

Radiation creation of cation defects in alkali halide crystals: Review and today's concept

(Review Article)

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Irradiation of alkali halide crystals creates pairs of Frenkel defects both in anion and cation sublattices. However, the particular nonimpact creation mechanisms (related to the decay of different electronic excitations) of cation Frenkel pairs are still unclear. At helium temperatures, there is yet no direct evidences of the creation of stable (long-lived) elemental cation defects. On the other hand, a number of complex structural defects containing cation vacancies and/or interstitials, were detected after irradiation of alkali halides at higher temperatures. Besides already proved mechanism related to the association of H and V_K centers into trihalide molecules, the following possibilities of cation interstitial-vacancy pair creation are analyzed as well: (i) a direct decay of cation or anion excitons, (ii) the transformation of anion Frenkel pairs, formed at the decay of anion excitons or $e-h$ recombination, into cation ones.

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1. Introduction

For about century alkali halide crystals (AHCs), ionic systems with simple electron and crystal structure, serve as model objects in studies of numerous physical processes

in solids. Radiation damage of materials exposed to different types of radiation belongs to these processes as well. Already in 1921, Röntgen and Ioffe revealed the coloration of NaCl under x-rays [1]. However, a systematic study of radiation-induced structural defects was stimulated by

the operation of the first fission reactor in late 1942. Already first experiments demonstrated drastic changes in the properties of reactor construction materials under intense neutron-gamma radiation. At present, the insufficient resistance of construction materials (mainly metals and alloys) against 14.1-MeV neutrons could be the Achilles heel for future industrial deuterium-tritium reactors. Overall, to meet the requirements of different technical applications, the processes of material damage should be thoroughly studied in order to increase the tolerance of functional materials, including inorganic wide-gap materials ($E_g > 5$ eV), against prolonged irradiation during their operation.

Frenkel and Wigner suggested that huge radiation damage in main reactor materials was related to the accumulation of Frenkel defects (FDs) — “vacancy-interstitial ($v-i$)” pairs formed due to elastic collisions of incident high-energy particles (neutrons or fission products) with the crystal nuclei (see [2] and references therein). This impact mechanism universal for solids is responsible for the radiation damage in metals and alloys. On the other hand, it was generally accepted long ago that the knockout mechanism with rather high threshold energy is not the dominant creation mechanism of $v-i$ pairs in wide-gap materials, including AHCs (see, e.g., [3–9]). In addition to collisions of charged incident particles with nuclei, the energy absorbed by the material during irradiation is also spent on the ionization or excitation of an electron subsystem forming thereby different radiation-induced electronic excitations (EEs). Varley considered consequence of double (multiple) ionization of a halogen ion with the formation of an unstable group of positively charged neighbor ions (7 in face-centered AHCs) ending by a knockout of a positively charged halogen ion X^+ into an interstice, i.e., formation of a $v-i$ pair [3]. However, it seems that even less-energy-needed nonimpact mechanisms of FD creation connected with the nonradiative decay of radiation-induced EEs are especially efficient in the majority of AHCs [4–9].

In many AHCs, the energy released at the decay of self-trapped(ing) excitons (STEs) or at the recombination of totally relaxed conduction electrons (e) and valence holes (h) exceeds the energy needed for the formation of a pair of FDs (a Frenkel pair), E_{FD} . These so-called excitonic and electron-hole mechanisms of FD creation in AHCs have been thoroughly studied [4–9]. It turned out that only about 5% of such structural defects are stable for days and months, while the majority of FDs are the short-lived ones ($\tau \sim 10^{-1} - 10^{-11}$ s) [7–11]. Just stable (long-lived, $\tau > 10^3$ s) FDs and their associations are responsible for the radiation damage/degradation of wide-gap materials and are the object of the present study.

It should be pointed out that the impact mechanism of FD creation was suggested for metals, i.e., the formation of metal vacancies and interstitials was considered. Later, the knock-out of oxygen atoms, in addition to magnesium ones, was also detected in ionic MgO single crystals [12].

Although Varley suggested the creation of $v-i$ Frenkel pairs in both anion and cation sublattice of AHCs, further studies demonstrated the efficient low-temperature creation of $v-i$ pairs only in an anion sublattice. Two types of FD pairs should be distinguished in AHCs [4–11]. Firstly, a classical Frenkel pair of charged point defects — an anion vacancy (v_a or an α center), which is positively charged with respect to a regular lattice, and a negatively charged interstitial halogen ion (i_a^- or an I center). The second pair of neutral FDs consists of an F center ($v_a e$, an electron trapped by an anion vacancy) and an interstitial halogen atom (i_a^0 or an H center). The processes of selective creation of stable $F-H$ and $\alpha-I$ pairs by vacuum ultraviolet (VUV) radiation which forms different intrinsic EEs (i.e., “creation spectra” of anion FD pairs) as well as the processes of FD thermal annealing and recharging of neutral Frenkel pairs (via tunnel process or by $e-h$ pairs) have been thoroughly studied using highly sensitive luminescence methods and theoretical modelling in many AHCs (see [4,6,13–21] and references therein).

On the other hand, the search for pairs of elemental cation FDs (v_c and i_c^+ or $v_c h$ and i_c^0) in AHCs has not yet been successful. Only cation defects being a part of more complex defect associations were detected by different experimental methods. As of 1980, the experimental manifestations of cation FDs in AHCs and their possible creation mechanisms were summarized in [22]. The aim of the present study is to analyze additionally the experimental manifestations of the creation of stable (long-lived) cation defects, i.e., pairs of cation FDs and their associations, in model AHCs. In particular, the decay of cation excitons, possible reasons of low efficiency of cation FD creation at low temperatures as well as tentative high-temperature creation mechanisms of stable cation FDs will be considered.

