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Model of first-stage *F*-center production in alkali halides containing divalent cation impurities

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A system of equations, describing the formation of *F* centers and their complements in irradiated alkali halides doped with divalent impurities, has been developed. These incorporate the stabilization of *H* centers and di-interstitial halogen defects at impurity-vacancy dipoles or aggregates of such dipoles, as well as radiation-induced interstitial detrapping mechanisms. Numerical and approximate analytical solutions of the equations reproduce the dynamic, temperature-dependent features of *F*-center growth found in experimental studies. They provide a new explanation of the experimentally observed relations between the growth of defects and the divalent-cation-impurity concentration; i.e., the square-root relation between first-stage *F* centers and such impurities, and the relation between the saturation concentration of H_D centers and these impurities.

I. INTRODUCTION

The rate of production of stable damage in irradiated alkali halides is considerably affected by the nature of the secondary reactions which occur after the primary production of *F* and *H* centers, the latter being chemically equivalent to interstitial halogen atoms. Impurities of various types play an important role in these reactions by acting as traps for the *H* centers which are mobile at quite low temperatures.[1-3]

Much attention has been given to the mechanisms by which impurities affect *F*-center production rates for irradiations performed near room temperature. It was recognized from early studies that substitutional divalent cation impurities have a striking effect on *F*-center growth curves. They result in an enhancement of the first, rapid stage of defect growth, while the late stage, corresponding to higher doses, is changed in a complicated manner.[1,4] It is now accepted from optical,[1] thermal-conductivity,[5] and electron-microscope studies[6,7] that clusters of halogen interstitials are a major product of high-dose irradiations. The presence of divalent cation impurities significantly alters the size and number of the clusters, suggesting a heterogeneous nucleation process. A mechanism of this type has been used recently by Aguilar *et al.*[8] to explain several features present in *F*-center growth curves. In order to understand these nucleation processes in detail, one must know the defect structures and mechanisms operative in the very early stages of their development, i.e., in the first stage of defect growth which has been the subject of considerable controversy.[1,4,9-20]

We note at the outset that there are undoubtedly several processes operative in the first stage as shown by the detailed studies of Hodgson and coworkers.[19,20] We shall concentrate on the *dominant* first-stage mechanisms in crystals doped with substitutional divalent impurities such as Ca^{2+} or Sr^{2+}. These systems have been extensively studied. Most of the early models have attributed the first stage to the exhaustion of preexisting defects.[1,4] It was supposed that such defects could be converted to *F* centers or could act as saturable traps for *H* centers. Isolated cation vacancies were assigned a major role as a result of the experimentally observed relation

$$f_0 \propto \sqrt{n_I} \ . \qquad (1)$$

Here f_0 is the concentration of *F* centers produced in the first stage and n_I is the concentration of divalent cation impurities. A relation of this form may be obtained by considering the association reaction between isolated cation vacancies (n_V) and isolated divalent cation impurities. This association process results in the formation of complexes known as impurity-vacancy (IV) dipoles, each consisting of a divalent cation impurity and a neighboring cation vacancy. Near room temperature the IV dipoles (n_D) exist in much greater numbers than the isolated cation vacancies.[1,4] In this approximation, it is simple to show that

$$\frac{n_V}{n_0} = \left(\frac{n_D}{\xi n_0}\right)^{1/2} \exp\left(\frac{-E_a}{2kT}\right) , \qquad (2)$$

where n_0 is the concentration of cation lattice sites, ξ is the number of equivalent orientations of the IV dipoles and E_a is the association energy. Since $n_D \gg n_V$, it follows that $n_D \simeq n_I$. Hence relation (1) appears to follow directly if the first-stage mechanism involves the exhaustion of isolated cation vacancies

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but not the considerably more numerous IV dipoles. A mechanism of this type which gained wide acceptance assumed the exclusive trapping of *H* centers by isolated cation vacancies.[11]

More recent work has, however, produced considerable evidence to show that IV dipoles are a major trap for halogen interstitials over a wide range of temperature. Hoshi *et al.*[12] demonstrated that *H* centers and di-interstitial halogen centers could be trapped by IV dipoles at temperatures at least as high as 195 K. ESR studies by Schoemaker[21] carried out at low temperatures revealed *H* centers near IV dipoles in various configurations. The measurements by Marat-Mendes and Comins[13–15] of ionic thermocurrents (ITC) and optical absorption bands in KCl(Sr) and KBr(Sr) irradiated near room temperature yielded a proportional relation between the growth of *F* centers and the destruction of IV dipoles. This relation held in both the first and the late stage of defect growth with numerical agreement within a factor of 2. *F*-center growth and IV dipole destruction were associated with the growth of ultraviolet absorption bands; for example in KCl(Sr) a prominent absorption band at 216 nm grew in proportion to the *F* band and as the square of a band at 316 nm until the latter saturated at low absorption. Annealing experiments[16] provided direct evidence that the ultraviolet bands are associated with trapped interstitial halogens. A mechanism similar to that of Hoshi *et al.*[12] in which an *H* center is trapped at an IV dipole followed by the trapping of a second *H* center to form a di-interstitial halogen provides a satisfactory explanation of these results.

Interstitial halogens may also be trapped by aggregates of IV dipoles. It is known that the state of aggregation determines the exact position and width of the absorption band near 220 nm in KCl(Ca) which is attributable to trapped di-interstitials.[22] The ITC measurements mentioned above[13] show that fewer IV dipoles are destroyed per *F* center created in crystals containing a larger proportion of dipole aggregates. Thermoluminescence and ESR studies[17,18] on crystals irradiated near room temperature yield effects which result from interstitial trapping at both IV dipoles and aggregates.

A further important point concerns the transition from the first to the late stage. In the ITC work of Marat-Mendes and Comins,[13–15] it was observed that this transition occurred when a large fraction of IV dipoles remained unaffected by the irradiation process.

These more recent results are incompatible with models of the first stage which involve the exhaustion of preexisting defects and also with the isolated cation vacancy model as an explanation for relation (1).

In the present paper we develop a model which accounts for relation (1) in a new way and in which the first stage is shown to be a dynamic saturation process where both trapping and detrapping of halogen interstitials occurs. The model incorporates the present understanding of the nature of the trapped interstitials and successfully reproduces the reversible changes in defect concentration which result from changes in temperature during irradiation.[14] A preliminary report of this work has been given recently.[23]

II. MODEL OF DEFECT GROWTH

We shall adopt a general approach applicable to crystals containing a variety of interstitial traps related to IV dipoles and their aggregates. This treatment can explain experimental observations with such crystals and can be easily restricted to simple special cases.

