

# The kinetics of diffusion-controlled annealing of Frenkel defects in alkali halide crystals

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The annealing kinetics of the strongly correlated (the so-called geminate) pairs of both neutral F,H centers as well as F, I centers entering secondary triplets ( $F \cdots I \cdots$  self-trapped hole) in KCl and KBr crystals is calculated. In this model diffusion of hole I and H centers and their annihilation with electron F centers at short relative distances stimulated by the elastic or Coulomb interaction are taken into account. It is demonstrated that F,H pairs are destroyed by tunneling recombination already at times  $\leq 10^{-4}$  s, i.e. much before the beginning of the thermostimulated experiments. A possible explanation of this contradiction is discussed.

## 1. Introduction

Radiation defects in alkali halides arise as a result of the non-radiative decay of self-trapped excitons (STE) accompanied by the creation of pairs of neutral and charged Frenkel defects: well-known F centers ( $v_a^+ e^-$ ) and interstitial halide atoms  $i_a^0$  (H centers) as well as anion vacancies  $v_a^+$  ( $\alpha$  centers) and interstitial halogen ions  $i_a^-$  (I centers) respectively [1]. The most informative method to determine the actual mechanisms of the defect formation and those of secondary defect reactions is the use of pulsed ionizing radiation with a very short time duration of the order of ns or ps [1,2]. From more than 20 years of investigations the following basic results were obtained: (i) F and H centers are primary Frenkel pairs. The observed formation time of F centers (faster than the nanosecond range in KCl and KBr) suggests that the higher excited states of STE is the precursor of the F center formation [2–4]; (ii) The main portion of F and H centers are destroyed by the mutual recombination right after the electron pulse [5,6] even at 2 K; (iii) It was first shown by the Sendai group that the decrease of the F and H absorption bands in KBr crystal after the pulsed electron irradiation at 8 K can be roughly decomposed into three exponentials having lifetimes of 300 ns, 15  $\mu$ s and 70  $\mu$ s [5,6]. It was observed in KCl crystals that F and H bands decay with almost identical lifetimes of  $\approx 2.8$   $\mu$ s,  $\approx 15$   $\mu$ s and  $\approx 2.2$   $\mu$ s,  $\approx 11$   $\mu$ s, respectively [3,7]. In KCl the fastest component with  $\tau = 100$  ns in F center annihilation was found by Latvian scientists [8–10].

It was first suggested in 1969 by Hirai and collaborators [5–7] that the basic physical mechanism of the synchronous annihilation of the complementary Frenkel defects observed in alkali halides even at LHeT, when they are definitely immobile, is tunneling transfer of an electron from the electron (F) center to the hole (H) center with further restoration of the perfect crystalline lattice. It was later shown theoretically [11,12] that at low temperature such tunneling recombination serves also as the major factor limiting defect accumulation under irradiation. The F and H center annihilation with almost the same lifetimes leads to the conclusion that both centers are created in geminate pairs with a short relative distance between partners and recombine with each other rapidly. Such pair-wise creation of F and H centers is supported by F-band half-width studies: in KCl it was found to be as large as  $\approx 0.3$  eV 20 ns after the electron shot, and to decrease to  $\approx 0.18$  eV 10  $\mu$ s later [3]. In the diffusion-controlled processes electron tunneling contributes mainly at low temperatures when defect mobility is also low [13]. Time-resolved investigations of F-center radiation-induced production have elucidated that in KBr and KCl crystals even at LHeT only about 5% of the total number of created F,H pairs avoid their rapid annihilation.

Along with tunneling recombination, the stability of Frenkel pairs is controlled by I and H center migration, stimulating their subsequent recombination with  $\alpha$ , F and F' centers (an F center with a trapped electron) [11,12]. These kinds of recombinations lead to the well-known multi-stage (kink) thermal annealing of F centers. Different methods of thermoactivation spectroscopy, such as thermostimulated luminescence (TSL), conductivity, depolarization, gas desorption,

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crystal volume change etc., were widely used for investigating the thermal stability of F,H;  $\alpha$ ,I pairs as well as their different combinations with close F' and  $V_k$  centers (self-trapped holes) created also under irradiation [14–18].

