SOME PROBLEMS OF CRYSTAL LUMINESCENCE

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1. INTRODUCTION

THE investigation of nonequilibrium states resulting from the absorption of light by nonmetallic crystals enables us to determine a number of crystal properties and characteristics and, particularly, the structure of their energy spectrum. The study of luminescence is one of the most important means of such investigations. The present article is concerned with those aspects of luminescence that are intimately associated with the exciton mechanism of crystal excitation.

The concept of an exciton as an excitation wave was first introduced by Frenkel[1] to describe the excited states of crystals that do not exhibit photoconductivity. Different exciton models are used for different kinds of crystals. In molecular crystals the exciton wave is usually pictured as an excitation of individual molecules moving in the form of a wave along the crystal (the Frenkel' exciton). In the case of ionic crystals and semiconductors we usually think either of an exciton with small radius, in which an electron excited at some lattice site remains within the first configuration sphere, or an exciton of large radius, in which an electron and hole move as two quasi-particles bound by Coulomb forces and forming a "quasi-hydrogen atom" with a radius that considerably exceeds the lattice constant (the Wannier-Mott exciton).

Luminous energy absorbed by a crystal undergoes a number of transformations involving a series of electron transitions that lead to luminescence, the photoelectric effect, changed populations of impurity levels, etc. The accompanying transport of energy through the crystal can be detected by investigating sensitized luminescence, photoconductivity etc. Photoexcitation energy is transported in a crystal mainly through the motion of excitons and the diffusion of hole-electron pairs. Since the forbidden band of molecular crystals is wide, and fundamental visible and near ultraviolet absorption produces excitons, the transfer of energy (neglecting the reabsorption of luminescence) in such crystals is conducted almost entirely by excitons.* On the other hand, in many semiconductors such as Ge, InSb, etc., energy is transported mainly by hole-electron pairs.

Study of the absorption and luminescence spectra of molecular crystals reveals a number of coincident bands and lines. Such coincidences have served as a criterion for determining the positions of pure electronic transitions associated in such spectra with molecular vibrations in the ground and excited states. These spectral properties as well as the fact that the low-temperature luminescence spectrum directly adjoins the long-wave absorption edge was interpreted as a proof of a direct relationship between fundamental absorption and luminescence in crystals. Since fundamental absorption in molecular crystals is associated with exciton production it was postulated that luminescence results from the same mechanism and that luminescence frequencies represent transitions from exciton levels. This will hereinafter be called exciton luminescence. Attempts have also been made to interpret luminescence in certain semiconductor crystals by associating it directly with the annihilation of excitons.[4,5]

It will be shown below that a thorough review of experimental data, together with a theoretical examination of the possible luminescence spectrum properties, furnishes proof that the luminescence which was previously interpreted as exciton-type is actually caused by emission from structural defects and impurities. Excitons play a part here by transferring excitation energy from the host lattice to these other centers.

The present article is not intended as a complete discussion of luminescence but only treats a few aspects of its complex nature, especially the role of excitons in the mechanism of luminescence. We shall not consider such important processes as the buildup and decay of luminescence or other interesting questions which have recently been discussed in a review article by V. L. Levshin.[6]

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*The photoconductivity first observed in 1910[2] in the case of anthracene and later in a number of other molecular crystals is very weak and results from impurities or surface levels.[3]

TABLE I

Crystal	Longest-wave strong fundamental absorption bands			
	Strongly polarized		Weakly polarized	
	ν (cm⁻¹)	λ (A)	ν (cm⁻¹)	λ (A)
Benzene[11]	37803 (∥ c) 37839 (∥ a) 37847 (∥ b)	2644.5 2642.0 2641.4	38351 38360	2606.7 2606.1
Naphthalene[12,55]	31476 (∥ a) 31580—676 (∥ b)	3176.1 3160.6	31960	3128.0
Anthracene[13]	25210 (∥ b)	3965.5	25380 25730	3939.0 3885.4
Naphthacene[14]	19390 (∥ b) 19920 (⊥ b)	5155.8 5018.7	—	—
Hexamethylbenzene[15]	35157 (⊥ b)	2843.5	35535 35690	2813.3 2801.1
Hexaethylbenzene[16]	35309 (∥ Nm)	2831.3	35650	2804.2
ψ-isocyanine[17]	17456 (parallel to polymer axis)	5727	18800	5317

It has been shown by a large body of experimental data that, as a rule. the luminescence spectrum of crystals excited in the fundamental absorption region is independent of the exciting wavelength.[7,8] From this it can be inferred that in an excited state a quasi-equilibrium distribution is established among energy levels of the host crystal. Also, in an ideal crystal at low temperatures, the luminescence spectrum will thus begin with the band corresponding to a pure electronic transition from the lowest excited state.*

The establishment of a quasi-equilibrium distribution during an excited state ($10^{-7} - 10^{-8}$ sec) can be understood by taking into account that this is aided by: (1) small separations of excited electronic levels compared with the separation between the first excited level and the ground level, (2) lattice perturbations resulting from highly excited states, (3) the partial intramolecular deactivation of excitation energy in crystals composed of monatomic molecules. These factors also account for the high rate of nonradiative transitions associated with the conversion of electron energy into phonon energy. Emission from the lowest excited state also to a certain extent furthers strong reabsorption of luminescence at shorter wavelengths. However, the theory in which reabsorption is a decisive factor[9] encounters a number of serious difficulties.[10]

The present article will discuss primarily low-temperature luminescence with a quasi-equilibrium distribution between excited levels of the host lattice. We shall not be concerned further with the details of the mechanism whereby the quasi-equilibrium distribution is established.

