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Creation of groups of spatially correlated defects in a KBr crystal at 8 K

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Abstract. The creation spectrum of triplets of spatially correlated defects (F centre + self-trapped hole, V_K centre + interstitial halogen ion, I centre) was measured for the first time in a KBr crystal at 8 K, using synchrotron radiation of 6–25 eV and highly sensitive luminescent methods. The spectrum of spatially correlated F and H centre creation by synchrotron radiation at 8 K was measured as well. The efficiency of F–V_K–I triplet creation is especially high at crystal irradiation by photons under the conditions of multiplication of electronic excitations when the absorption of one photon leads, respectively, to the formation of an electron–hole (e–h) pair and a secondary exciton (15.0–16.5 eV), or two e–h pairs (16.7–19.0 eV), or to the formation of a $3p^5s$ cation exciton (19.5–20.5 eV). It is shown that the formation of an F–V_K–I triplet is caused by the recharging of a primary F–H pair by an e–h pair or by a free exciton.

1. Introduction

Creation processes of point defects, dislocation loops, microvoids etc are successfully investigated in ionic dielectric crystals irradiated by particles or photons, the energy of which exceeds the value of the energy gap E_g by several orders of magnitude (see, e.g., [1, 2]). Powerful radiation sources and informative methods of optical, electron paramagnetic resonance (EPR) and thermoactivation spectroscopy (TAS) are used in these investigations. The creation mechanisms of various point defects under crystal irradiation by photons with energies close to E_g or exceeding this value by two to four times only have been much less studied. Conventional optical absorption and EPR methods are not sufficiently sensitive for the investigation of defect creation by means of weak sources of vacuum ultraviolet (VUV) radiation. Therefore, highly sensitive luminescent and photoelectric methods were used to study the mechanisms of radiation defect formation by VUV radiation in alkali halide crystals (AHCs) [3–10]. The creation of pairs of neutral and charged Frenkel defects—F centres and interstitial halogen atoms (H centres) or anion vacancies (α centres) and interstitial halogen ions (I centres)—was detected in AHCs irradiated by VUV radiation that selectively generates excitons or separated electrons and holes. Discharge sources of VUV radiation were used for the investigation of defect creation in the region 6–12 eV for KBr, KCl, RbBr, RbCl, CsBr and CsCl crystals in a temperature range of 4.2–300 K [3–10]. The use of synchrotron radiation (SR) made it possible to measure the creation spectrum of stable F centres in a wide region up to 32 eV at 295 K [11, 12]. The process

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of multiplication of electronic excitations (MEE), when one absorbed photon causes the formation of two or three electronic excitations (EEs), takes place under the irradiation of a KBr crystal by photons of $h\nu > 14$ eV. The processes of MEE have been investigated in KBr by means of photoelectric methods at 80 K [13] and by luminescent methods at 8 K [14, 15].

This study presents the creation spectrum of stable F centres and some other defects measured for the first time using SR of 6–25 eV at 8 K. The VUV irradiation of KBr at 8 K causes the formation of stable F–H pairs as well as more complex triplets of spatially correlated defects that include F centres. The associations of F centres with self-trapped holes (V_K centres) and interstitial anions (I centres) have been detected earlier in x-irradiated KBr crystals [16–19]. The efficiency of F–V_K–I triplet creation (as well as of other defect groups) should be especially high in the region of MEE, when the absorption of one photon leads, due to Auger processes, to the appearance of two or three EEs, the decay of which provides the simultaneous creation of several defects.

We paid special attention to the investigation of defect groups created by photons of definite energies in KBr at 8 K. Photons of 7 eV selectively generate anion Γ excitons, while separated electrons (e) and holes (h) are formed by 7.7 eV photons. The creation of stable F–H and α–I pairs by 7.0 and 7.7 eV photons has been studied earlier [5, 7, 20]. The threshold energies for the formation of both an electron–hole (e–h) pair and a secondary exciton or two e–h pairs by one photon are $E_t^0 = 15$ eV and $E_t^{\pm} = 16.8$ eV, respectively [14, 15]. Therefore, we have studied the defect formation by 15.8 and 17 eV photons. The formation energy of cation Γ excitons is $E_{ec} = 20$ eV and the photoionization energy of $3p^6$ K^+ is $E_{gc} = 20.5$ eV [21, 14, 22]. We investigated the process of defect creation by 20 and 23 eV photons also.

The formation of short-lived F–H pairs has been studied in detail in a KBr crystal irradiated by nanosecond electron pulses [23–25] or pico- and femtosecond laser pulses [24–26]. A KBr crystal irradiation under the conditions of MEE will be, in our opinion, most favourable for the creation of not only F–H pairs, but also groups of spatially correlated defects: F–V_K–I, F–V_K–H, H–H, H–V_K, F–I etc. The investigation of F–V_K–I triplet creation was a particular purpose of the present study.

