

Kinetics of non-steady state diffusion-controlled tunnelling recombination of defects in insulating crystals

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Abstract. The theoretical basis is developed for a previously presented method of experimental detection of reactions in insulators controlled by the interaction of diffusive defects and subsequent tunnelling recombination. The method involves measuring the increase (or decrease) in the recombination luminescence after stepwise increase in the temperature (i.e. defect mobility). It is shown theoretically that the inertial (about 100–300 s) transient process observed in pure solids—KCl, KBr, α -Al₂O₃ and the Na salt of DNA—strongly suggests self-trapping of the carriers participating in recombination whereas treatment of the defect (polaron) motion in terms of a continuous approximation allows us to estimate characteristic parameters of the motion and recombination.

1. Introduction

When studying the recombination luminescence in pure KBr crystals by means of the fractional glow technique described in detail by Tāle (1974, 1981) and Rosa and Tāle (1975), it has been observed for the first time that at temperatures close to those at which the self-trapped holes (V_K centres) become mobile the small (3–5 K) stepwise increase (or decrease) in the temperature leads to a very delayed change in the luminescence intensity I (Tāle and Gailitis 1971). Subsequently, such delayed reactions have been also found in other insulating solids, e.g. AlN (Rosa and Tāle 1975), Ba₃(PO₄)₂ (Tāle *et al* 1975). At temperatures of about 20 K or more below the TSL peak, when the V_K mobility is small, the transient time τ is several hundred seconds. When the temperature of TSL peak is approached, τ becomes greatly reduced to a value comparable with the time required to obtain an evenly distributed temperature within a sample.

This effect cannot be accounted for in terms of the standard theory of diffusion-controlled reactions (Waite 1957), where the reaction rate K is time dependent for a short transient period only when $K(t) = 4\pi DR_0 (1 + R_0/\sqrt{\pi Dt})$ (Nemzek and Ware 1975). Here D is the relative diffusion coefficient given by $D(T) = D_0 \exp(-E/kT)$, E is the diffusion activation energy and R_0 the clear-cut ('black sphere') recombination radius. After the transient period $\tau \gg R_0^2/D$ the steady state recombination regime is achieved, characterised by the constant reaction rate $K = 4\pi DR_0$ and the joint density $Y(=1 - R_0/r)$ of dissimilar defects is independent of D or T . (In our experiments, samples were kept at a given temperature for a sufficiently long time for the steady state

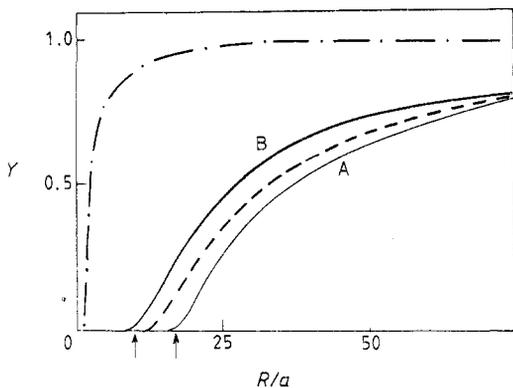


Figure 1. Quasi-steady distribution functions for V_K centres in KCl at 180 K (curve A) and 190 K (curve B): ---, recombination profile at an intermediate instant during the transition between these two quasi-states; -·-, with no tunnelling recombination.

regime to become established.) The stepwise increase in the temperature from T_1 to T_2 cannot, according to the standard theory, result in an inertial increase in I since the reaction rate instantly becomes $K = 4\pi D(T_2)R_0$, and $I = KC_A C_B$ in which C_A and C_B are the defect concentrations.

This is why delayed kinetics can appear only if the joint density $Y(r)$ or the recombination profile is dependent on $D(T)$. It is just the case for the *tunnelling recombination* of electron and hole defects (Rice and Pilling 1979, Kotomin and Doktorov 1982). Its probability (per second) is $W(r) = W_0 \exp(-r/a)$, where r is the distance between defects, and W_0 and a are constants; a equals half the Bohr radius of the electron centre which is usually more delocalised. Since the lifetime even for nearest electron-hole defects is usually comparable with that for diffusion hopping, the joint density should be dependent on the defect mobility D .

