Exciton Mechanisms of Energy Transfer to F^+ – and F – Centers in Anion-Deficient Crystals $\alpha - Al_2O_3$

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Abstract – The main result of the experiments and the simulation performed in this study was the corroboration and further development of the idea about a considerable role played by exciton mechanisms in the energy transfer to active centers in anion-deficient corundum crystals. According to modern representations, the direct excitation of F- and F^+-centers under ionizing radiation is due to excitons bound to these defects, while the energy to these centers is transferred, depending on temperature, by metastable free excitons or self-trapped excitons (STE's) of different types. As the concentration of anion vacancies increases, the probability of annihilation of the A and E types of STE's during excitation by ionizing radiation diminishes and STE's change from diffusion to the oriented motion towards vacancies. The processes of migration and energy transfer from A and E excitons to F^+- and F-centers are accelerated and, hence, the luminescence efficiency of these centers is improved.

1. Introduction

According to [1], the concept of electron excitations (EE's) is approximate. Strictly speaking, it does not suit well if the density of EE's in a crystal is high (pulsed electron beams (PEB's), laser radiation and, probably, synchrotron radiation (SR)) and the interaction between elementary excitations is no longer weak. This statement is in complete agreement with the data obtained in Refs. [2, 3]. These data suggest that the SR and PEB energy is transferred to F^+- and F-centers at least through two channels. In one of the channels, the transport mechanism incurs no migration losses because there is no delay between the pulse excitation and its relaxation involving short-lived F^+-centers. According to [2, 3], at the moment PEB's or SR hit, metastable F^+-centers are formed by displacement of ions not only in anion-deficient crystals, but also in stoichiometric crystals of α-Al_2O_3.

It also follows from [2, 3] that inertia processes of the energy transfer to active centers and its dissipation in the second channel, which are observed in α-$Al_2O_{3-\delta}$, are limited by the diffusion-controlled motion of STE's of the A and E types or similar entities. The final stage of this motion may include decomposition and/or annihilation of A and E excitons, the F→F^+ conversion stimulated by these excitons, and their deceleration near F^+- and F-centers, which is accom-

panied by the formation of defect-bound excitons (DBE's). Subsequently DBE's transfer their energy to F^+- and F-centers. All this adds up to the slower radiative de-excitation of these centers than in the first channel.

The fast and accelerative stages of the relaxation processes at hand are pronounced most clearly in the kinetics and time-resolved spectra of cathodoluminescence (CL) and X-ray luminescence (XL) of F^+-centers, which are discussed in detail elsewhere [2, 3]. Such data on singlet and triplet-singlet radiative transitions in F-centers are obviously insufficient so far. Therefore the models will be constructed focusing on processes that involve F^+-centers.
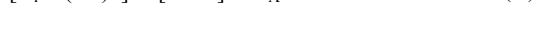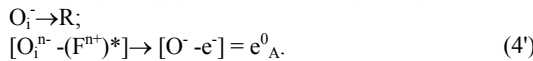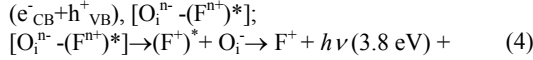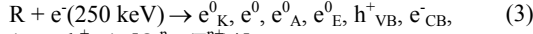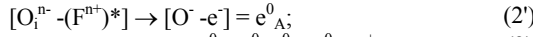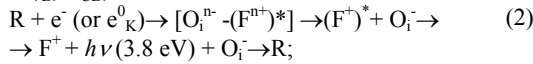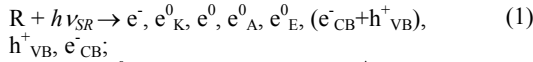
The simulation was performed assuming for simplicity that all traps were filled, the crystal was generally neutral, and the decomposition of an exciton, when one of its components was trapped, could be neglected. These assumptions are quite justified if one considers that PEB's and SR are extremely intensive and filling of traps is completed in few pulses. To conclude with, since spectral and kinetic data for the CL and the XL are somewhat different at room and nitrogen temperatures [2, 3], two models of the relaxation processes at $T \leq 200$ K and 200 K $< T \leq 300$ K will be presented. The conditional boundary near 200 K was chosen considering the known fact that STE's decompose or transform from the A to E type at $T > 200$ K [4].

