IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Theoretical simulation of V_K-centre migration in KCl. II. Phenomenological theory

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 7429

(http://iopscience.iop.org/0953-8984/4/36/016)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.96
The article was downloaded on 11/05/2010 at 00:31

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 4 (1992) 7429–7440. Printed in the UK

Theoretical simulation of V_K-centre migration in KCl: II. Phenomenological theory

E A Kotomin†, L N Kantorovich‡, I A Tale† and V G Tale†
† Institute of Solid State Physics, University of Latvia, Riga, Latvia
‡ Medical Academy, Riga, Latvia

Received 12 September 1991, in final form 7 April 1992

Abstract. An adequate theoretical basis is developed and presented for a non-stationary technique for the experimental detection of reactions in insulating crystals controlled by tunnelling recombination of mobile defects (hole centres) with electron centres. The effect of finite hop lengths of point defects in a crystalline lattice is carefully analysed. This method is based on measuring the inertial increase or decrease in the recombination luminescence intensity after a stepwise change of temperature (defect mobility). Theoretical analysis of the transient process observed experimentally for V_K centres in KCl:Tl crystals argues for their motion through 60° rotations with the frequency factor $S_r = 4 \times 10^{13}$ s^{-1}, very close to that obtained earlier in the optical dichroism studies.

1. Introduction

As is well known, V_K-centre motion in FCC alkali halides occurs mainly through 60° rotations [1]. From polarization experiments in KCl, the activation energy of these reorientations was found to be $E_a = 0.54$ eV and the relevant frequency factor $S_r = 4 \times 10^{13}$ s^{-1} [2]. The same value of E_a was obtained by means of the *fractional glow technique* (FGT), which is an extension of the standard thermostimulated luminescence (TSL) method and allows us to monitor with high accuracy the effective activation energy of the recombination process [3, 4].

In the previous paper [5] the quantum-chemical simulation of V_K-centre reorientation in KCl was carried out. The principal result was that the reorientation energy calculated (0.63 eV) is close to experimentally observed results and band hole formation (according to the hypothesis in [6–9]) is very unlikely.

In this paper we aim to analyse in detail the original method to detect small-radius hole centre migration in insulating crystals [3, 10]. The idea here is to impose, at the moment when the recombination intensity has reached its steady-state magnitude (at temperatures close to those at which hole centres become mobile), a small (3–5 K) stepwise temperature (mobility) stimulation. It results in a *very delayed increase* in the luminescence intensity I, which was interpreted as an additional argument for the slow motion of V_K in KBr by short hops (reorientations) rather than the long hops suggested in [6–9]. This effect has indeed since been observed in many insulating crystals, including AlN [11], $Ba_3(PO_4)_2$ [12], α-Al_2O_3 [13] and the Na salt of DNA [14].

A qualitative theoretical basis for these delayed reactions was presented quite recently [15], giving support to V_K *reorientational* motion. However, the agreement

between theory and experiment was only satisfactory because of the continuous diffusion approximation used. In this paper a more adequate and refined theory is developed that takes into account the *finite hop lengths* of defects in a crystalline lattice. We shall try to clarify which useful information could be obtained from the non-steady-state kinetics of mobile V_K recombination with electron centres. In particular, we suggest a novel phenomenological approach for estimating parameters of V_K motion, i.e. E_a and its frequency factor S_r (which are in good agreement with both experimental data and quantum-chemical calculations [5]), as well as the qualitative criterion that the process under study involves *electron tunnelling transfer* between electron and hole centres.

The plan of the paper is as follows. In section 2 we describe in detail the experimental technique used, and in section 3 the relevant experimental results obtained. Section 4 deals with the general theory of transient diffusion-controlled non-stationary kinetics with tunnelling electron transfer. Actual experimental data for V_K are interpreted in section 5 and a general conclusion of both papers is given in section 6.

2. Experimental technique

An optical cryostat with low thermal inertia has been used for the thermostimulated luminescence (TSL) studies, fractional glow technique (FGT) experiments and direct non-steady-state recombination kinetics measurements. The rapid change of the sample temperature has been attained by using a small-mass sample holder equipped with a radiation heating element (W-coil), together with a thermal switch between the sample holder and liquid nitrogen as the cooling agent (figure 1). The thermal switch is performed as follows. The copper sample holder is made up of a vertical thin-walled tube of stainless steel. The upper end of the tube is connected to a gas valve and the lower one to the bath (vessel) with liquid nitrogen. The level of liquid nitrogen is higher than the position of the sample holder.