In terms of the diffusion-controlled recombination accompanied by long-range tunnelling recombination (rather than the clear-cut radius R_0) the observed effect is due to slow transition between two joint densities (figure 1) corresponding to the temperatures T_1 and T_2 before and after the stepwise sample heating and cooling, respectively. For instance, if a sample is cooled, the excess concentration of closely dissimilar defects will disappear owing to the tunnelling recombination, and the density profile shifts to longer distances where the recombination and diffusive motion are balanced. On the contrary, if a sample is heated, rapidly moving V_K defects recombine with electron centres at shorter distances. In the steady state, $K = 4\pi DR^*$, where the effective recombination radius R^* depends on D (or T).

The long delay time observed (100–300 s) arises directly from the slow defect diffusion. In pure or slightly doped wide-gap insulating solids the only candidates are the self-trapped carriers (small-radius polarons) since unrelaxed electrons and holes have a very short lifetime and high mobility (see, e.g., Aluker *et al* 1987). Although such a qualitative interpretation was given by Tāle and Gailitis (1971) and by Tāle (1974) a long time ago, no quantitative analysis of the effect has been presented so far. The present paper develops such a theory and applies it to several greatly differing insulating solids.

2. Theory

A simple model for the delayed kinetics is derived from the following ideas. After the stepwise temperature (D) increase the second co-factor entering the reaction rate K —

the effective recombination radius R^* —changes simultaneously with the transition of the recombination profile between two steady states characterised by $Y(T_1)$, $R^*(T_1)$ and $Y(T_2)$, $R^*(T_2)$, respectively. Assuming that the transient time in I arises entirely from the diffusive passage for a distance $\Delta R = R^*(T_2) - R^*(T_1)$, making use of $\langle \Delta R^* \rangle^2 \propto Dt$, one obtains

$$\Delta I \propto \Delta K = 4\pi D \Delta R^* \propto D^{3/2} \sqrt{t}. \quad (1)$$

A more correct model is based on the direct solution of the diffusion equation incorporating tunnelling recombination (Rice and Pilling 1979, Kotomin and Doktorov 1982), which, in the dimensionless units $X = r/a$, $\tau = Dt/a^2$, reads

$$\partial Y / \partial \tau = D^* [Y'' + (2/X)Y'] - (W_0 a^2 / D) \exp(-X) \quad (2)$$

$$I \propto \int_0^\infty \exp(-X) Y(X) X^2 dX. \quad (3)$$

The solution of equation (2) depends on three independent parameters: a^2/D , W_0 and $D^* = D(T_2)/D(T_1)$. The latter parameter determines the relative increment in the intensity I since, at $t \rightarrow \infty$,

$$I(T_2)/I(T_1) = D(T_2)R^*(T_2)/D(T_1)R^*(T_1) \simeq D^* = \exp(-E\Delta T/T_1^2), \quad (4)$$

$$R^* \simeq aE/kT,$$

where R^* is the effective radius of the diffusion-controlled tunnelling recombination. Equation (3) gives an independent method of determining the diffusion activation energy E . On the contrary, the parameter a^2/D , which is the scale coefficient connecting the real time t and the dimensionless time τ , can be found by fitting the theoretical kinetics $I(\tau)$ to the experimental kinetics. Finally, the third parameter W_0 , which determines the form of the curve $I(\tau)$, enters equation (2) through the dimensionless parameter $W_0 a^2/D$ which characterises the strength of the tunnelling recombination relative to the diffusion. If the parameter a is known from independent measurements, say EPR (Grachev and Deigen 1978), one can obtain the pre-exponential factor of the diffusion coefficient $D_0 = S\lambda^2/6$. Also, we can estimate the hopping length λ of the defect or D_0 provided that the frequency factor S is known, e.g. by means of optical dichroism (Kabler 1972).

An advantage of our method is that the transition occurs between two well defined steady states (figure 1):

$$Y(r) = (2a/r) [K_0 \{2\sqrt{\beta_m} \exp[-(r - R_0)/2a]\}] \quad (5)$$

($\beta_m = W_0 a^2 \exp(-R_0/a)/D$, K_0 is the modified Bessel function of the first kind), which are *independent* of the initial defect distribution.

3. Experimental details

Along with the above-described study of the inertial increase (or decrease) in the luminescence intensity I , we have also carried out investigations which prove directly the tunnelling character of the luminescence and allow us to obtain the relevant activation energy by means of the fractional glow technique.

