

## ANNIHILATION OF EXCITONS AND EXCITON-PHONON INTERACTION\*

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IN 1931, the Soviet physicist Ya. I. Frenkel<sup>[1]</sup> advanced the hypothesis of existence in crystals of a particular type of electronic excitations that does not involve the appearance of free electrons and holes. Frenkel called this new type of excited state of a crystal the exciton. Owing to the identity of the unit cells of the crystal, this excitation can be transferred by resonance from one lattice site to another in the crystal, and thus the exciton moves in the crystal. Frenkel's ideas have been subsequently developed broadly in theoretical studies, both in the Soviet Union and abroad. Theoretical physicists have taken up the exciton hypothesis in attempts to explain various phenomena. However, the question of whether the exciton concept is only a speculative, theoretically-contrived notion, or whether such quasi-particles actually exist in crystals, has remained open for the following twenty years.

In 1951, direct experimental proof of the existence of excitons in a crystal was obtained.<sup>[2]</sup> The hydrogen-like optical spectrum of an exciton was found by direct experiments,<sup>[3]</sup> both the spectrum of its formation and of its annihilation. These experiments showed that in some crystals ( $\text{Cu}_2\text{O}$ ,<sup>[3,7]</sup>  $\text{CdS}$ ,<sup>[3-6]</sup>  $\text{CdSe}$ ,<sup>[3,8-10]</sup> etc.) the frequencies of the lines of the spectrum of energy levels of exciton states form hydrogen-like series. This showed that the electric charges involved in the entity (the exciton) that gives the hydrogen-like series of spectral lines are bound by Coulomb forces. This implied that an exciton can actually exist in crystals as a hydrogen-like quasiatom. Like positronium, it consists of an electron and a hole bound by Coulombic attraction, and it moves as a whole through the crystal.

Ideas concerning exciton states are currently widely adduced in treating optical, electrical, photoelectric, thermal, diffusional, and other phenomena in crystals, and in a number of phenomena in chemistry and biology. Various models have been constructed that describe exciton states in ionic, covalent, and molecular crystals.

The fundamental property of an exciton is its ability to migrate in the crystal. It is precisely because of this important property that excitons play such a large role in various processes that occur in crystals. A large number of experimental studies performed by different methods have been concerned with studying the motion of excitons. These studies are mainly concerned with studying energy transport by excitons in organic crystals (see, e.g. the reviews<sup>[11-13]</sup>). Energy transport by excitons in semiconductor crystals has been studied in less detail.<sup>[14]</sup>

The fact that an exciton has a velocity has been experimentally established in experiments on magnetic-

field inversion in  $\text{CdS}$  crystals,<sup>[15,16]</sup> from the spectra of transverse and longitudinal excitons in  $\text{ZnO}$ <sup>[17]</sup> and  $\text{CdS}$ ,<sup>[18]</sup> and in studying the spectrum of a quadrupole exciton transition in  $\text{Cu}_2\text{O}$ .<sup>[19]</sup> These experiments studied the motion only of excitons with very small wave vectors of the order of the wave vector of light. However, the excitons in a crystal are distributed over a rather broad range of wave vectors and kinetic energies. The extent of this range is determined by the temperature of the crystal. Hence, one can get a fuller picture of the motion of excitons in a band by studying the kinetic-energy distribution of the excitons.

We shall relate here the manifestation of the kinetic energy of excitons in the emission spectra of certain crystals. We shall treat crystals for which the effective-mass approximation is valid, and in which each exciton state is characterized by a definite wave vector and kinetic energy. This situation is characteristic of covalent and weakly ionic crystals. In strongly ionic and in molecular crystals, the motion of an exciton is as a rule not characterized by a wave vector, but occurs by "jumps" between different sites in the crystals.

Excitons arise in crystals in different ways. They can be excited directly by light or by particle impact, they can be formed by combination of free electrons and holes, and they can be created by other excitations in the crystal. Exciton states also disappear in the most varied ways. Excitons can dissociate into free electrons and holes that give rise to conduction in the crystal, they can transfer their energy to defects and impurities, and they can give rise to various elementary excited states in the crystal structure. Finally, radiative annihilation of excitons can occur when the energy of the exciton state is emitted in the form of light. Optical processes of creation and disappearance of excitons can be studied directly from spectra of exciton absorption and emission of crystals.

Let us consider a diagram illustrating the origin of the optical spectra of an exciton. Figure 1a shows schematically the energy spectrum of a crystal. The cross-hatched regions correspond to bands of allowed electron energies. Light can cause transitions of electrons between bands, and this process corresponds to the continuous intrinsic absorption spectrum. The horizontal lines in the band of forbidden energy states of an electron show the exciton levels. The arrows denote the processes of creation of excitons in different quantum states. It is precisely these transitions, which lie near the long-wavelength boundary of the continuous absorption, that are usually observed experimentally. In addition, transitions can occur between the exciton levels under the action of light. These transitions are shown in Fig. 1a by the left-hand set of arrows from  $n = 1$ . However, the crystal must already contain enough excitons in order for these transitions to be observed. Besides, there are also a number of experimental diffi-

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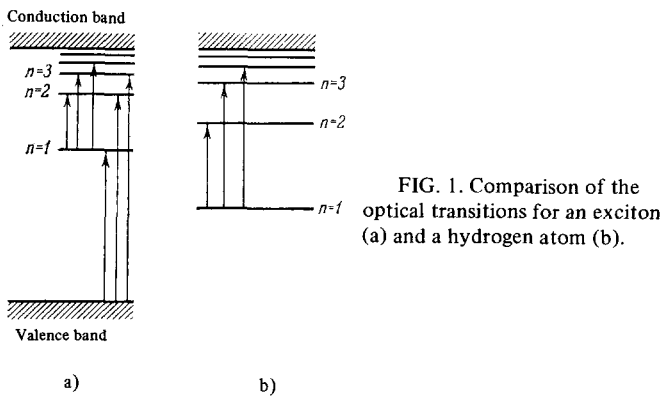


FIG. 1. Comparison of the optical transitions for an exciton (a) and a hydrogen atom (b).

