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# Kinetics of defect accumulation under electron irradiation in KBr at 4 K

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The kinetics of defect accumulation under electron irradiation have been studied in pure KBr in the temperature range where no defect is thermally mobile. Kinetics are given for $F$, $F^+$, $H$, $I$, and $V_k$ centers which constitute the main part of the centers created at 4 K in pure crystals. The concentrations lie up to a few $10^{19}$ cm$^{-3}$ and are measured by optical absorption. In the lower concentration range, the kinetics shapes are well explained by considering a local action of the stabilized interstitial centers on the newly created Frenkel pairs, causing their quick recombination. At concentrations higher than $10^{19}$ cm$^{-3}$, the decrease of the $F$-center creation yield is explained by the possibility of uncorrelated recombinations of the $F$ centers and the $H$ centers moving as dynamical crowdions, because their range becomes larger than the average separation between two centers in the crystal. The initial inhibition process for the creation of new defects is tentatively assigned to the deformation of the lattice in the vicinity of stabilized $I$ centers, causing the impossibility of a sufficient separation of a new Frenkel pair.

## I. INTRODUCTION

Kinetics of defect accumulation have contributed significantly in the past to the understanding of the phenomena involved in the formation and stabilization of defects created by irradiation in the alkali halides, especially at temperatures higher than or equal to 77 K.[1,2] Kinetics in the temperature range where no center is thermally mobile (typically 4 K) have not been extensively investigated, although they are of interest for several reasons, which are: (i) the absence of secondary reactions among mobile defects, (ii) a good knowledge of all elementary centers involved, (iii) results of pulsed experiments showing clearly that the neutral Frenkel pair ($F$ and $H$ center) is created as primary product of the irradiation.[3] So very low-temperature kinetics allow one to study elementary phenomena of defect creation without screening by thermally activated secondary reactions.

A typical feature of kinetics of 4 K is the formation of two kinds of Frenkel pairs: the neutral one ($F$-$H$), and the charged one ($F^+$-$I$). A realistic model for kinetics of 4 K must consider the transformation of the neutral pair into the charged one as a secondary reaction, whose efficiency might depend on the defect concentration in the crystal, because the ratio of the $F$- to the $F^+$-center concentrations varies with the center concentration.[4]

The presence of $F^+$ centers results in trapping of free electrons created as a component of electron-hole pairs, thus in the presence of an important population of $V_k$ centers to compensate their charge[5]: these centers are not stable in the crystal when the irradiation is discontinued, and a slow tunneling recombination among the electron of the $F$ center and the $V_k$ center takes place during ten minutes, accompanied by a phosphorescence. This fact is important for it causes one to observe too many $F$ centers and a smaller number of $F^+$ centers when they are measured under irradiation.

Previous experimental work on kinetics at 4 K concerns mainly the low-concentration range: measurements of the energy necessary to create a stable defect,[4,6] equilibria among centers to determine the structure of centers,[7] and the influence of the impurities on the crystals colorability.[8] The shape of the kinetics has been analyzed in the case of KCl heavily irradiated by protons,[9] but only for $F$ centers which exist in small quantity as compared to the $F^+$ centers at this temperature.

Kinetics at 4 K have also been computed numerically,[10] using rate equations taking into account all the possible reactions among the created centers. The solution gives a quasilinear growth for the sum of the $F$ and $F^+$ centers, with a growth rate saturating at high dose rates. Such equations cannot give a good descritpion of the observed center accumulation because they do not take into account the basically local character of the interactions among centers which is due to their absence of mobility.

This paper's purpose is to present an experimental study of the kinetics of all centers present under irradiation in KBr in 4 K, and to analyze the kinetics shapes by simple models based on local action of centers inhibiting the creation of new Frenkel pairs. KBr is choosen as a model crystal because of its important low-temperature colorability[11] and of the spectral position of its absorption bands, allowing one

TABLE I. Sequence of irradiation and optical absorption measurements in the 100-ms period.

$A$ : $\frac{1}{4}$ period. Irradiation
$B$ : $\frac{1}{4}$ period. Waiting for phosphorescence decay
$C$ : $\frac{1}{4}$ period. Zero compensation. Transmission measurement at $\lambda_1$
$D$ : $\frac{1}{4}$ period. Zero compensation. Transmission measurement at $\lambda_2$

to work in the conventional uv range. In the highest-concentration range, which can be reached relatively quickly with electron irradiation, the decorrelated recombination of $F$ and $H$ centers becomes important, and actually constitutes the limiting process for the growth of concentrations.

## II. EXPERIMENTAL CONDITIONS

All results have been obtained using nominally pure KBr crystals purchased from the Harshaw Chemical Co. The apparatus has been described elsewhere.[12] The 20- to 60-keV electron beam having a density between 0.1 and 20 $\mu$A cm$^{-2}$ creates defects in a thin layer (5.7 $\mu$m at 20 kV to 36.9 $\mu$m at 60 kV) at the surface of the crystal. The energy deposition rate $\dot{\epsilon}$ lies between $10^{19}$ and $2 \times 10^{21}$ eV cm$^{-3}$s$^{-1}$. Varying the electron beam energy allows concentration measurements between $10^{16}$ and $5 \times 10^{19}$ cm$^{-3}$, with optical densities (OD) smaller than 3 at the peak of the absorption bands.

