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Role of tunneling recombination in radiation-induced F-centre creation in alkali halide crystals at liquid helium temperatures

I Tāle, D Millers and E Kotomin
Semiconductors Physics Research Laboratory, Latvian State University, 19 Rainis Boulevard, Riga 226050, USSR

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Abstract. Computer simulations of the F-centre accumulation at liquid helium temperatures (LHT) in alkali halides, taking into account the spatial distribution and the tunneling recombination of the localized F- and H-centres, have been undertaken. The presented model easily explains known experimental data at these temperatures, that is: (i) the saturation and possible subsequent decay of the F-centre production rate, (ii) the existence of an abnormally high fraction of the aggregate (F_2, H_2, ...) centres (in contrast to random distribution), (iii) the formation of large loose aggregates, (iv) the existence of F-centre concentrations exceeding 10^{19} cm^{-3} and (v) the dependence of the production curve on the excitation intensity. A mechanism for loose-aggregates formation is proposed. The applicability of the present model at room temperature is discussed.

1. Introduction

It is well established that ionizing radiation produces halogen Frenkel pairs of centres in alkali halides, the primary products being F and H centres (Ueta *et al* 1969, Hirai *et al* 1971, Kondo *et al* 1972). A radiationless decay of excitons leading to the production of such Frenkel pairs involves motion of 'hot' interstitial atoms from the production site. During this motion, the interstitial loses excess energy and transforms into an H centre (X_4^{3-} molecule ion). A complementary F centre is localized below room temperature. At sufficiently low temperatures, an H centre is also localized. However, at higher temperatures (40 K in KCl), this latter becomes mobile and is free to make diffusion walks and possibly (i) to annihilate an F centre, (ii) to be trapped by an impurity cation or (iii) to form an immobile aggregate interstitial H_2 centre (Itoh *et al* 1967, Itoh and Saidoh 1969, Saidoh and Itoh 1973). At higher temperatures, H centres, probably due to diffusion, aggregate into large loose aggregates. (Direct evidence for this has been presented by Hobbs *et al* 1971.) The fate of the hot interstitial as well as the mobile H centre directly affects the F-centre production curve.

At temperatures which allow H-centre mobility (hereafter referred to as RT), Farge (1969) and Agullo-Lopez and Jaque (1973) presented a *phenomenological* model. This model describes the kinetics of F-centre accumulation, taking into account the three above-mentioned channels of the disappearance of the diffusing H centre.

Three stages of the F-centre production curve are associated with three appreciably different mechanisms. The initial state (I) is associated with a trapping of H centres by

saturable traps. The saturation of this process leads to the flat stage (II). At higher doses, interstitial clusters appear at this stage and become unsaturable traps for single H centres. This unsaturable sink induces a new growth of F-centre concentration (stage III). This phenomenological approach is based on traditional set differential equations (rate equations) and does not constitute a concrete physical mechanism of the F, H annihilation (cf § 4.4).

At temperatures where the H centres are localized (liquid helium temperatures, hereafter referred to as LHT), the situation is much more simple than at RT. Now each *regular* lattice site becomes capable of trapping an H centre at the moment of its formation. The presented phenomenological model (Hughes and Pooley 1971) of the F-centre accumulation at LHT is based on the idea of a clear-cut annihilation radius r_0. The pair of F, H centres, with separation $r > r_0$, does not interact but immediately annihilates if $r \leqslant r_0$. Just as at RT†, a concrete mechanism of the annihilation is not discussed. The distinctive feature of this model is e-fold decrease of the growth rate at large doses, but never real saturation. To explain the experimentally observed saturation (Hughes and Pooley 1971, Rabin and Klick 1960) and even the subsequent *decay* of the production curve, Hughes and Pooley (1971) supposed a speculative back-reaction. If protonic irradiation is the case, this back-reaction is the conversion: F-centre → U-centre. However, this particular mechanism does not seem to be the dominant cause of the mentioned decay.

Along with this decay complication, the clear-cut radius phenomenological model also cannot explain other experimental facts at LHT such as (i) the appearance of aggregate H_2 centres (Itoh *et al* 1967, Itoh and Saidoh 1969, Balzer *et al* 1969) and F_2 centres (Faraday *et al* 1961), (ii) the appearance of large aggretates of interstitials (Hobbs *et al* 1973) and (iii) the dependence of the F-centre production curve on irradiation intensity (Ritz 1964, Hughes and Pooley 1971).

