Simple model for the influence of impurity aggregates on the F-center production of alkali halides

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A simple heterogeneous nucleation model for F-center production in alkali halide crystals doped with doubly valent impurity ions in which the influence on the coloring efficiency of impurity aggregation during irradiation and/or the presence of aggregates in the sample at the start of the irradiation process is presented. The model is based on a set of ten nonindependent differential equations which were solved numerically by using a Runge-Kutta iteration procedure. It is shown that, within the hypotheses on which the model is based, the coloring efficiency may decrease as impurity concentration increases. Moreover, this simple theory accounts for a frequently observed unexplained experimental fact in the sense that the coloring curve for a heavily doped sample may cross that for a slightly doped one after the initial rise in such a way that more coloring is achieved during stage II of the F-center growth curve for the lower concentration. This model together with those previously reported provide a quite complete theoretical background to explain qualitatively the production of F centers in alkali halides doped with doubly valent impurity ions under different experimental conditions.

I. INTRODUCTION

Recently, theoretical models for F-center production in alkali halide crystals doped with doubly valent impurity ions (M^{2+}) have been developed by several workers.[1-3] In all these models, a heterogeneous nucleation process and the present understanding of the nature of the trapped interstitial centers have been incorporated. The numerical solutions of the kinetic equations involved in these models are generally in good qualitative agreement with the more important features of the experimentally determined effects of room temperature x-ray and/or γ-ray irradiation in these types of crystals. In some cases, semiquantitative agreement between model and experiment has been achieved. However, neither of these models, as they stand, may reproduce one of the unexplained experimental results frequently obtained[4-6] in the systems NaCl:Mn^{2+}, KCl:Pb^{2+}, and KCl:Sr^{2+}, in the sense that the coloring curve for a heavily doped crystal crosses that for a slightly doped one in such a way that more coloring is produced during stage II of the F-center growth curve for the lower concentration. With regard to this situation, Rubio and co-workers[7] suggested that if the radiation-induced process of impurity aggregation occurring during stage I of the coloring curve strongly competes with those leading to the formation of F centers, then the balance between them could result in lower coloring during stage II as impurity concentration increases, especially if the aggregates and/or precipitates formed during irradiation are some-

what less efficient than the isolated dipoles for enhancing coloring. This suggestion has been recently tested by some of the present authors[8] by analyzing the influence of radiation intensity and lead concentration in the room-temperature x-ray coloring of KBr. It was ascertained that the ionizing radiation induced lead aggregation and/or precipitation to the irradiated specimens as revealed by analyses of the emission and excitation spectra. The occurrence of this process was related to the observed decrease in the rate of F-center coloring. Moreover, it was established that lead aggregation induced by irradiation was the process responsible for the fact that the curves corresponding to very high impurity concentrations cross those for lower concentrations after the initial rise in such a way that the saturation level for coloring during stage II was lower as lead concentration increased above ~ 60 ppm

The main purpose of the present paper is to analyze, from a theoretical point of view, the influence of impurity aggregates and/or second-phase precipitates induced by irradiation on the room-temperature production of F centers in alkali halides doped with M^{2+} impurity ions.

II. MODEL OF DEFECT GROWTH

The basic assumptions of the model presented here are the following: (1) the capture of one interstitial defect (H) by the initially existing dipole traps (S_0) produces a center S_1 whose growth correlates with stage I of the F-

center coloring curve and (2) the trapping of one additional interstitial by S_1 generates a new center (S_2) whose stability is less than that of S_1. The additional trapping of one or more H defects by S_2 converts this center into a stable center A. In order to take into account the effect of impurity aggregation during the irradiation process, we assumed that the isolated dipoles originally present in the sample at the start of irradiation may form aggregate complexes such as dimers (P) and trimers (Q) during the time in which the irradiation is performed as a result of the enhanced rate of dipole aggregation by irradiation. The dimer complexes are able to capture one or two interstitial defects forming P_1 and P_2 centers, respectively. On the other hand, in order to make the model as simple as possible, we assumed that the trimer complex is the final product in the radiation-induced process of impurity aggregation. Although this assumption is a very rough approximation, it does not essentially alter the physical picture. Moreover, it can be easily removed in order to consider the effect of larger impurity aggregates on color center formation. Finally, it was considered that the trimer complexes are not able to capture the H defects. Therefore, these complexes represent in the model the large impurity aggregates or even the second-phase precipitates which are known to have less ability to trap the interstitial defects in comparison with those of the isolated dipoles and dimer complexes[9-12]

