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Franck–Hertz effect in cathodo- and photoluminescence of wide-gap materials

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ABSTRACT

A brief overview of previously obtained and novel data on the manifestations of an analogue of Franck–Hertz effect in photo- and cathodoluminescence of wide-gap inorganic materials is presented. On the example of NaCl:Tl⁺ and MgO:Cr³⁺ single crystals, the excitation processes of the luminescence of 6s²Tl⁺ ions and 3d³Cr³⁺ ions by 5–15 keV electrons or 5–20 eV photons at 6–420 K have been studied. The rapid processes of the direct energy transfer to Tl⁺ by hot conduction electrons or to Cr³⁺ centers by hot electrons and/or hot valence holes have been separated from rapid excitonic and more inertial electron–hole processes.

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1. Introduction

The main goal of the present paper is to sum up long-standing investigations of the solid-state analogue of Franck–Hertz effect (FHE) in gases – a resonant excitation of luminescent impurity centers and structural defects by hot (non-relaxed) conduction electrons or/and valence holes in wide-gap materials (WGM, $E_g > 6$ eV) – performed at the Institute of Physics, Tartu. In such materials, the separation of FHE in low-temperature photo- and cathodoluminescence (PL and CL, respectively) is of obvious interest for both fundamental studies and various technical applications, such as the elaboration of novel spectral transformers for neon luminescent tubes and xenon plasma display panels or the increase of WGM radiation resistance by weakening hot electron–hole (e – h) recombination with the creation of Frenkel defects (Lushchik et al., 2006).

In 1914, James Franck and Gustav Hertz (Nobel Prize in 1925) performed the now-famous experiment on the interaction of slow electrons of various kinetic energies with a mercury vapor and detected an ultraviolet emission (4.9 eV) of free Hg atoms resonant to electron energy losses. Niels Bohr repeatedly cited this experiment as the most illustrative confirmation of quantized model of the atom, when atoms absorb and emit discrete amounts of energy. From the modern standpoint, the resonant behavior of the excitation function of free mercury atoms by electrons of ~ 4.9 eV corresponds to spin-restricted singlet–triplet $^1S_0 \rightarrow ^3P_1$ electron transitions caused by an effective electron exchange. In the case of

totally allowed $^1S_0 \rightarrow ^1P_1$ electron transitions of free Hg atoms the excitation function smoothly increases with the rise of the kinetic energy of incident electrons above the threshold value.

At the beginning of 1960s, William Schockley and Viktor Vavilov separated an elementary act of multiplication of e – h pairs in narrow-gap semiconductors. Thereafter, PL with quantum yield $QY > 1$ was obtained in alkali iodides doped with mercury-like Tl⁺ and In⁺ ions (Ilmas et al., 1965). The exciting photon of vacuum ultraviolet (VUV) radiation was transformed into two or three quanta of visible emission of impurity centers. This so-called “photon multiplication” phenomenon was thoroughly studied at the Institute of Physics (Tartu, Estonia) in a number of alkali halide crystals (AHC), pure and doped with s^2 - and d^{10} -impurity ions. The analysis of the obtained luminescence data as well as of literature data on photoelectron spectra of AHC thin films allowed revealing two main mechanisms of photon multiplication connected with the creation of several electronic excitations by one exciting photon. A hot conduction electron with a sufficient energy, formed at the exciting photon absorption, is able to create a secondary exciton or a secondary e – h pair. The subsequent radiative exciton decay and the recombination of a secondary and a primary cold e – h pairs cause the appearance of two emission quanta per one exciting photon.

The application of synchrotron radiation allowed for a further detailed study of the excitonic and e – h multiplication mechanisms in AHC (Ivanov et al., 1973; Lushchik et al., 1996; Feldbach et al., 2000). The elementary mechanisms of photon multiplication have been studied in binary and complex metal oxides as well (Lushchik et al., 2005, 2006). The separation and elucidation of the third multiplication mechanism in WGM – the solid-state analogue of FHE appeared to be much more complicated (Lushchik et al., 1966,

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1998, 2005; Feldbach et al., 1997; Kirm et al., 1997; Makhov et al., 2008). The process of the direct excitation of impurity centers by hot conduction electrons or valence holes is rather fast (nanoseconds) and hardly distinguishable from the low-inertial excitonic mechanism. To account for the mechanism of electroluminescence in wide-gap semiconductors of ZnS:Cu⁺ and ZnS:Mn²⁺, the impact excitation of luminescent impurities by conduction electrons accelerated in an electric field was suggested (Piper and Williams, 1952; Bhattacharyya et al., 1993).