It should be noted that only an approximately quasi-equilibrium distribution is physically meaningful; the extent of the departure from quasi-equilibrium depends on a number of factors determining the rate of relaxation processes. Under certain favorable conditions this deviation can in principle be quite large. At the conclusion of this article we shall briefly discuss the factors which can disturb quasi-equilibrium.

2. LUMINESCENCE OF IDEAL CRYSTALS

Ideal crystals contain no impurities or defects and therefore possess regular translational symmetry. Experimental studies (Table I) show that the lowest fundamental excited states detected in the absorption spectrum of molecular crystals are usually states of free excitons. Evidence for this is provided by the strong polarization of the first fundamental absorption bands, which, according to the theory of Davydov,[18] indicates that these bands are associated with the production of free excitons.

We shall begin with a discussion of optical transions, in which phonons do not participate. It follows from translational symmetry that the only allowed transitions are those in which the exciton wave vector **k** is equal to the light wave vector **q**.

*We shall not here consider properties associated with triplet states and phosphorescence in particular.

Since for visible and ultraviolet light q is considerably smaller than the reciprocal lattice constant the point $k = q$ is very close to the center of the Brillouin zone. Because of the selection rule $k = q$ the position of the point $k = 0$ in the exciton band and especially the structure of the band about this point have a decisive effect on the luminescence spectrum. A theoretical analysis shows that the exciton band possesses a complicated structure and that the point $k = 0$ can be either an extremal or a saddle point of the surface E (k). Finally, the point $k = 0$ can be located at the junction of a few exciton bands with complicated non-analytic dispersion E (k). When an optical transition is allowed for extremely long waves, in a number of instances E (k) becomes discontinuous at this point.[19,20] Calculations of exciton bands in crystals with different symmetries have not yet been made, so that we have no reliable information concerning the energy position of the point $k = 0$ or the dispersion law in its vicinity. However, a number of considerations indicate that, as a rule, the bottom of the band is located at $k \neq 0$.

In quasi-equilibrium the excited state possesses excitons with different values of k belonging to all exciton bands of the crystal. Since kT is small at low temperatures (at 4°K, $kT \cong 3$ cm^{-1}) the great majority of excitons will be close to the bottom of the lowest exciton band. This nonuniform filling of exciton band states has an important effect on the luminescence spectrum.

Let the bottom of the lowest exciton band represent a state with $k \neq 0$, while states with $k = 0$ in this and other exciton bands are higher with separations that considerably exceed kT. The concentration of excitons with $k = 0$ is then small, so that luminescence without phonon participation is considerably attenuated. When these transitions still appear in the spectrum the corresponding bands will naturally be strongly polarized, but the intensity ratios of the components will differ from those in the absorption spectrum due to different populations of levels with $k = 0$ in different exciton bands.

We shall now consider indirect transitions participated in by phonons which are assumed to be weakly coupled to excitons, as is evidently the case in many crystals.[21,22] The quantum-mechanical probabilities of indirect optical transitions are then considerably smaller than the probabilities of direct transitions not involving phonons. However, due to the small populations of states with $k = 0$ (when $k \neq 0$ at the bottom of the band), at low temperatures the luminescence intensities of indirect transitions from the bottom of the ex-

citon band may be comparable with those of direct transitions and may even be several times greater than the latter. As a result the luminescence spectrum associated with a certain group of exciton bands will lose its similarity with the corresponding absorption spectrum.[23] This is shown first of all by the disappearance or extreme attenuation of luminescence bands which coincide with exciton absorption bands.

In this connection it must be emphasized that because of weak exciton coupling the small populations of states with $k = 0$ results directly in the inhibition of luminescence from exciton states as a whole. This will result in general attenuation of luminescence and an increased role for nonradiative transitions.

Strong coupling between excitons and phonons may result in excitation which deforms the crystal,[24] with a band that is below the free exciton band in an undeformed lattice. With a quasi-equilibrium distribution, a large fraction of the exciton states go over into states of deforming excitations at the instant of emission. The luminescence spectrum will then consist of broad bands shifted in the long-wave direction compared with the absorption spectrum and, as in the preceding case, will not exhibit coincidence with absorption bands.[25]

Strongly polarized absorption bands associated with the creation of free excitons[18] have been observed in the spectra of a number of molecular crystals. Crystals of condensed aromatic hydrocarbons have been subjected to especially thorough investigation.[11-16] A careful study of the luminescence data from these crystals shows that in all analyzable cases there is no coincidence between bands of low-temperature luminescence and the lowest fundamental absorption bands due to excitons.* This agrees with the theoretical view given above concerning the conditions for and the character of exciton luminescence.

