INTERSTITIAL STABILIZATION IN IRRADIATED ALKALI HALIDES AT 77 K

G. GUILLOT and A. NOUAILHAT

Laboratoire de Physique de la Matière (*) Institut National des Sciences Appliquées de Lyon
20, Avenue Albert-Einstein, 69621 Villeurbanne Cedex, France

Résumé. — Dans les halogénures alcalins irradiés à 77 K, la cinétique de croissance des centres F est fonction des réactions secondaires ayant lieu après le processus primaire de création de la paire de Frenkel. Le taux de création des centres F est fixé par la compétition entre divers processus secondaires : recombinaison des interstitiels libres avec les centres F et piégeage des interstitiels par des impuretés.

La forme de la cinétique est reliée au nombre d'impuretés capables de stabiliser les interstitiels et de donner lieu à la nucléation d'amas. Dans les cristaux les plus purs, la loi en $t^{0.8}$ de la cinétique des centres F est interprétée par la croissance de larges agglomérats (jusqu'à quelques centaines d'interstitiels) nucléés sur des impuretés résiduelles. Ces amas ont un rayon de capture qui croît avec leur taille. Dans les cristaux impurs contenant en particulier du sodium et du lithium (environ 50 ppm), ces impuretés agissent comme points de nucléation pour des agrégats de petites tailles (environ 10 interstitiels) qui constituent des pièges non saturables. Les rapports des rayons de capture des amas au rayon de piégeage des centres F sont déterminés.

Abstract. — In alkali halides irradiated at 77 K the growth kinetics of F centers is a function of the secondary reactions taking place after the primary Frenkel pair creation process. The F center creation rate is fixed by the competition between various secondary thermally activated processes : free interstitial recombination with F centers and the trapping of interstitials by impurities.

The kinetics shape is related to the number of impurities able to stabilize the interstitials and to give rise to cluster nucleation. In the purest crystals, the $t^{0.8}$ law for the F center kinetics is accounted for by the growing of large clusters (to a few hundred of interstitials) nucleated at some residual impurities. These clusters have an increasing trapping radius with the size. In the impure crystals, containing specially sodium and lithium (typically 50 ppm), these impurities act as nucleation sites for small size clusters (up to about 10 interstitials) constituting non saturable traps. The ratios of the cluster capture radii to the F center capture radius are determined.

Introduction. — When an alkali halide is irradiated by an ionizing radiation, a F center and a H center are the primary products of irradiation [1]. An important problem in the field of radiation damage in these materials is the part of halogen interstitials. So, during the last years, much work about the secondary processes related to the behaviour of these defects after their creation has been done [2, 3, 4]. Actually, in spite of a big amount of experimental results, no generally accepted model has been proposed.

A well known method for the study of these mechanisms consists to analyse the F center coloration kinetics as a function of the energy dose.

We have made systematic studies of the F center creation kinetics under electron irradiation at concentrations between $10^{16}/\text{cm}^3$ and $10^{19}/\text{cm}^3$ as a function of various parameters : chemical nature and purity of the samples, thermal and mechanical treatments, radiation intensity and irradiation temperature. We limited our investigations to the temperature range between 77 K-250 K because for most

alkali halides, the H center is the only thermally mobile defect at these temperatures [5].

1. Experimental procedures. — We will only consider results on KBr which can be considered as a typical alkali halide. The crystals are of two origins : Harshaw, with only few ppm of impurities [6] and Korth, more impure and containing a few ppm of sodium [7, 8].

The samples are irradiated with medium energy electrons at a temperature regulated between 77 K and 300 K. The optical absorption of the F band is measured continuously under electron irradiation [9].

For KBr, taking into account the energy deposition rate $\dot{E}$, which can vary between

$$10^{19} \text{ and } 5 \times 10^{21} \text{ eV/cm}^3 \cdot \text{s},$$

the penetration depth of the irradiation, the defect production energy and the secondary reactions, which govern the kinetics, we can measure F center concentrations over three orders of magnitude ($10^{16}/\text{cm}^3$ to $5 \times 10^{19}/\text{cm}^3$) with irradiation times of about 10^3 seconds.

(*) Equipe de recherche associée au C. N. R. S.

2. Experimental results. — **2.1 F CENTER CREATION AS A FUNCTION OF IRRADIATION TIME.** — The figures 1 and 2 show that the F centers grow with irradiation time t following the relations :

$$DO(F) \sim t^{0.8} \quad \text{for Harshaw crystals}^{(1)} \quad (1)$$

$$DO(F) \sim t^{0.5} \quad \text{for Korth crystals}^{(1)} \quad (2)$$

$DO(F)$: optical density of the F band.

FIG. 1. — Growth kinetics of F centers in KBr (H) irradiated with electrons ($V = 20$ kV, $j = 2$ $\mu\text{A}/\text{cm}^2$, $T = 77$ K).

FIG. 2. — Optical density at the F band maximum as a function of the square root of time in KBr (K up) ($V = 30$ kV, $j = 1$ $\mu\text{A}/\text{cm}^2$, $T = 90$ K).

