Temperature dependence of F-centre accumulation efficiency in doped alkali halides

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Abstract. A model explaining the temperature dependence of the efficiency of F-centre accumulation in doped alkali halides (as well as F_2-centre destruction), observed in the course of steady-state experiments, has been developed. The model takes into account three- (or one-) dimensional continuous diffusion of H centres, resulting in a primary process, and their decay due to the diffusion-controlled: (i) annihilation, (ii) tunnelling recombination with F centres, and (iii) localization by pre-existing defects (or recombination with F_2 centres). The probability of an F centre surviving depends upon the temperature and initial spatial distribution function within a genetic F–H pair at the moment of its production. The model indicates that diffusion-controlled accumulation *is not* described by the Arrhenius relation of energy being equal to that of diffusion. The effective energy is independent of temperature only for a particular form of the initial distribution; otherwise, it has a value a few times less than the diffusion energy and slowly decreases with temperature. An estimate for KBr is close to that observed experimentally. The relative efficiency of F–H *tunnelling* recombination decreases and that of annihilation correspondingly increases with temperature. Pulse radiolysis experiments are briefly discussed in connection with the model presented.

1. Introduction

Recently a series of experimental studies have been made on the mechanism of F-centre formation and accumulation in alkali halides (Crawford 1968, Sonder and Sibley 1972, Kabler 1975, Elango *et al* 1976). It has been shown that, if the temperature rises between liquid nitrogen temperature (LNT) and room temperature (RT), the efficiency of F-centre accumulation during steady-state experiments increases in many doped alkali halides, e.g. $KBr:Ca^{2+}$ (Vitol *et al* 1967), $KBr:Li^+$ (Guillot *et al* 1975), $KCl:Pb^{2+}$ (Sonder 1973), $KCl:Ca^{2+}$, $NaCl:Ca^{2+}$ (Vitol *et al* 1967) etc. This growth of the accumulation efficiency obeys the Arrhenius relation, with the effective energies of KBr and KCl (0.025 eV and 0.07 eV, respectively) being essentially less than those of H-centre diffusion. These same energies have been reported from studies of the destruction of pre-existing F_2 centres (Sonder 1972, 1973, 1975, Guillot *et al* 1975).

The purpose of this paper is to develop the phenomenological theory, taking into account primary and secondary processes of defect production, leading to F centre accumulation. Secondary processes take into account diffusion of H centres and their annihilation, tunnelling recombination and trapping in doped alkali halides. It will be

demonstrated that the observed temperature growth of F-centre accumulation efficiency may be understood by taking into account a *decrease* of tunnelling recombination efficiency with temperature, without assuming any specific potential of close F–H pairs, as Sonder (1972, 1973, 1975) does, or exciton decay near the defect, as Townsend (1976a, b) does.

2. Primary and secondary processes of defect production

An accumulation of F centres in steady-state experiments consists of two *distinct* successive stages: (*a*) *primary* process involving: (i) formation of a hot (non-relaxed) exciton, (ii) its motion and relaxation, (iii) a radiationless decay into a localized F centre and a mobile ('hot') atom X^0, (iv) motion of the latter up to loss of primary momentum, and (v) localization in the form of an H centre; (*b*) the series of *secondary* processes between defects (see below).

It has been calculated (Smoluchowski *et al* 1971, Dienes and Smoluchowski 1976) that, in alkali halides, the appreciable separation of an F centre and an H centre may be realized through a series of focused collisions in the $\langle 110 \rangle$ direction. (On the other hand, *unambiguous experimental evidence* of this mechanism is very complicated, cf Hall *et al* (1976).) The duration of this series does not exceed a few ps and its length *decreases* with the temperature (cf also Agranovich and Kirsanov (1976)). So, at the end of the very rapid primary process, genetic pairs of F–H centres arise, being spatially correlated (i.e. the probability of finding a single H centre sharply decreases starting with certain mutual F–H distances).

