Kinetics of F-center formation and interstitial stabilization mechanism in alkali halides irradiated at 77 K *

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In pure crystals of KBr electron irradiated at 77 K, the F-center concentration is proportional to the 0.8th power of the irradiation dose and the dose rate dependence of the defect formation is very small. A model is proposed in which the F creation rate is fixed by the secondary reactions taking place after the primary Frenkel pair creation: recombination of free interstitials with F centers and interstitial capture by traps. To account for all our experimental results and electron microscopy observations, we show that clusters of V_4 centers (di-interstitials) are nucleated inhomogeneously in the proximity of some residual impurities. The V_4-center cluster originates from the interaction between a mobile interstitial and another one temporarily trapped by an impurity, and develops then by capture of H-center pairs. We put in evidence a dependence of the interaction volume on the cluster size.

I. INTRODUCTION

It is now rather well known that, in alkali halides, the nonradiative recombination of an electron with a self-trapped hole generates an F center and its complementary interstitial defect, the H center, that is an interstitial halogen atom.[1,2] The F centers are immobile up to high temperatures (above 400 K) whereas H centers become mobile at quite low temperature (above 40 K in KBr).[3]

Thus the fate of the F and H centers which are the primary defects depends in a complex way on the irradiation conditions, the temperature, and the crystal purity. The question we are concerned with in this publication is "What is the stabilization process necessary for the halogen interstitial to avoid its quick recombination with F centers and to produce stable defects at 77 K?" Little very direct verification of the structure of the interstitial center produced above liquid-nitrogen temperature has been obtained. The optical measurements show that among interstitial centers only the V_4 centers are produced at 77 K in very pure crystals.[4] There are many evidences that the V_4 center is a defect involving two interstitial halogen atoms.[4-6]

On the other hand, electron-microscopy observations showed that irradiation at low temperatures leads to the formation of perfect interstitial dislocation loops which require both interstitial halogen and interstitial alkali metal.[7,8] The currently accepted explanation for the growth of such loops is that when two H centers come together (either as a result of their thermally activated movement or during their production) they com-

bine to form a halogen molecule which then "digs its own hole" in the lattice by displacing a lattice anion and a neighboring lattice cation on to the edge of the dislocation loop, the molecule then occupying the pair of sites so vacated.[7,9,10]

Another problem is what takes place in the initial nucleation stage of the loop: Is the nucleation homogeneous or heterogeneous even in the purest crystals presently obtainable?

To understand all these problems, we propose to study the macroscopic production kinetics of defects which are not related to the primary process but only to the defect interaction and defect migration.[11,12] This method is often successfully used by scientists working in the field of irradiation defects in metals though they do not create optically active defects as in alkali halides.[13,14]

Actually, in spite of a great number of experimental results and although kinetics equation for alkali halides have been given by several authors,[3,12,15,16] a model generally accepted has not yet been proposed. This is due to the fact that the various authors obtained very-different-form creation curves because of very different experimental conditions: irradiation temperature, dose rate, crystal purity.

We have systematically studied the growth kinetics of F centers up to high concentrations in very pure alkali halides irradiated with electrons as a function of various parameters (energy deposition rate, temperature). We limited our investigations to the temperature range between 77 and 250 K because for most alkali halides the H center is the only thermally mobile defect at these temperatures.[3] Careful analysis of the results taking into

account all the experimental results lead us to a more conclusive model for the mechanism of the stabilization process of the halogen interstitial.

II. EXPERIMENTAL CONDITIONS

All our results have been obtained using pure KBr crystals purchased from the Harshaw Chemical Company. We will only use results on KBr which can be considered as a typical alkali halide. Harshaw crystals contain only a few ppm of impurities.[17]

The samples are irradiated with medium-energy electrons at a temperature regulated between 77 and 300 K. We measure continuously the optical absorption of the F band during the electron irradiation. Because of the small penetration depth of the electrons, the energy deposition rate ϵ which can easily vary between 10^{19} and 5×10^{21} eV/cm^3 sec, and of the defect-production energy it is possible to measure the optical density at high concentrations of F centers (from 10^{16} cm^{-3} to 5×10^{19} cm^{-3}) with rather short irradiation times (maximum of 10^3 sec).