Using the EPR technique, as well as the photo- and thermostimulated luminescence, F,H correlated annealing was studied in detail [18]. Four stages at 35, 42, 47 and 52 K were observed in KCl. At 35 K close F,H pairs are annealed which could be transformed, by F-light, into  $\alpha$ ,I pairs. In pure KCl, the fraction of such pairs is about 30% whereas in KCl–Rb ( $7 \times 10^{-3}$  mole%) it is already 90% of the total number of F,H pairs. In its turn, high-temperature H centers (42, 47, 52 K) cannot be converted by the F-light into  $\alpha$ ,I pairs which argues for their considerable separation. The TSL peaks at 43 and 55 K [17] are 40–100 times weaker than the main I peak [14,16] at 39 K.

## 2. Theory

### 2.1. Tunneling recombination

It is clear that at temperatures below H center delocalization  $T_d$  tunneling recombination is the predominant recombination mechanism of their concentration decay. As the temperature exceeds  $T_d$  this tunneling is accelerated by hole center diffusion. Lastly, at high enough temperatures diffusion becomes so fast that H centers approach their complementary F centers *before* electron tunneling occurs, and annihilate with them restoring perfect the crystalline lattice [13]. Both tunneling recombination and diffusion-controlled annihilation depend on the relative distance between partners via the exponentially changing overlap of the wave functions of F and H centers in the former case and a number of hops necessary for their encounter in the latter case.

It is clear from experimental results quoted in section 1, that primary Frenkel defects – F and H centers – are strongly spatially correlated at their birth and their relative distances hardly exceed several nearest neighbours (NNs). This conclusion is also supported by recent molecular dynamics simulations [19] and by the theory of the temperature dependence of F center accumulation [20]. Quantum-mechanical calculations of the F,H center tunneling recombination in KCl [21] yield the parameter values  $W_0 = 10^{13} \text{ s}^{-1}$  and  $a = 0.5 \text{ \AA}$  defining the tunneling probability per unit of time known to be [13]  $W(r) = W_0 \exp(-r/a)$ , where  $r$  is the relative distance between the defects. This equation with parameters  $W_0$ ,  $a$  just mentioned yields the lifetime for the three kinds of F,H NNs oriented along the  $\langle 110 \rangle$  axis to be  $\approx 1 \text{ ns}$ ,  $1 \text{ \mu s}$  and  $1 \text{ ms}$  respectively. Thus, the lifetime for the 2 NN is in good agreement with the experiment. For the 1 NNs theory gives an

underestimate, very likely due to the neglect of the mutual perturbation of very close defects. Lastly, disagreement for the 3 NNs could be due to the fact that the component with  $\tau \approx 15 \text{ \mu s}$  corresponds to H centers in another configuration, different from the  $\langle 110 \rangle$  axis. Indeed, it is easy to calculate that H centers with coordinates (3,1,0) have a lifetime  $\approx 10 \text{ \mu s}$  – in a good agreement with experimental data. The same calculation has demonstrated that tunneling recombination is non-radiative and results in the formation of  $\alpha$ ,I charged defects. In principle, the tunneling recombination probability  $W(r)$  depends also on the angle between the H center axis and the straight line connecting its center with the F center. However, it cannot change qualitatively the results just presented. In contrast to the ground state, the tunneling recombination of the *excited* F centers with H is predicted to be radiative with a photon energy  $\approx 3 \text{ eV}$ ; this was indeed confirmed later experimentally [22]. The static tunneling recombination of immobile defects is characterized by the recombination radius [13]  $R^*(t) \approx a \ln(W_0 t)$ : all pairs of electron and hole centers with  $r < R^*(t_0)$  recombine at the time  $t_0$ . It is easy to estimate that at LHeT all F,H centers which are closer than the fourth neighbours along the  $\langle 110 \rangle$  axis recombine in 24 hours. This conclusion agrees well with steady-state ODEPR studies [23] where only such pairs of defects were detected.