The optical system is shown in Fig. 1 and gives the optical transmission at two wavelengths simultaneously. To avoid perturbation of the optical measurements by the intrinsic luminescence and phosphorescence emitted by the crystal at very low temperature, irradiation and measurements are made periodically, with a cycle described in Table I. To chop the irradiation does not influence the shape of the kinetics. To obtain the concentrations from the OD's, we have used the oscillator strength values listed in Table II; to calibrate $F^+$-center concentrations, we have used results described in a previous paper[5] which refer to equilibria among $F$, $F^+$, and $V_k$ centers when the electron irradiation is discontinued. These results are also used to determine the respective contribution of the $V_k$ and $H$ centers to the 380-nm absorption band, assuming that the purely electronic reaction $F + V_k \rightarrow F^+$ is no longer effective ten minutes after the irradiation has been switched off. So the concentration of $V_k$ centers is experimentally determined to be 6.5% of the sum of the $F$ and $F^+$-center concentrations. This amount corresponds to the number of $F^+$ centers having trapped an electron, and transformed into $F$ centers. So to have the concentrations of centers at the equilibrium, we must subtract it from the number of $F$ centers and add it to the number of $F^+$ centers. All our results will be corrected in this way.

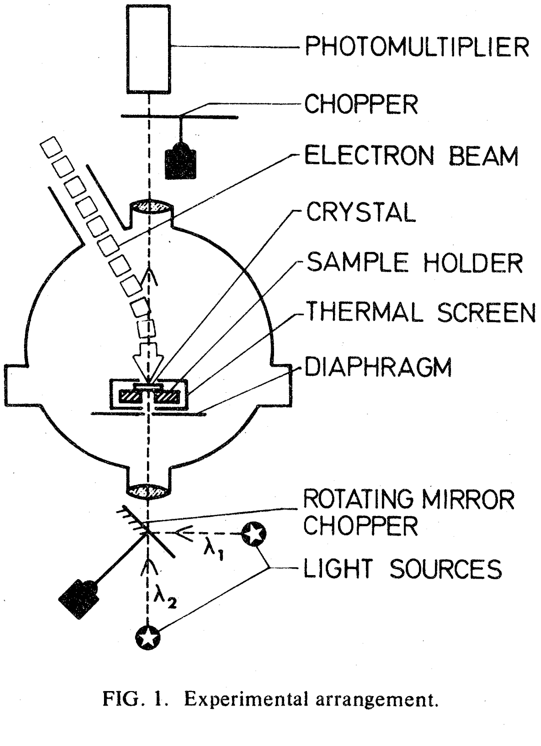

FIG. 1. Experimental arrangement.

TABLE II. Numerical data for KBr at 4 K.

| Center | $F$ | $F^+$ | $H$ | $I$ |
|---|---|---|---|---|
| Absorption (eV) | 2.06 | 6.1 | 3.2 | 5.4 |
| Oscillator strength $f$ (from Ref. 13) | 0.54 | see text | 0.32 | $0.082 f_{F^+}$ |

## III. EXPERIMENTAL RESULTS

Experimental accumulation kinetics have been measured as a function of the dose for all centers. Two general features are first pointed out:

(i) The kinetics depend only on the dose received by the crystal. No dependence on the energy deposition rate $\dot{\epsilon}$ has been evidenced in the range allowed by the apparatus. Furthermore, the energy necessary to create a vacancy center is found to be the same as found under x or high-energy electron irradiation,[6] where $\dot{\epsilon}$ is much smaller. The electron irradiation interruptions of any duration do not trouble kinetics as a function of dose, as pointed out in Ref. 5.

(ii) The total concentration of defects grows monotonically as a function of the dose. This is right for all centers separately, provided there is no transformation or agglomeration between centers, as for $H$ centers agglomerating into $H_2$ centers at concentrations higher than $10^{18}$ cm$^{-3}$.

The kinetics of defects (e.g., $F$ and $F^+$ centers) are all proportional to the logarithm of the dose at their beginning. This is expressed mathematically by

$$x = A \ln(d/B + 1) , \tag{1}$$

where $x$ is the defect concentration, $d$ is the dose, and $A$ and $B$ are phenomenological parameters. This form is the same as the one found by Hughes and Pooley[9] for $F$ centers in KCl at both room and liquid-helium temperature before saturation, where the kinetics are explained by a very simple forbidden volume model; this model provides a basis for the case of KBr at 4 K, where we attempt to give a physical sense to the parameters and notions involved.

To take into account the role of interstitials, we first consider their behavior relative to their complementary vacancy centers. Then, the kinetics of vacancy centers ($F$ and $F^+$ centers) are studied as a function of the dose. An analytical form is found for them and simple models are proposed for several concentrations regimes.