The typical dose rate used is $\epsilon = 10^{20}$ eV/cm^3 sec which leads to a typical defect generation rate of 10^{17} cm^{-3} sec^{-1} because about 10^3 eV are necessary to create a Frenkel pair in KBr at 77 K.[18]

III. EXPERIMENTAL RESULTS

A. F-center creation as a function of irradiation time

Figure 1 shows that the F centers grow with irradiation time t following the relation
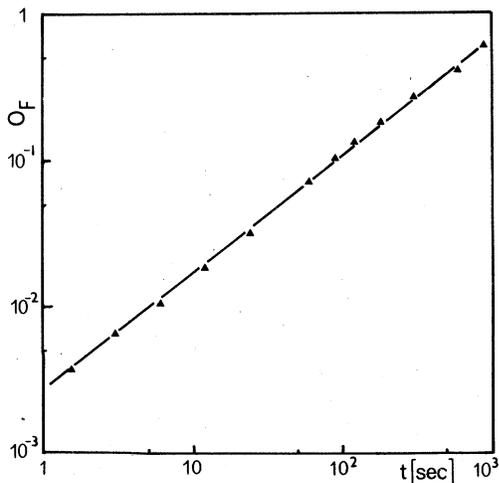
FIG. 1. Growth kinetics of F centers in ultrapure KBr irradiated with electrons ($V=20$ kV, $j=2$ μA/cm^2, $\Theta = 77$ K). An optical density of 1 corresponds to 10^{19} F centers/cm^3.
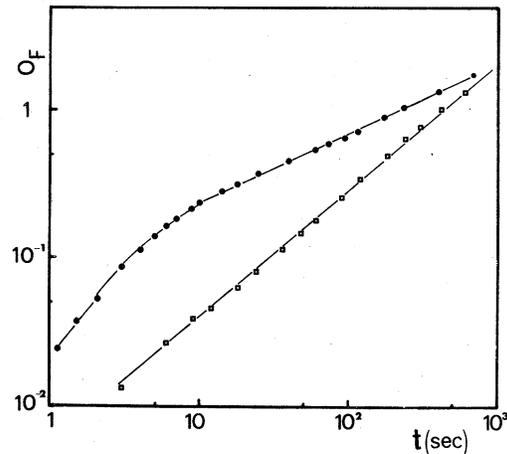
FIG. 2. Growth kinetics of F centers in KBr under electron irradiation ($V=45$ kV, $j=2$ μA/cm^2, $\Theta = 77$ K) in KBr (Harshaw) and KBr (Korth). An optical density of 1 corresponds to 5×10^{18} F centers/cm^3.

$$O_F \sim t^{0.8}, \tag{1}$$

where O_F is the optical density at the maximum of the F band.

This power law is valid over two orders of magnitude for center concentration and three orders of magnitude for dose. KBr samples of Harshaw origin and of Korth origin which are known as much more impure[19,20] have been also irradiated at 77 K with a smaller energy deposition rate to see the presence of "a first coloration stage" before the law.[1] Figure 2 gives some evidence of such a "first stage" up to 4×10^{17} F centers/cm^3 in KBr (Korth) which is due to the formation of H_A(Na) centers by trapping of mobile interstitials by sodium impurities.[20] In KBr (Harshaw), there is no evidence of a first coloration stage and the relation (1) is valid from 10^{16} cm^{-3} up to 10^{19} cm^{-3}.

B. F center growth as a function of the energy deposition rate

The energy deposition rate per unit volume ϵ on a crystal irradiated by electrons is

$$\epsilon = Vj/ed \tag{2}$$

with d the penetration depth of the electron accelerated with a high voltage V (the penetration depth laws of electrons in alkali halides are always of the form $d \propto V^m$, for KBr $m=1.7$)[21]; j is the density of the electron beam, V is the accelerating voltage of the electrons, and e is the electron charge.

Figure 3 shows that for a fixed irradiation time and accelerating voltage the F-band optical density is proportional to j:

$$O_F \propto j.$$
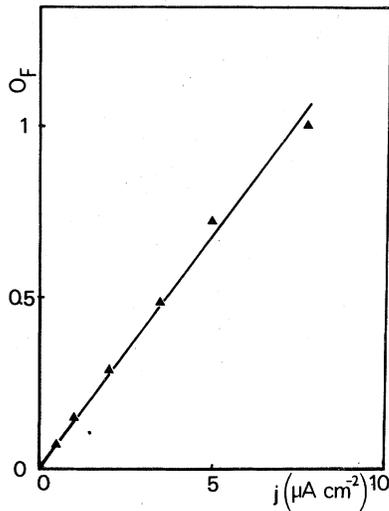
FIG. 3. Optical density at the *F*-band maximum as a function of the elctron density *j* in pure KBr (irradiations during 5 min at $V = 20$ kV, $\Theta = 77$ K). An optical density of 1 corresponds to 2×10^{19} *F* centers/cm^3.