### 2.2. Diffusion-controlled recombination

Next we have calculated the kinetics of F,H diffusion-controlled recombination in the steady-state experiments with slow temperature increase. The mathematical formalism incorporating defect diffusion and elastic interaction is described in detail in refs. [13,15]. The elastic interaction energy is  $E = -\alpha/r^3$ , where  $r$  is the distance between defects and  $\alpha$  is the elastic interaction constant [13].

The diffusion-controlled annihilation of F,H centers in KBr crystal during the linear heating is plotted in Fig. 1 for three kinds of NNs. The major conclusion suggests itself, i.e. the elastic interaction affects the survival probability of defects,  $P_s$ , drastically even for 3 NNs. Naturally,  $P_s$  depends also on the relative distance between the defects. The temperatures of the H center annealing (34–37 K) are in good agreement with actual experimental data [16,24]. In the more realistic case of simultaneous annealing of several kinds of F,H pairs they have different relative distances. The step structure was observed only for 1 NNs and 2 NNs; even for combined 2 NNs and 3 NNs the decay curve is rather smooth. The kinetics of the correlated annealing of pairs of close F,I centers stimulated by elastic attraction was calculated recently in ref. [25]. (I centres arise as a product of F,H tunneling recombination after

irradiation,  $F + H \rightarrow \alpha + I$ , or under irradiation,  $H + e \rightarrow I$ ; in the latter case F,I defects are well-correlated in space.) Studies of the effect of simultaneous annealing of several kinds of F,I pairs [25] show that a well-pronounced step-structure is observed only for pairs closer than 4 NNs – like in the case of F,H pairs.

Similar results were obtained also for KCl crystal except that F center decay occurs at higher temperature ( $T > 45$  K) than in KBr due to a larger activation energy of H center diffusion; it is in agreement with the experimental data. Fig. 2 shows that the survival probability for the fourth neighbours along the  $\langle 110 \rangle$  axis is quite high and even for such well-separated pairs depends considerably on the strength of elastic

