

Secondary excitons in alkali halide crystals

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The peculiarities of multiplication of electronic excitations have been investigated in wide-gap alkali halide crystals where, in contrast to semiconductors, free and self-trapped excitons as well as free and self-trapped holes coexist. In particular, the luminescent methods for separation and quantitative investigation of the formation processes of secondary excitons have been elaborated. These methods are based on the investigation of the dependence of the intensity ratio for two different emissions from the same crystal as a function of the energy of exciting photons. The excitation spectra of triplet (π) and singlet (σ) emissions of self-trapped excitons as well as of impurity luminescence have been measured, using synchrotron radiation of 12 to 32 eV, for high-purity KI, KBr, and doped KI:Na, KI:Tl, KBr:I, KBr:Tl crystals at 8 K. The analysis of the intensity ratio spectra for two emissions allowed us to separate the regions of secondary triplet exciton formation in KI (13–15 and 26.5–29 eV) and KBr (15–17 and 28–30 eV). The threshold photon energy for the formation of a secondary exciton has been experimentally determined to be equal to 13.1 ± 0.2 eV in KI and 15.2 ± 0.2 eV in KBr. The probability of secondary exciton formation by hot photoelectrons reaches the main maximum at 0.5–0.7 eV above the value of threshold energy. The energy transport to impurity centers by free triplet secondary excitons has been revealed in KI:Na and KBr:I crystals. The decay of $3p^5 4s$ cation excitons in KI and KBr, generated by 20-eV photons, leads to the formation of a double amount of electron-hole pairs.

I. INTRODUCTION

In semiconductors electronic excitations (EE's) formed by radiation in the long-wavelength region of intrinsic absorption are being investigated in detail. The effect of multiplication of electron-hole ($e-h$) pairs was revealed at the irradiation of semiconductors by photons with energy exceeding the value of the energy gap E_g by several times. Inelastic scattering of hot photoelectrons (photoholes), created due to the photoabsorption, on valence electrons leads to the formation of two to three $e-h$ pairs (see, e.g., Refs. 1 and 2).

In comparison with semiconductors EE's have some peculiarities in wide-gap ionic crystals. In alkali halides (AH's) a strong electron-phonon interaction causes a transformation of a hole into a self-trapped state. As a result, a dihalide X_2^- molecule located at two anion lattice sites, i.e., V_K center, is formed.³ At low temperatures V_K centers are immobile and their hopping motion becomes possible at $T=100-200$ K.³ The phenomenon of self-trapping of excitons was also detected for AH's at low temperatures. In some crystals (NaI, NaBr), a X_2^- hole component of a self-trapped exciton (STE) can be considered as a V_K center, while in the majority of AH's the symmetry of the STE differs from the symmetry of the V_K center.⁴

In spite of a strong electron-phonon interaction in the relaxed exciton states, the coexistence of free excitons (FE's) and STE's, caused by an activation barrier between the states of FE's and STE's, has been revealed at liquid helium temperatures in alkali iodides and in some bromides.⁵ For molecular crystals the same effect was predicted by Rashba.⁶ The energy transfer by FE's at large distances to luminescent impurity centers⁷ as well as the typical edge emission at the

direct optical formation of FE's (Ref. 8) appear due to the coexistence of FE's and STE's in AH's. Although there is no activation barrier between energy states of free and self-trapped holes, the holes, optically formed at band-to-band transitions, have time to migrate before self-trapping at tens of interanion distances and to ionize impurity centers.^{9,10}

The coexistence of free and self-trapped EE's in AH's causes the fundamental peculiarities in the processes of multiplication of electronic excitations (MEE's). Besides the universal mechanism for semiconductors and insulators, which involves the creation of secondary $e-h$ pairs by hot photoelectrons, the excitonic mechanism of MEE's has been detected in AH's doped by luminescent impurities.¹¹ This mechanism provides the energy transport to impurity centers. The investigation of the excitonic mechanism of MEE's has been extended to low temperatures using the emission of STE's.¹²⁻¹⁴ However, several secondary effects (selective reflection of radiation by a crystal surface, nonradiative decay of mobile EE's at the surface, etc.) impede the investigation of the excitonic mechanism. Recently, we have developed a method which allowed us to separate and quantitatively investigate, in KBr, the process of secondary exciton (SE) formation by synchrotron radiation (SR) due to the inelastic scattering of photoelectrons on valence electrons.¹⁵ This method is based on the analysis of the intensity ratio spectrum for two different emissions from the crystal, one of which is induced mainly by excitons and the other by $e-h$ recombinational processes. We have later succeeded in applying this method to NaCl (Ref. 16) and $YAlO_3$ crystals.¹⁷

The aim of the present study was to investigate quantitatively the formation processes of SE's or $e-h$ pairs by SR for pure and doped AH's at 8 K. A comparison of our experi-

mental data with the results on MEE processes in AH's, previously obtained either by other optical¹⁸ or photoelectric^{19–22} methods, allowed us to prove the existence of SE's in AH's and to discuss the detailed mechanisms of their formation.