### A. Interstitial centers as complementary to vacancy centers

#### 1. *I and $F^+$ centers*

Because of their charge, two $I$ centers must undergo a repulsive interaction. So there is no possible agglomeration and identical accumulation kinetics for $I$ and $F^+$ centers are to be expected. This is shown in Fig. 2, where different penetration depths have been used because of optical absorption characteristics of the two kinds of centers. The proportionality of the kinetics allows one to replace the $I$-center concentration by the $F^+$-center concentrations.

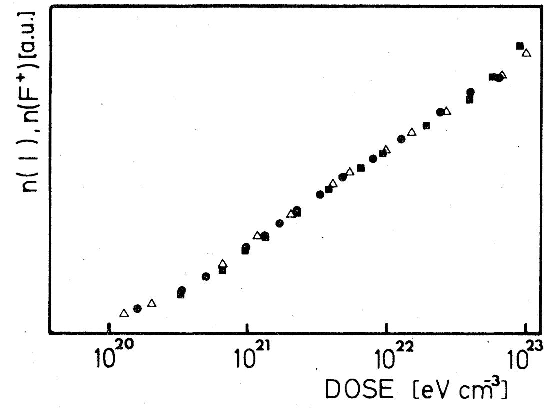

FIG. 2. $I$- and $F^+$-center accumulation kinetics in KBr under electron irradiation at 4 K, (● $I$ centers, $V = 55$ kV, $j = 1$ $\mu$A cm$^{-2}$; ■ $I$ centers, $V = 55$ kV, $j = 2$ $\mu$A cm$^{-2}$; Δ $F^+$ centers, $V = 20$ kV, $j = 1$ $\mu$A cm$^{-2}$).

#### 2. *H, $H_2$, and F centers*

$H$ centers are known to undergo a strong attractive interaction to form $H_2$ and more complex aggregates.[14] So, the complementary behavior of the $H$, $H_2$, and $F$ centers must be considered simultaneously. Figure 3 shows a quadratic growth of the $H_2$-center concentration versus $F$-center concentration. This curve is explained in the same way as the quadratic relation found by Itoh and Saidoh for the $H$ and $H_2$ centers,[15] because the $F$- and $H$-center concentrations are equal in the low-concentration range where no $H$-center agglomeration occurs significantly. Taking into account the quadratic relation $n(H_2) = k[n(F)]^2$, we can deduce the behavior of the $n(H)/n(F)$ ratio. We must have

$$n(H) + 2n(H_2) = n(F) \tag{2}$$

and

$$n(H)/n(F) = 1 - 2kn(F) \tag{3}$$

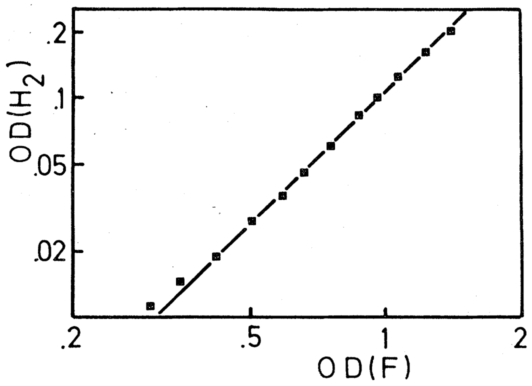

FIG. 3. Quadratic relation among $F$- and $H_2$-center concentrations in KBr under electron irradiation at 4 K ($V = 55$ kV, $j = 2$ $\mu$A cm$^{-2}$).

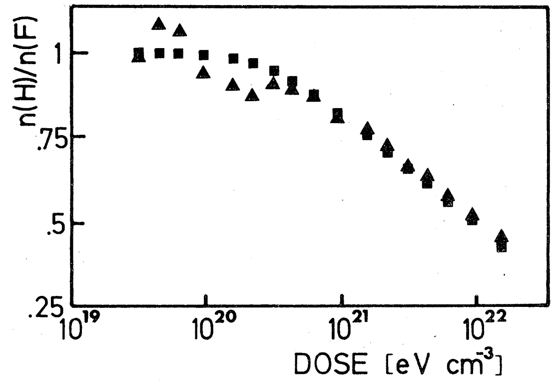

FIG. 4. $n(H)/n(F)$ ratio in KBr under electron irradiation at 4 K ($V=55$ kV, $j=2$ $\mu$A cm$^{-2}$). ▲ experimental points; ■ calculated points, according to $n(H)/n(F)=1-2kn(F)$.

as shown in Fig. 4.

We can determine the factor $k$ from several experimental curves, including data from Itoh and Saidoh's paper. Numerical values are given in Table III and are in good agreement if we consider that they originate from very different types of experiments.