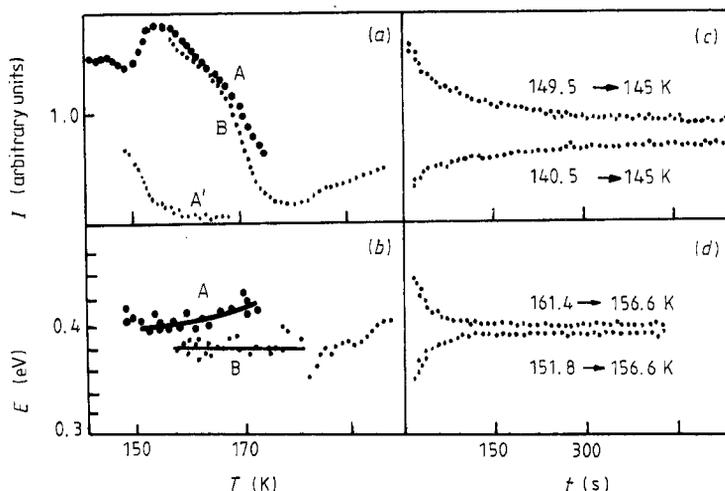


Figure 2. The transient kinetics for V_K centres in KBr: (a) the TSL curves; (b) activation energies; (c), (d) two delayed kinetics (the relevant initial and final temperatures are given).

3.1. KCl and KBr

In these crystals, delayed kinetics have been observed at stimulation temperatures which coincide with the low-temperature tail of the TSL peak (170 K and 200 K), arising from V_K centre migration and tunnelling recombination with immobile electron centres, respectively. The activation energy for V_K centres in undoped KBr crystals, purified by a zone refining 60 times, depends on the thermal preparation of a sample. In quenched crystals with a high concentration of dislocations, $E = 0.4$ eV and it slightly increases on the high-temperature side of the TSL peak. On the contrary, for the annealed samples, $E = 0.38$ eV remains constant in a whole temperature range of the TSL. Because steady state luminescence takes a long time to set in for the specific oscillating heating regime used in the fractional glow technique required to measure E , the average heating rate is at least two orders of magnitude less than that generally used for the TSL studies (0.15 K s^{-1}). This is why the V_K recombination process is observed in the temperature range 150–175 K (figure 2). The luminescence spectrum remains the same at temperatures of the TSL peak as well as for the *static* tunnelling luminescence (immobile defects) measured at liquid-nitrogen temperature (LNT) after x-ray excitation at $180 \text{ K} > T > 130 \text{ K}$. According to Grabovskis and Vitol (1979), this luminescence peak with the maximum at 2.2–2.3 eV results from the F– V_K tunnelling recombination. In all measurements of the diffusion-controlled luminescence, samples were excited at 80 K and then heated to the temperature at which V_K centres become mobile; they were then kept at this temperature for 20 min and step-like heated again. The heating rate was about 3 K s^{-1} , but the time required for the temperature to settle to a new value is 3–5 s.

The delayed kinetics are linear in the coordinates ΔI against \sqrt{t} (figure 3(a)) over at least 1.5 orders of magnitude in time. From the slope of this curve using equation (1), one can obtain $E = \frac{2}{3} \partial(\ln I) / \partial(-1/kT)$. However, the corresponding magnitude of $E = 0.2$ eV (figure 3(b)) is about a factor of 2 smaller than the value of $E = 0.4$ eV from optical dichroism and the fractional glow technique—see discussion below.

In order to increase the efficiency of the V_K centre accumulation, we have also investigated KCl crystals slightly doped with Tl (0.1 mol%) since, at low temperatures,