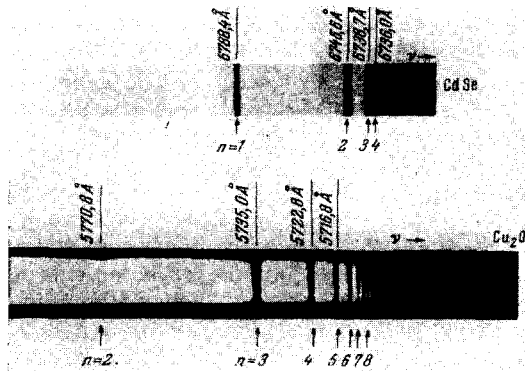


FIG. 2. Hydrogen-like absorption spectra of excitons in CdSe and Cu<sub>2</sub>O crystals at 4.2°K.

culties that interfere with observing optical transitions between exciton levels. Therefore, such transitions have not yet been observed experimentally.

As we have noted, in a number of crystals, the absorption spectra that correspond to exciton-creation processes are groups of narrow lines arranged in a hydrogen-like series. An example of this is the absorption spectra of Cu<sub>2</sub>O and CdSe crystals shown in Fig. 2. The experimental observation of hydrogen-like exciton absorption spectra confirms the analogy between the exciton and the hydrogen atom.

However, we should note a fundamental difference between the optical spectra of atoms and excitons. With atoms, we are concerned with transitions within a pre-existing system. However, with excitons we observe optical processes of creation and annihilation of the system per se (the exciton). Figure 1b shows schematically the optical transitions between the energy levels in a hydrogen atom. As we see by comparing Figs. 1a and b, the analog of optical transitions in the atom is transitions between exciton levels. As we noted above, the latter have not been observed experimentally. The observable exciton absorption and emission spectra have no analogs in the optical spectra of atoms. Hence, it is more correct to compare an exciton with another hydrogen-like system, rather than a hydrogen atom: a positronium atom, which can also be created by electromagnetic radiation. Radiative annihilation of excitons, which gives rise to exciton luminescence, has much in common with radiative annihilation of positronium atoms.

A radiative annihilation process has characteristic

features that distinguish it from other radiative processes, e.g., luminescence of atoms in a gas. In particular, the motion of the radiating system is manifested in different ways in these two processes.

When an atom undergoes a radiative transition, the energy of the emitted light quantum is determined by the energy difference  $E_0$  of the excited and ground levels of the atom. Moreover, because of the thermal motion of the atom, the frequency of the emitted light will be subject to a Doppler shift proportional to the velocity of the atom. The existence of a velocity distribution of the atoms in the gas has the result that a line is observed in the luminescence spectrum whose center corresponds to the excitation energy  $E_0$  of the atom, while the width is due to the Doppler effect. The width varies with the gas temperature, owing to the variation in the mean thermal velocity of motion of the atoms. The line has a symmetrical shape that is well described by a Gaussian distribution. Study of the shapes of such lines has served as one of the confirmations of the correctness of the kinetic theory of gases. Thus, the luminescence spectra of free atoms directly manifest the velocity of motion of the atoms. If we know the temperature (and hence the mean kinetic energy of the particles) of the emitting system, then we can determine the mass of the emitting particles from the velocity distribution.

In a process of radiative annihilation, the emitting system vanishes, and its energy (internal and kinetic) is totally transformed into radiation energy. Hence, annihilation spectra manifest the kinetic energy of the particles, rather than the velocity. We can directly determine the temperature of the emitting system from the kinetic-energy distribution of the particles. However, this distribution gives us no possibility of determining the mass and velocity of the particles separately, since the kinetic energy is the product of the mass and the square of the velocity of the particles. In order to measure these quantities separately, one must set up an additional experiment that permits one independently to determine one of these quantities, e.g., the velocity of motion of the particle. In the annihilation of positronium atoms, such an experiment could be a direct measurement of the momentum in an angular-coincidence system. For an exciton, its velocity could be determined from the spectrum of transitions between exciton levels. Indeed, these transitions are fully analogous to optical transitions in atoms, and the line shapes of these transitions should manifest a Doppler broadening that would permit one to determine the velocity.

Let us examine in more detail the process of radiative annihilation of excitons. If the crystal satisfies the effective-mass approximation, and the extrema of the energy band lie in the center of the Brillouin zone (the point  $k = 0$ ), then the relation of the exciton energy to the value of its wave vector will have the form

$$E_{\text{ex}} = E_0 + E = E_0 + (\hbar^2 k^2 / 2M), \quad (1)$$

where  $k$  is the wave vector of the exciton, and  $M$  is the total mass of the exciton, which is equal to the sum of masses of the electron and the hole.