2. Experimental

It is generally accepted that imperfections (impurities, as grown defects) strongly influence both the efficiency of radiation-induced defect creation and the subsequent defect stabilization. Therefore, highly pure AHCs were used in the present study. Single crystals were grown by the Stockbarger method or by the Kyropoulos method in “helium atmosphere” from highly pure salt after a special purification cycle involving a melt treatment in the correspondent halogen gas flow (Cl_2 for KCl, etc.) and a manifold recrystallization (up to 50 times) from the melt (see [23–26] for details). The content of main impurities (except homologous ones) estimated by means of spectroscopic methods was usually less than 1 ppm for halogen and alkali metal impurity ions and of $10^{-1} - 10^{-2}$ ppm for divalent metals and hydroxide. Single crystals doped with certain amount/type of impurity ions were grown by the same procedure.

The main photoluminescence experiments were carried out using synchrotron radiation (SR) facilities in Lund (BL52

at MAX-I and the undulator beamline I3 at MAX-III Laboratory) and Hamburg (SUPERLUMI station of HASYLAB at DESY). The reflection and excitation spectra were normalized to equal quantum intensities of exciting light falling onto the crystal. The reference signal from a sodium salicylate coated mesh was recorded for normalization. The excitation spectra were measured for time-integrated signal or for the emission detected within a time window (length Δt) correlated with the excitation pulse (delayed by δt). Creation spectra of point defects as well as of different TSL peaks by VUV radiation of 6.5–10.5 eV were measured using a homemade setup based on a single grating vacuum monochromator VMR-2 and the exciting photons from the hydrogen discharge in a flow capillary tube. The creation spectra of FDs by VUV radiation (including synchrotron radiation) and thermal annealing of radiation defects were measured using highly sensitive luminescence methods elaborated earlier in Tartu (see, e.g., [6,14,15,27,28]).

3. Experimental manifestations of cation defects in AHCs

As it was already mentioned in Introduction, the radiation-induced creation of elementary anion FDs (α -I and F -H pairs) was revealed and thoroughly studied in AHCs. The creation of cation FDs with symmetrical structure (v_c and i_c^+ or v_ch and i_c^0) was also suggested long ago (see [3,4,6] and references therein). Note that the determined formation energies of Schottky (v_a or v_c) and Frenkel defects under thermal equilibrium conditions in AHCs are significantly lower than those of anion excitons and values of E_g (see Refs. 6, 8, 29–31 and Table 1). Therefore, the excitonic and e - h mechanisms of FD creation, which provide efficient creation of anion FDs, could be, in general, responsible for the radiation creation of pairs of cation FDs as well.

However, up to now there is a lack of data on elementary cation FDs in AHCs, especially on their creation at helium temperatures. This is partly due to tentative location of absorption bands related to cation FDs. It was clearly demonstrated that the absorption of halogen ions surrounding v_a (i.e., absorption of α centers) in AHCs lies only slightly below the exciton absorption [4,14,17,24], while i_c^+ and v_c related absorption bands are tentatively located in the region of fundamental absorption. The absorption of halogen ions perturbed by neighbor i_c^+ is expected at lower energies, but it could be overlapped with a so-called Greek γ band connected with the absorption of halogen ions nearby i_a^- . The absorption of i_c^0 is expected in NIR spectral region, where the absorption of F -type centers and aggregates is dominant. In addition, there are more basic reasons impeding the creation/detection of cation FDs in AHCs, which will be considered in the following sections. At first, however, we briefly review the existing experimental manifestations of the creation of cation defects, or more complex structural defects involving ele-

Table 1. Calculated formation energies of Schottky (E_{Sch}) and Frenkel anion (E_{Fa}) and cation defects (E_{Fc}); peak position of the absorption/reflection bands of anion and cation excitons (E_{ea} and E_{ec}); minimum ionization energies of anions and cations (E_{ga} and E_{gc}) at helium temperatures (all values are in eV). The data are summarized on the basis of [6,8,25,29–31,47–59]

	E_{Fc}	E_{Fa}	E_{Sch}	$E_{ga} (\equiv E_g)$	E_{ea}	E_{ec}	E_{gc}
LiF	3.63	8.97	2.66	14.5	13.08	61.9	~65
LiCl	2.47	6.26	1.92	9.4	8.67	60.75	~64
LiBr	2.15	6.00	1.87	7.6	7.23	60.44	~63.5
LiI	1.50	5.47	1.54	6.1	5.94	59.8	~63.5
NaF	4.39	6.01	3.19	12.3	10.66	33.20	~36
NaCl	3.32	5.48	2.58	8.8	7.97	33.55	~36
NaBr	3.06	5.46	2.54	7.13	6.73	33.36	~35
NaI	2.61	5.36	2.34	5.86	5.63	33.18	~35
KF	3.83	4.00	2.74	10.8	9.88	20.0	
KCl	3.37	4.4	2.69	8.7	7.78	20.3	~20.8
KBr	3.27	4.52	2.73	7.4	6.83	19.8	~20.7
KI	3.02	4.6	2.64	6.3	5.86	20.1	~20.7
RbF	3.81	3.35	2.5	10.3	9.54	16.1	~17.0
RbCl	3.21	3.94	2.62	8.2	7.54	16.2	~17.2
RbBr	3.13	4.1	2.69	7.25	6.64	16.2	~16.6
RbI	2.97	4.29	2.66	6.37	5.76	16.3	
CsF	3.49	4.42	2.19	9.8	9.27	13.03	
CsCl	4.33	4.39	1.82	8.4	7.85	13.22	~14.1
CsBr	4.05	4.55	1.9	7.3	6.88	13.12	~13.8
CsI	3.53	4.62	1.86	6.1	5.81	13.06	

mentary cation ones, by radiation of different types at temperatures above 77 K.