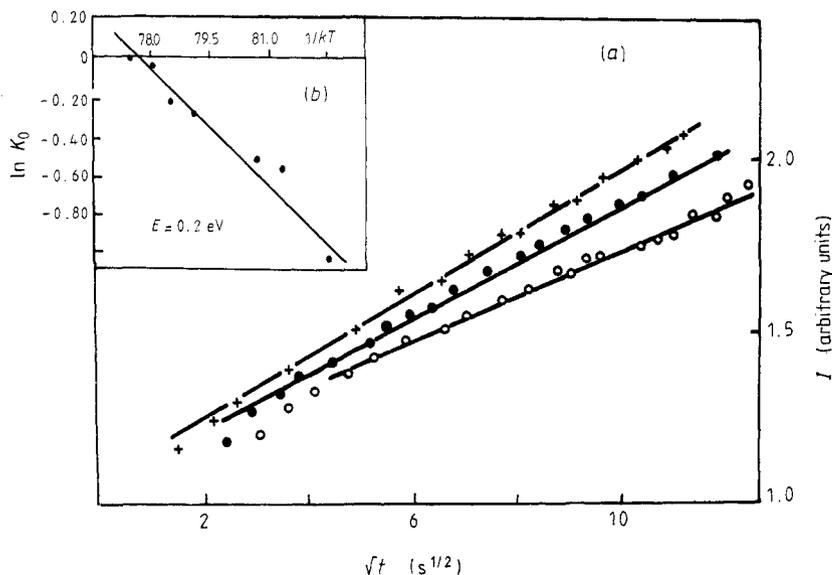


Figure 3. The kinetics of figure 2 plotted in coordinates I against \sqrt{t} . (a) The stepwise temperature increase is performed up to the temperatures of 145 K (\circ), 147 K (\bullet) and 149 K ($+$). (b) An estimate of the activation energy using a plot of the recombination intensity against temperature.

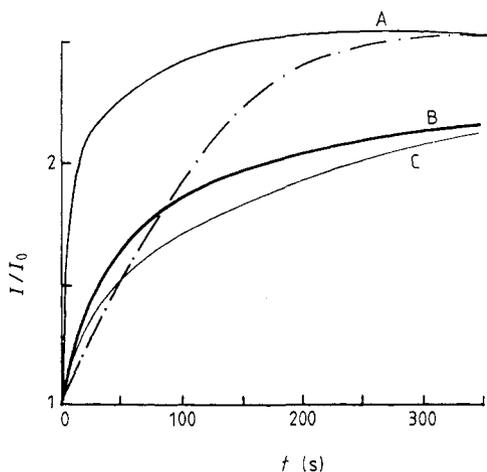


Figure 4. The transient kinetics for KCl:Ti (0.1 mol%) for $a^2/D = 5$ (curve A), $a^2/D = 70$ (curve B) and $a^2/D = 100$ (curve C). (175 \rightarrow 180 K; V_K TSL peak at 200 K): - - -, experimental results.

Tl ions trap electrons and remain stable above the V_K TSL peak. The luminescence spectra of both tunnelling and diffusion-controlled recombination again coincide ($E_{\max} = 2.7$ eV), indicating that for doped KCl the V_K -Tl⁰ recombination predominates.

A comparison of the experimental kinetics of the increase in luminescence with the computer calculations (figure 4) demonstrates their essential difference which is discussed below.

3.2. α -Al₂O₃

The undoped samples are characterised by a minimal number of anion defects and reveal the main TSL peak at 220 K. The spectral content ($E_{\max} = 4.3$ eV) of the relevant

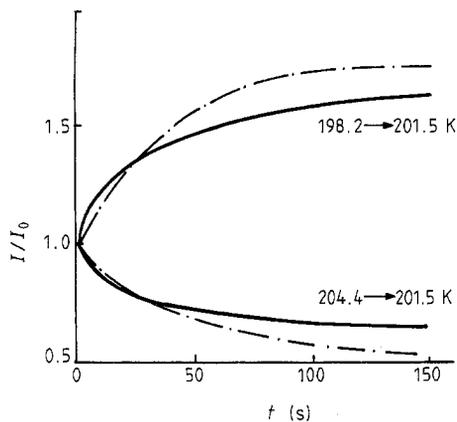


Figure 5. The same as figure 4 for $\alpha\text{-Al}_2\text{O}_3$ ($E = 0.7$ eV; TSL peak at 220 K): —, theory; - - -, experimental results.

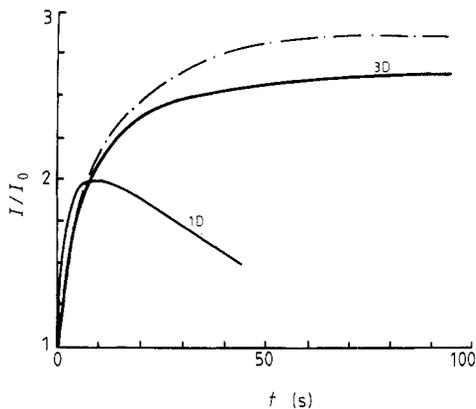


Figure 6. The same as figure 4 for the Na salt of DNA ($E = 0.4$ eV; 141 \rightarrow 146 K; TSL peak at 160 K): —, theory; - - -, experimental results.

luminescence coincides with the tunnelling spectrum. The latter is excited by x-rays with the same efficiency at $T < 200$ K; that is, a decrease in the production efficiency of defects involved in the tunnelling recombination coincides with the temperature region of the TSL peak (Kulis 1987, Kulis and Rachko 1987).

