Short Notes

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The Kinetics of Correlated Annealing of F, I Centres in KBr Crystals

By

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I centres (interstitial halide ions) are known to be the most mobile radiation-induced defects in alkali halides, and therefore they play an essential role in the processes of low-temperature defect annealing. The analysis of the experimental data [1 to 4] shows that I centres recombine not only with their complementary α-centres (anion vacancies, v_a^+) but also with $F(\alpha + e^-)$ and V_k (self-trapped hole, e_s^+) centres, which makes the problem of separation of the annealing of α, I pairs of centres and F, H pairs rather complicated. An additional problem arises from the fact that primary F, H centres can be transformed under irradiation into other centres via trapping of free holes and electrons,

$$F(v_a^+e^-) + H(i_a^0) + e^- + e^+ \rightarrow F(v_a^+e^-) + I(i_a^-) + e_s^+ , \tag{1}$$

$$F(v_a^+e^-) + H(i_a^0) + e^- + e^+ \rightarrow F'(v_a^+2e^-) + H(i_a^0) + e_s^+ . \tag{2}$$

In the reaction (1) an I centre is created due to free electron trapping by an H centre; this process can result in crowdion formation. Computer simulations of this process (cf.[5]) have shown that an interstitial ion created in this way could be displaced for a rather long distance from a vacancy; this distance has been estimated in [3] to range up to seven interionic spacings in KCl crystals. Therefore, one can expect a wide F, I distribution of inter-pair separations including well-correlated defects as well as almost randomly distributed defects. The annealing of defects within close pairs and uncorrelated pairs is controlled by an elastic interaction of defects and by free I centre migration, respectively.

In this note, we consider *the kinetics of the correlated annealing of pairs of close F, I centres stimulated by elastic attraction.* The mathematical model of the kinetics of correlated annealing is described in detail in [6] for primary Frenkel defects, i.e. F, H centres. The model is based on the theory of diffusion-controlled annihilation stimulated by the elastic defect interaction. This interaction arises if at least one of the point defects has an anisotropic double-force tensor **P**. In the elastic-dipole approximation the corresponding interaction energy is proportional to the third power of the inverse distance r [7 to 9],

$$U(\boldsymbol{r}) = \alpha[\Theta, \varphi]/r^3 . \tag{3}$$

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In the particular case of F, H centres studied in detail in [10] it has been shown that attraction takes place when the line connecting these two defects is along the [001] axis, whereas the molecular axis of H is parallel to the [110] axis. For KBr it has been found that $\alpha = -3$ eV Å^3. To do similar calculations for F, I centres, we use here the relevant equations for the interaction energy from [11] and the double-force tensor of an I centre in KBr from [12]. We found $\alpha = -4$ eV Å^3, which is 30% greater than for F, H pairs. This effect is due to different values of $P_0 = 1/\sqrt{6}\,(2P_{zz} - P_{xx} - P_{yy})$, where P_{ii} is the diagonal matrix element of the double-force tensors for I and H centres [13]. Since *both* α and I centres are almost isotropic, we assume their interaction to be angular-independent. The annihilation radius $r_0 = 3$ Å, which is close to the interionic spacing was earlier used by us in the kinetics of F, H recombination [6]. The activation energy for I centre hopping is $E_a = 0.06$ eV [14, 15] (see also [2]; in the diffusion coefficient $D = D_0 \exp(-E_0/kT)$ the pre-exponential factor is $D_0 = 3 \times 10^{13}$ Å^2 s^{-1}.

The results of our calculations are presented in Fig. 1 and 2. The conclusion we draw from Fig. 1 is that an increase of the distance l between the partners of an F, I pair from the nearest-neighbour distance (1 NN) to the fourth-nearest neighbours (4 NN) results in an increase of both the corresponding annealing temperature by about 1 K per one-step increase of the degree of neighbourhood, and in a higher survival probability, i.e. higher fraction of I centres not recombining with their 'own' F centres. In our calculations this probability is 0.1 for 1 NN and 0.2 for 4 NN. If there were no elastic interaction, the survival probability would obey the very simple relation $P = 1 - r_0/l$, from which one expects the values 0.45 and 0.69 for 1 NN and 4 NN, respectively. This convincingly demonstrates the importance of the elastic interaction even for relatively distant defect pairs. Fig. 2 shows the effect of the simultaneous annealing of *several* kinds of defects. The obvious result is that a *well pronounced* recovery stage is only observed for nearest-neighbour pairs, whereas badly resolved stages already emerge for 3 NN and 4 NN pairs. With an increase from

