temperatures only the levo-polarized excitons can interact strongly with the lattice vibrations. The point $q = 0$ corresponds to a maximum in the energy of these excitons, and hence they are able to produce lattice phonons at the expense of their own energy, and thus change their quasi-momenta.

The dextro-polarized excitons, for which the point $q = 0$ corresponds to an energy minimum, cannot interact so readily with the lattice, since the necessary phonons are present at low temperatures in infinitesimally small amounts.

Thus, circular dichroism should be observed at low temperatures ("left-handed" light should be more strongly absorbed than "right-handed").

*Here and below, the spectra of so-called "pure" crystals will be discussed, i.e., crystals into which no special impurities have been introduced. Thus, we are not considering here an entire group of interesting phenomena appearing in the spectra of frozen solutions of organic compounds at low temperatures. These phenomena have been observed by É. V. Shpol'skiĭ and his associates (the "Shpol'skiĭ effect"). For further details, see reference 16.

However, exciton luminescence under these conditions should be difficult, since "left-handed" excitons "rolling" into the region of large q would leave the "conservation" surface. Then, without the interference of defects, they would no longer be able to give rise to luminescence. According to the above-mentioned mechanism for transitions at defects, the presence of defects may lead to luminescence lines which need not occur in resonance coincidence with the absorption lines. (These lines must correspond to lower frequencies.) On the other hand, as is known, Samoïlov,¹⁸ in observing the spectrum of the isotropic optically-active sodium uranyl acetate at low temperatures, found a resonance coincidence between the long-wave absorption lines and the principal luminescence lines. In addition, it turned out that these lines in the absorption spectrum are characterized by large circular dichroism, while in the luminescence spectrum these lines are completely circularly polarized. Here, just that component was emitted which was absorbed. The magnitude of the circular dichroism $\Gamma = (\kappa_+ - \kappa_-) \kappa$ in defect absorption* may be of the order of $2\pi l/\lambda$, where κ is the absorption coefficient of the light, l is the value of the dimensions of the defect, and λ is the wavelength of the light. Since Samoïlov observed a value $\Gamma \approx 1$, we arrive at the conclusion that his experiments cannot be explained on the basis of a mechanism of transitions of electrons at defects.

In connection with what has been stated above, it is of interest to discuss a mechanism of transformation of excitons into transverse photons at a defect without concomitant localization of the electronic excitation energy. It is especially convenient to carry out this discussion in the language of polaritons, since in this case the perturbing action of the defect is the only perturbing influence. The interaction between excitons and transverse photons with any binding strength is taken into account even in the zero-order approximation. The mechanism discussed here corresponds to an intra-band transition at constant energy (Fig. 1d). This process may become actual in the case in which the region of small quasi-momentum does not correspond to a stable minimum in the exciton energy, i.e., precisely when exciton luminescence is difficult.

Before proceeding to the results of the calculations, we shall make one remark. If we carry out an analysis of the energy of the polariton oscillations of the lower branch, we find the following. Outside the "conservation" surface, polaritons fundamentally possess "exciton" energy (i.e., energy of the movement of electrons). Hence, these polaritons may interact strongly with the lattice vibrations, since it is precisely the electrons, rather than the field,† which in-

teract directly with the nuclei in the lattice. For the electrons, processes of radiationless transformation of the energy of electronic ("exciton") excitation into heat are probable. On the contrary, for practically all polaritons having quasi-momenta lying within the "conservation" surface, the exciton part of the energy is small, while the energy of the field of the transverse photons predominates. Hence, these polaritons interact weakly with the lattice vibrations, and are able to reach the surface of the crystal and produce observable light.

Thus, from what has been said, it follows that the model of intra-band transitions presented above, (i.e., transitions in which a polariton with a quasi-momentum outside the "conservation" surface is transformed into a polariton with a quasi-momentum within the "conservation" surface) may lead to the transformation of electronic excitation energy into observable light.

If an equilibrium energy distribution of the polaritons is attained before emission takes place, the frequency of the luminescence line at low temperatures will be determined by the energy of a polariton at the minimum point (Fig. 1d, point A_0).