TABLE III. Experimental values of the coefficient $k$ of Eq. (3).

| Measurement type | $k$ (cm$^3$) |
|---|---|
| $n(H)/n(F)$ ratio | $2.1\times10^{-19}$ |
| $n(H_2)/[n(F)]^2$ ratio | $4.33\times10^{-19}$ |
| $n(H_2)/[n(H)]^2$ ratio (in Ref. 15) | $1.39\times10^{-19}$ |

### B. $F$ and $F^+$-center kinetics

#### *1. General description of the kinetics*

Figure 5 shows the $F$ and $F^+$ growth kinetics as a function of the dose. A typical logarithmic growth is pointed out in the dose range lower than a few $10^{22}$ eV cm$^{-3}$ (zone I). For higher doses (zone II), the $F$-center concentration grows linearly versus dose (Fig. 6), whereas the $F^+$-center concentration is always logarithmic. At concentrations higher than $10^{19}$ $F$ centers cm$^{-3}$ (zone III), a square-root law is observed for the $F$ centers as a function of the dose (Fig. 7). $F^+$ centers have not been measured in this concentration range. A simple phenomenological representation of $F$- and $F^+$-center growth kinetics in zone I and II is given by the relation

$$x=A\ln(d/B+1)+Cd\ , \tag{4}$$

which is the same as relation (1), except the linear term which describes zone II of $F$-center kinetics. The square-root law valid in zone III for $F$ centers has the same form as the $F$-center kinetics observed at 77 K, where interstitials are mobile. This suggests that a model very different from the one valid in zones

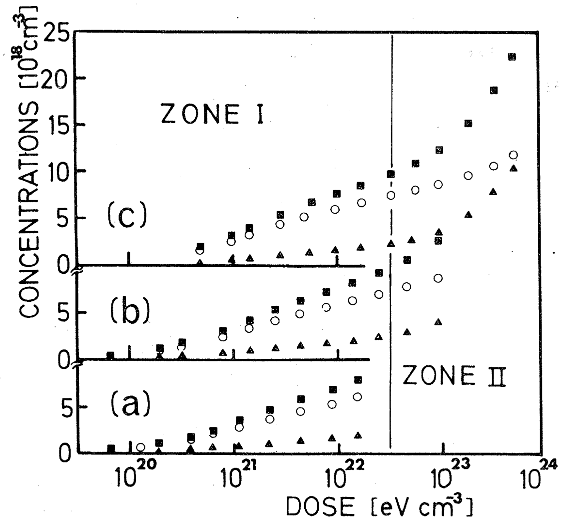

FIG. 5. $F$ (▲) and $F^+$ (○) center accumulation kinetics and their sum (■) in KBr under electron irradiation at 4 K. [$V=20$ kV, $j=0.2$ $\mu$A cm$^{-2}$ (a); $j=1$ $\mu$A cm$^{-2}$ (b); $j=3$ $\mu$A cm$^{-2}$ (c).]

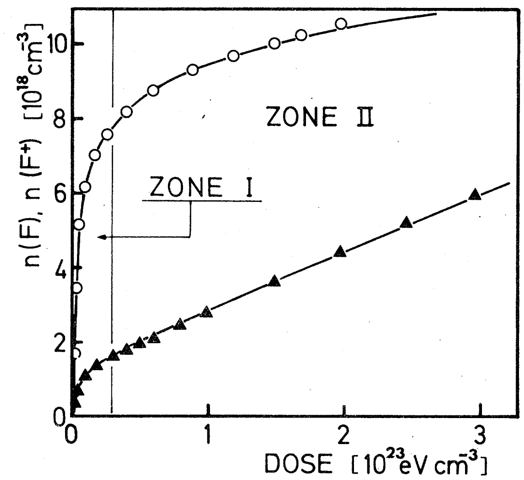

FIG. 6. $F$ (▲) and $F^+$ (○) center accumulation kinetics in KBr under electron irradiation at 4 K. ($V=20$ kV, $j=3$ $\mu$A cm$^{-2}$). The curves are according to Eqs. (8) and (10) with the following set of parameters: $v=7.2\times10^{-19}$ cm$^3$, $R^+=1.3\times10^{-2}$ eV$^{-1}$, $R=2.05\times10^{-3}$ eV$^{-1}$, $R_0=1.4\times10^{-5}$ eV$^{-1}$.

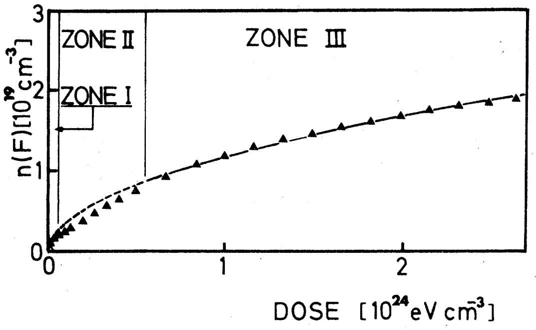

FIG. 7. *F*-center accumulation kinetics in KBr under electron irradiation at 4 K ($V=20$ kV, $j=10$ $\mu$A cm$^{-2}$). The curve is according to Eq. (17) with $2R_0\sigma_T n(T)/\sigma_F = 1.4\times10^{14}$ center eV$^{-1}$ cm$^{-3}$ to fit the points in zone III.

I and II must be found in this case, taking into account decorrelated recombinations between *F* and *H* centers.