Then with Eqs. (1) and (2)

$$O_F \propto \epsilon t^{0.8} . \tag{3}$$

If we recall that Eq. (2) is written with the hypothesis that the deposition rate is homogeneous, therefore the coloration profile is also homogeneous and the *F*-center concentration under irradiation at 77 K increases according to

$$F = K' \epsilon t^{0.8} . \tag{4}$$

It is possible to check this relation by measuring on different samples the *F*-center optical density as a function of *V* (with fixed *j* and *t*). We have

$$O_F \propto Fd ,$$

then with (2) and (4)

$$O_F \propto V .$$

The *F*-center optical density is porportional to the accelerating voltage of the electrons (Fig. 4). Relation (4) shows that the dose rate dependence of the defect formation is relatively small.

C. Influence of the irradiation temperature θ

We limited our investigations to the range of temperature where only the *H* centers are mobile and the vacancies are frozen in (typically from 77 to 200 K in KBr).[3] It is evident that the phenomena become much more complicated when we must take into account secondary reactions due to the mobility of vacancies.[22]

No law change is observed in KBr in this temperature range and the constant *K'* only increases with Θ (Fig. 5) according to
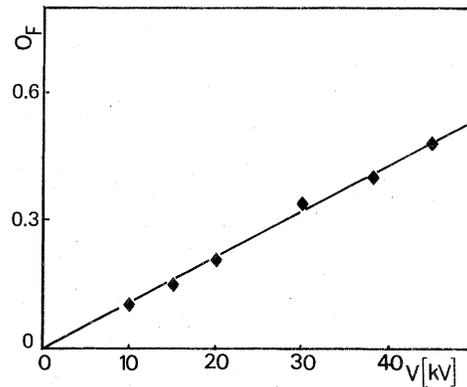
FIG. 4. Optical density at the *F*-band maximum as a function of the electron accelerating voltage *V* in pure KBr (irradiations during 3 min, $j = 2$ μA/cm^2, $\Theta = 77$ K).

$$K' \propto \exp(-W/k\Theta) \tag{5}$$

with $W = 0.023 \pm 0.005$ eV.

D. Influence of various treatments before irradiation

It is well known that the form of the kinetics curves depends notably on the various mechanical and thermal treatments that samples have undergone.[3] We have studied three types of treatments able to modify the crystal state before irradiation: (i) a plastic deformation, (ii) a doping of the pure Harshaw crystals, (iii) an electron preirradiation at 300 K.

1. Plastic deformation at 300 K

A 5% cold work does not change (in a limit of 10%) the concentration of *F* centers created for a fixed irradition time and the form of the kinetics.
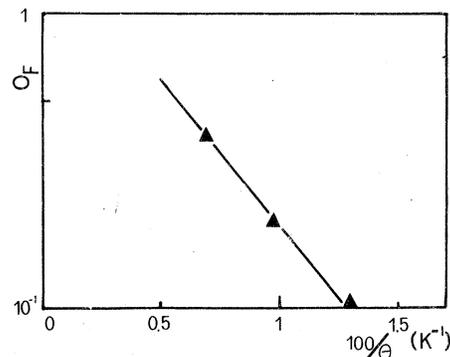
FIG. 5. Variations of *K'* as a function of irradiation temperature in KBr (we simply put the optical density obtained after 400 sec of irradiation).

2. Doping of pure crystals

We have doped some KBr (Harshaw) crystals by heterodiffusion with various monovalent and divalent impurities. After a first coloration stage, the growth kinetics of F centers is no more a $t^{0.8}$ law but varies according to a square root of irradiation time.[23]

3. Preirradiation at 300 K

An electron irradiation at 300 K up to an F-center density of about 1.5×10^{18} cm^{-3} followed by a coloration at 77 K does not affect the kinetics parameters in the range of the concentration we study.

IV. INTERPRETATION AND DISCUSSION

We must explain the experimental observations that the vacancy concentration is proportional to the 0.8th power of the irradiation dose and that the formation rate is practically independent of the dose rate. We can note that in the same range of concentrations a similar relation has been obtained by Sonder for KCl,[16] and that Sonder has also found that the growth of the F center is almost independent of the dose rate.[16] The model must also take into account the fact that the interstitial centers are V_4 centers involving two interstitial halogen atoms and forming interstitial clusters. By the cluster, it is simply meant that the distribution of the V_4 center is not uniform but rather concentrated under the influence of a long-range lattice distortion.

A. Introduction of the model

The F-center creation rate is a function of the various thermally activated secondary processes taking place after the primary Frenkel-pair creation event: a free-halogen interstitial can either recombine with an F center or be trapped in some unknown place. For the quantitative investigations of our results we start from the following reaction equations which are based on the treatment of diffusion-limited reactions by Waite[24]:

$$\frac{di}{dt} = \alpha\epsilon - \sigma_F iF - \left(\frac{di}{dt}\right)_s ,$$
$$\frac{dF}{dt} = \alpha\epsilon - \sigma_F iF \tag{6}$$

with i and the F concentrations of free-halogen interstitials and F centers; α is the primary production efficiency of Frenkel pairs, and σ_F is the coefficient which fixes the recombination rate between interstitials and vacancies ($\sigma_F = 4\pi R_F D$ with R_F the reaction radius for recombination of F and

H centers, and D is the interstitial diffusion coefficient).[25] $(di/dt)_s$ is the stabilization rate of interstitials by all the possible processes.