It is pertinent here to consider also the inverse process $B \rightarrow A$ (Fig. 1d). This process, due to the exciton character of polaritons outside the "conservation" surface, must lead to the appearance of absorption due to defects, but not associated with the excitation of local states. The probability of $B \rightarrow A$ transitions is proportional to the number of final polariton states per unit of energy. In cubic crystals, this quantity is proportional to the quantity $q^2 \frac{dq}{\alpha E_{pol}(q)} \Big|_{q=q(\omega)}$, where $q(\omega)$ is determined by the condition $\hbar\omega = E_{pol}(q)$. Here the value of q is taken to be outside the region of "conservation". Near the point A_0 , $E_{pol}(q) \approx E_0 + \alpha(q - q_0)^2$. Hence

$$\frac{dq}{dE} \sim \frac{1}{\sqrt{\hbar\omega - E_0}} \quad (\hbar\omega \gg E_0),$$

and thus the absorption has a maximum at $\hbar\omega = E_0$, in resonance coincidence with the luminescence line. Naturally, since in this case the absorption is proportional to the number of defects, it may be considerably weaker than the absorption associated with the excitation of polaritons near the "conservation" surface (ordinary exciton absorption).

Here it is pertinent to note that in the mechanism being discussed, the frequency E_0/\hbar , which corresponds to the absorption and luminescence in resonance coincidence, characterizes the position of the energy minimum of the exciton band, but is not connected with the structure of the defects.

In this sense, the absorption and luminescence occurring in resonance coincidence at the frequency E_0/\hbar may be designated as having exciton character,

*By analogy with the circular dichroism of optically-active molecules in solution (see, e.g., reference 19).

†This refers to the field of the radiation in the spectral region of the exciton absorption band.

in spite of the fact that their intensities, polarization, and position in the spectrum may be subject to the influence of external factors (the latter is due to the possible influence of internal stresses on the form of the exciton band).

In order to carry out numerical estimates of the probability of the transition $A \rightarrow B$ (Fig. 1d), we shall use the macroscopic model of long-wavelength polaritons discussed in reference 20. This paper generalizes the results of Huang²¹ to crystals of arbitrary symmetry, and permits us to take into account spatial dispersion.

This treatment, which has been carried out in conjunction with Yu. V. Konobeev, consists in the following. As in reference 21, a Hamiltonian is constructed corresponding to the associated equations of motion given in reference 20 for the vectors of the dipole moment per unit volume and the electric induction. Then with the aid of normal modes of vibration, the Hamiltonian is written in the form of a sum of Hamiltonians. Each of the latter is of the oscillator type, and corresponds to one of the possible types of polaritons. In a perfect crystal, the polaritons cannot transform into one another (the law of conservation of quasi-momentum). However, the presence of defects permits such transitions. For the sake of simplicity, the crystal is assumed in the calculations to be cubic and optically inactive. The form of defect was chosen to be a spherical cavity of radius l . The desired probability of transition of the polariton from state A to state B was determined with the use of the quantum theory of perturbations. The result was that this probability per second per single defect is expressed by the following formula:

$$W_1 = \frac{8\pi (E_{\text{exc}}^2(0) + \hbar^2 \omega_0^2)^{1/2}}{3\hbar^4 c^2 d^3 N} \left(\frac{\hbar^2 \omega_0^2}{E_{\text{exc}}^2(0)} \right) \left(\frac{\hbar^2 c^2 q_B^2}{E_{\text{exc}}^2(0)} \right) \left(\frac{\hbar^2 c^2 q_A^2}{\hbar^2 \omega^2} \right)^2 f^2(q_A l). \quad (5)$$

In this expression, the following symbols are used: N is the number of molecules in the total volume of the crystal, q_A is the quasi-momentum of a polariton in state A, q_B is the quasi-momentum of a polariton in state B; the function $f(x)$ is determined by the relation

$$f(x) = \frac{\sin x - x \cos x}{x^3}; \quad (6)$$

$\hbar\omega$ is the energy of a polariton in state A or B, and d is the lattice parameter of the crystal.