The purpose of the present paper is to discuss a rather simple model easily accounting for the mentioned experimental data and based on the *tunneling* mechanism of annihilation. This universal mechanism occurs at all doses, temperatures and irradiation sources. It does not mean that this mechanism is predominant in all cases but we hope to demonstrate its importance for the annihilation of localized electron–hole centres at LHT and, taking additional suppositions, even at RT (§ 4.4).

2. Tunneling recombination

There exists a well established mechanism of tunneling recombination of spatially separated electron and hole centres in alkali halides *and*, in particular, F, H centres (Dexter 1954, Delbecq *et al* 1966, 1974, Ueta 1967, Ueta *et al* 1969, Hirai *et al* 1971). A tunneling recombination of F, H centres leads to their conversion into F^+, I centres (Vitol 1969, Smoluchowski *et al* 1971). This mechanism occurs for both mobile and immobile hole centres (Dexter 1954, Bogan 1969) and therefore *both* phenomenological theories (ie at LHT and at RT) may be based on it. We believe that only this mechanism for annihilating spatially separated and *localized* centres can explain the decay of F centres after removing the irradiation (Bogan *et al* 1973, Delbecq *et al* 1974).

† Herrmann and Pinard (1971) carried out the computer simulations of the F-centre production curve based on a prohibited-volume approximation. They related this prohibited volume to the RT case. However, their results can be applied directly to LHT if we take prohibited volume in the sense of Hughes and Pooley (1971, § 4.3).

In the case of semiconductors, it has been shown (eg Curie 1967, Williams 1968) that the recombination probability $W(r)$ (ie spontaneous temperature-independent electron transfer) of the donor–acceptor pair depends on the separation, r, between defects in the following form:

$$W(r) = W_0 \exp(-r/r_B), \tag{1}$$

where W_0 is constant and r_B is half the Bohr radius of the more diffuse wavefunction of the donor or acceptor. This relation appears due to the calculation of the squared matrix element $\langle n | \boldsymbol{p} | m \rangle$ of the spontaneous transfer. Such a calculation is based on three suppositions: (i) The wavefunction of one (or both $\langle n |, | m \rangle$) states is hydrogen-like ($\Psi \propto \exp(-r/2r_B)$). (ii) The defects do not perturb each other (the isolated-defects approximation being valid if r exceeds a few lattice spacings). (iii) The wavefunctions have a spherical symmetry and hence $W(r)$ is independent of the angles.

Electron and hole centres in alkali halides exhibit tunneling recombination, analogous to donor–acceptor pairs in semiconductors. However, the use of relation (1) in this case needs further justification. A strict justification is obviously the quantum mechanical calculation of the mentioned matrix element, $\langle n | \boldsymbol{p} | m \rangle$, based on the actual wavefunctions of defects; for example, an F centre ($| m \rangle$) and the centre produced due to tunneling (H + electron).

Such a rather complex calculation has not been carried out as yet. However, in the case of alkali halides, one can *qualitatively* justify relation (1) in the following way.

It is known that when the separation r between the electron and its defect exceeds a few lattice spacings, a continual approximation in the Hamiltonian is valid and leads to an effective-mass approximation and a hydrogen-like behaviour of the wavefunction. (Such an asymptotic hydrogen-like behaviour of the wavefunction of a colour centre is rather common and holds in both semiconductors and alkali halides.) For example, there is a large body of theoretical calculations of F centres in alkali halides where its ground wavefunction has been described as hydrogen-like at all r (see the review by Fowler 1968). This is in agreement with ESR and ENDOR measurements. The phenomenological relation (1) is widely used for describing electron–hole recombination at low temperatures in alkali halides and is in good agreement with experimental data (Bogan *et al* 1973, Gailitis 1972, Tale and Gailitis 1971, Delbecq *et al* 1974). The relation (1), justified above, will be also used in the present paper.