There exist three *qualitatively* distinct secondary reactions involving radiation-induced as well as pre-existing defects, namely:

(*a*) A *tunnelling* recombination of spatially separated electron–hole centres is a *temperature-independent* process, due to which it appears to be one of the most important processes around liquid helium temperature (LHT) (e.g. Tāle *et al* 1975a). Decay through the tunnelling recombination of nearest and next-nearest F–H pairs around LHT occurs with two distinctive times, each having a value a few µs (Ueta *et al* 1969, Kondo and Hirai 1971, Kondo and Ueta 1972, Karasawa and Hirai 1972). It is believed that for quantitative estimates we may employ probability for tunnelling recombinations in the form (cf Bogan *et al* 1973, Tāle *et al* 1975a (§ 2), Delbecq *et al* 1974):

$$w(r) = w_0 \exp(-r/r_B), \tag{1}$$

where w_0 is a constant,† r_B is half the Bohr radius of an F centre and r is the separation between electron–hole defects.

(*b*) At higher temperatures where H, I centres are mobile, there arise two kinds of diffusion-controlled reactions:

(*i*) These are reactions occurring *immediately* if a pair of defects approach to within a certain distance r_0 (the so-called *clear-cut radius*), namely: (i) *annihilation* of pairs of the complementary defects (F–H, F^+–I), (ii) *localization* of mobile H centres by pre-existing defects, and (iii) *aggregation* of mobile H centres.

(*ii*) *Diffusion-controlled tunnelling* recombination of essentially separated defects which approach each other due to diffusion has been considered recently (Kotomin 1975, Fabrikant and Kotomin 1974, 1975, Pilling and Rice 1975). It was shown that

† For many donor–acceptor pairs in semiconductors, w_0's typical magnitude is $\simeq 10^7$ s^{-1} (Dean 1973, Vink 1974). The same value may be also estimated for F, H centres using the two mentioned decay times.

the annealing process involving thermal diffusion of the hole (H, V_k) centres and their tunnelling recombination with electron centres (e.g. F) can be described (after a transient period) by a rate equation with rate constant $k = 4\pi D_0 R_{qs}(T) \exp(-E/kT)$ D_0 being the pre-exponential factor of the diffusion coefficient, E the activation energy of diffusion and R_{qs} the effective radius of the *quasi-steady tunnelling recombination* (QSTR), which decreases with temperature.

It is clear at present that the initial distribution function within F–H pairs, resulting from the primary process, and the fate of the diffusing H centres during secondary annealing *directly affects* the F-centre accumulation (as well as F_2-centre decay).

Sonder (1973, 1975) presented a simple model of the latter processes based on rate equations†. In such an approach, the probability that a mobile H centre will be trapped (and, consequently, an F centre will survive) is determined by the trapping and recombination cross sections and by macroscopic concentrations of traps and F centres (cf equation (3) of Sonder (1973)). The temperature dependence, according to Sonder, arises from the growth of the probability that an H centre does leave its 'own' nearby F centre and will participate in the mentioned reactions. The activation energy of such a separation is supposed to be due to a specific form of the potential at small mutual separation‡. This model, however, is too rough an approximation, because: (i) to obtain the Arrhenius relation only *one* kind of nearest pairs must exist, which is doubtful, (ii) the rate-equation-model itself *cannot* take into account the *spatial correlation* of defects, which is obviously very important in the diffusion-controlled process in question; all the more so since tunnelling recombination, sharply dependent on the mutual spatial separation of defects, is involved, and (iii) this model assumes time and temperature independence of trapping and recombination radii.

Quite recently it has been qualitatively assumed (Kotomin 1975, Tāle *et al* 1975b) that the growth of the efficiency of F-centre accumulation with temperature is caused by a *decrease* of the QSTR radius, which results in a relative increase of the role of trapping and aggregation processes competing with recombination.

The present paper is concerned with a quantitative analysis of this idea for the case of doped crystals.

3. Proposed model

3.1. Initial suppositions

3.1.1. The primary process of defect formation results in the appearance of a series of isolated genetic F, H centres (Hirai *et al* 1971, Kondo and Hirai 1971, Kondo and Ueta 1972, Karasawa and Hirai 1972, Ueta *et al* 1969, Bradford *et al* 1975). Each pair is described by the initial spatial distribution function $u_0(r, T)$. It is supposed that, during its motion, the hot interstitial is not captured by any defect. We assume also that the exciton does not decay near the defect (cf Townsend 1976a, b, Nouailhat *et al* 1976) because its electronic state and mobility are not known.