2. Experimental details

The main objects of our investigation were single KBr crystals grown in the Institute of Physics, Tartu, by the Kyropoulos method in 'helium atmosphere'. Before growing a 'special purity' salt undergoes a purification cycle involving a melt treatment in Br_2 gas flow and 50-fold recrystallization from the melt. The content of Ba^{2+}, Sr^{2+} and Ca^{2+} impurity ions was less than 0.01 ppm and that of Na^+ and I^- ions less than 3 ppm. Only the concentration of Cl^- was about 50 ppm.

The main experiments were carried out at beamline 52 in the MAX-Laboratory in Lund, Sweden (550 MeV storage ring). Relevant details for the experimental setup have been described in previous papers [11, 14]. Freshly cleaved samples were mounted in a cold-finger cryostat (8–300 K). The reflection spectra for the (100) plane of KBr and the creation spectra were measured under ultrahigh-vacuum conditions (10^{-9} mbar). The luminescence from a sample was analysed using a 0.3 m grating monochromator and a Hamamatsu R585 photomultiplier operating in the photon counting mode.

At the measurement of the creation spectra the crystal was irradiated by an equal number of photons at each of several energies. The reference signal for normalization (for equal quantum irradiation dose) was recorded from a sodium salicylate coated mesh.

The previously irradiated crystal was stimulated by 2.05 ± 0.03 eV photons, from a double monochromator, in the maximum of the F absorption band (so-called F stimulation). This photostimulation causes the excitation (but not ionization) of F centres up to the 2p state in KBr at 8 K. A second monochromator was used to detect σ luminescence of self-trapped excitons (STEs). According to Kabler [27], σ luminescence of an STE in KBr at 4.5 K has the maximum at 4.42 eV and corresponds to radiative decay of the STE, the hole component of which is a self-trapped hole, V_K centre. The F stimulation of an irradiated crystal causes the appearance of this σ luminescence if the distance between an F and a V_K centre, R_{FV}, is a few d (d is an interanion distance along [110]). The excitation of an F centre up to the 2p state increases the effective radius of an electron component of the F centre and makes possible the tunnel transfer of an electron from F to a V_K centre, forming an STE.

Instead of a V_K centre, an interstitial halogen atom (an H centre, that is, a Br_2^- molecule situated at one anion site [28]) can be located near an F centre. Such an F–H pair is stable in KBr at 5 K if the interdefect distance equals $R_{FH} = 4$d [29]. An optical excitation of the F centre up to the 2p state provides a rapid tunnel recharging of an F(2p)–H pair with the formation of an α–I pair (an electron transfer from F to H) [6, 7, 20]. According to theoretical estimates [30] the recharging of F(1s)–H pairs occurs non-radiatively, while the recharging of F(2p)–H pairs can be accompanied by the tunnel luminescence. This photostimulated luminescence (PSL), caused by the tunnel recharging of F(2p)–H pairs, was detected in CsBr, KBr, KCl [6, 20] as well as in KI and RbI crystals [31]. The tunnel luminescence band of F(2p)–H pairs has the maximum at 2.6 eV in a KBr crystal irradiated at 4.2 K [20].

The light sum (S_F) of 4.42 or 2.6 eV luminescence stimulated in the maximum of the F absorption band ($h\nu_s = 2.05$ eV) was taken as a measure of spatially correlated F and V_K or F and H centres, respectively, created by SR. The F stimulation of a crystal led to a total destruction of defect pairs, the interdefect distances (R_{FH} and R_{FV}) of which were small enough for realization of the tunnel processes. Besides the spatially correlated defects, radiation produces in KBr at 8 K F centres which are spatially separated from H or V_K. The amount of these separated defects can be decreased due to the photoionization of F centres by photons of 2.5–2.6 eV. Direct measurements of photoconductivity at 10 K in additively coloured KBr crystals showed that 2.5–2.6 eV photons generate electrons in the conduction band [32]. In order to totally destroy all V_K centres, produced by radiation at 8 K, the crystal was periodically heated up to 220 K.

TAS methods were used to detect the F–V_K–I and F–V_K–H triplets, formed by VUV radiation at 8 K. It was shown earlier that the thermal annealing of I centres in KBr occurs in two stages, at 17–30 K [33, 16, 7]. The annealing of H centres in KBr takes place in a wide temperature range 30–60 K [16, 34]. At 30–45 K interstitial atoms recombine with correlated F centres while at higher temperatures there occurs the association of H with impurities or other H centres [34] as well as with V_K [35]. The complex study of KBr crystals, irradiated at 8 K, by means of optical and TAS methods led to the conclusion that F stimulated 4.42 eV luminescence, which can be annealed by a crystal heating up to 27 K, arises due to the processes in F–V_K–I triplets of spatially correlated defects [16, 33].