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

It is easy to show that the set of our experimental results is not in agreement with the solutions of the kinetics equations (6) in the following cases (see Appendix A):

(a) The interstitials are trapped by saturable traps. This would lead to a quasiexponential law for the formation kinetics of the F centers with a saturation value.[20]

(b) The traps are nonsaturable: their concentration and their capture cross section are constant. If $\sigma_T T \ll \sigma_F F$ we find that the F-center concentration follows a square-root law as a function of dose. Durand et al.[15] and Sonder[16] proposed such a model to interpret the experimental F-center creation in LiF and KCl.

(c) Isolated di-interstitial centers (V_4 centers) are formed by random collision of two free interstitials. In this case the F-center density would obey

$$F \propto \epsilon^{2/3} t^{1/3} . \tag{7}$$

All the kinetics equations comprising processes (a), (b), and (c) cannot account for the experimental observations that the vacancy concentration is given by (4) and that the growth curve is not dependent on the dose rate.

B. Nucleation of the clusters

It has been shown by Hobbs et al.[7] that the clusters of interstitials are formed even at liquid-nitrogen temperature where the interstitial centers show exclusively the V_4 absorption band.

The clusterization should take place in such a way that the electronic structure of each V_4 center is not strongly influenced. Therefore it is suggested that an interstitial is stabilized temporarily in the vicinity of a V_4 center under the influence of the strain field and the temporary stable interstitial atom in turn traps another interstitial atom to become a V_4 center. This new V_4 center may be separated from the original V_4 center by a distance of probably a few lattice spacings. Repetition of such processes results in the clusterization of the V_4 center. Such kind of clusterization of the interstitial atoms may lead to the clusters of the di-interstitials suggested by Hobbs to explain the results of the electron microscopic

observations.[7]

These clusters can be nucleated either homo-geneously or heterogeneously but what takes place in the initial nucleation stage of the loop is not yet clear. Agullo-Lopez and Jaque,[26] in order to interpret the growth kinetics of F centers in NaCl x irradiated at 300 K, have supposed that the interstitials were stabilized in the form of clusters homogeneously nucleated at di-H centers formed in the perfect lattice by the random collision of two migrating interstitials. In this model often used for metals, it is easy to show that the number of nuclei is a function of irradiation density.[27] This is not in agreement with Hobbs' observations which show that the density of aggregates is not affected by the variation of ϵ over three orders of magnitude and that impurity doping is known to make the clusters distributed sparsely: a large number of small clusters is formed.[7] Therefore there is little doubt that the nucleation is hetero-geneous and involves impurity ions even in the purest crystals presently obtainable. Moreover, homogeneous nucleation would lead to loop densities one or two orders of magnitude lower than observed.[28]

We suppose that a defect serves as a nucleus of the clusterization and the structure of the cluster is the densely populated V_4 center in the proximity of the defect. The nucleation of the clusters occurs in the proximity of an impurity. In a very recent work Itoh assumed that the nucleation takes place in a perfect site once a V_4 center is formed.[29]

We make the assumptions that some traps in concentration T cm^{-3} can temporarily stabilize the interstitials during a time τ_s. It is well known that the capture cross section of an H center by an H center already trapped around an impurity to form a di-interstitial is much larger than the one corresponding to the stabilization by an impurity.[30,31] Therefore the temporary trapping of interstitials tends to favor cluster formation.

According to the calculation made in Appendix B, one expects a value of $\Gamma = 10^{-2}$ (ratio of the probability of homogeneous and heterogeneous nucleation) with a reasonable concentration of 10^{16} traps/cm^3. Therefore most of the clusters of V_4 centers are nucleated on impurities and originate from the interaction between a mobile H center and another temporarily trapped by an impurity.

C. Interpretation of the results

The reactions described in the preceding paragraph can be expressed as follows:

perfect lattice $\rightleftharpoons H + F$

$$H + T \rightleftharpoons H_T + T$$

$$H_T + H + T \rightarrow H_2 + T \qquad (8)$$

$$H_2 + H + T \rightleftharpoons (H_2)H_T + T$$

$$(H_2)H_T + H + T \rightarrow (H_2)_2 + T$$
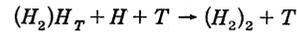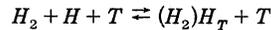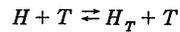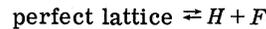
and so on, in which T is the concentration of traps which stabilize the interstitials.