Photostimulation in the absorption bands of either the F centres (6 eV) or V centres (3.3 eV) of samples which had undergone x-ray excitation at 300 K and then cooled to LNT, has led us to a conclusion about the *hole* nature of centres producing the TSL peak at 220 K. (Note that it is the first low-temperature hole peak in $\alpha\text{-Al}_2\text{O}_3$.) Pure $\alpha\text{-Al}_2\text{O}_3$ samples reveal delayed kinetics of the increase in luminescence (figure 5) similar to those observed above for alkali halides, but here agreement between theory and experiment is essentially better than for KCl and KBr.

The observation of such kinetics in perfect pure $\alpha\text{-Al}_2\text{O}_3$ has been interpreted by Kulis (1987) and Kulis and Rachko (1987) as due to *hole self-trapping* and slow hole migration, in line with the preliminary continuum theory calculations of hole polarons in this crystal (Cox 1981).

3.3. Na salt of DNA

Samples obtained from Reanal Co. (Hungary) were subjected to x-ray excitation at LNT for 15–20 min. The principal TSL peak is observed at 160 K. The luminescence peaks at 3.1 eV and is the same for the tunnelling recombination (at LNT) and that detected in the temperature interval of the TSL peak (Butlers 1987, Tăle and Butlers 1987). This biopolymer also reveals the delayed increase in the luminescence shown in figure 6. All the above-described experimental facts—observation of tunnelling luminescence the efficiency of which (as indicated by plots of intensity against excitation temperature) decreases at the temperature of the TSL peak, the slow increase in the luminescence in the temperature range of this TSL peak after stepwise increase in temperature, the coincidence of the luminescence spectra for tunnelling and TSL—argue strongly in favour of diffusion-controlled tunnelling recombination. Since for the denatured samples of Na salt of DNA or in double-helical RNA we do not obtain delayed kinetics of the type under study, this indicates that it is the conformational instability of the Na salt of DNA which leads to carrier self-trapping.

4. Discussion

As noted above, the delayed kinetics under study can be fitted quite well by means of equation (1), yielding $\Delta I \propto \sqrt{t}$, but the corresponding estimate of E is essentially less than the experimental value. First, it follows from the assumption that the transient kinetics could be described in terms of the time-dependent recombination radius accompanied by a parallel shift of the recombination profile. However, the calculations using equations (2) and (3) have demonstrated clearly that after a stepwise temperature increase a short-distance part of the profile is the first to be distorted, whereas its long-distance tail changes very slowly (cf. figure 1). This behaviour leads to a rapid 50% increase in I in a short time accompanied by a further slow increase over a much longer time.

A comparison of the theory with experimental data for V_K in KCl and the hypothetical self-trapped holes in $\alpha\text{-Al}_2\text{O}_3$ and in the Na salt of DNA is given in figures 4–6. In the first case the best fit is obtained for $a^2/D = 50 \pm 20$ s and $E = 0.53$ eV. Making use of the latter and half the Bohr radius of its electronic partner—the TI^0 centre— $a \approx 1$ Å (Grachev and Deigen 1978), we obtain $D_0 = (12 \pm 5) \times 10^{-3}$ cm² s⁻¹. On the contrary, the optical dichroism studies (Kabler 1972) yield a value of $D_0 = 4 \times 10^{-3}$ cm² s⁻¹. The agreement is regarded as satisfactory, taking into account also that a certain portion of the V_K centres recombine, in particular, at F centres ($a = 0.5$ Å).