The basic ideas mentioned above can easily be reduced to the following equations:

$$\frac{df}{dt} = g - \sigma i f , \tag{1}$$

$$\frac{di}{dt} = g - \sigma i (f + s_0 + s_1 + s_2 + n_a^{2/3} a) + \beta s_1$$

$$+ \alpha s_2 - \sigma i (p_0 + p_1 + p_2) + \gamma p_1 + \eta p_2 , \tag{2}$$

$$\frac{ds_0}{dt} = -\sigma i s_0 + \beta s_1 - c_1 (s_0^2 + s_0 p_0) , \tag{3}$$

$$\frac{ds_1}{dt} = -\sigma i s_1 + \sigma i s_0 - \beta s_1 + \alpha s_2 , \tag{4}$$

$$\frac{ds_2}{dt} = \sigma i s_1 - \sigma i s_2 - \alpha s_2 , \tag{5}$$

$$\frac{da}{dt} = \sigma i s_2 , \tag{6}$$

$$\frac{dp_0}{dt} = -\sigma i p_0 + \gamma p_1 + \frac{c_1}{2} (s_0^2 - 2 s_0 p_0) , \tag{7}$$

$$\frac{dp_1}{dt} = \sigma i p_0 - \sigma i p_1 - \gamma p_1 + \eta p_2 , \tag{8}$$

$$\frac{dp_2}{dt} = \sigma i p_1 - \eta p_2 , \tag{9}$$

$$\frac{dq_0}{dt} = c_1 s_0 p_0 , \tag{10}$$

where f, i, s_0, p_0, and q_0 represent the concentration of F centers, free interstitials, empty dipole traps, empty dimer traps, and trimers, respectively. s_1, s_2, p_1, p_2, and a denote the concentration of the interstitial centers

described previously.

In the equations above it is considered that the ionizing radiation creates F and H centers at a rate g. Equation (1) gives the production of F centers which is reduced by possible recombination with mobile halogen defects. Equation (2) gives the production of free interstitial defects, their possible recombination with F centers and their trapping at S_0 (dipoles), P_0 (dimers), S_1, S_2, P_1, and A centers. This equation also includes the halogen detrapping terms βs_1, γp_1, αs_2, and ηp_2 which are expected to be dependent on radiation intensity and temperature. Equation (3) expresses the evolution of the initial concentration of empty dipole traps. The reduction in this concentration is the result of halogen trapping, as well as of dimer and trimer formation. It is important to notice that the rate constant for dimer formation (C_1) has been considered to be equal to that of trimer formation for the sake of simplicity. Moreover, considering the low probability of three-body encounters, it was assumed that trimer formation is only the result of the encounter of a dipole with a dimer. On the other hand, we assumed, appealing to the experimental evidence, that the dimer complexes are equally as efficient as the isolated dipoles for enhancing coloring.[8-11] Therefore, the values for the capture rates for H trapping, as well as for the detrapping constants associated with centers P_1 and P_2, were considered to be equal to those of centers S_1 and S_2.