On the basis of (1), the mean value of the tunneling radius $\hat{r}(t) = r_B \ln(W_0 t)$, $(t \gg W_0^{-1})$ has been estimated (Gailitis 1972, Bogan *et al* 1973). Pairs of defects with separation $\hat{r}(t)$ give the predominant contribution to the recombination intensity at decay moment t. The magnitude of r_B for F centre may be derived from the kinetics of tunneling decay and is of the order of 0·8 lattice spacings in KCl (Bogan *et al* 1973). W_0 is of the order of $10^6\ s^{-1}$ (Ueta *et al* 1969). One can easily estimate that the mean radius $\hat{r}(t)$ at usual experimental times ($\gtrsim 10^3$ s) exceeds 10 lattice spacings and, consequently, *tunneling may be the important back-reaction* during the accumulation of electron and hole centres (Bogan *et al* 1973).

3. The model and computer simulations

3.1. The chosen model

We consider the model as follows:

(i) Well separated localized genetic pairs of F, H centres appear simultaneously in

the anionic sublattice at the production rate of α pairs $s^{-1}cm^{-3}$. This kind of formation is supported by the data of Smoluchowski *et al* (1971). The motion of hot interstitials during the primary act of defect production is not taken into account; we are only interested in the final result—the localized H centre. Each centre occupies one lattice site.

(ii) Both F and H centres are distributed randomly over the volume as well as inside the genetic pair. There is a correlation between the components (F, H) of genetic pairs in real experiments (eg Ueta *et al* 1969, Hirai *et al* 1971). However, such a correlation cannot yield qualitatively new effects in our model. Our model especially does not contain any spatial correlations of centres in the *primary* process of defect formation. Speaking of the above-mentioned LHT model, one can foresee that in such a case, centre distribution will always remain random due to neglect of the overlap of the prohibited volumes of the equivalent centres. However, correlations appear in the framework of the present tunneling model (§4.2), due to the strong dependence of the recombination probability on the separation between defects†.

(iii) The only back-reaction taken into account is the above-mentioned tunneling recombination $F + H \rightarrow F^+ + I$. At LHT, the primary pair of defects (F, H centres) as well as the products of their tunneling (F^+, I centres) are immobile and these defects may annihilate and restore a perfect lattice only if the mutual separation in F, H (or F^+, I) pairs is not greater than 1–2 lattice spacings. The fraction of such pairs at low and intermediate doses (considered in the present paper) is rather small and we neglect their contribution to the accumulation process. However, one *must* take into account the annihilation process at temperatures where H, I centres are mobile as well as with great doses (saturation region). The probability for every given F_i–H_j ($i, j = 1, \ldots, N$ where N is the number of defect pairs in the volume) pair (not a genetic pair unless $i = j$) to live τ seconds before tunneling is

$$P_{ij}(\tau) = \exp[+W_{ij}(r)\tau] = \exp[+W_0\tau \exp(-r_{ij}/r_B)].$$

The total probability, P_l, for any given centre (say, F_l, where $l \in [1, N]$) to live τ seconds means the probability of finding N pairs F_l–H_j ($j = 1, \ldots N$) containing this centre. It is easy to obtain that

$$P_l(\tau) = \prod_{j=1}^{N} P_{lj}(\tau) = \prod_{j=1}^{N} \exp[-W_0\tau \exp(-r_{lj}/r_B)]. \tag{3}$$

(iv) The process is treated as a Markov one, that is, the value $P_l(\tau)$ for any defect at a given moment t does not depend on its creation moment.

3.2. Computer simulations

The analytical calculations of the presented model involving spatial effects are complicated, and computer simulations are undertaken. The reaction volume V has been chosen as $92a \times 92a \times 92a$ cubic array ($a = 5$ Å). The accumulation process has been treated as production of genetic pairs separated by decay periods $\tau = 1/(\alpha V)$. The Cartesian coordinates of each centre have been chosen at random in the interval 0–$92a$. A fraction of the pairs disappears during each decay period τ. An F_l centre ($l = 1, 2, \ldots, N$) is supposed to survive only if $P_l \geqslant \xi_l$, ξ_l being a random number $\in [0,1]$ and P_l is calcu-

† Such correlations must appear also in prohibited-volume approximation accounting for the mentioned overlap of the prohibited volume.