We are thus faced with the essential problem of determining the nature of this crystal luminescence. It must be established whether or not this "near" luminescence (near an electronic transition in the absorption spectrum) originates in satellite bands whose intensity increases through excitation redistribution in the exciton bands. It is important to establish to what extent the increased inhibition of exciton luminescence affects the spectra of different crystals. It should be noted that at higher tem-

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*Coincidence with absorption bands has been detected in the luminescence of a number of rare-earth salts. We shall not analyze this effect since the exciton mechanism apparently plays a small part in absorption by these substances and has still not been sufficiently studied.[26]

peratures, when kT is greater than or of the order of the band width, such inhibition disappears and the relative intensity of exciton luminescence may be expected to increase. However, the probabilities of nonradiative transition increase at the same time; in general this can reduce the overall brightness.

When the first excited state is a localized excitation the luminescence band will be shifted in the long-wave direction with respect to the weakly polarized absorption band by only the amount of the Stokes shift. With weak exciton-phonon coupling the two bands will practically coincide. It must be noted that in the case of localized excitations all of the characteristics of exciton absorption are least pronounced and their spectral properties are similar to those of local centers.

The situation may be similar in the case of semiconducting (ionic, semipolar, and valence) crystals. Here transitions not involving phonons are also allowed only from states with $k = q$. Therefore, with not too strong exciton-phonon coupling and $k \neq 0$ at the bottom of the exciton band, exciton luminescence is inhibited and diffuse as a result of phonon participation.

Many such crystals possess a large refractive index, so that we may expect the creation of Mott excitons. We then have $k = 0$ at the bottom of the exciton band when $k = 0$ pertains to the bottom of the electron band and the top of the hole band.*

In a number of crystals, such as Si or Ge, for which the structure of electron and hole bands is known, the edge of one of these is displaced from the point $k = 0$.[28] We may thus expect the inhibiting of exciton luminescence in a number of semiconducting crystals, but with the difference that the effective masses of Mott excitons are small and the bands are correspondingly broad (~ 1 ev), considerably exceeding kT over the entire important temperature region. Therefore, when the minimum of the energy surface is displaced from the point with $k = 0$, effects associated with the inhibition of exciton luminescence must be especially strong.

In the case of large-radius excitons two additional factors inhibit exciton luminescence. First, the quantum-mechanical probability of an optical

transition decreases in different instances as the cube or even the fifth power of a small parameter which is equal in order of magnitude to the ratio between the atomic radius and the exciton radius.[22] Secondly, large-radius excitons have a small binding energy which may amount to only 10^{-2}—10^{-3} ev;[29] exciton levels are then sparsely populated even at low temperatures and exciton luminescence is suppressed by a thermal barrier.

We shall now consider the case where the bottom of the exciton band is located at $k = 0$. We then observe a group of absorption bands corresponding to transitions to different excited exciton levels; for a cubic crystal with favorable structure of the electron and hole bands these absorption bands may comprise a hydrogen-like series.[22,30-32] With a quasi-equilibrium distribution established in the excited state luminescent emission will occur only from levels within the range $\sim kT$ above the lowest exciton state. At low temperatures a single luminescence band will thus be observed, agreeing in frequency with the first absorption band. When a transition from the lowest exciton state is forbidden by symmetry considerations luminescence will be altogether absent. It should be noted that for Mott excitons, because of the great width of the exciton band, the bands of vibrational overtones (satellites) in the luminescence spectrum will be wider than for local centers with the same radius of states and with the same electron-phonon coupling. When the dispersion of vibrational frequencies can be neglected the width of satellite bands for local centers is vanishingly small, whereas for exciton bands at low temperatures it is of the order kT and at high temperatures may reach the order of $E(k_0)$ where k_0 is of the order of the reciprocal of the exciton states radius (since excitons interact most strongly with vibrations for which $1/k$ is larger than or of the order of the exciton radius). Even when the vibrational branches show no dispersion the vibrational structure may thus becomes extremely diffuse.

The problems discussed in this section, especially those relating to molecular crystals, may be partly solved by considering the luminescence of impure crystals.

3. LUMINESCENCE OF CRYSTALS CONTAINING IMPURITIES

As has been shown above, at low temperatures the exciton luminescence of crystals is strongly inhibited. However, this does not mean that excitons do not participate in the luminescence mechanism; on the contrary, they may play a large part in electronic processes related to luminescence.

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*A general condition for $k = 0$ at the bottom of the Mott exciton band is a zero sum for the electron quasi-momentum k_e at the bottom of the electron band plus the hole quasi-momentum k_h at the top of the hole band.[27] This condition could, generally speaking, be satisfied even when k_e and k_h simultaneously correspond to definite points of symmetry on the boundaries of the Brillouin zone, but examples of this character are still unknown.