A brief consideration of experimental manifestations of FHE in PL of WGM, taking NaCl single crystals as an example, will be given in Section 2. Section 3 contains data on low-temperature CL of MgO single crystals in support of a solid-state analogue of FHE in metal oxides.

2. Manifestations of FHE in photoluminescence of WGM

Fig. 1 shows a simplified energy-band diagram of a typical WGM – a NaCl single crystal doped with mercury-like Tl⁺ ions with a 6s² ground-state configuration. The minimum energy for the direct optical formation of an anion exciton with $n=1$ in NaCl equals $E_e = 8$ eV, the energy gap is $E_g = 8.75$ eV and the total width of the valence band (v-band) is $E_v \approx 3$ eV. Fig. 1 also demonstrates the energy levels of a Tl⁺ impurity center in NaCl:Tl, that are located within the energy gap and correspond to ¹S₀, ³P₁ and ¹P₁ states of a free Tl⁺ ion. The energetic position of the ¹P₁ level (~6.2 eV) with respect to the bottom of a conduction band (c-band) is experimentally determined by measuring the excitation spectra of recombination luminescence and photoconductivity.

Fig. 2 demonstrates the excitation spectra of the A emission (4.27 eV, ³P₁ → ¹S₀) of Tl⁺ centers in NaCl:Tl⁺ measured using synchrotron radiation at 8 K (SUPERLUMI station of HASYLAB at DESY, Hamburg). The spectra were measured for time-integrated luminescence as well as for the emission detected within two time windows (length Δt) correlated with the excitation pulses of synchrotron radiations (delayed by δt). The parameters for the fast emission component were Δt = 10 ns and δt = 2 ns and for the slow one – Δt = 250 ns and δt = 200 ns. The spectra contain three bands:

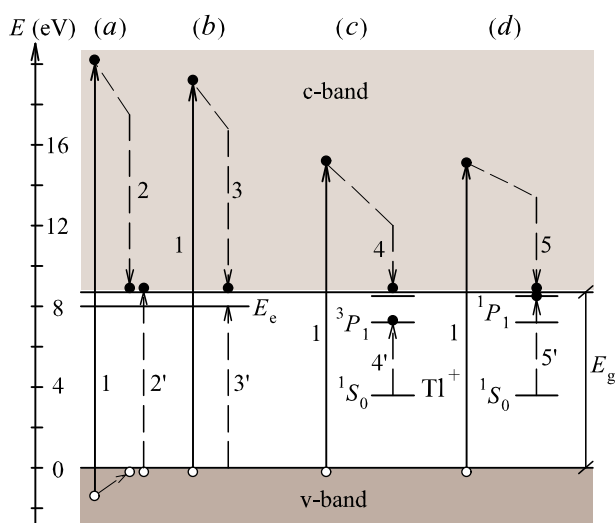


Fig. 1. A simplified energy-band diagram for a NaCl:Tl⁺ crystal. The multiplication processes connected with the creation of a secondary *e-h* pair (case a) or a secondary anion exciton (case b) by a hot conduction electron as well as the excitation of a Tl⁺ impurity center by a hot electron (cases c and d) due to non-radiative Auger transitions (2 → 2', 3 → 3', 4 → 4', 5 → 5'). All the processes start with the absorption of an exciting photon (arrow line 1). The inclined dashed arrow lines demonstrate non-radiative transitions at carrier relaxation inside energy bands.