The set of Eqs. (4)—(6) and (8) and (9) gives the evolution of the interstitial centers S_1, S_2, A, P_1, and P_2, respectively, while Eqs. (7) and (10) express the concentration of dimers and trimers as a function of the irradiation time. Finally, it should be pointed out that one of the most important assumptions implicitly accepted in these equations is that the capture rates for H trapping by dipoles, dimers, F centers, S_1, S_2, and P_1, except for the capture by the aggregate center A, have been considered to be equal $(\sigma = 10^{14} \text{ cm}^{-3} \text{sec}^{-1})$. For center A, the capture rate σ_a was assumed to be proportional to the surface of the interstitial cluster, i.e., $\sigma_a = n_a^{2/3} \sigma$ where n_a is the mean number of interstitials per cluster. However, different values of the rate coefficient should probably be used for the various interstitial traps. In order to take this fact properly into account it is necessary to have a very detailed knowledge of the trapping cross sections for the whole series of interstitial aggregates. Unfortunately, this knowledge is not available now. In any case this detailed model will be only applicable to a given crystal system and therefore of little general use. Moreover, the assumptions above are not essential to the model, and if necessary can be removed. On the other hand, the values employed in the numerical calculations for the detrapping constants $\beta = 10^{-2} \text{ sec}^{-1}$ and $\alpha = 5 \text{ sec}^{-1}$ are the same as those employed previously.[2,3] In all cases the value of g was taken to be equal to $10^{14} \text{ cm}^{-3} \text{sec}^{-1}$ which corresponds to a dose rate of $10^{16} \text{ eV cm}^{-3} \text{sec}^{-1}$ if one assumes[2] that the creation of each F-H pair requires that of 100 eV. With the numerical values for the parameters involved in the rate equations, the concentration of the various defect species can be obtained as a function of the irradiation dose for several values of the initial concentration of dipoles, aggregate complexes, and C_1. In order to do this,

the rate equations were solved numerically by using a Runge-Kutta iteration program on a VAX-11/780 computer.

III. RESULTS AND DISCUSSION

A. $p_0 = 0$ and $q_0 = 0$

This particular situation corresponds to the case in which all the impurity ions are in solution in the sample forming isolated dipoles at the start of irradiation. Figure 1(a) illustrates the effect of the value for the rate constant C_1 on the F-center coloring curve for a selected impurity concentration of $s_0 = 12 \times 10^{17}$ cm^{-3}. In the same figure, the coloring curves for other impurity concentrations, i.e., $s_0 = 3 \times 10^{17}$ and $s_0 = 5 \times 10^{17}$ cm^{-3} are also included for the sake of comparison. In order to obtain these latter curves we considered that impurity aggregation induced by irradiation is negligible for impurity concentrations up to 5×10^{17} cm^{-3}. This assumption is reasonable if one takes into account the experimental results obtained in alkali halides doped with either strontium, europium, or calcium ions.[6,10,13] Therefore, in order to obtain the coloring curves for $s_0 = 3 \times 10^{17}$ and $s_0 = 5 \times 10^{17}$ cm^{-3},

the value of $C_1 = 0$ was employed in the calculations. In Fig. 1(b) a similar situation is presented for an impurity concentration of 16×10^{17} cm^{-3}. The values employed for C_1 in order to obtain the coloring curves portrayed in Fig. 1 are in the range of the magnitudes which have been determined for this constant in the studies of the aggregation kinetics of M^{2+} impurities in the alkali halides.[14,15]

Figure 2 displays the corresponding evolution of the interstitial centers S_1, S_2, P_1, P_2, and A as a function of the irradiation dose for an impurity concentration of 12×10^{17} cm^{-3} and for two different values for the rate constant C_1. In the same figure the average number (n_a) of halogen interstitials forming the center A, as well as the number of F centers produced as a function of dose are also plotted for comparison. It is observed that the growth of the F-coloring curve during stage I correlates with the growth of the S_1 and P_1 interstitial centers.

Figure 3 outlines the corresponding evolution of the concentration of dipoles, dimers, and trimers as a function of the irradiation dose.