Their role is the transfer of absorbed energy from the host lattice to defects and impurities at which emission occurs. In their motion through the crystal excitons are scattered by phonons; when the exciton lifetime considerably exceeds the average time between two collisions with phonons exciton propagation can be described by a diffusion equation.[33-36]

Interactions with impurity centers can destroy excitons,* and under favorable conditions this process may be accompanied by impurity luminescence. (The simultaneous luminescence of several different kinds of impurities in a crystal is, of course, possible.) Many experiments have confirmed the participation of excitons in luminescence through this mechanism. The exciton mechanism for transferring energy from an absorbing center to an emitting center has been used to account for sensitized luminescence of many molecular and semiconducting crystals.[41]

The transfer of excitations in crystals (especially semiconductors) may also be accomplished by means of hole-electron pairs. It is of great interest to determine the type of excitation associated with luminescence. This has been done by Lashkarev and Karkhanin for the semiconducting crystal Cu_2O.[42] More than 90% of the photoelectrons were removed from the sample by an electric field of a few hundred v/cm. The fact that this did not weaken luminescence appreciably indicated that photoelectrons do not participate in the emission, which is excited directly by excitons.

In order to ascertain to what extent the excitons that induce luminescence are able to diffuse, experiments were performed to determine the diffusion length of an exciton, which is the distance of excitation energy transfer. Lashkarev and Karhanin[33] estimated the diffusion length of excitons at about 1μ from the dependence of the infrared luminescence efficiency of Cu_2O crystals on absorption. (Considerable surface quenching occurs here.) The same order of magnitude is obtained for the diffusion length of CdS crystals by examining the spectral distribution of photoconductivity and the absorption coefficient,[43] assuming an exciton mechanism of photocurrent excitation.

The familiar violet luminescence of anthracene has been investigated more carefully than that of other molecular crystals. Appreciable anthracene luminescence appears at a concentration of 10^{-7} — 5×10^{-7} per mole in a mixed anthracene-naphthalene crystal.[44] At these concentrations anthra-

cene molecules are separated by a distance of about 0.1μ, which was taken to be the order of magnitude of the exciton diffusion length in naphthalene. Another investigation[45] indicates that in order to obtain the correct dependence of quantum efficiency, for emission by anthracene-naphthacene crystals, on naphthacene concentration the exciton diffusion length in anthracene must be set at $\sim 0.15\mu$. An investigation of exciton migration through thin polycrystalline layers of anthracene[46] indicated a diffusion length of 0.05μ.

Certain luminescence properties can be ascertained by comparing the absorption and luminescence spectra of solid solutions and mixed crystals at low temperatures. These spectra have been very useful in elucidating fundamental crystalline absorption,[47] since the narrow impurity lines and branching of the series permit very reliable determinations of molecular vibrational frequencies.

An essentially new result was obtained by investigating the absorption and luminescence spectra of impure crystals such as tolane and dibenzyl with an admixture of stilbene;[48,49] this is the fact that both an electronic transition and each of its combinatiions with molecular vibrations is represented in these spectra by a group of lines. Line intensity in each group varies depending on the original impurity content of the melt and the conditions of crystal growth. As a whole the spectra of these crystals can be regarded as the superpositions of a few close series of bands and lines, with all band intensities in a given series varying simultaneously. Such a spectrum may result from the fact that different kinds of impurity centers are formed when one kind of molecular impurity is introduced. The concentrations of these centers determine the relative line intensities in each of the indicated groups, i.e., the relative intensities of the series.

In order to account for the observed spectra of mixed crystals we may advance either of two hypotheses concerning the structure of the different centers resulting from a single impurity. According to the first hypothesis it is possible that impurity molecules above a certain concentration form complexes consisting of two or more molecules. According to the second hypothesis stilbene molecules with a bent bridge connecting noncoplanar benzene rings, will, on entering the tolane lattice consisting of long flat molecules, suffer strong deformation, which changes the valence angles of bonds between benzene rings.* These changes may

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*The cross section for exciton interaction with impurity centers has been calculated theoretically a number of times.[37, 38, 39, 40]

*The possibility of such distortions of stilbene molecules is shown by the presence of two molecular types in the stilbene lattice, differing in their orientation about the crystal axes and in the valence angle of bonds between benzene rings.

TABLE II. Variable line structure at the beginnings of impure crystalline spectra

Stilbene in tolane[48]* (different specimens)						Pyrene in different paraffin solvents[51]				3,4-Benzpyrene in different paraffin solvents[51]						Corone in different paraffin solvents[51]			Phenol in benzene		Naphthacene in different solvents[53]				Stilbene in dibenzyl[49]* (different specimens)		
Absorption			Lumines-cence			Luminescence				Absorption		Luminescence				Luminescence			Absorption		Absorption		Lumines-cence		Abs.	Lumines-cence	
1	2	3		1	2	Pentane	Hexane	Heptane	Octane	Hexane	Octane	Pentane	Hexane	Heptane	Nonane	Heptane	Hexane	Octane	1	2	Dibenzyl	Tolane	Dibenzyl	Tolane	1	2	3
29456	29470	29486		29458	29468	26850	26855	26871	26875						24758	23457	23468	23479					20529				29660
29486	29480	29505		29468		26896	26909			24805	24806	24806		24772	24791		23547	23539	23517		20576	20649	20553	20651		29690	29692
29517	29497	29530		29528	29620	26918			26928	24819		24819	24821	24791	24803	23547						20687	20576	20690			29779
29545	29507	29553		29619	29672	26942				24832	24823				24825		23547					20726	20609	20724	29791		29791
29569	29530			29643						24842		24843	24844	24847										29815			29815
29666	29545									24862		24865												29832	29835	29838
	29553									24898	24876													29855		29855
	29565										24895													29870	29902	29870
	29610										24900													29878		
	29631																							29904		
	29641																									
	29666																									

*The strongest bands are given.

evidently vary depending on the way in which impurity molecules are incorporated into the crystal (such as the replacement of type I or II molecules in the elementary tolane cell[50]). A decision between these two hypotheses could be reached by studying the concentration dependence, but we still lack such experimental information.

