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Kinetics of Defect Accumulation and Recombination

I. General Formalism

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A general theory of the kinetics of radiation-induced defect accumulation and recombination in solids and liquids limited by spatial correlations of Frenkel defects is presented and developed. Kinetic equations are solved making use of the superposition approximation. For the first time a correlation of the *similar* defects is taken into account, which arises indirectly due to *dissimilar* defect recombination. A radiation-induced accumulation of immobile defects proves clearly a formation of loose aggregates of the similar defects. It is shown that a defect concentration grows with time t proportionally to $1 - \exp(-2\mu_0 v_a t)$, μ_0 is the rate of defect production per unit volume and time, v_a being an annihilation volume. The less the initial defect correlation is in genetic (Frenkel) pairs, the greater is the defect concentration under saturation at high doses.

Es wird eine allgemeine Theorie der Erzeugungs- und Rekombinationskinetik von Frenkeldefekten vorgeschlagen und entwickelt, die die Abstandskorrelation von unbeweglichen sowie beweglichen Defekten berücksichtigt. Die kinetischen Gleichungen werden in der Superpositionsnäherung gelöst, in der zum ersten Mal die Korrelation zwischen *gleichartigen* Defekten, die mittelbar durch Rekombination zum Vorschein kommt, nicht vernachlässigt wird. Es wird die Entstehung von porösen Clustern von gleichartigen Defekten bei Bestrahlung bewiesen. Es wird gezeigt, daß die Defektdichte mit der Zeit t proportional $1 - \exp(-2\mu_0 v_a t)$ wächst, wo μ_0 die Produktionsrate der Erzeugung der Defekte und v_a das Annihilationsvolumen sind. Die Sättigungsdichte ist um so kleiner, je stärker die Abstandskorrelation des Frenkelpaares bei Erzeugung ist.

1. Introduction

As well understood now, a correct theory describing the kinetics of radiation-induced defect accumulation and recombination in solids and liquids has to be based on a hierarchy of equations for the many-particle distribution functions (DF) [1 to 6].

These DF's yield a probability description of a spatial defect distribution (hereafter referred to as "defect structure"). Serious mathematical difficulties restrict the set of equations to those for the one-particle DF (defect concentration) and pair (joint) DF's describing the spatial correlation of the similar (A-A, B-B) and dissimilar (A-B, B-A) defects.²⁾

There exist two kinds of spatial defect correlations: (i) a correlation of different-kind defects arising due to a primary process of radiation-induced creation of "genetic" pairs of close defects (e.g. Frenkel pairs consisting of vacancies and interstitials in crystals); (ii) a correlation of both the similar and dissimilar defects arising in the course of numerous secondary processes (production of new defects, defect recombina-

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²⁾ Recombination can be usually described by a reaction between two kinds of defects, $A + B \rightarrow C$. $C = 0$ for an annihilation mechanism when a perfect crystal lattice is restored whereas $C \neq 0$ means the formation of another defect pairs, $A' + B'$, e.g. due to tunneling recombination [7].

tion and motion) which change the defect structure. Namely the second-kind correlations determine the behaviour of the steady-state defect concentration under saturation.

Despite a number of papers dealing with the defect accumulation kinetics (e.g. [4a, 8 to 10]), the spatial defect correlation was not correctly considered as yet, due to which the defect concentration growth with time was not analytically correctly described. Still unsolved remain some problems of the kinetics of the diffusion-controlled defect recombination incorporating defect correlations of both mentioned kinds. The purpose of this paper is to present and develop a unified phenomenological theory covering both above-mentioned problems.

The generally accepted way of describing a defect structure [1 to 4] being quite correct formally, remains rather complicated and unsuitable for problems in question. Since the kinetics of defect accumulation and recombination deals with a system (crystal) with variable number of particles (defects), a special description method is needed. The DF's $W = W(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{r}'_1, \dots, \mathbf{r}'_{N'})$ introduced in [1 to 4] determine the many-particle probability $W d\mathbf{r}_1 \dots d\mathbf{r}_{N'}$ to find at a moment t an interstitial No. 1 in a unit volume $d\mathbf{r}_1$ at \mathbf{r}_1, \dots , a vacancy N' in a unit volume $d\mathbf{r}_{N'}$ at $\mathbf{r}_{N'}$. Since all interstitials (vacancies) are identical, their enumeration in W is not necessary and leads in particular to complicated combinations (cf. [2 to 4]).

Qualitatively speaking, the way developed below of describing possible defect system states can be compared with the generally accepted approach [1 to 4] as a secondary quantization formalism in a quantum field theory with the formalism of wave functions for equivalent particles in "standard" quantum mechanics. (As well known, a variable number of particles necessitates the former.)

