

Bound-exciton Auger recombination induced by acoustic phonons

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Experimental and theoretical investigations were made of a new process representing modulation of the quantum efficiency of the luminescence of excitons localized at neutral donors by a flux of nonequilibrium phonons. The temperature dependence of the internal quantum efficiency of the same lines in the exciton luminescence spectrum of CdS crystals was determined for an equilibrium phonon system. The reduction in the quantum efficiency under these conditions was attributed to a transition of exciton-impurity complexes to an excited state. It was found that in the case of excited states of the complexes characterized by zero total angular momentum an effective Auger recombination channel competed successfully with a channel representing optical decay of bound excitons. A comparison of the theoretical calculations of the quantum efficiency with the experimental results demonstrated the important role of the Auger process induced by acoustic phonons in the recombination effects occurring at low temperatures. Experiments revealed a new type of local excitations associated with oscillations of a hole in an adiabatic potential created by the core of a donor and by two electrons.

INTRODUCTION

Investigations of the exciton luminescence of direct-gap semiconductor crystals have established the important role played by excitons localized at impurities and defects: "giant" oscillator strengths make these excitons the main channel of radiative recombination of nonequilibrium carriers.¹ However, it is surprising why such exciton complexes do not manifest Auger nonradiative recombination. In fact, if three particles are separated by distances of the order of the Bohr exciton radius $a \sim 10^{-7}$ – 10^{-6} cm, the conditions then correspond to an effective density of free carriers amounting to $n \sim 10^{18}$ – 10^{21} cm⁻³. In the case of interband transitions, Auger recombination would be highly effective at such carrier densities. We therefore investigated both experimentally and theoretically the role of the Auger nonradiative channel in the formation of the spectra of the exciton-impurity luminescence.

In the case of the ground state of a bound exciton the Auger recombination is suppressed by the selection rules associated with the laws of conservation of the angular momentum or its projection along a specific axis. The total angular momentum of an exciton-impurity complex (EIC) is not affected by its decay. Since an electron in an EIC has zero orbital momentum and a hole band is formed from p -type wave functions, it follows that in the case of nonradiative decay the total angular momentum of an EIC should be transferred to a fast electron generated as a result of the Auger decay. We shall show later that in the case of an EIC in the ground state such a transfer of the angular momentum to a fast electron reduces considerably the probability of the Auger process and makes it noncompetitive compared with the radiative recombination. This forbiddenness is lifted for specific excited states of an EIC corresponding to local vibrations of the center of mass of an exciton bound to a defect. The total momentum of an EIC then vanishes, so that the process of decay occurs without transfer of momentum to a fast electron. We shall show that the probability of the Auger decay of such an excited state of an EIC is several orders of

magnitude higher than the probability of the Auger decay from the ground state. Therefore, the Auger process should be manifested in the transfer of an EIC to an excited state.

We shall report an investigation of the quantum efficiency of the luminescence of EICs in CdS crystals under the conditions such that these complexes were excited by a flux of nonequilibrium acoustic phonons or by an increase in temperature from 1.3 to 50 K. It was established that the excitation of EICs activates the nonradiative recombination channel characterized by a small activation energy $E_+ = 2.5$ meV. We attributed this channel to Auger recombination and described all the experimental results by a simple theoretical model. We determined the characteristic Auger time for an exciton bound to a neutral donor in CdS and excited to the first vibrational state, corresponding to the motion in the plane perpendicular to the c axis. The activation energy E_1 was found to be equal to the energy of this excitation.

The results of our experimental investigation are given in Sec. 1; Sec. 2 provides an analysis of a phenomenological model used to describe the kinetics of the EIC luminescence in the presence of an effective nonradiative channel, whereas Sec. 3 is devoted to a theoretical analysis of the Auger recombination of EICs in the ground and excited states. The main results are discussed in the Conclusions.

1. EXPERIMENTAL RESULTS

The kinetics of recombination of bound excitons in cadmium sulfide crystals was investigated. A study was made of the luminescence due to excitons localized at donor impurities.¹ The spectroscopic binding energy of an exciton for centers of this type was $\epsilon_0 = 7.8$ meV. A change in the binding energy with the chemical nature of the center did not exceed 0.25–0.5 meV. We investigated CdS samples with donor concentrations of 10^{15} – 10^{16} cm⁻³, some of which were weakly compensated (in this case the line due to excitons bound to acceptor impurities was absent from the luminescence spectra) and the others were fairly strongly compensated (in this case the ratio of the intensities of the lumines-

cence of excitons bound to donors and acceptors was $\leq 1/2$). Crystals were grown from the vapor phase and were platelets 20 μm thick with the hexagonal c crystal axis in the plane of the plate. The experiments involving nonequilibrium phonons were carried out at $T = 1.3$ K. Nonequilibrium acoustic phonons were injected into a crystal from a thermal generator in the form of a metal film evaporated on the surface of a sample opposite the illuminated surface. The luminescence of our samples was recorded in the reflection geometry. The metal film was excited by nitrogen laser pulses of $\sim 10^{-8}$ s duration. The intensity of the nonequilibrium acoustic phonon flux arriving in the excitation region and the spectrum of these phonons were determined using a phonon spectrometer.² The spectrum of nonequilibrium phonons from a thermal generator exhibited a characteristic feature: a change in the degree of laser heating (characterized by the radiation intensity I_0) of the metal film had practically no effect on the spectrum of the phonons injected into the semiconductor sample and altered only the occupation numbers of the phonon states. The total energy of the system of phonons injected into the semiconductor was proportional to the intensity I_0 of the nitrogen laser radiation. The luminescence was recorded using a photon counting system and the spectra were stored in the memory of a computer and then subjected to an automated analysis.

In addition to a study of the influence of nonequilibrium phonons on the formation of exciton spectra, we also studied the temperature dependences (in the range $T = 1.3\text{--}50$ K) of the intensity of the luminescence due to excitons localized at shallow donors. At temperatures in this interval we were unable to separate the luminescence of the bound excitons from the background of the long-wavelength wing of the luminescence line of the free excitons.