II. LUMINESCENT METHODS OF INVESTIGATION OF SECONDARY EXCITONS

The energies of optical formation of excitons are $E_e=5.5–8.5$ eV and the energy gaps are $E_g=6–9$ eV for alkali iodides, bromides, and chlorides. Consequently, secondary excitons in these AH's can be formed by photons of $h\nu>E_g+E_e=11–17$ eV. We used SR of 5–32 eV in order to investigate excitons and especially SE's in AH's at 8 K. At these conditions an intensive luminescence of STE's is observed and the mean free path of FE's before self-trapping in iodides and in some of the bromides is about several thousands of the lattice constant.^{5,8}

The experiments were carried out at beam line 52 in MAX-Laboratory in Lund, Sweden (550 MeV storage ring). Relevant details of the experimental setup have been described in previous papers.^{15,17} The excitation spectra were measured at equal quantum intensities of the excitation falling onto the crystal. A typical optical slit width of a primary monochromator was 0.16–0.24 nm. In order to obtain a fresh surface, the crystals were cleaved *in situ* under ultrahigh vacuum conditions (10^{-9} mbar). Cubic-face-centered KI and KBr crystals of high purity as well as crystals doped by homologous impurity ions (KBr:I and KI:Na) were the main objects of the present study. Single KBr and KI crystals were grown by the Stockbarger method from salts after a special purification cycle involving a melt treatment in Br_2 gas flow (for KBr) and a manifold recrystallization from the melt. The content of impurity ions was on the level of 0.01–3 ppm. Only the concentration of Cl^- in KBr and Br^- in KI was about 20 ppm. The content of impurity ions in a doped crystal was estimated by means of optical methods and is given in parentheses: KBr:Tl (300 ppm), KBr:I (50 ppm), KI:Tl (100 ppm), and KI:Na (10 ppm).

Quantitative studies of SE formation and the separation of this process from electron-hole formation are based on the investigation of the efficiency ratio spectrum for two different emissions from the same crystal. One of the selected emissions (intrinsic or impurity) should be mainly excited by triplet excitons, whereas the other emission should be due to the recombination of electrons with holes. We have recently applied this method to pure KBr and NaCl, where the triplet π component of STE luminescence can be mainly excited via the excitonic mechanism, while the singlet σ luminescence of STE's arises due to the $e-h$ mechanism.^{15,16} The reasons for the dominant appearance of STE π emission on the direct optical formation of excitons with $n=1$ as well as σ emission on the recombination of electrons with self-trapped holes have recently been discussed in detail.²³ The optical formation of FE's with $n=1$ leads mainly to the creation of "off-center STE's," while the recombination of electrons with relaxed holes causes the formation of "on-center STE's."^{4,23,24}

We have elaborated another version of the efficiency ratio method, which is based on a difference in the values of mean

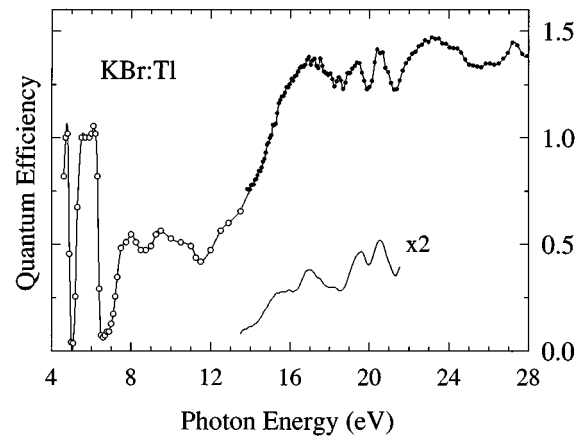


FIG. 1. Excitation spectra of Tl^+ -center emission in a KBr:Tl crystal at 295 K (\circ and \bullet) and 72 K (solid line). Radiation from a discharge source was used in measurements (\circ) in the spectral range up to 13.5 eV. The quantum efficiency of Tl^+ emission on the direct excitation of impurity ions by 4.8-eV photons is taken equal to unity.

free path l of free excitons and holes before self-trapping in AH's. This difference is caused by the existence of an activation barrier between the energy states of FE's and STE's and its absence at the self-trapping of holes.^{5,6} At low temperatures the values of l for holes are significantly smaller than those for FE's.⁵ This is why, at optimum concentration of luminescent impurity centers, the excitonic mechanism leads to more effective excitation of impurity luminescence than the $e-h$ mechanism. We have recorded sequentially the excitation spectra for two different emissions from the crystal using identical recording conditions (the same slit width, step size, etc.). The influence of a selective reflection of SR by a crystal surface can be excluded and the near-surface losses significantly reduced if we use the intensity ratio spectrum for these two emissions, connected with excitonic and $e-h$ mechanisms, respectively.

III. ELECTRON-HOLE MECHANISM OF MEE'S

In cubic AH's the minimum of an s -like conduction band and the top of a p -like valence band are located at the Γ point of the Brillouin zone. An analysis of the optical characteristics of KBr and KI has shown that at 10 K the value of E_g equals 7.55 and 6.31 eV, respectively.²⁵ Figure 1 presents the excitation spectrum of Tl^+ center luminescence for a KBr:Tl crystal at 295 K. The direct excitation of Tl^+ impurity centers in the regions of A , B , and C absorption bands (4.8, 5.6, and 6.0 eV, respectively) leads to the appearance of a broadband emission (3.2–4.2 eV) with a quantum yield $\eta=0.9\pm 0.1$.¹⁴ The efficiency of Tl^+ luminescence is low on the direct formation of excitons by 6.6 ± 0.1 -eV photons, and the value of η starts increasing at $h\nu>7$ eV up to a practically constant value $\eta\approx 0.5$ at 7.6–14 eV. The $e-h$ pairs are formed at band-to-band transitions. After a fast relaxation, holes undergo the transformation into a self-trapped state forming V_K centers in KBr.³ At 295 K, the V_K centers are highly mobile and interact with Tl^+ , thereby forming Tl^{2+} centers. The recombination of an electron with Tl^{2+} takes place via an excited state of Tl^+ and leads to the appearance

of TI^+ luminescence. In KBr:Tl (300 ppm), less than half of the e - h pairs recombine with TI^+ emission, while the recombinations in other e - h pairs mainly induce the formation of point defects (F centers, etc.).¹⁴ The efficiency of TI^+ emission sharply increases at $h\nu > 14$ eV, and the value of η exceeds unity in the range 15–28 eV. Similar to many other systems,¹¹ the so-called effect of photon multiplication is observed in KBr:Tl . More than one e - h pair is formed after the absorption of one photon, causing the appearance of recombinational luminescence with $\eta > 1$. The quantum yield of the photoelectron emission also exceeds unity in the region of 22–29 eV in a thin film of KBr at 295 K.^{19,22}