Both models are based on the assumption that different absorption centers are formed with a small difference $(30 - 100 \text{ cm}^{-1})$ between their excitation energies. The absorption spectrum will then contain overlapping series of bands representing the excitation of these centers. The vibrational frequencies determined from the different series are almost in agreement; this results from the slight distortion of impurity molecules in the lattice.

The idea of a few different types of impurity centers has also been confirmed by experimental data on impurity luminescence. When the average separation of impurity molecules is smaller than or of the order of the exciton mean free path, absorption of light by the host lattice leads to impurity luminescence. However, because of the spatial separation of emission centers and the impossibility of energy exchange between them, even at very low temperatures the luminescence spectrum should contain a few resonance bands representing pure electronic transitions in different centers. The intensities of these bands will naturally increase with growing concentration of a given type of center. The spectra of mixed stilbene-tolane and stilbene-dibenzyl crystals have revealed a few luminescence bands coinciding with the origins of series observed in the absorption spectrum (Table

II); the luminescence band intensity and absorption band intensity varied similarly between different samples.

E. V. Shpol'skiĭ and his coworkers[51] have observed the same effect in detailed studies of the fluorescence spectra of coronene and pyrene solid solutions (T = 77° K) in paraffin solvents (n-hexane, n-heptane, n-octane etc.). A large number of narrow bands were found, grouped into highly developed vibrational series in which practically all bands are doublets. There is an especially noteworthy difference in the magnitude of the doublet splitting in different solvents. The phosphorescence spectra of these solutions were investigated at the same time;[51] the separations of doublet components in these spectra differed from those in the fluorescence spectra. Similar series of bands were observed in the fluorescence spectra of 3,4-benzpyrene solutions. Single lines or groups of 4 to 5 lines were observed depending on the solvent. Simultaneous study of the absorption and fluorescence spectra of pyrene solutions in hexane showed that the first fluorescence doublet corresponds to an absorption doublet and that the doublet components are resonance lines. Similar studies of coronene fluorescence in different solvents[52] have suggested that the doublet structure of the bands results from two possible orientations of impurity molecules in the lattice of the solvent.

A systematic investigation of the absorption and luminescence spectra of solid solutions of naphthacene and of a large group of organic solvents[53] has revealed the varying structure and varying multiplet character of individual bands. A few different types of impurity centers are also apparently pres-

ent here. The different polarization of individual bands and series of bands may be considered from the point of view of impurity center anisotropy or on the basis of the properties of impurity absorption close to exciton bands of the solvent crystal.[54]

Naphthalene luminescence, which is of special interest, has been investigated and discussed frequently. As we know, luminescence at 20°K begins with the $\nu = 31060$ cm^{-1} band, which coincides with a weak absorption band. Absorption spectrum studies of crystals with varying purity has proved[55] that the intensity of this band varies over a broad range. In samples subjected to the most thorough purifying process (zone melting) the 31060 cm^{-1} band is practically absent from the absorption spectrum and is strongly attenuated in the luminescence spectrum. The direct introduction of different impurities showed that this band is due to β-methylnaphthalene. Therefore the familiar luminescence of naphthalene crystals also does not come from a perfect lattice.

4. LOW TEMPERATURE LUMINESCENCE

Many crystals exhibit bright luminescence especially at low temperatures. Emission frequently results from the presence of impurities but even so-called "pure"* crystals are sometimes strongly luminescent, with spectra marked by a number of peculiarities including, first of all, varying band intensities and positions.

Variable luminescence spectra of molecular crystals were first noted in reference 57; at T = 20°K different anthracene crystals were found to possess the same luminescence bands with different widths and intensity ratios.

During recent years a number of papers have been published containing direct or indirect indications of variation in crystal absorption and luminescence spectra. In many cases an energy gap was detected between strong absorption and strong luminescence bands which did not result trivially from a forbidden pure electronic transition (as in the case of benzene; cf., for example, references 58, 59, and 11).

In many compounds weak variable absorption bands were detected at the long-wavelength edge of the strong fundamental absorption bands. The former are from 100 to 1000 times weaker than the latter, are observed only in relatively thick specimens, are often strongly polarized and cannot be combined into a single system with the strong bands.

*Following Arkhangel'skaya and Feofilov,[56] by "pure" crystals we mean those to which no activator has been added.

In an investigation of fine structure at the fundamental absorption edge of CdS crystals at 20°K it was found[60] that not only in different specimens but even in different parts of the same specimen in the interval 20,400 − 20,600 cm^{-1} the intensities, polarization, and positions of narrow lines may vary. From the great variability of these bands even in a single specimen it was inferred that they cannot be associated with intrinsic absorption by an ideal lattice (including exciton absorption) but result from the presence of defects. It was suggested that these bands were close to continuous absorption because they do not result from the excitation of weakly bound electrons belonging to defects, but rather from electronic transitions in host-crystal ions adjacent to defects (i.e., they resemble α and β bands in the spectra of alkali halide crystals[61]).