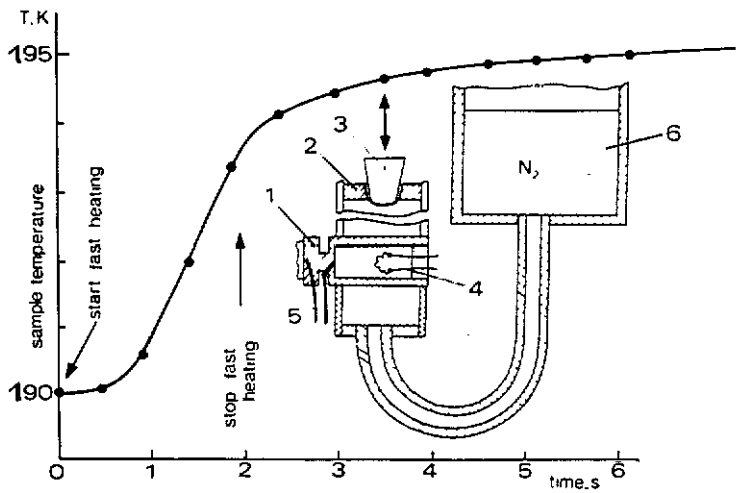

Figure 1. Full curve: time dependence of the stepwise sample heating. Schematic diagram of the low-inertia cryostat: 1, sample holder; 2, tube; 3, gas valve; 4, radiation heater; 5, thermocouple, 6, liquid nitrogen bath.

On opening the gas valve, liquid nitrogen contacts directly with the sample holder, thus leading to rapid cooling of the sample to liquid-nitrogen temperature (LNT). Closure of the valve interrupts the rapid cooling because the produced nitrogen vapour squeezes out liquid nitrogen from the tube and heat transfer from the holder to the liquid nitrogen is reduced to a minimum. The given final temperature of the holder is settled and kept constant using the radiation heater controlled by a PI-type thermoregulator and the embedded thermocouple. The minimum settling time of the temperature can be reached if the thermocouple is placed directly on the surface of the holder, which absorbs the radiation energy of the heater.

The holder is heated quickly when the gas valve is closed and the heating element is switched on to maximum power. Almost all the heat is accumulated by the holder. In practice, the temperature increase rate depends on the heating power only. The settling time of the final temperature in the case of fast heating is close to that of fast cooling.

The total time of the stepwise heating (or cooling) is defined by both the time required for fast heating (or cooling respectively) and the settling time of the final temperature of the holder (figure 1). The former depends on the temperature difference and the rate of fast heating (cooling), in the present cryostat being about 3 K s^{-1}. The temperature settling time of the holder, measured by a second thermocouple placed between the sample and the sample holder, is about 3–5 s, i.e. close to the thermal inertia of halide samples of thickness of about 0.5 mm.

A Brookdeal-type 5C1 single-photon-counting system equipped with a FEU-106 photomultiplier tube (PMT) has been utilized for the recombination luminescence intensity measurements, the counting time being 1 s. The spectral compositions of both the TSL and the *tunnelling luminescence* (TL) have been investigated using two luminescence measuring channels—an integral and a spectral one. The latter was equipped with an SPM-2-type grating monochromator. By registration of the TSL or the TL spectrum, the ratio of the signal in the spectral channel to the signal in the integral channel was calculated at each photon energy, thus taking into account changes in the recombination luminescence intensity in the course of the relaxation process under study.

3. Experimental results

Two major characteristic TSL peaks occur in KCl crystals activated with 30 ppm Tl (figure 2(*a*)). The peak at 210 K is caused by motion and recombination of V_K centres. The peak is observed in pure samples and its temperature corresponds to the temperature region of decay of the electron spin resonance (ESR) signal of the self-trapped holes [1]. The other peak at 300 K is known in Tl-doped KCl and corresponds to ionization of the activator Tl^0 centres. Both peaks differ in their spectral composition of the recombination luminescence (figure 2(*b*)). Decay in V_K-centre concentration results in the main luminescence band peaking at 3.0 eV with a half-width 0.75 eV [16]. The same luminescence band occurs in the TL spectra of Tl-activated KCl crystals (curve 1 in figure 2(*b*)) and has been interpreted earlier as a direct radiative electron transfer between the ground states of spatially close Tl^0 and V_K centres [17]. Therefore, the thermostimulated migration of V_K centres ends with their tunnelling recombination with an electron localized at a Tl^+ impurity. It should be mentioned that some of the migrating V_K centres (as follows from investigation

of the decay of the absorption spectra) after pulse excitations are captured by Tl^+ ions, leading to the growth of the Tl^{2+}-centre concentration [6, 7]. (The mechanism of Tl^+-centre ionization by the V_K centre remains unclear in detail. Thermostimulated ionization of Tl^0 centres leads to the distinctive activator luminescence band at 4.27 eV caused by recombination of released electrons with Tl^{2+} centres, which are still thermally stable at this temperature.)