In this formula, the first term  $E_0$  corresponds to the internal energy of the exciton state, while the second term  $E$  is the kinetic energy of the exciton. If the exciton gas is in thermal equilibrium with the crystal struc-

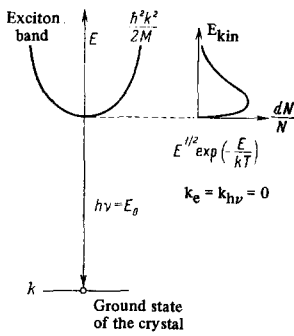


FIG. 3. Energy diagram explaining the conservation of energy and of wave vector in the process of phononless exciton annihilation.

ture, then the relative number of particles of kinetic energy  $E$  at the temperature  $T$  will be given by the Maxwell formula:

$$dN/N \sim E^{1/2} \exp(-E/kT) dE. \quad (2)$$

In the process of radiative annihilation, an exciton vanishes and a light quantum is emitted. In addition, this process can be accompanied by simultaneous emission or absorption of phonons. The fundamental laws governing various annihilation processes are defined by the laws of conservation of energy and quasimomentum.

In phononless annihilation, the energy and momentum of the exciton are fully imparted to the photon (Fig. 3). The energy of exciton states in crystals usually amounts to several electron volts. The momentum of photons of this energy is very small in comparison with the mean momentum of thermal motion of excitons, even at very low temperatures.\* Hence, only excitons of very low momenta can participate in radiative phononless annihilation. The kinetic energy  $E$  of such excitons is negligibly small, and the energy of the emitted quanta will be almost exactly equal to the internal energy  $E_0$  of the exciton state.

The reverse process of creation of excitons by light obeys the same conservation laws, and only light quanta can be absorbed that have energies almost exactly coinciding with the internal energy  $E_0$  of the exciton states. Thus, the selection rules for momentum result in appearance in the spectrum of direct excitonic absorption of narrow lines whose energies correspond to the bottom of the exciton bands.

It is interesting to note that Doppler broadening must be totally absent in the spectra of phononless transitions involving formation or disappearance of excitons. The law of conservation of momentum in phononless optical transitions unambiguously fixes the wave vector of the excitons being annihilated, both in magnitude and in direction. The size of the wave vector of the exciton is determined by the energy of the photon, which satisfies the law of conservation of energy. The direction is determined by the direction of observation, since the directions of motion of the exciton being annihilated and the emitted photon coincide. Hence, all excitons that participate in phononless annihilation have the same velocity. As we have noted above, a Doppler effect should be manifested only in optical transitions between exciton levels.

\*In fact, the wave vectors of photons in the visible are of the order of  $10^5 \text{ cm}^{-1}$ , whereas the mean wave vector of thermal motion of excitons is of the order of  $10^6 - 10^7 \text{ cm}^{-1}$ .

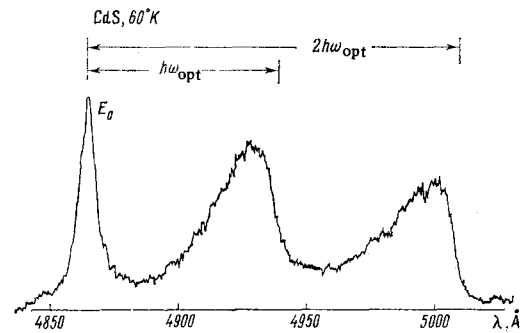


FIG. 4. Exciton luminescence spectrum of CdS crystals ( $T = 60^\circ\text{K}$ ).

The width of the phononless lines in exciton spectra of pure crystals is determined by the non-steady-state character of the exciton states, which is due to scattering of excitons by phonons. This broadening is analogous to the broadening of atomic lines in the spectra of gases by collisions. With rising temperature, the probability of scattering of excitons by phonons increases, and the phononless lines in exciton spectra broaden.<sup>[20]</sup> Recent experimental and theoretical studies have shown that the most probable event in crystals having an appreciable ionic character is scattering of excitons by longitudinal optical phonons.<sup>[21]</sup> As a rule, the energy of such phonons amounts to several hundred reciprocal centimeters, and the number of them in the crystal at low temperatures is small. Hence, at temperatures up to  $\approx 80^\circ\text{K}$ , the phononless lines in the free-exciton spectrum of most crystals are insignificantly broadened. In cuprous oxide crystals, according to measurement of the absorption spectrum of the line  $n = 2$  of the yellow series, this broadening amounts to  $8 \text{ cm}^{-1}$ .<sup>[22]</sup> In the CdS crystal, the broadening of the  $n = 1$  lines of the A and B series, which we have measured from the reflection spectrum, is also small, being about  $10 \text{ cm}^{-1}$  (over the temperature range from  $4.2$  to  $77^\circ\text{K}$ ).

Whenever the minimum of the exciton band is not at the point  $k = 0$ , the process of phononless annihilation of excitons is generally impossible, and also the reverse process of direct absorption.<sup>[23]</sup> In this case, the optical exciton spectrum will lack narrow absorption lines and phononless annihilation lines in resonance with them.

Let us turn to the results of experimental studies of exciton luminescence spectra of certain crystals at low temperatures. Figure 4 shows the exciton luminescence spectrum of CdS crystals at  $60^\circ\text{K}$ .\* One distinctly observes in the spectrum an emission line due to phononless annihilation of excitons in the  $n = 1$  state of the series  $\Gamma_9 - \Gamma_7$ . The position of this line in the spectrum almost coincides with the position of the corresponding exciton absorption line.

In addition to the phononless line, the exciton luminescence spectrum of CdS crystals (see Fig. 4) also exhibits lines shifted toward lower energies with respect to the resonance value  $E_0$  by the amount of one or two longitudinal optical phonons ( $h\omega_{\text{opt}} = 305 \text{ cm}^{-1}$ ). These lines are due to radiative annihilation of excitons with

\*At lower temperatures ( $T \lesssim 30^\circ\text{K}$ ), the luminescence spectra of CdS crystals contain in this region a large number of narrow, intense emission lines arising from crystal-lattice defects (the so-called "bound excitons"). These lines vanish from the spectrum as the temperature is raised above  $40^\circ\text{K}$ .