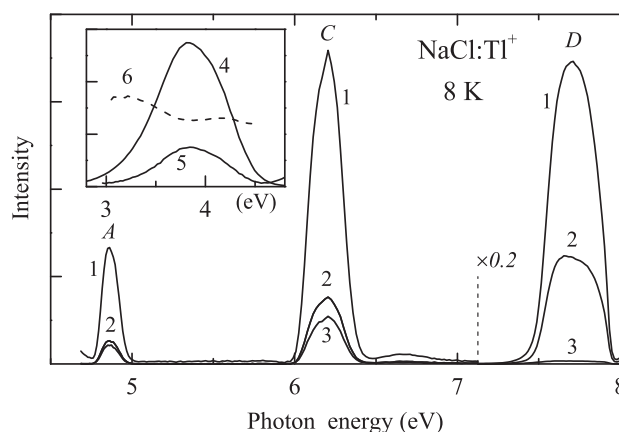


Fig. 2. The excitation spectra of A emission (4.27 eV, ³P₁ → ¹S₀) of Tl⁺ centers measured for time-integrated (curve 1), slow (Δt = 250 ns and δt = 200 ns, curve 2) and fast (Δt = 10 ns and δt = 2 ns, curve 3) components in NaCl:Tl⁺ at 8 K. Inset shows the emission spectra measured for slow (4) and fast (5) components and the intensity ratio spectrum for slow/fast emissions (6) in NaCl on the excitation by 7.7 eV photons at 8 K.

the A excitation (absorption) band peaked at 4.78 eV corresponds to ¹S₀ → ³P₁ electron transitions in a free Tl⁺ ion; the C-band (6.2 eV) is related to ¹S₀ → ¹P₁ singlet–singlet transitions and the so-called D-band (a non-elementary band at ~7.7 eV directly adjoins the exciton absorption bands), which is caused by the excitation and ionization of the chlorine ions surrounding the impurity ion.

According to Fig. 1, a photon of $h\nu > 20$ eV forms a hot conduction electron which is able to create a secondary *e-h* pair due to the non-radiative Auger transition (case a, arrow lines 2 and 2'), while the energy excess of a hot conduction electron (with respect to the bottom of the c-band), formed by an exciting photon of $h\nu = 18$ –20 eV is sufficient to create a secondary exciton (case b, 3 and 3'). Even a lower energy of exciting photons ($h\nu = 15$ –17 eV) is needed for the direct excitation of impurity centers by hot conduction electrons, i.e., for the realization of a solid-state analogue of FHE in NaCl:Tl⁺ (case c, arrow lines 4 and 4' or case d, 5 and 5').

A comparison of the excitation spectra of impurity center luminescence in doped crystals with the photoemission spectra from thin films had a beneficial effect on the separation of FHE from other mechanisms of photon multiplication in WGM. Earlier, this comparison had been made for RbCl:Tl⁺ and RbCl:Ag⁺ crystals (Feldbach et al., 1997; Lushchik et al., 1998). Fig. 3 shows the energy distribution curves of the emitted electrons on the excitation of an extra pure NaCl evaporated film by 14.7–17.5 eV photons at 295 K.

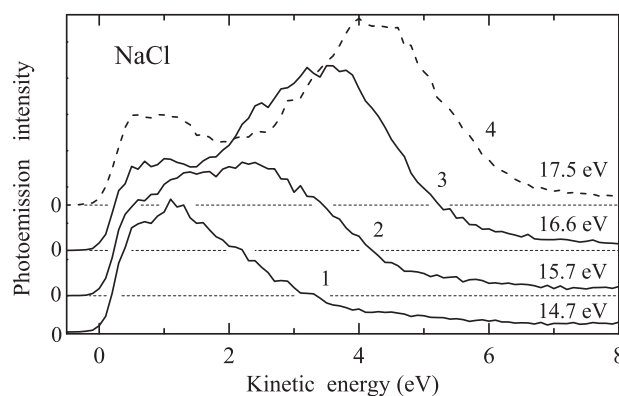


Fig. 3. Energy distribution curves of the emitted electrons of a NaCl thin film for various exciting photon energies at 295 K.

The photoelectron spectra were measured at beam-line 6A2 at the UVSOR facility (Okazaki, Japan). The kinetic energy (E_{kin}) of the emitted electrons is given relative to the vacuum level, while the energy of the conduction electrons inside a crystal is higher by a value of an electron affinity $\chi = 0.7$ eV.

According to Fig. 3, photons of $h\nu = 15.7$ eV already create the electrons with $E_{\text{kin}} = 4.3$ eV, which are able (χ should be taken into account) to excite Ti^+ up to 3P_1 state. A further radiative transition to a ground state ($^3P_1 \rightarrow ^1S_0$) results in the A emission of Ti^+ centers. In case $h\nu = 16.6$ eV, hot conduction electrons excite Ti^+ centers even up to a higher 1P_1 singlet state. The inset in Fig. 2 shows the emission spectra measured for the fast ($\Delta t = 10$ ns, $\delta t = 2$ ns) and slow ($\Delta t = 250$ ns, $\delta t = 200$ ns) component in NaCl at the excitation by 7.7 eV photons at 8 K. Such exciting photons fall within a non-elementary D excitation band of Ti^+ centers adjacent to the exciton absorption. The intensity ratio spectrum for the slow and fast emission components makes it possible to separate the A emission of Ti^+ centers (~ 4.2 eV) and a more inertial emission (~ 3.35 eV) associated with self-trapped excitons.