Reference to Fig. 1 shows that the process of impurity aggregation may strongly compete with those leading to the formation of F centers. Moreover, depending on the value employed for C_1 the amount of coloring for a heavily doped crystal may be lower than that for a slightly doped one not only during stage II but also during stage
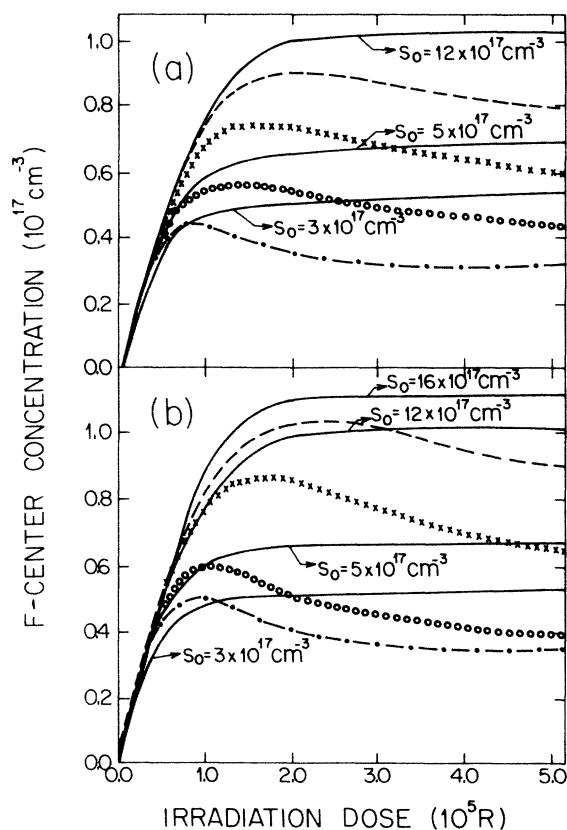

FIG. 1. (a) Computer-simulated F coloring curves as a function of impurity concentration for the case $p_0 = 0$, $q_0 = 0$. The effect of the value for the rate constant C_1 on the coloring curve corresponding to $s_0 = 12 \times 10^{17}$ cm^{-3} is also shown for $C_1 = 0$, ————; 3.5×10^{-4} sec^{-1}, — — —; 10^{-3} sec^{-1}, $\times$; 5×10^{-3} sec^{-1}, O; and 10^{-2} sec^{-1}, —·—·. (b) The same as in (a) but for an impurity concentration of $s_0 = 16 \times 10^{17}$ cm^{-3}.
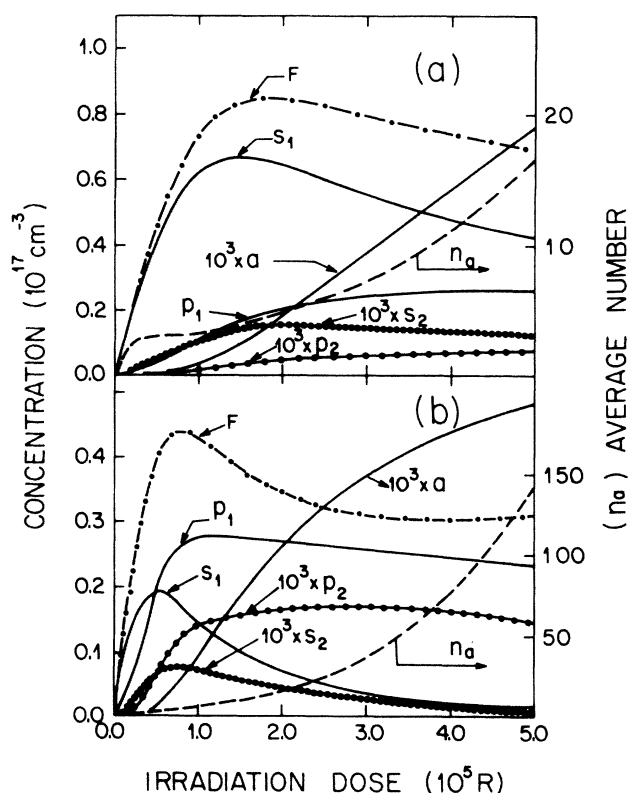