2. Model Considered

2.1 Model of defect structure

In the generally accepted approach [1 to 10] a crystal is considered as a continuum due to which a number of important features of a discrete crystal are lost, e.g. (i) the number of defects has always an upper limit given by a value of the order of the number of elementary cells in a crystal; (ii) the volume per defect is always finite. Therefore a finite crystalline volume can contain only a finite number of defects (cf. [10]). Under certain conditions the discreteness of the crystalline lattice might be unimportant (e.g. for large recombination radii), but it still yields a physical justification for the mathematical model of a defect structure given below.

Let us put into accordance with a crystal a lattice whose sites are defined by a set of vectors, $\{\mathbf{r}\}$. (Keeping in mind a further transition to a continuous model (Section 3.2), it should be stressed that the actual choice of the lattice is unimportant due to which the theory could be also applied to disordered crystals and liquids.) Such a lattice as a mathematical object is required for a preliminary stage of development of a new formalism incorporating a finite volume of defects. Hence for both simplicity and concreteness consider a simple cubic lattice with a volume per lattice site (cell volume) $v = a^3$, a is the lattice constant. A lattice constant is used below as a length unit due to which the cell volume, v , is dimensionless and equals unity.

In terms of the considered model a defect structure is defined uniquely by a complete set of "population numbers", $\{v_{\mathbf{r}}\}$. Possible cell states are

- a) $v = \alpha$ (vacancy),
 - b) $v = \beta$ (interstitial),
 - c) $v = \gamma$ (defectless state).
- (2.1)

The theory described below could be also extended to include more complicated defects (e.g. crowdions) through extension of the set (2.1). At any rate, a limited set of cell states (2.1) should be considered when analyzing possible elementary processes in a crystal (Section 2.3).

2.2 Distribution functions

The stochastic processes considered, i.e. Frenkel pair creation, defect motion, and recombination change the number of defects in a crystal and their relative distribution. These processes are incorporated in our model through a stochastic change of cell populations, ν_r . A complete probability description of a physical state of a crystal containing N cells ($N \rightarrow \infty$) is given by the many-particle DF,

$$P_{\nu_1 \dots \nu_m}(\mathbf{r}_1, \dots, \mathbf{r}_m); \quad m = N \quad (2.2)$$

with the recurrent relations defining DF's of lower order

$$\sum_{\nu_m} P_{\nu_1 \dots \nu_m}(\mathbf{r}_1, \dots, \mathbf{r}_m) = P_{\nu_1 \dots \nu_{m-1}}(\mathbf{r}_1, \dots, \mathbf{r}_{m-1}). \quad (2.3)$$

Evidently

$$\sum_{\nu} P_{\nu}(\mathbf{r}) = 1. \quad (2.4)$$

The DF (2.2) is the probability to find at a moment t the cells with coordinates $\mathbf{r}_1, \dots, \mathbf{r}_m$ in the states ν_1, \dots, ν_m .

The DF (2.2) is defined only for non-coinciding pairs of coordinates, otherwise $P \equiv 0$. Since defects arise and recombine by pairs, one can easily obtain

$$P_{\alpha}(\mathbf{r}) = P_{\beta}(\mathbf{r}) = c, \quad P_{\nu}(\mathbf{r}) = 1 - 2c. \quad (2.5)$$

Independence of the one-particle DF's on \mathbf{r} was assumed in (2.5) which is the case for homogeneously excited crystals. The dimensionless concentrations, c (i.e. the probability to find an arbitrary cell occupied irrespectively by a vacancy or an interstitial) is related to the "usual" concentration, c^* , by the simple equation $c^* = c/v$. A transition to dimensional variables is trivial.

For joint DF's one has

$$P_{\nu\nu'}(\mathbf{r}, \mathbf{r}') = P_{\nu\nu'}(\mathbf{r} - \mathbf{r}') = P_{\nu\nu'}(\mathbf{r} - \mathbf{r}'). \quad (2.6)$$

Independent DF's are

$$\left. \begin{aligned} X_{\nu} &= P_{\nu\nu}(\mathbf{r} - \mathbf{r}'); \quad \nu = \alpha, \beta, \\ Y &= P_{\alpha\beta}(\mathbf{r} - \mathbf{r}') = P_{\beta\alpha}(\mathbf{r} - \mathbf{r}'), \end{aligned} \right\} \quad (2.7)$$

whereas the dependent DF's (defined by (2.3)) are

$$\left. \begin{aligned} Q_{\nu} &= P_{\nu\nu}(\mathbf{r} - \mathbf{r}') = c - X_{\nu} - Y; \quad \nu = \alpha, \beta, \\ U &= P_{\nu\nu'}(\mathbf{r} - \mathbf{r}') = 1 - 4c + 2X + 2Y, \\ X &= \frac{1}{2}(X_{\alpha} + X_{\beta}). \end{aligned} \right\} \quad (2.8)$$

where

The DF's X_{ν} , Y describe spatial joint correlations of the similar and dissimilar defects, respectively.