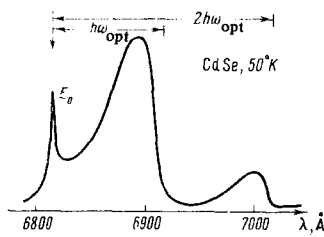


FIG. 5. Exciton luminescence spectrum of CdSe crystals ( $T = 50^\circ\text{K}$ ).

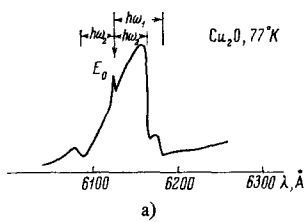
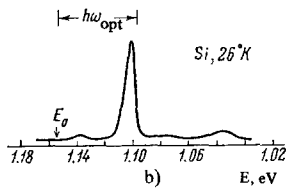


FIG. 6. Exciton luminescence of crystals of  $\text{Cu}_2\text{O}$  [7] ( $T = 77^\circ\text{K}$ ) and Si [24] ( $T = 26^\circ\text{K}$ ).



simultaneous emission of optical phonons, and they have a characteristic asymmetric shape resembling that of a Maxwell distribution. The width of these lines varies strongly with the temperature, and is of the order of  $kT$ . Conversely, the phononless free-exciton line and the emission line of immobile "bound excitons" hardly vary in width with varying temperature. We can naturally conclude that the shape of the exciton-phonon annihilation lines reflects the kinetic-energy distribution of the excitons, as is manifested in the radiative-annihilation spectrum as the excitons interact with phonons.

The exciton-luminescence spectra of other crystals also exhibit similar asymmetric emission lines that are shifted by the amount of energy of optical phonons with respect to the phononless exciton-annihilation line. Figure 5 shows the emission spectrum of a CdSe crystal at  $50^\circ\text{K}$ . As we see by comparing Figs. 5 and 4, the exciton luminescence spectra of CdSe and CdS crystals are analogous. The temperature-dependence of these spectra is also the same. The energy of a longitudinal optical phonon ( $h\omega_{\text{opt}}$ ) as manifested in the exciton luminescence of CdSe amounts to  $210\text{ cm}^{-1}$ .

The luminescence spectrum of  $\text{Cu}_2\text{O}$  crystals at  $77^\circ\text{K}$  (Fig. 6a) shows [7] a weak, narrow phononless-annihilation exciton line of the yellow series that coincides in resonance with the absorption line  $n = 1$ . Moreover, the spectrum contains two lines of characteristic shape on the long-wavelength side of the resonance line. They are due to radiative annihilation of excitons with simultaneous excitation of phonons in the crystal. These lines are shifted with respect to the resonance line by the amount of the optical-phonon energies  $h\omega_1 = 145\text{ cm}^{-1}$  and  $h\omega_2 = 105\text{ cm}^{-1}$ . A line occurs in the short-wavelength region of the spectrum that results from annihilation of excitons with simultaneous disappearance of phonons from the crystal. The probability of such a process at

FIG. 7. Energy diagram explaining the conservation of energy and of wave vector in annihilation of an exciton with simultaneous excitation of a phonon.

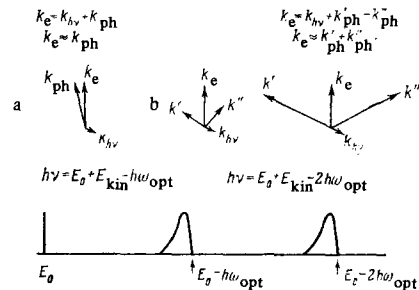
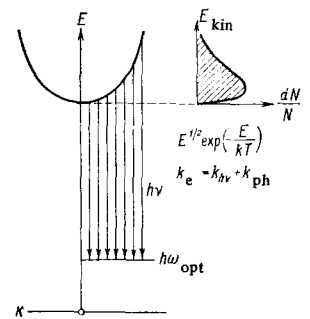


FIG. 8. Laws of conservation of energy and of wave vector in one-phonon (a) and two-phonon (b) exciton annihilation.

$77^\circ\text{K}$  is rather large, since the phonon energy  $h\omega_2 = 105\text{ cm}^{-1}$  is comparable with the mean energy of thermal vibrations of the crystal at this temperature.

In silicon crystals, the minimum of the lowest exciton band occurs at a point  $k \neq 0$ , and the process of phononless radiative annihilation of excitons is forbidden by the law of conservation of momentum. In fact, the emission spectrum of silicon does not manifest a phononless exciton annihilation line. However, one observes a process of radiative annihilation of excitons with simultaneous excitation of a transverse optical phonon  $h\omega_{\text{opt}} = 465\text{ cm}^{-1}$  (with a peak at  $1.10\text{ eV}$ ) [24] (see Fig. 6b). More attentive study of the exciton luminescence spectrum of silicon crystals [25] makes it possible to observe also lines due to interaction with other phonons.

Emission due to annihilation of excitons with simultaneous excitation of phonons in the crystal has recently been observed also in many other crystals (SiC, Ge, ZnO, diamond). [26-28]

As we can see from the cited examples, the phenomenon of radiative annihilation of excitons with simultaneous excitation of phonons in the crystal is general among crystals. In this process, the kinetic energy of the excitons is directly manifested, and study of such processes can give direct information on the motion of excitons in crystals.