Examination of the thermostimulated luminescence in KCl:Tl by means of the FGT shows that for the impurity concentrations under consideration the processes of V_K-centre recombination and Tl^0-centre ionization are *monoenergetic* with activation energies of 0.54 and 0.71 eV respectively. Note that the activation energy of V_K-centre recombination observed by FGT *coincides* perfectly with the value estimated from the polarization experiments [2].

Curve 2 in figure 3 shows the characteristic transient kinetics observed after stepwise heating of a sample by 5 K. (Zero time in figure 3 is taken as the moment of onset of the fast rise of sample temperature.) In our luminescence kinetics, no non-inertial components have been observed at all. Moreover, in most cases of stepwise heating experiments, the error in the measurements of the initial luminescence intensity does not exceed 1.5%. Only when the time of settling of the quasi-stationary luminescence intensity becomes comparable to the time of such stage heating does the luminescence intensity partly increase simultaneously with the temperature growth. Therefore, the contribution (proposed in [6, 7]) of long-range band hole flights due to V_K-centre breaking to the total reaction rate cannot exceed 1–1.5%, at least at moderate temperatures.

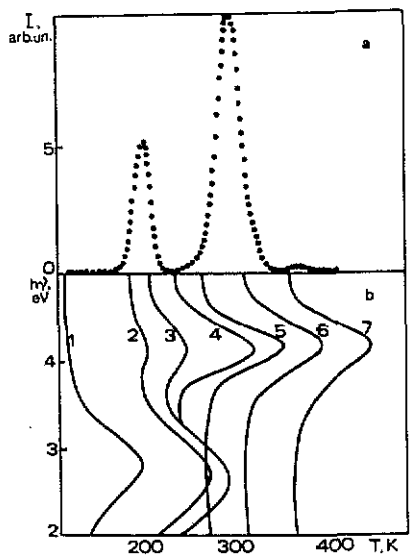

Figure 2. (*a*) TSL of KCl:Tl (0.03 mol%) excited at 80 K by x-rays. (*b*) TL (curve 1) and TSL (curves 2 to 7) spectra taken at corresponding temperatures.

Let us now discuss the mutual spatial distributions of the reacting centres in the decay kinetics both after pulsed excitation and in the transient kinetics after stepwise heating. The former obviously involves *all* kinds of V_K centres created and therefore is affected by the *initial* mutual distribution function of V_K–A^+ defects and is usually

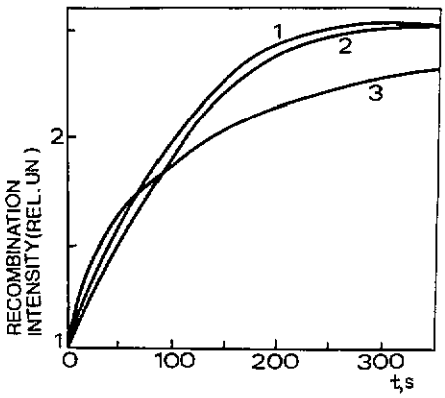

Figure 3. A comparison of experimental delayed kinetics of an increase in V_K luminescence intensity after sudden change of their mobility (temperature increase from 175 to 180 K) in KCl with theory: curve 1, hopping kinetics for $\lambda = 2a$ obtained by means of equation (4.5); curve 2, experimental curve; curve 3, continuous diffusion ($\lambda \to 0$) approximation [15], equation (4.3).

believed to be random. The latter depends on the mechanism of production of V_K and Tl^0 centres and in doped crystals can be, in principle, non-random. However, in this case the transient kinetics is determined only by the small change in the part of the stationary distribution function of defects close to the effective recombination radius (see below), which can be calculated analytically and does not depend on the initial distribution function. The low lifetime of V_K centres (more than an order of magnitude less than the theoretical one based on a random initial distribution function) observed in the pulse experiments should arise necessarily in the transient kinetics if there were flight motion of band holes, which *is not the case*. Thus, the conclusion suggests itself that the shortening of the V_K-centre lifetime results from a *correlated initial distribution* of V_K and impurity Tl^+ centres. Therefore, the absence of a non-inertial component in the transient kinetics puts into question the breaking of an X_2^- chemical bond during V_K reorientation, at least in crystalline KCl. (Analogous results were observed by us also in KBr.) Consider now the interpretation of transient kinetics in more detail.

4. Theory of transient hopping-controlled tunnelling reactions

4.1. General comments

First, note that the effect of inertial increase in the recombination intensity after stepwise defect mobility stimulation *cannot* be accounted for in terms of a standard theory of diffusion-controlled reactions [15, 18–20]. In terms of this latter reaction rate, K is time-dependent during a short transient period only when

$$K(t) = 4\pi D R_0 (1 + R_0/\sqrt{\pi D t}).$$

Here D is the relative diffusion coefficient given by

$$D(T) = D_0 \exp(-E_a/kT)$$

E_a is the activation energy and R_0 the clear-cut (*black-sphere*) recombination radius.