The rise of the number of v_c results in the enhancement of ionic conductivity easily measured at high temperatures in highly pure AHCs. The temperature dependence of ionic conductivity was analyzed in AHCs preliminary exposed to x-rays (see [22,32] and references therein). Based on associative/nonassociative character of radiation-induced conductivity it was concluded that both single v_c and divacancies v_av_c were created in KCl, KBr, NaCl, NaBr. Optical characteristics of EEs localized near divacancies, the number of which can be increased by irradiation as well as by thermal quenching or plastic stress, have been also determined in a number of AHCs [24] and even in MgO [33]. More complex associations of radiation-induced divacancies (tentatively, quartets $v_av_c v_av_c$) were experimentally detected via electron microscopy of freshly cleaved surfaces of the irradiated samples decorated with gold in order to increase the defect size [34,35].

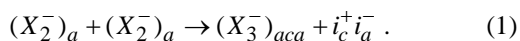
The association of v_c with a self-trapped hole (a V_K center), i.e., a so-called V_F center (v_ch) was also revealed by Känzig using the EPR method in LiF [36] and further investigated by EPR and optical methods in many other irradiated AHCs (see, e.g., [4,6,22,28,37]). A V_F center is defined as a dihalide X_2^- quasimolecule situated at two neighbor anion sites (i.e., V_K center) but the axis of which

is curved due to a nearby v_c . Creation spectrum of V_F centers by VUV radiation in the region of exciton absorption was measured in RbBr at 190 K using a sensitive luminescent method [37]. At higher temperatures, V_F centers become mobile, associate with other structural defects and, thus, participate in the formation of trihalide molecules (see text below).

Besides divacancies and V_F centers one more type of structural defects that contain v_c was thoroughly studied in many AHCs with both fcc or bcc lattice structure. Soon after the discovery of the first color center — an F center with typical absorption band in visible spectral region, a UV absorption band was also detected in x-irradiated AHCs and ascribed to the so-called V -type centers (V_2 , V_3 , V_4 and V_7) [38]. The absorption of V -type centers was found to be close to the absorption of polyhalide molecules in water solution and it was suggested that V_2 centers in fcc alkali chlorides and bromides correspond to linear trihalide molecules located in two anion and one cation sites along $\langle 100 \rangle$ crystallographic directions, $(X_3^-)_{aca}$ [39].

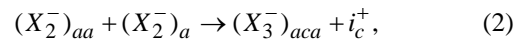
A further detailed investigation of the related UV absorption bands induced by x-irradiation at 77–300 K as well as of the products of their thermal and photo-dissociation (appearance of V_F centers was detected by the EPR method as well) confirmed the radiation creation of v_c that are part of $(X_3^-)_{aca}$ centers in fcc KCl, KBr, RbCl, RbBr and bcc CsBr single crystals (see [6,22,28,32,34,35,40–44] and references therein). The orientation of $(X_3^-)_{aca}$ centers along $\langle 100 \rangle$ in fcc AHCs and along $\langle 111 \rangle$ in bcc CsBr was experimentally proved via the measurements of optically induced dichroism in the region of V_2 absorption bands. Note that the number of $(X_3^-)_{aca}$ centers, which can be also considered as a $v_c h_i^0$ association, linearly increased with the irradiation dose and reached 10^{17} – 10^{18} cm $^{-3}$, i.e., exceeded by at least two orders of magnitude the concentration of pre-irradiation/as-grown v_c in the highly pure AHCs used for these investigations. The creation of $(X_3^-)_{aca}$ centers was also detected after the irradiation of AHCs with VUV photons that form anion excitons or e - h pairs in the regime of one- or two-photon absorption. In the former case, trihalide molecules were detected via the corresponding peak of thermally stimulated luminescence (TSL), while typical absorption bands were directly detected in the latter case, when crystals were preliminarily irradiated with XeCl-laser emission.

It was suggested that cation FDs, for instance v_c participating in an $(X_3^-)_{aca}$ center, can arise due to the energy released at the interaction of anion FDs — two H centers [45,46]. Interstitial halogen atom, an H center constitutes a dihalide X_2^- molecule located at one anion site. The interaction of two H centers could be performed in the following way:



The process requires the radiation creation of a pair of cation FDs, v_c - i_c^+ . Note that possible creation of anti-Schottky defects, interstitial dipoles $i_c^+ i_a^-$ was suggested already in [47] and the corresponding experimental data were considered in [6,22]. According to theoretical estimates [45,46], the reaction (1) was not exothermal one in regular lattice sites, while could be realized at the surface or near the edge of interstitial dislocation loops, the formation of which was detected by the electron microscope [48]. The aggregation of two H centers near single point defects (e.g., v_c or v_a), both pre-irradiation ones or formed already during irradiation, with the creation of cation FDs was also considered (see [6,22] and references therein).

The efficiency of $(X_3^-)_{aca}$ center creation by VUV radiation or x-rays depends on temperature and is the highest at 180–200 K, while x-irradiation at 4.2 K does not cause the creation of v_c that are part of $(X_3^-)_{aca}$ centers [6,41]. In KCl and KBr with sufficient concentration of impurity electron traps, the number of V_K centers can be accumulated during x-irradiation at 80–200 K. At such temperatures, H centers are rather mobile and able to interact with still immobile V_K centers by the following reaction:



the final products of which contain v_c and i_c^+ [6,22,34,35]. It is worth noting that V_K - H association can result in the formation of $(X_3^-)_{aca}$ centers in highly pure AHCs as well. Although the initial amount of radiation-induced V_K centers in these AHCs is small, their number can increase significantly via the transformation of mobile anion interstitial atoms according to the reaction $i_a^0 + v_a \rightarrow V_K$. This process was experimentally proved in RbBr crystals where thermal stability of i_a^0 exceeds that for i_a^- [35].

In addition, more complex radiation damage involving cation sublattice was also detected in AHCs: intrinsic crystallites on the crystal surface, small cavities in the crystal bulk, interstitial and vacancy dislocation loops, metallic colloids of different size, etc. (see, e.g., [6,20,22,35,48,49]). Summarizing this section we can conclude that there are many experimental manifestations of the radiation creation of FDs in cation sublattice (mainly as components of more complex structural defects) at rather high temperature. Nevertheless, the creation of cation FDs can be explained, in general, by the direct decay of various EEs, including cation related ones, into pairs of cation FDs or via the interaction of anion FDs formed at the decay of anion excitons or recombination of e - h pairs. It is worth noting that the formation energy of cation FDs in NaBr and NaCl is lower than that for anion FDs (see Table 1). At helium temperature, the efficiency of anion FD creation in NaCl and especially NaBr is very low, and a search for cation FDs in these crystals seems to be promising [6,20,50].