### 2. *Bases for a simple model for kinetics*

A model for very low-temperature growth kinetics of defects must take into account two experimental evidences: (i) no center is thermally mobile[16] and (ii) the Frenkel pairs are correlated. The first point indicates that one must consider local properties to explain the decrease of the Frenkel-pair creation efficiency. A mathematical representation for it is the assumption of a forbidden volume, where the Frenkel pair cannot be formed, around some types of centers. The second point can be deduced from first-order recombination kinetics of neutral Frenkel pairs observed both after a pulsed irradiation in KBr at 8 K (Ref. 17) and during thermal recombination states.[18] It suggests that a newly created Frenkel pair is fragile and can be caused to recombine by a little perturbation in its neighborhood.

Hughes and Pooley[9] have given a simple model in the case of only one type of created center (*F*) having an associated forbidden volume $v$. It gives a logarithmic growth as a function of the dose for centers with the following hypotheses: the forbidden volumes associated to the centers can be superposed; the creation rate is a constant *R* out of the forbidden volume and vanishes in the forbidden volume.

The result is

$$x=\frac{1}{v}\ln(vRd+1)\ , \tag{5}$$

which allows us to define the parameters *A* and *B* of relations (1) and (4). If there is a residual creation rate for defects equal to $R_0$ in the forbidden volume, we have the following law:

$$x=\frac{1}{v}\ln[v(R-R_0)d+1]+R_0d\ . \tag{6}$$

If we have no linear part in the kinetics (e.g., $F^+$ centers), the parameter $R_0$ is equal to zero. *R* is the initial defect formation rate.

The real case is more complex because of the two types of Frenkel pairs created at 4 K, which are not formed independently. One must first examine which center is responsible for the forbidden volume. The order of magnitude of the forbidden volume we find is $6\times10^{-19}$ cm$^3$; on the basis of this value, the nature of the center responsible for it can be discussed.

During the Frenkel-pair formation, the interstitial is the mobile entity which moves as a "dynamical crowdion". A decorrelated recombination can be caused by its fall into a vacancy center. Assuming a propagation distance of about 10 interionic distances,[19] volume $v$ should be $7\times10^{-22}$ cm$^3$ with an interaction radius between the vacancy and the interstitial of one interionic distance (simple fall of the interstitial into the vacancy), and $2\times10^{-20}$ cm$^3$ with an interaction radius of three interionic distances (minimal separation to have a stable pair). These values are much smaller than the experimental ones. In order to determine the role of the *F* center as responsible for the forbidden volume, an experiment on the creation rate of *F* and $F^+$ centers in crystals containing defects created at 77 K has been performed. The creation rate of defects is measured by the sum of the initial slopes of kinetics at 4 K. As a result of Eq. (5), it decreases according to $\exp\{-v[n(F)+n(F^+)]\}$; the values of $v$ for defects created at 77 and 4 K are given in Table IV and differ much, which shows that the *F* center is not involved.

Interstitial centers can cause a forbidden volume bound to deformation of their neighborhood (see Sec. IV). Their elastic interaction with the lattice has been measured and the strains they induce are known to be important, especially for the *I* center.[13] Moreover, *I* centers are much more numerous than *H* centers. In the following model, we assume that *I* centers are the only centers responsible for the lowering of the creation efficiency of new Frenkel pairs which will be discussed.

TABLE IV. Forbidden volume $v$ associated to *F* and $F^+$ centers for crystals irradiated at 4 and 77 K.

| Temperature of pre-irradiation | 4 K | 77 K<br>$[n(F^+)=0]$ |
|---|---|---|
| $v$ (cm$^3$) | $6.2\times10^{-19}$ | $1.24\times10^{-19}$ |

### *3. Model for the real case of F- and $F^+$-center accumulation kinetics*

Two possibilities for the limitation of $F$ and $F^+$ growth are to be considered: (i) The neutral and charged pairs are caused to recombine after the transformation $F-H \rightarrow F^+-I$; in this case, the $F$- and $F^+$-center kinetics have to be described independently. (ii) The interstitials inhibit the primary process of creation, or the Frenkel pairs recombine before the transformation $F-H \rightarrow F^+-I$; in this case, we must describe the sum $n(F)+n(F^+)$ as a function of the dose, and the transformation reaction giving account for the observed $n(F^+)/n(F)$ ratio.

*a. Variant* (i). Let $v$ be the forbidden volume associated to the $I$ center, $R^+$ and $R'$ the initial formation rate of $F^+$ and $F$ centers, respectively, and $R_0$ the formation rate for $F$ centers in the forbidden volume. Following Hughes and Pooley,[9] we can write for $F^+$ centers

$$\frac{dn(F^+)}{dd}=R^+e^{-vn(F^+)}, \tag{7}$$

which immediately gives

$$n(F^+)=\frac{1}{v}\ln(R^+vd+1) . \tag{8}$$

If $F$-center creation is limited by $I$ centers with a residual creation rate $R_0$, we can write

$$\frac{dn(F)}{dd}=\mathrm{R}e^{-vn(F^+)}+R_0 , \tag{9}$$

where $R=R'-R_0$ and

$$n(F)=\frac{R}{R^+v}\ln(R^+vd+1)+R_0d . \tag{10}$$

These relations fit well our experimental results, as shown in Fig. 6.