By way of concluding this section, it should be mentioned that Fig. 1 presents a significantly simplified energy diagram of a NaCl crystal with a relatively narrow valence band ($E_v \approx 3$ eV). The separation of FHE from the fast excitonic and $e-h$ mechanisms of photon multiplication in binary and complex metal oxides runs into obvious problems due to a sharp rise of E_v up to the value of E_g in these WGM. For instance, the value of $E_v \approx 6.6$ eV can be experimentally estimated from the spectra of fast intraband luminescence measured under excitation of MgO crystals by nanosecond single 300 eV electron pulses (Lushchik et al., 2006).

3. Manifestations of FHE in cathodoluminescence

Luminescent WGM have been successfully used for years as cathodoluminophors. The recombination of totally relaxed conduction electrons and valence holes mainly takes place at the final stage of the interaction of 50–5 keV electrons with WGM. The excitation of WGM by an electron beam was used over years at the Institute of Physics, Tartu, as a convenient way of investigating energy transfer processes to luminescent impurities – both mainly inertial $e-h$ processes and usually fast excitonic ones (see, e.g., Soovik and Eksina, 1964; Lushchik et al., 2005). The spectra of electron energy losses in WGM have been measured in many laboratories. These spectra demonstrated that, besides the creation of $e-h$ pairs and small-radius excitons, the energy is also spent on the so-called near-surface losses connected with the formation of electronic excitations, the energy of which is lower than that needed for bulk exciton creation (E_c). In the WGM with a high concentration of impurity ions or defects, these low-energy losses can be caused in part by FHE.

Recently, the spectra of steady CL were measured using a two-channel system with a double VUV (4–11 eV) and a double prism monochromator (1.8–6.0) at the excitation of pure and doped WGM (LiF, NaCl, MgO, Al_2O_3 , Y_2O_3 , YAlO_3 , $\text{Lu}_3\text{Al}_5\text{O}_{12}$, Gd_2SiO_5 , CaSO_4 , etc.) by an electron beam at 5–8 K. The main experiments were performed with 5 keV electrons (100 nA, ~ 2 mm $^{-2}$ spot). In the case of 15–20 keV electrons, the possible charging of the irradiated single crystal was eliminated by the sputtering of a thin layer of Au (~ 10 nm) on the sample surface. After the electron irradiation was stopped, it was possible to register the spectra of phosphorescence at a low temperature and the thermally stimulated luminescence (TSL) curves of the irradiated WGM with a heating rate of $\beta = 10$ K min $^{-1}$.

It is worth noting that 1–2 s after the electron irradiation was stopped (the measurements of CL spectra usually take 10–25 min), the intensity of impurity or defect-related emission drastically

decreased by 3–4 orders of magnitude, weakened by a factor of 10 within a minute and continued its slow damping. At a further crystal heating, the TSL was measured above a pedestal of tunnel phosphorescence that is practically independent of temperature in a wide range.

In the present paper, the manifestations of FHE in CL will be illustrated on the example of MgO and $\text{MgO}:\text{Cr}^{3+}$. The MgO single crystals were grown in our laboratory from a highly pure starting material by a variation of the arc fusion method. In MgO, $E_g = 7.782$ eV and an exciton has a large radius and a low oscillator strength. The formation energy of this Wannier-Mott-type exciton with $n = 1$ equals $E_e = 7.77$ eV. The thermal quenching of exciton emission (nearly resonant with exciton absorption) occurs already at 80 K and all excitons undergo ionization at 80–300 K. So far, there is no experimental evidence of the self-trapping of excitons, electrons and holes in the bulk of MgO crystals. Even at low temperatures ($T < 80$ K), the creation efficiency of free excitons by 3–30 keV electrons is at least an order of magnitude as low as of separated e and h . Hence, mainly rapid $e-h$ recombination near/at impurity centers is in real competition with the fast energy transfer from an MgO matrix to impurities/defects via FHE.