The decay kinetics under consideration can arise only when the joint density $Y(r)$ depends on $D(T)$ and thus the transient process corresponds to its *inertial* passage from one steady state $Y(D_1)$ to another one $Y(D_2)$ corresponding to a new defect mobility (D). This is just the case for the tunnelling recombination of electron and hole defects [21–25]. (In the particular case of V_K centres, the tunnelling character of their recombination with electron F, Tl^0 centres is well established [17, 26].) Its probability (per unit time) is $W(r) = w_0 \exp(-r/a)$, where r is the distance between dissimilar defects, w_0 and a are constants depending on the nature of the defects involved and the recombinative mechanism (radiative or radiationless) and a equals half the Bohr radius of the electron centre, which is usually more delocalized.

In our particular case D means the V_K diffusion coefficient, since it becomes mobile in alkali halides at temperatures when electron centres are definitely immobile. The joint density in which we are interested has the following form [23, 24]:

$$Y(r) = (2a/r)K_0\left\{2\sqrt{\beta_m}\exp[-(r-R_0)/2a]\right\} \tag{4.1}$$

where K_0 is the zero-order modified Bessel function of the first kind, and the dimensionless parameter $\beta_m = w_0 a^2 \exp(-R_0/a)/D$ characterizes the *strength* of the tunnelling recombination. The greater the tunnelling parameters w_0 and a, the greater is β_m and the better pronounced is the shift of the recombination profile to longer distances. On the other hand, increase in D (or T) reduces β_m and leads to the profile shift to shorter distances (see figure 1 in [15] as an illustration). Tunnelling recombination is called *strong* as $\beta_m \gtrsim 10$ [23]. In this regime the effective recombination radius

$$R_{\text{eff}} = R_0 + a\ln(\gamma\beta_m) \simeq aE_a/kT \gg R_0 \qquad \gamma = 1.78 \tag{4.2}$$

is independent of the hard-sphere radius R_0 at defect contact. Note that for large r, $Y(r) = 1 - R_{\text{eff}}/r$.

4.2. Continuous diffusion approximation

To investigate the delayed kinetics quantitatively, the transient process was described in terms of the following equation [15] for the joint correlation function of dissimilar defects:

$$\partial Y/\partial\tau = D^*[Y'' + (2/x)Y'] - \beta_m e^{-x} \tag{4.3}$$

and the recombination luminescence intensity

$$I_{(\tau)} \propto \int_0^\infty e^{-x}x^2 Y(x,\tau)\,dx. \tag{4.4}$$

This model is based on two assumptions: (i) defect motion can be described as a *continuous* diffusion with the relevant Laplace operator Δ; (ii) defect recombination is so slow that concentrations are practically constant and change in intensity I arises entirely due to the change of the reaction rate $K(\tau)$. (This assumption is experimentally controlled [15].) The dimensionless units used in equations (4.3) and

(4.4) are $x = r/a$, $\tau = Dt/a^2$ and $D^* = D(T_2)/D(T_1)$. Therefore, the solution of these equations is defined by three parameters: D^*, a^2/D and w_0. The first parameter determines the relative increase in the ordinate scale (intensity)

$$I(T_2)/I(T_1) = D(T_2)R_{\text{eff}}(T_2)/D(T_1)R_{\text{eff}}(T_1) \simeq (T_2/T_1)\exp(-E_a\Delta T/kT_1^2) \tag{4.4a}$$

where $\Delta T = T_2 - T_1 \ll T_1$ is the temperature increment (stimulation), which gives an independent way to determine the activation energy E_a.

Proceeding in this way, the theoretical estimate $S_r^t \simeq (12 \pm 5) \times 10^{13}$ s^{-1} was obtained [15], compared with the experimental value $S_r^e \simeq 4 \times 10^{13}$ s^{-1} [2]. The activation energy $E_a = 0.53$ eV also agrees well with optical dichroism studies (yielding 0.54 eV) as well as with transient absorption studies ($E_a = 0.54 \pm 0.05$ eV [6, 7, 27]). However, only satisfactory agreement was achieved since both curves have rather different behaviour (see section 5). We attribute this to the roughness of the continuous diffusion approximation, since the V_K reorientation hop length $\lambda = a_0/2\sqrt{2}$ [2] (a_0 is the lattice constant) is $\simeq 2.1$ Å, being *greater* than the distinctive recombination parameter $a \lesssim 1$ Å [28]. It means that a single hop takes the defect immediately into (or out of) the recombination region [23], and a more adequate formalism is required here.