We assume that the ionizing radiation creates *F* and *H* centers at a rate *p*. The *H* centers (denoted by i) are mobile or free. They may be trapped singly at IV dipoles or dipole aggregates in j possible configurations to form H_D-type centers (denoted by n_{1j}) or in the form of trapped di-interstitial halogen defects (denoted by n_{2j}). We shall use the Sonder-Sibley notation[1] for defects which have known structures. It is supposed that j such trapped di-interstitial configurations exist, since following Hoshi *et al.*,[12] the formation of the di-interstitial halogen proceeds by the trapping of a second interstitial at an H_D-type center. The success of this mechanism in explaining the origin of the square-law relation between the n_1 and n_2 centers before the saturation of the former, over a wide range of temperature, has been described in the literature.[12,16] We include interstitial detrapping processes *initiated by the radiation*, the presence of which we shall show experimentally. It is to be noted that the concept of interstitial detrapping has been used by other authors in their kinetic schemes.[8,19,20] The kinetic equations are

$$\frac{df}{dt} = p - \sigma i f \ , \tag{3}$$

$$\frac{di}{dt} = p - \sigma i f - \sum_j [\alpha_{1j} i (n_{Dj} - n_{2j} - n_{1j}) + \alpha_{2j} i n_{1j} - K_{1j} n_{ij} - 2K_{2j} n_{2j}] \ , \tag{4}$$

$$\frac{dn_{1j}}{dt} = \alpha_{1j} i (n_{Dj} - n_{2j} - n_{1j}) - \alpha_{2j} i n_{1j} - K_{1j} n_{1j} \ , \tag{5}$$

$$\frac{dn_{2j}}{dt} = \alpha_{2j} i n_{1j} - K_{2j} n_{2j} \ , \tag{6}$$

$$f = i + \sum_j (n_{1j} + 2n_{2j}) \ . \tag{7}$$

Equation (3) gives the growth of F centers (f) which is limited by recombinations with free interstitial halogens (i). Equation (4) expresses the production, recombination, and trapping of free interstitials. It also includes the detrapping terms $K_{1j}n_{1j}$ and $K_{2j}n_{2j}$. The K_{ij} have the form $B_{ij}\exp(-E_{ij}/kT)$, where the B_{ij} are expected to depend on the radiation intensity. The n_{Dj} are the initial concentrations of possible interstitial traps introduced by the divalent impurities. The sets of equations (5) and (6) describe the growth of the F-center complements n_{1j} and n_{2j}. Equation (7) expresses the production of vacancy and interstitial defects in equal numbers and ignores F-aggregate centers which are in a negligibly small concentration. The rate constants σ, α_{1j}, and α_{2j} may be estimated using $(Z\nu/N_i)$. N_i is the concentration of interstitial sites and Z is the number of sites surrounding a defect for certain annihilation or trapping of an interstitial. ν has the form $\nu_0\exp(-E_m/kT)$, where E_m is the migration energy of the H center and ν_0 is an attempt frequency.

We now proceed to obtain approximate analytical solutions of the kinetic equations in two situations, using the relative concentrations of the H_D centers and the trapped di-interstitials to distinguish these. Experimentally observed results and direct numerical solutions of the kinetic equations are used as a check on the validity of the assumptions and approximations used.

A. Growth of defects near room temperature ($n_{2j} >> n_{1j}$)

Near room temperature, except for irradiation times which are very small compared with the full development of the first stage, the trapped di-interstitial centers (n_{2j}) greatly exceed the H_D centers (n_{1j}) in concentration.[13]

Under irradiation, the interstitial halogens are stabilized rapidly.[1] For these conditions we assume that the concentration of free interstitials attains a small quasistationary concentration i_s obtained by setting $di/dt=0$ in Eq. (4). (For a discussion of the stationary state hypothesis see, e.g., Benson.[24]) Thus

$$i_s=\frac{p+\sum_j(K_{1j}n_{1j}+2K_{2j}n_{2j})}{\sigma f+\sum_j[\alpha_{1j}(n_{Dj}-n_{2j}-n_{1j})+\alpha_{2j}n_{1j}]} . \tag{8}$$

From the experimental results of Marat-Mendes and Comins on KCl(Sr) irradiated near room temperature,[13] it is seen that the H_D centers rapidly attain a very small maximum value and then decrease slowly. This behavior, as we shall see in Sec. V, is duplicated by the direct numerical solutions of the rate equations for appropriate values of the parameters. The quasistationary values of the n_{1j} are obtained from the set of equations (5) by setting $dn_{1j}/dt=0$. Hence

$$(n_{1j})_s=\frac{\alpha_{1j}(n_{Dj}-n_{2j})}{\alpha_{1j}+\alpha_{2j}} , \tag{9}$$

where we assume $(\alpha_{1j}+\alpha_{2j})i_s >> K_{1j}$ is an appropriate condition for the efficient creation of the trapped di-interstitial centers (n_{2j}). We use the values for $(n_{1j})_s$ as being representative of the concentration of these centers throughout the F-center growth curve without introducing serious error.

Substitution of the $(n_{1j})_s$ and i_s into Eq. (3) gives the rate of growth of F centers as

$$\frac{df}{dt}=p-\sigma f\left[\frac{p+\sum_j 2K_{2j}n_{2j}}{\sigma f+\sum_j \frac{2\alpha_{1j}\alpha_{2j}}{\alpha_{1j}+\alpha_{2j}}(n_{D_j}-n_{2j})}\right] , \tag{10}$$

where

$$\sum_j K_{1j}n_{1j} << \sum_j 2K_{2j}n_{2j}$$

when

$$n_{1j} << n_{2j} .$$

We now examine Eq. (10) in the light of the observed relation (1). In the simplest case of a dominant interstitial trap of concentration n_D Eq. (10) reduces to

$$\frac{df}{dt}=p-\sigma f\left[\frac{p+K_2 f}{\sigma f+\alpha(n_D-f/2)}\right] . \tag{11}$$

Here $\alpha=2\alpha_1\alpha_2/(\alpha_1+\alpha_2)$ and, using Eq. (7), $f \simeq 2n_2$ for i, $n_1 << n_2$.

A saturation in F-center production, corresponding to the termination of the first stage, occurs when $(df/dt)_{f=f_0}=0$. This yields a quadratic equation in f_0 which has a physically meaningful solution

$$f_0=\left[\frac{p\alpha n_D}{B_2\sigma}\right]^{1/2}\exp\left[\frac{E_2}{2kT}\right] \tag{12}$$

for $(p\alpha/2)^2 << 4p\alpha\sigma K_2 n_D$.

