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Aggregation of Frenkel defects under irradiation: a mesoscopic approach

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The radiation-induced aggregation of Frenkel defects in solids is studied in terms of a mesoscopic approach. The asymmetry in elastic interactions between mobile interstitials (I–I) and between interstitials and vacancies (I–V) plays a decisive rôle in the aggregation of similar defects. The conditions for defect aggregation are studied in detail for NaCl crystals. The critical dose rate for aggregation has been calculated as a function of the temperature as well as the aggregation rate as a function of temperature and dose rate. Furthermore, the rôle of deep traps (like impurities and di-vacancies), reducing the mobility of interstitials, and the rôle of dislocations serving as sinks for interstitials, are studied. The aggregation appears to reach a maximum at a distinct temperature which is in agreement both with experiment and the Jain–Lidiard theory. The model also predicts a shift of this maximum towards lower temperatures if the dose rate is decreased. The consequences of the model for the disposal of nuclear waste in rock salt formations are briefly discussed.

1. Introduction

The study of radiation-induced defects in alkali halides has been started many decades ago. A subproblem which has attracted much attention because of its particular fundamental and applied interests is the kinetics of the formation of alkali metal colloids and halide gas bubbles under irradiation. This process of aggregation of primary defects is an experimentally well established phenomenon for relatively high temperatures and high irradiation intensities [1]. This aggregation process is in particular of great importance with respect to plans for disposal of nuclear waste in rock salt formation [2–4] and usage of NaCl crystals for high-level dosimetry [5].

For the quantitative analysis of the kinetics of this defect accumulation, a number of models have been presented which differ both by physical pre-assumptions and by mathematical formalisms. The mathematical formalisms can roughly be classified into three categories: macroscopic, mesoscopic and microscopic approaches.

The first method is based on kinetic rate equations which describe the change of the concentrations of primary defects and their aggregates as a function of

time. These macroscopic concentrations are averaged over the entire volume of the crystal and thus do not depend on the positions of the defects. This approach has proven to be rather successful in describing many important features of the radiolysis processes in alkali halides and in particular in NaCl [6–8].

In the mesoscopic approach of defect accumulation and clustering, the distribution of point-defects is characterized by space-dependent concentrations of vacancy (V) and interstitial (I) defects. The recombination kinetics are treated in a mean-field procedure, neglecting spatial correlations between defects and their impact on the reaction kinetics. The mesoscopic approach predicts that a nontrivial behavior (i.e. a non-homogeneous distribution) may arise if elastic attractions between point defects are taken into account [9]. Non-homogeneous distribution, which implies clustering of similar defects, manifests itself as a breaking of the translational symmetry of the defect distribution due to the emergence of spatial modulations of the averaged defect concentrations.

In the microscopic approach [10,11], the defect distribution is characterized by the defect–defect correlation functions. This allows one to take into account relative spatial distributions of similar (I–I, V–V) and dissimilar (I–V) defects and thus to incorporate the influence of defect correlations on the recombination kinetics. Within this approach, it is possible to show that the very nature of the recombination process

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I. FUNDAMENTAL PROCESSES

provides a tendency towards clustering of similar defects on a microscopic scale.

In this paper, we will present results of a new version of the *mesoscopic* approach which is suitable for the description of radiolysis processes in alkali halides. Martin [9] has shown that the occurrence of an inhomogeneous defect distribution in the mesoscopic approach requires a certain asymmetry between similar and dissimilar defects. This asymmetry can be produced by either a large difference in concentrations of the two primary defects, or by a difference in the interactions between the defects. In Martin's model, asymmetry was accomplished by the introduction of dislocation sinks at which interstitials (which are far more mobile than vacancies) disappear, such that the concentration of interstitials becomes very small. This causes the attraction between pairs of vacancy defects to become more important than that between pairs of vacancy–interstitial defects, simply because the latter pairs practically do not exist. In this paper, we present a new variant on the mesoscopic approach by taking into account that there exist direct asymmetries in the effective interactions between defects that may give rise to clustering, even in dislocation-free crystals. Furthermore, we take into account the influence of impurities, which may act as traps for interstitials, and study the resulting modifications of the segregation behavior.