2. The Model at $T \leq 200$ K

In accordance with experimental data [2, 3], the XL and CL kinetics of F^+-centers in anion-deficient α-$Al_2O_{3-\delta}$ samples with a small concentration of vacancies ($C_{Va} \leq 10^{17}$ cm^{-3}) include three stages: the inertialess development after the excitation pulse ($0 < t < t_{min}$), the buildup ($t_{min} < t < t_{min} + \Delta t_b$), and the slow relaxation ($t > t_{min} + \Delta t_b$) with the constants τ_1, τ_b and τ_2 respectively. Therefore the assumed model of transformation of PEB and X-ray SR energies in α-$Al_2O_{3-\delta}$ at $T \leq 200$ K includes three stages, which may branch.

At the first stage ($0 < t < t_{min}$), the reaction (1) causes generation of fast electrons (e^-) due to the external photoeffect, free electrons and holes (e^-_{CB}, h^+_{VB}), electron-hole pairs (EHP's or $e^-_{CB} + h^+_{VB}$), STE's of the A and E types (e^0_A, e^0_E), and metastable free excitons (FE's or e^0), including those of the K type (e^0_K). According to (2), the interaction of fast

electrons ($E_{e\_max} = h\nu_{SR\_max} = 60$ keV) and other high-energy EE's (K-excitons, etc.) with the lattice (R) leads to the formation of metastable excited F^+-centers, which are quickly relaxed by radiation and annihilate. Such F^+-centers can be formed by the reaction (2), for example, through the intermediate stage when the quasi-molecule $[O_i^{n-}\text{-}(F^{n+})^*]$ appears. Here O_i^{n-} is an oxygen ion with the charge n^- ($n = 0, 1, 2$) displaced to an interstice and $(F^{n+})^*$ is an excited center of the F type with the charge n^+. It is the charge transitions in this quasi-molecule that can explain the formation of a metastable F^+-center in the excited state by the reactions (2) and (4) and an A-exciton by the reactions (1) and (3) and by the branches (2') and (4') at the beginning of the quasi-molecule rearrangement. It is significant that such rearrangements take 10^{-10}–10^{-12} s and their analysis presents an independent problem, which cannot be solved so far for engineering reasons. Nevertheless, studies of this kind are performed at a picosecond resolution [5] and confirm our ideas.
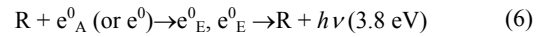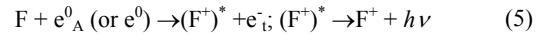
$$R + h\nu_{SR} \rightarrow e^-, e^0_K, e^0, e^0_A, e^0_E, (e^-_{CB}+h^+_{VB}), \quad (1)$$
$$h^+_{VB}, e^-_{CB};$$
$$R + e^- \text{ (or } e^0_K) \rightarrow [O_i^{n-}\text{-}(F^{n+})^*] \rightarrow (F^+)^* + O_i^- \rightarrow \quad (2)$$
$$\rightarrow F^+ + h\nu (3.8 \text{ eV}) + O_i^- \rightarrow R;$$

$$[O_i^{n-}\text{-}(F^{n+})^*] \rightarrow [O^-\text{-}e^-] = e^0_A; \quad (2')$$
$$R + e^- (250 \text{ keV}) \rightarrow e^0_K, e^0, e^0_A, e^0_E, h^+_{VB}, e^-_{CB}, \quad (3)$$
$$(e^-_{CB}+h^+_{VB}), [O_i^{n-}\text{-}(F^{n+})^*];$$
$$[O_i^{n-}\text{-}(F^{n+})^*] \rightarrow (F^+)^* + O_i^- \rightarrow F^+ + h\nu (3.8 \text{ eV}) + \quad (4)$$
$$O_i^- \rightarrow R;$$
$$[O_i^{n-}\text{-}(F^{n+})^*] \rightarrow [O^-\text{-}e^-] = e^0_A. \quad (4')$$

It is seen from experiments that the determining component of the relaxation time constant τ_{1_XL} at the first stage during SR excitation is the lifetime of an F^+-center in the excited state, τ_{F+}, which is equal to 2.1 ns. This fact may be attributed to several reasons. One of the reasons is that EE's, especially high-energy ones, are formed most efficiently near defects. One more reason is that penetrability of X-ray quanta is very high. Therefore, high-energy EE's, which are induced by X-ray SR, practically do not migrate and produce short-lived metastable F^+-centers almost instantaneously.