lated by equation (3). This procedure, being performed for all F centres, leads to the disappearance of, say, k F centres during a given decay period. After F centres, the same procedure is employed for H centres. Corresponding probabilities (see equation 3) take, of course, into account *all* F centres existing during a given decay period, including F centres which have just disappeared. The only restriction is that the number of disappearing H centres must be equal to k because centres recombine in pairs. The procedure chosen does not associate any disappearing H centre with any *concrete* (eg nearest) F centre. If there exists a pair of close F, H centres, their decay probabilities are rather large and they are very likely to disappear as a pair, but there *is* also the chance that one (or both) defects will recombine with another more distant centre†. The recombination parameters have been taken as $r_B = 0{\cdot}8a$ and $W_0 = 10^6\ s^{-1}$ (see § 2).

4. Results and discussion

In this section, the obtained results are presented and compared with those for the LHT model and known experimental data.

4.1. Accumulation curves

Figure 1 shows the F-, H-centres accumulation curve, $dF/d(\alpha/t)$, at two different primary production rates α. As one can see, up to $10^{17}\ cm^{-3}$, the concentration of accumulated centres increases proportionally to the dose ($\alpha \times$ time). Above this point, the accumulation rate decreases due to an appreciable tunneling process. For lower α, deviation begins at lower concentration because the increase of the period $\tau \propto \alpha^{-1}$ between the production of two successive F–H pairs leads to a greater annihilation probability (cf equation 2). This dependence of the accumulation curve on the irradiation intensity is in good agreement with the experimental data of Hughes and Pooley (1971) and cannot

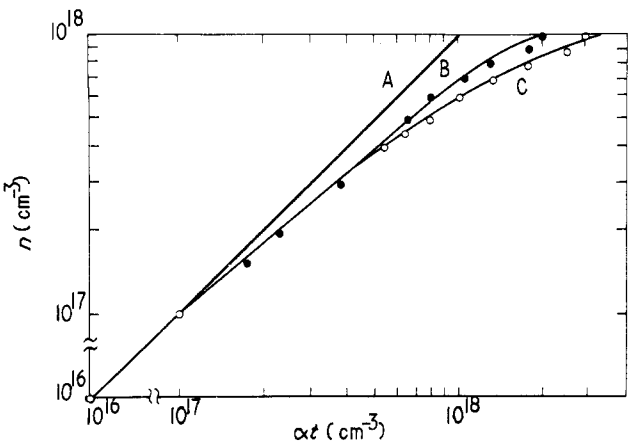

Figure 1. The simulated production curves: A, absence of recombination; B, $\alpha = 10^{19}\ s^{-1}cm^{-3}$; C, $\alpha = 10^{16}\ s^{-1}cm^{-3}$. The divergence between the straight line A and the F, H centre accumulation curve yields the concentration of both tunneling products (F^+, I centres) and aggregate (F_2, H_2, ...) centres.

† There is another possible procedure of disappearance: to apply the random-number method to every one of the N^2 pairs (F_i–H_j where $i, j = 1, 2, \ldots, N$) instead of our $2N$ centres. Our simulations show that this yields the same results as described above.

be explained by their model. It seems to be quite reasonable that our model will yield saturation for greater doses, and an earlier deviation leads to a lower saturation level which is also in agreement with the experimental data. However, at present, our computer simulations have not been carried out up to saturation level due to the appreciable calculating time. The physical meaning of predicted saturation and subsequent decay is discussed in § 4.3.

Half the produced centres accumulate at $10^{18}\,cm^{-3}$ if $\alpha = 10^{19}\,cm^{-3}s^{-1}$, whereas if $\alpha = 10^{16}\,cm^{-3}s^{-1}$ only one third do so. The first number ($\frac{1}{2}$) is formally in excellent agreement with the experimental results of Hirai *et al* (1971). However, Hirai *et al* observed an appreciable pairing of F, H centres which is not taken into account in our model and obviously would increase our estimate. On the other hand, we used $r_B = 0{\cdot}8$ a (Bogan *et al* 1973) which is, perhaps, an overestimate and compensates for the absence of correlations.

Our model shows that, as a rule, newly-produced centres annihilate with already existing ones, but not with genetic partners. The fraction of genetic pairs in recombination does not exceed a few per cent, but would be greater if one took into account non-random distribution between the components of genetic pairs.