If we assume for a numerical estimate of W_1 that

$$\hbar^2 \omega_0^2 / E_{\text{exc}}^2(0) \approx 0.1, \quad l \approx 3d, \quad d = 5 \cdot 10^{-8} \text{ cm}, \quad E_{\text{exc}}(0) \approx 2.5 \text{ eV}, \\ q_A l = 0.75, \quad \hbar q_B c / E_{\text{exc}} \approx 1, \quad \hbar q_B c / \hbar \omega \gg 1,$$

we find that $W_1 \approx (1/N) 10^{12} \text{ sec}^{-1}$. If $q_A l = 0.6$, $W_1 \approx 2.5 (10^{12}/N) \text{ sec}^{-1}$, etc. The total probability of the process discussed here is equal to the product $W_1 n$, where n is the number of defects in the total volume of the crystal. In order that this process may take place within the lifetime of an exciton τ ($\tau \approx 10^{-8}$

sec), it is necessary that the concentration of defects be such that the inequality $W_1 n \lesssim 1/\tau$ be fulfilled. It follows from this inequality that the concentration of defects n/N must be of the order of $10^{-5} - 10^{-4}$ or greater.

The estimate thus carried out suffers from a certain arbitrariness, since such quantities as l and q_A are quite unknown. We shall therefore consider that

$$W_1 \approx \frac{1}{N} (10^{10} - 10^{13}) \frac{1}{\text{sec}}.$$

We note that the probability of the transition $B \rightarrow A$ is at least $q_A^2/q_B^2 \approx 10^3$ times larger (if $q_A \approx 1/4 d$) than that of the process $A \rightarrow B$, due to the greater density of the final states.

The process discussed above of the transformation of exciton energy into light at a defect, without a stage corresponding to the localization of the exciton energy at the defect, competes with the process of capture of the exciton by a local level, when such exists in association with the existence of the defect.

In order to estimate the role of both mechanisms, we must make a quantitative comparison of the probability value W_1 calculated above with the probability of capture of an exciton by the defect at low temperatures.

In order to estimate this probability, we may attempt to use data on the probability W_2 of exciton capture, for example, by impurity molecules in anthracene. Thus, a calculation from experiments on the luminescence of anthracene containing naphthalene as an impurity at room temperature²² leads to a value of $W_2 \approx (10^{13}/N) \text{ sec}^{-1}$. This value agrees with theoretical estimates.²³ However, these estimates were carried out for room temperature. For temperatures of the order of 20° K , the value found in references 22 and 23 must be decreased, according to reference 23, by the factor $\sim e^{-U/kT}$, where U is the energy interval from the bottom of the exciton band $E_{\text{exc}}(0)$ to the local level. If we consider that the luminescence and absorption lines in resonance coincidence in anthracene (see reference 17) are due to the excitation of local levels, then the value of U must be at least $\geq 100 \text{ cm}^{-1}$.* This fact decreases the value of W_2 found in reference 22 by a factor of approximately 10^4 .†

Thus, the estimates carried out for anthracene favor the model studied above for transitions $A \rightarrow B$ (Fig. 1). We note that this model naturally explains the experiments of Samoilov,¹⁸ which were performed

*If the quantity U is defined experimentally as the distance from the levels in resonance coincidence to the band of strong absorption in anthracene, then the value of U assumed above must be increased several-fold.

†It was found in reference 24 that the intense transfer of energy from anthracene to tetracene at room temperature practically disappears at $T = 4^\circ \text{ K}$.

on the optically-active crystal sodium uranyl acetate. In Figs. 1e and 1f, the approximate shapes of the exciton and polariton bands in such a crystal are shown, the crystal being dextrorotatory. Anomalous circular dichroism appears in this case, due to the fact that there is no possibility of transitions of the type $B \rightarrow A$ for dextro-polarized polaritons with energy $E < E_{\text{exc}}(0)$. Hence, only the levo-polarized component can be absorbed in this case.

We must note that, in addition to the transitions of the type $A \rightarrow B$, transitions of the type $A \rightarrow B_1$ are also possible, where the point B_1 corresponds to the same energy as B , but to a different polarization. These transitions turn out to be possible, due to the fact that the directions of the quasi-momenta at the points A and B_1 need not be identical.

Transitions of the type $A \rightarrow B_1$ may lead to a certain depolarization of the long-wavelength absorption and luminescence in resonance coincidence which were discussed above.

It is probable that in some crystals, there may exist groups of luminescence lines appearing both as a result of localization of electronic excitation energy at defects, and without such localization. In this regard, we note that the kinetics of the emission of these lines must differ in the cases of different mechanisms.