Figure 1 presents the dependence of the number of F–V_K–I triplets (that is proportional to S_F) on the dose D_e of KBr irradiation by 7.7 or 15.8 eV photons at 8 K. The absolute value of D_e varies from 10^{13} to 3×10^{15} photons cm^{-2}. At low values of D_e the dependence is linear, while at higher D_e it becomes sublinear. However, there is no saturation even at $D_e = 3 \times 10^{15}$ photons cm^{-2}. The sublinear behaviour of $S_F(D_e)$ is connected with the fact that the growth of D_e increases the number of radiation defects as well as the efficiency of the reverse process—destruction of already formed defects during crystal irradiation.

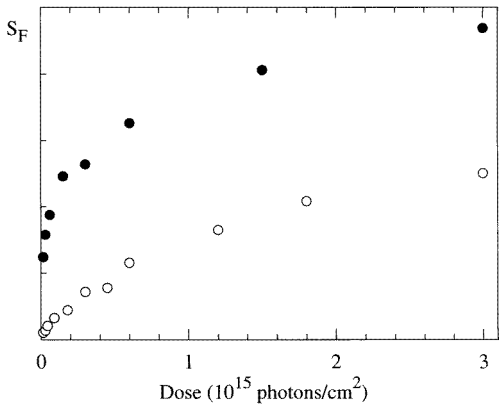

Figure 1. Dependence of the light sum of 4.42 eV photostimulated luminescence S_F on the dose of a KBr crystal irradiation by photons of 7.7 eV (○) and 15.8 eV (●) at 8 K. The previously irradiated crystal was stimulated in the maximum of the F absorption band ($h\nu_s = 2.05$ eV).

According to figure 1 the increase of S_F slows down since $D_e = 3 \times 10^{14}$ photons cm^{-2} in the case of KBr irradiation by 7.7 eV photons, which generate single e–h pairs. However, the same process with 15.8 eV photon irradiation takes place at significantly lower values of D_e because the absorption of one photon of 15.8 eV leads to the formation of two EEs: an e–h pair and a mobile secondary exciton in KBr at 8 K [14]. At low values of D_e the efficiency of triplet creation by photons of 15.8 eV is several times higher (from 10 to three times depending on the value of D_e). However, at high values of D_e the ratio of efficiencies is close to 2. Measuring the spectrum of F–V_K–I triplet creation by SR, we used, for technical reasons, the dose of KBr irradiation $D_e = 3 \times 10^{14}$ photons cm^{-2}, i.e. our dose corresponds to the beginning of the sublinear dependence of $S_F(D_e)$.

To be more precise, we measured the creation spectrum of F stimulated 4.42 eV luminescence, which arises due to the tunnel recharging of F and V_K centres in spatially correlated defect groups. It will be shown in section 4 that the majority of F–V_K–I triplets (with the exception of a crystal irradiation by 15.8 eV photons) can be annealed at 18 to 27 K due to the beginning of hopping diffusion of I centres at small distances (up to 10 interionic distances). The annealing of a small fraction of spatially correlated F and V_K centres takes place at higher temperatures (30–45 K) and is tentatively connected with the processes in F–V_K–H triplets (H centres become mobile and recombine with F centres).

3. Spectra of defect group creation by VUV radiation

3.1. Creation of F–V_K–I triplets

Figure 2 presents the reflection spectrum measured for KBr in the region up to 9.5 eV. According to [36] and [37] the intensive reflection peaks at 6.81 and 7.30 eV are connected with the formation of $\Gamma(3/2, 1/2)$ and $\Gamma(1/2, 1/2)$ excitons with $n = 1$, respectively. Γ excitons with $n = 2$ can be formed in the regime of two-photon absorption at $h\nu \geqslant 7.3$ eV [37]. The value of the energy gap is $E_g = 7.55$ eV in KBr at 8 K. The reflection maxima in the region 8.1–9.1 eV correspond to the formation of EEs with d-type electron component at the L point of the Brillouin zone [38]. The irradiation of a KBr crystal by 7.7 eV photons leads to the creation of e–h pairs near the Γ point, i.e. with 'cold' holes, while 8.1 to 9.1 eV photons generate e–h pairs with 'hot' holes.

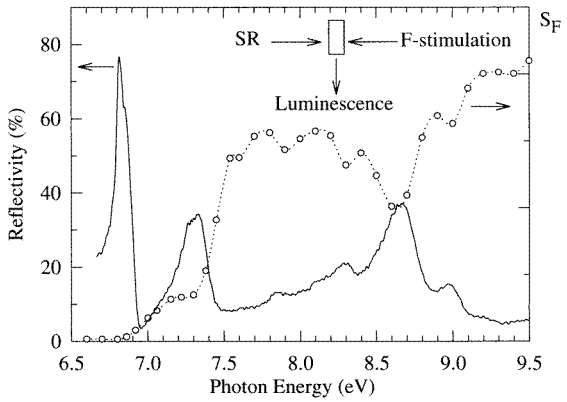

Figure 2. Spectrum of F–V_K–I triplet creation (○) and the reflection spectrum (solid line) measured for KBr at 8 K. The light sum of 4.42 eV photostimulated luminescence S_F is taken as a measure of triplets created by VUV radiation (see text for details). The inset shows the geometry for measuring the creation spectrum.