FIG. 2. Computer-simulated evolution of the concentration of the various traps with irradiation dose for a selected impurity concentration of $s_0 = 12 \times 10^{17}$ cm^{-3}; (a) $C_1 = 5 \times 10^{-4}$ sec^{-1} and (b) $C_1 = 10^{-2}$ sec^{-1}.
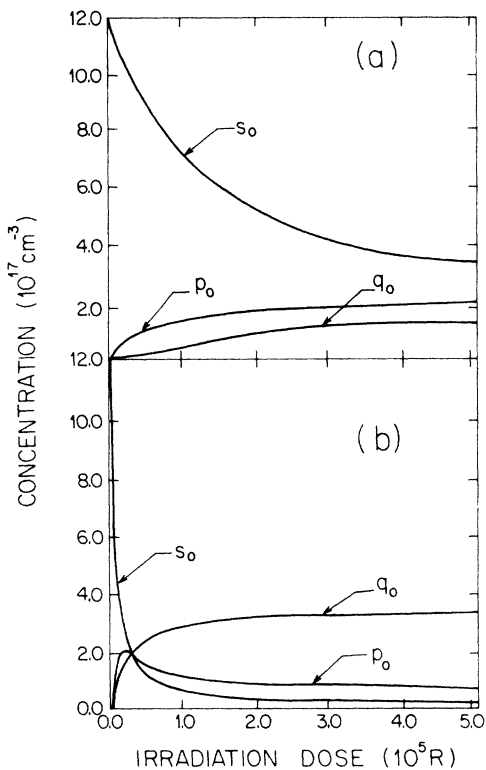
FIG. 3. Computer-simulated evolution of the concentration of dipoles (s_0), dimers (p_0), and trimers (q_0) as a function of the irradiation dose for a selected impurity concentration of 12×10^{17} cm^{-3}: (a) $C_1 = 5 \times 10^{-4}$ sec^{-1} and (b) $C_1 = 10^{-2}$ sec^{-1}.

I of the F-center coloring curve. This result is to be expected if one considers that increasing the value of C_1 enhances the formation of trimer complexes which are assumed to be inefficient traps for the trapping of the mobile halogen defects. In contrast with this result, if the trimer complexes are assumed to be equally as efficient as the isolated dipoles and dimer complexes for enhancing coloring, then the coloring will increase with impurity concentration and the crossing of the coloring curves is not produced.

B. $p_0 \neq 0$ and $q_0 = 0$

The coloring curves presented in the subsection above were obtained on the assumption that all the impurity ions were in solution in the crystal before irradiation. However, it is a well-known experimental fact that depending on impurity concentration large aggregates and/or second-phase precipitates may be present in the sample even after a quenching treatment from high temperatures. The presence in the sample of these aggregate complexes at the start of irradiation may considerably enhance the impurity aggregation, since they can act as important nucleation centers. Therefore, it is expected that they alter the rate of production of color centers more than in the case discussed above especially if the aggregate complexes are inefficient traps for the H defects.

In order to analyze this situation within the bounds of the theoretical model presented here, coloring curves were obtained as a function of the amount of the impurity which was assumed to be in solution, as well as forming aggregates in the sample before irradiation. The results are portrayed in Fig. 4. In order to obtain these curves we considered as before that only isolated dipoles were present in the sample at the start of irradiation for impurity concentrations up to 5×10^{17} cm^{-3}. Also, it was assumed that impurity aggregation induced by irradiation was negligible up to this concentration. In Fig. 4(a) the effect of the value for C_1 on the F coloring curve corresponding to an impurity concentration of 12×10^{17} cm^{-3} is presented. In order to obtain these curves we considered that 10×10^{17} impurity ions cm^{-3} were forming dipolar complexes (s_0) while 2×10^{17} cm^{-3} were in the form of dimers (p_0) at the start of irradiation. In Fig. 4(b) a similar situation is illustrated for an impurity concentration of 24×10^{17} cm^{-3}. For this latter concentration, only 50% of the impurity was considered to be in solution before irradiation. The other 50% was assumed to be forming dimer complexes.
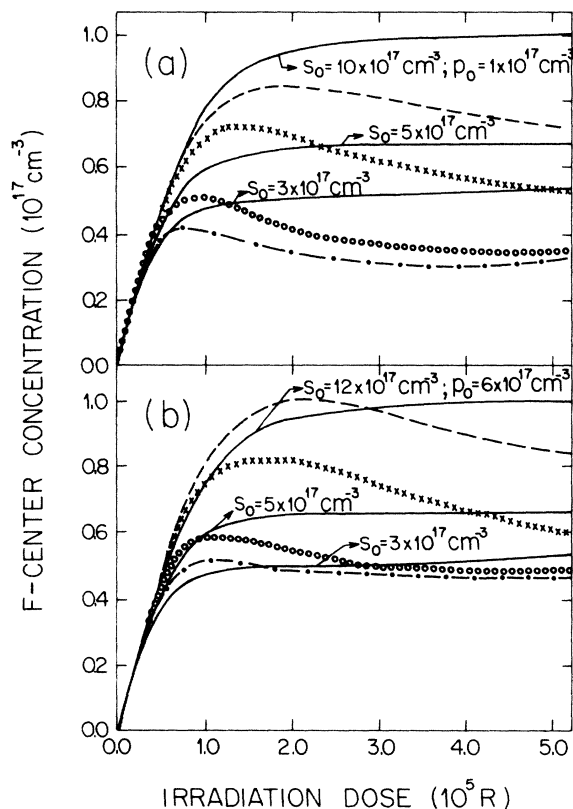