At high concentrations, the model becomes unavailable, due to the use of too rough approximations. In particular, the role of processes not related to the forbidden volume is neglected, especially possible decorrelated recombinations which become important.

*b. Variant* (ii). We assume that the $I$ centers limit both the creation of new vacancy center ($F$ or $F^+$) and the transformation of a vacancy center into $F^+$ centers, with forbidden volumes respectively equal to $v$ and $w$.

The vacancy centers are created with an initial rate equal to $S'$ and with a residual rate $S_0$ in the forbidden volume. The initial probability of transformation is given by $P$. So we can write

$$\frac{d[n(F)+n(F^+)]}{dd}=Se^{-vn(F^+)}+S_0 , \tag{11}$$

for the vacancy creation rate, with $s=S=S'-S_0$ and

$$\frac{dn(F^+)}{dd}=\frac{d[n(F)+n(F^+)]}{dd}Pe^{-wn(F^+)} , \tag{12}$$

which means that in order to create an $F^+$ center, we must have the creation of a vacancy center ($F$ or $F^+$) followed by a transformation whose probability is $Pe^{-wn(F^+)}$. To integrate relation (11), we consider that since the $F^+$ centers are much more numerous than the $F$ centers on zone I (about 10 times), the ratio $n(F^+)/[n(F)+n(F^+)]$ varies few around its average value in zone I; thus we can define a forbidden volume $u$ associated to either $F$ or $F^+$ centers, which is proportional to $v$ and defined by $n(F^+)v=[n(F)+n(F^+)]u$.

So Eq. (11) becomes

$$\frac{d[n(F)+n(F^+)]}{dd}=Se^{-u[n(F)+n(F^+)]}+S_0 \tag{13}$$

and the solution is

$$n(F)+n(F^+)=\frac{1}{u}\ln(Sud+1)+S_0d . \tag{14}$$

Equation (12) gives the repartition of $F$ and $F^+$ centers in the $n(F)+n(F^+)$ sum. We can write

$$\frac{d[n(F)+n(F^+)]}{dn(F^+)}=\frac{dn(F)}{dn(F^+)}+1=\frac{1}{P}e^{wn(F^+)} \tag{15}$$

which gives

$$n(F)=\frac{1}{Pw}(e^{wn(F^+)}-1)-n(F^+) . \tag{16}$$

These relations fit well the experimental results at the beginning of the curves (Fig. 8); but if the theory is

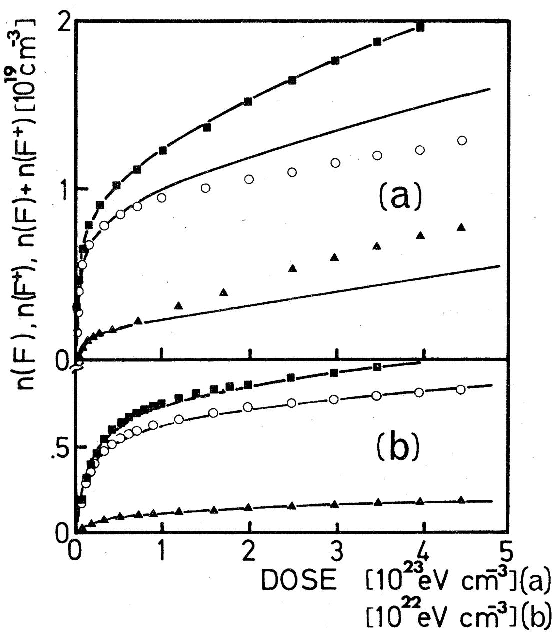

FIG. 8. $F$ (▲) and $F^+$( (○) center accumulation kinetics and their sum (■) in KBr under electron irradiation at 4 K ($V=20$ kV, $j=3$ $\mu$A cm$^{-2}$). The curves are according to Eqs. (14) and (16) with the following set of parameters: $u=6.2\times10^{-19}$ cm$^3$, $S=1.3\times10^{-2}$ eV$^{-1}$, $S_0=1.65\times10^{-5}$ eV$^{-1}$, $w=2.8\times10^{-20}$ cm$^3$, $P=0.935$.

in good accordance with the kinetics of all vacancy centers in zone II, it is however not possible to find values of $P$ and $w$ giving a good fit for $F$ and $F^+$ kinetics separately in this zone.

#### *4. Model at very high concentrations of F centers*

Very high-defect concentrations (about $4\times10^{19}$ $\text{cm}^{-3}$) are due to the residual formation of $F$ centers in the forbidden volume. They exist mainly in KBr and not in KCl where a saturation of $F$-center kinetics has been observed under proton[8] and x irradiation.[7] Zone III of the $F$-center kinetics is characterized by a growth of the $F$-center concentration which is no longer linear. The shape of the law is a 0.5 power of the dose (Fig. 7).

To explain this law, we consider the range of a dynamic crowdion in the lattice when an interstitial is formed, which has been found to be about 10 interionic distances and is equal to the average separation of two centers in KBr for a concentration of $1.38\times10^{19}$ $\text{cm}^{-3}$. One expects in zone III an important role of the decorrelated recombinations of Frenkel pairs, as in the case of temperatures where only the interstitials are thermally mobile (e.g., LiF at room temperature, KBr at 77 K).