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† Another rate-equation model of H-annealing has been considered quite recently by Dienes and Smoluchowski (1976).

‡ Another effect of *close* pairs—short stochastic walks of crowdions near traps—has quite recently been considered by Smoluchowski (1976). *Neglecting* the potential distortion, he found that the effective energy of motion in the presence of a trap is *higher* than without a trap, which cannot explain the experimental results in question.

3.1.2. In the course of secondary diffusion-controlled processes, H centres decay through three channels: (i) tunnelling recombination with genetic F centres (in accordance with equation (1)), yielding F^+– I pairs, (ii) annihilation of the same F centres if their relative distance is less than the annihilation radius ρ, and (iii) localization by any pre-existing defects or destruction of F_2 centres.

3.1.3. The motion of an H centre is rather complicated (Itoh 1972, Dienes and Smoluchowski 1976) and includes *linear* jumps as well as 60° rotations, which results in three-dimensional walks (cf § 3.5).

3.1.4. A general statement of the problem must take into account blurring of the components of different genetic pairs leading to aggregation of mobile H centres, a competition between two H centres to recombine with an F centre (and vice versa), etc. These are processes of primary importance for *pure* crystals. We shall restrict ourselves to the case of doped crystals where the dominant channels of H-centre disappearance are those of supposition § 3.1.2. We shall also estimate the effect of the recombination of H centres with 'foreign' F centres, neglecting aggregation of H centres (§ 3.3). An H centre is supposed to be trapped at a certain distance R from its F centre. A simple calculation indicates that, for a trapping radius $r_0 \simeq 10 \text{ Å}$ and a concentration of traps $C = 10^{19}$ cm^{-3}, $R \simeq 100 \text{ Å}$, which is about five times greater than the mean distance between traps. A more careful analysis must also take into account the real distribution of traps with respect to the F centres; this is important, for example, for the kinetics of further tunnelling recombination between F and H_A centres (Vitol and Grabovskis 1973), but *not* for the temperature dependence in question (cf § 3.3).

3.1.5. We consider only steady-state experiments during which all H centres have time to disappear by the above-mentioned channels and, consequently, the probability of an F centre surviving (or an F_2 centre disappearing) equals the probability of H-centre trapping. Since we do not take into account the above-mentioned F–H_A tunnelling recombination, the time of the H-centre walks, for the sake of simplicity, can be taken to be infinity.

3.2. Probability for an F centre surviving and its temperature dependence

In terms of mathematics the problem reduces to the calculation of the probability, P, of surviving:

$$P = - D \int_0^\infty dt \int_S \nabla u \, dS = - 4\pi R^2 \int_0^\infty \frac{\partial u}{\partial r}\bigg|_R dt \tag{2}$$

where $u(r, t)$ is the solution of the diffusion equation

$$\frac{\partial u(r, t)}{\partial t} = D\nabla^2 u(r, t) - w_0 \exp{(- r/r_B)}u(r, t), \tag{3}$$

with the boundary conditions, taking into account the trapping and annihilation,

$$u(R, t) = 0, \qquad u(\rho, t) = 0 \tag{3a}$$

(cf also the end of § 3.3), the diffusion coefficient for H centres being $D = D_0 \exp{(- E/kT)}$.

It is shown in the Appendix that

$$P = \frac{4\pi \int_\rho^R r^2 u_0(r, T) u_{qs}(r, T)\, dr}{1 - R_{qs}/R},$$ (4)

where

$$u_{qs}(r, T) = \frac{2r_B}{r}\left(K_0[z(r)] - \frac{k_0[z(\rho)]}{I_0[z(\rho)]}I_0[z(r)]\right),$$ (5)

with $z(r) = \alpha \exp(-r/2r_B)$, $\alpha = 2r_B(w_0/D)^{1/2}$ and where I_0 and K_0 are modified Bessel functions, describes the radial part of the quasi-steady distribution forming after the transient period and *independent* of initial distribution (Fabrikant and Kotomin 1975, § 3). The QSTR radius entering into equation (4) is

$$R_{qs}(T) = r_B\left(\frac{E}{kT} + \ln\frac{w_0 r_B^2}{D_0} + 2C + \frac{2K_0[z(\rho)]}{I_0[z(\rho)]}\right)$$ (6)

and also includes the *annihilation* through the latter term; C is the Euler constant (0.577)†.