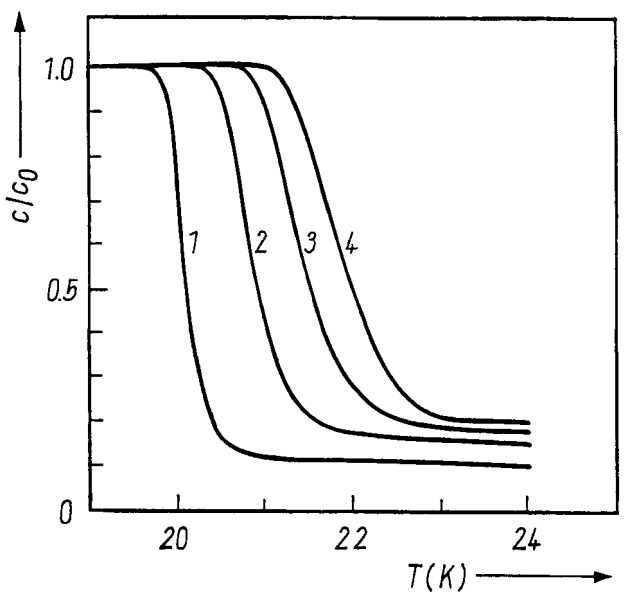

Fig. 1. Decay of the F, I pair concentration by thermally activated recombination, as calculated by means of the theory described in the text. The heating rate is chosen as 0.1 Ks^{-1}. Curves 1 to 4 correspond to 1 NN to 4 NN, respectively, with relative F, I separations amounting to 5.465 Å; 7.182 Å; 8.563 Å, and 9.747 Å, respectively. The other parameters are given in the text

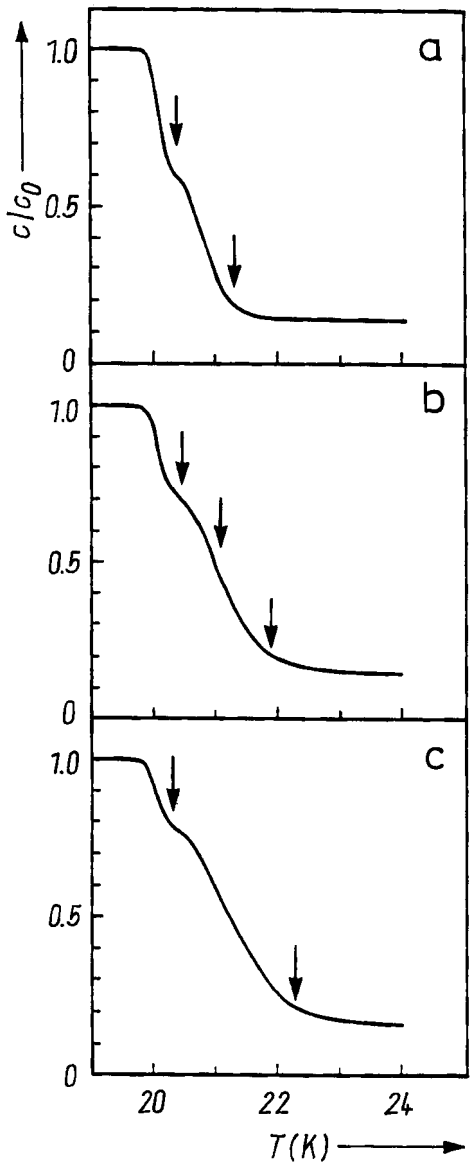

Fig. 2. Effect of simultaneous recombination of different kinds of NN defects present in equal concentrations: a) 1 NN + 2 NN; b) 1 NN + 2 NN + 3 NN; c) 1 NN + 2 NN + 3 NN + 4 NN. The arrows show kinks in the recovery stages

1 NN to 4 NN the amplitude of the first stage decreases and slightly shifts to lower temperatures.

Let us now discuss briefly the relevant experimental data. Annealing of I centres was experimentally studied more than once [1 to 3, 5, 14 to 16]. Based on optical measurements [15], the I centre recombination has been assumed to occur exclusively with the complementary α centres. However, further thermally-stimulated conductivity (TSC) and thermostimulated luminescence (TSL) investigations have demonstrated that I centres also recombine with F and F′ electron centres. It has been discussed in [2] that many-stage correlated annealing of H + V_k and F + F′ centres with I centres delocalized below 30 K leads to a charge (e^-) release observed in the TSL experiments, thermostimulated depolarization current, thermostimulated charge diffusion, as well as in the recombination emission of self-trapped excitons. Up to ten substages were observed, depending on the irradiation conditions. These are likely to be determined by processes of delocalization, diffusion, and recombination of I centres having *different spatial distributions* and configurations relative to their recombination partners within defect pairs (I ... α), as well as triplets, quartets (I ... F ... V_k), (I ... F′ ... V_k ... V_k), etc. The recovery stage of *uncorrelated* (unperturbed) I centres in KBr was observed at 27 to 28 K [1, 2, 17], whereas substages at lower temperature are caused by *perturbed* I centres, involved in defect pairs, triplets, etc. [2]. In the present note we have simulated one of these mechanisms, namely, the F, I pair recombination. The corresponding temperature region, 20 to 22 K, found in our calculations agrees well with that observed in TSC and TSL experiments [18]. Our theoretical results are of particular importance in interpreting TSC data [19], since free electrons can arise only due to such *secondary* processes. In [19] *three* stages at 20, 22, and 24 K were observed, which is in agreement with Fig. 2b.

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