Thus for irradiations at constant temperature and intensity, $f_0 \propto \sqrt{n_D}$. This leads directly to relation (1), i.e., $f_0 \propto \sqrt{n_I}$ since near room temperature $n_I \sim n_D$ in heat-treated crystals containing single IV dipoles and $n_I \propto n_D$ for crystals containing a dominant dipole aggregate, e.g., a trimer.[25] In the more complicated case of crystals containing both IV dipoles and their aggregates, relation (1) can be obtained only if the trapping and detrapping rate constants are essentially independent of the type of trap, i.e.,

$\alpha_{1j}=\alpha_1$, $\alpha_{2j}=\alpha_2$, and $K_{2j}=K_2$. Thus

$$\frac{df}{dt}=p-\sigma f\left[\frac{p+K_2\sum\limits_j 2n_{2j}}{\sigma f+\alpha\sum\limits_j(n_{Dj}-n_{2j})}\right] , \qquad (13)$$

which reduces to Eq. (11) since $f \simeq \sum_j 2n_{2j}$ for i, $\sum_j n_{1j} << f$, $n_D=\sum_j n_{Dj}$, and $n_2=\sum_j n_{2j}$.

Thus relation (1) may be obtained provided a dipole aggregate of n dipoles behaves as n isolated dipoles in trapping interstitials. Experimental results are consistent with this interpretation since F-center growth curves in the first stage in, e.g., KCl(Sr) (Ref. 13) and KCl(Pb) (Ref. 26) are virtually independent of the state of aggregation of the IV dipoles. The breakdown of relation (1) in NaCl(Mn) (Ref. 17) appears to result from the variety of Mn charge states present leading to the conditions discussed above being invalid.

B. Growth of defects when $n_{1j} > n_{2j}$.

This condition applies in general for short irradiation times and for longer times at low temperatures.[27]

Approximate analytical solutions of the kinetic equations can be obtained in the special case $n_{1j} >> n_{2j}$. More general numerical solutions of the rate equations for the condition $n_{1j} \gtrsim n_{2j}$ will be described later.

The quasistationary free interstitial concentration, using Eq. (8), is

$$i_s=\frac{p+\sum\limits_j K_{1j}n_{1j}}{\sigma f+\sum\limits_j \alpha_{1j}(n_{Dj}-n_{1j})} , \qquad (14)$$

provided $n_{1j} >> n_{2j}$, $K_{1j}n_{1j} >> K_{2j}n_{2j}$, and $\alpha_{1j}(n_{Dj}-n_{1j}) >> \alpha_{2j}n_{1j}$. These conditions will arise from a relatively small value for the α_{2j}.

Substitution of i_s into the set of equations (5) yields

$$\frac{dn_{1j}}{dt}=\alpha_{1j}(n_{Dj}-n_{1j})\left[\frac{p+\sum\limits_j K_{1j}n_{1j}}{\sigma f+\sum\limits_j \alpha_{1j}(n_{Dj}-n_{1j})}\right] -K_{1j}n_{1j} . \qquad (15)$$

In crystals doped with a particular divalent impurity, H_D centers will be of two basic types: H centers at isolated IV dipoles and at various aggregates of dipoles. The total concentration of H_D centers from Eq. (7) is $n_1=\sum_j n_{1j} \simeq f$ for i_s, $\sum_j 2n_{2j} << f$. Thus

$$\frac{dn_1}{dt}=\sum_j\frac{dn_{1j}}{dt} =\frac{p\sum\limits_j \alpha_{1j}(n_{Dj}-n_{1j})-\sigma\sum\limits_j K_{1j}n_{1j}\sum\limits_j n_{1j}}{\sigma\sum\limits_j n_{1j}+\sum\limits_j \alpha_{1j}(n_{Dj}-n_{1j})} . \qquad (16)$$

In the simplest case of a dominant trap with concentration n_D,

$$\frac{dn_1}{dt}=\frac{p\alpha_1(n_D-n_1)-\sigma K_1 n_1^2}{(\sigma-\alpha_1)n_1+\alpha_1 n_D} . \qquad (17)$$

The H_D-type centers will grow according to Eq. (17) and will attain a saturation value n_{1s} when

$$\left[\frac{dn_1}{dt}\right]_{n_1=n_{1s}}=0 .$$

Hence

$$n_{1s}=\left[\frac{p\alpha_1 n_D}{B_1\sigma}\right]^{1/2}\exp\left[\frac{E_1}{2kT}\right] \qquad (18)$$

$$\text{for } (p\alpha_1)^2 << 4p\alpha_1 K_1\sigma n_D .$$

Thus we see that $n_{1s} \propto \sqrt{n_D}$ for irradiations at constant temperature and intensity provided we are working in the extreme condition $n_{1j} >> n_{2j}$.

In the case of several interstitial traps (as discussed in Sec. II A), relation (18) is obtained if the rate constants are essentially independent of the type of trap, i.e., $\alpha_{1j}=\alpha_1$ and $K_{1j}=K_1$. Here

$$\frac{dn_1}{dt}=\sum_j\frac{dn_{1j}}{dt} =\frac{p\alpha_1\sum\limits_j(n_{Dj}-n_{1j})-\sigma K_1\left[\sum\limits_j n_{1j}\right]^2}{(\sigma-\alpha_1)\sum\limits_j n_{1j}+\alpha_1\sum\limits_j n_{Dj}} , \qquad (19)$$

which reduces to the form of Eq. (17) if $n_D=\sum_j n_{Dj}$ and $n_1=\sum_j n_{1j}$. Relation (18) follows provided a dipole aggregate of n dipoles behaves as n isolated IV dipoles in trapping interstitials.

III. EXPERIMENTAL PROCEDURE

Single crystals of KCl of nominal purity were obtained from Karl Korth, Kiel, Germany and cleaved to an approximate size $(10\times10\times1)$ mm^3. The samples were attached using GE4027 varnish to the copper cold finger of a temperature-controlled optical cryostat.

Irradiations were performed at various temperatures using x-rays from a Philips tungsten target tube operated at 80 kV and 16 mA. The x-ray beam was filtered through 0.5-mm Al, 0.4-mm Fe, and 1.0-mm amorphous silica before striking the crystal placed 7.5 cm from the target. Calculations using a Kramers distribution for the bremsstrahlung radiation[28] and allowing for attenuation by the filters indicate a nearly uniform energy deposition and hence defect concentration throughout the crystal.

Optical-absorption measurements were carried out with a Cary 17 spectrophotometer. The crystals were rapidly cooled to 77 K for all absorption measurements, using a consistent procedure with an average cooling rate of ~ 0.5 K s^{-1}. This procedure minimizes thermally activated post-irradiation decay processes and bleaching effects of the measuring light.

F-center concentrations were calculated from the Gaussian form of the Smakula equation[29] using an oscillator strength of 0.55. Absorption coefficients for other defects were measured at the peak of the respective bands after subtraction of background absorption.

IV. EXPERIMENTAL RESULTS

Certain of the theoretical predictions can be compared directly with existing data in the literature and will be discussed in a later section. Other conclusions require direct experimental verification. We have investigated the predicted dynamic, temperature-dependent, saturation behavior in the growth of defects as well as the effect of radiation-induced interstitial detrapping. Both of these aspects of the theory have not been previously studied in detail.