The dependence of the CL intensity (I_{CL}) on temperature has been measured at the cooling down (400 \rightarrow 6 K) of $\text{MgO}:\text{Cr}^{3+}$. MgO crystals with a concentration of Cr^{3+} impurity ions of 0.01 at.% were also grown in our laboratory. The absorption and emission of chromium centers in the region of 1.5–6.0 eV have been earlier studied in detail for the same crystals (Küçk et al., 2000). To avoid a high irradiation dose, short-run (30 s) pulses of an electron beam (5 keV, 50 nA mm $^{-2}$) and a subsequent 60 s pause were used at the cooling of $\text{MgO}:\text{Cr}^{3+}$ with $\beta = 10$ K min $^{-1}$ (see Fig. 4). Only cooling below 45 K was performed under steady electron irradiation. The emission of Cr^{3+} ions (~ 1.76 eV) was selected through a double monochromator. In 1–2 s after a pulse of an electron irradiation was stopped, the intensity of CL drastically decreased. A repeated switch of an electron beam (except for the first time) caused a sharp jump

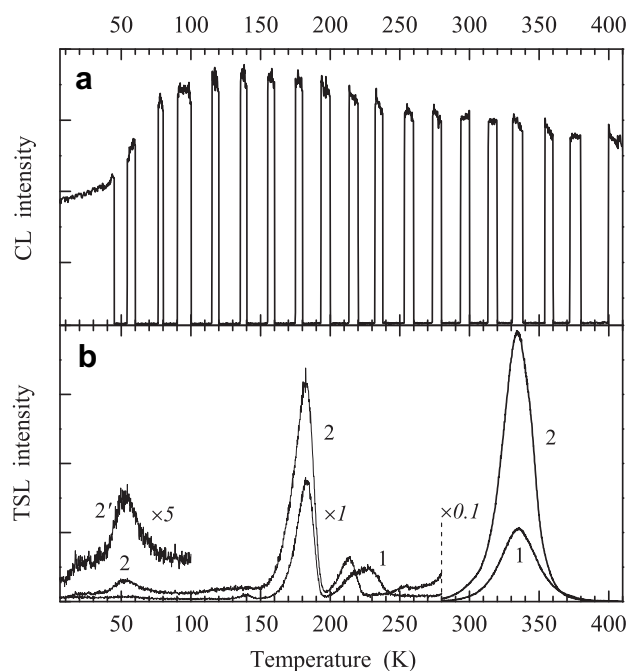


Fig. 4. a) The dependence of the CL intensity on the cooling temperature (400 K \rightarrow 6 K) for a $\text{MgO}:\text{Cr}^{3+}$ (0.01 at. %) crystal under excitation by 5 keV electrons. (b) The TSL curves measured for 3.4 eV (curve 1) and 3.2 eV emission (curves 2 and 2') in the MgO crystals irradiated by 15 keV electrons at 6 K. The samples were previously annealed at 1575 K (1) or plastically deformed ($\epsilon = 4\%$) at 295 K (2, 2'). $\beta = 10$ K min $^{-1}$.

of a signal (not depicted in the figure) and the conversion thereof into a quasi-steady CL (this CL is shown) occurs in 1–2 s. According to Fig. 4a, the intensity of CL (for a Cr^{3+} -emission) slightly increases with a cooling of the sample down to 170 K, remains nearly constant down to 115 K and significantly decreases down to about 55% from the maximum value at 80–40 K. The same dependence of $I_{\text{CL}}(T)$ can be obtained again after an additional preheating of the sample to 600 K. A direct measuring of the pulse annealing of the EPR signal of paramagnetic centers in a $\text{MgO}:\text{Cr}^{3+}$ crystal irradiated at 80 K showed that the decay of the Cr^{1+} centers formed via electron trapping by Cr^{3+} occurs at ~ 170 K (Kärner et al., 1980). However, the main part of Cr^{3+} centers can be restored only at 330–420 K, when holes free themselves from V^0 , V_{OH} and V^- centers and recombine with Cr^{2+} centers.

The results presented in Fig. 4a testify that a solid-state analogue of FHE provides in $\text{MgO}:\text{Cr}^{3+}$ a considerable contribution to a fast (10^{-3} – 10^{-6} s) component of CL associated with ${}^2T_1 \rightarrow {}^4A_2$ and ${}^2E \rightarrow {}^4A_2$ radiative transitions in Cr^{3+} centers. This conclusion is especially apparent for the temperature region of 400–180 K, when the competition with the excitons ionized at such temperatures is excluded and Cr^{1+} centers are unstable. However, the situation is more complicated at low temperatures.