A specific feature of stage 1 in the case of PEB's is that in accordance with the model, quasi-molecules $[O_i^{n-}\text{-}(F^{n+})^*]$ appear by the reaction (3) immediately at the initial moment when $\delta t \approx 0$. As distinct from the SR excitation, the displacement of O_i^{n-} relative to $(F^{n+})^*$ in the quasi-molecule is larger than the lattice constant, because the electron energy ($E_e = 250$ keV) is higher than the energy of X-ray quanta ($E_{max} = 60$ keV). As a result, the lifetime of a metastable F^+-center under exposure to PEB's is longer than in the case of the SR excitation ($\tau_{1\_CL} > \tau_{1\_XL}$) and is equal to 25–50 ns. This lifetime determines the fast relaxation time constant τ_{1_CL} at stage 1 by the reaction (4). The decrease in

τ_{1_CL} with growing C_{Va}, which was observed experimentally in Ref. [3], can be explained by the decrease in the distance between the components O_i^{n-} and F^{n+} of the quasi-molecule. This distance directly depends on the growing probability that aggregates of the F_n type are formed near O_i^{n-}.

The second stage ($t_{min} < t < t_{min} + \Delta t_b$) at $T \leq 200$ K is characterized by the buildup of the XL and the CL of F^+-centers in anion-deficient samples, which predominantly contain F-centers before and after excitation. Since parameters of the CL and XL bands at 3.8 eV, which are measured at the moments of the buildup and the slow decay, coincide with their counterparts for F^+-centers [2, 3], it is reasonable to assume that STE's (or FE's) redistribute the charge in the F-center, leading to the formation of an excited F^+-center by the reaction (5). Moreover, the data [6] suggests that, probably, metastable FE's are playing progressively larger role in the F→F^+ conversion as the temperature is reduced from the nitrogen to helium point. The proposed model is not contradictory either to the fact that the buildup stage is absent or cannot be detected in samples with a high initial concentration of F^+-centers [2, 3]. An essential component of stage 2 is the growth of the concentration of E-type STE's, which shows up as the buildup of their luminescence [3, 7]. This growth is most probably due to reactions like (6).
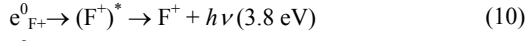
$$F + e^0_A \text{ (or } e^0) \rightarrow (F^+)^* + e^-_t; (F^+)^* \rightarrow F^+ + h\nu \quad (5)$$

$$R + e^0_A \text{ (or } e^0) \rightarrow e^0_E, e^0_E \rightarrow R + h\nu (3.8 \text{ eV}) \quad (6)$$

At the third stage ($t > t_{min} + \Delta t_b$), spare STE's of the A type (or FE's) transform to DBE's by the reaction (7) near F^+-centers formed at the second stage in all anion-deficient samples. Excitons bound to F^+-centers can be formed directly by the reaction (7) omitting the intermediate stage (5) in samples with a considerable concentration of stable F^+-centers. Stage 3 may include concurrently the formation of DBE's near F-centers by the reaction (8) and the continued generation of E-excitons by the reaction (9). Obviously, the probability of formation of E-excitons relative to DBE's increases at both the second and third stages as the concentration of anion vacancies diminishes.

$$F^+ + e^0_A \text{ (or } e^0) \rightarrow e^0_{F+} \quad (7)$$
$$F + e^0_A \text{ (or } e^0) \rightarrow e^0_F \quad (8)$$
$$e^0_A \text{ (or } e^0) \rightarrow e^0_E \quad (9)$$

EE's formed at the third stage can be relaxed in several directions depending on the concentration of anion vacancies in samples. If C_{Va} is low, the 3.8-eV luminescence of STE's of the E type with the decay time constants τ_{E2} and τ_{E3} (reactions (10) and (11)) are admixed to the XL and LC of F^+-centers. For this rea-

son, decay curves of the XL and CL at 3.8 eV in anion-deficient and stoichiometric samples are similar at large times (t > t_{min} + Δt_b) [3].

$$e^0_{F+} \rightarrow (F^+)^* \rightarrow F^+ + h\nu\,(3.8\ eV) \qquad (10)$$
$$e^0_E \rightarrow R + h\nu\,(3.8\ eV) \qquad (11)$$