H_T is the H center temporarily trapped at T which distorts the lattice and interacts very efficiently with another free one. The species $(H_2)_n H_T$ are not stable but those denoted $(H_2)_n$ are stable.

Very recently Itoh formulated all the above reactions (8) by a series of simultaneous equations (in this case nucleation is homogeneous and T are the H_2 themselves formed at first).[29]

After a nucleation period which is certainly very short because of the high dose rates used, we can write that we are in stationary conditions for the concentration of the free interstitial:

$$\frac{dF}{dt} = \alpha\epsilon \frac{R_T T_0}{R_T T_0 + R_F F} \qquad (9)$$

with T_0 the concentration of impurities which have a binding energy of the order of the interstitial migration energy, and R_T the trapping radius of the impurities.

$R_T T_0$ must be considered as a mean term because certainly there are various sorts of traps with different capture radii.

The reciprocal damage rate,

$$\frac{dt}{dF} = \frac{1}{\alpha\epsilon}\left(1 + \frac{R_F}{R_T T_0} F\right), \qquad (10)$$

is more convenient because its deviation from linearity shows whether the reaction rate constant of a cluster with interstitials is constant or not.

Figure 6 shows this quantity (determined from the kinetics of Fig. 1) as a function of F-center concentration and hence of the cluster size. In the very pure crystals, $R_T T_0$ increases as a function of irradiation time and the experimental results are interpreted by the growth of clusters having a capture cross section increasing with their size.

If $R_T T_0 \ll R_F F$ and R_T is a function of the number of trapped interstitial, relation (10) gives an F-center growth curve of the form

$$F \propto (\alpha\epsilon t)^n \quad \text{with } \tfrac{1}{2} < n < 1. \qquad (11)$$

For example, if R_T is only a geometrical cross section proportional to the circumference of the dislocation loops, that is, $R_T \propto (F/T_0)^{1/2}$, we found that the F center kinetics will obey
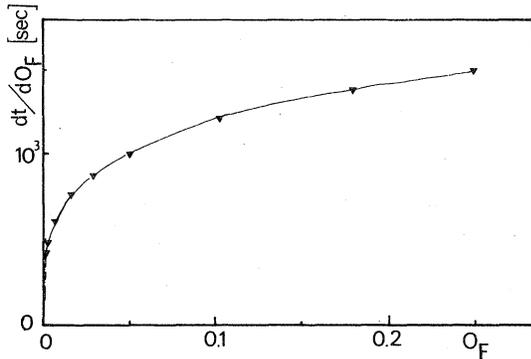
FIG. 6. Reciprocal damage rate dt/dO_F as a function of F-center concentration in pure KBr (the analyzed curve is the kinetics of Fig. 1).

$$F \propto (\alpha \epsilon t)^{0.66}. \qquad (12)$$

From results of Fig. 6, we can determine the variation of the trapping radius of the interstitial aggregates as a function of the number of F centers created (Fig. 7). As a matter of fact, we have a complex variation of R_T with F/T_0 for V_4 centers clusters. If the V_4 centers are well separated, they can be treated as individual entities: in this case R_T is simply the sum of the capture radius of the impurity R_{T_0} and of the trapping radius of each stabilized interstitial R_i. The above assumption is certainly an overestimate of the cluster growth and hence of the vacancy formation yield since the strain field of each constituting the V_4 center may overlap. In fact, in the clusters the inner interstitials 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

$$R_T = R_{T_0} + \frac{F}{T_0} \cdot R_i \left(\frac{F}{T_0} \right) \qquad (13)$$

we can describe the evolution of R_T.
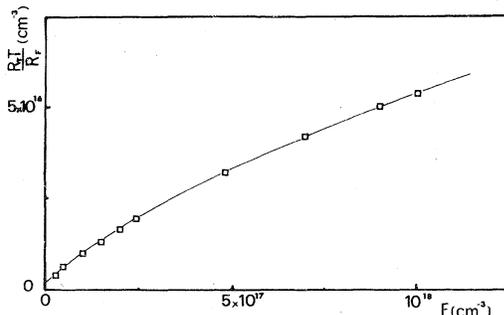
FIG. 7. Trapping radius R_T of the interstitials clusters as a function of F-center concentration in pure KBr (the scale is R_T multiplied by the constant T/R_F).

In this relation F/T is the average number of interstitials per aggregate, R_{T_0} is the trapping radius of the trap that acts as nucleus, and R_i is the contribution of each stabilized interstitial at the cluster trapping radius.