Let us examine the process of radiative annihilation of an exciton with simultaneous excitation of an optical phonon. It is precisely these phonons that are manifested in the exciton luminescence spectra of most crystals. When an exciton is annihilated with simultaneous excitation of one or several phonons, the momentum of thermal movement of the exciton can be transferred to the phonons. Excitons of any kinetic energy can participate in these annihilation processes, in distinction from the phononless process (Fig. 7). Figure 8 illustrates the

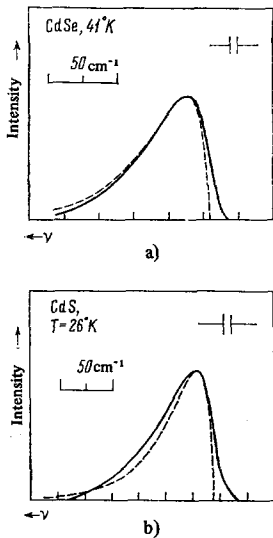


FIG. 9. Comparison of the experimental contour (solid curve) of the two-phonon exciton-annihilation line in CdS and CdSe crystals with Maxwellian distribution curves at the same temperatures (dotted curves).

laws of conservation of momentum and energy for a one-phonon and a two-phonon process.

The law of conservation of energy (see Fig. 8) implies that the process of annihilation of an exciton with excitation of one phonon corresponds in the emission spectrum to a line shifted to longer wavelengths with respect to the phononless line by the amount of energy of the optical phonon. Since the energy of optical phonons hardly depends on the value of the momentum, we can expect that the shape of the line for one-phonon annihilation of excitons will reflect the Maxwellian kinetic energy distribution of the excitons.

The process of annihilation of an exciton with excitation of two optical phonons (see Fig. 8) fundamentally obeys the same rules as the process of one-phonon annihilation. Just as with one-phonon annihilation, the emission spectrum manifests the kinetic energy distribution of the excitons, and the line for two-phonon annihilation of excitons is shifted to longer wavelengths by the amount of energy of two optical phonons with respect to the phononless line.

However, there is a substantial difference in the formulation of the law of conservation of momentum for the one-phonon and two-phonon processes. In the two-phonon annihilation of an exciton of momentum  $k$ , phonons of momenta  $k'_{\text{ph}}$  and  $k''_{\text{ph}}$  are excited, and they satisfy the equality  $k_e = k'_{\text{ph}} + k''_{\text{ph}}$ . Here the law of conservation of momentum can be satisfied in many ways, and the momenta  $k'_{\text{ph}}$  and  $k''_{\text{ph}}$  can take on different values. In one-phonon annihilation, however, the momentum of the created phonon can have only one value  $k_{\text{ph}} \approx k_e$  (see Fig. 8).

As will be shown below, this fact leads to a substantial difference in the shapes of spectra of one-phonon and two-phonon annihilation. Moreover, the large number of possible combinations of phonons in the two-phonon process substantially increases its probability. In spite of the fact that this process is of higher order than the one-phonon process, the intensity of the two-phonon emission lines of CdS and CdSe crystals is comparable with that of the one-phonon lines, as we see from Figs. 4 and 5.

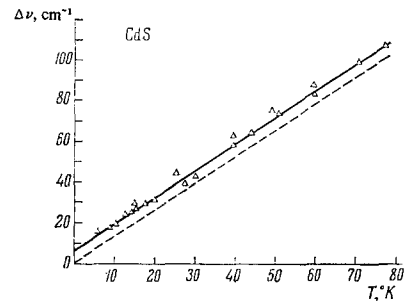
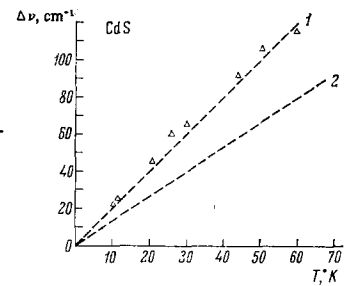


FIG. 10. The increase with temperature of the half-width  $\Delta\nu$  of the two-phonon exciton-annihilation line in CdS crystals (solid curve). The dotted curve shows the increase with temperature in the half-width of a Maxwellian distribution  $E^{1/2} \exp(-E/kT)dE$ .

FIG. 11. The increase with temperature of the half-width  $\Delta\nu$  of the one-phonon exciton-annihilation line in CdS crystals (1). Curve 2 is the increase with temperature of the half-width of a Maxwellian distribution.



In conjunction with V. A. Abramov and A. I. Ekimov, the present authors have conducted a detailed study of the shapes of emission lines that result from one-phonon and two-phonon annihilation of  $n = 1$  excitons of the series  $\Gamma_9 - \Gamma_7$  in CdS and CdSe crystals at temperatures from  $4^\circ$  to  $77^\circ \text{K}$ . As the studies showed, the line shapes and the temperature-dependence of the exciton luminescence spectra are perfectly identical for these two crystals. We can assume that the exciton-phonon annihilation spectra will obey the same rules in other crystals of the  $A_{II}B_{VI}$  group as well.

The emission lines due to exciton-phonon annihilation in the spectra of CdS and CdSe crystals have a characteristic shape that resembles the shape of the Maxwellian kinetic-energy distribution (see Figs. 4 and 5). Comparison of the contour of the spectral lines arising from two-phonon annihilation of excitons in these crystals with the Maxwellian distribution curves at the same temperatures (Fig. 9) shows that the kinetic-energy distribution is well described by the Maxwell formula. The shape of the two-phonon annihilation lines in CdS and CdSe crystals approximates the Maxwellian shape throughout the studied temperature range. As we see from Fig. 10, the half-width of the two-phonon line varies with the temperature in approximately the same way as the half-width of the Maxwellian distribution  $dN/N \sim E^{1/2} \exp(-E/kT)dE$ , which increases with the temperature as  $1.9 \text{ kT}$ .