As C_{Va} increases, the probability of DBE's forming near F^+- and F-centers grows and the kinetics of the XL and the CL at 3.8 eV is increasingly determined by the reaction (10), i.e. the luminescence of F^+-centers. The 3-eV XL and CL of F-centers, which are excited due to the decomposition of DBE's by the reaction (12) and the capture by the reaction (13) of F^+-centers released from shallow traps, are enhanced simultaneously.

$$e^0_F \rightarrow F^* \rightarrow F + h\nu\,(3\ eV); \qquad (12)$$
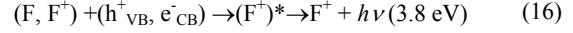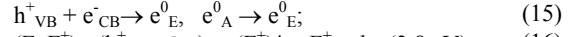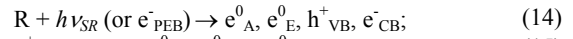$$F^+ + e^-_t \rightarrow F^* \rightarrow F + h\nu\,(3\ eV) \qquad (13)$$
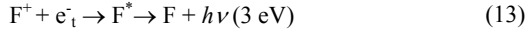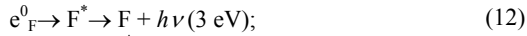
So, one of the main carriers of the X-ray SR and PEB energy is, at least near nitrogen temperatures, STE's of the A type, which diffuse in the lattice and transform to the E type by the reaction (6) or are localized near F^+- and F-centers by the reaction (5).
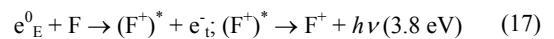
3. The Model at 200 < T ≤ 300 K

The experimental data reported in Refs. [2, 3] were used for construction of the second model of relaxation processes taking place in α-$Al_2O_{3-\delta}$ crystals at 200 K < T ≤ 300 K and involving F^+- and F-centers. According to these data, as T increases from 200 to 300 K, the stages of the fast decay and the buildup either disappear or cannot be detected in XL and CL decay curves of F^+-centers, while the luminescence intensity of F^+- and F-centers sharply grows. Moreover, spectral and kinetic luminescence properties of F^+- and F-centers differ little upon exposure to SR and PEB's. Some important corollaries follow from these considerations. Firstly, since these kinetics do not include the fast relaxation stage with $\tau \leq \tau_{F+}$, it may be concluded that even if metastable F^+-centers, which are formed by displacements, appear, their number is small. Then their generation cannot have a significant effect on the phenomena studied. Secondly, vanishing of the buildup stage in the kinetics, the decrease in τ_2, and the considerable growth of the XL and the CL of F^+-centers suggest the acceleration of the F→F^+ conversion and the excitation energy transfer to F^+-centers. In our opinion, the reason is the increasingly important part played by the exciton mechanism of the PEB and SR energy transfer and the migration of excitons to active centers, which accelerates with growing T. This conclusion is well substantiated by the data [6] pointing to a high efficiency of the exciton photoexcitation of F^+- and F-centers at T = 300 K. Thirdly, it follows from the above comments that the second

model should be much simpler than the model at T ≤ 200 K.

X-ray quanta and STE's of the A and E types are formed by the reaction (14) at 200 K < T ≤ 300 K similarly to the case of T ≤ 200 K. According to [8], E-excitons can be formed by the recombination assembly of EHP's and from STE's of the A type by the reaction (15). Moreover, the inertialess increase in the CL and XL intensity of F^+-centers is observed immediately after the excitation pulse. This increase, specifically, follows the instrument function, which is measured in the SR channel with a subnanosecond resolution. This fact confirms the assumptions made in Ref. [9] and suggests that reactions like (16) are possible if the excitation density is high. Significantly, the reaction (16) can give rise to two processes: the instantaneous F→F^+ conversion and the fast (without the buildup) excitation of F^+-centers.

$$R + h\nu_{SR}\ (or\ e^-_{PEB}) \rightarrow e^0_A,\ e^0_E,\ h^+_{VB},\ e^-_{CB}; \qquad (14)$$
$$h^+_{VB} + e^-_{CB} \rightarrow e^0_E,\quad e^0_A \rightarrow e^0_E; \qquad (15)$$
$$(F, F^+) + (h^+_{VB}, e^-_{CB}) \rightarrow (F^+)^* \rightarrow F^+ + h\nu\,(3.8\ eV) \qquad (16)$$