The investigation of luminescence[60,62] has revealed the coincidence of luminescence origins with a number of absorption lines in an interval of ~ 200 cm^{-1} (Fig. 1). At 20°K, where kT = 14 cm^{-1}, the simultaneous presence in the luminescence spectrum of a few resonance bands separated by such a large spectral interval is possible only if the quasi-equilibrium distribution is essentially destroyed in the excited state. Since the width of this interval is of the order of phonon energies, if the levels under consideration belonged to excitons a quasi-equilibrium distribution among them could easily be established through one-phonon transitions. On the other hand, considerably disturbance of the quasi-equilibrium distribution is easily accounted for by associating individual luminescence series with optical transitions at different spatially separated lattice defects. Therefore a comparison of the luminescence and absorption spectra provides strong arguments for the "defect" character of emission.*

*We note that the variability of narrow absorption and luminescence bands close to the fundamental absorption edge does not by itself nearly prove their connection with electronic transition in local centers. Indeed, it can be postulated in principle that these bands result from otherwise forbidden transitions to exciton states (or from exciton states) that are allowed near defects. Additional data are needed to permit a decision between these two possibilities. In addition to the considerations concerning the establishment of the quasi-equilibrium distribution the strong polarization of most bands provides an argument for the "defect" character of absorption and luminescence.[60] Finally, at low temperatures the removal of forbiddenness can result in a narrow absorption band coinciding with a luminescence band only if the bottom of the exciton band is at k = 0 and the lattice defect is of a very special character (a smooth deformation extending over many lattice spacings).
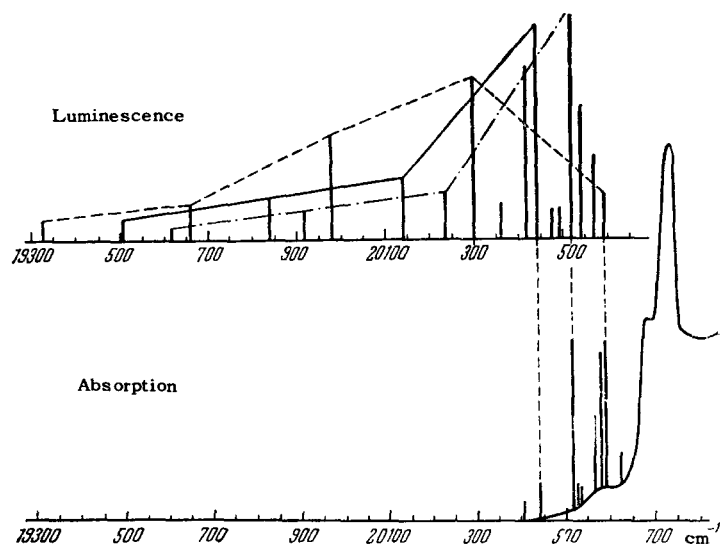
FIG. 1. Absorption and "blue" luminescence line spectra of the same CdS crystal at 20°K. The luminescence spectrum shows vibrational series with an interval of about 300 cm^{-1}. The bands at the beginning of the luminescence spectrum were attenuated by reabsorption.

Several hypotheses have been advanced to account for the variability of long-wave bands in the absorption spectrum of anthracene. According to Sidman[63] the weak bands at the fundamental absorption edge result from the excitation of localized excitons. The variability of these bands results from the fact that they are strongly influenced by various crystal distortions such as dislocations. The higher polarization ratio in the short-wave luminescence region (5:1) compared with that in the absorption spectrum (2.5:1) is taken as evidence that luminescence occurs at points where lattice symmetry is impaired.[64] Aside from the objectionable hypothesis that these bands correspond to localized excitons, it seems likely that the bands are associated with lattice imperfections. Indeed, in a comparison of the absorption and luminescence spectra of many anthracene crystals prepared in different ways, at 20° K, it was established that weak variable absorption bands coincide with strong bands among the first luminescence bands (Fig. 2).[65] From these observations it was inferred that the luminescence of crystalline anthracene takes place from local levels created near various lattice defects.

An investigation of the spectra of crystalline stilbene yielded similar results.[66] In order to elucidate the nature of the defects responsible for stilbene luminescence, specimens were subjected to heat treatment, which resulted in considerable redistribution of luminescence line intensities. It can be inferred from this result that the given defects are created by thermal motion during annealing and are frozen in during quenching (thermal defects). This agrees with the fact that the vibrational frequencies in the luminescence spectrum agree with known vibrational frequencies of stilbene molecules.