In our studies of the temperature-dependent defect growth it was necessary to be able to observe the saturation concentration of *F* centers in cases where the irradiations were performed at low temperature. These saturation levels are considerably larger than those produced at room temperature and correspond to relatively high absorbance values. For this reason we have carried out our studies in KCl which was not deliberately doped, but contained sufficient residual divalent cation impurities to yield an obvious first-stage defect growth. The absorption bands formed in the neighborhood of 230 nm in the crystal resulting from the trapped di-interstitial halogen defects behave in the same manner as absorption bands formed in this wavelength region in deliberately doped crystals.

Figures 1 and 2 show the experimental growth curves for *F* centers and the trapped di-interstitial defects (V_2^m centers). We use this latter notation for consistency with previously published work.[16,17,30] Three crystals were used in this group of studies. Crystal *A* was irradiated at sequentially lower tem-

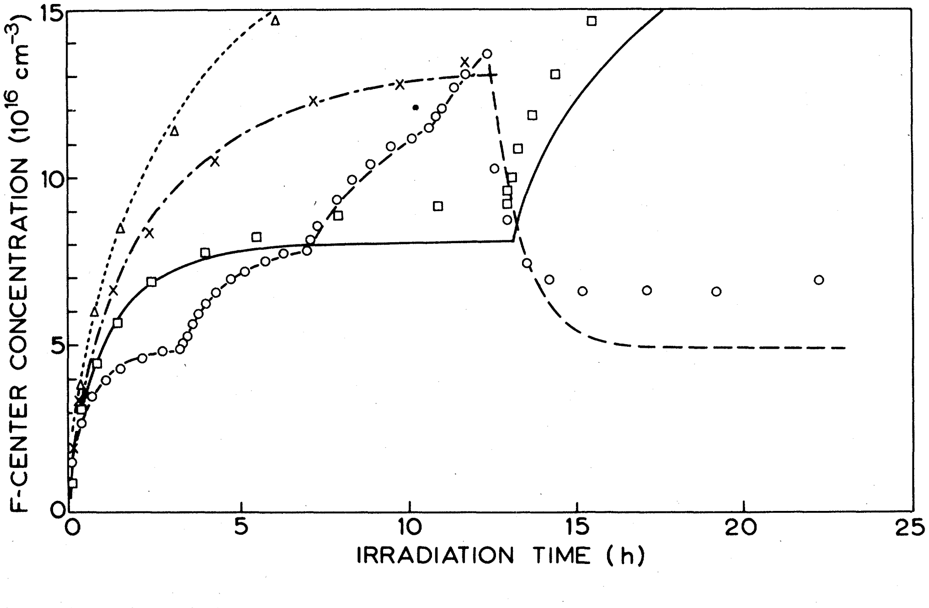

FIG. 1. Experimental and theoretical growth curves for *F* centers in KCl crystals. Open circles: *F*-center growth and decay in crystal *A* irradiated sequentially at 293, 273, 253, 233, and 293 K. Open squares: *F*-center growth for crystal *B* irradiated at 273 K. Crosses: *F*-center growth for crystal *C* irradiated at 253 K. Open triangles: *F*-center growth for crystal *D* irradiated at 233 K. The dashed, full, dot-dash, and dotted curves are the corresponding theoretical growth curves for *F* centers for crystals *A*, *B*, *C*, and *D*, respectively. Values of the theoretical parameters: $p = 6.3\times10^{13}$ cm^{-3} s^{-1}, $n_D = 1.4\times10^{17}$ cm^{-3}, $E_m = 0.075$ eV (Ref. 3), $\sigma = 8.6\times10^{-9}\exp(-E_m/kT)$ cm^{-3} s^{-1}, $\alpha_1 = 0.03\sigma$, $\alpha_2 = 1.5\sigma$, $K_2 = K_1 = 50.1\exp(-E_2/kT)$ s^{-1}, $E_2 = 0.32$ eV.

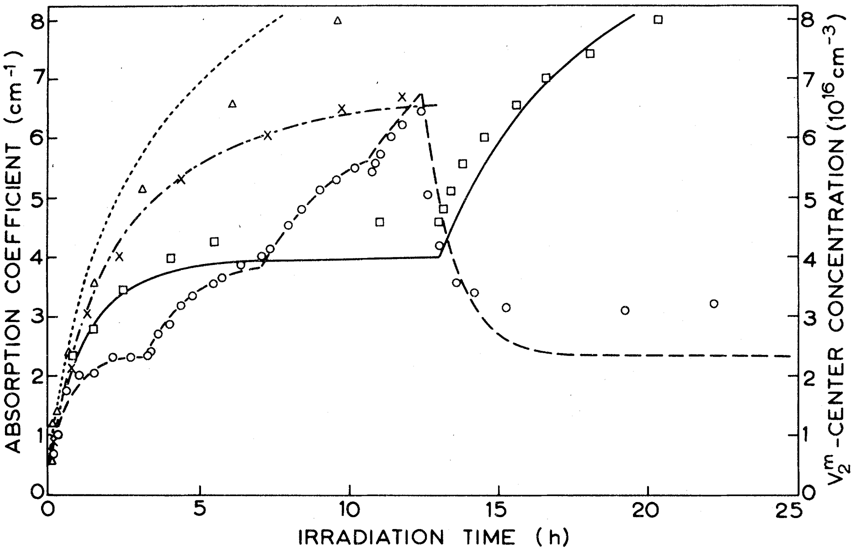

FIG. 2. Experimental and theoretical growth curves for V_2^m centers in KCl crystals. The growth curves correspond to those shown in Fig. 1 for F centers and are produced in the same crystals and using the same theoretical parameters.

peratures between 293 and 233 K and showed significant increases in the quasisaturation level of F-center growth (f_0) as the temperature of irradiation was reduced. After the irradiation at 233 K, the temperature of irradiation was restored to 293 K. This resulted in a rapid reduction in the F-center concentration and the growth curve finally followed an extrapolation of the original growth curve at 293 K. As we shall verify, the rate of reduction is considerably faster than that produced by thermal bleaching alone, confirming the presence of a radiation-induced back reaction. Crystal B was irradiated at 273 K, followed by a further irradiation at 233 K, crystal C was irradiated at 253 K, and crystal D at 233 K. In each case it is seen that the quasisaturation F-center concentration attained is characteristic of the temperature of irradiation as predicted by the model. The results for the V_2^m centers (Fig. 2) show a similar pattern as would be expected for defects which are the major complements of the F centers. Although H_D-center concentrations were too low to be measured in the present experiments, the experimental results on KCl(Sr) obtained by Marat-Mendes and Comins[13] (see Sec. II A) can be compared with theory and will be discussed in the following section.