4.3. Hopping-controlled kinetics

Studies of the kinetics of solvated electrons in polar liquids and energy transfer in activated crystals have stimulated several attempts to derive kinetic equations that were correct for *arbitrary* hopping lengths $0 < \lambda < \infty$ [29, 30]. Burstein *et al* [31] have indeed derived the general equation sought and investigated it analytically for the steady-state regime and assuming exponential hopping length distribution, known as the Torrey model. Since we are interested in *transient* kinetics and a single hop length describing V_K reorientation in a crystalline lattice, the Torrey model is no longer valid, and the relevant equations were solved by us numerically. The hopping analogue of equation (4.3) now reads

$$\frac{\partial Y(x,t)}{\partial \tau} = -\left(\tau_0^* + \tilde{w}_0 e^{-x}\right) + \frac{\tau_0^*}{2x\tilde{\lambda}} \int_{|\tilde{r}-\tilde{\lambda}|}^{\tilde{r}+\tilde{\lambda}} Y x \, dx. \tag{4.5}$$

The dimensionless units used are: $\tau = t/\tau_0(T_1)$ (τ_0 being the defect *waiting time* before a hop from a given lattice site), $\tilde{w}_0 = w_0\tau_0$, $x = r/a$ and $\tilde{\lambda} = \lambda/a$. The parameter $\tau_0^* = \tau_0(T_1)/\tau_0(T_2)$ is the ratio of waiting times before and after mobility change (it is nothing but D^* in equation (4.3) since $D = \lambda^2\nu/6 = \lambda^2/6\tau_0$).

It could be easily checked that, as $\lambda \to 0$, the use of the Taylor expansion of $Y(x,t)$ leads immediately to the continuous equation (4.3); the diffusion operator Δ arises (there) due to combination of the first and third terms.

In another extreme case, $\lambda \gg a$, one arrives immediately at [31]

$$Y(x,\tau) = \frac{1}{1+\tilde{w}_0 e^{-x}} + \frac{\tilde{w}_0 e^{-x}}{1+\tilde{w}_0 e^{-x}} \exp(-\tau - \tilde{w}_0 e^{-x}). \tag{4.6a}$$

As $\tau \gg \tilde{w}_0^{-1}$, the steady-state is achieved:

$$Y(x,\tau) = 1/(1+\tilde{w}_0 e^{-x}). \tag{4.6b}$$

This recombination profile corresponds to the reaction rate (see equation (4.4))

$$K = \tfrac{4}{3}(\pi a^3/\tau_0)(\ln^3 \tilde{w}_0 + \pi^2 \ln \tilde{w}_0) \qquad \text{as } \tilde{w}_0 > 1. \tag{4.7}$$

When tunnelling recombination becomes very strong, $\ln \tilde{w}_0 \gg 1$, the reaction rate transforms into a very simple and physically transparent expression:

$$K = \tfrac{4}{3}\pi R_w^3/\tau_0$$

where $R_w = a \ln \tilde{w}_0$ is the recombination sphere radius.

From figure 4 one can conclude that the recombination profiles differ greatly in two extreme cases of long (a) and short (b) hops. In the former case it is quite symmetric and increases rapidly, saturating already at $r \simeq 10a$. In contrast, in the latter case it increases very slowly, saturating only at $r \gtrsim 100a$. (The *time development* of the steady-state formation as a function of λ has been studied in detail in [32].)

In the present paper we are interested in the *passage* between two steady states corresponding to two different mobilities (D values). Such a transient kinetics is visualized in figure 5 for hop lengths varying from $20a$ to $1a$. Three general conclusions suggest themselves: (i) the short-distance part of the profile shifts at first, producing a rapid increase in intensity I, whereas its further saturation is achieved due to relatively slow long-distance tail stabilization; (ii) decrease in the hop length results in the smooth recombination profiles resembling that for the diffusion limit (figure 4(b)); (iii) the passage time increases rapidly as λ decreases. (The same conclusion was drawn for the transient time necessary to form the steady-state profile itself [32].)

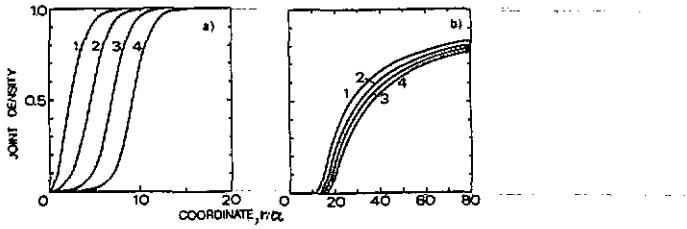

Figure 4. The steady-state joint density for dissimilar defects in two extreme cases of very long hops (a) and small hops (b). Curves 1 to 4: $w_0 = 10^1, 10^2, 10^3, 10^4$ (a); and $\lambda = 0.5a, 0.2a, 0.1a, 0.05a$, $w_0 = 10^4$ (b).