Figure 1 shows the differential luminescence spectra induced by nonequilibrium acoustic phonons in the range of frequencies corresponding to the recombination of excitons both free and localized at shallow and neutral donors. It is clear from this figure that a reduction in the intensity of the zero-phonon luminescence (ZPL) lines of the EICs was not accompanied by an equivalent increase in the integrated intensity of the phonon wings of the spectrum and there was no increase in the intensity of the free-exciton luminescence. Therefore, there was a reduction in the intensity in the radiative recombination channel and this could be explained in a natural manner by activation of a nonradiative recombination process.³ Since the maximum quantum energy of nonequilibrium acoustic phonons in our experiments did not exceed values of the order of 4 meV (Ref. 2), we concluded that the characteristic activation energy of this nonradiative process was located in the low-frequency range $\hbar\omega < 4$ meV. Estimates of the characteristic energies of the processes of this type were obtained from the temperature dependences of the EIC luminescence intensity. An increase in temperature caused quenching of the luminescence. This quenching was due to the following factors. Firstly, the electron-phonon interaction enhanced the probability of radiative recombination involving acoustic phonons, so that an increase in temperature increased the occupation numbers of the phonon states. This should result in a corresponding reduction in the ZPL. Secondly, an increase in temperature could increase the rate of nonradiative recombination of excitons localized at the impurity centers. This was the process of

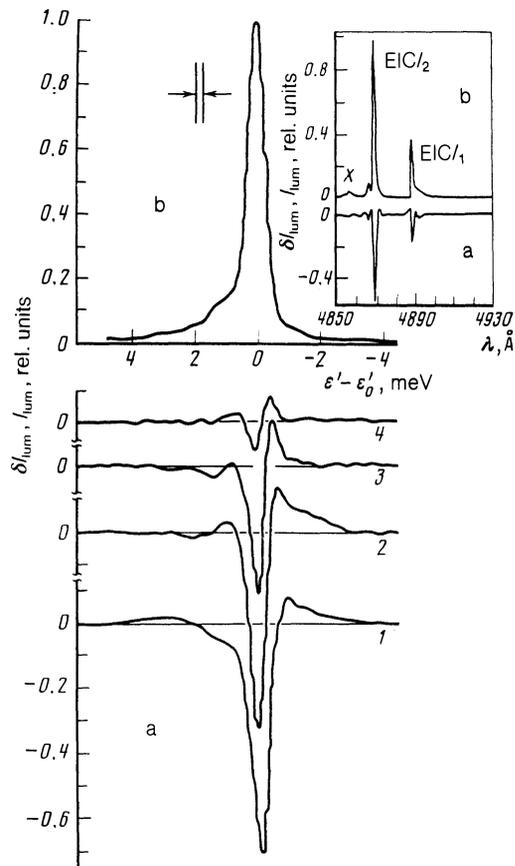


FIG. 1. Luminescence spectra of excitons bound to donors: a) differential; b) in the absence of phonons at $T = 1.3$ K. The values of the volume density of the energy of nonequilibrium phonons E_{Σ} (J/cm^3) are taken from Ref. 2: 1) 3.8×10^{-2} ; 2) 1.4×10^{-2} ; 3) 3.4×10^{-3} ; 4) 8.0×10^{-4} . The inset shows the luminescence spectra of CdS in the exciton part of the spectrum: a) differential; b) in the absence of phonons at $T = 1.3$ K; X is the free exciton line, the EIC line I_2 represents an exciton bound to a donor, and EIC I_1 is the luminescence line of an exciton bound to an acceptor.

greatest interest to us because it was intimately related to the change in the quantum efficiency of the luminescence in the investigated spectral range. Thirdly and finally, an increase in temperature caused dissociation of EICs. The population of the localized exciton states then decreased and this caused quenching of the corresponding radiative recombination line.

The problem of a redistribution of the intensity of the luminescence between the ZPL and the phonon wings could be investigated relatively easily and identified in the experiments under discussion (see, for example, Ref. 4). We formulated (see below) phenomenological and microscopic nonradiative recombination models describing all the experimental results on the changes in the quantum efficiency of the luminescence in the case of interaction of equilibrium or nonequilibrium phonons with EICs and used the results to explain the temperature dependences of the nonradiative recombination.

The experimental temperature dependences of the luminescence intensity are usually analyzed employing the relationship⁵

$$I(T) = I(T=0) / \left\{ 1 + \sum_i c_i \exp(-E_i/T) \right\}, \quad (1)$$

where E_i is the characteristic activation energy and the coefficients c_i represent the relative probabilities of recombination in channels responsible for the luminescence quenching. We shall regard $I(T)$ and $I(0)$ as the integrated values of the luminescence line intensities subject to allowance for their spectral profiles. The experimental results presented in Fig. 2 are described satisfactorily by Eq. (1) when two characteristic energies $E_1 = 2.5$ meV and $E_2 = 7.7$ meV and the corresponding coefficients $c_1 = 5-10$ and $c_2 = 200$ are assumed. Therefore, the traditional method for the analysis of the dependences $I(T)$ leads to the conclusion that there are two characteristic energies of the quenching of the EIC luminescence spectrum and one of these energies (E_2) is identical with the energy of localization of an exciton at a neutral donor (ε_0), so that the corresponding quenching process can be regarded as thermal activation of a bound exciton. The first activation energy level corresponds, as shown below, to the excitation of vibrational motion of an exciton bound to a donor. This level decays mainly by the Auger process. It should be noted that a similar dependence with two activation energies has been reported earlier (see, for example, Ref. 6 describing the results on GaAs), but the process of nonradiative recombination with characteristic energies less than the energy of localization of an exciton at a shallow impurity center is identified here for the first time. The energy level E_1 of the EICs decays entirely by the nonradiative process, as demonstrated by the observation that the luminescence line originating from this state is absent from the experimentally observed absorption and luminescence spectra. Therefore, the results obtained demonstrate the importance of the excited states of the EICs in the processes of

nonradiative recombination of excitons. We shall show later that the most striking observation is that the transfer of the EICs to this state by a flux of nonequilibrium phonons has a direct effect on the quantum efficiency of the luminescence. We shall now consider a very simple model which allows for the influence of the nonradiative decay channel on the investigated luminescence spectra.