4. Decay of cation excitons

Among different intrinsic EEs, the decay of which can result in the creation of cation FD pairs in AHCs, the so-called cation excitons (CEs, e_c^0) — excited states of alkali metal ions are of particular interest. The formation energy of CEs and other cation EEs (photoionization of cations forms $e-h_c$) exceeds those for anion ones by several times, for instance E_{ec} varies from ~ 13 eV in Cs-halides up to ~ 62 eV in lithium halides (compare E_{ea} and E_{ga} with E_{ec} and E_{gc} in Table 1) [51–57]. Note that the position of the most intense reflection/absorption peak (so-called B peak) was usually used as E_{ec} in Table 1. On the basis of the experimentally proved efficient nonradiative decay of anion excitons (AEs, e_a^0) into pairs of anion FDs (α -I and F -H pairs), it was suggested long ago (see [22]) that just the decay of CEs can provide favorable conditions for the creation of FDs in a cation sublattice of an AHC. However, CE decay into cation FDs can be also realized via intermediate transformation of CEs into anion EEs (e.g., $e-h_a$ pairs) that thereafter create anion and/or cation FDs.

The processes of multiplication of EEs, when one exciting photon forms several anion EEs ($e-h_a$ pairs and e_a^0), were investigated in details using SR of a wide spectral region covering the formation of cation EEs in Cs-, Rb-, K- and Na-halides (see, e.g., [6,16,25,58–65] and references therein). In addition, the creation spectra of FDs (mainly F centers) by SR of 6–40 eV were measured in a number of AHCs (KCl, KBr, RbCl, NaCl) using highly sensitive luminescent methods [27,66–69]. Keeping in mind possible mechanisms of cation FD creation, we considered and analyzed below the existing data related to a narrow spectral region covering the direct creation of CEs and the beginning of the cation photoionization in AHCs grouped in accordance with the alkaline metal.

4.1. Caesium halides

The excitation spectra of STE luminescence have been measured for CsCl and CsBr crystals in the formation region of cation EEs [58,60]. In Cs-halides, the structure of cation-related EEs have been thoroughly studied via reflection spectra at 30–400 K as well [51,52]. In CsCl, the reflection peak at ~ 13.2 eV belongs to $5p^5 6s$ Cs^+ excitons, while photoionization of caesium ions starts at ~ 14.0 eV (the values of E_{ec} and E_{gc} are only slightly different in other Cs-halides). Based on the experimental data it has been concluded that E_{gc} exceeds E_{ga} less than twice and the decay of cation EE into double amount of anion EEs (i.e., multiplication process) is impossible in CsCl and CsBr for energetic reasons.

In addition, starting from the exciting photon energy of E_{gc} one more decay channel of EEs competitive to the creation of cation FDs — the radiative decay with the appearance of a special type of fast luminescence — is realized in CsBr [70] as well as CsCl and CsF crystals

[59,71]. This so-called crossluminescence (core-valence or Auger-free luminescence) arises due to the recombination of electrons from the valence band with the holes formed in the cation core band during the excitation process.

The ~ 265 and ~ 370 K TSL peaks related to the hopping diffusion of V_F centers and thermal dissociation of $(X_3^-)_{aca}$ centers, respectively, have been detected in a CsBr crystal preliminarily irradiation at 100 K with 13.2-eV photons forming CEs [72]. However, this result can not be definitely considered as the decay of CEs into cation FD pairs, because intermediate processes with the participation of anion FDs are not still excluded.

4.2. Rubidium halides

In the reflection spectra of RbCl at 20 K, the peak at ~ 16.1 eV is ascribed to $4p^5 5s$ Rb^+ excitons and the threshold for cation photoionization lies at ~ 17 eV [53]. The excitation spectra of intrinsic and impurity emissions in RbCl, RbBr and RbI crystals as well as the spectrum of F -center creation by SR in RbCl have been measured [59,60,62,65,66].

As an example, Fig. 1 presents the fragments of the excitation spectra for intrinsic STE and Tl^+ -impurity emissions, the reflection spectrum measured for RbCl and RbCl:Tl crystals at 8 K as well as the creation spectrum of stable F centers in RbCl:Tl (300 ppm) measured at 295 K using SR in the region of cation EE formation (see also [62,66]). The threshold photon energy for the multiplication process with the formation of two anion $e-h_a$ pairs has been estimated as 17 eV and one photon of ~ 16 eV forms both $e-h_a$ and a secondary e_a^0 (the corresponding regions

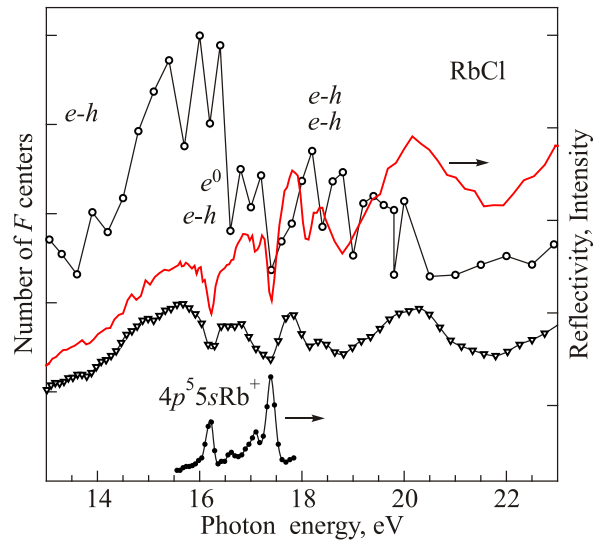


Fig. 1. The reflection spectrum (\bullet) and the excitation spectra for time-integrated signals of Tl^+ emission (4.03 eV, ∇) and π -STE emission (2.23 eV, solid line) measured for RbCl and RbCl:Tl (300 ppm) crystals at 8 K. The creation spectrum of stable F centers by SR measured for RbCl:Tl at 295 K (\circ). Light sum of a typical luminescence was taken as a measure of radiation-induced defects (see text for details).