According to Fig. 1, cooling of KBr:Tl down to 72 K freezes the hopping diffusion of V_K centers and decreases the efficiency of TI^+ center luminescence by 7–8 times. However, even at 72 K a part of the holes, generated by 17–22-eV photons, is still able to reach TI^+ ions and ionize them with subsequent radiative recombination of electrons and TI^{2+} centers. This effect can be interpreted (similar to other systems^{9,10}) as a low-temperature migration of hot primary and secondary holes toward impurity centers. The coexistence of free and self-trapped holes determines two different e - h mechanisms of MEE's in AH's. It is important to mention that the threshold energies for these two mechanisms at $T \neq 0$ K can be different because relaxed or partly relaxed holes are formed not only due to photoionization of the anions situated at regular lattice sites, but also on the ionization, by photons of lower energy, of halogen ions which are displaced from equilibrium positions on account of thermal fluctuations. In the last case a hole is formed directly in a self-trapped state and can participate only in a hopping migration, not in a coherent one.

IV. EXCITONIC MECHANISMS OF MEE's

Besides e - h processes, also excitonic processes play an important role at the irradiation of a semiconductor by photons, the energy of which is lower than the value of E_g . However, the contribution of excitonic processes to semiconductor absorption at $h\nu > E_g$ is extremely low due to a large effective radius of an exciton and a small value of the oscillator strength. In wide-gap AH's an effective exciton radius is comparable with the lattice constant and the oscillator strength for transitions with the formation of excitons is large. This circumstance significantly facilitates the investigation of the excitonic processes even on the background of intensive band-to-band transitions.

Let us consider some typical results by the example of KI and KI:Na crystals. Figure 2 shows the emission spectra of KI on the excitation by photons of various energy. The irradiation of the crystal by 7.7- or 13-eV photons, which create separate electrons and holes, causes the appearance of two well-known emission bands at 4.15 and 3.31 eV. These singlet (σ) and triplet (π) components of STE emission arise due to the recombination of electrons with relaxed self-trapped holes. The so-called E_x emission (2.8–3.2 eV) can be also excited in the region of the generation of e - h pairs at 8 K. The E_x emission band is not elementary and has not been strictly interpreted yet. In some works the E_x emission is interpreted as the third emission band of STE's,²⁴ while a part of the emission in this spectral region is undoubtedly

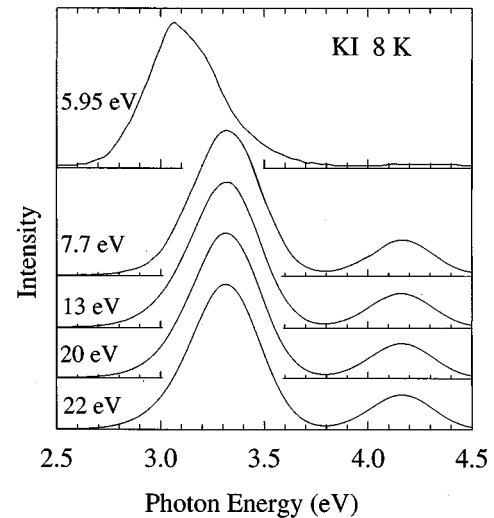


FIG. 2. Emission spectra of a KI crystal on the excitation by 5.95–22-eV photons at 8 K. Every emission spectrum is normalized to unity at its maximum.

connected with the radiative annihilation of STE's near homologous impurity ions (Br^- and Na^+).²⁶ According to Fig. 2 the irradiation of KI by 5.95-eV photons causes the effective emission of 2.8–3.2 eV, while σ and π emissions of STE's are weakly excited in this case. The 5.95-eV photons generate $\Gamma(1/2,3/2)$ orthoexcitons (the first number indicates the angular momentum of an electron j_e and the second of a hole j_h) with total angular momentum $J=1$.²⁶ Photons of 5.95 and 5.83 eV effectively excite the emission at 2.85 and 3.05 eV caused by the decay of STE's near Na^+ or Br^- impurity ions, respectively, in KI.²⁶

Our experimental data for KI and KI:Na show that the intrinsic luminescence of STE's dominates on the recombinational formation of STE's with the participation of relaxed V_K centers. On the other hand, the impurity emission, connected with small concentration of impurity centers (1–10 ppm), can be effectively excited due to the direct optical formation of $\Gamma(1/2,3/2)$ excitons. The same result was obtained earlier for KI and KI:Tl and interpreted as the direct manifestation of the coherent migration of FE's at large distances toward impurity centers at 8 K.^{5,7} The activation barrier between energy states of FE's and STE's can be overcome due to thermal fluctuations on heating of KI up to 20–50 K. This causes the increase of STE π emission and the decrease of the mean free path of FE's as well as lowering of the efficiency of impurity luminescence. The edge emission of FE's sharply decreases in the same temperature range 20–50 K also.^{5,8} It was shown earlier²⁷ that the recombination of electrons with V_K centers does not excite the edge emission of FE's. By means of these well-known peculiarities of excitons, we have succeeded in separating the e - h and the excitonic mechanisms of MEE's in doped KI. Even in a crystal with a small concentration of impurity ions, FE's, with large values of the free mean path, can excite an emission of impurity ions, whereas holes do not reach impurity centers at low temperatures because of their fast self-trapping. The subsequent recombination of electrons with self-trapped holes leads mainly to the appearance of STE σ emission.