A further experiment was performed on crystal D to compare the effects of thermal and radiation-induced detrapping of the interstitials. The crystal was irradiated at 233 K such that a suitable defect concentration within the first stage but approaching the quasisaturation level was attained, as already shown in Figs. 1 and 2. The irradiation was then stopped and the temperature raised rapidly to 293 K. The crystal was thermally bleached at this temperature, the bleaching being interrupted at appropriate intervals for rapid recooling to 77 K and optical measurements. The thermal-bleaching program was continued until the rate of change in defect concentration was very small. At this stage the crystal was reirradiated with x rays also at 293 K. The results are shown in Fig. 3. It is clear that the effect of thermal bleaching is quite small over the time scale corresponding to the irradiations. Furthermore the F- and V_2^m-center concentrations attained after a considerable period of thermal bleaching at 293 K bear no obvious relation to the concentration resulting from an irradiation at this temperature. On the other hand, the effect of the radiation-induced bleaching is substantial and is much more rapid than the thermal bleaching. The final concentrations attained correspond to an extrapolation of the defect growth curves produced at 293 K as seen by comparison with Figs. 1 and 2.

V. NUMERICAL SOLUTIONS OF THE KINETIC EQUATIONS

These solutions permit a direct comparison with experimental data and a check on the validity of the approximations and restrictions used in the analytic treatment.

We have solved Eqs. (3)–(7) numerically subject to the attainment of a small quasistationary concentration in the free interstititial concentration, i.e., using Eq. (8). As we have shown by Eq. (13), relation (1) is obtained for the conditions $\alpha_{1j}=\alpha_1$, $\alpha_{2j}=\alpha_2$,

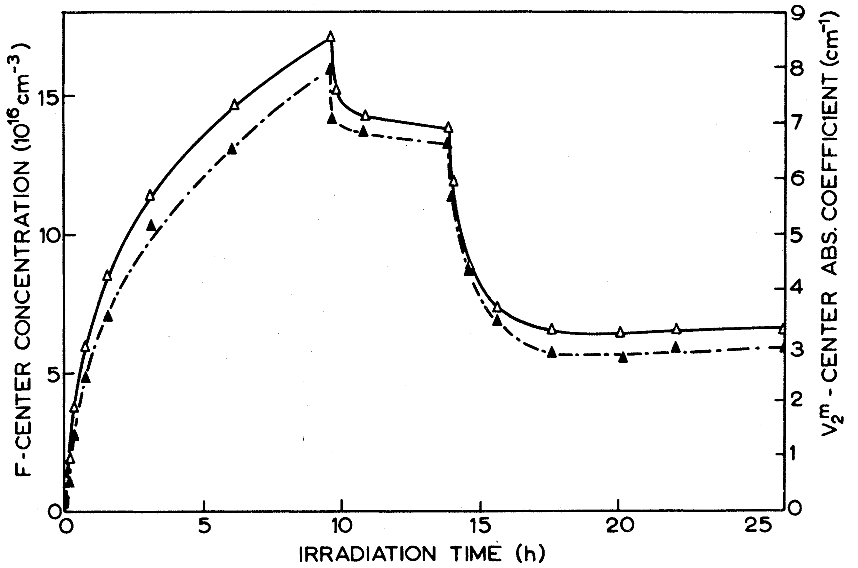

FIG. 3. Effects of thermal and radiation-induced bleaching on *F* and V_2^m centers in crystal *D*. Open triangles: growth and decay of *F* centers during sequential processes consisting of an x irradiation at 233 K, thermal bleaching at 293 K, and radiation-induced bleaching during x irradiation at 293 K. Closed triangles: growth and decay of V_2^m centers during the same sequence.

$K_{1j}=K_1$, $K_{2j}=K_2$, and $n_D=\sum_j n_{Dj}$. We have incorporated these conditions into our numerical treatment.

The primary defect production rate p was determined from the initial slope of the growth curve at 293 K in Fig. 1. The rate coefficient σ was estimated using the relation $(Z\nu_0/N_i)\exp(-E_m/kT)$, where $Z=4\pi r^2\langle b\rangle N_i$ is the number of sites surrounding an *F* center leading to certain interstitial capture.[31] Here r is the capture radius, $\langle b\rangle$ is the average change in *F*-center–interstitial separation during a jump, N_i is the interstitial site concentration, ν_0 is the attempt frequency, and E_m is the migration energy of an *H* center. These quantities were estimated or determined as follows: $p=6.3\times10^{13}$ cm^{-3}s^{-1}, $E_m=0.075$ eV (Ref. 3), $\sigma=8.6\times10^{-9}\exp(-E_m/kT)$ cm^{3}s^{-1}, with $r=6.7$ Å, $\langle b\rangle=4.4$ Å, and $\nu_0=3.5\times10^{12}$ Hz.[32] The rate coefficients α_1 and α_2 were supposed to have a form similar to that of σ, but with values of Z appropriate to the respective processes of interstitial stabilization. We estimate n_D as 1.4×10^{17} cm^{-3}, which is a realistic concentration of divalent impurity-associated traps in a relatively pure crystal.

As discussed in Sec. IV, *F*- and V_2^m-center concentrations were measured but the exact behavior of the H_D-center concentration is uncertain in our experiments. According to the approximate Eq. (11) which leads to relation (1), the behavior of *F*-center growth is largely controlled by K_2 provided K_1 lies within an appropriate range of values. We have adopted the simplest procedure by setting $K_1=K_2=B_2\times\exp(-E_2/kT)$, where E_2 was directly determined from the temperature dependence of f_0 as 0.32 eV. With these prior estimates and determinations, α_1, α_2, and B_2 were adjusted to fit the experimental growth curves. Good fits were obtained with $\alpha_1=0.03\sigma$, $\alpha_2=1.5\sigma$, and $B_2=50.1$ s^{-1}. We note that the general behavior for both *F* and V_2^m centers is quite well reproduced by the calculated growth curves in Figs. 1 and 2. In particular the dynamic temperature dependence of the saturation of the first stage is clearly evident. There are deviations at higher doses between the calculated and experimental curves. Since in the present work we are interested in first-stage behavior, we have not included terms describing clustering of interstitials beyond the di-interstitial stage in the kinetic equations. Terms of this type, when included, are able to account for late-stage behavior rather well.[8] As expected, for small H_D-center concentrations, the *F*-center growth curves are not sensitively dependent on K_1. Indeed computations using Eq. (11) directly lead to growth curves very similar to those with the full solutions. Thus although this simpler equation is satisfactory as a description of *F*-center production near room temperature, a more detailed understanding of the interrelationships between *F* centers and their complements, the H_D and V_2^m centers, requires the full solutions.

We have thus extended our calculations to other aspects of the growth of defects which have a direct bearing on published experimental data. Calculations of the early growth of *F*, H_D, and V_2^m centers using the same parameters as before are shown in Fig. 4.