2. KINETICS OF THE LUMINESCENCE OF EXCITON-IMPURITY COMPLEXES IN THE PRESENCE OF AN EFFECTIVE RECOMBINATION CHANNEL

The results of Sec. 1 allow us to account for the kinetics of bound excitons by a model with just two energy levels: a ground state with a binding energy ε_0 and an excited level of energy ε_1 . We shall assume that the excitons localized in the ground state of the EICs decay radiatively and the process can be described by a characteristic optical recombination time τ_R . The excitons in the excited state recombine nonradiatively and their lifetime in the case of such decay is τ_N . In view of the absorption and emission of acoustic phonons of energy $\hbar\omega = \varepsilon_0 - \varepsilon_1$ the system goes over from the ground to the excited state and the changes in the populations of these two states are manifested by changes in the quantum efficiency of the EIC luminescence. We shall write down the rate equations for the populations of the ground n_0 and excited n_1 states on the assumption that the rate of generation of localized excitons in the ground state is g :

$$dn_0/dt = g - (\tau_R^{-1} + W_{\uparrow})n_0 + W_{\downarrow}n_1,$$

$$dn_1/dt = W_{\uparrow}n_0 - (W_{\downarrow} + \tau_N^{-1})n_1, \quad (2)$$

$$W_{\uparrow, \downarrow} = W_0(N_{ph} + 1/2 \mp 1/2), \quad (3)$$

where W_{\uparrow} and W_{\downarrow} are the probabilities of transitions between the investigated states of the EICs as a result of the absorption or emission of an acoustic phonon of energy $\hbar\omega$; N_{ph} are the occupation numbers of these states in the phonon spectrum. In the case of thermal activation of the EICs the occupation numbers of the phonon states are described by the Planck formula

$$N_{ph} = [e^{\hbar\omega/T} - 1]^{-1}.$$

In the case of the transitions induced by nonequilibrium phonons the number N_{ph} is governed by the spectral characteristics of the phonon flux arriving from the thermal generator. We shall at this stage not specify the excitation process, but we shall find from Eq. (2) the steady-state populations n_0 and n_1 :

$$\begin{aligned} n_0 &= g\tau_R \frac{1 + W_{\downarrow}\tau_N}{1 + W_{\downarrow}\tau_N + W_{\uparrow}\tau_R}, \\ n_1 &= g\tau_R \frac{W_{\uparrow}\tau_N}{1 + W_{\downarrow}\tau_N + W_{\uparrow}\tau_R}. \end{aligned} \quad (4)$$

We shall define the quantum efficiency η of the EIC luminescence as the ratio of the number of decays of the EICs accompanied by the emission of optical radiation (n_0/τ_R) to the total number of decays ($n_0/\tau_R + n_1/\tau_N$) (naturally, under steady-state conditions we have $g = n_0/\tau_R + n_1/\tau_N$). The following expression for the quantum efficiency η is derived from Eq. (4):

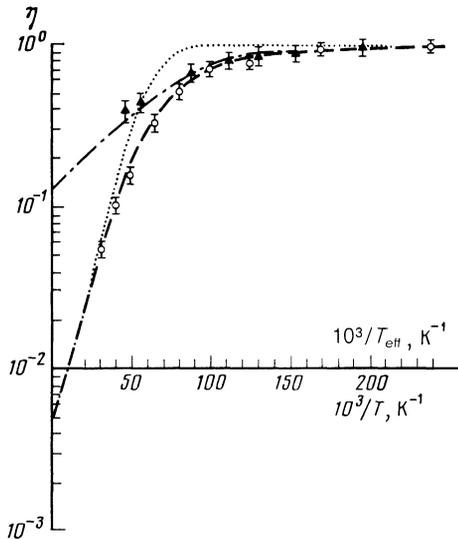


FIG. 2. Dependences of the internal quantum efficiency of the luminescence on temperature in the absence of nonequilibrium phonons (\circ) and of the occupation numbers on the effective temperature in the presence of nonequilibrium acoustic phonons (\blacktriangle). The dashed curve is calculated on the basis of Eqs. (1) and (23) assuming that $E_1 = 2.5$ meV, $E_2 = 7.7$ meV, $c_1 = 7$, $c_2 = 200$. The chain curve is calculated from Eq. (22) on the assumption that $\hbar\omega = \varepsilon_0 - \varepsilon_1 = 2.5$ meV and $c_1 = 7$. The dotted line is calculated on the basis of Eq. (1) on the assumption that $E_2 = 7.7$ meV and $c_2 = 200$.

$$\eta = [1 + W_1 \tau_n / (1 + W_1 \tau_N)]^{-1}. \quad (5)$$

The expression in Eq. (5) is simplest in certain limiting cases. For example, if the rate of nonradiative transitions is considerably higher than the rates of all the other processes, the quantum efficiency

$$\eta = 1 / (1 + W_1 \tau_R)$$

is governed only by the competition between two processes: optical decay from the ground state and release of an exciton to an excited state as a result of phonon absorption. If $W_1 \tau_R \ll 1$, then during the optical recombination time there is no significant transfer of the EICs to the excited state and the quantum efficiency approaches the limit $\eta \rightarrow 1$. However, if there is active "mixing" of the states ε_0 and ε_1 , so that $W_1 \tau_R \gg 1$, the quantum efficiency is much smaller than unity: $\eta \propto (W_1 \tau_R)^{-1}$. In the second limiting case, when the times of the phonon-assisted transitions are considerably less than the characteristic nonradiative time, the quantum efficiency can be expressed in terms of the ratio of the radiative and nonradiative recombination times:

$$\eta = \left[1 + \frac{\tau_R}{\tau_N} \frac{N_{ph}}{N_{ph} + 1} \right]^{-1}.$$