2. Model

We assume that the primary radiation-induced Frenkel defects in alkali halides (F and H centers) are created randomly at a rate P per unit volume and time, having mobilities:

$$D_{x} = D_{x}^{0} \exp\left(\frac{-E_{x}}{kT}\right), \qquad x = V, I. \tag{1}$$

For NaCl, we may use $E_I = 0.1$ eV [12], $E_v = 0.8$ eV [13] and $D_x^0 \approx 2 \times 10^{-3}$ cm^2/s. If unsaturable traps for interstitial defects with concentration C_T are present, the effective diffusion coefficient is reduced to the value $\tilde{D}$, where:

$$\tilde{D}^{-1} = D^{-1} + 4\pi C_T R_T \nu^{-1} \exp\left(\frac{E_B + E_x}{kT}\right). \tag{2}$$

Here E_B denotes the binding energy to the trap, R_T the trap capture radius, and ν an attempt frequency of the order of magnitude of the Debye frequency.

For H centers in NaCl, several kinds of traps have been reported, including cation impurities (Li), cation vacancies and di-vacancies ($v_a v_c$). The latter type of defects are known to have large binding energies for H centers: it has been calculated [14] that $E_B \approx 1.5$ eV in KCl. The di-vacancies are believed to be responsible for anomalous high-temperature (Thermo-Stimulated

Luminescence) TSL peaks observed in heavily irradiated NaCl and KCl. Evidence for the radiation-induced formation of di-vacancies in alkali-halides was given by several authors [15].

Elastic interaction between point defects is known to decay with the relative distance as [16]:

$$E_{xy}(r) = -\hat{E}_{xy}/r^3, \qquad x, y = I, V, \tag{3}$$

In both ionic solids and metals, the hierarchy for the interactions is: $E_{II} > E_{IV} > E_{VV}$. Detailed calculations for KBr yielded [17]: $E_{II} = 0.3$ eV; $E_{IV} = 0.05$ eV and $E_{VV} = 0.02$ eV for nearest-neighbor defects. We have adopted these values in our calculations for NaCl. When a F and a H center approach each other to a distance equal to or less than R_a ($= a$; the lattice distance) it is assumed that the two defects recombine and restore the perfect lattice.

The formalism of the new mesoscopic method is described elsewhere [18] in more detail. The method is based on time-dependent equations for the diffusion-controlled evolution of the spatially averaged concentrations of the primary defects: $c_v(r, t)$ and $c_I(r, t)$, interacting according to Eq. (3). The (in)stability of the homogeneous steady-state is studied by introducing small fluctuations in the concentrations. It is shown that these fluctuations will not be damped, but on the contrary, will increase in amplitude if the dose rate P is above a certain critical limit given by:

$$\ln(P_{cr}) = 2\ln\left(\frac{kT}{\Delta_{el}}\right) + \ln(D) + \ln\left[(1+\epsilon)^2 4\pi R_a\right], \tag{4}$$

where $D = D_I + D_v$, $\epsilon = D_v/D_I$ and where:

$$\Delta_{el} = \left[\hat{E}_{II} + \epsilon\hat{E}_{vv} - (1+\epsilon)\hat{E}_{VI}\right]f(0). \tag{5}$$

Δ_{el} is a measure of the asymmetry between the interactions between similar and dissimilar defects and $f(0)$ is the Fourier transform of the elastic potential (Eq. (3)) at $k = 0$. From Eq. (4) it could be readily concluded that if $D_I \gg D_v$, $\ln(P_{cr})$ would increase in first approximation linearly with the temperature. But, since vacancy defects in alkali halides are assumed to have a finite mobility, ϵ also changes with temperature. This feature gives rise to new effects in comparison with the case of metals [9,18] where vacancy defects are considered to be more or less immobile. In general it can be stated that the larger the asymmetry in the elastic defect interactions is, the larger the fraction Δ_{el}, and the smaller the critical dose rate P_{cr} will be. The aggregation rate for $P > P_{cr}$ is characterized by a frequency $\omega'(k, T)$, which is proportional to $(P/4 \pi D R_a)^{1/2}\Delta_{el}/kT$ [18] which will be discussed below, in Fig. 2.