2.3 Models of elementary processes

Starting from possible states of a cell (2.1), the following elementary processes could be considered:

a) The primary process of a Frenkel pair creation:

$$\gamma_r \gamma_{r'} \rightarrow \alpha_r \beta_{r'}; \quad (2.9a)$$

secondary processes:

b) creation-induced recombination

$$\beta_r \alpha_{r'} \rightarrow \gamma_r \gamma_{r'}, \quad (2.9b)$$

c) creation-induced motion

$$\gamma_r \alpha_{r'} \rightarrow \alpha_r \gamma_{r'}, \quad \beta_r \gamma_{r'} \rightarrow \gamma_r \beta_{r'}; \quad (2.9c)$$

d) defect recombination

$$\alpha_r \beta_{r'} \rightarrow \gamma_r \gamma_{r'}, \quad (2.9d)$$

e) defect motion is described by (2.9c).

From the strict physical viewpoint the probability of processes (2.9b), (2.9d) is defined not by initial states of cells at \mathbf{r} and \mathbf{r}' only but is a functional of states of all those cells which lie on possible particle trajectories between \mathbf{r} and \mathbf{r}' . Since such a rigorous approach would be too complicated, elementary processes (2.9a), (2.9d) are assumed to be Markovian stochastic processes dependent only on initial states of two cells at \mathbf{r} and \mathbf{r}' and completely determined by the transfer probabilities (per unit time) μ and σ . The creation rate $\mu(|\mathbf{r} - \mathbf{r}'|)$ and the recombination rate $\sigma(|\mathbf{r} - \mathbf{r}'|)$ are spherically symmetric functions of coordinates. Processes (2.9b) and (2.9c) are not of independent interest because they could be incorporated in recombination and migration processes through redefinition of their rates.

The concept of elementary cells, their populations (2.1), and DF's similar to (2.2) are widely used in statistical physics of phase transitions (the so-called "lattice models"). It should be stressed that the index m in (2.2) is not connected with the number of defects in a crystal due to which our mathematical approach could be applied to systems with both constant and variable number of defects.

3. Kinetic Equations

3.1 Lattice statement

Consider the time development of one-particle and joint DF's.

1. Defect creation (eq. (2.9a))

$$\left. \frac{\partial c}{\partial t} \right|_c \equiv \left. \frac{\partial P_\alpha(\mathbf{r})}{\partial t} \right|_c = \sum_{\mathbf{r}'} \mu(\mathbf{r} - \mathbf{r}') P_{\gamma\gamma}(\mathbf{r} - \mathbf{r}'), \quad (3.1a)$$

$$\left. \frac{\partial X_r}{\partial t} \right|_c \equiv \left. \frac{\partial P_{rr}(\mathbf{r} - \mathbf{r}')}{\partial t} \right|_c = \sum_{\mathbf{r}''} [\mu(\mathbf{r} - \mathbf{r}'') P_{\gamma\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') + \mu(\mathbf{r}' - \mathbf{r}'') P_{\gamma\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')] , \quad (3.1b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_c \equiv \left. \frac{\partial P_{\alpha\beta}(\mathbf{r} - \mathbf{r}')}{\partial t} \right|_c = \mu(\mathbf{r} - \mathbf{r}') P_{\gamma\gamma}(\mathbf{r} - \mathbf{r}') + \sum_{\mathbf{r}''} [\mu(\mathbf{r} - \mathbf{r}'') P_{\gamma\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') + \mu(\mathbf{r}' - \mathbf{r}'') P_{\alpha\gamma\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')] . \quad (3.1c)$$

The physical meaning of different terms in these equations is quite evident (cf. [4]).

2. Defect recombination (annihilation) (2.10).

$$\left. \frac{\partial c}{\partial t} \right|_a \equiv \left. \frac{\partial P_\alpha(\mathbf{r})}{\partial t} \right|_a = - \sum_{\mathbf{r}'} \sigma(\mathbf{r} - \mathbf{r}') P_{\alpha\beta}(\mathbf{r} - \mathbf{r}'), \quad (3.2a)$$

$$\left. \frac{\partial X_\nu}{\partial t} \right|_a \equiv \left. \frac{\partial P_{\nu\nu}(\mathbf{r} - \mathbf{r}')}{\partial t} \right|_a = - \sum_{\mathbf{r}'} [\sigma(\mathbf{r} - \mathbf{r}'') P_{\nu\nu'}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') + \sigma(\mathbf{r}' - \mathbf{r}'') P_{\nu\nu''}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')]; \quad \nu = \alpha, \nu' = \beta \text{ or } \nu = \beta, \nu' = \alpha, \quad (3.2b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_a \equiv \left. \frac{\partial P_{\alpha\beta}(\mathbf{r} - \mathbf{r}')}{\partial t} \right|_a = - \sigma(\mathbf{r} - \mathbf{r}') P_{\alpha\beta}(\mathbf{r} - \mathbf{r}') - \sum_{\mathbf{r}''} [\sigma(\mathbf{r} - \mathbf{r}'') P_{\alpha\beta\beta}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') + \sigma(\mathbf{r}' - \mathbf{r}'') P_{\alpha\beta\alpha}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')]. \quad (3.2c)$$

3. Defect migration

Defect migration could be considered as random walk in a lattice. However, taking into account the results of Sections 3.2, 3.3 we shall restrict ourselves to the case of a continuous diffusive motion.