Figure 2 shows also the spectrum of F–V_K–I triplet creation measured for KBr in the region of 6.5–9.5 eV at 8 K. The light sum S_F of the 4.42 eV tunnel recombination luminescence, stimulated in the maximum of the F absorption band, is taken as a measure of defect groups created by SR. A comparison of this creation spectrum with the reflection spectrum, the features of which were interpreted earlier [36–38], allows us to conclude that PSL of 4.42 eV is practically absent at the direct formation of $\Gamma(3/2, 1/2)$ excitons with $n = 1$ by 6.7–6.9 eV photons. A weak PSL can be detected after KBr irradiation by photons of 6.92–7.30 eV, i.e. after a sharp gap in the reflection spectrum which is usually connected with the formation of longitudinal excitons and the beginning of the upper polaritonic branch.

A sharp increase of the intensity of 4.42 eV PSL takes place at $h\nu > 7.3$ eV in the formation region of Γ excitons with $n = 2$. The value of S_F is approximately constant at 7.6–8.1 eV, where separated electrons and holes are formed, and changes slightly in the region 8.2–9.1 eV. It is necessary to mention that the spectrum of $S_F(h\nu)$ is not corrected for the reflection of VUV radiation by the crystal. The value of reflectivity varies from 7 to 37% in the spectral region of 7.6–9.1 eV.

Photons of 7 eV generate Γ excitons with $n = 1$, which undergo self-trapping and decay with the creation of short-lived ($\tau < 1$ μs) as well as stable F–H pairs at 8 K. Figure 3 presents the stimulation spectrum of 2.6 eV PSL measured for a KBr crystal previously irradiated by 7.00 ± 0.05 eV photons (irradiation dose is $D_e = 3 \times 10^{13}$ photons cm^{-2}). The contour of this stimulation spectrum is approximately the same as the shape of an F absorption band measured for an additively coloured KBr crystal at 10 K [32]. The stimulation spectrum of 4.42 eV PSL, that reflects the creation of F–V_K–I triplets, has been measured for KBr irradiated by 7.7 eV photons. According to figure 3, the 4.42 eV tunnel luminescence can be effectively stimulated not only in the region of the F absorption band (1.95–2.15 eV) but at 2.15–2.25 eV also. Crandall showed [32] that at 10–20 K the quantum yield of photoconductivity, caused by the ionization of isolated (single) F centres, is close to unity in the region of $h\nu > 2.7$ eV but sharply decreases down to zero at 2.2 eV. The K absorption band of F centres has an indistinct maximum in the region 2.28–2.36 eV and corresponds mainly to the excitation of an F centre up to the 3p state. A high-energy edge of the K band is connected with the excitation of an F centre up to higher states also. The

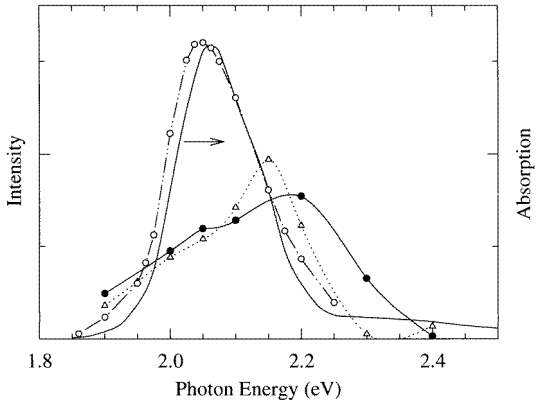

Figure 3. Stimulation spectra of 2.6 eV (○) and 4.42 eV (● △) luminescence in a KBr crystal previously irradiated by photons of 7.0 eV (○), 7.7 eV (●) and 20 eV (△) at 8 K. Absorption spectrum of single F centres measured in additively coloured KBr crystal at 10 K [32].

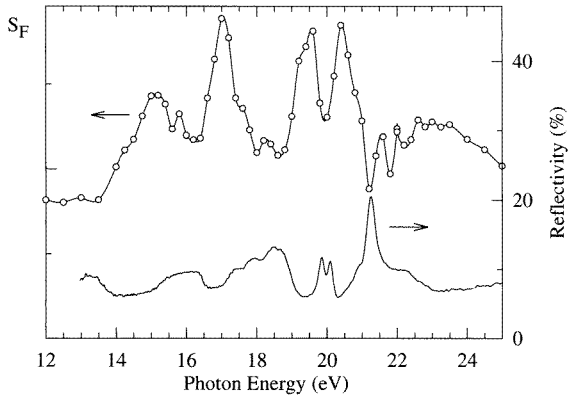

Figure 4. Spectrum of F–V_K–I triplet creation (○) and the reflection spectrum (solid line) measured for KBr at 8 K. See text and caption of figure 2 for details.

excitation of F centres, that are parts of F–V_K–I and F–V_K associations, up to the 3p state enables the effective tunnelling of an electron of an F centre to a V_K centre situated at larger distance R_{FV} than that at the excitation of F centres up to the 2p state. It is also necessary to take into account that the 3p state of an F centre is strongly disturbed by the long-range electric field, which is caused by the presence of a V_K centre spatially correlated with the F centre. However, the 1p and 2p states of the F centre do not undergo a similar disturbance.