3. Results

From the general aggregation condition (Eq. (4)), it can easily be deduced that, if there would not be any traps for the highly mobile H centers, the critical dose rate for aggregation would be unrealistically high. If, however, H center trapping by deep traps (e.g. divacancies) is taken into account, the critical dose rate is reduced to reasonably low values even for very small concentrations of traps C_T. At low temperatures, where $(C_T R_T \exp((E_I + E_B)/kT) \gg 6a^{-2} \exp(E_I/kT)$, the instability curves are expected to shift down by one order of magnitude if C_T increases by one order of magnitude. This effect can be observed in particular in Fig. 1 for the solid and long-dashed curves. The solid line is almost linear for the temperature range of this figure since the term $\ln(D)$ in Eq. (4) is dominant here.

The introduction of traps, however, also causes the aggregation to be *limited* to a certain range of temperatures. This temperature range shifts to higher temperatures if the concentration of traps is increased. The upper temperature limit is reached when the mobility of the vacancy defects becomes larger than that of the interstitials and Δ_{el} (Eq. (5)) becomes negative due to large values of $\epsilon = D_V/D_I$. In NaCl, the upper limit for Δ_{el} is reached for $\epsilon \geq 6$, if we assume the trapping energy for the interstitial defects by di-vacancies to be 1.5 eV [14]. For $C_T = 10^8$ cm^{-3} this happens below 300 K and is not seen in Fig. 1. For $C_T = 10^{10}$ cm^{-3} (which is probably a more reasonable value), the upper

Fig. 2. Dispersion curves showing the rate of aggregate formation versus the reciprocal wavelength of periodical concentration fluctuations. Parameters are shown in the figure. For $T > 370$ K, the defect distribution is homogeneous, i.e. $\omega' < 0$.

temperature limit is well observed in Fig. 1 ($T_c = 310$ K). To stress this effect, the instability curve for the case of *immobile* vacancy defects is shown in this figure by a long-dashed line. In order to check how much our results are sensitive to the parameters of traps (first of all: their binding energies), we have performed calculations for $E_B = 1$ eV and found nearly the same effects as reported for C_T ranging from 10^{15} to 10^{17} cm^{-3}.

The transition rate for the homogeneous distribution changing into a system consisting of aggregates of similar defects is shown in Fig. 2 as a function of the temperature. At low temperatures, aggregation is very slow due to low mobilities of the defects. As the temperature increases, the transition rate increases too until a maximum is reached. This maximum in the transition rate corresponds in real space to an average distance between the aggregates of about five lattice distances. A further increase of the temperature (and the mobility of interstitial defects) leads to a gradual decrease of the aggregation since the relative difference in the elastic interactions between similar and dissimilar defects, $(\hat{E}_{II} - \hat{E}_{IV})/kT$, becomes small [9,18].

Decreasing the trap concentration for a fixed dose rate leads to a decrease of the temperature at which optimal aggregation occurs since the instability conditions are more rigid for higher temperatures (Fig. 1). By the same reasons, the optimal aggregation temperature becomes lower if the dose rate is decreased. It is obvious that the aggregation rate is much larger at lower temperatures since the mobilities of the defects are much smaller.