In investigations of the temperature dependences of the quantum efficiency $\eta(T)$ we have to supplement the two-level scheme described above by a new channel associated with the possibility of release of an exciton to a free state. It follows from the calculations that the possibility of dissociation of the EICs at temperatures $T \sim \varepsilon_0$ gives rise to the following characteristic activation term in the denominator of the expression for η :

$$\eta = \left[1 + \frac{W_1 \tau_R}{1 + W_1 \tau_N} + \frac{N_{ex}(T)}{n_D} \exp\left(-\frac{\varepsilon_0}{T}\right) \right]^{-1}, \quad (6)$$

where

$$N_{ex}(T) = 2(m_h T / 2\pi \hbar^2)^{3/2}, \quad m_h = (m_{\perp}^2 m_{\parallel})^{1/2},$$

m_{\parallel} and m_{\perp} are the longitudinal and transverse masses of holes, n_D is the concentration of neutral donors in the investigated semiconductor crystal, and N_{ex} is the effective number of states in the continuous spectrum of the exciton band participating in the thermal dissociation process. Comparing the expression for the quantum efficiency with Eq. (1), we can see that our expression applies to the thermal activation processes as well as to the processes representing any other mechanism of the excitation of an EIC to a state with a nonradiative decay channel.

Clearly, the most convincing method for the identification of a transition is selective excitation of a specific transition and a study of its response to such excitation manifested in the spectrum of the radiative recombination of the EICs. The existence of an excited state of the EICs with an excitation energy $\Delta\varepsilon = \varepsilon_0 - \varepsilon_1$ is of the greatest interest. Although the thermal activation experiments suggest the existence of an activation level with an energy $E_1 = 2.5$ meV, nevertheless, the process of excitation of transitions with the energy $\hbar\omega = \Delta\varepsilon$ provides an unambiguous proof of their existence and more detailed information not only on the energy levels of the system, but also on the kinetic characteristics of the states participating in the process. We shall now turn to the experimental results on nonequilibrium phonons. We shall first consider the question of determination of the quantum efficiency η in this case. The problem is that the dependence

(1) used to describe the luminescence quenching does not allow for the "transfer" of some of the intensity of the ZPL to the phonon wings.⁷ It is therefore necessary to separate this contribution in order to analyze the luminescence quenching, which is entirely due to the nonradiative recombination process. This can be done (as shown below) only in experiments on nonequilibrium phonons. We shall therefore consider the temperature dependence⁷ describing the luminescence in the form of a band comprising the ZPL and the phonon wings. We can show that the quantum efficiency depending on the phonon nonequilibrium can be found from

$$\delta J / J_0 = 1 - \eta / \eta_0. \quad (7)$$

where δJ and J_0 are the absolute values of the integrated intensity of the differential signal representing the ZPL and the phonon wings, and of the equilibrium low-temperature luminescence; η and η_0 are the internal quantum efficiencies in the presence of nonequilibrium phonons and under nonequilibrium conditions. Equation (7) is derived on the assumption that the crystal excitation rates in the presence and absence of nonequilibrium phonons are the same. In experiments this is achieved by using a modulation method (see, for example, Ref. 2). We can see from Eq. (6) that if $N_{ph} \rightarrow 0$ (or $T \rightarrow 0$), we have $\eta \rightarrow 1$. Therefore, experiments on nonequilibrium phonons make it possible to separate the contribution of just the nonradiative recombination to the luminescence quenching process. We therefore investigated the dependences of η on the energy and occupation numbers N_{ph} of nonequilibrium acoustic phonons generated in a sample. The first part of the task was performed using a phonon generator representing a metal film evaporated on a sample and "heated" by a laser pulse. This generator created a phonon spectrum in the frequency band 0–4 meV with a maximum at 1.5–2 meV. As pointed out above, the occupation numbers N_{ph} varied with the rate of excitation of the metal film, whereas the form of the spectrum was practically unaffected. This circumstance was convenient in the design of experiments on the dependences of the states of the spectrum of nonequilibrium phonons on the occupation numbers. We did not induce transitions between the bound state of the EICs and the states of free motion of excitons, because there were no phonons of energy 7–8 meV in the nonequilibrium spectrum. Figure 2 shows the dependence of η on the effective temperature:

$$T^* = \hbar\omega \ln^{-1} [1 + 1/N_{ph}]_{\hbar\omega=2,5 \text{ meV}}.$$

Clearly, in the temperature range $T^* = 1.3$ –20 K the "nonequilibrium" values of η agreed satisfactorily with the results of measurements of η under equilibrium conditions in the phonon subsystem. At higher effective temperatures of nonequilibrium phonons there was no rapid quenching of the luminescence of the kind observed at equivalent temperatures in the equilibrium case. This demonstrated clearly that the transitions induced by nonequilibrium phonons did not affect the states in the continuous spectrum and, consequently, they did not affect the characteristic activation energy 7.8 meV. Therefore, the experimental results on the quantum efficiency η obtained in the presence of nonequilibrium phonons yielded the energy of the excited state of the EICs and the pre-exponential factor describing, in accordance with Eq. (5), the relative probabilities of decay of the EICs in various channels and the rates of the phonon transi-

tions: $\Delta\varepsilon = \varepsilon_0 - \varepsilon_1 = 2.5$ meV, where $W_0/\tau_R/(1 + W_0\tau_N) = 7$. We shall consider later a theoretical model which can be used to calculate the probability of nonradiative transitions $1/\tau_N$, as well as the probabilities of the absorption W_1 and emission W_1 of acoustic phonons in transitions between the investigated states of the EICs, which makes it possible to find the dependence of the quantum efficiency on the temperature T or the effective temperature T^* (in the presence of nonequilibrium phonons the value of T^* is governed by the occupancy numbers of the phonon states at the frequency $\hbar\omega = \Delta\varepsilon$).