From (13) and Fig. 6, we find for the pure crystals

$$(R_{T_0}/R_F)T_0 \approx 2 \times 10^{15} \text{ cm}^{-3}. \qquad (14)$$

The present model can explain the broad features of the experimental observations, i.e., the quasi-lack of the dependence on the dose rate and the $t^{0.8}$ dependence. Furthermore it gives an idea of the nucleation of the interstitial clusters.

The small dependence of F as a function of the dose rate can be explained either by a distribution of the cluster size which would be a function of ϵ or by a small homogeneous nucleation rate (by formation of V_4 centers in the perfect lattice).

D. Discussion

1. Behavior as a function of the irradiation temperature θ

Relations (4) and (9) show that the coefficient K' is a function of α, R_T, and R_F. By supposing that the trapping radii and the number of traps remain constant in the range of temperatures 77-200 K, F is a function of Θ if α varies with Θ. Taking into account (4) and (9) and though relation (9) cannot be integrated because of the complex variation of R_T with F (Fig. 6), we are waiting for α to appear as ϵ in K'.

From our experimental results, K' varies exponentially with Θ with an activation energy of 0.023 ± 0.005 eV (Fig. 5). From the model this implies that the primary production efficiency of the Frenkel pairs follows an Arrhenius law:

$$\alpha = \alpha_0 \exp(-E/k\Theta), \quad E = 0.023 \pm 0.005 \text{ eV}. \qquad (15)$$

The variation of $\alpha(\Theta)$ and the value of the activation energy E of the process is in very good agreement with the value found by measuring $\alpha(\Theta)$ from kinetics of disappearing F_2 centers by interstitial capture.[18,32] At present, it is not clear if the increase of α with Θ is due to an increase of the escaping process by a statistical increase in the F-H average distance either because of the primary energy distribution,[2] or because of a thermally activated migration process on the distance covered by the crowdion,[33] or because of the correlated recombination probability depending on the temperature due to the form of the F-H interaction at small distances.[32]

The experimental result of the increase of α following an Arrhenius law found by measuring F-center kinetics at different temperatures brings,

however, a precise criterion for verification of the proposed model for defect accumulation under irradiation at 77 K.

2. Behavior as a function of the various treatments (plastic deformation and doping)

A 5% plastic deformation does not change the form and the parameters of F-center coloration kinetics. This result is coherent with the proposed model. If we suppose a concentration of traps of 10^{16} cm^{-3} in pure crystals and that a length of 10 Å characterizes these traps at the beginning of irradiation for interstitial trapping, the capture total length (10^9 cm/cm^3) is then about three orders of magnitude more important than the total length of the dislocations introduced by the coldwork (about 5×10^7 cm/cm^3 according to Ref. 34).

This rough estimation is in good agreement with that of Hobbs et al.[7]: it is necessary to have a dislocation density of about 10^9 cm/cm^3 to present the nucleation of the loops usually observed in as-cleaved crystals.

The introduction of impurities in pure crystals changes the kinetics. It is known that impurities have two main effects on the coloration curves: on the one hand, they increase defect production at 77 K by a factor of 2 to 5; on the other hand, they produce a more important curvature of the kinetics.[35] This effect has been found for monovalent as well as for divalent impurities and cannot be due to the chemical properties of the dopant. By arguing very qualitatively, it seems reasonable to suppose that in crystals where many nucleation sites exist, the interstitial clusters have small sizes and their capture cross section must be determined by a strain field which in first approximation does not depend on the size of agglomerates. This behavior of nonsaturable traps explains the square root of dose found in impure crystals.[12]

3. Discussion of traps

Figure 8 gives a diagram for the interaction potential model between a trap and an interstitial. The interaction can be divided in two parts [Fig. 8(b)]: (i) a very high interaction near the trap which leads to a mechanical instability of interstitials (in the case of vacancies) or to a deep trapping (in case of impurities). This region of high interaction is "the absorption region"; (ii) out of this domain, there is a small long-range interaction as the elastic interaction.

Schroeder et al.[36,37] have shown that for isotropic attractions the effective radius of reaction is approximatively given by the distance at which the gain in potential energy is equal to the thermal
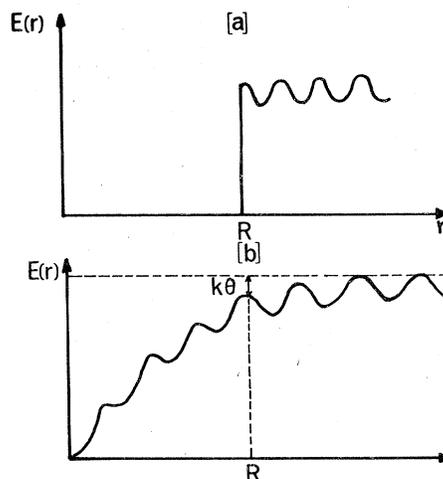
FIG. 8. Interaction potentials (schematic) (a) cutoff potential which defines the reaction radius R; no interaction for $r > R$. (b) Long-range potential: R is approximatively determined by the point where the potential energy gained equals the thermal energy: $-E(R) = k\Theta$.