So, following Refs. 2 and 20, we must have

$$n(F)\simeq\left(2R_0\frac{\sigma_T n(T)}{\sigma_F}\right)^{1/2} d^{1/2}\,, \tag{17}$$

in which $\sigma_F$ and $\sigma_T$ are, respectively, the capture probability for the interstitial to recombine with a $F$ center or to be trapped by nucleation germs $n(T)$ which are nonsaturable traps. If we consider that $n(T)$ is approximately constant in zone III (see discussion), this law fits well with the high dose and concentration part of the $F$-center kinetics (Fig. 7).

## IV. DISCUSSION

The experimental data obtained show that models using forbidden volumes are adequate for a description of the interactions between centers and newly formed Frenkel pairs. The nature of the responsible center as well as the mechanism of the inhibition limiting the growth of concentration must be discussed as a function of the hypothesis made for the models.

### A. Nature of the center responsible for the forbidden volume and elastic perturbations caused by the defects in the lattice

Experimental results show that the $I$ center can be considered as the main responsible center for the forbidden volume. The contribution of the $H$ center to the latter is difficult to evaluate experimentally since the thermal stabilities of $H$ and $I$ centers are not very different in KBr.[16] The main reason leading us to neglect the $H$ center is the value of the ratio of the $I$ to the $H$ concentration in zone I lying between 5 and 10, which shows that the global contribution of $H$ centers is in any case much smaller than the one of $I$ centers, even assuming an equal individual contribution of both centers. Another reason is that the perturbation caused by an $I$ center in its neighborhood is known to be more important than the one caused by an $H$ center. It has been measured in the following ways: (i) thermal-conductivity measurements showing that the $I$ center has a large scattering cross section for phonons[21]; (ii) variation of the volume of crystals containing $I$ and $H$ centers[22]; (iii) radiation-induced hardening measurements, showing a much stronger interaction between $I$ centers and dislocations than between $H$ centers and dislocations, when they are associated to a monovalent impurity[23]; (iv) measurements of the double force tensor of $H$ centers[14] and $I$ centers[24] by x-ray scattering.

As we shall see in Sec. IV B, most probably the mechanism inhibiting the formation of a new Frenkel pair is not an electronic transfer from the exciton in its precursor state to a defect, but is rather bound to lattice deformations; consequently, although points (i)–(iv) do not constitute a proof to the role of $I$ centers in the mechanism, they strengthen the hypothesis of the $I$ center being the main responsible center for the forbidden volume.

### B. Mechanism inhibiting the formation of new Frenkel pairs

The creation of a stable Frenkel pair is known to consist of[25]: (i) a photochemical reaction, allowing transformation of the energy of an exciton into kinetic energy of matter; (ii) the separation of a newly formed pair ("dynamic crowdion" process); (iii) a charge-transfer process (transformation of a neutral pair into a charge one) at very low temperature.

Reaction (iii) is not experimentally known to occur before or after reaction (ii). Recently, Aboltin *et al.*[26] have proposed a mechanism for the formation of charged Frenkel pairs where charge transfer occurs when the pair is separated by only one interionic distance along ⟨110⟩. Experiments by Kondo *et al.*[17] show that the decrease of $F$ and $H$ concentrations after pulsed irradiation is not correlated to a corresponding increase of $F^+$ and $I$ centers. It argues for reaction (iii) preceding reaction (ii). Unfortunately, although the $F$-$H$ pair has been proved to formed in a few picoseconds after irradiation, which has led to thinking that the $F^+$-$I$ pair derived from the $F$-$H$ pair, no experiment has been able to give information on the formation of the $F^+$-$I$ pair kinetics in the picosecond range; so the sequence of reactions (ii) and (iii) cannot be determined directly.

The nature of the inhibition process can originate from two different interactions: (a) an electronic energy transfer from the excitonic state responsible for the Frenkel-pair formation and (b) an elastic action on the created Frenkel pair, causing it to recombine quickly. A transfer mechanism from the precursor state to $\mathrm{Na}^+$ impurity in KBr at 4 K has been invoked by Tanimura *et al.*[27] to explain the anticorrelation between the pair formation efficiency and the $\mathrm{Na}^+$ perturbed exciton luminescence as a function of the $\mathrm{Na}^+$ concentration. But, in our case, this mechanism should not be considered because it is contradictory to the constant efficiency of the pair formation process observed at 77 K (Ref. 2); an exciton-defect transfer is pointed out from the luminescent states in KI at the $H_2$ centers at 77 K,[28] but the Frenkel-pair precursor state is not concerned. In the same way, the intrinsic luminescence of KBr at 4 K is quenched by the $H$ centers.[5]