Our results contradict the results of Aluker *et al* (1986, 1987), obtained from the V_K trapping on the TI^+ activator ions and setting D_0 to be one to two orders of magnitude greater than that derived from the dichroism studies. Aluker *et al* (1986, 1987) have interpreted their experiments as a breaking of the chemical bond within the X_2^- quasi-molecule (V_K centre) during reorientations which occurs rather seldom (once for about every 100 hops) but which results in a very long (100 Å or greater) migration of a free hole before becoming self-trapped. However, as has been discovered recently by Dyachenko *et al* (1988), F centres, and probably V_K centres are spatially well correlated with Tl centres in alkali halides. On this basis the results of Aluker *et al* (1986, 1987) could be reinterpreted as a relatively short-distance V_K migration with the generally accepted hopping lengths.

The effective radius of the $\text{TI}^0\text{-}V_K$ tunnelling recombination calculated via equation (4) is 20 Å at 180 K which agrees with the experimentally found value of 35 ± 7 Å for *static* recombination (Nesterova 1981), in which case the radius should be greater since defects do not approach each other owing to diffusion.

Our estimate of the characteristic parameter a^2/D for hypothetical self-trapped holes in $\alpha\text{-Al}_2\text{O}_3$ is 30 ± 10 s (figure 5). Further calculation, say of D_0 , requires knowledge of the parameter a , which could be derived from, for example, the optical ionisation energy I of the relevant, and still to be identified, electron centre ($a \approx \hbar/\sqrt{2mI}$). Finally, a similar estimate for the Na salt of DNA is $a^2/D = 7 \pm 3$ s. In order to choose between 1D and 3D recombinations in this case, we have calculated equations (2) and (3) for 1D and 3D diffusive motions. The conclusion drawn from figure 6 is that 1D motion terminated by tunnelling recombination with the electronic centre lying along the same helix does not occur since in that case no quasi-steady state is reached and the recombination profile changes monotonically with time. This effect has been obtained earlier for the 'black sphere' model, where $K \propto t^{-1/2}$ (Rughooputh *et al* 1987). However, it does not exclude combination of the helical motion with 3D tunnelling recombination.

Note finally that agreement between theory and experiment for V_K centres is qualitative only; there are no physically plausible parameters W_0 , a^2/D , E which could fit the

experimental curve well in figure 3; a theoretical curve always increases more sharply but saturates much more slowly at a longer time. This seems to arise from the continuum approximation of the diffusion used in equation (2), which holds, strictly speaking, if the hopping length is less than half the Bohr radius a . For V_K centres the so-called *mixed* recombination mechanism (Kotomin and Doktorov 1982) takes place when $a \ll \lambda \ll R^*$. The solution of the corresponding equations generalising equation (2) could, at least in principle, also yield the additional parameter λ/a . Qualitatively the difference between theory and experiment (figure 3) could be interpreted as follows. In a continuum approximation, diffusion and recombination arise immediately, whereas the defect in fact should perform several hops for recombination. On the contrary, at long periods of time the continuum description yields too slow an increase in I compared with the exact model since well separated defects approach each other by finite-length hops. Owing to qualitative agreement of theory and experiment, only the parameter W_0 cannot now be reliably calculated.

5. Conclusion

The above-described method for the study of diffusion-controlled tunnelling recombination in irradiated insulators enables us to obtain the relative defect diffusion coefficient D and the effective radius R^* of the tunnelling recombination, both of which are temperature dependent. The key idea is to employ the *non-steady* state recombination regime since it is impossible to find D and R^* from the quasi-steady reaction rate $K \propto DR^*$. This requires knowledge of half the Bohr radius a which could be found from the optical ionisation energy or EPR. It is shown that the *very fact* that the recombination intensity increases so slowly after a stepwise increase in temperature (i.e. defect mobility) in undoped solids argues strongly that the tunnelling recombination is involved and that carriers are likely to be self-trapped so that the relevant small-radius polarons are slightly mobile and hop over short distances only. In particular, we have demonstrated that it occurs in a wide class of insulating solids with very different chemical bondings—ionic (KCl and KBr), semi-covalent (α -Al₂O₃) and biopolymer (Na salt of DNA). The above-described philosophy could also be valid for heavily doped wide-gap solids with carrier tunnelling over impurities, e.g. Al₂O₃:Cr.

Since the interpretation of the kinetic experiments is always based on some spatial distribution of defects, which is usually unknown, e.g. for $V_K - \text{TI}$ or $V_K - \text{F}$ centres in alkali halides the quantum chemical simulation (Shluger *et al* 1986) could help to answer the question of whether the V_K centre band could be broken during its reorientation. It could also be useful to clarify the spatial structure of the self-trapped hole in α -Al₂O₃.

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