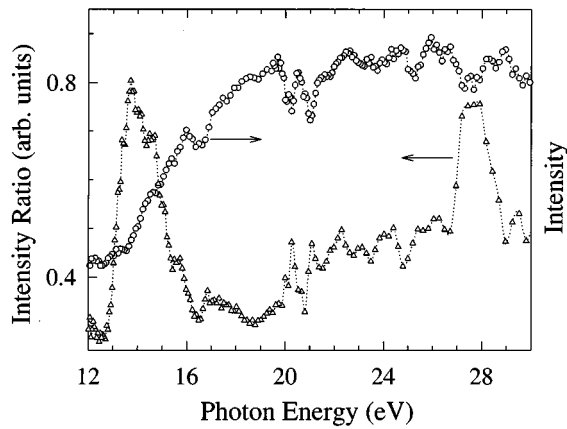


FIG. 3. Excitation spectrum of 4.15 eV σ emission of STE's (\circ) and the intensity ratio spectrum (Δ) for impurity emission of Na^+ centers (2.9 eV) and σ emission of STE's measured for a KI:Na crystal at 8 K.

In Fig. 3 we present the excitation spectrum of STE σ emission (4.15 eV) measured in the region of 12–30 eV for KI:Na at 8 K. The intensity of σ emission (I_σ) increases between 13.5 and 19 eV and is approximately constant in the range 19–30 eV. Similar to other AH's, the numerous minima of I_σ in KI:Na correlate with the intrinsic reflection (absorption) maxima for a KI crystal.²⁸ We have measured the excitation spectrum of 2.9 eV luminescence which corresponds mainly to the π emission of STE's near Na^+ impurity centers. Figure 3 also shows the intensity ratio spectrum for this STE emission near Na^+ and for STE σ emission (I_{Na}/I_σ). The I_{Na}/I_σ spectrum represents the ratio of two processes, the excitation of impurity emission by FE's and the recombinational formation of STE's. The value of I_{Na}/I_σ is practically constant at 12–13 eV, sharply increases in the region of 13–14 eV, and then decreases in the range up to 16.5 eV. The second maximum of I_{Na}/I_σ occurs at 26.5–29.0 eV. We interpret these two maxima of I_{Na}/I_σ as an increased efficiency of anion exciton formation in these spectral regions. The formation of SE's is observed on the background of photocreation of primary e - h pairs (12–14.5 eV) and of primary as well as secondary e - h pairs (14.5–19 eV). Besides electron transitions between valence and conduction bands, the transitions starting from the core $5s^2$ shell of the I^- ions also occur in the range 16–19 eV in KI. In this region the complicated structure of the spectra, presented in Fig. 3, can be partly connected with the transitions from the core $5s^2$ I^- shell.

A fragment of the I_{Na}/I_σ spectrum at 12–18 eV for KI:Na is reproduced in Fig. 4(a) together with the intensity ratio spectrum I_{TI}/I_σ for total emission of TI^+ centers (there are two components of TI^+ emission at 3.7 and 2.8 eV) and STE σ emission in KI:Tl at 8 K. There are typical maxima of I_{Na}/I_σ and I_{TI}/I_σ in the region 13–15 eV. The concentration of impurity ions in KI:Tl (100 ppm) is by an order of magnitude higher than in KI:Na (10 ppm). This explains the more obvious (relative to the regions 12–13 and 15–18 eV) maximum in KI:Na. In KI:Tl the TI^+ emission can be excited not only by secondary FE's, but also due to the recombination of electrons with TI^{2+} centers formed by hot (unrelaxed) holes. In KI:Na the mean free path of holes before self-

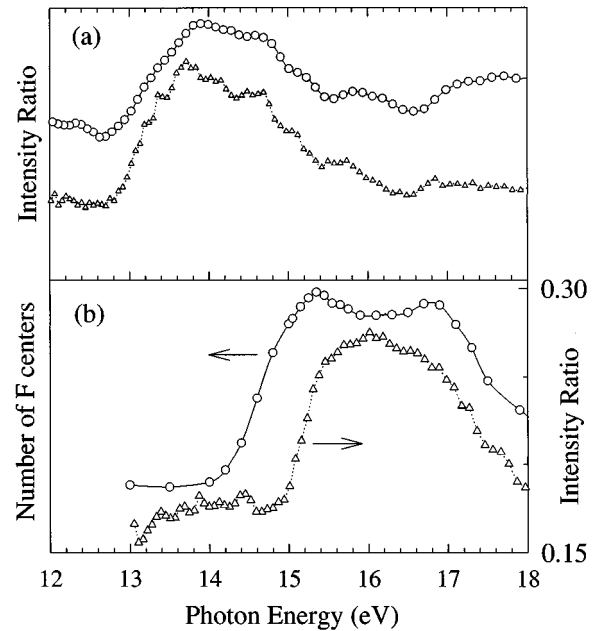


FIG. 4. (a) The intensity ratio spectrum (\circ) for total emission of TI^+ centers (components at 3.7 and 2.8 eV) and σ emission of STE's (4.15 eV) measured for a KI:Na crystal at 8 K. The intensity ratio spectrum (Δ) for impurity emission of Na^+ centers (2.9 eV) and σ emission of STE's measured for a KI:Na crystal at 8 K. (b) The intensity ratio spectrum (Δ) for π (2.3 eV) and σ (4.42 eV) emissions of STE's measured for a KBr crystal at 8 K. The spectrum of F -center creation (\circ) by synchrotron radiation measured for KBr:Tl at 295 K using the luminescent method. The light sum of TI^+ impurity luminescence stimulated in the maximum of F -absorption band was taken as a measure of F centers created by SR.

trapping is not sufficient for their localization near Na^+ impurity ions, the concentration of which is low (10 ppm).