The hierarchy of equations for DF's is cut-off by making use of the well-known superposition approximation by Kirkwood for three-particle correlations

$$P_{\nu\nu'\nu''}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \approx \frac{P_{\nu\nu'}(\mathbf{r} - \mathbf{r}') P_{\nu'\nu''}(\mathbf{r}' - \mathbf{r}'') P_{\nu\nu''}(\mathbf{r}'' - \mathbf{r})}{P_\nu(\mathbf{r}) \cdot P_{\nu'}(\mathbf{r}') \cdot P_{\nu''}(\mathbf{r}'')}. \quad (3.3)$$

3.2 Continuous statement

The joint DF's X_ν and Y in (3.1), (3.2) are defined on discrete numbers of lattice sites. It is convenient to interpolate these functions in intermediate regions assuming these DF's to be continuous functions of coordinates. It could be done by making use of integrals instead of lattice sums in (3.1), (3.2). When using (3.3), after simple manipulations (e.g. transition to relative coordinates $(\mathbf{r} - \mathbf{r}') \rightarrow \mathbf{r}$) one gets the following basic set of equations:

$$\left. \frac{\partial c}{\partial t} \right|_c = (\mu U * 1), \quad (3.4a)$$

$$\left. \frac{\partial X_\nu}{\partial t} \right|_c = \frac{2Q_\nu}{c(1-2c)^2} (\mu U * Q_\nu), \quad (3.4b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_c = \mu U + \sum_{\nu=\alpha,\beta} \frac{Q_\nu}{c(1-2c)^2} (\mu U * Q_\nu); \quad (3.4c)$$

$$\left. \frac{\partial c}{\partial t} \right|_a = - (\sigma Y * 1), \quad (3.5a)$$

$$\left. \frac{\partial X_\nu}{\partial t} \right|_a = - \frac{2X_\nu}{c^3} (\sigma Y * Y), \quad (3.5b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_a = - \frac{2Y}{c^3} (\sigma Y * X) - \sigma Y. \quad (3.5c)$$

In (3.4), (3.5) for compactness the spatial convolution has been introduced

$$(A * B) = \int A(\mathbf{r}') B(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \equiv \frac{2\pi}{r} \int_0^\infty dr' r' A(r') \int_{|r-r'|}^{r+r'} d\varrho \varrho B(\varrho). \quad (3.6)$$

Relations (3.4), (3.5) seem formally like those used in a continuous statement of the problem (cf. [4 a, b]). However, unlike the usual approach, the discreteness of a crystalline lattice was taken into account here. E.g. due to the condition $X_r \geq 0$, $Y \geq 0$ in (2.5) and (2.8) one easily obtains the relations

$$c < 0.5, X_r, Y < c \quad (X_r, Y \rightarrow c^2 \text{ if } r \rightarrow \infty).$$

The DF's X_r and Y are not defined by (3.4) and (3.5) for $r < 1$, because by the definition (2.2) all joint "lattice" DF's become zero at $|\mathbf{r} - \mathbf{r}'| < 1$. However, the functions A and B enter the integrand (3.6) multiplying r' and ϱ , respectively, and hence their values are relatively small for $r < 1$. Due to this one can use (3.4), (3.5) at $r < 1$ also, i.e. to define DF's X_r and Y for small relative distances.

The creation, $\mu(r)$, and recombination, $\sigma(r)$, rates can be presented in form of unit step functions

$$\mu = \mu_0 f(r); \quad f = \frac{1}{v_c} \theta(R_c - r), \quad (3.7)$$

$$\sigma = \sigma_0 g(r); \quad g = \frac{1}{v_a} \theta(R_a - r). \quad (3.8)$$

Here μ_0, σ_0 are measures of the power of creation and recombination processes. The radii $R_c (v_c = (4\pi/3) R_c^3)$ and $R_a (v_a = (4\pi/3) R_a^3)$, $R_c > R_a$, describe maximum relative distances at which defects are still created and recombine, respectively.

The introduction of a clear-cut recombination radius, R_a , corresponds to the above considered annihilation mechanism of close Frenkel pairs observed for crystals of arbitrary nature (irrespective of whether they are metals or insulators).