Finally, Fig. 3 shows that the concentration of ag-

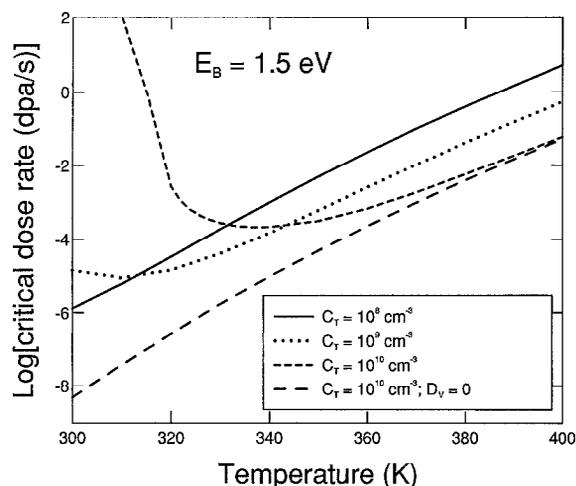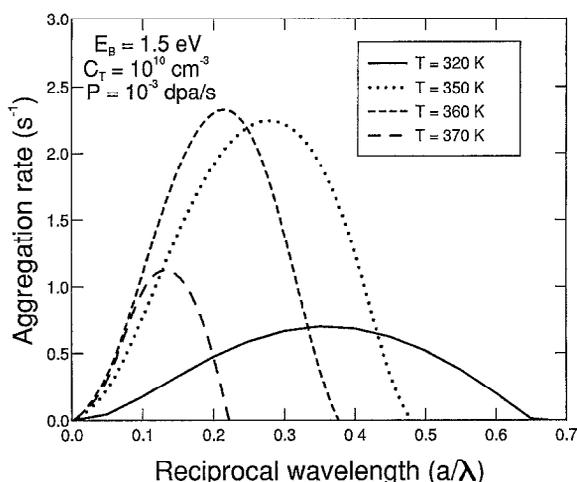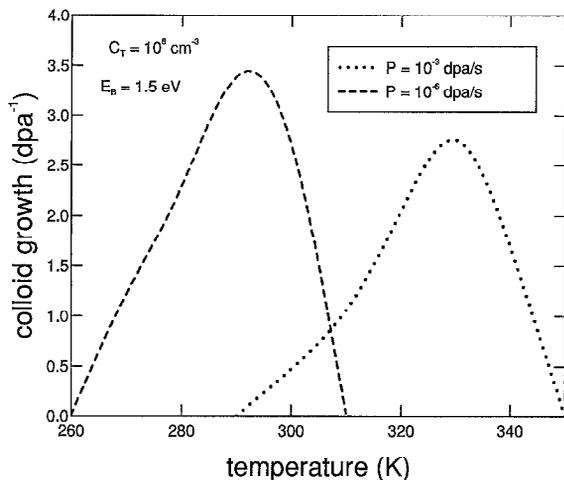

Fig. 1. Instability diagram showing the critical dose rate versus temperature. Binding energy of the traps $E_B = 1.5$ eV; trap concentrations and dose rates are shown in the figure. $R_a = a$ (lattice spacing); $E_{II} = 0.3$ eV; $E_{IV} = 0.05$ eV, and $E_{vv} = 0.02$ eV. For a given temperature, aggregation takes place in the dose rate regime *above* the critical dose rate curves shown in this figure.

Fig. 3. The concentration of aggregates as a function of temperature for two dose rates.

From a practical point of view, our model leads to the following conclusions: 1) the (experimentally observed) aggregation of F and H centers in NaCl, at temperatures above RT requires the existence of deep traps for H centers which probably only can be provided for by di-vacancies; 2) the rate of aggregate-growth as a function of the temperature shows a bell-shape; 3) lowering dose rates leads to a shift of the optimum temperature for defect clustering towards lower values; and 4) the final aggregate concentration for a given dose only slightly depends on the dose rate.

The last two conclusions are relevant to the question of the disposal of nuclear waste in rock salt formations. Namely, they suggest that storage in deep (= warm) geological formations will lead to lower concentrations of permanent radiation damage, and that laboratory experiments (using relatively high radiation intensities) might provide reliable estimates for in situ situations where dose rates will be appreciably smaller.

gregates is a bell-shaped function of the temperature. It shifts to lower temperatures and slightly increases in amplitude if the dose rate is decreased.