are marked in figure). Unfortunately, e_a^0 and $e-h_c$ (formed close to the threshold of cation photoionization) in RbCl are located in the same energy region. Therefore, it is rather difficult to separate secondary $e-h_a$ and e_a^0 formed via the decay of primary anion or cation EEs. Note that the peculiarities in the excitation spectrum of impurity emission at 14–16 eV (i.e., below the creation region of secondary e_a^0) are related to the third mechanism of EE multiplication — the direct excitation of Tl^+ ions by hot conduction electrons (see, e.g., [62]). At 295 K, a photon from CE region produces $e-h_a$ and e_a^0 and the latter is responsible for the especially efficient creation of stable F centers at 14.5–15.5 eV (for details see text related to Fig. 2).

In RbBr and RbI with lower threshold energies for multiplication processes, the decay of each e_c^0 or $e-h_c$ leads to the formation of two $e-h_a$ pairs [60,65]. Note that the mixing of exciting photon energy regions typical of the multiplication of anion EEs and of the decay of cation EEs impedes the interpretation of the observed results in rubidium halides. In addition, the possibility to excite crossluminescence by photons with the energy above E_{gc} in RbF should be taken into account as well [71].

4.3. Potassium halides

In potassium halides, the formation energy of CEs significantly exceeds the threshold energies for multiplication processes when an exciting photon becomes able to form two anion EEs: a $e-h_a$ and a secondary e_a^0 or two $e-h_a$ pairs (see for details [6,27,61,62]). Therefore, it is easier to separate the decay products of cation EEs on the background of anion EE multiplication. Based on the excitation spectra for intrinsic or impurity emissions, the threshold photon energies for the formation of secondary e_a^0 and $e-h_a$ pairs have been determined for KCl, KBr and KI crystals (see [58,59,61,68]). K^+ -related EEs (e_c^0 and $e-h_c$) were investigated at 20 K in all potassium halides [54].

Figure 2 presents the excitation spectrum of STE emission in KBr at 8 K. The multiplication process with the formation of both $e-h_a$ and a secondary e_a^0 starts above 15.4 eV, while two anion $e-h_a$ pairs can be formed by an exciting photon above 17 eV (the corresponding regions are marked in figure) [58–60]. Figure 2 shows also the fragments of the creation spectra of stable F centers (295 K) and $F-H$ pairs (8 K) in KBr:Tl and KBr crystals measured using SR of 13–23 eV (see also [27,68]). Special highly sensitive luminescence methods were elaborated in Tartu for the detection of small amounts of FDs induced by VUV radiation in the region of crystal fundamental absorption (see, e.g., [6,14,15]). The light sum of typical luminescence was taken as a measure of F ($F-H$) centers created by a prescribed number of photons at each of several energies. At 295 K, F centers, created by SR in a form of $F-H$ pairs, survive due the association of mobile complementary H centers with V_K resulting in the formation of $(X_3^-)_{aca}$ centers. The efficiency of F -center creation is es-

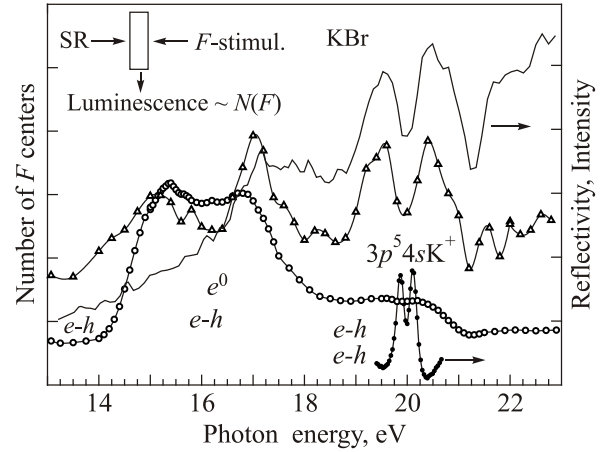


Fig. 2. The excitation spectrum for a time-integrated signal of STE emission (σ -component at 4.4 eV, solid line) measured for a KBr crystal at 8 K. The reflection spectrum (\bullet) and the creation spectra of stable F centers by synchrotron radiation measured for KBr at 8 K (Δ) and KBr-Tl at 295 K (\circ). Light sum of a typical luminescence was taken as a measure of radiation-induced defects (see text for details). The inset shows the geometry for measuring the creation spectrum via a luminescent method.

pecially high at 15–17 eV due to nonradiative decay of secondary e_a^0 . The creation efficiency of F centers at $e-h_a$ recombination is lower, while the efficiency value doubles if an exciting photon creates two $e-h_a$ pairs instead of one $e-h_a$ (the corresponding regions are marked in Fig. 2). It is important, that there are practically no changes of creation efficiency in the region of $3p^5 4s K^+$ excitons (spin-orbit splitting can be seen at 8 K). In KBr, a secondary e_a^0 is not formed at the decay of an e_c^0 .

The analysis of the creation spectrum of stable F centers by SR at 295 K in a KCl:Tl crystal led to similar conclusions [67]. Therefore, according to our experimental data, CEs in KBr (and in other potassium halides) decay with the formation of two $e-h_a$ pairs, each of which subsequently provides the creation of anion FDs ($F-H$ pairs). Note that the situation is more complicated if the exciting photons form secondary e_a^0 at 8 K (see Fig. 2). At low temperature, secondary e_a^0 in KBr are highly mobile and before self-trapping and decay into FDs can participate in other processes (recharging of already existing defects, excitation of impurity centers, etc.).