This power law is valid over two orders of magnitude for center concentration and energy dose.

KBr samples of both origin have been also irradiated at 77 K with a smaller energy deposition rate to see the presence of a *first coloration stage* before the laws (1) and (2).

We have given some evidence of a first coloration stage of exponential type up to 4×10^{17} F centers/ cm^3

⁽¹⁾ We shall note the crystals of Harshaw and Korth respectively by the symbols H and K up.

in KBr. This stage corresponds to the formation of $H_A(\text{Na})$ centers by trapping of mobile interstitials by the sodium impurities [10].

In KBr (H), the F center kinetics does not show any first stage of coloration and the relation (1) is good from $10^{16}/\text{cm}^3$ to $10^{19}/\text{cm}^3$. Some KBr (H) crystals doped by heterodiffusion with various monovalent and divalent impurities show a F center growth kinetics according to a square root of irradiation time [9].

2.2 F CENTER GROWTH AS A FUNCTION OF THE ENERGY DEPOSITION RATE. — The energy deposition rate per unit volume $\dot{\varepsilon}$ is :

$$\dot{\varepsilon} = \frac{Vj}{ed} \quad (3)$$

with e : electron charge,

d : penetration depth of the electrons accelerated with a high voltage V .

We have shown that the F center concentration increases according to :

$$F = K' \dot{\varepsilon} t^{0.8} \quad \text{for KBr (H)} \quad (4)$$

$$F = K(\dot{\varepsilon} t)^{0.5} \quad \text{for KBr (K up)} \quad (5)$$

2.3 INFLUENCE OF THE IRRADIATION TEMPERATURE T_i . — For the impure samples of KBr (K up) between 77 K and 120 K, the number of F centers increases proportionally to the square root of the irradiation time according to (5)

from 5×10^{17} to 10^{19} defects/ cm^3 ,

K increasing with the irradiation temperature. For $T_i > 140$ K, the relation (5) is not valid and the F center kinetics varies according to the law (1) found in KBr (H) (figure 3).

Contrary to impure samples, no law change is observed in KBr (H) between 77 K and 145 K, the constant K' only increases with T_i (Fig. 3).

FIG. 3. — Growth kinetics of F centers in KBr (K up) at 77 K ($\star$) and 145 K ($\star$), in KBr (H) at 77 K ($\bullet$) and 145 K ($\circ$) ($V = 20$ kV, $j = 2$ $\mu\text{A}/\text{cm}^2$).

It appears then clearly that the growth kinetics shape of the F centers is related to the number of impurities able to stabilize the mobile interstitials.

3. Discussion. — 3.1 INTRODUCTION OF THE MODEL.

— The growth kinetics of F centers is function of the secondary reactions taking place after the primary Frenkel pair creation process. The F center creation rate is then fixed by the competition between various secondary thermally activated processes : a free interstitial can either recombine with a F center or be trapped by impurities.

However, Agullo Lopez *et al.* [11] have supposed, to interpret the growth kinetics of F centers in NaCl X-irradiated at 300 K, that the interstitials were stabilized in the form of clusters homogeneously nucleated at di-interstitials formed by random collision of two migrating interstitials. In this model, it is easy to show that the number of nuclei is a function of irradiation density [12]. This is in discrepancy with Hobbs' observations in electron microscopy which show that the density of aggregates is not affected by the variation of $\dot{\epsilon}$ over three orders of magnitude [13].

Recently, we have shown that a few ppm of impurities are sufficient for the interstitial cluster nucleation to take place only on the residual impurities and not by an homogeneous nucleation process [10]. It seems then that clustering of free interstitials by random collision of two migrating H centers cannot be considered as the first step in the formation process of aggregates.

For the quantitative investigation of the results we start with the following reaction equations which are based on the treatment of diffusion-limited reactions by Waite [14] :

$$\begin{aligned} \frac{di}{dt} &= \alpha \dot{\epsilon} - 4\pi D R_F i F - 4\pi D R_T i T \\ \frac{dF}{dt} &= \alpha \dot{\epsilon} - 4\pi D R_F i F. \end{aligned} \quad (6)$$

In these equations i , F and T are respectively the concentrations of free interstitials, F centers and traps. We suppose that T is constant. α is the primary production efficiency of Frenkel pairs, $\dot{\epsilon}$ the energy deposition rate per unit volume. D is the diffusion coefficient for mobile interstitials. R_F is the reaction radius of a F center for the recombination with a migrating interstitial and R_T is the capture radius of the trapping impurity.

In this model, the interstitial interaction with F centers (or traps) is described by a spherical interaction volume. Out of this sphere, the halogen interstitial can migrate freely and as soon as it enters into it, the corresponding reaction (recombination or stabilization) takes place.