There exist two distinct temperature ranges, which we will refer to as 'low' and 'high' temperatures, namely $\alpha \gg 1$ for low temperatures and $\alpha \ll 1$ for high temperatures. For low temperatures, the QSTR radius is independent of ρ:

$$R_{qs}(T) \simeq r_B\left(\frac{E}{kT} + \ln\frac{w_0 r_B^2}{D_0} + 1.154\right)$$ (7)

and has a value of a few tens of Å (see figure 1a). For high temperatures, the QSTR radius reduces almost to ρ and weakly depends on the temperature:

$$R_{qs}(T) \simeq \rho + \frac{2w_0 r_B^3}{D_0}\exp\left(-\frac{\rho}{r_B} + \frac{E}{kT}\right).$$ (8)

3.3. Different initial distributions

Obviously, P in equation (4) depends on the concrete form of the initial distribution function $u_0(r, T)$, so let us now consider three different forms for u_0:

(a) The simplest is the δ-like form

$$u_0 = \frac{\delta(r - l)}{4\pi r^2}.$$ (9)

For this initial distribution, P becomes

$$P = \frac{u_{qs}(l, T)}{1 - R_{qs}/R}.$$ (10)

From (10), the conclusion can be drawn that P weakly depends on the concentration of traps if $R_{qs} \ll R \simeq 100\,\text{Å}$ holds, which *a posteriori* justifies our rough description of the trapping. If $\alpha \exp(-l/r_B) \ll 1$, one gets

$$P(l, T) \simeq \frac{1 - R_{qs}/l}{1 - R_{qs}/R} \simeq 1 - \frac{R_{qs}}{l} = 1 - \frac{\rho}{l} - \frac{\alpha^2 r_B \exp(-\rho/r_B)}{2l}.$$ (11)

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† It should be emphasized that although equation (4) contains the R_{qs} forming only after the transient period $\tau \simeq R_{qs}^2/D$, equation (4) correctly describes the transient process. If τ is zero, one obtains the well known result (see, for example, Schroeder 1970) $P = 1 - R_{qs}/l$, where l is the initial δ-like separation and $R \to \infty$.

From (11), a few important conclusions concerning high temperatures can be drawn : (i) the contribution of tunnelling recombination is small, whereas annihilation becomes a dominant factor, (ii) the saturation level for the probability of surviving is directly determined by the annihilation radius ρ and the initial separation l within an F–H pair (see figure 1), and (iii) an accurate choice of w_0, D_0 is not very important, because they determine only a small correction (cf § 3.4).

(b) Another, more real, distribution function is

$$u_0(r) = \frac{N \exp(-r/r')}{4\pi r},$$

where the average separation within a pair is $2r'$.

A simple calculation indicates that, in this case at low temperatures, $P \propto D^{r_B/r'}$; that is, the Arrhenius relation *holds* with effective energy $E^* = E(r_B/r')$. Since $r' > r_B$, E^* is a few times less than the diffusion energy E.

(c) Finally, if random distribution is the case, i.e. $u_0 = 1/[(4\pi(R^3 - \rho^3)]$, one gets (at *all* temperatures)

$$P = 1 - \tfrac{3}{2}\frac{R_{qs}(T)}{R} + O\left(\alpha^2 \frac{r_B^3}{R^3}\right).$$

In conclusion, bearing in mind that the recombination of H centres with 'foreign' F centres in Sonder's experiments is an appreciable factor, let us estimate this effect.

To consider that a diffusing H centre can pass through the trapping radius R and approach a foreign F centre, let us assume that this effect may be considered as the *reflection* of an H centre from the boundary at $r = R$. This corresponds to the replacement of equation (3a) by the so-called *radiation boundary condition* (e.g. Waite 1957, Peak and Corbett 1972)

$$u(R, t) + \beta \frac{\partial u(r, t)}{\partial r}\bigg|_R = 0, \tag{3b}$$

where β describes the reflection probability.