In order to influence drastically the e - h recombination, the number of point and quasi-two-dimensional structural defects was significantly increased in the MgO crystals by a plastic deformation along [001] direction. Fig. 4b shows the TSL curves (measured for 3.4 and 3.2 eV emissions) for two MgO crystals. The first crystal was annealed at 1575 K (2 h) in an effort to anneal the dislocations and other defects while the second one was plastically deformed at 295 K (the thickness was decreased by $\epsilon = 4\%$). Plastic deformation causes a sharp enhancement of the TSL peaks at 335 and 50 K. According to EPR studies, the 335 K peak is connected with the release of one of two holes from a V^0 center (two holes in a field of a cation vacancy, $v_c hh$). The peak at 50 K is, in our opinion, associated with the electron release from shallow traps – bivalencies ($v_a v_c$), the number of which is significantly increased in the deformed sample.

At low temperatures, the electron trapping at $v_a v_c$ is in competition with the direct excitation of Cr^{3+} centers by hot conduction electrons. As a result, the intensity of CL drastically decreases at the cooling of a deformed MgO crystal from 185 to 35 K. The dependence of the CL intensity on the cooling temperature (the measurements were performed in the same way as for $\text{MgO}:\text{Cr}^{3+}$ – see Fig. 4a) shows that I_{CL} decreases by a factor of 8 in the region of 180–35 K (for undeformed $\text{MgO}:\text{Cr}^{3+}$ I_{CL} at 35 K was only twice as low as at 180 K). The defects formed in a deformed crystal serve as efficient centers of electron localization.

The excitation spectra for 2.9 and 5.2 eV emissions in virgin and plastically deformed ($\epsilon = 4\%$, $T = 295$ K) MgO crystals have been measured using synchrotron radiation at 8 K. The efficiency of a broadband luminescence at ~ 2.9 eV sharply increases in the deformed sample in a wide spectral region of $h\nu = 6.7$ – 7.5 eV. Similar broad non-elementary excitation bands of luminescence connected with the absorption of anions surrounding $v_a v_c$ were revealed in many AHC (Lushchik et al., 1991). The emission of 5.2 eV is effectively excited in a narrow region slightly below and above the exciton resonance. According to theoretical estimates (Seitz, 1954), the presence of v_c causes the shift of neighbor anion absorption toward a short-wavelength region with respect to the absorption of anions in a regular lattice. It is worth noting that ~ 5 eV emission is well-expressed in MgO and $\text{MgO}:\text{Al}^{3+}$ crystals and is caused by the recombination of electrons with V^- and V_{Al} centers incorporating v_c (Kärner et al., 1980). The experiments with plastically deformed and preheated MgO crystals allow us to ascribe the low-temperature attenuation of the process of a fast (μ s

scale) energy transfer to Cr^{3+} centers by hot electrons and holes to an interception of e and h by structural defects, the number of which can be decreased due to the preheating of a single crystal or can be increased by even a weak plastic deformation.

4. Concluding remarks

According to the photoelectron spectra and electron energy losses spectra measured by several authors, hot electrons, the energy of which is less than that needed for the creation of secondary excitons and e - h pairs but is sufficient for the direct excitation of impurity ions and structural defects, are formed at the final stages of electronic excitation relaxation under irradiation of WGM by incident electrons or VUV radiation. In the WGM doped with various impurity ions, the manifestations of the direct energy transfer by hot conduction electrons and, tentatively, by hot valence holes to luminescent impurity centers were detected earlier in PL excited by VUV radiation of $h\nu = (1.5$ – $4)E_g$ or CL excited by 1–15 keV electrons. In the present study, novel data on a solid-state analogue of FHE are provided on the example of $\text{NaCl}:\text{Ti}^+$ and $\text{MgO}:\text{Cr}^{3+}$ single crystals. It is established that the creation energy of a pair of Frenkel (E_{FD}) defects is higher than E_g in NaCl at $T < 100$ K and in MgO in the whole investigated temperature region (4–600 K). This inequality $E_{\text{FD}} > E_g$ provides a high radiation resistance of these materials against non-impact mechanisms of radiation damage and promotes the investigation of FHE.

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