The half-width of the one-phonon annihilation line increases more rapidly with the temperature than that of the Maxwellian distribution. Figure 11 shows the temperature-dependence of the half-width of the one-phonon line in the CdS crystal. The temperature increase in the half-width of the line that is observed experimentally fits a growth in the half-width of the curve as  $E^{3/2} \exp(-E/kT)$ , which increases as  $2.9 \text{ kT}$ .

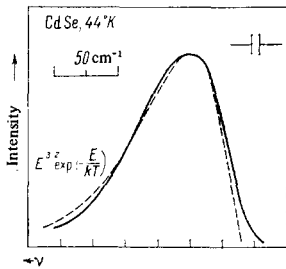


FIG. 12. Comparison of the experiment contour (solid curve) of the one-phonon exciton-annihilation line in CdSe crystals at  $T = 44^\circ\text{K}$  with the curve of  $E^{3/2} \exp(-E/kT)$  drawn for the same temperature (dotted curve).

The half-width of the one-phonon line in CdSe crystals has the same temperature-dependence. Comparison of the line contours for one-phonon annihilation in CdS and CdSe crystals with curves of  $E^{3/2} \exp(-E/kT)$  drawn for the same temperatures shows that this formula describes well the shape of the observed line. Figure 12 shows such a comparison for the spectrum of CdSe crystals at  $44^\circ\text{K}$ .

The width of exciton-phonon annihilation lines should be determined not only by the kinetic-energy distribution of the excitons, but also must include an additional broadening due to scattering by excitons by phonons. However, as we have mentioned, study of the width of phononless lines shows that this broadening at temperatures below  $80^\circ\text{K}$  is considerably less than the width of the kinetic-energy distribution. Within the limits of accuracy of our measurements, we could not detect this additional broadening.

The experimentally-established shape of a one-phonon annihilation line  $E^{3/2} \exp(-E/kT)$  differs from the shape  $E^{1/2} \exp(-E/kT)$  of the Maxwellian distribution by the factor  $E$ . This additional factor results from the dependence of the probability of exciting an optical phonon by an exciton on the magnitude of the momentum of the exciton. In a one-phonon annihilation process, an exciton of momentum  $k_e$  produces a phonon of approximately equal momentum  $k_{ph}$ . As our experimental results imply, the probability of this process is proportional to  $E$  or to  $k^2$ .

A theoretical study of the probability of interaction of excitons with optical phonons has been performed by Ansel'm and Firsov.<sup>[29]</sup> According to the results of this study, the probability of exciton-phonon interaction is approximately proportional to  $k^2$  for small momentum values. The excitons in thermal equilibrium with the crystal at low temperatures have precisely these momentum values. Thus, the relation of the probability of exciton-phonon interaction to the magnitude of the momentum that we have determined experimentally agrees with the theoretical results of Ansel'm and Firsov.

For a two-phonon process, as analysis of the spectrum implies, the probability of interaction between an exciton and a phonon does not depend on the size of the wave vector of the exciton. This is explained by the fact that each exciton in a two-phonon annihilation can give rise to different phonon pairs, and the selections of these phonon pairs are about the same for different thermal excitons. Consequently, the probability of a two-phonon process will be about the same for different excitons, and the spectrum should manifest only the kinetic-energy distribution of the excitons. Indeed, experiment shows that two-phonon exciton lines have a

Maxwellian shape. The simple qualitative considerations given here are confirmed by recent theoretical studies describing the shapes of exciton-phonon emission lines.<sup>[30,31]</sup>

The differing formulation of the law of conservation of momentum for processes of one- and two-phonon annihilation not only results in differing shapes of the corresponding emission lines, but it also gives rise to a change in the relative intensities of these lines with temperature. As we have noted above, the probability of one-phonon annihilation of an exciton is proportional to the square of its momentum. The mean thermal momentum of the excitons increases with increasing temperature of the crystal. Consequently, the overall probability of one-phonon annihilation increases, as does the intensity of the one-phonon emission line. As study of the shape of the two-phonon line shows the probability of two-phonon annihilation does not depend on the exciton momentum in the first approximation. If we know the expression describing the contours of the one- and two-phonon emission lines, we can calculate the ratio of their integral intensities as a function of the temperature:

$$S = \frac{I_{f=1}}{I_{f=2}} \sim \frac{\int_0^\infty E^{3/2} \exp(-E/kT) dE}{\int_0^\infty E^{1/2} \exp(-E/kT) dE} \sim T, \quad (3)$$

where  $I_{f=1}$  and  $I_{f=2}$  are the integral intensities of the one- and two-phonon annihilation lines.

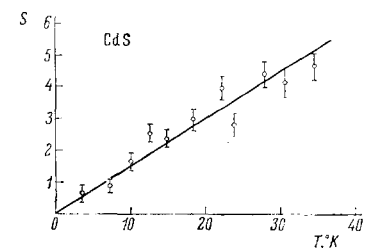
Equation (3) implies that the relative intensity  $S$  of the lines must vary linearly with the temperature. Indeed, such a linear increase with temperature of the relative intensity of the exciton-phonon annihilation lines is observed in CdS and CdSe crystals. Figure 13 shows the experimental temperature-dependence of the ratio of intensities of the one- and two-phonon annihilation lines in the CdS crystal.