The stimulation spectra for 4.42 eV luminescence in the case of a KBr crystal irradiation by 14, 17 or 23 eV photons are close to the spectrum obtained after crystal irradiation by 7.7 eV photons and depicted in figure 3. However, the stimulation spectrum for 4.42 eV PSL induced by 20 eV photons differs significantly. The reason that causes this difference will be discussed later.

Figure 4 shows the creation spectrum of F–V_K–I triplets measured in the region 12–25 eV for KBr at 8 K. The light sum S_F of 4.42 eV PSL ($h\nu_s = 2.05$ eV) was taken as a

measure of triplets created by SR ($D_e = 3 \times 10^{14}$ photons cm^{-2}). The value of S_F is low at 12.5–14.0 eV, where one exciting photon produces only one e–h pair, starts to increase at 14.5 eV and doubles at 17 eV. The sharp increase of S_F occurs in the region of MEE where hot photoelectrons form secondary anion excitons (15.0–16.5 eV) or secondary e–h pairs (16.7–19.0 eV). The value of S_F reaches a maximum at 17 eV, near the threshold energy for the creation of two 'cold' (with small kinetic energy) spatially correlated e–h pairs by one photon. Rapid recombination of one of these pairs causes the creation of spatially correlated F and H centres. A hole from the second e–h pair gets localized forming a V_K centre. An electron from the second e–h pair is captured by an H centre with the formation of an extra Cl^- ion in an anion row along the [110] direction [9]. After displacement by a several interanion distances from its 'birth place' this ion, mobile even at 8 K, localizes in a tetrahedral interstitial site of a crystal lattice thus forming an I centre immobile at 8 K [19]. An absorption of a 17 eV photon provides a favourable situation for the creation of an F–V_K–I triplet according to the reaction

$$e + h + e + h \rightarrow F + H + e + V_K \rightarrow F + He + V_K \rightarrow F\text{–}V_K\text{–}I. \qquad (1)$$

An absorption of one 18–19 eV photon leads to the generation of two e–h pairs as well. However, these pairs are 'hot' ones (carriers have significant kinetic energy). In case of a crystal irradiation, that generates hot carrier quartets, the probability of the creation of F–V_K–I triplets with small interdefect distances decreases. In the region of 14.5–16.7 eV the situation is more complicated. Secondary excitons (SEs), formed by hot photoelectrons, have a high mobility [22] and at 8 K they are able to leave their birth place causing the decrease of F–I–V_K creation efficiency.

According to figure 4 the efficiency of 4.42 eV PSL is high after crystal irradiation by 19.5–20.5 eV photons that generate cation $3p^5 4s\ \Gamma$ excitons [21, 14]. For energetic reasons cation excitons can decay with the formation of two e–h pairs. Recently we have revealed this effect in KBr:Tl at 295 K [11]. At the decay of cation $3p^5 4s\ \Gamma$ excitons, the energy transfer from an excited K^+ ion to two neighbouring halogen ions and the formation of two hot photoelectrons and two cold holes is expected. Holes transform into two especially close V_K centres. The recombination of one of photoelectrons with a V_K provides the creation of an STE. An F–H pair formed at the non-radiative decay of this STE is spatially very close to the second V_K. So, a strong perturbance of excited states of an F centre, as a part of an F–H–V_K triplet, is expected. The experimental data testify on behalf of our hypothesis on the decay mechanism of cation excitons. The stimulation spectrum of 4.42 eV luminescence in 20 eV photon irradiated KBr has a maximum at 2.15 eV (see figure 3), i.e. not at the maximum of the K band (2.25–2.35 eV) as in the case of an additively coloured crystal nor at 2.2 eV as in the case of KBr irradiation by 7.7, 14, 17 or 23 eV photons, which form F–V_K–I triplets. The decay of cation excitons, generated by 20 eV photons, leads to the creation of a triplet with extremely small distance R_{FV} between F and V_K centres.

However, the situation is different at a crystal irradiation by photons of $h\nu > 21$ eV, which cause the photoionization of cations. Photons of 23 eV produce conduction electrons and the holes in the $3p^6$ shell of K^+, which are later filled up by electrons from the $4p^6$ shell of Br^-. The energy released during this process (>11 eV) is non-radiatively transfered to a Br^- ion causing the formation of a secondary e–h pair. So, the absorption of one 23 eV photon leads to the creation of two e–h pairs with hot electrons and holes and the formation of two extremely spatially close V_K centres is not expected in this case. The efficiency of F–V_K–I triplet creation by 23 eV photons is significantly lower than that by 20 eV photons which generate cation excitons (see figure 4).