energy:

$$-E(R) = k\Theta. \tag{16}$$

The mechanism of the stabilization of the interstitial appears to be due to elastic interaction. This interaction between the H center and other defects has been calculated by Dienes et al.,[38] Bachmann and Peisl,[39] and Diller.[10]

Table I give the interaction radii of an interstitial atom with different traps calculated from Bachmann and Itoh's results[4,39] using Schroeder's criterion. The large difference between the interaction volume of an H center has been ascribed to the largeness of the elastic distortion around the H center.

These values are in good agreement with Saidoh's results for the interaction volumes obtained from the dynamic experiment and the thermal annealing experiments.[5,33]

From the kinetic analysis of the F-center coloration curves, we can estimate the ratio R_{T_0}/R_F from (14) by taking an approximate concentration of impurities of 5×10^{15} cm^{-3}:

$$R_{T_0}/R_F = 0.4 .$$

This value is in rather good agreement with the ratio of R_{Na}/R_F in Table I. As the Na impurity is typical of the traps which can act as a nucleation center, we can conclude that the experimental results are consistent with theoretical calculations on interactions between H center and traps in alkali halides.

In our model we suppose that the concentration

TABLE I. Interaction radius between an intersitial and the Na impurity, the F center, and another H center (unit of atomic distance) from Refs. 4 and 39.

R_{Na}	R_F	R_H
1	1.8	3.2

of traps remains constant. This is certainly a very crude approximation since electron microscopy observations show that the number of interstitial dislocation loops can decrease with increasing irradiation dose due to the possibilities of coalescence of close loops.[40] On the other hand as the loops grow larger, their strain fields extend to increasingly larger distances. Both effects can influence our phenomenological capture radius although in opposite senses.

4. Experimental verification of the proposed model: F_2 center disappearing by recombination with free interstitials

From relation (9) it is easy to show that if we create an excess of F_2 centers at 77 K, the F_2 centers disappear by recombination with free halogen interstitials according to

$$\frac{dF_2}{dt} = -\alpha\epsilon \frac{R_{F_2}F_2}{R_F F + R_{F_2}F_2 + R_T T_0}, \tag{17}$$

where F_2 and R_{F_2} are, respectively, the concentration and the capture radius of the F_2 center.

If in these experiments, the density of F centers is constant and high enough to make the term $R_F F$ preponderant, the F_2 centers will disappear according to a first-order kinetics, the time constant of which is proportional to the F-center concentration and inversely proportional to the dose rate ϵ (Fig. 9). These results have been analyzed in detail by Sonder[32] and us[18] and support very well the model of interstitial trapping.

In conclusion, the main experimental results on F-center growth kinetics in pure crystals (variations versus time and irradiation temperature, absence of dose rate dependence) can be accounted for by the growth of aggregates of V_4 centers which have a capture cross section increasing with their size. It is concluded that even in pure specimens all interstitial loops are nucleated at some residual impurity sites during irradiation at 77 K.

ACKNOWLEDGMENTS
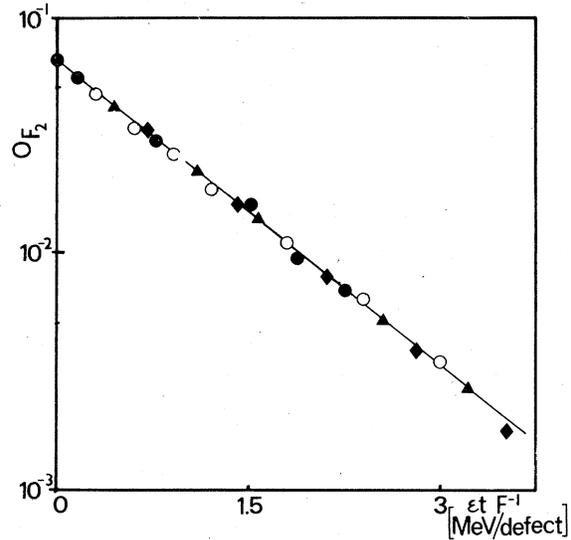
FIG. 9. Decrease of the F_2 band at 77 K as a function of $\epsilon t /F$ for different values of the electronic density j in KBr ($V = 30$ kV; ●, $j = 1$ $\mu A/cm^2$; ○, $j = 2$ $\mu A/cm^2$; ▲, $j = 3.5$ $\mu A/cm^2$; ◆, $j = 4.7$ $\mu A/cm^2$).