In figures 6 and 7 the relative increase in reaction rate is plotted for the same λ values as in figure 5. One can see that, for large λ, a change of the distinctive parameter $w_0\tau_0$ affects the transient kinetics considerably (cf curves 1 and 3 in figure 6). As λ decreases, this effect is less pronounced and for $\lambda = 1a$ the situation is *inverted*: the curve for greater values of the $w_0\tau_0$ parameter lies *lower* (see curves 3 and 4 in figure 7). Note also that, for small λ, the intensity (reaction rate) increases very smoothly as compared to large λ values.

A transient process for some more small λ values corresponding to the *continuous* diffusion limit was treated in [15], but qualitatively the effect could also be seen from figure 4(b): the passage from curve 4 to 1 corresponds to *two* orders-of-magnitude change of mobility D (since $D \sim \lambda^2$) unlike the *one* order-of-magnitude change shown in figure 5.

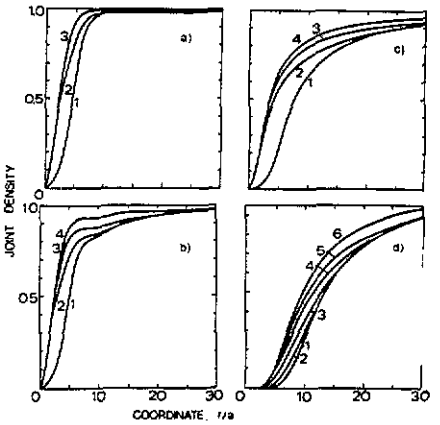

Figure 5. Transient kinetics for joint densities after mobility was increased by an order of magnitude versus hop length λ: $\lambda = 20a$ (*a*), $10a$ (*b*), $5a$ (*c*), $1a$ (*d*), $w_0\tau_0 = 10^2$. Figures in these curves indicate time (in units t/τ_0) after mobility change: (*a*) curves 1 to 3, $t = 0$, 0.15, 4; (*b*) curves 1 to 4, $t = 0$, 0.15, 0.4, 3; (*c*) curves 1 to 4, $t = 0$, 1.2, 5, 400; (*d*) curves 1 to 6, $t = 0$, 1.2, 5, 20, 10^3, 10^4.

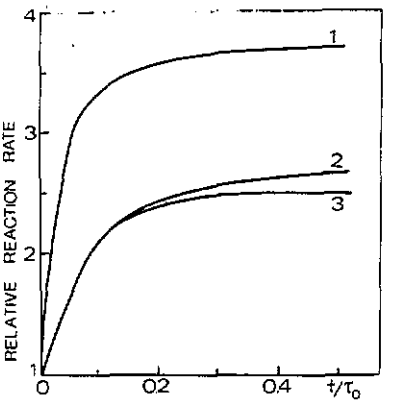

Figure 6. Relative change of the reaction rate after mobility was increased by an order of magnitude versus time: curve 1, $\lambda = 20a$, $w_0\tau_0 = 10^3$; curve 2, $\lambda = 10a$, $w_0\tau_0 = 10^2$; curve 3, $\lambda = 20a$, $w_0\tau_0 = 10^2$.

In conclusion of this section we would like to note that an order-of-magnitude increase in mobility ($\propto \tau_0^{-1}$) results in essentially a smaller change of the reaction rate (intensity) since (as follows from equation (4.7) in the hopping regime)

$$I(T_2)/I_0(T_1) = K(T_2)/K_0(T_2) = [R_w(T_2)/R_w(T_1)]^3\tau^* \simeq \tau^*\{1 - (\ln\tau_0^*)/[\ln w_0\tau_0(T_1)]\}^3 . \tag{4.8}$$

For $w_0\tau_0(T_1) = 10^3$ and $\tau_0^* = 10$ we get $I(T_2)/I(T_1) \simeq 3$, in good agreement with curve 1 in figure 6. In contrast, in the opposite continuous diffusion limit and with strong tunnelling recombination

$$I(T_2)/I(T_1) = D^* R(T_2)/R(T_1) = D^* T_1/T_2 = D^*(1 - \Delta T/T_2) \tag{4.9}$$

which practically coincides with $D^*(= \tau_0^*)$, since $\Delta T \ll T_2$.

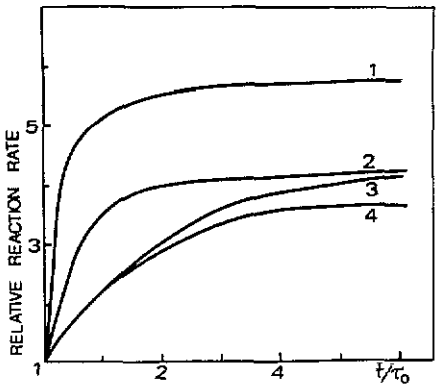

Figure 7. The same as figure 6 for small hop lengths: curve 1, $\lambda = 5a$, $w_0\tau_0 = 10^3$; curve 2, $\lambda = 5a$, $w_0\tau_0 = 10^2$; curve 3, $\lambda = 1a$, $w_0\tau_0 = 10^2$; curve 4, $\lambda = 1a$, $w_0\tau_0 = 10^3$.