3.2. Creation of spatially correlated F and H centres

The creation spectra of stable F–H pairs were measured earlier for CsBr, KCl and KBr crystals using VUV radiation of 6.5–10.0 eV at 4.2 K [6, 8, 20]. In KBr the spectrum covers the regions of photocreation of Γ excitons with $n = 1$ and $n = 2$ as well as the region of band-to-band transitions. The light sum of 2.6 eV PSL ($h\nu_s = 2.05$ eV) was taken as a measure of F–H pairs. For the first time we have expanded these measurements to the region of MEE (12–24 eV), i.e. the region where secondary anion excitons, secondary e–h pairs and cation EEs should be taken into account.

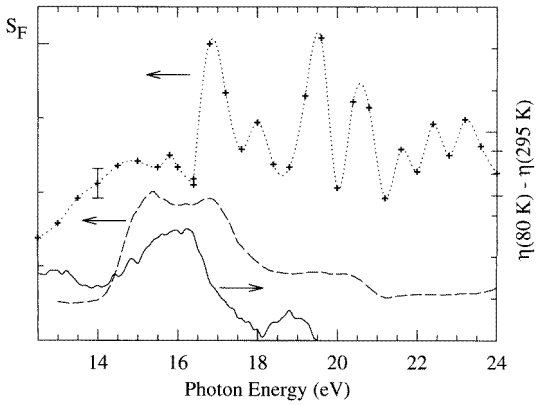

Figure 5. Spectrum of F–H pair creation (+) by SR measured for KBr at 8 K. The light sum of 2.6 eV photostimulated tunnel luminescence S_F is taken as a measure of F–H pairs (see text for details). The F-centre creation spectrum (dashed line) of a KBr:Tl sample at 295 K [11]. The difference of photoelectric yield (solid line) measured for a thin film of KBr at 80 and 295 K [13].

Figure 5 shows the creation spectrum of stable F–H pairs measured for a KBr crystal at 8 K ($D_e = 10^{15}$ photons cm^{-2}). The light sum of 2.6 eV PSL was taken as a measure of F–H pairs created by SR. There is a significant difference between this spectrum and the creation spectrum of stable F centres measured earlier [11] in KBr:Tl at 295 K using luminescent methods (a fragment of the latter spectrum is depicted in figure 5 also). The main difference between two spectra is observed in the region 14.5–16.5 eV where photons produce hot electrons able to form SEs. At 295 K SEs undergo a rapid self-trapping and decay with the creation of immobile F and mobile H centres. Stabilization of an H centre occurs due to its interaction with a V_K centre (which is formed by the same photon as a secondary exciton) and the formation of a Br_3^- trihalide molecule [11]. However, at 8 K a fraction of SEs in KBr are highly mobile and before self-trapping they migrate large distances, causing, for example, an efficient excitation of impurity ion luminescence in KBr:I [22]. In pure KBr a fraction of mobile SEs interacts with F and H centres as well as with other defects created by VUV radiation resulting in the recharging of defects and the formation of defect associations.

In figure 5 we present also the difference of photoelectric yields η for a KBr thin film measured by Ejiri *et al* [13] at 80 and 295 K. The value of η significantly increases in some regions of the spectrum at the cooling of a KBr film down to 80 K. The maximum of this increase takes place at 14.5–16.6 eV, i.e. in the region where one absorbed photon produces an e–h pair and an SE. At crystal heating 80 $\rightarrow$ 295 K the efficiency of SE decay

with the formation of stable F centres increases, while the probability of exciton migration into near-surface layers and photoemission efficiency decrease.

The efficiency of 2.6 eV PSL (and spatially correlated F and H centres) in a KBr crystal at 8 K has a maximum at 16.5–17.3 eV, close to the threshold for the formation of secondary e–h pairs. A rapid recombination of an electron with a self-trapping hole, before its transformation into a totally relaxed V_K centre leads to the effective creation of F–H pairs. A secondary hole (from a secondary e–h pair) undergoes a rapid self-trapping near an F–H pair forming, as a result, an F–H–V_K triplet. The majority of secondary electrons become localized at H centres, transforming them into I centres (and F–H–V_K triplets into F–V_K–I). Nevertheless, a fraction of primary F–H pairs and F–H–V_K triplets can be detected by means of 2.6 eV PSL after crystal irradiation by 17 eV photons.

4. Thermal annealing of defect groups formed by VUV radiation

4.1. Annealing of defects created due to the decay of excitons

Luminescent TAS methods have been used in order to identify the types of interstitial (I or H centres) that participate in defect groups created by VUV radiation. Figure 6 presents the annealing curve of the intensity of F flash, I_F. A KBr crystal was irradiated at 4.2 K by 7.00 ± 0.05 eV photons ($D_e = 3 \times 10^{13}$ cm^{-2}), which generate excitons with $n = 1$, and then heated up with a rate of about 0.03 K s^{-1}. In the process of heating the crystal was periodically stimulated by 2.05 eV photons with constant intensity. Such pulsed F stimulation causes the tunnel recharging of F(2p)–H pairs and the appearance of 2.6 eV PSL (F flash). The value of I_F increases in the region 18–23 K, while the decrease of I_F occurs at 25 to 32 K and from 37 to 43 K. The decrease of I_F is accompanied by a weak thermally stimulated luminescence (TSL) with the main peak at 28 K and significantly less intensive peaks at 37 and 43 K.

