

Kinetics of correlated annealing of radiation defects in alkali halide crystals

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Kinetics of the correlated annealing of pairs of neutral (F–H) Frenkel defects in the KBr crystal is treated theoretically, taking into account defect diffusion, and annihilation at short distances stimulated by an elastic interaction. It is shown that an elastic interaction affects the annealing kinetics and the survival probability of close geminate defects considerably. The widespread description of the correlated annealing in terms of a first-order reaction fails for close defects yielding effective energies which in fact differ essentially from an activation energy of diffusion, E_a , even if it is corrected by an interaction energy. The effect of the initial distribution of defects over relative distances is studied. It is concluded that the several-stage annealing of defect concentrations often observed in thermostimulated experiments in alkali halides does not necessarily mean recombination of close Frenkel defects which differ in initial distances.

1. Introduction

Low temperature ionizing irradiation (X- and γ -rays, electron beam, etc.) of alkali halides produces various types of defects. Among them of a key importance are primary Frenkel pairs of F, H centres (vacancy with an electron and an interstitial halide atom, respectively) which are created via the nonradiative decay of self-trapped excitons [1–4]. Since kinetic energy of an interstitial atom leaving a vacancy behind is relatively small (1–2 eV [3]), primary F–H spatially defects are well correlated in so called geminate pairs. The same is true for Frenkel defects in metals [5].

The stability of Frenkel pairs is controlled by I and H centre delocalization stimulating subsequent recombination with α , F and F' (F centre with a trapped electron) centres [6]. This recombination leads to the well-known multi-stage thermal annealing, which was investigated by different methods [6–15].

In this paper we consider theoretically the kinetics of correlated F, H annealing in order to suggest a correct formalism necessary for interpreting actual experimental data. We consider KBr as an experimentally well-studied example. The H centre annealing in this crystal was investigated in detail [6–13]. It is shown to be accompanied by TSL [6,9] as in the case of a random (i.e. uncorrelated with α centres) distribution of I centres. As follows from studies [6], H-centre annealing leads to several TSL peaks ranging from

$T = 32$ to 60 K. It is generally-accepted that the stage at 20 – 30 K is not related to mobile H centres but arises due to secondary reactions initiated by migrating I centres [6,9,11]. The H centres trapped by impurities or dimer centres (H_A, H_2, \dots) are not observed at this stage [16]. A more detailed treatment of experimental data for KBr crystal will be given elsewhere [17], whereas preliminary theoretical analysis of this problem is given in [18,19]. Based on results of our calculations we suggest caution in interpreting many-stage annealing kinetics and moreover, the effective pseudo-monomolecular activation energies. In conclusion, the role of tunnelling recombination in recombination kinetics of correlated F, H centres is discussed.

2. Theoretical

The energy of elastic (dipole–dipole) interaction between point lattice defects is [5,20]

$$\phi(\mathbf{r}) = \alpha/r^3. \quad (1)$$

The H centre under study is an example of a strongly anisotropic defect: it is an X_2^- molecular occupying a single anion site [21]. Therefore, its elastic interaction is also anisotropic. However, since the temperature at which it begins to rotate is much lower than that at which it begins to hop, we can assume confidently that H centers always strive for an energetically profitable

position; thus one could perform *upper* bound estimates considering the case of the isotropic attraction with a constant α corresponding to the relative orientation with *maximum* attraction between F, H centres. According to the calculations [22], $\alpha_{\max} \approx -3 \text{ eV } \text{\AA}^3$ in KBr.

Our model treated below assumes that H defect created at a given distance l from its complementary F centre undergoes random walks and annihilates it when approaching to within a certain small distance R_0 (so-called clear-cut reaction radius). By fitting results of our continuous model to computer simulations of random walks on a discrete lattice [23], we obtained $R_0 \approx \text{\AA}$ in KBr, very close to interionic spacing. When one incorporates the elastic attraction, the energy barriers for H centre hopping in the direction of an F centre lowers and thus stimulates their annihilation.