3. AUGER RECOMBINATION OF LOCALIZED EXCITONS

As mentioned earlier, the purpose of the present section is to discuss at microscopic levels all the processes governing the quantum efficiency. We shall begin with a calculation of the probabilities of nonradiative Auger decay. In the case of excitons localized at shallow donors the Auger recombination process is accompanied by the release to the conduction band of a fast electron with energy $\varepsilon(k_f)$ practically equal to the width of the band gap E_g of a semiconductor crystal. Since the Auger process involves participation of a fast electron with the quasimomentum

$$k_f = \left[\frac{2m_c}{\hbar^2} E_g \right]^{1/2},$$

a characteristic small parameter is encountered in the Auger recombination problem

$$\alpha = (k_f a)^{-1} = (E_D/E_g)^{1/2} \ll 1,$$

where

$$E_D = \hbar^2/2m_c a^2, \quad a = \hbar^2 \kappa^2 / m_c e^2,$$

a is the Bohr radius of the ground state of the donor, E_D is the corresponding binding energy, κ is the permittivity of the medium, and m_c is the electron effective [we shall ignore from now on a possible deviation from the parabolic dispersion law $\varepsilon(k)$ of the conduction band]. The physical meaning of this small parameter is as follows: the probability of finding in an EIC a particle with a large quasimomentum $k \sim k_f$ is low and since the characteristic values of the electron momenta in an EIC are of the order of a^{-1} , its smallness is described by the parameter $\alpha = a^{-1}/k_f \ll 1$. In fact the Auger process probability can be represented by series in powers of the small parameter α and in our case it is sufficient to consider the lowest order in α .

Since an EIC consists of two electrons and a hole, the wave functions of the initial and final states should be antisymmetrized in terms of the electron coordinates. It follows from Ref. 8 that in this case the Auger decay probability is

$$\tau_N^{-1} = 2\pi \hbar^{-1} \bar{\rho}(\varepsilon_f) \langle |V_a + V_b|^2 \rangle, \quad (8)$$

where the angle brackets denote averaging over the angles of emission of a fast Auger electron, $\bar{\rho}$ is the energy density for the final states in the conduction band, V_a and V_b are the matrix elements for the process of Auger recombination accompanied by release of an electron to the band from donor and exciton states, respectively⁸:

$$\begin{aligned} V_a &= \int e^{-i\mathbf{k}_f \mathbf{r}} u_c^*(\mathbf{r}) \varphi_D(\mathbf{r}) u_c(\mathbf{r}) \\ &\quad \times \frac{e^2}{\kappa |\mathbf{r} - \mathbf{r}'|} F^*(\mathbf{r}') u_v^*(\mathbf{r}') \varphi_{ex}(0) u_c(\mathbf{r}') d^3r d^3r', \\ V_b &= \int e^{-i\mathbf{k}_f \mathbf{r}} u_c^*(\mathbf{r}) \varphi_{ex}(\mathbf{r} - \mathbf{r}') u_c(\mathbf{r}) \\ &\quad \times \frac{e^2}{\kappa |\mathbf{r} - \mathbf{r}'|} F^*(\mathbf{r}') u_v^*(\mathbf{r}') \varphi_D(\mathbf{r}') u_c(\mathbf{r}') d^3r d^3r'. \end{aligned} \quad (9)$$

The notation in Eq. (9) is as follows: φ_D and φ_{ex} are the envelopes of the electron Bloch function for a donor and an exciton; F is an envelope for the motion of a hole in a bound exciton; u_c and u_v are the Bloch amplitudes for the bottom of the conduction and valence bands. We shall not specify as yet the nature of the wave functions, but we shall analyze the matrix elements V_a and V_b .

First of all, we note that the characteristic values of the coordinate $r \sim k_f^{-1}$ are considerably smaller than a and, consequently, than the quantity $r' \sim a$, which is governed by typical dimensions of the region of hole motion in a bound exciton. In this case the matrix element V_a splits into independent integrals in terms of the variables r and r' :

$$V_a = \varphi_{ex}(0) J_{cv} \int \varphi_D(\mathbf{r}) e^{-i\mathbf{k}_f \mathbf{r}} d^3r, \quad (10)$$

$$J_{cv} = \frac{e^2}{\kappa} \int \frac{1}{r'} F^*(\mathbf{r}') u_v^*(\mathbf{r}') u_c(\mathbf{r}') d^3r'. \quad (11)$$

We shall now discuss the integral J_{cv} representing the overlap of the hole and electron wave functions. The symmetry of the wave functions at the bottom of the conduction band and at the top of the valence band is very different in the case of direct-gap semiconductor crystals. For example, in the case of CdS the Bloch amplitudes u_c have the Γ_7 symmetry and transform like the s function:

$$u_c = |s, \pm 1/2\rangle,$$

whereas

$$u_v = |2^{-1/2}(x \pm iy); \pm 1/2\rangle$$

has the symmetry of the Γ_9 type (and the spin functions $|1/2\rangle$ and $|-1/2\rangle$ describe states with the spin projection $m_s = \pm 1/2$ along the optic axis $Z \equiv c$ of the crystal, which is selected as the quantization axis of the states in the valence band). The projections of the total momentum of the states at the bottom of the conduction band and at the top of the valence band with the same spin orientation differ by $\Delta m = \pm 1$. This symmetry gives very definite selection rules for the dipole matrix elements of an optical interband transition:

$$d_{cv} = \langle u_v | \mathbf{r} | u_c \rangle,$$

which is polarized at right-angles to the Z axis. We shall show that these symmetry properties are important for the calculation of the matrix element of the Auger decay of an EIC or, more exactly, they determine the magnitude of the overlap integral J_{cv} . We shall do this by finding the wave function of hole motion $F(\mathbf{r})$. The motion of the center of mass of an exciton in an EIC can be identified with the motion of a heavy hole which exhibits small oscillations in a spherically symmetric potential created by the electron component of the EIC. In the adiabatic approximation in respect