3.3 The case of small defect concentration

Of our main interest is the case of small defect concentration, $c \ll 1$, which holds at large annihilation volumes, $v_a \gg 1$ and rapid annihilation, as is usually the case. The DF's X_r and Y are of the order of c^2 almost at all distances. When neglecting in (3.4) c compared with 1 and X_r, Y as compared with c , one obtains

$$\left. \frac{\partial c}{\partial t} \right|_c = \mu_0, \quad (3.9a)$$

$$\left. \frac{\partial X_r}{\partial t} \right|_c = \mu_0 2c, \quad (3.9b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_c = \mu_0 (2c + f). \quad (3.9c)$$

The condition $c \ll 1$ used is also needed for the validity of the diffusion equations (3.10) where an independent motion of the similar defects is assumed. The change of DF's due to the relative motion of defects (we consider a diffusive motion here (cf. [11])) is

$$\left. \frac{\partial c}{\partial t} \right|_{\text{diff}} = 0, \quad (3.10a)$$

$$\left. \frac{\partial X_\nu}{\partial t} \right|_{\text{diff}} = 2D_\nu \hat{L} X_\nu, \quad (3.10b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_{\text{diff}} = D \hat{L} Y, \quad (3.10c)$$

where $D = D_\alpha + D_\beta$, and the diffusion motion operator is

$$\hat{L} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right). \quad (3.11)$$

In the present part of the paper we shall restrict ourselves to the case of radiation-induced immobile defect accumulation assuming their instant annihilation. For simplicity we shall neglect defect diffusion which is valid at low temperatures or for heavily doped crystals when just created defects become rapidly immobilized by impurities.³⁾ Neglect of diffusion leads to $X_\alpha = X_\beta = X$ and therefore the index ν will be often omitted below.

4. Instantaneous Annihilation

4.1 Small defect concentration

Simultaneous use of (3.5) and (3.9) gives the complete set (in terms of joint DF's) of kinetic equations

$$\frac{\partial c}{\partial t} = \mu_0 (1 - \eta^{-1} (gY * 1)), \quad (4.1a)$$

$$\frac{\partial X}{\partial t} = 2\mu_0 \left(c - \eta^{-1} \frac{X}{c^3} (gY * Y) \right), \quad (4.1b)$$

$$\frac{\partial Y}{\partial t} = \mu_0 \left(2c + f - \eta^{-1} gY - \eta^{-1} \frac{2Y}{c^3} (gY * X) \right) \quad (4.1c)$$

with $\eta = \mu_0/\sigma_0$. Let us define $Y(r \leq R_a) \equiv \eta h$. The set of equations (4.1) can be rewritten

$$\frac{\partial c}{\partial t} = \mu_0 (1 - (gh * 1)), \quad (4.2a)$$

$$\frac{\partial X}{\partial t} = 2\mu_0 \left(c - \frac{X}{c^3} (gh * Y) \right), \quad (4.2b)$$

$$\frac{\partial Y}{\partial t} = \mu_0 \left(2c + f - \frac{2Y}{c^3} (gh * X) \right); \quad r > R_a, \quad (4.2c)$$

$$\eta \frac{\partial h}{\partial t} = \mu_0 \left(2c + \frac{1}{v_c} - \frac{h}{v_a} - \eta \frac{2h}{c^3} (gh * X) \right); \quad r \leq R_a. \quad (4.3)$$

(In (4.3) the relations (3.8) are also used).

³⁾ General results for the diffusion-controlled recombination are given in Section 4.4, but in detail this theory will be discussed in the second part of the paper.

On intuitive grounds one could expect the condition of rapid annihilation to be $\eta \ll 1$ (a more careful analysis yields $\eta \ll c_0^2$, where c_0 is given by (4.6)). Under this condition (4.3) is nothing but a differential equation with a small parameter η multiplying the derivative. Assuming instantaneous annihilation ($\eta = 0$ or $\sigma_0 = \infty$), one gets the degenerate equation with the simple solution

$$h = v_a \left(2c + \frac{1}{v_c} \right). \quad (4.4)$$

For finite $\eta \ll 1$ the solution of (4.3) could be expressed through an asymptotic series expansion in powers of η , where (4.4) is the coefficient multiplying η^0 .

Since a distinctive annihilation time is usually a few orders less than a typical diffusive hop [4], (4.4) seems to be quite satisfactory.⁴⁾

Substitution of (4.4) in (4.2a) gives

$$\frac{\partial c}{\partial t} = 2\mu_0 v_a (c_0 - c) \quad (4.5)$$

with a saturation concentration

$$c_0 = \frac{1}{2v_a} \left(1 - \int_0^{R_a} 4\pi f r^2 dr \right) = \frac{1}{2} \left(\frac{1}{v_a} - \frac{1}{v_c} \right). \quad (4.6)$$

The case of an instantaneous annihilation is of special interest because one can obtain easily an analytical relation for the concentration growth with time (or irradiation dose, $\mu_0 t$)

$$c = c_0 (1 - \exp(-2\mu_0 v_a t)). \quad (4.7)$$

The relation (4.7) has been found earlier empirically (e.g. [12, 13]).⁵⁾ One can see from (4.6) that a maximum saturation concentration, $1/2v_a$, is reached for uncorrelated Frenkel pairs. Their correlation ($v_c \neq \infty$) reduces c_0 down to zero for very correlated pairs, $R_c \rightarrow R_a$ (cf. [4a]).

To understand the dependence of c_0 on v_c , one has to consider spatial correlation of defects (Section 5).