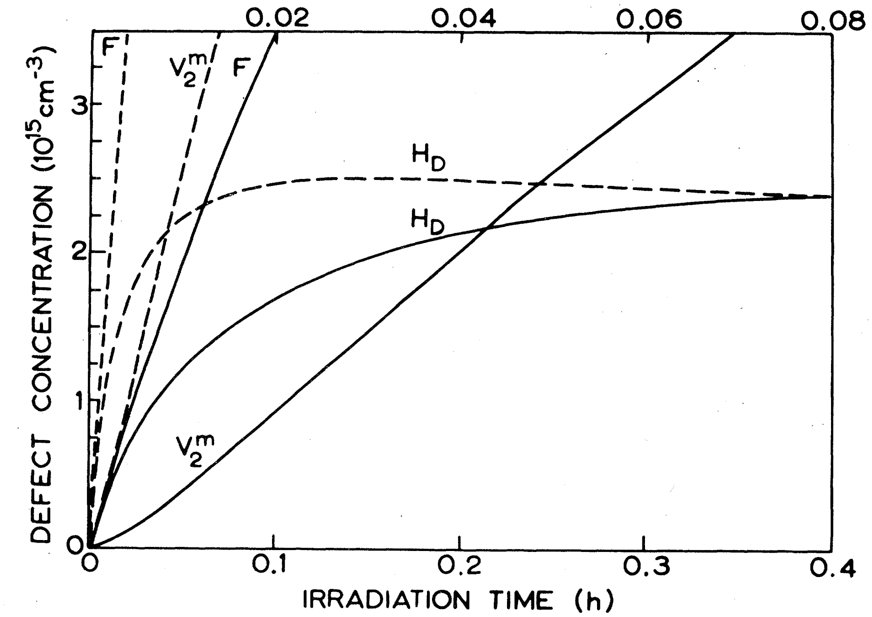

FIG. 4. Early growth of F, V_2^m, and H_D centers calculated using the theoretical parameters reported in the text and in the caption for Fig. 1. The temperature used was 293 K. The upper (shorter) time scale refers to the solid curves, while the lower (longer) time scale applies to the dashed curves.

The calculated growth curves are in good qualitative agreement with results obtained by Marat-Mendes and Comins[13] on KCl(Sr) (see Fig. 3 of their paper). The important features which are reproduced are the initial suppression at low doses of the V_2^M-center growth while the H_D centers grow as important complements of the F centers, the subsequent faster growth of the V_2^m centers which eventually grow as the major complements of the F centers, and the saturation behavior of the H_D centers, which, with the chosen parameters, undergo a distinct decrease in concentration after reaching a maximum. This type of behavior is typical of intermediate products in growth processes and provides strong support for the basic concepts of the model. A further aspect of these results is shown in Fig. 5 where we have plotted logarithmically the V_2^m-center concentration against the H_D-center concentration. It is clear that the square of the H_D-center concentration is proportional to the V_2^m-center concentration until saturation of the former defects occurs. These results are directly comparable with experimental data, especially that in Fig. 4 of Hoshi *et al.*[12] We note that the constant of proportionality for the relation $(H_D)^2 \propto (V_2^m)$ is temperature dependent.[16] This behavior can be reproduced theoretically by a relatively slow reduction in the ratio α_2/α_1 corresponding to a different temperature variation in the interstitial trapping cross sections. The required variation makes little difference to the growth curves for F and V_2^m centers near

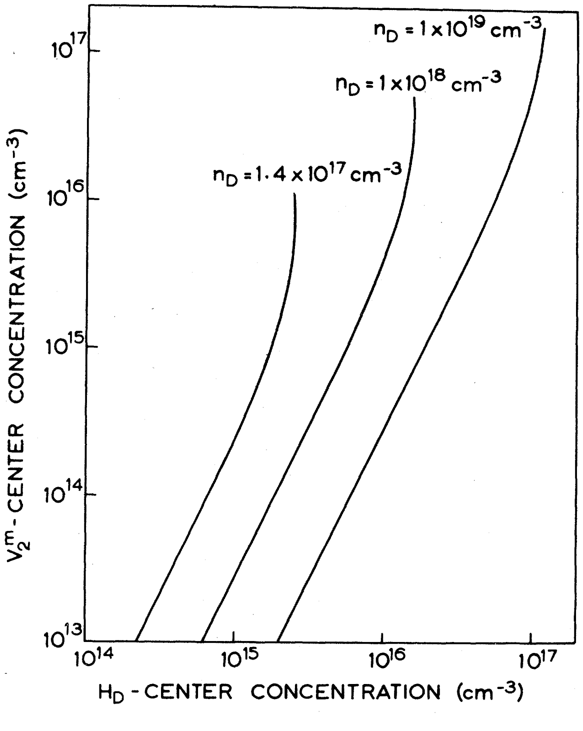

FIG. 5. Logarithmic plots of V_2^m-center concentration against H_D-center concentration calculated for various dominant interstitial trap concentrations n_D. The temperature used was 293 K. Other parameters are the same as for Fig. 1.

room temperature since under these circumstances the H_D centers are in low concentration.

In Fig. 6 we have plotted logarithmically the quasisaturation level of the *F*-center concentration (f_0) against the concentration of the dominant interstitial trap (n_D) over a wide range. Here we have used two different primary defect production rates (p) corresponding in practice to relatively high and low intensities, respectively. As is seen, relation (1), i.e., $f_0 \propto \sqrt{n_D}$ holds well over several orders of concentration and can be compared with experiment.[1,4,10,11] It is interesting to note that for high values of p, corresponding to large radiation intensities, some curvature in the plot is found, particularly for the lower impurity concentrations. This corresponds to a situation where the inequality $(p\alpha/2)^2 << 4p\alpha\sigma K_2 n_D$ in Eq. (12) does not hold. In the range of impurity concentrations, usually used for studies of this type (5×10^{17} to $5 \times 10^{19}\ \mathrm{cm}^{-3}$) little curvature is observed.

In Sec. II B we studied the saturation concentration of the H_D centers (n_{1s}) as a function of the dominant trap concentration n_D, finding that $n_{1s} \propto \sqrt{n_D}$ holds strictly in the case where $n_{1j} >> n_{2j}$, i.e., the H_D center concentration greatly exceeds that of the V_2^m centers. By adjustment of the parameters we can duplicate a range of conditions. As seen in Fig. 7 we find that $n_{1s} \propto n_D^q$, where $0.5 \leq q \leq 1.0$.