3.2 INTERPRETATION OF THE RESULTS. — The set of equations (6) leads to the following relation at times larger than the interstitial lifetime :

$$\frac{dF}{dt} = \alpha \dot{\epsilon} \frac{R_T T}{R_T T + R_F F}. \quad (7)$$

The reciprocal damage rate :

$$\frac{dt}{dF} = \frac{1}{\alpha \dot{\epsilon}} \left(1 + \frac{R_F}{R_T T} F \right) \quad (8)$$

is more convenient, because its deviation from linearity shows whether R_T is constant or not.

The figure 4 shows this quantity (determined from the kinetics of figures 1 and 2) as a function of the F center concentration. The difference in the behaviour of both sorts of crystals is clearly seen.

Fig. 4. — Reciprocal damage rate $dt/d(DO_F)$ as a function of F center concentration in KBr (K up) (▲) and KBr (H) (○) (the analyzed curves are the kinetics of figures 1 and 2).

3.2.1 Ultra pure crystals. — In the very pure samples of Harshaw, $R_T T$ increases as a function of irradiation time. T being supposed constant, the capture cross section of traps must vary with the number of trapped interstitials, i. e. with the cluster size.

We can therefore determine the variation of the trapping radius of the interstitial aggregates as a function of the number of F centers created (Fig. 5). We have to expect a complex variation of the quantity R_T in this case. If the interstitials are well separated around the impurity, they can be treated as individual entities ; in this case, R_T is simply the sum of the capture radius of the impurity R_{TO} and of the trapping radius of each stabilized interstitial R_i . If the interstitials are more numerous and lie close together, the

Fig. 5. — Trapping radius R_T of the interstitial clusters as a function of F center concentration in KBr (H). (The scale is R_T multiplied by the constant T/R_F .)

inner ones are screened by the outer ones and the effective radius R_i of a stabilized interstitial decreases with increasing number of interstitial per cluster. Therefore, by :

$$R_T = R_{TO} + \frac{F}{T} R_i \left(\frac{F}{T} \right) \quad (9)$$

we can describe the evolution of R_T (F/T = average number of interstitials per aggregate).

From (9) and figure 4, we find for the pure crystals :

$$\frac{R_{TO}}{R_F} T \simeq 2 \times 10^{15} / \text{cm}^3.$$

We think that we have formation of clusters of V_4 centers which are di-interstitials [15].

These V_4 centers are certainly formed by interaction between a mobile H center with another H center which is temporarily stabilized by the impurity or the aggregate [10]. These ideas are in accordance with the fact that the H center trapped by a defect or by an impurity distorts the lattice and interacts efficiently with another H center which moves thermally [16, 17].

So, in the ultra pure crystals, the F centers growth kinetics can be accounted for by the growth of aggregates of V_4 centers nucleated at some residual impurities and having a capture cross section increasing with their size.

3.2.2 Impure crystals. — For the impure samples of Korth, R_T is constant versus F centers concentration (Fig. 4). We find $R_T \cdot T / R_F \simeq 1.5 \times 10^{17} / \text{cm}^3$. This behaviour is typical of non saturable traps (with a constant capture cross section). At high concentrations of defects ($R_T T \ll R_F F$), the relation (7) shows that the F center kinetics will be a square root law as a function of irradiation dose, which is experimentally observed.

Qualitatively it seems reasonable to suppose that

in crystals where many nucleation sites exist, the interstitial clusters have small sizes [13] and their capture cross section must be determined by a strain field which does not depend on the size of agglomerates.

Considering our experimental results, we shall suppose that the sodium impurity is responsible for this behaviour. Indeed, the transition from relation (2) to relation (1) for a 145 K irradiation seems obviously connected to the fact that $H_A(\text{Na})$ centers are no longer stable beyond 120 K [15].

Moreover, this is confirmed by the fact that crystals doped with a few ten ppm of lithium, follow at 145 K a square root law after a first exponential stage [10]. Now the $H_A(\text{Li})$ center is stable up to about 240 K [15].

Monovalent impurities (sodium or lithium) are saturable traps (H_A center formation), but they can also act as nucleation sites for the growth of small aggregates. A H center highly distorts the lattice [16]. We can then suppose that a H center temporarily trapped around one H_A center has an important capture cross section for a mobile one. So, there is a high probability to form small clusters of di-H (V_4 center) which can act as non saturable traps around the impurity.

Conclusion. — In alkali halides irradiated at 77 K the reaction rate of defects is fixed by the secondary reactions of the interstitial after the primary production of the Frenkel pair : non correlated recombination with F centers or trapping by impurities.

The F center kinetics shape is a function of the number of impurities which can act as nucleation sites. In ultra pure crystals, big clusters having a capture cross section increasing with their size are created. In the impure ones (specially with monovalent impurities like sodium) these impurities act as nucleation sites for small size clusters which are non saturable traps.

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DISCUSSION

L. W. HOBBS. — I would like to make a comment about your non saturable interstitial traps. We know of course from electron microscopy, that these traps are associated with interstitial dislocation loops. The number of such loops continuously decreases with increasing irradiation dose due to the possibilities of

coalescence of close loops. On the other hand, as the loops grow larger, their strain field in general extend to increasingly larger distances. Both effects will influence your phenomenological capture radius although in opposite senses.