An elastic interaction resulting in a decrease of the defect formation efficiency is much more probable; it has been suggested before in the case of crystals doped with ions larger than the host crystal ion. So Hirai,[29] in $\mathrm{KBr:I^-}$, assigns the decrease of the formation efficiency of defects to a reflection process of the dynamic crowdion on substitutional $\mathrm{I}^-$, causing a correlated recombination. In $\mathrm{KBr:Rb^+}$, Tanimura *et al.*[30] have observed a decrease of the defect creation efficiency due to the presence of $\mathrm{Rb}^+$, which is not compensated by any new luminescence emission. The interaction between the $H$ center and the $\mathrm{Rb}^+$ ions is calculated and found to be repulsive which causes a recombination of the Frenkel pair. Another strain-induced mechanism causing Frenkel-pair recombination might be due to the lowering of the lattice's symmetry in the vicinity of an $I$ center. It would be similar to the case of $\mathrm{MgF_2}$ (Ref. 31) which has lower symmetry and where no stable defects are observed: although the photochemical reaction is efficient, the crowdion process does not permit a sufficient separation of the pair.

We have seen that although it is impossible to evaluate the respective contributions of $H$ and $I$ centers, the latter seem more likely to be responsible for the limiting process, on the basis of a larger perturbation caused in the lattice. On the other hand, the two variants of the model using only a forbidden volume associated to the $I$ center account well for experimental results measured at the beginning of the $F$ and $F^+$ kinetics. The mechanism of limitation of the concentration growth is found to cause a recombination of a newly formed Frenkel pair; the better fit obtained with different actions on $F$ and $F^+$ centers allows us to conclude that the recombination occurs after the charge transfer from the $F$ to the $H$ center resulting in $F^+$ and $I$ centers. It excludes the possibility of an action of the $I$ centers on the excitonic state precursor of the Frenkel pair. Thus an action related to the strain field around the $I$ center seems most likely on the basis of analogies with other cases of lowering of the pair creation efficiency by large dopants such as $I^-$ or $\mathrm{Rb}^+$ in KBr.

### C. Interstitial stabilization and decorrelated recombinations at high concentrations

The $F$-center kinetics in zone II show that there is a residual formation rate in the forbidden volume. The $\frac{1}{2}$ power law observed in zone III is consistent with this assumption, if we consider a decorrelated recombination model to limit the growth of the $F$ centers.

The nature and concentration of the interstitial traps involved in Eq. (17) have to be discussed. $H$ centers are known to aggregate at high concentrations of defects at 4 K, so it is possible to consider that $H$ centers constitute saturable traps for other $H$ centers moving as dynamical crowdions. As their concentration has been shown to decrease after a maximum at $10^{18}\ \mathrm{cm^{-3}}$, we can extrapolate their concentration at the beginning of zone III assuming an exponential law whose initial slope is given by Eq. (3). We find that the $H$-center concentration is smaller than 1% of the $F$-center concentration in zone III; consequently all neutral interstitial centers exist as $H_2$ centers or higher $H$-center aggregates.

The distribution of $H_2$ centers as aggregates has been measured by electron microscopy[32]; at temperatures where centers are not thermally mobile ($T < 30$ K), the measured concentration of aggregates is about $10^{16}\ \mathrm{cm^{-3}}$, which is larger than at 77 K where aggregates are more important. This value, which is small compared to the maximum concentration of $H$ centers, is an inferior limit because only sufficiently large aggregates are observed in electron microscopy.

Assuming a trap concentration $n(T)$ equal to $10^{18}$ $\mathrm{cm^{-3}}$, i.e., that all $H$ centers are nucleation germs, we can evaluate the ratio of the capture probabilities by $F$ and interstitial centers, respectively, from the coefficient of Eq. (17). From Fig. 7, we have

$$2R_0\sigma_T n(T)/\sigma_F = 1.4\times10^{14}\ F\ \mathrm{eV^{-1}\ cm^{-3}}\ .$$

From zone II of the $F$-center kinetics, we have

$$R_0 = 1.4\times10^{-5}\ F/\mathrm{eV}\ .$$

Then, we have

$$n(T)\sigma(T)/\sigma(F) = 5\times10^{18}\ \mathrm{cm^{-3}}\ ;$$

therefore

$$\sigma_T/\sigma_F \simeq 5\ ,$$

which is not very different from the ratio of the geometrical sections of $H_2$ and $F$ centers.

At $n(F) = 2 \times 10^{19}$ cm$^{-3}$, we have $\sigma_T n(T)/\sigma_F n(F) = 0.25$ and the hypothesis that trapping by interstitials is negligible compared to trapping by $F$ centers is only approximate, but its validity increases with the $F$-center concentration.

## V. CONCLUSION

We have given a description of the growth kinetics of all defects created in KBr by irradiation at 4 K. Several models have been given for the kinetics in a very large concentration range, taking into account the results of previous work in the field of defect creation by irradiation in alkali halides as well as the properties of the Frenkel pairs at liquid-helium temperature. The mechanisms involved in the lowering of the defect creation rate by the presence of defects are most likely related to the deformation of the lattice around the existing defects. The high-concentration range for $F$ centers is explained by the decorrelated recombination of $F$ and moving interstitial centers. Our results suggest an independent limitation of $F$- and $F^+$-center growth, thus independent formation processes. This conclusion could be confirmed only by a time-resolved experiment on the formation of charged Frenkel pairs.

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