of the parameter $m_c/m_h \ll 1$ considered by us the amplitudes of the hole oscillations are sufficiently small so that expanding the "electron" potential near the equilibrium position, we obtain oscillatory motion of a hole with the wave function of the ground state⁸:

$$F_0(\mathbf{r}) = F_{\parallel}(z)F_{\perp}(\boldsymbol{\rho}),$$

$$F_{\parallel}(z) = \pi^{-1/4} \Delta_{\parallel}^{-1/2} \exp(-z^2/2\Delta_{\parallel}^2), \quad (12)$$

$$F_{\perp}(\boldsymbol{\rho}) = \pi^{-1/2} \Delta_{\perp}^{-1} \exp(-\rho^2/2\Delta_{\perp}^2), \quad (13)$$

where Δ_{\parallel} and Δ_{\perp} are the amplitudes of the hole oscillations along directions parallel and perpendicular to the optic axis Z . The ratio of Δ_{\parallel} and Δ_{\perp} is governed by the anisotropy of the effective mass of a hole in the band Γ_0 :

$$\Delta_{\perp}/\Delta_{\parallel} = (m_{\parallel}/m_{\perp})^{1/4},$$

where $m_{\perp} = 0.7m_0$ and $m_{\parallel} = 5m_0$ for CdS. In calculation of the energies of the corresponding oscillations

$$1/2 \hbar \omega_{\parallel} = \hbar^2/2m_{\parallel}\Delta_{\parallel}^2, \quad \hbar \omega_{\perp} = \hbar^2/m_{\perp}\Delta_{\perp}^2$$

it is necessary to know the "stiffness" of the potential created by the electron system of the EIC in the hole motion case.⁸ Therefore, the values of the oscillation energy are quite readily calculated using the available models of the EIC potential and can be found for the majority of specific cases.⁹ It is more important to consider the reasons for the suppression of the Auger recombination process in the ground state of an EIC and of the strong Auger recombination in the excited state. We can readily show that the first excited states of an EIC are formed by a combination of vibrational excitations along the Z axis and along directions perpendicular to Z (one should point out that in the case of adiabatic systems with $m_c/m_h \ll 1$ the electron excitations are characterized by excited states of the EIC higher on the energy scale). We shall now concentrate our attention on the excited state of the motion of a hole with the projection of the angular momentum $m = \pm 1$ along the axis and with the following envelope of the Bloch functions

$$F_{m=\pm 1}(\mathbf{r}) = F_{\parallel}(z)F_{\perp}(\boldsymbol{\rho}) \rho e^{\pm i\varphi}/\Delta_{\perp} \equiv F_{\parallel}(z)F_{\perp}(\boldsymbol{\rho})(x \pm iy)/\Delta_{\perp}. \quad (14)$$

It should be noted that rotation about the Z axis effectively represents a linear combination of oscillations of a hole polarized in a plane perpendicular to the optic axis Z of a crystal. In order to avoid terminological confusion, we shall call the momentum due to the envelopes $F(\mathbf{r})$ the rotational momentum.

The wave-function overlap integral J_{cv} vanishes if a hole is in the ground state. This is a consequence of the symmetry of the system: the wave function of the ground state of the system is always even and integration of this wave function in the expression for J_{cv} together with the odd function $u_v(\mathbf{r})$ and any other radial functions gives zero net result. The same result can be obtained using the properties of periodicity of the Bloch amplitudes $u_c(\mathbf{r})$ and $u_v(\mathbf{r})$ and calculating J_{cv} by expanding a smooth envelope in terms of the intracell variable ξ when the coordinate of a particle is $\mathbf{r} = \mathbf{R} + \xi$ and \mathbf{R} are the vectors of the lattice sites in a crystal:

$$J_{cv} = \int d^3R \int \frac{d^3\xi}{v_0} |\mathbf{R} + \xi|^{-1} F_0^*(\mathbf{R} + \xi) u_v^*(\xi) u_c(\xi)$$

$$= \langle u_v | u_c \rangle \int d^3R R^{-1} F_0^*(\mathbf{R}) + \langle u_c | \xi | u_c \rangle \int d^3R \nabla_R \left[\frac{F_0^*(\mathbf{R})}{R} \right]$$

$$= \mathbf{d}_{cv} \int d^3R \nabla_R [R^{-1} F_0^*(\mathbf{R})] = 0,$$

where v_0 is the volume of a unit cell in the crystal. We can also say that a state in the valence band may be filled as a result of Auger recombination, and this can be described by altering the projection of the momentum by $\Delta m = \pm 1$ in the case of an "exciton" electron (this is obtained because of the Bloch amplitudes which differ by $\Delta m = \pm 1$). The EIC then dissociates under the action of internal forces, so that the total momentum (or more correctly its projection along the Z axis) remains unaltered. Consequently, the only variant of the decay is the transfer of the momentum to a fast electron, which is formed as a result of such a process. The case $r \sim k_f^{-1} \ll r'$ under discussion corresponds to the retention in the Coulomb electron-electron interaction of only the monopole term, which corresponds to a transition without the transfer of momentum to a fast electron. Clearly, such a process is forbidden by the law of conservation of momentum, as is demonstrated by the vanishing of the corresponding matrix element. Naturally, a transition accompanied by the transfer of momentum to a fast electron is allowed if we include terms of higher order in the multipole expansion of the electron-electron interaction $e^2/\kappa|\mathbf{r} - \mathbf{r}'|$. In fact, the process of transfer of the momentum $\Delta m = \pm 1$ corresponds to inclusion of the dipole term in the expansion

$$\frac{e^2}{\kappa|\mathbf{r} - \mathbf{r}'|} = \frac{e^2}{\kappa r'} + \frac{e^2}{\kappa r'} \frac{\mathbf{r}\mathbf{r}'}{r'^2} + \dots \quad (r \ll r').$$

However, the dipole terms contain a small parameter of the type $r/r' \sim \alpha$ (since $r \sim k_f^{-1}$ and $r' \sim \Delta_{\perp} \sim a$), so that the probability of the Auger process gives rise to an additional small term $\sim \alpha^2$. Therefore, the process of the Auger decay of the ground state of an exciton is accompanied by the transfer of momentum $\Delta m = \pm 1$ to a fast electron and it is allowed only in orders higher in terms of the parameter α than the Auger process without the transfer of momentum.