Since each *annihilated* pair transfers into an F^+, I pair, it is clear from figure 1 that the ratio F^+/F greatly increases with dose and decreases with α growth at the same dose. A number of investigators have reported a large ratio F^+/F at LHT (eg Ritz 1966, Behr *et al* 1967) and the growth of the number of F^+ centres with dose (Behr *et al* 1967).

4.2. Spatial correlations of centres

As has been mentioned (§3.1), any spatial correlation of centres may arise only due to secondary (tunneling) processes.

Figure 2 shows the probability densities of finding the nearest centre at a distance r from the given one placed at the origin. There are four such distribution functions,

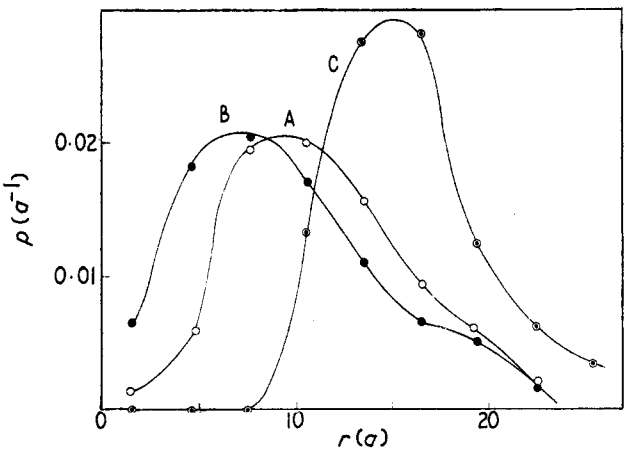

Figure 2. Probability densities of finding the nearest centre at a distance r from the given centre. $\alpha = 10^{16}\,s^{-1}cm^{-3}$, concentration $10^{18}\,cm^{-3}$. A, absence of recombination—random (Poisson) distribution; B, the distribution functions of equivalent centres (F–F = H–H); C, the distribution functions of different centres (F–H = H–F). The tunneling recombination induces a fraction of paired centres exceeding the random (Poisson) distribution (cf A and B at first abscissa points corresponding to nearest neighbours).

that is: F–F, F–H, H–F and H–H, because a given centre and its nearest neighbour may be either of two (F or H) types. In the framework of the present model, one can interchange the assignation of F, H centres and thus there exist only *two* different distribution functions, that is, for the equivalent (F–F = H–H) and unequivalent (F–H = H–F) centres.

Curve A corresponds to the absence of tunneling annihilation, that is, a random (Poisson) distribution of F, H centres over the volume. The two distribution functions, F–F and F–H, are now also equivalent and the mean value of separation $\bar{r}$ between centres corresponds to the well known nearest-neighbour result: $\bar{r} = 0{\cdot}5542(N)^{-1/3}$ where N is the concentration of F centres. Curves B and C correspond to the distribution functions of equivalent (B) and unequivalent (C) centres at the same total concentration and exhibit changes due to tunneling recombination. Curve B has a shift to the region of lower separations, that is, more close pairs F–F, H–H of the same type of centres

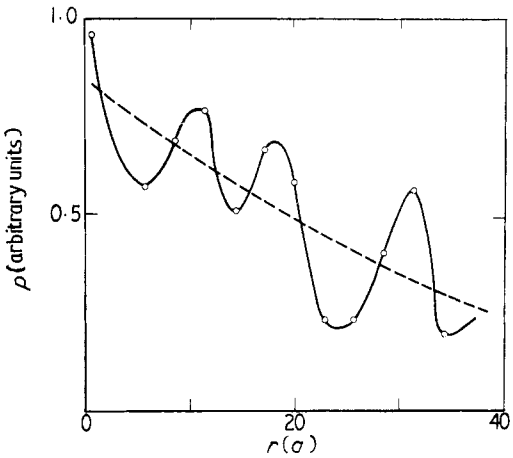

Figure 3. Probability density of finding centres of the same type at a distance r in unit volume (full curve). The broken curve is for the case of a random distribution of centres, decay being due to the finite dimension of a cube (see text).