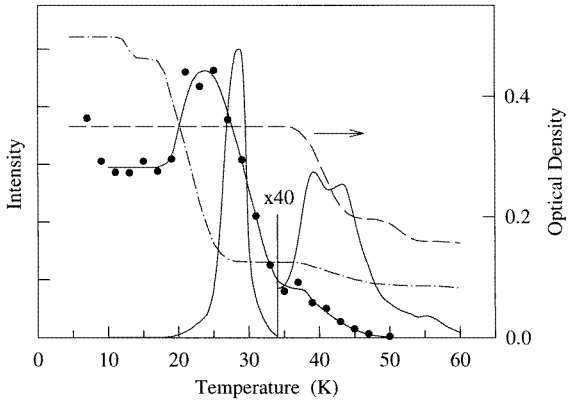

Figure 6. Thermal annealing of the intensity of F flash (●) and α flash (— · —) and thermally stimulated integrated luminescence (solid line) for KBr irradiated by 7.0 eV photons at 4.2 K. The annealing of the optical absorption of H centres (– – –) for KBr x-irradiated at 4.2 K and heated up to 30 K.

In addition to F–H pairs, irradiation of KBr by 7 eV photons at 4.2 K creates α–I pairs also [7, 9, 29], the presence of which can be testified to by the appearance of typical α luminescence of 2.55 eV (α flash, I_α) under photostimulation of an irradiated crystal in

the maximum of the α absorption band (6.15 eV). The annealing of I_α (see figure 6) is caused by hopping diffusion of I interstitials and their recombination with anion vacancies. The recombination of spatially correlated α and I centres takes place at 18 to 27 K, while at higher temperatures highly mobile I interstitials interact with genetically uncorrelated α centres and with F centres. The recombination of I and F centres provides the appearance of conduction electrons and their subsequent radiative interaction with V_K and H centres.

Figure 6 shows also the annealing curve of the optical absorption of H centres (the band maximum at 3.26 eV) induced in KBr by x-irradiation (50 kV, 20 mA, 1 hour) at 4.2 K. In order to suppress an optical absorption connected with V_K centres (maximum at 3.22 eV), the irradiated crystal was pre-heated up to 30 K. The main annealing of H centres is observed at 35 to 45 K and is accompanied by weak TSL peaks at 37 and 43 K. These TSL peaks arise due to partial recombination of H with F′ centres (F centre with an additional captured electron).

The above-mentioned data combined with additional information on the annealing of radiation defects in x-irradiated KBr crystals [16–19] allow us to interpret the increase of the intensity of 2.6 eV PSL at 18–24 K (see figure 6) as the increase of a number of H centres and F–H pairs due to the recombination of mobile I centres with V_K (both being members of F–V_K–I triplets). The decrease of I_F at higher temperatures is caused by the recombination of F with 'alien' I centres (initially separated by tens of interanion distances d from F centres). Conduction electrons, formed at such F–I interactions, recombine mainly with V_K centres. The annealing of I_F at 35 to 45 K is connected with the recombination of mobile H with F centres.

Γ excitons with $n = 1$, generated by 7 eV photons in KBr, undergo self-trapping and efficiently decay into F–H pairs. However, this process, investigated in detail at helium temperatures [6, 7, 9], is not the only way of free exciton relaxation. In KBr at 4–30 K, free excitons (e^0) migrate before self-trapping at large distances and can interact with F–H pairs. The effective cross-section of the interaction of exciton polaritons with defects is especially large in the case of spatially extended defects, e.g., H centre which produces around itself an extensive region of elastic deformation [28]. A KBr irradiation in the region of the exciton absorption band makes possible the formation of defect triplets according to the reaction

$$F + H + e^0 \rightarrow F + He + V_K \rightarrow F\text{–}V_K\text{–}I. \tag{2}$$

However, this reaction does not take place at the irradiation of KBr:Cl ($D_e = 3 \times 10^{13}$ photons cm^{-2}), either by 6.7 eV photons, that generate EEs localized near imperfections, or by 7.7 eV photons that provide band-to-band transitions at the Γ point and form e–h pairs with cold holes, which rapidly become self-trapped and are able to interact with other self-trapping holes [20]. The significant increase of I_F (temperature range 18–23 K in figure 6) is typical only for KBr irradiation by 7 eV photons that generate highly mobile free excitons. The value of I_F for 4.42 eV PSL decreases more than twice from 18 to 25 K in KBr irradiated by 7.7 eV photons. This decrease is connected with the thermal annealing of F–V_K–I triplets.