The boundary condition chosen leads to the replacement of equation (4) by

$$P = \frac{4\pi \displaystyle\int_\rho^R r^2 u_0(r, T) u_{qs}(r)\, dr}{1 - (R_{qs}/R)(1 - \beta/R)}. \tag{4a}$$

One can see that mixing of the genetic pairs leads to a *decrease* of P, but *does not* change its temperature dependence in doped crystals and is a *second-order effect* if $R_{qs} \ll R$.

3.4. Model of finite lifetime with clear-cut recombination radius

Since the probability of tunnelling recombination in the form of equation (1) is not at present strictly justified for alkali halides, it is interesting to also examine other kinds of probability per unit time. The simplest pretendant is

$$w(r) = \begin{cases} w_0 = \text{constant}, & r \leqslant r_0 \\ 0, & r > r_0. \end{cases} \tag{12}$$

The principal circumstance is that here the lifetime $\tau = w_0^{-1}$ is finite, i.e. such a recombination is *inertial* and during diffusion a pair of defects can approach one another to

within the critical distance r_0 and drift apart *without recombination*. It is easy to obtain now

$$R_{qs}(T) = r_0 \left(1 - \frac{2}{\alpha} \tanh \frac{\alpha}{2}\right), \qquad \alpha = 2r_0 \left(\frac{w_0}{D}\right)^{1/2}. \tag{13}$$

At high temperatures ($\alpha \ll 1$), the QSTR radius decreases as D^{-1}:

$$R_{qs}(T) = \frac{r_0 \alpha^2}{12} = \frac{r_0^3 w_0}{3D_0} \exp(E/kT). \tag{14}$$

If the initial distribution is δ-like, one gets (cf equation (11)):

$$P = \frac{1 - R_{qs}/l}{1 - R_{qs}/R}, \qquad l > r_0. \tag{15}$$

A comparison of equations (14) and (8) (with $\rho = 0$) leads to the conclusion that, at *high* temperatures, the actual recombination law (with finite lifetime) is not important because the contribution of tunnelling recombination is small. Obviously, this is so because of the *inertial* character of the tunnelling recombination—the more mobile an H centre is, the higher is the chance that it can pass near an F centre without recombination. At high temperatures, the small value of the parameter $\alpha = (12r_B/d) (w_0/v)^{1/2}$ (where v is the frequency of jumps) $= (12 \, r_B/d) (\tau_1/\tau_r)^{1/2}$ means that the lifetime, τ_1, of an H centre in a site near an F centre becomes *less* than the finite time, τ_r, necessary for recombination.

3.5. Linear motion of an H crowdion

Under certain circumstances, e.g. due to distortion of the potential of a close F–H pair or if the frequency of linear jumps of an H centre greatly exceeds that of the rotations above certain temperatures (cf Dienes and Smoluchowski 1976, § 3), an H centre can undergo *one*-dimensional diffusion instead of the three-dimensional one considered above.

It is easily obtained that, for a δ-like initial separation and $\alpha \exp(-l/2r_B) \ll 1$, one gets

$$P = \frac{l}{R} \frac{1 - R_{qs}/l}{1 - R_{qs}/R} \tag{16}$$

(cf equation (11)). If the initial distribution is of the form $\exp(-x/r')/r'$, then $P \propto D'^{r'_B/r'}$ (cf § 3.3(*b*)).

3.6. Concrete estimates

3.6.1. F-centre accumulation efficiency in KBr. Concrete estimates require a more detailed analysis of the motion of an H centre. The energy, E_r, and the frequency factor, v_{0r}, of 60° rotations are unambiguously determined by ESR (Bachmann and Känzig 1968). Annealing experiments concerning *free* H centres have been interpreted in terms of first-order kinetics with activation energy 0·09 eV (see § 3 of Dienes and Smoluchowski (1976)). According to the quite recent theory of Smoluchowski (1976), this is the activation energy, E_L, of *linear* jumps. The corresponding value of v_{0L} is, however, a matter of dispute. For its estimate, Dienes and Smoluchowski (1976) use the Debye temperature of the crystal, which seems to be both unjustified and an overestimate. Using both the

theoretical and experimental data that F–H centres are separated by 7–10 lattice constants (see the penultimate paragraph of this subsection) and the lifetime of an H centre (Ueta 1967), one gets $v_{0L} \simeq 5 \times 10^{10}$ s^{-1}, i.e. two orders of magnitude less than the mentioned estimate.