5. Analysis of the delayed recombination kinetics of V_K centres

The theory developed in section 4 above can now be applied to the actual experimental data for V_K centres in KCl:Tl [15] (see that paper for more experimental details). The relevant delayed kinetics of the luminescence increase is plotted in curve 2 of figure 3, whereas theory based on a continuous approximation is shown in curve 3. The obvious conclusion could be drawn that the agreement is only qualitative: the theoretical curve increases more rapidly but saturates more slowly than the experimental one. In figure 3 the result of *hopping-controlled* theory for $\lambda/a = 2$ (equation (4.5)) is plotted in curve 1. In the spirit of our approach, the best fit is obtained by varying the abscissa scale parameter τ_0, which is found to be 50 (the same factor as sought in continuous theory represented in section 4). Obviously, better agreement is reached now, indicating clearly the importance of the incorporation of *finite* hop lengths into recombination kinetics.

Fitting of the ordinate scale factor yields $E_a = 0.53$ eV, close to the earlier experimental estimate $E_a = 0.54$ eV for 60° reorientations [2, 6]. Keeping in mind [2] that V_K reorientation by 90° requires considerably higher energy (its probability is less by two orders of magnitude), one comes to the conclusion that V_K motion occurs *via 60° reorientations.*

Now making use of this E_a and the relation

$$1/\tau_0 = S_r \exp(-E_a/kT)$$

we arrive immediately at the frequency factor $S_r \simeq 4 \times 10^{13}$ s^{-1}, in excellent agreement with that obtained by means of optical dichroism [2].

Since the theoretical curve, equation (4.3), is rather insensitive to the choice of another dimensionless parameter $w_0\tau_0$, we could only estimate its order of magnitude, being $10^{10\pm2}$. This value agrees with the product of $\tau_0 \simeq 50$ just obtained and the typical pre-exponential factor of radiative tunnelling transitions $w_0 = 10^8$ s^{-1} [21, 22]. The effective recombination radius estimated from equation (4.7) is about $20a$. Making use of the value of half of the Bohr radius of the electron centre with which V_K recombines (Tl^0, $a \simeq 1$ Å, ENDOR data [28]), we obtain $R_w \simeq 20$ Å—the same value as in the continuous diffusion approximation [15]. Note that it is in reasonable

agreement with experimentally found $R \simeq 35 \pm 7$ Å for *static* recombination [33]. (It is clear that the diffusion radius should be *smaller* due to defect mutual approach before recombination.) The conclusion that the main electronic partner is Tl^0 comes from both luminescence [15] and absorption [34] spectra.

6. General conclusion

Summing up, both approaches employed—quantum-chemical simulations [5] and phenomenological kinetic theory—argue for the 60° reorientational mechanism of V_K-centre motion.

Turning now to the kinetic studies, discussed in this paper, their common bottleneck is the assumption about the relative spatial distribution of defects. In stationary experiments studying V_K recombination during the transient period, all spatially correlated dissimilar defects recombine and thus we start with the *steady-state* profile [10–15], which can be calculated theoretically. Its achievement is seen from the nearly constant recombination intensity. (According to [34], the share of correlated $\{V_K\text{–}Tl^0\}$ geminate pairs depends considerably on the excitation energy, constituting about 10% for x-rays.) On the other hand, the interpretation of the pulsed experiments of V_K trapping by impurities resulting in the idea of long-range hole hops (flights) is based on a *random* spatial $V_K\text{–}Tl^+$ distribution. Despite the fact that it seems to be intuitively reasonable, there exist however experimental data indicating that excitons have a *greater probability* to decay into radiation defects in the vicinity of impurities [16, 35–37]. Therefore of fundamental importance would be further careful analysis of the $V_K\text{–}Tl^+$ spatial correlation; if it happened to be the case, experimental findings [6–8] could be reinterpreted in terms of the usual V_K reorientational motion but at much shorter distances. This criticism also refers to picosecond time resolution studies [19] of steady-state formation based on the treatment of short-time reaction rate $K(t) \propto t^{-1/2}$ dependence, which is valid for a random initial distribution only.

Acknowledgments

Many thanks are due to E Aluker, A Burstein, V Chernov, A Doktorov, A Popov and A Shluger for illuminating discussions. One of us (EK) thanks also Professor A Blumen for his hospitality during the author's visit to Bayreuth University and for criticism of this work, which contributed greatly to its improvement.