FIG. 4. Computer-simulated coloring curves as a function of impurity concentration for the case $p_0 \neq 0$, $q_0 = 0$. The effect of the value for the rate constant C_1 on the coloring curve corresponding to $s_0 = 10 \times 10^{17}$ cm^{-3} and $p_0 = 1 \times 10^{17}$ cm^{-3} is also portrayed for $C_1 = 0$, ——; 3.5×10^{-4} sec^{-1}, — — —; 3.5×10^{-3} sec^{-1}, $\times$; 5×10^{-3} sec^{-1}, $\circ$; and 5×10^{-2} sec^{-1}, —·—·. (b) The same as in (a) but for the case $s_0 = 12 \times 10^{17}$ cm^{-3} and $p_0 = 6 \times 10^{17}$ cm^{-3}.

The evolution of the interstitial centers S_1, S_2, P_1, P_2, and A as well as of the dipole, dimer, and trimer complexes as a function of the irradiation time is quite similar to those presented in Figs. 2 and 3. The main difference is that the growth in the concentration of trimer complexes occurs faster in this case due to the presence of dimers at the start of irradiation.

Reference to Fig. 4 shows that the coloring curve for a heavily doped crystal may cross those for slightly doped ones after the initial rise. As before, the crossover point is strongly dependent on the value employed for the rate constant C_1.

The coloring curves portrayed in Figs. 1 and 4 are similar to those experimentally determined in the systems NaCl:Mn, KCl:Pb, and KCl:Sr as a function of impurity concentration.[4-6] This fact suggests that the unexplained experimental observation reported in these investigations in the sense that less coloring was produced during stage II of the F-center growth center for the heavily doped samples than that produced in slightly doped ones may be due to: (a) impurity aggregation induced by either ionizing radiation or annealing temperature during irradiation and/or (b) the presence in the sample of impurity aggregates which are not efficient traps for the halogen interstitials at the beginning of the irradiation process. Unfortunately, the experimentally determined coloring curves in the former two systems mentioned above were obtained with a broad band x-ray spectrum and energy deposition rates were not reported. This fact prevents a comparison with the theoretical predictions of the model. However, for the system KCl:Sr the coloring curves were reported as a function of irradiation dose; therefore, a comparison of these results with the predictions of the model appears to be possible in this system.

In order to make this comparison as meaningful as possible, crystals of KCl doped with similar strontium concentrations as those employed to obtain the coloring curves were grown in our laboratory. The concentration of isolated dipoles was then determined in the samples after they were heated for 1 h at 600 °C and then cooled down onto a copper block at room temperature. In order to perform these determinations, ionic thermocurrent measurements were carried out with the experimental setup described previously.[16] It was found that within experimental error ($\pm 10\%$) and for strontium concentrations up to ~ 60 ppm (9×10^{17} cm^{-3}) all the Sr ions were in solution in the cooled samples. For a 165-ppm-doped sample (24×10^{17} cm^{-3}), however, only $\sim 12 \times 10^{17}$ cm^{-3} were found to be in solution in the crystal. This result indicated that $\sim 50\%$ of the impurity ions were forming aggregates in the cooled sample.