Substitution of (4.4) in (4.2b), (4.2c) gives

$$\frac{\partial X}{\partial t'} = \frac{c}{v_a} - \left(2c + \frac{1}{v_c} \right) \frac{X}{c^3} (g * Y), \quad (4.8a)$$

$$\frac{\partial Y}{\partial t'} = \frac{1}{2v_a} (2c + f) - \left(2c + \frac{1}{v_c} \right) \frac{Y}{c^3} (g * X); \quad r > R_a \quad (4.8b)$$

with $t' = 2\mu_0 v_a t$, $Y(r \leq R_a) = 0$, because $\lim_{\eta \rightarrow 0} Y = \lim_{\eta \rightarrow 0} \eta h = 0$. The existence of (4.7) simplifies the calculation of the DF's X and Y . Let us define $X = c_0^2 X_0(r')$, $Y = c_0 Y_0(r')$, $c = c_0 s$, $r = R_a r'$, $R_c = R_a \kappa$. In new variables the annihilation radius R_a becomes unity, $v_a' = 4\pi/3$, $v_c' = (4\pi/3) \kappa^3$, $g(r') = (v_a')^{-1} \theta(1 - r')$.

⁴⁾ However, a finite recombination time and a more complicated dependence $\sigma = \sigma(r)$ are actual, e.g. for the tunneling recombination of defects in insulators (cf. [7], where $\sigma \sim \exp(-r/\text{const})$).

⁵⁾ It should be stressed that an analysis of accumulation curves for immobile F centres in KCl crystal has led to an estimate of R_a containing about 3000 lattice sites [10]. This order of magnitude exceeds the typical R_a in metals [4] and argues that the tunneling mechanism of F centre recombination (but not annihilation) is a limiting factor of their accumulation (cf. [14]).

The ratio of (4.8) and (4.7) becomes (primes are omitted below)

$$\frac{\partial X_0}{\partial s} = \frac{2}{1-s} \left[s \frac{\kappa^3}{\kappa^3-1} - \left(s + \frac{1}{\kappa^3-1} \right) \frac{X_0}{s^3} (g * Y_0) \right], \quad (4.9a)$$

$$\frac{\partial Y_0}{\partial s} = \frac{2}{1-s} \left[\frac{\kappa^3}{\kappa^3-1} \left(s + \frac{\theta(\kappa-r)}{\kappa^3-1} \right) - \left(s + \frac{1}{\kappa^3-1} \right) \frac{Y_0}{s^3} (g * X_0) \right], \quad r > 1. \quad (4.9b)$$

In the steady-state $s = 1$ and the DF's have the asymptotics $\lim_{r \rightarrow \infty} X_0, Y_0 = 1$. The steady-state DF's X_0, Y_0 satisfy

$$X_0(g * Y_0) = 1, \quad (4.10a)$$

$$Y_0(g * X_0) = 1 + \frac{1}{\kappa^3-1} \theta(\kappa-r); \quad r > 1. \quad (4.10b)$$

4.2 Basic equations for DF's

The above given way of derivation of (4.5), (4.8) by studying the limiting case $\sigma_0 \rightarrow \infty$ in (4.3) can be extended.

Let $\delta Y / \delta t$ be the rate of change of Y within an annihilation sphere ($r \leq R_a$) caused by both defect creation and motion. Then in the case of an instantaneous annihilation one puts $Y(r \leq R_a) = 0$, whereas in (3.5) in spatial convolutions σY should be replaced by $v_a g(\delta Y / \delta t)$, i.e.

$$\left. \frac{\partial c}{\partial t} \right|_a = - \left(\theta \frac{\delta Y}{\delta t} * 1 \right), \quad (4.11a)$$

$$\left. \frac{\partial X_v}{\partial t} \right|_a = - \frac{2X_v}{c^3} \left(\theta \frac{\delta Y}{\delta t} * Y \right), \quad (4.11b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_a = - \frac{2Y}{c^3} \left(\theta \frac{\delta Y}{\delta t} * X \right) \quad (4.11c)$$

with $\theta = \theta(R_a - r) = v_a g$.

Relation (4.11a) should be specially discussed. There is reason to believe that (4.11a) holds irrespective whether the supposition approximation (3.3) was used or not. Thus if $\eta \rightarrow 0$ the last term in (4.3), obtained in superposition approximation and describing three-particle correlations within the sphere $r < R_a$, tends to zero. This term is of the order of η_1 . Really, when assuming that the probability Y_1 to find an interstitial at a distance $r^1 \leq R_a$ from a vacancy is of the order of η , it seems quite reasonable that the probability to find two interstitials at $r_1 < R_a, r_2 < R_a$ from a vacancy is of the order of $Y_1 Y_2 \approx \eta^2$. Namely this follows from the supposition approximation (3.3) which gives a self-consistent result. It is hard to imagine a reason why the last term in (4.3) could be of the order of $\eta^0 = 1$ because use of the supposition approximation does not, as a rule, lead to such a great error. From the above said, (4.5), (4.6) obtained under the condition $c \ll 1$ ($v_a \gg 1$) seem to be quite reliable.