4.4. Sodium halides

Figure 3 presents the fragments of the reflection spectra and the excitation spectra for STE emissions measured for four sodium halides at 10 K (see also [25,60,63,64]). The spectral regions, where an exciting photon forms from one up to four $e-h_a$ pairs are marked as well. In NaCl, an exciting photon with the energy slightly below e_c^0 decays into 3 $e-h_a$ pairs, while a deep dip (exceeds selective reflection losses) in the excitation spectra for impurity and intrinsic emissions is interpreted as the formation of an e_a^0 instead of

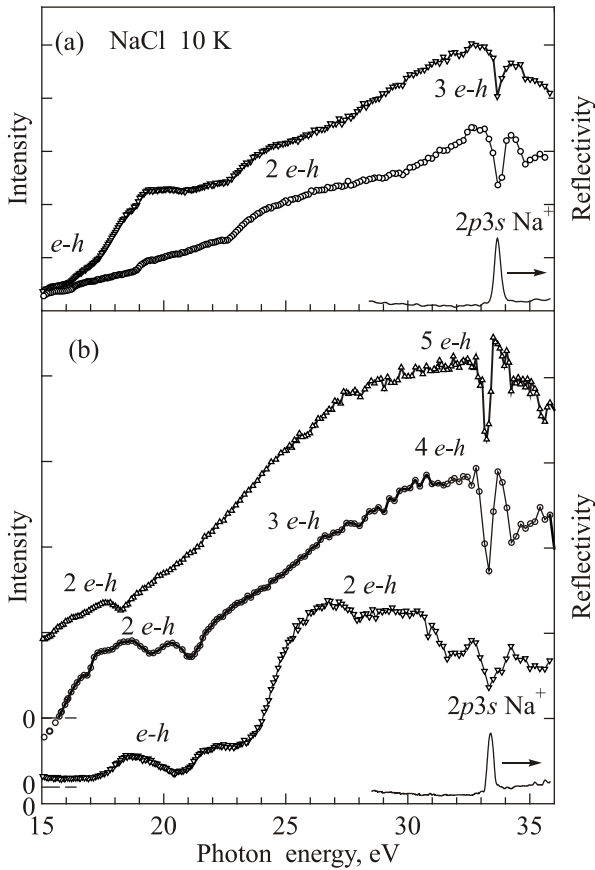


Fig. 3. (a) The reflection spectrum (solid line) and the excitation spectra for time-integrated signal of Ag^+ emission (5.17 eV, ∇) or a fast component of σ -STE emission (time window of $\Delta = 12$ ns and $\delta = 2.4$ ns; 5.5 eV, \circ) measured for NaCl and NaCl:Ag (600 ppm) crystals at 10 K. (b) The reflection spectrum (solid line) and the excitation spectra for time-integrated signals of STE emission measured for NaF (π -component at 2.6 eV, ∇), NaBr (4.62 eV, \circ) and NaI (4.28 eV, Δ) crystals at 10 K.

one of $e\text{-}h_a$ pairs. The similar situation is realized in other sodium halides: a cation exciton decays into an anion exciton and a few $e\text{-}h_a$ pairs (one in NaF). The decay mechanism of e_c^0 in NaBr, NaCl and NaI can be ascribed to the Auger process connected with the energy transfer from an e_c^0 to two neighbor anions: one of anions will be in an excited state (i.e., e_a^0), while the ionization of the second anion leads to the appearance of a hot (high-energy) conduction electron able to form one-three $e\text{-}h_a$ pairs.

In NaCl, the efficiency of FD creation depends on irradiation temperature and is very low at $T < 120$ K. The creation spectrum of stable F centers by SR at 12 K was measured in a highly pure NaCl [69]. The deep dip exactly at the energy of e_c^0 creation, similar to that in the excitation spectra and indicating on the formation of e_a^0 , was detected in the creation spectrum as well. It has been concluded that just the recombination of nonrelaxed $e\text{-}h_a$ pairs is mainly responsible for the creation of $F\text{-}H$ Frenkel pairs at low temperatures, while an e_a^0 (both formed directly or via an e_c^0 decay) does not decay into an $F\text{-}H$.

4.5. Lithium halides

The formation of e_c^0 and $e\text{-}h_c$ in lithium halides occurs in a far VUV region (~ 62 and ~ 67 eV, respectively in LiF) and corresponding data on photoabsorption at 295 K have been presented in [57]. This spectral region is not very suitable for optical measurements using SR. Therefore, there are only few fragmented data on the behavior of different emissions and creation of FDs for the region of cation EE formation in lithium halides. Although low-temperature excitonic and $e\text{-}h$ processes under LiF excitation with SR of 6–40 eV have been thoroughly studied (see, e.g., [26,73]), there is a lack of data on the behavior of different emissions and FD creation in the region of cation EE formation.

According to [26,73], the photocreation of spatially close an e_a^0 and an $e\text{-}h_a$ by one ~ 30 -eV photon (i.e., in the region of EE multiplication providing increased local density of EEs) cause the formation of groups of spatially correlated anion defects (for instance, $F\text{-}I\text{-}V_K$ triplets), which manifest themselves via typical TSL peaks during a subsequent heating of irradiated LiF crystals. The 13 K TSL peak did not arise after crystal irradiation by photons that selectively form e_a^0 or $e\text{-}h_a$, while this peak was detected after LiF irradiation by photons either from multiplication (30 eV) or $1s2p$ Li^+ exciton formation (62 eV) regions. In our opinion, the decay of an e_c^0 leads to the formation of an e_a^0 (similar to the case of Na-halides) and two or three $e\text{-}h_a$ pairs, the decay/recombination of which results in the creation of anion FDs. The suggestion on e_a^0 appearance is consistent with the fact that the efficiency of lithium atom ejection from a crystal surface at the 62-eV photon excitation is the same as in the case of e_a^0 formation by 13-eV exciting photons [74].