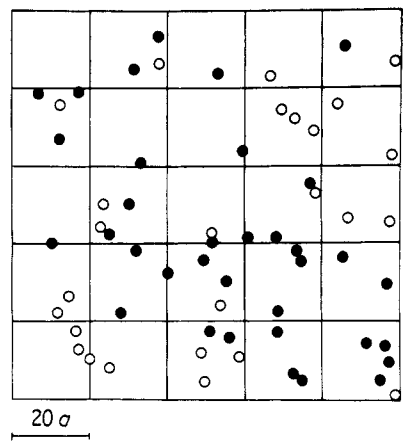

Figure 4. Projection of the coordinates of centres onto the xy plane from layer $z = 30$–$60\,a$. The points ● are H centres and ○ are F centres. One can see two H_2 centres.

appear than in case A. The fraction of aggregate (F_2, H_2) centres exceeds appreciably that in the Poisson distribution (cf curves A, B at minimal separation r). Faraday *et al* (1961), Itoh *et al* (1967) and Itoh and Saidoh (1969) reported the same result. Curve C exhibits an *absence* of F, H centres at mutual distances less than 8 lattice spacings (40 Å). These results may be reasonably interpreted in terms of the formation of *loose aggregates* consisting of centres of the same type.

Figure 3 shows the probability density of finding centres of the same type at a distance r from a given one at the origin in unit volume; that is, the number of F (or H) centres in the shell layer $(r, r + \Delta r)$ divided by its volume $4\pi r^2 \Delta r$. The results obtained have been averaged over all centres in the origin. In the case of a random distribution and infinite volume, it should obviously be constant, independent of r. The *finiteness* of volume leads to a slow decay with r (see figure 3) because of the absence of a fraction of the centres at a distance r from the given one placed at a distance less than r from the cube

face. The periodical structure observed (figure 3) can be reasonably associated with the previously mentioned loose aggregates and allows us to estimate roughly the size of the aggregate, as well as inter-aggregate separation, to be about 10 lattice constants (50 Å). Large interstitial aggregates have been directly observed at LHT by Hobbs *et al* (1973) and their size is in accord with our estimate.

The non-uniform distribution of centres over the volume can be observed by a direct projection of the centre coordinates into the xy plane (figure 4).

The large observed macroscopic concentration of F centres (Faraday *et al* 1961, Ritz 1966) can be attributed to the existence of the mentioned aggregates, because a *random* distribution of centres cannot exceed $10^{18}\,\mathrm{cm}^{-3}$ due to the large tunneling probability of close electron–hole centres (cf § 2 and Bogan *et al* 1973).

4.3. Cluster formation

Let us briefly and schematically discuss the process of cluster formation (figure 5). Consider a newly produced H centre (B). If the latter is produced near an F centre, tunneling is very likely to occur (C), but if it appears near another H centre without any F centre in the neighbourhood, such a pair of single H centres has a large chance of surviving (D). The stability of such an H-centre formation against the appearance of a nearby F centre increases with the number of H centres inside it.

Two processes occur due to increase of the dose and decrease of the fraction of the centres surviving during their natural choice, $F/\alpha t$, namely: (i) the formation of loose aggregates containing centres of the same type in the form of isolated and aggregated

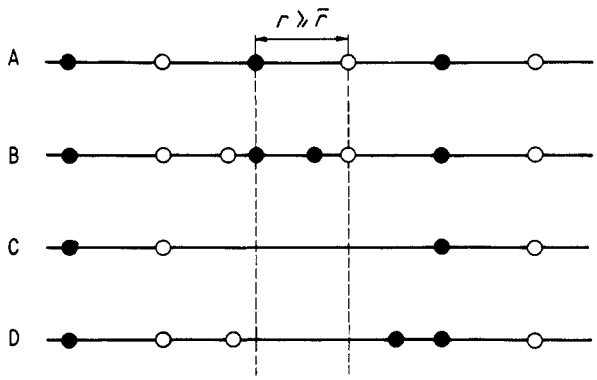

Figure 5. Proposed process of cluster formation. A, random distribution of centres ($\bar{r}$—average distance of tunneling); B, appearance of newly created defects pair; C, after recombining nearest defects via tunneling; D, nucleation of cluster.

centres and (ii) the growth of the number of aggregate centres (F_2, H_2, F_3, H_3 etc) in such a loose aggregate. It is believed that at high macroscopic concentrations ($\sim 10^{19}\,\mathrm{cm}^{-3}$), such a loose aggregate will transform into a compact cluster and then into a colloid.