In the limiting case of uncorrelated Frenkel pairs, $v_c = \infty$, one obtains from (4.6) that the saturation concentration of defects of A - or B -kind is $(1/2) v_a$. The probability to find a defect of arbitrary kind (irrespective of A or B) is $P_A + P_B = 2c_0$, i.e. the average volume per arbitrary-kind defect is v_a . At first sight such a low saturation concentration, $(1/2) v_a$, seems to be surprising because one could easily imagine a defect distribution *without* aggregates of the similar defects (whose formation will be

proved in Section 5) with a *higher* concentration. For instance, a compact distribution of spheres, containing defects of one kind in their centres, whereas other-kind defects are placed in sited between spheres, yields $c'_0 = 0.742/v_a > c_0$. The generally accepted viewpoint [10, 14, 17, 18] is that aggregation of the similar defects *increases* considerably the saturation concentration. Thus our results break down the intuitive idea that the non-equilibrium system tends to a spatial structure with a *maximum* defect concentration. From (4.8) the conclusion can be drawn that defect configurations with $c'_0 > c_0 = 1/2v_a$ are unstable and dissolve during irradiation.

4.3 Accumulation of uncorrelated Frenkel defects for arbitrary concentration

In the limiting case $v_c \rightarrow \infty$ equations (3.4) could be simplified. For an instantaneous annihilation one gets

$$\frac{\partial c}{\partial t} = \mu_0(1 - 2c) [(1 - 2c) - 2v_a(gQ * 1)], \quad (4.12a)$$

$$\frac{\partial X}{\partial t} = 2\mu_0(1 - 2c) \left[Q - \frac{2v_a X}{c^2} (gQ * Y) \right], \quad (4.12b)$$

$$\frac{\partial Y}{\partial t} = 2\mu_0(1 - 2c) \left[Q - \frac{2v_a Y}{c^2} (gQ * X) \right]; \quad r < R_a. \quad (4.12c)$$

These equations allow, in principle, to take into account the effect of almost complete saturation of a crystal by defects in the case $v_a \approx 1$ (small annihilation volumes comparable with the lattice constant). It should be stressed that (4.12) gives $c_0 < 1/2v_a$. Strictly speaking, for $v_a \approx 1$ the continuous approach used is not quite correct, but real crystals break down at much lower defect concentrations than $c_0 \leq 1$.

4.4 Defect diffusion

The approximation of an instantaneous annihilation, generally accepted in the theory of diffusion-controlled reactions [2 to 5], affects kinetic equations in the following way. The condition $Y(r \leq R_a) = 0$ yields the Smoluchowski' boundary condition $Y(R_a) = 0$ for the DF Y . Due to the linearity of (4.11) in $\delta Y/\delta t$, the contributions of creation and diffusive processes could be considered independently. A creation, affected by an instantaneous annihilation, is defined by (4.5) and (4.8). Defect diffusion necessitates to add new terms. Spatial convolutions in (4.11) could be written as

$$\left(\theta \frac{\delta Y}{\delta t} * B \right) = \frac{2\pi}{r} \int_0^{R_a} \frac{\delta Y}{\delta t} r'^2 \varphi(r') dr', \quad (4.13)$$

where

$$\varphi(r') = \frac{1}{r'} \int_{|r-r'|}^{r+r'} B(\varrho) \varrho d\varrho. \quad (4.14)$$

Substitution of $\delta Y/\delta t$ from (3.10b) in (4.13) and integration twice by parts give

$$\left(\theta \frac{\delta Y}{\delta t} * B \right) = \frac{2\pi D}{r} Y'(R_a) R_a^2 \varphi(R_a); \quad Y'(r) = \frac{\partial Y}{\partial r}. \quad (4.15)$$

Derivation of (4.16) used the condition $Y(r \leq R_a) = 0$ due to which other terms in (4.15) become zero.

Define the flux through the recombination sphere as

$$\Phi = 4\pi R_a^2 D Y'(R_a). \quad (4.16)$$

Substitution of (4.15) in (4.11) and use of (3.10) give the contribution of defect diffusion affected by an instantaneous annihilation in kinetics equations

$$\left. \frac{\partial c}{\partial t} \right|_{\text{diff}} = -\Phi, \quad (4.17a)$$

$$\left. \frac{\partial X_\nu}{\partial t} \right|_{\text{diff}} = -\Phi \frac{X_\nu}{r R_a c^3} \int_{|r-R_a|}^{r+R_a} Y(\varrho) \varrho d\varrho + 2D_\nu \hat{L} X_\nu, \quad (4.17b)$$

$$\left. \frac{\partial Y}{\partial t} \right|_{\text{diff}} = -\Phi \frac{Y}{r R_a c^3} \int_{|r-R_a|}^{r+R_a} X(\varrho) \varrho d\varrho + D \hat{L} Y. \quad (4.17c)$$

The relations (4.17) are of independent interest because if defect creation is absent (irradiation is switched off), they describe the kinetics of the diffusion-controlled defect recombination, such a kinetics will be considered in detail in the second part of the paper. In turn, an analytical analysis of defect accumulation incorporating diffusion is very complicated (cf. [8]) and in the next section we restrict ourselves to the case of negligible diffusion.