For elaboration on the model in the region of slow relaxation, it is necessary to refer to individual experimental data. As the concentration of F^+-centers grows, the constant τ_{XL} in the XL kinetics of F^+-centers at T = 300 K decreases from ~20 ns to the value approaching the lifetime of the excited state of an F^+-center (τ_{F+} = 2.1 ns). Therefore, some analogy to the low-temperature case can be drawn. Such dependences were observed at 80 K for slow components of the XL and CL kinetics of F^+-centers and were related in the foregoing to the curtailment of the time of the $e^0_A \rightarrow e^0_{F+}$ transformation by the reaction (7) as the concentration of F^+-centers was reduced. Since at T > 200 K the lifetime of an A-exciton is too short (τ_A < 1 ns, see [4]) and it efficiently transforms to the E type in perfect crystals, the E-exciton may be the main candidate for the excitation energy transfer to F^+- and F-centers in anion-deficient α-$Al_2O_{3-\delta}$. Similarly to STE's of the A type at T < 200 K, E-excitons participate in some processes throughout their radiation lifetime τ_{R_E} at 200 K < T ≤ 300 K. They may annihilate by radiation according to the reaction (11), may partially convert F- to F^+-centers by the reaction (17), and may transform to excitons bound to F- and F^+-centers by the reactions (18) and (19). At the final stage of relaxation DBE's can, in turn, excite F^+- and F-centers, which are genetically related to DBE's, according to the reactions (10) and (12) described above.

$$e^0_E + F \rightarrow (F^+)^* + e^-_t;\ (F^+)^* \rightarrow F^+ + h\nu\,(3.8\ eV) \qquad (17)$$
$$e^0_E + F^+ \rightarrow e^0_{F+} \qquad (18)$$
$$e^0_E + F \rightarrow e^0_F \qquad (19)$$

It is thought that as C_{Va} increases, the probability of the radiative annihilation of STE's by the reaction

(11) decreases both at moderate and low temperatures, while the chaotic motion of E-excitons becomes more and more ordered and oriented towards anion vacancies. Simultaneously τ_{R_E} decreases from the maximum possible value, which approaches τ_E (~20 ns at $C_{Va} \approx 0$ and T = 300 K, see [4]), to ~τ_{F+}. These processes facilitate the reactions (10) and (17)-(19) and, hence, lead to the decrease in the radiation lifetime τ_{R2_F+} of metastable F^+-centers formed through the conversion. The curtailment of τ_{R2_F+} with growing C_{Va} shows up in experiments as the decrease in τ_{XL} [2, 3] and the size of the curtailment is nearly the same as that of τ_{R_E}. Moreover, if C_{Va} is large, the direct formation of e^0_{F+} and e^0_F (for example, FE→DBE or EHP→DBE) may be much more efficient and the intermediate stages (18)-(19) may be omitted.

Thus, the presented interpretation of the kinetic data for the CL and the XL, which were measured at 295 K, produces additional evidence to the involvement precisely of E-excitons in the excitation energy transfer to F^+-centers. Not the least significant is the fact that over the interval of 200–300 K the decay time constant in the kinetics of the CL and the XL at 3.8 eV is limited by τ_{R_E} as the upper bound and τ_{F+} as the lower bound.

4. Conclusion

One of significant results of the simulation is the confirmation and further development of the earlier idea about the exciton mechanism of excitation of active centers in anion-deficient corundum crystals. According to the advanced representations, the direct excitation of F- and F^+-centers under the action of X-ray SR and PEB's is due to bound excitons, while the energy is transferred to these centers by free metastable excitons or self-trapped excitons of different types depending on the temperature. It is assumed that at helium temperatures the trend of the transfer kinetics, especially its fast component with $\tau \leq 1$ ns, is limited by the motion of metastable FE's. The radiation lifetime of STE's of the

A type determines the duration of the buildup (τ_b ~ 15–50 ns) and the slow decay (τ_2 ~ 80–400 ns) of the radioluminescence of F^+-centers at 80 K $\leq$ T < 200 K. The shorter radiation lifetime of STE's of the E type governs the faster exponential kinetics of the luminescence of the same centers (τ ~ 2–20 ns) at T $\geq$ 200 K.

If the concentration of anion vacancies increases, the radiative annihilation of STE's of both types during excitation by ionizing radiation becomes less probable and STE's change from diffusion to an oriented motion towards vacancies. The processes of migration and energy transfer from A- and E-excitons to F^+- and F-centers are accelerated and, hence, the luminescence efficiency of these centers is considerably improved.

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