Annealing kinetics of defects in geminate pairs could be described through joint correlation functions of dissimilar defects [18], giving the probability density to find a pair of F, H defects at a relative distance r . For an arbitrary defect interaction $\phi(r)$ it reads [24]:

$$\frac{\partial Y(r, t)}{\partial t} = D \left[\Delta Y + \frac{1}{kT} \nabla \cdot (Y \nabla \phi) \right], \quad (2)$$

with the boundary and initial conditions

$$Y(r \leq R_0, t) = 0$$

$$Y(r, 0) = \delta(r - l) / 4\pi l^2. \quad (3)$$

Here D is the diffusion coefficient,

$$D = D_0 \exp(-E_a/kT), \quad (4)$$

E_a is the incoherent hopping activation energy, T – temperature, D_0 the pre-exponential factor.

The portion of defects recombined until the moment t is given by a flux through annihilation sphere

$$\left[\omega(t) = \frac{C}{C_0} = \int_0^t dt' 4\pi R_0^2 D \frac{\partial Y}{\partial r'} \right]_{r=R_0}. \quad (5)$$

In the particular case of the elastic interaction, eq. (1), and after substitution $Y = y/r$, eq. (2) reads [18]

$$\frac{\partial y}{\partial t} = D \left[y'' - \frac{3gy'}{r^4} + \frac{9gy}{r^5} \right], \quad (6)$$

with $g = \alpha/kT < 0$.

The survival probability of a geminate pair $\omega(t \rightarrow \infty)$ (i.e. a portion of H centres which after prolonged walks left their complementary F centres without recombination) defines directly temperature dependence of the F centre accumulation [18,25].

The idea that the latter kinetics of correlated recombination could be described in terms of the pseudo-first-order process is widespread [8,26]

$$\frac{dC}{dt} = -KC, \quad (7)$$

with the reaction rate $K \propto \exp(-E^*/kT)$. The *effective* activation energy E^* which was expected to be either coinciding with diffusion activation energy E_a [26] or E_a corrected by an energy of elastic interaction [8,27]. If it were the case, the plot $\ln(C^{-1}dC/dt)$ vs $(1/kT)$ has to give a straight line with a slope equal to E^* .

On the other hand, it is clear that eq. (7) is only an approximation since $C(t) \approx \text{const.}$ at small and large times respectively (defects are just started an approach each other to recombine or those which survived have separated already at a large distance).

3. Results and discussion

The theoretically calculated decay of F, H pair concentration during KBr linear heating is plotted in fig. 1 for two different initial distances corresponding to the first nearest neighbours (nn) along $\langle 110 \rangle$ axis (direction in which STE decay into defects [1–3]) and next, 2nn along $\langle 100 \rangle$ axis. The obvious conclusion