The accumulation rate, $\mathrm{d}F/\mathrm{d}(\alpha t)$, greatly decreases in the course of loose-aggregate formation because a newly produced centre has a chance to survive only if it appears inside a loose aggregate of the same type, the probability of such a process obviously decreasing with a decrease in the size of the loose aggregate.

The experimentally observed decay of single centre concentration at LHT (Hughes and Pooley 1971) can be associated with the transfer of the loose aggregates into clusters when the aggregate is so dense that each newly produced centre (F, say) either *annihilates* or becomes a *nearest* neighbour of an already existing F centre (which yields F_2 and corresponds to the disappearance of two single F centres). At higher doses, this must be the case for further conversion $F_2 + F \rightarrow F_3$ etc. Unfortunately, these details remain a matter of speculation until computer simulations are carried out up to this region. Hughes and Pooley (1971) observed a surprisingly low number of F_2 centres (however, see §4.4).

At present, there is no certain information at LHT about the loose aggregates consisting of the F centres. However, the F, H centres are equivalent within the framework of our model and consequently form similar aggregates. A more realistic model must take into account the motion of hot interstitial atoms during which the latter can: (i) form H centres, (ii) annihilate an F centre, (iii) form a di-H centre or (iv) be trapped in a cation impurity. The present model is restricted by the first process; the three other processes violate the F, H equivalence and cause the predominant formation of *interstitial* aggregates.

The appearance of loose aggregates and clusters violates the primary uniform distribution of centres throughout the volume. This is caused both by fluctuations in the primary distribution of centres and the dependence of tunneling recombination on the respective spatial distribution of centres due to which viable fluctuations favouring clustering have a larger chance of survival.

Finally, one can predict the aggregates to be much more stable (viable) systems and their decay after switching off the excitation should proceed much more slowly as compared with the decay law for a random distribution of F and H centres.

4.4 Room temperature

The model presented above involved the tunneling *annihilation* of *localized* F, H centres. However, both the model and the obtained results are likely to be valid at RT in the case where the contribution of the diffusing H centres in the total recombination intensity is negligible. This is the case if (i) the temperature is sufficiently high that an H centre is rapidly trapped (eg by a cation impurity, forming an H_A centre) and (ii) the impurity (and other traps) concentration is sufficiently high for such a rapid trapping†. In such a situation, the diffusion induces a rapid localization of the H centres, formally similar to the localization at LHT.

The applicability of the model is argued by numerous experiments at RT; for example: eg: (i) the saturation of the accumulation curve at electron irradiation and its subsequent decay associated with the *appreciable growth* of the number of F_2 centres (Vaisburd *et al* 1965), (ii) the dependence of the accumulation curve on the irradiation intensity (Hughes and Pooley 1971) and (iii) the accumulation of a high F-centre concentration exceeding 10^{19} cm^{-3} (Soul 1970).

However, the study of processes at intermediate temperatures and low impurity concentration as well as the kinetics of loose-aggregates formation (whose growth is greatly stimulated by temperature (Hobbs *et al* 1973)) need further careful computer simulations.

† A similar situation has been discussed by Sonder (1969).

5. Conclusion

Following the idea of tunneling recombination of F, H and H_A centres, the model of radiation-induced centres accumulation is presented. The model is valid at LHT and partly at RT. The latter explains a large body of experimental results including: (i) the saturation and subsequent decay of the accumulation curve at LHT as well as at RT, (ii) the formation of loose interstitial aggregates at LHT and (iii) the appearance of F_2, H_2 centres at LHT in numbers greatly exceeding the Poisson (random) distribution.

The paired aggregate centres at LHT appear due to *two* processes, namely: (i) the trapping of a hot interstitial by an H centre during the *primary* process of defects formation (Itoh and Saidoh 1969) and (ii) the probability of two H (or F) centres, *by chance* appearing as nearest neighbours, to survive is greater than that of two isolated centres (present model). No doubt the first process will stimulate the second one.

To extend this model, one has to take into account the diffusion walks of H centres at RT. Such a computer simulation, being rather complex, will allow us to understand the temperature dependence of the accumulation process as well as to study the kinetics of aggregate formation at RT.

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