Thus, all the differences that are observed between the spectra of one-phonon and two-phonon annihilation of excitons arise from the different way in which the law of conservation of momentum is formulated for the two processes. The marked manifestation of these differences in the emission spectra is evidence that the observed phenomenon is a process of annihilation specifically of free excitons, without transfer of momentum to an impurity or defect.

Detailed study of exciton luminescence spectra shows that emission from excitons is a typical process of annihilation of free particles. As we have noted, radiative annihilation of positronium atoms is an analogous process. The difference between these two processes consists in the amount of energy liberated upon annihilation.

The internal energy of exciton states in crystals

FIG. 13. The experimental temperature-dependence of the ratio  $S$  of the intensity of the one-phonon line to that of the two-phonon line in the exciton luminescence spectrum of CdS crystals.



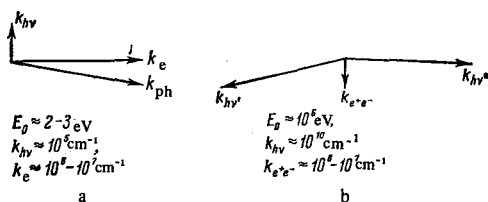


FIG. 14. Conservation of energy and momentum in the annihilation of excitons (a) and of positronium atoms (b).

usually amounts to several electron volts. If the energy of the exciton is completely transformed into the energy of a light quantum, then the wave vector of such a quantum will be of the order of magnitude of  $10^5 \text{ cm}^{-1}$ . The most probable thermal momenta of excitons, even at low temperatures, as expressed in the same units, amount to  $10^6-10^7 \text{ cm}^{-1}$ , and they cannot be borne away by a photon. Hence, only a small fraction of the excitons participate in phononless annihilation, namely those having very small momenta. Conversely, excitons of any kinetic energy can participate in the process of radiative annihilation with simultaneous excitation of phonons that bear away the thermal momentum (Fig. 14).

In the case of a positronium atom, the total internal energy of the electron-positron system amounts to  $10^6 \text{ eV}$ . The wave vector of a light quantum of such an energy is of the order of  $10^{10} \text{ cm}^{-1}$ , and its momentum considerably exceeds the thermal momenta of the positronium atoms. Hence, one-photon annihilation of free positronium atoms is impossible. In two-photon annihilation, the momenta of the two light quanta compensate one another, and their sum becomes equal to the thermal momentum of the positronium. Hence, radiative annihilation of free positronium atoms always occurs by emission of two or more phonons.

Thus, in order to permit free particles of any kinetic energy to participate in the annihilation process, emission of no less than two particles is necessary. In annihilation of excitons, these particles are a photon and a phonon (or two phonons). In annihilation of positronium atoms, two or three photons are emitted.

The law of conservation of momentum is the fundamental selection rule determining the nature of an annihilation process. Hence, a change in the form of this conservation law can cause a substantial change in the annihilation spectrum. For example, one-photon annihilation of a positronium atom can occur upon collision with a heavy nucleus. Here the momentum of recoil of the emitted photon is transferred to the nucleus. However, this process can no longer be considered to be a process of annihilation of free particles.

An analogous phenomenon has been observed in the exciton luminescence spectrum of silicon crystals.<sup>[25]</sup> As we know, the absolute minimum of the conduction band in Si crystals is displaced from the point  $k = 0$  in the  $[1, 0, 0]$  direction, and optical transitions to exciton states without participation of phonons are forbidden. However, a line has been observed in the exciton luminescence spectra that arises by annihilation of excitons without creation or disappearance of phonons in the crystal. Here the emission spectrum manifested excitons having all kinetic energies, and the emission line had a characteristic Maxwellian shape. It was estab-

lished that the intensity of this line in different specimens was proportional to the concentration of the isoelectronic impurity of carbon atoms. The reason for appearance of this line is the breakdown of the law of conservation of momentum in the crystal structure at sites where its periodicity is violated by the foreign, but isoelectronic atoms of carbon. Thus, the excitons cannot be considered to be free particles in this process as well.

The manifestation of the kinetic energy of excitons in an exciton-phonon annihilation spectrum is the most direct proof of the motion of excitons in crystals. In the described cases, the shape of the observed annihilation lines indicates that the excitons can be considered to be a gas of free quasiparticles in thermal equilibrium with the crystal structure. This means that the exciton band is parabolic within the studied interval of kinetic energies, while the kinetic-energy distribution of the excitons obeys well the Maxwell-Boltzmann statistics. Although excitons are particles of integer spin, and they must obey the Bose statistics, we could not detect deviations from the Boltzmann statistics under the conditions of our experiments, in which the concentrations of excitons were small, but the temperatures relatively high. Study of the shapes of lines arising from radiative annihilation of excitons with simultaneous emission of phonons makes it possible to study the structure of exciton bands and the statistical kinetic-energy distribution of excitons in the band. In addition, these lines make it possible to study processes of exciton-phonon interaction.

In conclusion, we shall take up briefly one of the interesting aspects of the process of exciton-phonon radiative annihilation, the possibility of using this process as an active mechanism for obtaining stimulated emission. The problem of laser action from exciton transitions in crystals for which the intrinsic absorption edge arises from indirect transitions was first taken up by Basov and his associates.<sup>[32]</sup>

Let us consider phononless exciton and exciton-phonon radiative transitions from the standpoint of stimulated emission. When a crystal is excited, electron-hole pairs are created, and these subsequently are partly bound into excitons, and can become annihilated with emission. The strongest emission must be expected for excitons in the  $n = 1$  state, since the greatest number of excitons will occur specifically on this level in the process of establishment of thermal equilibrium.