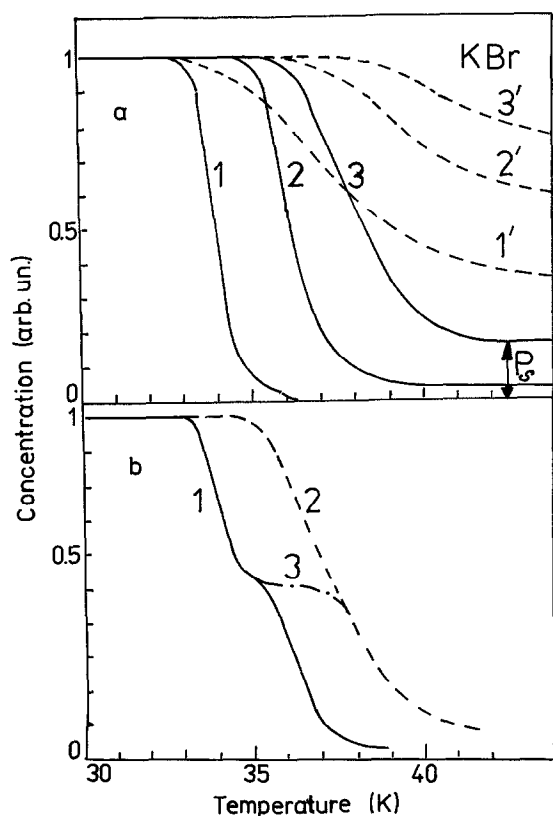


Fig. 1. The calculated kinetics of diffusion-controlled recombination of close (geminate) F,H centers in KBr for single-kind pairs (a) and combination of several kinds of pairs (b). In (a) full lines incorporate an elastic interaction of defects whereas broken lines neglect it. The relative distance between defects: curve 1: 4.2 Å (1 NNs); curve 2: 6 Å (2 NNs); curve 3: 8.5 Å (3 NNs).  $P_s$  is the F center survival probability. The parameters used are: the heating rate 0.1 K/s,  $E_a = 0.09$  eV, elastic constant  $\alpha = -3$  eV Å<sup>3</sup>,  $R_0 = 3$  Å<sup>3</sup>,  $D_0 = 1.5 \times 10^{11}$  Å<sup>2</sup> s<sup>-1</sup>. In (b) curve 1 corresponds to the mixture of 1 NNs and 2 NNs (in equal concentrations); curve 2: 2 NNs and 3 NNs whereas curve 3: 1 NNs and 3 NNs. Tunneling recombination of defects is neglected.

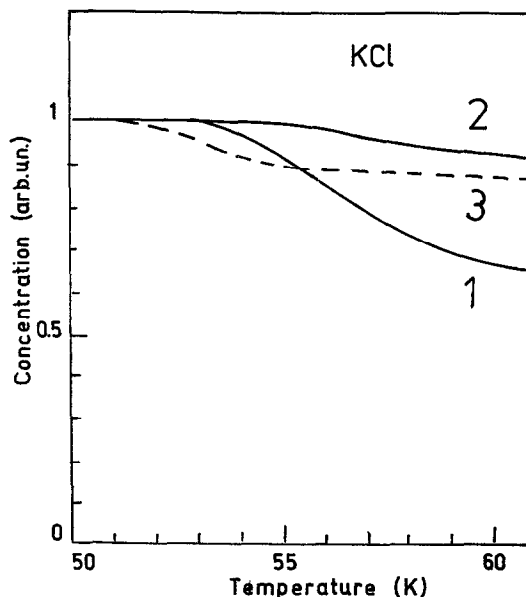


Fig. 2. The diffusion-controlled recombination of F,H centers in KCl which are 4th neighbours along the  $\langle 110 \rangle$  axis ( $d = 17.76$  Å). Curve 1 is the diffusion-controlled recombination stimulated by elastic interaction, curve 2 for non-interacting defects and curve 3 shows the effect of tunnelling recombination.

interaction;  $P_s = 0.65$  and  $0.92$  for  $\alpha = 3.3$  eV Å<sup>3</sup> and  $\alpha = 0$  respectively. Incorporation of *tunneling recombination* reduces both the step temperature and the survival probability. However the latter remains quite large ( $P_s \approx 0.86$ ); the existence of a large portion of defects separated by such distances was confirmed experimentally [23].

### 3. Discussion and conclusion

What was presented in section 2 demonstrates a certain contradiction in the traditional interpretation of the multi-step structure in F center annealing observed in alkali halides. If it arised due to several kinds of close F,H pairs with different separation (as it is usually thought [24,26]), these pairs would be definitely destroyed by the tunneling recombination at  $t < 10^{-4}$  s, i.e. long before the steady-state annealing experiments started! One of possible explanations could be shortcomings of our model or mathematical formalism, in particular the use of the continuum diffusion approximation. However, the same conclusion that the step structure could be resolved only for 1 NNs–3 NNs whereas the contributions of all other kinds of more distant H centers is smoothed has been also drawn recently in direct Monte Carlo simulations [19]. This all suggests the idea that the many-stage annealing observed could originate either from a set of *secondary*

reactions between Frenkel defects rather than their correlated annealing (see ref. [25]) or from those close F<sub>i</sub>H defects whose tunneling recombination is prohibited by some reasons (e.g. spin orientation).