Figure 4(b) depicts the intensity ratio spectrum (I_I/I_σ) for the 3.5 eV luminescence, caused by I^- center excitation by FE, and the σ emission of STE's (4.42 eV) in KBr:I at 8 K. Similar to the intensity ratio spectrum for π and σ components of STE's, measured previously in a pure KBr crystal,¹⁵ the value of I_I/I_σ stays approximately constant at 13.5–15 eV, sharply increases in the range 15–16 eV, and then decreases to the initial value at 18 eV. We interpret the maximum in the I_I/I_σ spectrum as a direct manifestation of SE formation. The region of SE formation in KBr is shifted by 2 eV toward higher energies relatively to that in KI. The value of this shift agrees well with the differences between the values of E_g (7.55 and 6.31 eV) and E_e (6.76 and 5.83 eV) for these crystals.

All the above-mentioned data support undoubtedly the existence of the excitonic mechanism of MEE's, which can be experimentally detected on the background of the e - h mechanism (see Sec. III) by the analysis of the intensity ratio spectra for two emissions of the crystal. A comparison of the behavior of excitation spectra for impurity luminescence and STE emission shows that in a crystal at 8 K (with a small concentration of impurity centers) the energy transfer to these centers occurs with the participation of FE's. According to our analysis, the initial stage of MEE's at low temperatures is connected with the formation of highly mobile

TABLE I. Threshold photon energies for the formation of secondary excitons (E_{th}^0) and secondary electron-hole pairs (E_{th}^{\pm}); formation energies for transverse and longitudinal excitonic states (E_e^T and E_e^L) and paraexcitons (E_e^p) with different angular momentum for an electron (j_e) and a hole (j_h) (J is a total angular momentum); energy gaps (E_g) and binding energies for paraexcitons (E_B). All energy values (in eV) are obtained in the temperature range 4.2–10 K.

	j_e	j_h	J	KI	KBr	NaCl
E_{th}^0				13.1	15.2	18.0
E_{th}^{\pm}				14.0	16.5	19.5
E_g	1/2	3/2		6.31 ^a	7.55 ^a	8.77 ^a
E_e^p	1/2	3/2	2	5.83 ^b	6.76 ^f	
E_e^T	1/2	3/2	1	5.85 ^c	6.79 ^f	7.97 ^a
E_e^L	1/2	3/2	1	5.95 ^d	6.95 ^g	8.17
E_e^T	1/2	1/2	1	6.80 ^a	7.30 ^a	8.10 ^a
E_e^L	1/2	1/2	1	6.90 ^e	7.45 ^g	8.30
E_B	1/2	3/2		0.48	0.79	0.80

^aRef. 25.

^bRef. 31.

^cRef. 32.

^dRef. 33.

^eRef. 34.

^fRef. 35.

^gRef. 36.

secondary FE's, the energy of which can be effectively transferred at large distances to impurity centers.

A natural question arises whether the immediate formation of SE's in a localized state is possible under certain conditions. Our experimental results are in favor of the direct formation of localized SE's at least at 295 K. It is known (see, e.g., Ref. 29) that heating of AH's leads to a significant increase of the Urbach tail of fundamental absorption, which is caused by the direct formation of excitons in a self-trapped state. At 10–20 K the intrinsic absorption of KBr sharply decreases from the maximum value 10^6 cm^{-1} at 6.79 eV down to 10^2 cm^{-1} at 6.72 eV, while at room temperature the same decrease of the absorption constant occurs between 6.65 and 6.2 eV, i.e., in a significantly wider energy region.²⁹ We have succeeded in revealing the process of SE decay with the formation of an F - H pair of Frenkel defects in KBr:Tl at 295 K by measuring the creation spectrum of stable F centers.³⁰ A fragment of this spectrum is reproduced in Fig. 4(b). A comparison of the spectrum of F -center creation with the spectrum of I_1/I_σ for KBr:I shows that the function of SE formation at 8 K has a sharper rise than that at 295 K. The range 14.2–15.2 eV, connected with the formation of SE's by hot photoelectrons in KBr at 295 K, can be considered as an analog of the Urbach tail of exciton absorption. In our opinion, SE's can be formed at 295 K either in a free state (as at 8 K) or directly in a localized state. Quantitative investigation of this effect has still to be performed, however.

V. CREATION OF SECONDARY EXCITONS BY HOT PHOTOELECTRONS

Important information about the formation of SE's can be obtained by the analysis of the threshold photon energies E_{th}^0 for the creation of SE's. Table I presents our experimentally determined values of E_{th}^0 (accuracy ± 0.2 eV) along with the

threshold energies for the formation of secondary e - h pairs, E_{th}^{\pm} (accuracy ± 0.3 eV) for AH's at 8 K. The values E_{th}^0 and E_{th}^{\pm} are compared with the previous values of E_g , obtained by many authors. Comparisons are also made of the energies of the direct generation of Γ excitons with $n=1$ in different electronic states and the binding energies of Γ paraexcitons, $E_B = E_g - E_e^p$ (E_e^p is the formation energy of $\Gamma(1/2, 3/2)$ paraexcitons with $J=2$). All energies, presented in Table I, were obtained in the temperature range 4.2–10 K.