Using the obtained estimate of v_{0L} and putting $r_B = 2$ Å (Fowler 1968) and $w_0 = 10^7$ s^{-1}, one finds that the temperatures referred to in § 3.2 as *low* and *high* lie below 130 K and above 200 K, respectively, i.e. above the latter temperature, tunnelling recombination is inefficient.
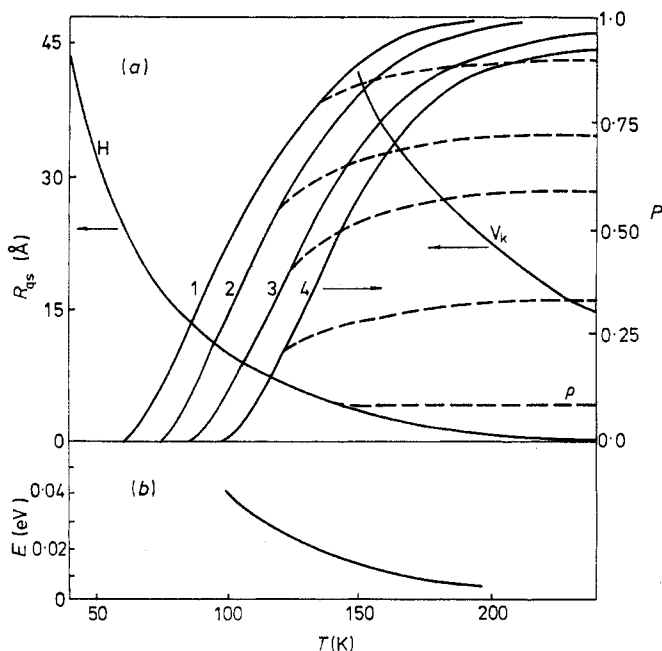

Figure 1. (a) Left-hand scale—the calculated values of the quasi-steady tunnelling recombination radii for an H centre and a V_k centre versus temperature. Right-hand scale— the probability for an F centre surviving for different initial separations l within a pair: curve 1, $l = 10r_B$; 2, $7r_B$; 3, $5r_B$; 4, 3 r_B ($r_B = 2$Å) (cf figure 5 of Saidoh and Itoh (1975)). Full curves correspond to zero annihilation radius ρ, broken curves to $\rho = 2r_B$. (b) The effective energy describing the F-centre accumulation efficiency and corresponding to curve 2 above for $\rho = 0$.

Figure 1 (a) shows the corresponding probability P of an F centre surviving as a function of temperature and initial δ-like separation l (see equation (10)). One can see that P monotonically increases with T and strives for saturation at high temperatures; an increase of l leads, roughly speaking, to a shift of P as a whole to lower temperatures. The saturation level, in accord with equation (11), is determined by the initial separation l and the annihilation radius.

Figure 1(b) shows the effective energy, $\partial \ln P / \partial (-1/kT)$, calculated for $l = 7r_B$. Its value is of the order of a few times 10^{-2} eV—in agreement with the experiment— but slowly *decreases* with the temperature. One can also easily include the temperature dependence of *primary* process assuming, for example, that the length of separation l *decreases* twice from 7 r_B at 100 K to 3·5 r_B at 200 K—in accordance with theory (Dienes

and Smoluchowski 1976). The corresponding effective energy in this case does not, however, essentially differ from that in figure 1(*b*).

The conclusion can also be drawn from figure 1(*a*) that the actual magnitude of the QSTR radius is $\simeq 40$ Å at temperatures slightly above that of the delocalization of an H centre, but sharply decreases with increasing temperature, almost coinciding with the annihilation radius at 200 K. For comparison, figure 1(*a*) also shows the QSTR radius for the V_k centre.