## References

- [1] R.T. Williams and K.S. Song, *Self-Trapped Excitons* (Springer, Berlin, 1993).
- [2] M. Hirai, *Rev. Solid State Sci.* 4 (1990) 431.
- [3] M. Hirai, Y. Kondo, T. Yoshinari and M. Ueta, *J. Phys. Soc. Jpn.* 30 (1971) 440.
- [4] R.T. Williams, J.N. Bradford and W.L. Faust, *Phys. Rev. B* 18 (1978) 1978.
- [5] T. Karasawa and M. Hirai, *J. Phys. Soc. Jpn.* 33 (1972) 1728; 40 (1976) 769.
- [6] Y. Kondo, M. Hirai and M. Ueta, *J. Phys. Soc. Jpn.* 33 (1972) 151.
- [7] Y. Kondo, M. Hirai, T. Yoshinari and M. Ueta, *J. Phys. Soc. Jpn.* 26 (1969) 1000.
- [8] V.V. Gavrilov, S.A. Chernov and S.E. Etsin, *Sov. Phys. – Solid State* 24 (1982) 2481.
- [9] S.E. Etsin, *Proc. Latv. Acad. of Sci. Phys. No. 5* (1984) p. 30;  
S. Chernov, V.V. Gavrilov and S.E. Etsin, *Proc. Latv. Acad. Sci. No. 6* (1983) 27.
- [10] S.E. Etsin, Ph.D. Dissertation, Riga (1986);  
S. Nesterova, Ph.D. Dissertation, Riga (1983).
- [11] I. Tale, D. Millers and E. Kotomin, *J. Phys: Solid State Phys.* 8 (1975) 2366.
- [12] E. Kotomin, Ph.D. Dissertation, Univ. of Latvia, Riga (1975).
- [13] E.A. Kotomin and A. Doktorov, *Phys. Stat. Solidi B* 114 (1982) 287.
- [14] Ch.B. Luschik, in: *Physics of Radiation Effects in Crystals*, Ser. Modern Problems in Condensed Matter Sciences, eds. R.A. Johnson and A.N. Orlov (North-Holland, 1986) p. 473.
- [15] E.A. Kotomin, A.I. Popov and R.I. Eglitis, *J. Phys.: Cond. Matter* 4 (1992) 5901.
- [16] D.E. Aboltin, V.I. Grabovskis, A.R. Kangro, Ch.B. Lushchik, A.A. O'Konnell-Bronin, I.K. Vitol and V.E. Zirap, *Phys. Status Solidi A* 47 (1978) 667.
- [17] E.A. Vasil'chenko, A.Ch. Luschik, N.E. Luschik, Kh.A. Soovik and M.M. Tajirov, *Sov. Phys. – Solid State* 23 (1981) 271.
- [18] A.Ch. Luschick and Ch.B. Luschik, *Proc. Russian Acad. Sci.* 56 (1992) 88.
- [19] P.V. Bochkanov, V.I. Korepanov and V.M. Lysitzin, *Sov. Phys. – Proc. Higher Schools No. 3* (1989) 16; V.M. Lysitzin, *Proc. Latv. Acad. Sci., Phys. No. 3* (1990) 59.
- [20] E.A. Kotomin and A.S. Chernov, *Sov. Phys. – Solid State* 22 (1980) 1515.
- [21] A. Shluger, E. Kotomin and L. Kantorovich, *Solid State Commun.* 42 (1982) 749.
- [22] E.A. Vasil'chenko and M.M. Tajirov, *Proc. Inst. Phys. Estonian Acad. of Sci.* 53 (1982) 172.
- [23] W. Meise, U. Rogulis, F.K. Koschik and J.M. Spaeth, *Proc. Int. Conf. on Defects in Insulating Materials* (World Scientific, 1993) p. 1078.
- [24] M. Saidoh and N. Itoh, *J. Phys. Chem. Sol.* 34 (1973) 1165.
- [25] A.I. Popov, E.A. Kotomin and R.I. Eglitis, *Phys. Status Solidi B* 175 (1993) K39.
- [26] N. Itoh, *Adv. Phys.* 31 (1982) 491.