The possibility of cooperative absorption of a photon by two ions with direct formation of two excitons in solids has been proposed by Dexter.³⁷ According to theoretical estimates, the probability of this process is by several orders of magnitude lower than that of photon absorption with the formation of one EE. Experimental evidence of the formation of two excitons due to the cooperative absorption of a photon is not yet available. The threshold energy for this process is expected to be $E_{\text{th}} = 2E_e$. The values of E_{th}^0 (see Table I) are significantly higher than $2E_e$. Furthermore, one photon of $h\nu \geq E_{\text{th}}^0$ undoubtedly creates an e - h pair and an exciton. In pioneering work on the detection of SE formation in AH's at 295 K, it was proposed that $E_{\text{th}}^0 = E_g + E_e$ and $E_{\text{th}}^{\pm} = 2E_g$.¹¹ So $E_{\text{th}}^{\pm} - E_{\text{th}}^0 = E_g - E_e = E_B$. At the same time it was also proposed that in AH's the effective mass for a hole is more than one order of magnitude larger than that for an electron. Our experimental values of E_{th}^0 and E_{th}^{\pm} satisfy the inequalities $E_{\text{th}}^0 > E_g + E_e$, $E_{\text{th}}^{\pm} > 2E_g$, and $E_{\text{th}}^{\pm} - E_{\text{th}}^0 > E_B$. An attempt at a qualitative interpretation of these inequalities will be made below.

An interband impact ionization is the most probable creation mechanism of several e - h pairs by one photon of $h\nu \geq E_{\text{th}}^{\pm}$. An inelastic scattering of a sufficiently energetic electron on valence electrons leads to the formation of a secondary e - h pair. From a quantum-mechanical point of view, the impact ionization is equivalent to the intraband Auger transition with the formation of a secondary e - h pair

owing to the energy release at a transition of a primary photoelectron to a lower level inside a complicated conduction band.

Generally, the strict theoretical estimation of E_{th}^{\pm} in crystals with complicated conduction and valence bands is a difficult task (see, e.g., Ref. 2) which has not been solved yet. In order to elucidate the main peculiarities of the e - h mechanism of MEE's in cubic-face-centered AH's, it is useful to consider a simplified form of the theory for a system with two parabolic energy bands, the extrema of which are located at the Γ point of the Brillouin zone, $\mathbf{k}=0$.³⁸ The process of impact ionization by hot photoelectrons takes place according to the laws of conservation of the energy and the quasi-impulse (wave vector \mathbf{k}). The direct interband transition with a photon absorption causes the creation of a hot conduction electron with effective mass m_e and a hot hole in a valence band with effective mass m_h . The energy absorbed by a crystal, $h\nu - E_g$, is divided between a photoelectron and a photohole in accordance with the ratio m_h/m_e . If the interaction with phonons is neglected and $m_e/m_h < 1$, a hot photoelectron gains a larger part of the photon energy. This primary electron is able to ionize a crystal and to create a secondary e - h pair if its energy E_i exceeds the value of E_g . The inequality $E_i > E_g$ must be fulfilled in order to conserve the total wave vector on the inelastic scattering with the formation of a secondary e - h pair. In this case the threshold photon energy for the impact ionization of a crystal by a hot photoelectron³⁸ is

$$E_{\text{th}}^{\pm} = 2E_g(1 + m_e/m_h). \quad (1)$$

The value of E_{th}^{\pm} equals $2E_g$ in crystals with $m_e \ll m_h$. If $m_e = m_h$, $E_{\text{th}}^{\pm} = 4E_g$ and an electron and a hole are both able to form a secondary e - h pair.

If the interaction of a hot photoelectron with phonons is taken into account, the conservation of \mathbf{k} takes place even at $E_i = E_g$ and the threshold energy for the formation of a secondary e - h pair³⁹ is given by

$$E_{\text{th}}^{\pm} = E_g + E_g(1 + m_e/m_h). \quad (2)$$

Figure 5(a) illustrates the situation described by the formula (2) for different values of m_e/m_h . In crystals with $m_e/m_h = 0$, E_{th}^{\pm} equals $2E_g$, and at $m_e/m_h = 1/3$, E_{th}^{\pm} equals $7E_g/3$. The maximum value $E_{\text{th}}^{\pm} = 3E_g$ corresponds to the case $m_e/m_h = 1$, when a hot photoelectron and a hot photohole both have sufficient energies to form a secondary e - h pair (participation of phonons provides the conservation of the total wave vector). In AH's $m_e < m_h$ and the total width of a valence band $E_v < E_g$, which is why only photoelectrons take part in the process of MEE's. In all crystals $E_{\text{th}}^{\pm} > 2E_g$ because a part of the absorbed energy is transferred to a photohole. In order to obtain the experimentally determined values of E_{th}^{\pm} for KI, KBr, and NaCl crystals, the values of m_e/m_h , 0.22, 0.18, and 0.22, respectively, must be used in formula (2).

Using a simplified theory, we have obtained the threshold photon energy for SE formation [compare with formulas (2) and (1)] as