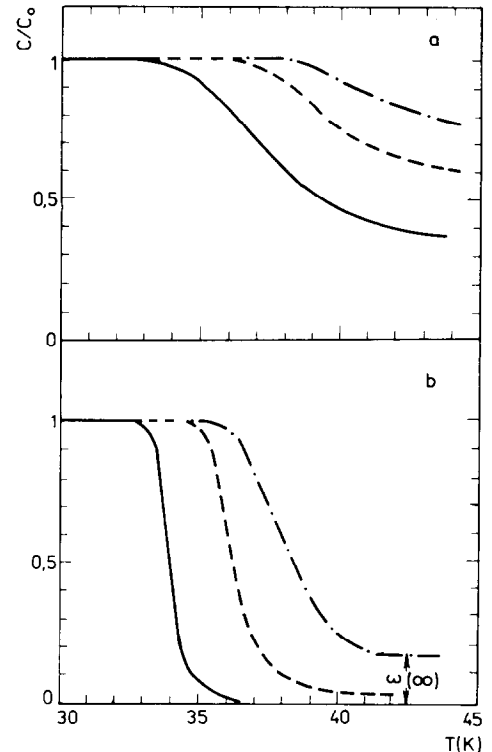


Fig. 1. Calculated kinetics of diffusion-controlled correlated annealing of F, H pairs in KBr neglecting (a) and taking into account (b) their elastic interaction. Initial relative distances between defects: — 4.2 Å (nn), — — 6 Å (2nn) and - - - 8.5 Å (3nn). The survival probability $\omega(\infty)$ is shown in the figure below. The parameters used: $\beta = 0.1 \text{ Ks}^{-1}$, $E_a = 0.09 \text{ eV}$, $\alpha = -3 \text{ eV } \text{\AA}^3$, $R_0 = 3 \text{ \AA}$, $D_0 = 1.5 \times 10^{11} \text{ \AA}^2 \text{ s}^{-1}$.

Table 1

Estimates of the effective energies E^* (in eV) of F, H annealing in KBr based on a model of pseudo-first-order kinetics

Initial separation l [Å]			
Elastic			
constant	4.2 (nn)	6.0 (2nn)	8.5 (3nn)
$\alpha = 0$	0.06	0.08	0.09
$\alpha = -3 \text{ eV \AA}^{-3}$	0.17	0.12	0.10

can be drawn that the survival probability depends considerably on an initial separation between defects but even more on the strength of an elastic interaction. A plot of this kinetics in the above discussed coordinates ($\ln(C^{-1}dC/dt)$ vs $(1/kT)$) yields effective energies E^* given in table 1. When elastic interaction is neglected, we have $E^* < E_a$; whereas if it is incorporated, $E^* > E_a$. This latter fact contradicts an intuitive idea [8] that $E^* \approx E_a - |\alpha|/l^3$.

In both cases ($\alpha = 0$ and $\alpha > 0$) E^* strives for E_a , as l increases. We simulated also the case of *weakly* correlated defects considering a quasi-uniform distribution within the separation interval $l = 15\text{--}55 \text{ \AA}$. Here E^* obtained (0.086 eV) is indeed very close to the given E_a (0.09 eV).

It is shown [18,19] that for a strong elastic interaction, the survival probability obeys the Arrhenius law

$$\omega(\infty) \propto \exp(g/l^3) = \exp(\alpha/k_B T l^3), \quad (8)$$

with the effective energy $E^* \approx \phi(l)$ – the elastic interaction energy at the place of a pair birth. It was found experimentally [28] that for low doses the F-centre accumulation efficiency in KBr could be indeed approximated by the Arrhenius law with $E^* \approx 0.017 \text{ eV}$

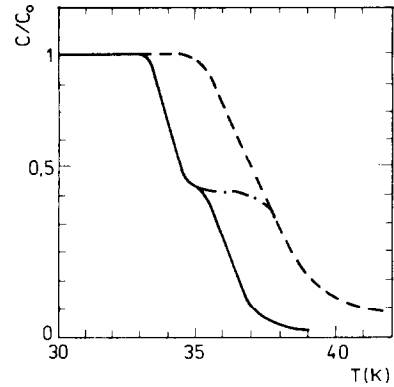


Fig. 2. Correlated annealing of F, H pairs in the case of several kinds of Frenkel pairs. — nn and 2nn, - - - 2nn and 3nn, - · - · nn and 3nn. Partial concentrations of defects are taken equal and an elastic interaction is taken into account.

(instead of generally accepted 0.03 eV [21] observed at higher doses) thus arguing for a preferential F, H centre creation at a *second* neighbour distance (see also [29] and discussion below).

Since the actual distribution function can involve several kinds of pairs separated by different distances we have simulated this effect in fig. 2. (In all cases considered *partial* defect concentrations at different distances were taken the same thus to give after summation unity (i.e. C_0), irrespective of a number of lattice sites in relevant positions.)

The step structure for the simultaneous nn and 2nn defect annealing is more pronounced than for 2nn and 3nn. Note that the smooth latter curve lies just *between* two curves corresponding to 2nn and 3nn only (see fig.