In fact, the lines corresponding to transitions at defects are thus due to a two-stage mechanism, and need not in general show an exponential decay law. On the other hand, the mechanism of exciton luminescence unassociated with the localization of energy at the defects must lead to an exponential decay of the luminescence.

In conclusion, we shall make a remark with regard to the possible role of triplet states in the exciton luminescence of molecular crystals.

Because of the exchange interaction between electrons belonging to different molecules, a triplet state is able to move through the crystal, and may in principle give rise to a band of "triplet" excitons. However, the width of this band will be infinitesimally small in comparison with the width of the band of "singlet" excitons.

This fact is due both to the smallness of the overlap integrals of the wave functions of neighboring molecules and to the fact that the smallness of these overlap integrals will result in the localization of the triplet excitation in a molecule for a sufficient period of time to produce a local lattice deformation.

Hence, we shall consider the triplet state in a crystal to be a state in which one of the molecules is in the triplet state, together with a local lattice deformation.

In the excitation of luminescence, a certain fraction of the molecules goes over from the singlet excited state into the triplet state.^{25,26,27}

Then, owing to the long lifetime of triplet states, an appreciable fraction of the molecules in the crystal

may be in the triplet state during steady-state irradiation (this refers, of course, to the superficial layer of the crystal where the absorption of light fundamentally takes place). In this regard, we recall, for example, that in reference 28 when an exciting illumination of high intensity was used, about 80% of all the molecules were excited to the triplet state, etc.

In the study of luminescence spectra at low temperatures, the intensity of the exciting light may not be very large. Thus the number of molecules occurring in the triplet state may also not be very large. Nevertheless, this possibility must not be ignored. The point is that a long-lived molecule in the triplet state will show an effect on "singlet" excitons similar to that shown on these excitons by a defect in the crystal structure.

First, there may appear in the neighborhood of the triplet-state molecule a local singlet level in which an exciton may generally be captured, with subsequent quenching or emission.

Second, an exciton for which luminescence is forbidden by the selection rule for the wave vector may be scattered by such a defect, and then be able to transform into light without localization at the defect (the mechanism discussed above).

In order that triplet states may play an appreciable role, they must have a concentration of the order of $10^{-5} - 10^{-4}$ or greater, at least in the superficial layer.

The intensity of luminescence lines corresponding to processes occurring in the interaction of "singlet" excitons with defects produced by the presence of triplet-state molecules must be proportional to the square of the intensity of the exciting light. This condition is due to the fact that not only the number of singlet excitons, but also the number of triplet molecules is proportional to the intensity of the exciting light.

On the other hand, the intensity of luminescence lines due to the interaction of excitons with defects existing prior to irradiation is proportional to the first power of the intensity of the exciting light. Hence, a study of the dependence of the intensity of particular luminescence lines of a molecular crystal on the intensity of the exciting light may permit us to elucidate the possible role of triplet states in the exciton luminescence of molecular crystals. Of course, before we search for such effects, we must make a more precise estimation of the possible concentration of triplet-state molecules in each concrete case.

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Translator's Comments – This paper gives some new information on the subject of chemiluminescence of chlorophyll, which has been discussed at length in a recent collected volume of papers from a conference on photosynthesis held in the U. S.¹ The particular contribution of this paper is that of demonstrating the existence of chemiluminescence under *in vitro* conditions in systems simpler than the *in vivo* chemiluminescence of leaves, etc., but showing considerable analogy to the *in vivo* systems. The demonstration of chemiluminescence during the reoxidation of photoreduced chlorophyll was an especially clear example of the phenomenon. Chemiluminescence of chlorophyll in various forms after irradiation in the presence of oxygen is apparently related, but the mechanism in this case may not be as simple as would be indicated by its designation as photooxidation of chlorophyll. Unfortunately, the spectrum of the chemiluminescence could not be measured, but only its position roughly estimated by experiments with light filters. Nevertheless, the described experiments show promise in providing simple model systems in which the chemiluminescence of chlorophyll and its relation to photosynthesis may be studied.

¹Research in Photosynthesis, ed. H. Gaffron, Interscience, New York, (1957).

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