A large number of weak bands adjacent to the long-wave fundamental absorption edge are quite generally observed in the absorption spectrum of many molecular and semiconducting crystals. These bands are usually variable and their polarization, intensity and spectral position are strongly affected by external factors. These lines coincide with the shortest wavelengths among luminescence bands, and on this basis they have been interpreted as pure electronic transitions in the host-crystal lattice. However, in all similar substances that have thus far been studied to a sufficient extent the impurity ("defect") character of these absorption bands and the related luminescence has been reliably established. This has been shown for such molecular crystals as anthracene,[65] naphthalene,[55] stilbene,[66] tolane, phenanthrene[67] etc., as well as for the semiconducting crystals CdS, ZnS, AgI, PbI$_2$, HgI$_2$ etc.[56,68,60,62]

In this connection it is appropriate to call attention to the luminescence and absorption spectra of
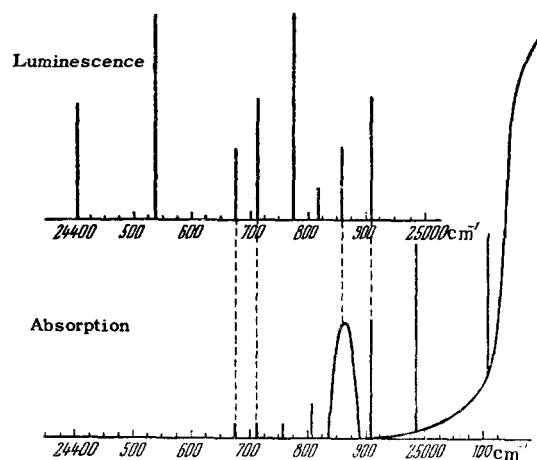

FIG. 2. Absorption and luminescence spectra of the same anthracene crystal at 20°K.

polymers such as l,l'-diethyl-pseudo-isocyanin chloride (ψ-isocyanin).[17] It has been shown that the luminescence band of this polymer (5727 A) coincides exactly with the narrow absorption band generated by polymerization, which is polarized along the polymer axis. A direct proof of exciton energy transfer along the polymer chain and of the exciton character of this absorption band was the strong quenching of luminescence by an extremely small admixture of pyrokatechin. One molecule of pyrokatechin to 10^3—10^6 molecules of ψ-isocyanin strongly quenches the luminescence of the polymer.

It seems to us that ψ-isocyanin and a few related polymers exhaust the cases in which the exciton nature of luminescence has been proved convincingly. In view of the ideas discussed above it is not surprising to find luminescence of this character. Unlike a three-dimensional crystal the polymer chain of ψ-isocyanin can be regarded as a one-dimensional structure. Also the fact that luminescence and absorption in the $\lambda = 5727$ A band are polarized along the polymer axis makes it very likely that the bottom of the exciton band is located at $k = 0$. In this case the inhibition of luminescence discussed above will disappear. One should also note that the investigations of ψ-isocyanin were conducted at room temperature.

Since in molecular crystals the excited defect levels are located, as already mentioned, next to the fundamental absorption edge, we may expect a number of peculiarities as regards the intensities and polarization of the corresponding lines and, specifically, considerable departure from the model of an oriented gas.

When an excited pure electronic level of an impurity molecule or host molecule in an irregular position (i.e., the level of an "anomalous" molecule) is near the exciton band edge of a molecular crystal the quantum state of this local center is complex.[54] The excitation is not entirely concentrated in the anomalous molecule but extends over a number of close-lying molecules of the regular lattice, and the region involved increases in size as the excited local center level approaches the exciton band edge. This composite character of the excitation accounts for a number of peculiarities in the intensity and polarization of absorption bands (and thus of luminescence band polarization), which depend strongly on the structure of the exciton band near its edge and the distance of the band from the excited local center electron level. When the band edge at which the local level is found corresponds to $k = 0$ the intensity of the corresponding absorption band will be unusually high. Otherwise it may be considerably attenuated. The polarization of local center bands may differ strongly from polarization according to the oriented gas model, and under certain conditions the bands may be fully polarized.

When the anomalous molecule is oriented at some angle to the crystallographic axes strongly polarized absorption bands may, in general, result from two additional mechanisms: the formation of complexes with a distinct structure, and the propagation of excitation waves through the sublattice of anomalous molecules. Each of these mechanisms should produce a multiplet, consisting of a few bands, out of each nondegenerate level of the anomalous molecule, and at least one band should be present in each spectral component. In addition, the form of the spectrum should depend strongly on the concentration of anomalous molecules. On the other hand, the mechanism described above is evidently the only one which can account for a single band that is practically fully polarized along a direction in the crystal making an angle with the anomalous molecule. At not too high concentrations of anomalous molecules the spectrum due to this effect remains unchanged. These differences should make it possible to distinguish the influences of the different mechanisms experimentally.

It may be noted that the optical properties of molecular crystals can be described in some approximation using the oriented gas model, which possesses the advantage of extreme simplicity. However, all progress in understanding the spectral properties of the crystals depends on departures from the oriented gas model and the use of a theory that consistently takes intermolecular interaction into account. This is true both for the characteristic splitting and strong polarization of exciton bands in molecular crystal spectra and for the anomalous polarization of absorption bands and of local-center luminescence bands, close to exciton bands.