References

[1] Kabler M N 1972 *Point Defects in Solids* (New York: Plenum) pp 171–207
Hayes W and Stoneham A M 1985 *Defects and Defect Processes in Non-Metallic Solids* (New York: Wiley)
[2] Keller F J and Murray R B 1966 *Phys. Rev.* **150** 670
Keller F J, Murray R B, Abraham M M and Weeks R A 1967 *Phys. Rev.* **154** 812
[3] Tale I 1981 *Phys. Status Solidi* a **66** 65; 1982 *DS Thesis* Institute of Physics, Latvian Academy of Science, Salaspils
[4] Tale V 1987 *PhD Thesis* Institute of Physics, Estonian Academy of Science, Tartu
[5] Shluger A L, Kantorovich L N, Heifets E N, Shidlovskaya E K and Grimes R W 1992 *J. Phys.: Condens. Matter* **4** 7417

[6] Aluker E D, Gavrilov V V, Deutch R G and Chernov S A 1987 *Transient Radiation-Induced Processes in Alkali Halide Crystals* (Riga: Zinatne)
[7] Aluker E D, Chernov S A and Gavrilov V V 1984 *Sov. Phys.–Solid State* **26** 1879; 1986 *Sov. Phys.–Solid State* **28** 168
[8] Pirogov F 1979 *Proc. Latv. Acad. Sci.* **6** 45
Aluker E D, Deutch R G, *et al* 1980 *Sov. Phys.–Solid State* **22** 3689
[9] Pirogov F 1985 *Proc. Latv. Acad. Sci.* **5** 60
[10] Tale I A and Gailitis A 1971 *Proc. Acad. Sci. USSR* **35** 1336
[11] Rosa I and Tale I 1975 *Czech. J. Phys.* A **29** 810
[12] Tale I, Kulis P and Kronhaus V 1975 *J. Lumin.* **20** 343
[13] Kulis P 1987 *PhD Thesis* University of Riga
[14] Butlers P 1987 *PhD Thesis* University of Riga
[15] Kotomin E, Tale I, Tale V, Butlers P and Kulis P 1989 *J. Phys.: Condens. Matter* **1** 6777
[16] Delbecq C J, Ghosh A K and Yuster P H 1967 *Phys. Rev.* **154** 797
[17] Grabovskis V Ja and Vitols I K 1979 *J. Lumin.* **20** 337
[18] Waite T R 1957 *Phys. Rev.* **107** 471
[19] Nemzek T L and Ware W R 1975 *J. Chem. Phys.* **62** 477
Sipp B and Voltz R 1983 *J. Chem. Phys.* **79** 434; 1985 *J. Chem. Phys.* **83** 157
[20] Tanimura K and Itoh N 1981 *J. Phys. Chem. Solids* **42** 901
[21] Dean P 1973 *Prog. Solid State Chem.* **8** 1
[22] Vink A T 1974 *J. Lumin.* **9** 159
[23] Doktorov A B and Kotomin E A 1982 *Phys. Status Solidi* b **114** 3
[24] Rice M and Pilling S 1979 *Prog. React. Kinet.* **9** 34
[25] Zamaraev K I and Klairutdinov R F 1989 *Long-Rangem Electron Transfer in Chemistry* (Amsterdam: Elsevier)
[26] Delbecq Ch J, Toyozawa Y and Yuster P H 1979 *Phys. Rev.* B **9** 4497
[27] Deutch R G 1990 *DS Thesis* Institute of Physics, Latvian Academy of Science, Salaspils
[28] Grachev V and Delgen M 1978 *Sov. Phys.–Usp.* **125** 631
[29] Burstein A I and Zusman L D 1975 *Sov. Opt. Spectrosc.* **38** 588
[30] Vugmeister B E 1978 *Phys. Status Solidi* b **90** 711
[31] Doktorov A B, Kypriyanov A A and Burstein A I 1978 *Sov. Phys.–JETP* **47** 623; 1985 *Sov. Phys.–JETP* **61** 516
[32] Kotomin E 1991 *Dynamical Processes in Condensed Molecular Systems* (Singapore: World Scientific) p 414
[33] Nesterova S 1981 *Proc. Latv. Acad. Sci.* **3** 44; 1982 *PhD Thesis* Institute of Physics, Latvian Academy of Science, Salaspils
[34] Aksenov O, Aluker E, Lusis D and Mezina I 1980 *Phys. Status Solidi* a **57** 129
[35] Hirai M 1990 *J. Phys. Chem. Solids* **51** 737
[36] Kalnins A, Pliavina I, Popov A and Tale A 1990 *Phys. Status Solidi* b **161** 85; 1991 *Latv. Phys. Tech. J.* 1992
[37] Dyachenko S, Nagli L and Pirogov F 1988 *Phys. Status Solidi* a **88** 87