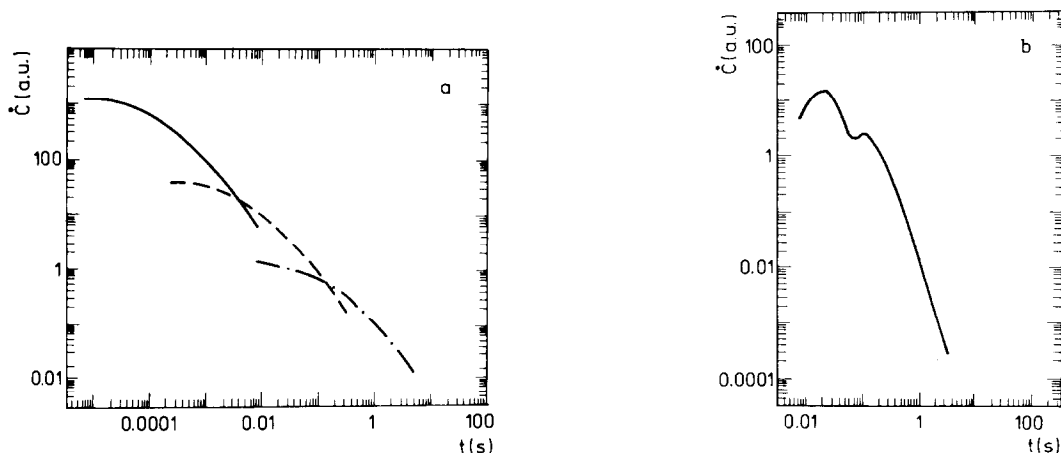


Fig. 3. (a) Kinetics of isothermal decay of F, H centres at 60 K, 50 K and 43 K (—, - - -, - · - · respectively). Initial distribution consists of nn and 2nn (in equal concentrations). Elastic interaction is neglected. (b) The same as full curve above but taking into account an elastic interaction.

1). For 4nn and 5nn the decay is very smooth and the survival probability high.

In order to distinguish between the kinetics of monomolecular recombination of geminate pairs and *bimolecular* recombination of defects belonging to different pairs (e.g. when pairs become mixed due to diffusion), the plot of $\log(dC/dt)$ vs $\log t$ can be useful [8]. From the point of view of standard bimolecular kinetics [24] we have

$$I\alpha \frac{dC}{dt} = -K(t)C^2, \quad (9)$$

with the reaction rate [$K(t) = 4\pi DR_0(1 + R_0/\sqrt{\pi Dt})$].

As $t \rightarrow \infty$, eq. (9) yields $C \propto t^{-1}$ (or $I \propto t^{-2}$). That is, the plot in coordinates $\log I$ vs $\log t$ yields a straight line. Moreover, this curve has a steeper decay at short times which has been indeed observed experimentally more than once in different materials [30–32]. However, in the case of geminate pairs the kinetic curves reveal an opposite effect shown in fig. 3a: the initial decay state typically is quite flat. Incorporation of elastic interaction makes it possible to resolve efficiently different kinds of close defects (if any) (fig. 3b).

All of the above discussion supports the same conclusion: multi-stage annealing kinetics can be observed in alkali halides for very close defects only, typically no further than 4th neighbours. However, it is well known from pulse experiments [1–4] that close F, H centres in KBr (as well as in other alkali halides) disappear rapidly due to electron tunnelling from the electron to the hole centre.

This process being temperature independent is the only recombination channel at LHeT. Typical lifetimes observed for three kinds of nearest F, H centres are 0.3 μ s, 12 μ s and 70 μ s. It means that defects still existing at the time-scale of the steady-state experiments can no longer be close.

Therefore, we suggest that experimentally observed many-state kinetics originate from a set of *secondary* reactions between Frenkel defects rather due to their correlated annealing. (This is the more so for α , I pairs where up to 10 annealing stages reported [4].)

Of great interest would be a similar study for correlated annealing of Frenkel defects in metals.

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