As stated in § 3.3, the Arrhenius relation *holds* for the initial distribution function, which decays exponentially with distance *r*. However, the *actual* type of initial spatial distribution within the F–H pair presents a very complicated problem. Pulse radiolysis experiments (Ueta 1967, Ueta *et al* 1969, Kondo and Hirai 1971, Kondo and Ueta 1972, Karasawa and Hirai 1972, Bradford *et al* 1975) indicate clearly that the main portion of the F, H centres are closely paired and disappear at around LHT over a period of μs through tunnelling recombination. Another series of experiments (Känzig and Woodruff 1958 a, b, Itoh and Royce *et al* 1966, Itoh and Saidoh 1970, Srivasan and Compton 1965) indicates a prolonged existence of well-separated pairs; e.g. Saidoh and Itoh (1973 a, b) reported lifetimes of 10^4 s for H centres just after their delocalization. Following an estimate for the effective radius of tunnelling recombination of localized defects (Bogan *et al* 1973) $\hat{r}(t) = r_B \ln w_0 t$, this time one obtains $\hat{r} \simeq 8$ lattice constants, which agrees well with the other estimates.

It seems quite possible that close pairs may be due to the fact that either the main portion of hot halogen atoms do not have an energy falling within the rather narrow interval necessary for a successful collision sequence, or, get momentum in the wrong direction (cf Smoluchowski *et al* 1971, Smoluchowski 1975, Dienes and Smoluchowski 1976). The other ejected atoms cover, however, large distances by means of a collision sequence. Inertial annealing experiments observe only a diffusion-controlled disappearance of the latter; otherwise distinct H-centre lifetimes could not be obtained (cf Ueta 1967, Saidoh and Itoh 1973a, figure 2). On the other hand, close pairs can play an important role in the *accumulation* of F centres. Conditions for one-dimensional diffusion of H centres is not clear at present†.

3.6.2. Destruction of pre-existing F_2 centres. Bearing in mind the results obtained at the end of § 3.3 (equation (4a)), one can deduce that the present model may be applied to those steady-state experiments concerning the destruction of pre-existing F_2 centres (Sonder 1973, 1975, Guillot *et al* 1975). The model yields *the same* effective energy as occurs in F-centre accumulation, which has already been observed in KCl and KBr by the above-mentioned authors.

It should be added in conclusion that our model assumes that all the walking H centres disappear during a steady-state experiment. This is not so at rather low temperatures *T* such that $4[D(T)\tau/\pi]^{1/2} < R$ (where τ is the duration of the experiment), due to which a portion of slowly diffusing H centres do not have enough time to approach the F centres and thus disappear, leading to the observation of a certain concentration of F centres (which decreases with temperature).

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† Dienes and Smoluchowski (1976) suppose that this arises at high temperatures ($\gtrsim 180$ K in KBr) because $v_{0L} \gg v_{0r}$. However, our estimate yields $v_{0L} \approx v_{0r}$. Perhaps an H centre undergoes such motion near an F centre due to the distorted potential, which becomes three-dimensional motion at large distances. A careful analysis of such motion is rather complicated.

4. Discussion and conclusion

The present paper demonstrates that the temperature dependence of a steady-state accumulation of radiation-induced F centres in doped alkali halides as well as a destruction of pre-irradiating F_2 centres can be understood by taking into account the *decrease* of the efficiency of the tunnelling recombination with increasing temperature. The probability of an F centre surviving depends on the temperature as well as on the initial distribution function within the genetic F–H pair resulting from the primary process. Annihilation alone *cannot* provide any temperature dependence.

A choice between our model and that of Sonder is rather complicated. However, other more important problems exist. Firstly, steady-state experiments for *pure* crystals exhibit a temperature growth of accumulation with the *same* effective energy, as in doped crystals (Vitol *et al* 1967). This means that the role of impurities in this process seems to be non-decisive; perhaps the aggregation of H centres is the main trapping factor (e.g. in Saidoh and Itoh's (1973a, b, 1975) experiments, the interaction volume of a replacement sequence with an H centre is ten times greater than that for Na^+—see, however, Townsend (1976a, b)). Secondly, a radiolysis experiment with pulses shorter than the time $w_0^{-1} \sim \mu$ s of tunnelling recombination of the nearest F–H pairs indicate the *same* effective energy irrespective of whether we have pure or doped crystals (Saidoh *et al* 1975, Aluker *et al* 1976).