$$E_{\text{th}}^0 = E_g + E_e(1 + m_e/m_h) \quad (3)$$

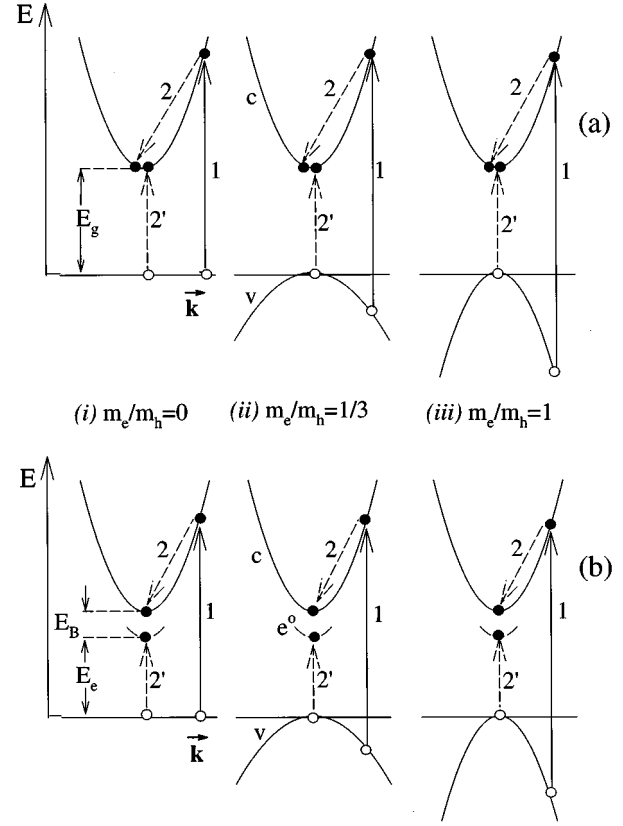


FIG. 5. Simplified model of the formation of secondary electron-hole pairs (a) and secondary excitons (b). Energy of a conduction band (c), a valence band (v), and excitons (e^0) as a function of the wave vector (\mathbf{k}) for three different values of the ratio of effective masses for electrons (m_e) and holes (m_h). Solid arrows (1) depict the process of a photon absorption with the formation of a primary e - h pair. Dashed arrows (2 and 2') show the Auger transition (with the participation of phonons) with the formation of secondary e - h pairs (a) or excitons (b).

if the interaction of hot photoelectrons with phonons is taken into account and

$$E_{\text{th}}^0 = E_g + E_e(1 + 2m_e/m_h) \quad (4)$$

if it is neglected. Figure 5(b) illustrates the impact excitation of a crystal with the formation of SE's [according to formula (3)] for different values of m_e/m_h .

Using formulas (2) and (3), we obtain

$$E_{\text{th}}^{\pm} - E_{\text{th}}^0 = E_B(1 + m_e/m_h). \quad (5)$$

This difference equals $2E_B$ if $m_e/m_h = 1$ and E_B if $m_e/m_h \ll 1$. Our experimental values of E_{th}^{\pm} and E_{th}^0 satisfy the inequality $2E_B > E_{\text{th}}^{\pm} - E_{\text{th}}^0 > E_B$. In formulas (1) and (4) the interaction of hot photoelectrons with phonons is neglected and

$$E_{\text{th}}^{\pm} - E_{\text{th}}^0 = E_B(1 + 2m_e/m_h). \quad (6)$$

In this rough approximation the difference equals $3E_B$ in crystals with $m_e/m_h = 1$. By using the values E_{th}^0 , E_g , and E_e^0 from Table I in formula (3), it is possible to estimate the values of m_e/m_h for KI, KBr, and NaCl (0.17, 0.13, and 0.16, respectively). These values are smaller than those

based on the data on the formation of secondary e - h pairs in the same crystals. The difference of the m_e/m_h values, obtained in various ways, illustrates the approximate form of formulas (2) and (3). The parabolic approximation for the dispersion in conduction and valence bands is justified in a limited region around $\mathbf{k}=0$ only.

Besides the analysis of E_{th}^0 , important information about the process of SE formation in AH's can be obtained from the intensity ratio for excitonic and recombinational emissions at $h\nu > E_{th}^0$. According to the data on electron impact spectroscopy for free atoms,⁴⁰ in the case of weakly allowed optical transitions (e.g., $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^3P_2$ transitions in a Hg atom), the intensity of atomic emission sharply reaches the maximum with an electron energy increasing above the threshold value. For the states of free atoms, transitions to which are allowed by selection rules (e.g., $^1S_0 \rightarrow ^1P_1$ transition in a Hg atom), the intensity of emission increases slowly and reaches the maximum at an energy exceeding the threshold value by 2–3 times. Our experimental results show that in KI and KBr the value of the intensity ratio for excitonic and recombinational emissions sharply increases in the region of 0.5–0.7 eV above the value E_{th}^0 . In AH's such a behavior is expected not for the formation of spin-singlet $\Gamma(1/2,1/2)$ excitons, but for spin-triplet $\Gamma(1/2,3/2)$ paraexcitons with $J=2$ and $\Gamma(1/2,3/2)$ orthoexcitons with $J=1$. According to the data in Table I, the formation energy of $\Gamma(1/2,1/2)$ longitudinal orthoexcitons, $E_c^L(1/2,1/2)$, in KI exceeds the value $E_g(1/2,3/2)$, whereas, in KBr, $E_c^L(1/2,1/2) \approx E_g(1/2,3/2)$. Consequently, the formation of $\Gamma(1/2,1/2)$ SE's in KI and KBr must be expected in the same spectral region as the creation of secondary e - h pairs. Therefore $\Gamma(1/2,1/2)$ excitons are not responsible for the main maxima in the intensity ratio spectra for KI (13.8 eV) and KBr (15.8 eV). Hot photoelectrons form mainly $\Gamma(1/2,3/2)$ paraexcitons and $\Gamma(1/2,3/2)$ longitudinal orthoexcitons in KI and KBr crystals. The difference between energy states of these excitons is 0.13 and 0.17 eV for KI and KBr, respectively (see Table I). Unfortunately, our experimental accuracy is not sufficient to distinguish between triplet para- and orthoexcitons.

It was recently shown⁴¹ that the multiplicity is not changed due to the transition FE \rightarrow STE and the optical generation of free paraexcitons leads to the formation of triplet STE's. From our data (see also Refs. 15 and 23), which show that the triplet π emission of STE's is dominant on the formation of SE's with $n=1$, we can conclude that hot photoelectrons create mainly triplet FE's. It is important to mention that contrary to photons, which directly generate transverse polariton excitons, hot photoelectrons form longitudinal SE's without a polaritonic component.³⁵

VI. DECAY OF CATION EXCITATIONS

Besides excitons, the hole component of which is localized at halogen ions (anion excitons), photons with significantly higher energy can in AH's create so-called cation excitons. The hole component of these cation excitons is localized at alkaline metal ions. In KCl, KBr, and KI, cation excitons have an electronic configuration $3p^5 4s K^+$ and they have been investigated in detail (see, e.g., Ref. 28).