In the case of an excited state of an EIC $F_{\pm 1}(\mathbf{r})$ of Eq. (14) this forbiddenness is lifted. In fact, the total momentum of an EIC including the rotational motion of a hole is zero, so there is no need to "transfer" momentum to the fast electron created by the Auger decay. The overlap integral J_{cv}^1 which appears in the case of the Auger recombination of an excited state of an EIC can be calculated directly by the substitution in Eq. (14):

$$J_{cv}^1 = \frac{e^2}{\kappa} \int \frac{1}{r'} F_{\parallel}(z') F_{\perp}(\boldsymbol{\rho}') \frac{(x' + iy')^*}{\Delta_{\perp}} u_v^*(\mathbf{r}') u_c(\mathbf{r}') d^3r'$$

$$= \frac{e^2}{\kappa} \frac{d_{cv}}{\Delta_{\perp}} \int \frac{d^3R}{R} F_{\parallel}(z) F_{\perp}(\boldsymbol{\rho})$$

$$= 2\pi (\pi^{1/2} \Delta_{\parallel})^{1/2} \left(\frac{d_{cv}}{\Delta_{\perp}} \right) \frac{e^2}{\kappa}, \quad \mathbf{R} = (z, \boldsymbol{\rho}), \quad (15)$$

where d_{cv} is the dipole moment of a matrix element of an interband transition.¹¹ Therefore, the rotational motion of a hole simulates the dipole matrix element of the transition d_{cv} , but because of the smoothness of the hole envelope (varying over a distance of the order of Δ_{\perp}) the matrix ele-

ment V_a contains a small factor d_{cv}/Δ_1 . The second integral in the expression for V_a given in Eq. (10) corresponds to the wave function of a donor in the k representation when the quasimomentum is large: $k \sim k_f \gg a^{-1}$. Using the equation for the donor wave function in the k representation, we obtain an asymptotic expression for

$$\tilde{\varphi}(\mathbf{k}) = \int \varphi_D(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d^3r$$

if $k \gg a^{-1}$:

$$\begin{aligned} \tilde{\varphi}(\mathbf{k}) &= -\frac{1}{\varepsilon(\mathbf{k}) + E_D} \int U(\mathbf{k}-\mathbf{k}') \tilde{\varphi}(\mathbf{k}') \frac{d^3k'}{(2\pi)^3} \\ &\approx -\frac{U(\mathbf{k})}{\varepsilon(\mathbf{k})} \int \tilde{\varphi}(\mathbf{k}') \frac{d^3k'}{(2\pi)^3} = -\frac{2m_c}{\hbar^2 k^2} U(\mathbf{k}) \varphi_D(0), \end{aligned} \quad (16)$$

where $U(\mathbf{k})$ is the Fourier component of the impurity potential and $\varphi_D(0) = (\pi a^3)^{-1/2}$. Clearly, in the case under discussion the main role is played by short distances $r \sim k_f^{-1}$ near the donor center, where k_f^{-1} is of the order of the lattice constant. In this case the existence of a "core" part of the impurity potential and its variation over scales comparable with the lattice constant increase $\tilde{\varphi}(k_f)$ considerably compared with the long-range Coulomb part of the impurity potential. The "core" part $U(\mathbf{k})$ does not determine the energy of a shallow donor, where $k \sim a^{-1}$ are important, and can give rise only to a weak chemical shift. Therefore, if $k \sim k_f$, we have $\tilde{\varphi}(\mathbf{k}) = \text{const}/k^2$. The value of $\varphi(k)$ can be calculated exactly for the zero-radius potential:

$$\tilde{\varphi}(k_f) = [8\pi(2m_c E_D / \hbar^2)^{1/2}]^{1/2} / k_f^2 = (8\pi\alpha)^{1/2} k_f^{-3/2}, \quad (17)$$

which will be used in our later estimates. Substituting Eqs. (17) and (15) into Eq. (10), we obtain the following expression for V_a :

$$V_a = 4\pi e^2 \kappa^{-1} (d_{cv}/\Delta_1) (2\pi^{1/2} \Delta_1)^{1/2} \alpha^2. \quad (18)$$

We must point out once again that in the calculation of the matrix element V_a for the Auger transition from the ground state of an EIC we obtain, because of the forbiddenness rules, the quantity containing a higher degree of the small parameter α .

We shall not discuss in detail the procedure for calculation of the matrix element V_b , but simply point out that it has a smaller value than V_a (Ref. 8). The probability of the Auger recombination of an EIC in an excited state is obtained by the substitution of Eq. (18) into Eq. (8):

$$\tau_N^{-1} = 64\pi^{3/2} (E_g/\hbar) \alpha^5 (d_{cv}^2/\Delta_1 a) (m_\perp/m_\parallel)^{1/2}. \quad (19)$$

It should be pointed out that in the framework of the adiabatic approximation used by us we have $m_c \ll m_h$, and the binding energies of an exciton and a shallow donor are equal, but the results obtained above can be generalized also to the case of deep impurity centers when $E_D > E_{ex}$. Therefore, the above formula for the nonradiative Auger decay probability is expressed in terms of microscopic parameters of the semiconductor crystal (E_g , d_{cv} , and α) and in terms of the parameter Δ_1 of an excited state participating in the process. It is interesting to obtain numerical estimates of the Auger decay rate. The dipole matrix element d_{cv} can be obtained from

the experimental data on optical transitions exhibited by excitons localized at neutral donors.¹ The characteristic amplitudes of the oscillations of a hole can be estimated to be of the order of the value which agrees with the "dimensions" of the wave function for bound excitons obtained from the formula