Nevertheless, a possible conclusion can be drawn that some common *primary* process is involved in all the types of experiments, e.g. the temperature dependence of the probability that an unrelaxed exciton will decay through a channel, leading to F-centre formation (cf also Elango (1975), Karasawa and Hirai 1976, Townsend 1976, Nouailhat *et al* 1976).

It should also be noted in conclusion that the explanation of the temperature growth in question being due to an increase in the average range of the replacement sequence with temperature (Saidoh *et al* (1975) and references therein) *is not self-consistent*, because:

(*i*) A great proportion of the dynamic crowdions disappear even during as short a period as 200 ns through aggregation trapping or recombination, and consequently a model taking into account *secondary* reactions (e.g. Sonder's one) should be employed, where the effective energy *is not* equal to that of diffusion, as Saidoh *et al* (1975) suppose. On the other hand, this supposition led to the concept of an excited H centre.

(*ii*) Saidoh *et al* present an expression for the escape probability for an H centre from its own ('genetic' in our terms) F centre and declare that this increases if the replacement sequence increases, neglecting *for no reason* the probability of further H-centre trapping or recombination with other F centres, as a result of which they get an *unreal* recombination radius of about 17 lattice constants and a length of the replacement sequence of the order of 500 (!) lattice constants (at 200 K), which must *necessarily* lead to neglected secondary reactions.

(*iii*) Saidoh and Itoh (1975) themselves note that F-centre production yield is higher in crystals with lower replacement sequences.

The interaction volume begins to increase with temperature at about 50 K (in KBr), which argues for an H-centre controlled process. However, the displacement of an H centre in the ground state (with our estimate of v_{0L}) during 200 ns is very small ($\simeq 10$ Å) and so the question remains open.

Acknowledgments

Appendix

To obtain the probability that an H centre be trapped during infinite time

$$P = -D \int_0^\infty dt \int \nabla u \, ds = -4\pi R^2 D \int_0^\infty \left(\frac{\partial u(r, t)}{\partial r}\right)_R dt, \tag{A1}$$

it is necessary to consider the equation for $u(r, t)$

$$\frac{\partial u(r, t)}{\partial t} = D\nabla^2 u(r, t) - w_0 \exp(-r/r_B)u(r, t).$$

Integrating both sides of the latter over t and assuming the solution to be spherically symmetric, one obtains

$$D\frac{d^2 V}{dr^2} - w_0 \exp(-r/r_B)V = -ru_0(r), \tag{A2}$$

where

$$V(r) = r\int_0^\infty u(r, t)\, dt.$$

A general solution of equation (A2) satisfying the annihilation condition $V(\rho) = 0$ *is*

$$V(r) = \frac{b}{D}v_{qs}(r) + \frac{2r_B}{D}\{G_2(r)I_0[z(r)] - G_1(r)K_0[z(r)]\} \tag{A3}$$

where $z(r) = \alpha \exp(-r/2r_B)$, b = constant, $\alpha = 2r_B(w_0/D)$, $v_{qs} = u_{qs}r$ (see equation (5)),

$$G_1 = \int_\rho^r r'u_0(r')I_0[z(r')]\, dr',$$

$$G_2 = \int_\rho^r r'u_0(r')K_0[z(r')]\, dr'.$$

For $r \gg R_{qs}$ (see equation (6)) neglecting terms of the order $z(r)$ one obtains from (A3)

$$\frac{V(r)}{r} \simeq \frac{b}{D}\left(1 - \frac{R_{qs}}{r}\right) + \frac{2r_B}{Dr}\left\{G_2(r) - \left[\frac{r}{2r_B} - \ln\frac{\alpha}{2} - c\right]G_1(r)\right\}. \tag{A4}$$

The constant b can be obtained, employing the radiation boundary condition at $r = R$

$$u(R, t) + \beta(\partial_r u(r, t))_R = 0.$$

which after integration over t has the form

$$V(r) + R\beta\left(\partial_r \frac{V}{r}\right)_R = 0.$$

Substituting (A4) into (A1) one gets

$$P = -4\pi R^2 D \int_0^\infty dt \left(\partial_r \frac{V}{r} \right)_R = \frac{4\pi \int_\rho^R r^2 u_0(r) u_{qs}(r)\,dr}{[1 - (R_{qs}/R)][1 - (\beta/R)]}. \tag{A5}$$

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