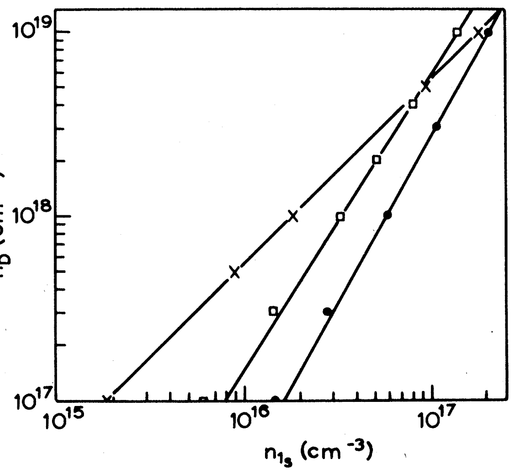

FIG. 7. Logarithmic plots of the dominant interstitial trap concentration (n_D) against the saturation concentration of the H_D centers (n_{1s}) for different values of the parameters. Parameters common to all plots: $p = 6.3 \times 10^{13}\ \mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, $E_m = 0.075$ eV (Ref. 3), $T = 195$ K, $\sigma = 8.6 \times 10^{-9} \times \exp(-E_m/kT)\ \mathrm{cm}^3\,\mathrm{s}^{-1}$, $K_1 = 50.1 \exp(-0.20/kT)\ \mathrm{s}^{-1}$, $K_2 = 50.1 \exp(-0.32/kT)\ \mathrm{s}^{-1}$, $\alpha_1 = 0.03\sigma$. Crosses: $\alpha_2 = 50\alpha_1$, open squares: $\alpha_2 = 10\alpha_1$, closed circles: $\alpha_2 = \alpha_1$. The results indicate a relation of the form $n_{1s} \propto n_D^q$. The respective values of q for the three plots are crosses $q = 1.0$, open squares $q = 0.62$, closed circles $q = 0.54$.

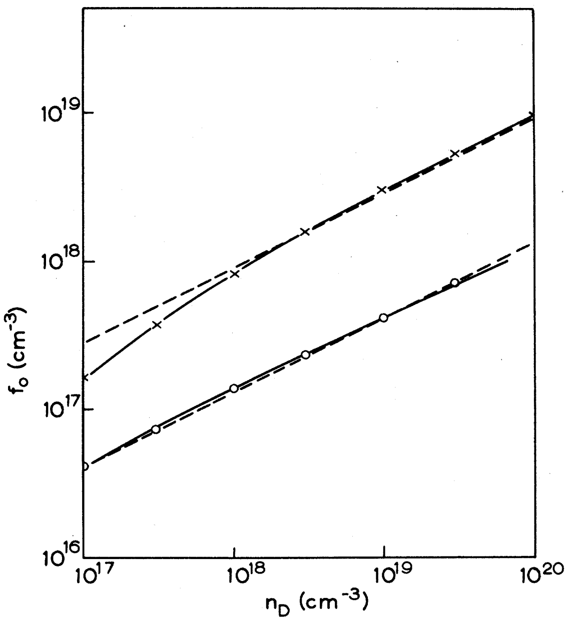

FIG. 6. Logarithmic plots of the quasisaturation level of the *F*-center concentration (f_0) against the concentration of the dominant interstitial trap (n_D) calculated for two values of the primary defect production rate (p) at $T = 293$ K. Circles: $p_1 = 6.3 \times 10^{13}\ \mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, crosses: $p_2 = 50p_1$. Other parameters are as for Fig. 1. The dashed lines correspond to a strictly square-root relation.

In comparing the calculated results with those obtained experimentally, we refer to the papers by Hoshi *et al.*[12] and by Itoh and Ikeya[27] in which this relation was studied in KBr(Ca) for irradiations at 195 K. We have reexamined their results in the light of the predictions of the model. In Fig. 4 of Hoshi *et al.*[12] the concentration of H_D centers is plotted as a function of the concentration of trapped di-interstitial centers (known as D_3 centers in KBr) for three different concentrations of Ca^{2+} impurity. From these results it may be seen that the concentration of H_D centers at saturation (n_{1s}) is comparable to that of the trapped di-interstitials or D_3 centers $(n_{1s} \gtrsim n_2)$. On the basis of our model, we would expect the relation $n_{1s} \propto n_D^q$ with $q > 0.5$. In fact we calculate $q \sim 0.6$ for the Hoshi *et al.* data. On the other hand the data in Fig. 6 of Itoh and Ikeya[27] yields $q \sim 0.5$. We note, however, that these results include data for crystals from varied origins; those with the two highest impurity concentrations are different from the samples with lower impurity levels. Moreover, in heavily doped specimens, precipitation of the impurity may take place to some degree.[33] For these reasons it would seem reasonable to recalculate q from the published data excluding that where the use of crystals from different origins and high impurity contents occur simultaneously. In this case we also find $q \sim 0.6$.

As far as the intensity dependence of the quasisaturation level f_0 is concerned, we need to examine Eq. (12). The overall intensity dependence will depend on two terms, p and B_2, which are both expected to be intensity dependent. Since $f_0 \propto \sqrt{p/B_2}$ for constant n_D and T, we see that a measured intensity dependence of f_0 in an experiment will not give the separate intensity dependences of p and B_2, but only their ratio. The experimental results on KCl (Ref. 34) and NaCl (Ref. 35) show that $f_0 \simeq kI^{0.4}$ where I is the radiation intensity. The intensity dependence of the primary defect production rate p can be estimated in principle from the initial portion of the F-center growth curves. However it is by no means certain that this dependence is maintained throughout the growth curve; in fact Pooley[36] has suggested that the relation between p and I may vary depending on the intensity and the concentration of electron trapping defects and under certain conditions one might expect $p \propto I^{3/2}$. The relation between B_2 and I is more obscure and will obviously depend on the nature of the interstitial detrapping process. If for example the process involves electron capture by the trapped di-interstitial defects as suggested previously by Marat-Mendes and Comins,[15] then an estimate of the intensity dependence of the electron density n_e in the conduction band would be relevant. Very simple arguments,[34] modified to consider electron trapping dominated by V_2^m centers, give $n_e \sim I^r$ where $0.5 \leq r \leq 1$. On such a model B_2 would also have this intensity dependence. The result $f_0 \propto I^{0.4}$ would require $p \sim I^{3/2}$ and $B_2 \gtrsim I^{1/2}$. On the other hand if $p \sim I$, then B_2 would have to be virtually independent of radiation intensity, which would appear unlikely considering the obvious effects of the radiation-induced bleaching observed.

For the sake of illustration, we have used the intensity dependences $p \propto I^{3/2}$ and $B_2 \propto I^{1/2}$ to calculate growth curves of F and V_2^m centers for various values of the intensity. These results are shown in Fig. 8. We note that the effects observed by Harrison[37] in which the quasisaturation F-center concentration (f_0) is characteristic of the intensity of irradiation are reproduced at least qualitatively.