4. Discussion and conclusions

The bell-shape of aggregate concentration as a function of temperature is consistent both with experiments [19,20] and with the macroscopic Jain–Lidiard theory [6,7]. The dose-rate dependence of position and intensity of its maximum is less firmly supported by experiments [21] but the trends predicted by our mesoscopic model coincide with results of macroscopic models [8].

As was suggested by Martin [9], an alternative aggregation mechanism could occur when very mobile interstitials are absorbed by dislocations. In this case, vacancy defects, largely dominating now in concentration, will aggregate due to their elastic attraction. The realization of one of the two aggregation mechanisms depends on the relation between the two corresponding relaxation times $1/\omega'$ and τ, necessary for the formation of the inhomogeneous defect distribution due to asymmetry in their elastic interactions, and that for the drain of interstitials to dislocations respectively [18]. Latter relaxation time can be estimated as $\tau \approx 1/\rho_d D_I$, where ρ_d is the dislocation density. A comparison between $1/\omega'$ and τ for two dose rates which differ by 3 orders of magnitude ($P = 10^{-3}$ dpa/s and 10^{-6} dpa/s) shows that for temperatures above 50°C for NaCl, the dislocation-controlled aggregation will be predominant, whereas for lower temperatures the aggregation is trap-controlled.

Acknowledgements

References

[1] A.E. Hughes and S.C. Jain, Adv. Phys. 28 (1979) 717.

[2] P.W. Levy, Nucl. Techn. 60 (1983) 231.

[3] J. Bergsma, R.B. Helmholdt and R.J. Heijboer, Nucl. Techn. 71 (1985) 597.

[4] W.J. Soppe and J. Prij, Nucl. Techn., in press.

[5] S. Owaki, K. Nobugai, T. Okada and K. Inabe, Radiat. Protect. Dosim. 34 (1990) 315.

[6] U. Jain and A.B. Lidiard, Philos. Mag. 35 (1977) 245.

[7] A.B. Lidiard, Philos. Mag. A39 (1979) 647.

[8] W.J. Soppe, J. Phys.: Condens. Matter 5 (1993) 3519.

[9] G. Martin, Fundamental Aspects of Radiation Damage in Metals, vol. 2, eds. T. Robinson and F.W. Young, Jr., (Gatlinburg, Tennessee, 1975) p. 1084.

[10] V.N. Kuzovkov and E.A. Kotomin, Rep. Prog. Phys. 51 (1988) 1479.

[11] V.N. Kuzovkov and E.A. Kotomin, Phys. Scripta 47 (1993) 585.

[12] E. Sonder and W.A. Sibley, Point Defects in Solids, vol. 1 (New York, Plenum, 1972) chap. 4.

[13] P.W.M. Jacobs, Diffusion in Materials, eds. A.L. Laskar, J.L. Bocques, G. Brebec and C. Monty (Kluwer, Dordrecht, 1990) p. 203.

[14] V.V. Gavrilov, A.V. Gektin, V.Ya. Serebryannyi and A.N. Varaksin, Sov. Phys. Sol. State 30 (1988) 870.

[15] A.V. Gektin, V.I. Smaushkova and N.V. Shiran, Opt. Spectr., 63 (1987) 184.

[16] K. Schröder and K. Dettmann, Z. Phys. B 22 (1975) 345.

[17] K. Bachmann and H. Peisl, J. Phys. Chem. Sol. 31 (1970) 1525.

[18] E.A. Kotomin and M. Zaiser, Appl. Phys. A 57 (1993) 117.

[19] A.E. Hughes, Radiat. Eff. 74 (1983) 57.

[20] A.E. Hughes, Radiat. Eff. 97 (1986) 161.

[21] J. Groote and H.R. Weerkamp, Radiation Damage in NaCl, Thesis, University of Groningen (1989).

I. FUNDAMENTAL PROCESSES