5. Creation mechanisms of cation defects

In wide-gap materials, besides the impact (knockout) mechanism, structural defects can be created at the nonradiative decay of different EEs. In a very short time radiation-induced high-energy EEs transform mainly into $e\text{-}h$ pairs and excitons. We will focus on the nonradiative decay of excitons into FDs, because excitonic states also arise at the intermediate stage of $e\text{-}h$ recombination.

Several criteria determining the realization of EE decay into FDs were considered [4,6,16]. In the majority of AHCs, the formation energy of an $e\text{-}h_a$ pair (E_{ga} in Table 1) and even of an e_a^0 is sufficient for the creation of FDs (the energetic criterion is fulfilled). The main reason for the transformation EEs \rightarrow FDs is the interaction with lattice vibrations which should cause the inertial displacement of ions from lattice sites. Therefore, the second, time criterion requires relatively long (with respect to period of effective lattice vibrations) residence time of an EE at a definite lattice site. This criterion is also fulfilled in many AHCs with self-trapping e_a^0 and valence holes h_a (formation of STE and V_K , respectively).

Thus, the following four possibilities of an anion exciton decay (in the process of its self-trapping) into anion and cation pairs of FDs with symmetric structure were suggested long ago [4]:

$$e_a^0 \rightarrow v_a e(F) + i_a^0(H), \quad e_a^0 \rightarrow v_a(\alpha) + i_a^-(J), \quad (3)$$

$$e_a^0 \rightarrow v_c h(V_F) + i_c^0, \quad e_a^0 \rightarrow v_c + i_c^+. \quad (4)$$

It has been already mentioned that only low-temperature creation of stable anion FD pairs is experimentally proved in AHCs. It has been also shown that the presence of local vibrations in pre-decaying EE states impedes the conversation of vibration energy into heat, promotes its concentration on a few lattice ions and can be considered as the third criterion of an efficient EEs \rightarrow FDs transformation [15].

Although the lifetime of high-energy EEs is shorter, the energetic and time criteria are fulfilled for CEs as well. According to the suggestion in [22], the decay of CEs can provide favorable conditions for the creation of FDs in a cation sublattice of an AHC:

$$e_c^0 \rightarrow v_c h(V_F) + i_c^0 \quad e_c^0 \rightarrow v_c + i_c^+. \quad (5)$$

However, numerous attempts to prove experimentally the reaction (5) in AHCs did not yet succeed. As it has been demonstrated in Sec. 4, CEs formed in caesium, rubidium, potassium, sodium and lithium halides by 13 to 62-eV photons are transformed mainly into several anion EEs ($e-h_a$ and e_a^0), each of which undergoes subsequent radiative or nonradiative decay. According to our experimental data for Na- and Li-halides, an e_c^0 decays into an e_a^0 and one to four $e-h_a$ pairs, which cause at low temperature the creation of anion FDs according to reactions (3).

Up to now we have considered the decay of excitons in a regular (defectless) lattice region and in case of a moderate excitation density. In general, the EE decay into defects is facilitated if the decay takes place in the neighborhood of the already generated (or as-grown) point defects such as v_a and v_c . In this case, the near-defect-localized e_a^0 can decay via reactions (4) and (3) with the formation of defects involving cation FDs ($v_a v_c$ and i_c^+ or $v_a v_c$ and i_a^- , respectively). The similar situation can be realized under the enhanced density of radiation-induced EEs (in the tracks of protons and swift heavy ions, groups of spatially correlated EEs at the multiplication process), if before the decay twin EE associations (e.g., $e_a^0 e_a^0$ or $e_c^0 h$) are formed. Both possibilities were considered in [22].

As it has been declared in Introduction, the creation of stable FDs (long-lived, $\tau > 10^3$ s) is the subject of the present study. Besides creation via EE decay, defects in a stable Frenkel pair should be spatially separated by a few interanion distances in order to leave the so-called instability zone and to avoid a spontaneous recombination of complementary (geminate) defects with the restoration of a regular lattice. At relatively high temperature, the hopping

diffusion of interstitials will promote the needed separation within Frenkel pairs, while elementary FDs remain immobile at helium temperatures and the sufficient interdefect separation for the formation of a stable Frenkel pair is questionable. For anion FDs, the crowdion-type motion of interstitials along closely packed anion chains can help to form stable Frenkel pairs [6,16,17].

The conditions for efficient realization of such crowdion separation were considered as the forth, "orientation" criterion of an efficient EEs \rightarrow FDs transformation (see [6,16,17,35]). On the other hand, the realization of crowdion-type movement of cation interstitials is unlikely, because small-size cations (with respect to anions) in the majority of AHCs do not form closely packed rows, along which the efficient crowdion motion in a cation sublattice can occur. In our opinion, just this circumstance explains the impossibility of stable cation FD creation at helium temperature. Even if EEs decay into cation Frenkel pairs, these are the pairs of short-lived defects with small interdefect distances.

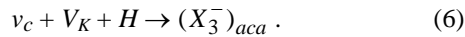
There are more opportunities for cation FD creation at high temperatures, when at least a part of radiation induced defects is already mobile. In AHCs, i_a^- become mobile slightly above liquid helium temperature, the hopping diffusion of paramagnetic $i_a^0(H)$ centers usually starts above 20 K, while the mobility of V_K and V_F hole centers manifests itself strongly above liquid nitrogen but still below room temperature (see, e.g., [4,13,14,16,26,35,68] and references therein).