$$\Delta_\perp \sim [\hbar^2/2m_\perp \varepsilon_0]^{1/2},$$

where ε_0 is the binding energy of the center of mass of an exciton. The Bohr radius of a donor is $a = 21 \text{ \AA}$, whereas the small parameter is $\alpha = 0.13$. Substitution of these values in Eq. (19) gives the Auger recombination time which is considerably shorter than the characteristic optical decay times of excitons in CdS: $\tau_N \sim 10^{-10} \text{ s}$. Therefore, the excited state of an EIC may represent a very effective channel for nonradiative decay, but its activity requires special conditions. In fact, at low temperatures, which are usual in the studies of bound excitons, an EIC is in the ground state and an excited state is poorly populated, so that the Auger recombination of bound excitons is unimportant. At high temperatures, when the dissociation of EICs takes place, the fraction of excitons localized at neutral donors is small, so that their role in the formation of the spectra is also unimportant. Consequently, the nonradiative channel under discussion is effective at temperatures in the range $\Delta\varepsilon \lesssim T \lesssim \varepsilon_0$. The role of this channel is manifested most strikingly when an EIC is subjected to a flux on nonequilibrium phonons, which transfer the EIC from the ground state to an excited one.

We shall conclude this section by noting that the parameters of the EIC potential in different substances may be those required for the Auger process to an excited state (with a specific projection of the linear or rotational momentum in the case of spherically symmetric models) which lie in the continuous spectrum of the exciton band. In this case the Auger process probability is considerably less than for a localized state under discussion here, so that all the effects of the competition between the radiative and nonradiative channels may disappear.

We shall now calculate the probabilities of phonon transitions between the ground and excited states of an EIC. The transition between the vibrational levels ε_0 and ε_1 have the following probabilities deduced using the conventional theory of the interaction of carriers with acoustic phonons:

$$W_{\downarrow, \uparrow} = W_0 (N_{ph} + 1/2 \pm 1/2),$$

$$W_0 = \frac{w^2}{2\pi\hbar\rho s^2} q^3 \left\langle \left| \int F_1^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} F_0(\mathbf{r}) d^3r \right|^2 \right\rangle, \quad (20)$$

where N_{ph} represents the occupation numbers of phonons at the frequency of a transition $\hbar\omega = \Delta\varepsilon$: w is the deformation potential constant; ρ is the density of the crystal; s is the velocity of sound; q is the momentum of an acoustic phonon for the relevant transition; the angular brackets denote averaging of the direction of the phonon momentum. In the derivation of Eq. (20) we ignored a possible anisotropy of the parameters w and s of a crystal. Using the explicit forms of the wave functions of the ground (13) and excited (14) states, we obtain the following expression for the phonon transition probabilities:

$$\begin{aligned} W_{\downarrow, \uparrow} &= \frac{w^2}{2\pi\hbar\rho s^2} \left(\frac{q}{2\Delta_\perp^2} \right) (N_{ph} + 1/2 \pm 1/2), \\ q &= \Delta\varepsilon/\hbar s, \quad m_\perp/m_\parallel \ll 1. \end{aligned} \quad (21)$$

Substitution of the numerical values of the parameters for a CdS crystal gives $W_{1,1} \sim 10^{11}(N_{ph} + 1/2 \pm 1/2) s^{-1}$ ($W_0 \approx 10^{11} s^{-1}$). We can see that the Auger process rate is less than the characteristic rate of phonon transitions at $N_{ph} \sim 1$, i.e., than the probability of a transition (accompanied by the emission of phonons) from the excited to the ground state. Using Eq. (21), we can now find the numerical values of the coefficients in the expression for the quantum efficiency of the luminescence of EICs subject to the condition of irradiation with nonequilibrium phonons:

$$\eta = \left[1 + \frac{W_1 \tau_R}{W_1 \tau_N + 1} \right]^{-1} \approx (1 + 11N_{ph})^{-1}, \quad (22)$$

where $\tau_R = 0.5 \times 10^{-9}$ s, in accordance with the experimental observations reported in Ref. 1. The temperature dependence of the quantum efficiency $\eta(T)$ is given by the relationship

$$\eta(T) \approx [1 + 11N_{ph} + 660(T/\epsilon_0)^{1/2} \exp(-\epsilon_0/T)]^{-1}, \quad (23)$$

where the Planck formula is used for the equilibrium value of N_{ph} . We can see from Fig. 2 that calculations based on Eqs. (22) and (23) give a dependence which is in good agreement with the experimental results for equilibrium and nonequilibrium phonon subsystems. It should be stressed that in calculation of the quantum efficiency of the luminescence of EICs we used no fitting parameters.

CONCLUSIONS

It follows that quenching of the exciton luminescence in direct-gap semiconductors (including cadmium sulfide) is due to nonequilibrium and equilibrium phonons and is associated with a transition of an EIC to an excited state. In the ground EIC state the Auger process is suppressed. This follows from the observation that for the same symmetry of the valence and conduction bands the total momentum of the corresponding state differs from zero. We need to transfer this momentum to a fast electron which reduces considerably the Auger process probability.

The active states responsible for the Auger decay are the excited states of EICs for which the total momentum vanishes. Experiments have revealed a new type of local vibrations of an EIC associated with the motion of a hole in the adiabatic potential created by the core of the donor and two electrons. The corresponding centers can be sources of resonance scattering of phonons in semiconductor crystals.

It should be pointed out that the process under consideration plays an important role in recombination effects also in other semiconductors at low temperatures. Clearly, quenching of the EIC luminescence characterized by a low activation threshold, observed for a number of semiconductor crystals and particularly for GaAs (Ref. 6), is due to the Auger decay from excited states of an EIC. This conclusion is supported by the observation that the appearance of free holes was observed simultaneously⁶ with quenching of the EIC luminescence.

¹The integral J_{cv}^1 can be calculated also by splitting into cells. Then, the integration procedure is carried out inside any cell with respect to ξ because the wave function of the rotational motion of a hole gives rise to a dipole matrix element in the zeroth order without expansion of the envelope $F(\mathbf{r})$ with respect to ξ , as was done for the ground state.

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