Phononless annihilation of an exciton corresponds in the energy diagram of the crystal to a transition from an exciton level to the ground state of the crystal.\* Since excitons are excited by way of the valence band and the conduction band in the discussed process, phononless excitation and emission of excitons occur in a three-level system. However, simultaneously with the radiative transitions in the crystal, reverse transitions occur from the ground state to the exciton level, accompanied by absorption of the emitted light. This absorption is very intense, and thus it interferes with laser action. In order to make the emission process predominate over absorption, one must attain an inverted population of the

\*Such transitions occur efficiently in crystals having allowed vertical transitions



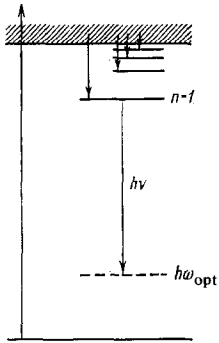


FIG. 15. Energy diagram for appearance of exciton-phonon stimulated emission.

ground state and the exciton level of the crystal. In order to do this, one must excite more than half of the maximum possible number of excitons in the crystal (a concentration of the order of  $10^{22} \text{ cm}^{-3}$ ). Such large concentrations of free excitons are hardly attainable, and laser action at the phononless lines of free excitons is not observed experimentally.

Conversely, the process of exciton-phonon radiative annihilation proves to be extremely favorable for obtaining laser action. This process corresponds to transition from an exciton level to a vibrational sublevel  $h\omega$  of the ground state of the crystal. When the excitons interact with the optical vibrations of the crystal, this sublevel occurs at an energy  $h\omega_{\text{opt}}$  above the valence band (Fig. 15). The overall process of excitation and emission occurs in a four-level system. For most crystals,  $h\omega_{\text{opt}} > kT$  up as far as room temperature. Consequently, the vibrational sublevel  $h\omega_{\text{opt}}$  is practically unoccupied at low temperatures. Thus there is always an automatic population inversion of the upper and lower levels for the discussed exciton-phonon transition. The absorption process that is the reverse of the radiative process is highly improbable. This creates favorable conditions for amplification and generation of light. Stimulated emission can involve more than one phonon.

Laser action by exciton-phonon transitions is actually observed experimentally. Figure 16 shows as an example the stimulated-emission spectrum of a CdSe crystal excited by an electron beam of density  $15 \text{ A/cm}^2$ . The temperature of the crystal is  $10^\circ \text{K}$  (the spectrum is taken from a study by Kurbatov, Mashchenko, Mochalkin, Britov, and the present authors<sup>[33]</sup>). Detailed correlation of spectra of the crystal as the excitation level was gradually raised and comparison with photoluminescence made it possible to establish that the emission band shown in the figure consists in free-exciton stimulated emission ( $n = 1, \Gamma_9 - \Gamma_7$  series) with simultaneous excitation of one longitudinal optical phonon. This emission shows all the features of stimulated emission: directionality, threshold, and mode structure (this is distinctly visible in the figure). It is interesting to note that in this case the contour of the phonon-replica exciton band in stimulated emission is very similar to the phonon-replica exciton contour in spontaneous emission (see Fig. 16). Laser action can also be observed in the second phonon replica.<sup>[34,35]</sup>

The exciton-phonon mechanism of stimulated emission is apparently general for most semiconductors. The exciton-phonon nature of the coherent emission has

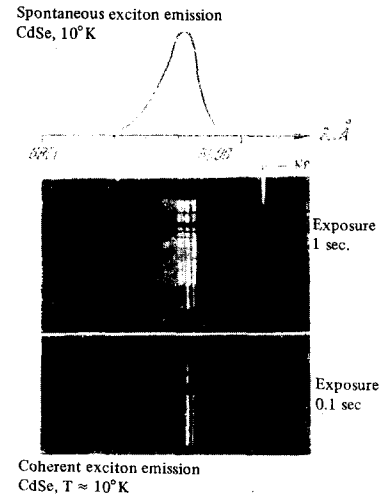


FIG. 16. Coherent free-exciton emission with simultaneous excitation of a longitudinal optical phonon in CdSe crystals ( $T \approx 10^\circ \text{K}$ ).

been established in crystals of CdS,<sup>[34-37]</sup> CdSe,<sup>[33,37]</sup> ZnO,<sup>[37]</sup> and in the mixed crystals CdS-CdSe<sup>[38]</sup> and ZnS-CdS.<sup>[39]</sup>

Since exciton-phonon processes are a property of the fundamental structure of the crystal, laser action by exciton-phonon transitions has a number of advantages over laser action by an impurity mechanism. In semiconductor crystals having reasonable concentrations of impurities and defects, such that radiative transitions are still observed, the intensity of emission from impurities (including emission from bound excitons) undergoes saturation at high excitation densities. On the other hand, no such saturation is observed for free excitons. This shows that at high excitation densities, the process of emission via free excitons is more efficient than that via an impurity. Indeed, the concentration of free excitons can attain very high values. Since the intrinsic emission of the crystal plays the dominant role in the stimulated emission when a crystal is intensively excited, there is no need to control rigidly the types and concentrations of impurities. It suffices merely that the fraction of radiationless transitions should not be too large. Thus, special introduction of impurities is not required in order to obtain suitable crystals.

An important merit of the exciton mechanism of emission is also its temperature stability. Both spontaneous and stimulated emission from excitons are observed over a broad temperature range, from liquid-helium to room temperature.<sup>[34,35]</sup> Apparently, the reason for this temperature stability of an exciton involves its ability to migrate through the crystal. While thermal vibrations cause an impurity to ionize, an increase in thermal energy for an exciton, can only increase its kinetic energy.

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Translated by M. V. King