Many credible manifestations of the creation of defect associations involving also elementary cation FDs by different radiation types at $T \geq 77$ K were detected. These complex radiation-induced defects — $v_a v_c$, $i_c^+ i_a^-$, V_F and $(X_3^-)_{aca}$ centers were considered already in Sec. 3. It has been proved experimentally that a $v_c-i_c^+$ Frenkel pair is formed as a result of two i_a^0 association nearby a pre-irradiation defect (or created at an earlier stage of irradiation) or the interaction of an i_a^0 with a V_K center (see reactions (1) and (2), respectively). A v_c created in a such way and the concentration of which exceeds significantly a possible amount of as-grown v_c , becomes a part of a $(X_3^-)_{aca}$ quasi-molecule situated at two anion and one cation lattice sites and created nearby an $i_c^+ i_a^-$ anti-Schottky defect or a single i_c^+ .

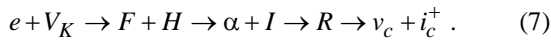
However, at the present moment it is rather difficult to prefer one of two possibilities to create a $v_c-i_c^+$ pair: (i) at the direct decay of an e_a^0 according to the reaction (4) or (ii) at the e_a^0 decay into anion FDs (reaction (3)) with their subsequent transformation into cation ones. Note that there are no proofs of the decay of e_c^0 into cation FDs at low or room temperature yet (see Sec. 4). The possible mechanisms of high-temperature creation of cation FDs were investigated and analyzed mainly for KCl and KBr single crystals [27,28,75]. Measuring the creation spectrum of stable F centers by the photons that selectively form e_a^0 or $e-h_a$ in

different energetic states at 80–300 K, we obtain simultaneously information on the creation efficiency of $(X_3^-)_{aca}$ centers that definitely contain radiation-induced v_c . At high temperatures, H centers (formed as F - H Frenkel pairs) are mobile and escape recombination with complementary and still immobile F only via association with other defects into trihalide molecules, the thermal dissociation of which in AHCs occurs at ~ 350 – 450 K and is accompanied by typical TSL peaks [4,22,28,32,34,37,42–44,67,75].

It was shown [28,75], that the creation efficiency of F (detected via typical luminescence) or $(X_3^-)_{aca}$ centers (detected via corresponding TSL peaks) in KBr and KCl is especially high if exciting photons with the energies around E_g form both e_a^0 and $e-h_a$. The similar result was obtained also for the multiplication region, when one exciting photon is able to form simultaneously two EEs: e_a^0 and $e-h_a$ [27,67]. The photocreation efficiency of $(X_3^-)_{aca}$ is especially high at $T > 170$ K, when V_K centers become mobile and interact with also mobile H near still immobile v_c according the reaction:



At low temperatures, reaction (6) can be realized only with the participation of hot (nonrelaxed) holes, while the main part of h undergoes self-trapping. If exciting photons generate $e-h_a$ pairs, the required h are formed and, in addition, the creation of v_c (i.e., $v_c-i_c^+$ pairs) is also possible via the following sequence of transformations (see also [28]):



According to Rowell and Sangster [29] (see also Table 1), the equilibrium formation energy for cation FDs in the majority of alkali chlorides, bromides and iodides is lower than that for a classical anion Frenkel pair. Therefore, in addition to heat release (phonon package), the energy released at the nonradiative decay of α - I with the restoration of a regular lattice (R in reaction (7)) is sufficient for $v_c-i_c^+$ creation as well [27,28,67,75]. At high temperature, a mutual spatial separation of cation defects is possible and results in the formation of long-lived $v_c-i_c^+$. It is generally accepted (see, e.g., [6]) that primary F - H pairs are formed at the decay of EEs (in our case at the e - h recombination), neutral defects partly undergo tunnel recharging with the formation of a classical anion α - I Frenkel pair. The possibility of reaction (7) is confirmed by the creation of $(X_3^-)_{aca}$ by XeCl excimer laser, the emission of which (in the two-photon regime) causes the formation of only $e-h_a$ pairs in the bulk of KBr at 180 K [35].

The manifestations of cation FD creation at 230–470 K were revealed, in particular, at the irradiation of KCl with photons in the region of the Urbach tail, i.e., at the direct formation of anion STEs [75]. Favorable conditions for $v_c-i_c^+$ creation arise at the transformation of one-halide STE (see [6,13,76]) into a usual two-halide one. In case of

one-halide STE configuration, two neighbor cations are closer to each other (while it is so for two anions in two-halide STE), and during transformation into a two-halide configuration the vibronic energy is concentrated at these cations with subsequent creation of $v_c-i_c^+$.

6. Conclusions

Despite numerous experimental manifestations of the radiation-induced complex structural defects containing cation ones, the particular nonimpact (EE-related) creation mechanisms of cation Frenkel pairs in AHCs are still unclear. At low temperatures, the decay of anion excitons or $e-h_a$ recombination leads to the formation of stable FDs only in an anion sublattice. It is suggested that only short-lived cation Frenkel pairs (if any) are generated via EE decay at helium temperatures, while only additional thermal energy allows a spatial separation of geminate defects and formation of long-lived $v_c-i_c^+$ pairs. In contrast to anion defects within F - H pairs, the crowdion-type defect separation in a cation sublattice is impossible.

At all temperatures, the energy used for the creation of cation excitons is transferred to neighbor anions: an e_c^0 decays into several $e-h_a$ pairs (plus an e_a^0 in sodium and lithium halides), which subsequently generate anion FDs in AHCs. At high temperatures, a $(X_3^-)_{aca}$ trihalide molecule located at two anion and one cation sites (i.e., v_c is definitely involved) is formed due to twin associations of H and V_K centers. Note that there are several possible ways to form the required v_c .

At present, it is rather difficult to choose between the direct decay of an e_a^0 into a $v_c-i_c^+$ pair or the e_a^0 decay into anion FDs with their subsequent transformation into cation ones. It is suggested that $v_c-i_c^+$ pairs can be formed due to the energy released at the high-temperature nonradiative recombination of anion interstitial ions with geminate vacancies, which were earlier generated at the $e-h_a$ pair recombination. One more possibility of high-temperature creation of stable $v_c-i_c^+$ pairs tentatively arises at the transformation of one-halide self-trapped exciton into a usual two-halide one. A rigorous assessment of two above-mentioned mechanisms still lies ahead.

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