APPENDIX A: THEORETICAL F CENTER CREATION KINETICS IN SOME SPECIAL CASES

On the basis of the interstitial-recombination model we can write

$$\frac{di}{dt} = \alpha\epsilon - \sigma_F iF - \left(\frac{di}{dt}\right)_s, \tag{A1}$$

$$\frac{dF}{dt} = \alpha\epsilon - \sigma_F iF.$$

By taking into account the extremely short life of the free interstitial we can consider in accordance with Farge and Sonder that we are immediately in stationary conditions, i.e., $di/dt = 0$.[15,16]

(a) The interstitial traps are saturable: a trap can stabilize only one or two interstitials

$$\left(\frac{di}{dt}\right)_s = \sigma_T iT ,$$

$T = T_0 - F$ (T_0 is the saturable trap concentration at $t = 0$), then

$$\frac{dF}{dt} = \alpha\epsilon \frac{R_T(T_0 - F)}{(R_F - R_T)F + R_T T_0}$$

which yields

$$\left(\frac{R_T - R_F}{R_T}\right) F + \frac{R_F}{R_T} T_0 \ln(1 - F/T_0) = -\alpha\epsilon t . \tag{A2}$$

In the case where $R_T \approx R_F$,[20] the F-center kinetics obey

$$F \approx T_0[1 - \exp(-t/\tau)]$$

with $1/\tau = \alpha\epsilon/T_0$.

(b) Nonsaturable traps:

$$\left(\frac{di}{dt}\right)_S = \sigma_T i T$$

with $\sigma_T T =$ const, then we obtain the expression

$$\frac{dF}{dt} = \alpha \epsilon \frac{R_T T}{R_T T + R_F F}$$

which gives if $R_T T \ll R_F F$:

$$F \simeq (2\alpha R_T T/R_F)^{1/2}(\epsilon t)^{1/2} \,. \qquad (A3)$$

(c) Formation of di-interstitials by interstitial aggregation at random

$$\left(\frac{di}{dt}\right)_S = \sigma_i i^2$$

with σ_i the capture cross section of a free inter-stitial for another free one.

In this case at high irradiation doses to have $4\sigma_i \alpha \epsilon/\sigma_F^2 F^2 \ll i$, the free interstitial density is

$$i \approx \frac{\alpha \epsilon}{\sigma_F F} - \frac{\sigma_i(\alpha \epsilon)^2}{\sigma_F^3 F^3}$$

which yields

$$F \approx [3\sigma_i(\alpha \epsilon/\sigma_F)^2 t]^{1/3} \,. \qquad (A4)$$

APPENDIX B: EVALUATION OF THE RATIO OF THE HETEROGENEOUS AND HOMOGENEOUS NUCLEATION RATE

As traps we understand here impurities which can form rather immobile complexes with the interstitials. These complexes should be stable for some time τ_S after which the interstitial dissociates again from the trap.

According to Refs. 14 and 41 the homogeneous and heterogeneous nucleation rate are, respectively, of the form

$$4\pi D R_{HH} i^2$$

and

$$4\pi D R_{H_T H} i i_T$$

with D the diffusion coefficient of the free interstitial: $r_0^2 \nu_0 \exp(-E_m/k\Theta)$, where r_0 is the distance of a single interstitial jump, ν_0 is the frequency factor, and E_m is the migrating energy of the free interstitial. $E_m = 0.09$ eV in KBr.[5] R_{HH} and $R_{H_T H}$ are, respectively, the interaction radii between two free H centers and between a free interstitial and a temporarily trapped H center; i and i_T are, respectively, the free-interstitial concentration and the trapped-interstitial concentration.

The ratio Γ of the homogeneous nucleation probability to the heterogeneous one will be equal to $\Gamma = i/i_T$ which in turn is equal to the ratio τ_m/τ_S where τ_m is the mean time of the interstitial diffusion between traps $(\tau_m = \frac{1}{4} D R_T T)$.

The defect trapping is described by two phenomenological parameters: the trapping radius R_T and the stabilization time τ_S. According to Refs. 14 and 41:

$$\tau_S = \frac{1}{\nu_0} \exp\left(\frac{E_m + E_L}{k\Theta}\right)$$

with E_L the binding energy of the trapped interstitial.

By making some very reasonable hypothesis, we can estimate the value of Γ. One obtains for $R_T = r_0 = 5 \times 10^{-8}$ cm, $\tau_S = 1$ sec which corresponds to a binding energy of $E_L = 0.11$ eV, $E_m = 0.09$ eV, $\nu_0 = 10^{13}$ sec^{-1}, $\Theta = 77$ K, the value $\Gamma \approx 10^{14}/T$.

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