The maxima at 19.85 and 20.1 eV, in the reflection spec-

trum for the (100) plane of KBr measured after cleaving of the crystal at 8 K, are connected with the excitation of K^+ at the Γ point of the Brillouin zone.²⁸ This doublet is caused by the spin-orbit splitting of cation Γ excitons. An intense reflection maximum at 21.23 eV is interpreted as the formation of $3p^5 4d$ cation excitations at the X point.²⁸ There are two shoulders, at 20.5 and 20.7 eV, in the region between Γ and X cation excitons. The shoulder at 20.7 eV is tentatively attributed to the photoionization threshold of $3p^6 K^+$.²⁸ The spectrum of F -center creation has been measured for KBr:TI by means of SR (12–32 eV) at 295 K, and the typical peculiarity in the spectrum was interpreted as a manifestation of the photoionization of the K^+ ion, $E_{gc} = 20.5 \pm 0.2$ eV.³⁰

The excitation spectra for π and σ emissions of STE's (2.3 and 4.42 eV) for KBr at 8 K have been investigated earlier.¹⁵ The intensity ratio I_π/I_σ for π and σ emissions of STE's is practically constant in the region 18.5–22.5 eV. We have previously shown¹⁵ that a 17–19-eV photon can form two e - h pairs. We can thus conclude that the decay of $3p^5 4s$ cation excitons in KBr leads to the formation of a double amount of e - h pairs as well.

The decay of cation excitons with the formation of a double amount of anion excitons has also not been detected in a KI crystal. Figure 2 shows that the direct generation of cation excitons by 20-eV photons causes the excitation of the same emission bands, as in a case of e - h pair formation by 7.7- or 13-eV photons. The irradiation of KI by 20- or 22-eV photons does not lead to an effective excitation of 2.8–3.1 eV luminescence, which dominates in the emission spectrum on the excitation by 5.95- or 5.83-eV photons, i.e., on the direct optical formation of anion excitons (see Fig. 2). The threshold energy for photoionization of $3p K^+$ has not been strictly determined in KI yet. We made an attempt to determine the value of E_{gc} using the intensity ratio spectrum I_{Na}/I_σ for the emission of STE's near Na^+ impurity ions and the σ emission of STE's in KI:Na at 8 K (see Fig. 3). Besides the maximum in the range 13–14.5 eV, analyzed in detail in Sec. V, there is a second maximum between 26.5 and 28 eV which should correspond to the formation of anion SE's by hot photoelectrons on the photoionization of $3p K^+$. According to all theoretical calculations and experimental estimates, the width of the cation valence band in KCl, KBr, and KI does not exceed 0.2 eV and the threshold photon energy for SE formation due to the photoionization of K^+ , E_{th}^{0c} , must be close to the value of $E_{gc} + E_e$. Taking $E_{th}^{0c} = 26.5 \pm 0.2$ eV and $E_e = 5.83$ eV, we obtain $E_{gc} = 20.7 \pm 0.2$ eV in KI. Exactly in this spectral region, between the absorption maxima of Γ and X cation excitons, there is a shoulder which has been tentatively interpreted as E_{gc} .²⁸ In KBr the second maximum of I_π/I_σ is located at 28–29 eV (Ref. 15) and our experimental estimate gives $E_{th}^{0c} = 27.5 \pm 0.2$ eV. In KBr at 8 K, $E_e = 6.8$ eV and $E_{gc} = E_{th}^{0c} - E_e = 20.7 \pm 0.2$ eV.

It should be mentioned that the binding energy for cation excitons in KBr and KI can be estimated as 0.8 and 0.6 eV, respectively. According to Table I, these values are close to the values of E_B for anion excitons.

VII. CONCLUSIONS

Methods for quantitative investigation of secondary excitons in AH's have been elaborated. The analysis of the inten-

sity ratio spectra for two emissions, excited by SR of 12–32 eV, allowed us to separate the regions of SE formation in KI (13–15 and 26.5–29 eV) and KBr (15–17 and 28–30 eV) crystals. The formation of a SE is caused by the photocreation of a primary conduction electron (in pair with a hole), the energy of which is sufficient to form a triplet SE. Low-energy regions of SE formation are connected with the photoionization of anions ($5p\text{ I}^-$ and $4p\text{ Br}^-$) and high-energy regions with the creation of hot photoelectrons at the photoionization of cations ($3p\text{ K}^+$). Taking KI:Na and KBr:I crystals as the example, we have revealed at 8 K an efficient energy transfer (at large distances) to impurity centers and the excitation of impurity luminescence by free triplet SE's.

The experimental determination of the threshold energies for the formation of SE's in KBr (15.2 ± 0.2 eV) and KI (13.1 ± 0.2 eV) allowed us to eliminate some of the proposed mechanisms for SE formation. In particular, the decay of a cation exciton with the formation of two anion excitons has not been detected. The formation of triplet SE's in AH's can be described as Auger transitions of hot electrons, generated by photons, to lower-energy levels inside the conduction band. This process can be roughly interpreted as an inelastic

scattering of hot photoelectrons on valence electrons (impact excitation of a crystal).

The values of the threshold energy for the e - h mechanism of MEE's (16.5 eV in KBr and 14 eV in KI) exceed $2E_g$ because a part of the photon energy absorbed by a crystal is transferred to a photohole. In doped AH's (e.g., KBr:TI), the formation of secondary e - h pairs by primary hot photoelectrons causes the excitation of recombinational impurity luminescence with the quantum yield $\eta > 1$. The decay of Γ -cation excitons ($3p^5 4s$) in KI and KBr, generated by 20-eV photons, leads to the formation of a double amount of e - h pairs.

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