As indicated above, the variable weak bands which are detected at the long-wavelength fundamental absorption edge of many crystals and which are associated with electronic transitions near lattice defects usually exhibit anomalous polarization. Such absorption bands have been detected in the spectra of crystals of anthracene,[65] stilbene,[66] phenanthrene,[67] etc. The anomalous polarization of luminescence bands has been investigated in the spectra of crystalline anthracene.[75] These experiments can serve as a basis for investigating the departure of "impurity" ab-

sorption and luminescence from the oriented gas model and for the detection of spectral characteristics that are predicted by theory.[54]

5. QUASI-EQUILIBRIUM DISTRIBUTION IN AN EXCITED STATE

We shall now consider problems connected with the establishing of a quasi-equilibrium distribution in an excited state. As already mentioned, this is not accomplished completely. The degree of deviation from the quasi-equilibrium distribution and its significance in different cases are determined by the duration and specific character of the given effect as well as by the rate of relaxation processes. For example, only nonequilibrium electrons participate essentially in the photoelectric effect (with energies of a few electron volts), so that the photoelectric effect possesses a very small relaxation time. On the other hand, we may expect that luminescence and the photoconductive effect, in which fast carriers do not play such a very large part and for which relaxation times are correspondingly large, will ordinarily be well described by the establishment of a quasi-equilibrium distribution in an excited state among levels of the host crystal.

The establishment of the quasi-equilibrium distribution can be divided into the process of establishing equilibrium between quasi-particles of the same kind (electrons, holes or excitons belonging to one band) and the establishment of equilibrium between quasi-particles of different kinds (for example, between different kinds of excitons or between excitons and hole-electron pairs). It is naturally easiest to establish equilibirum between quasi-particles of the same kind.*

Equilibrium between different kinds of excitons is established more easily than between excitons and hole-electron pairs. This results particularly from the fact that the association of electrons and holes leading to the formation of excitons is of bimolecular character, and that the relaxation rate is considerably reduced by the spatial separation of band carriers and by the shift of the quasi-equilibrium distribution toward ionized states. The rate of relaxation is determined to a considerable extent by the sequence of energy levels, their separations, coupling with phonons etc.

The rate at which quasi-equilibrium is established between local centers and excited states of the host crystal as well as between different spatially separated centers will, as a rule, be smallest.

Possible disturbances of the quasi-equilibrium distribution in an excited state can be illustrated by the optical and photoelectric properties of CdS crystals. The absence of unique correspondence between the absorption coefficient and the photocurrent near the strong absorption edge of these crystals[43,70,71] provides evidence that the spectral dependence of the photocurrent cannot be explained by the spectral dependence of the absorption coefficient alone; the photocurrent must depend explicitly on the exciting wavelength. This in turn indicates that light absorption by CdS crystals in this part of the spectrum is of a mixed character* and that there are departures from the quasi-equilibrium distribution. This inference is confirmed by the difference in the excitation spectra of "green" and "orange" luminescence of CdS crystals.[72]

It is still not clear how the quasi-equilibrium distribution is disturbed in this case since the nature of absorption in this part of the spectrum has still not been established. If we postulate fundamental absorption the observed effects are caused by departures from quasi-equilibrium between excitons and hole-electrons pairs. It has been suggested, however, that absorption in this part of the spectrum is at least partially due to impurities.[73,74] In that event the experimental data can be interpreted by assuming a departure from quasi-equilibrium between local centers and hole-electron pairs.

The results obtained by MacFarlane et al.,[29] who established a dependence between the quantum efficiency of the photoconductive effect in a germanium crystal and the exciting wavelength in the mixed fundamental absorption region, apparently prove the departure from quasi-equilibrium between excitons and hole-electron pairs at liquid hydrogen temperature.

6. CONCLUSION

We thus see from an analysis of the experimental data, as well as from special investigations undertaken to determine the basic characteristics of luminescence in crystals, that thus far (at least for low temperatures) no luminescence has been observed which exhibits the features and laws of exciton-type luminescence. A number of experiments have also confirmed the inhibition predicted by theory (Sec. 2) or even the practically complete absence of exciton luminescence when the bottom of the exciton band corresponds to $\mathbf{k} \neq 0$ and the exciton coupling is not too strong.

On the other hand, the same experimental data are in good accord with the concept of "impurity

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*This is confirmed experimentally by data on the diffusion of nonequilibrium carriers, their galvanomagnetic effects etc.

*That is, absorption in this spectral region produces different types of excited states.

luminescence" in the broadest sense of this term (Secs. 3 and 4). Thus the question raised in Sec. 2 as to whether "near" luminescence is associated with indirect transitions from the exciton band or with optical transitions in local centers has been decided in favor of the second hypothesis.

It follows that excitons produced in a crystal through the absorption of light are annihilated non-radiatively either in the host lattice or at impurities and defects, and that in the latter event "impurity" luminescence may be excited. The diffusion length of excitons is generally a structurally sensitive quantity which cannot be regarded as constant for a given substance and must depend on the chemical purity of the crystal and the degree of lattice perfection.*

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*It has still not been decided to what extent the diffusion length in different crystals is determined by annihilation in the host lattice or near imperfections. It is clear, however, that in crystals with high luminescence efficiency, such as anthracene, a decisive part is played by the transfer of excitation energy to centers responsible for luminescence. In crystals containing a considerable number of structural defects at which luminescence cannot take place the exciton diffusion length will naturally be reduced. This effect has been observed directly[69] in the sharp falling off of luminescence intensity when crystals are deformed mechanically.

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