VI. DISCUSSION

The theoretical model for first-stage F-center production provides a very different explanation for the origin of the observed experimental effects than that given by most models suggested in the past (see the Introduction). In particular, the total exhaustion of preexisting defects cannot provide an explanation of the dynamic and reversible changes in the quasisaturation level of the F centers and their major complements. These effects are satisfactorily explained by the new model. Furthermore the square-root relation between first-stage F centers and the concentra-

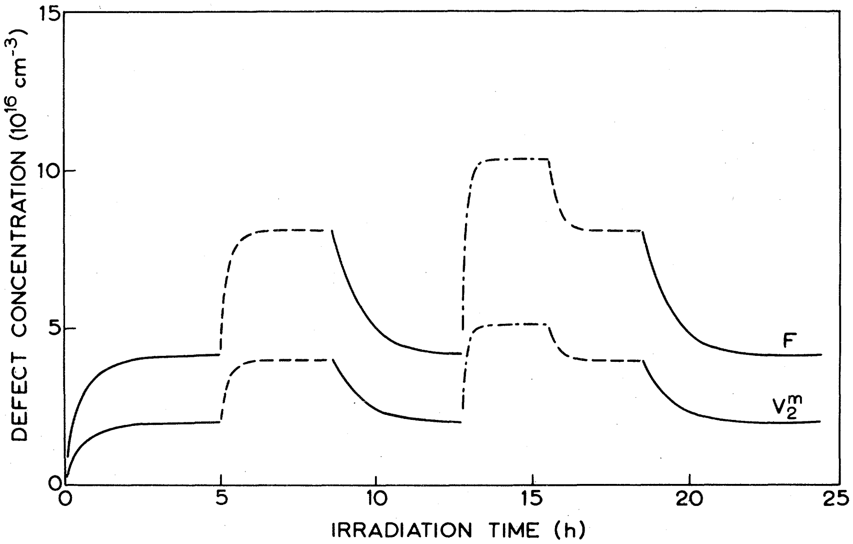

FIG. 8. Growth curves for F and V_2^m centers calculated for various relative intensities of irradiation. In the simulations, the primary rate p' for the different relative intensities was calculated using $p' = p(I_2/I_1)^{3/2}$; similarly $B_2' = B_2(I_2/I_1)^{1/2}$. Parameters used were $p = 6.3 \times 10^{13}$ cm^{-3} s^{-1}, $B_2 = 50.1$ s^{-1}, $n_D = 1 \times 10^{17}$ cm^{-3}, $T = 293$ K. Other parameters are as for Fig. 1. Solid curves $I_2/I_1 = 1$, dashed curve $I_2/I_1 = 5$, dot-dashed curve $I_2/I_1 = 10$.

tion of divalent impurities, relation (1), follows directly from the solution of the kinetic equations. The relation between the saturation concentration of the H_D centers and the concentration of impurities has been examined and the model gives a power-law relation $n_{1s} \propto n_D^q$ where the exponent q lies between 0.5 and unity. These conclusions appear to be supported by available experimental data[12,27] although further experiments would be valuable.

Other observed experimental results, such as the square-law relation between the V_2^m centers and the H_D centers before the saturation of the latter,[12,16] are well reproduced, as is the decay of the H_D centers after reaching a maximum concentration.[13] The extent of decay, depends on the parameters chosen and can be made negligible with an appropriate choice. This latter condition is evident in the results of Itoh and Ikeya[27] on KBr(Ca).

It is seen that the detrapping of interstitial halogens is an essential feature of the mechanism and we emphasize that the dominant process is *radiation induced,* rather than being *purely* thermally activated. Thermal activation is, of course, involved as part of the process. These conclusions arise from the experiment with crystal *D*. This shows that pure thermal bleaching results in a defect concentration bearing no obvious relation to that produced during irradiation at the same temperature. However radiation-induced bleaching and thermal activation together result in a dynamic saturation level characteristic of the temperatuare of irradiation. The rapid reduction of the defect concentration produced during an irradiation at 233 K by subsequent irradiation at 293 K shows the efficiency of the radiation-induced process which occurs in a time scale consistent with the period of the experiments.

The precise details of the radiation-induced detrapping process are not clear, but may involve electron capture by the trapped di-intersititial defects. This point of view was expressed in a previous paper.[15] There are distinct analogies between the rapid decay of defects during irradiation in which recombinations between interstitials and vacancy centers occur and similar overall effects which occur during optical bleaching experiments with light within the *F* band. Here, the *F* centers release electrons which are predominantly captured by the V_2^m centers and a mutual decay of these complementary defects occurs.

As far as the intensity dependence of the quasisaturation of the *F* centers is concerned, the model is able to reproduce the reversible changes in saturation concentration with changes in irradiation intensity.[37] The near-square-root-relation dependence on radiation intensity observed experimentally[34,35] can also be obtained provided appropriate intensity dependences for the primary defect production rate and the radiation-induced interstitial detrapping rate are assumed. However these assumptions are by no means firmly established and further experimental work in this area is needed.

We should comment on the nature of the defects formed as complements to the *F* centers. The H_D center, being paramagnetic, has been thoroughly investigated.[9,21] However the V_2^m center (or D_3 center) is less well understood. Schoemaker and coworkers[21] have observed defects consisting of di-*H* centers trapped near divalent impurities and IV dipoles at low temperatures by ESR and remark that similar nonparamagnetic centers are also possible. These would presumably correspond to the trapped di-halogen defects observed in the present experiments.

The somewhat controversial point as to the charge state of the trapped di-interstitial defect, i.e., Cl_2^0 or Cl_3^- has not as yet been satisfactorily resolved.[16,17] Raman scattering experiments[38] appear to offer the most promising approach to this question and we have such experiments in progress.

It should be noted that the present work has certain features in common (and certain differences in detail) with the model of Aguilar *et al.*,[8] both having been presented at a recent conference. The Aguilar *et al.* paper concentrates largely on the large-dose stage-III region in *F*-center production and this complements the present studies on first-stage production. We observe that both models calculate defect concentrations under steady-irradiation conditions which are appropriate to *in situ* measurements. Complex post-irradiation effects have been observed in KCl (Ref. 39) and NaCl(Refs. 40 and 41) which lead to differences between steady-state concentrations of defects and those measured subsequent to an irradiation period. These processes appear to be thermally activated and in NaCl have an activation energy of ~0.4 eV.[41] Our experimental procedures minimize these effects. With the cooling procedure adopted the sample will attain temperatures sufficiently low as to assure negligible decay in 1–2 min. Using the published data,[39] this would indicate a difference between the *in situ* values and ours by a few percent. It would appear that such mechanisms, while being important in a detailed understanding of the defect-production process, do not obscure the dominant relationships between defects and the overall functional forms of their growth behavior as predicted by the rate models and found in typical experimental studies.

Finally we note that reversible changes in the ultimate saturation level of defect production with changes in dose rate and temperature in very heavily irradiated KCl have been studied by Sonder and Templeton.[42] These effects appear similar to those observed in the present experiments and indeed the dominant activation energy determined (0.4 eV) lies fairly close to the 0.32 eV found here for the first stage. The basic concept of interstitial detrapping featured in both our model and that of Aguilar *et al.*[8] appears to account for these effects in a consistent manner. Indeed it is encouraging to see that models employing the same basic concepts are able to account for many of the outstanding features of defect-growth curves.

ACKNOWLEDGMENTS

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