5. Accumulation of Immobile Defects

Fig. 1 shows the results of computer calculations based on (4.9) for the time development of the joint DF's of the similar and dissimilar defects, X and Y . (For convenience instead of time the relative defect concentrations, c/c_0 are given.) Two extreme cases have been considered: a) the random creation of the Frenkel defects within pairs, b) the strong initial correlation within Frenkel pairs ($R_c/R_a = 1.5$).

One can conclude from the curves in Fig. 1a that when the relative concentration approaches 1/2, the share of close to similar defects ($A-A$, $B-B$) considerably exceeds that for the Poisson distribution. It means the formation of radiation-induced loose aggregates containing defects of the same-kind only (cf. [14]). Its typical size may be estimated as $2R_a$. The share of nearest similar defects (separated by $a = 0.1R_a$) exceeds the Poisson value twice at $c/c_0 = 0.5$, 3 and 10 times at $c/c_0 = 0.8$ and 0.99 , respectively. This is in qualitative agreement with the experiment for F_2 centres in alkali halides [15].⁶

The conclusion may be drawn that the powerful aggregatization process occurs mainly at high irradiation doses. The mean distance between loose aggregates slightly increases with time and amounts to about $1.5R_a$.

In the case b of the strong initial correlation the DF of the dissimilar defects, Y , has a very sharp peak at low concentrations within the interval $R_a \leq r \leq R_c$ ($= 1.5R_a$). Of extreme importance is the formation of a corresponding decay ("negative" correlation) for the DF of the similar defects within this interval. It indicates the *coupling* of two joint DF's. At the same time the formation of aggregates is here suppressed (along with a much lower saturation concentration) as compared with uncorrelated pairs. On approaching saturation the Y peak disappears as well as the

⁶ The emergence of loose aggregates of the similar defects in alkali halide crystals under powerful irradiation has also been observed experimentally [16].

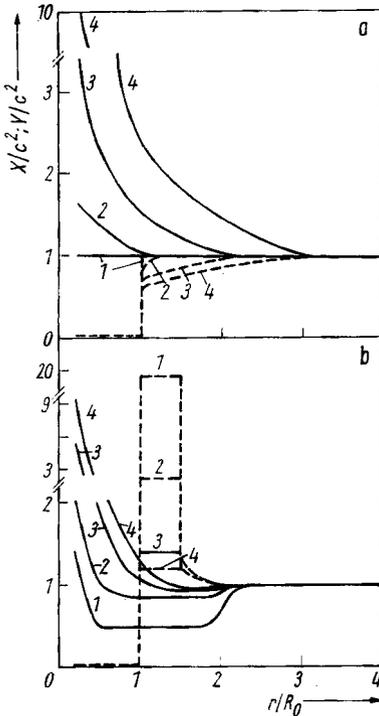


Fig. 1. Time (dose) development of the DF's of the similar defects, X , and dissimilar defects Y . Figures indicate the relative defect concentrations c/c_0 : (1) 0.05, (2) 0.5, (3) 0.9, (4) 0.99. — DF X , --- DF Y . Both DF's are normalized on c^2 . a) Uncorrelated pairs, b) strongly correlated pairs, $R_c/R_a = 1.5$

decay in the X . At saturation the X shows the formation of aggregates quite similar to the case of no initial correlation, but the mean size is about half that in the case of negligible correlation.

So what has been said above is the confirmation of the radiation-induced defect aggregation earlier obtained both experimentally [15, 16] and by computer simulations [14, 17, 18]. These computer simulations expect the emergence of loose aggregates irrespective of the recombination mechanism—annihilation in metals [17, 18] or tunneling recombination in insulators [14]. They expect a mean aggregate size close to $2R_a$, in good agreement with our results, but the saturation concentrations often considerably exceed our estimate $(1/2) v_a$. The cause of the latter discrepancy is not clear now.

6. Conclusion

In this part of the paper the basic equations, incorporating the spatial correlation of both the similar and dissimilar defects, describing defect accumulation and diffusion-controlled recombination have been derived. It is shown for the case of accumulation of immobile defects limited by their annihilation that an initial correlation within genetic (Frenkel) pairs results in "negative" correlations in the DF of the similar defects, i.e. both correlations are coupled.

It is proved that the accumulation of irrespective uncorrelated or correlated Frenkel defects stimulates the formation of loose aggregates of the similar defects earlier obtained experimentally and by computer simulations.

In the second part of the paper the effect of the correlation of the similar defects will be investigated in the case of diffusion-controlled defect annihilation which permits to extend pre-existing theories.

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