4.2. Annealing of defects formed under conditions of MEE

The process of F–V_K–I triplet creation in KCl and KCl:Tl crystals x-irradiated at 10 K has been investigated in detail by means of the EPR method [9, 19]. It was shown that low-temperature annealing of V_K centres is accompanied by the increase of the number of H centres. This effect is caused by the beginning of hopping diffusion of I centres at small distances. A fraction of mobile I centres, that participate in F–V_K–I triplets formed

by x-irradiation of KCl, interacts with V_K centres transforming them into H centres.

The process of F–V_K–I triplet creation in x-irradiated KBr was investigated using only optical methods [9, 19]. We have continued the study of this process applying, for the first time, SR in the energy region of MEE. The absorption of one 17 eV photon in KBr at 8 K leads to the creation of two e–h pairs (a primary pair and a secondary one) [14, 15]. The value of I_F for 4.42 eV PSL decreases approximately threefold at a crystal heating up to 26 K. This decrease is caused by the thermal annealing of F–V_K–I triplets. At temperatures below 18 K the hopping diffusion of I centres is practically frozen. In the region of 18–27 K, I centres are already mobile: they can migrate at small distances and recombine with F centres, that participate in F–V_K–I triplets. The annealing of practically all spatially correlated F and V_K centres that remained after KBr heating up to 27 K occurs from 39 to 45 K due to the hopping diffusion of H centres and its recombination with F centres from F–V_K–H triplets.

In the case of KBr irradiation by 15.8 eV photons the situation is more complicated. Figure 7 presents the dependencies of the light sum S_F of PSL on the temperature of the previous irradiation of KBr by photons of 15.8 eV ($D_e = 10^{14}$ cm^{-2}). The absorption of one photon of 15.8 eV leads to the formation of both an e–h pair and an SE [14, 15]. According to figure 4 the value of S_F for PSL of 4.42 eV in the case of 15.8 eV photon irradiation is significantly smaller than that for a crystal irradiated by 17 eV photons. The value of S_F for PSL of 4.42 eV slightly changes if the irradiation temperature varies from 8 to 30 K. We interpret such behaviour of $S_F(T)$ as the manifestation of a small amount of F–V_K–I triplets created by 15.8 eV photons. The dependence of S_F on the temperature of KBr irradiation by 15.8 eV photons in the case of 2.6 eV PSL is different (see figure 7): the value of S_F is practically constant at 15–26 K, increases at 27–30 K and then sharply decreases if the irradiation temperature varies from 32 to 45 K. The last temperature region corresponds to the annealing of F–H pairs (see section 4.1). Similar to the case of direct generation of excitons by 7 eV photons (see figure 6), the value of S_F for PSL of 2.6 eV increases in the temperature region of 27–30 K for a KBr crystal irradiated by 15.8 eV photons.

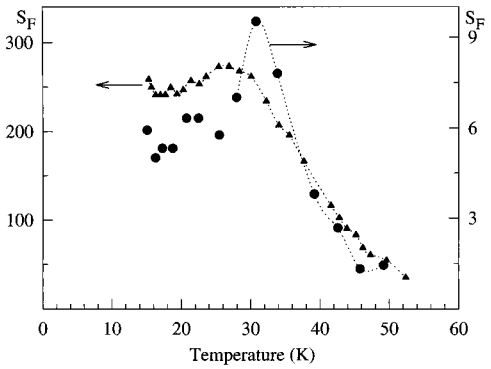

Figure 7. Dependence of the light sum of F stimulated luminescence of 2.6 eV (●) and 4.42 eV (▲) on the temperature of preliminary irradiation of KBr by photons of 15.8 eV.

The process of energy transfer by SEs to impurity centres was studied in KBr:I [22]. It was shown that SEs are highly mobile at 8 K and before self-trapping they migrate large distances from their birth place. The irradiation of KBr by 15.8 eV photons at 8 K creates two different defect groups. The formation of the first group is spatially localized by the

region of MEE and is connected with the rapid self-trapping of an exciton, decay of an STE into an F–H pair and interaction of this F–H with an e–h pair with the formation of an F–V_K–I triplet. However, the amount of such F–V_K–I triplets is small. Creation of the second group is caused by SEs which are able to migrate large distances from their birth place. These excitons undergo self-trapping and decay into F–H pairs.

5. Concluding remarks

We have undertaken the first complex study of the creation of the groups of spatially correlated defects by VUV radiation of 6–25 eV at 8 K. The results show that besides the well studied short-lived and stable F–H pairs as well as stable α–I pairs the irradiation creates in KBr more complicated defect associations, which include F centres, self-trapped holes (V_K centres) and interstitial halogen ions (I centres). The use of VUV radiation, that selectively generates in KBr anion excitons, electron–hole pairs, both an electron–hole pair and a secondary exciton, quartets of carriers or leads to the selective excitation and ionization of the $3p^6$ shell of the K^+ ion, allowed us to clarify the elementary mechanisms of creation and transformation of spatially correlated defect groups, which serve as seeds for the formation of more complex radiation damages.

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