With this information at hand, we tried to reproduce the experimentally determined curves using the present model. The results are shown in Fig. 5. One observes that a reasonable semiquantitative agreement between model and experiment is achieved using a value for the rate constant for aggregation $C_1 = 3.5 \times 10^{-4}$ sec^{-1} and the hypothesis mentioned above, i.e., (a) for impurity concentrations up to 5×10^{17} cm^{-3} the radiation-induced process of impurity aggregation is not important ($C_1 = 0$), and (2) the large aggregates represented in the model by
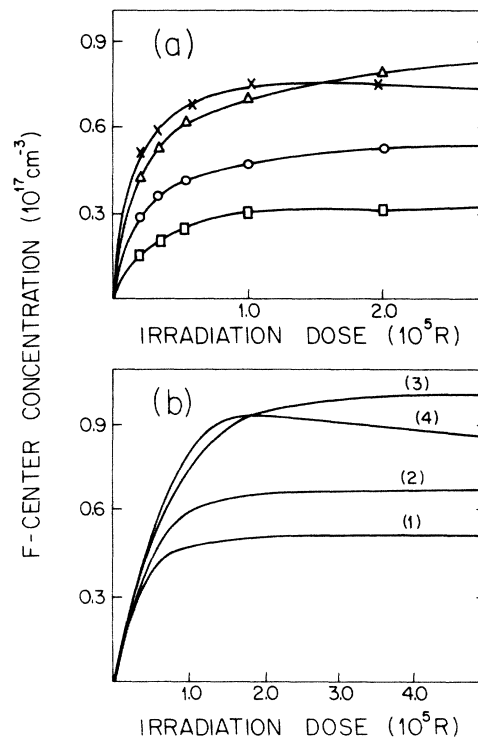

FIG. 5. (a) Experimentally determined evolution of the number of F centers produced as a function of impurity concentration in the system KCl:Sr (Ref. 6). $\square$, 2.7×10^{17} ions cm^{-3}; $\bigcirc$, 4.8×10^{17} ions cm^{-3}; $\triangle$, 9×10^{17} ions cm^{-3}; and $\times$, 24.6×10^{17} ions cm^{-3}. (b) Computer-simulated evolution for the same impurity concentration as described above. The values of C_1 used were for (1) and (2) $C_1 = 0$; (3) $C_1 = 10^{-5}$ sec^{-1}, and (4) $C_1 = 3.5 \times 10^{-4}$ sec^{-1}.

the trimer complexes are not able to capture the interstitials.

A comparison of the coloring curves portrayed in Figs. 1 and 4 indicates that in both cases, i.e., (a) $p_0 = 0$, $q_0 = 0$ and (b) $p_0 \neq 0$, $q_0 = 0$, the model may predict that the F-coloring curve for a heavily doped crystal crosses that for a slightly doped one. The time at which the crossing is produced, however, is considerably smaller for case (b) than for case (a) if one maintains the same value for C_1. Also, the magnitudes employed for C_1 in order to obtain the crossing of the coloring curves are smaller in the second case. Therefore, case (b) appears to be the more appropriate to explain the experimental results, especially if one considers the values reported for C_1. Therefore, the presence of impurity aggregates, especially in the heavily doped crystals at the start of the irradiation, may be the fact responsible for the unexplained experimental determination that lower coloring is sometimes achieved in heavily doped crystals than in slightly doped ones.

At this point, it should be pointed out that the case $p_0 \neq 0$, $q_0 \neq 0$ was not analyzed. This case will correspond within the bounds of the theoretical model presented here, to the experimental situation in which large aggregates or even second-phase precipitates exist in the crystal at the beginning of the irradiation process. These precipitates are expected to be present in "as-grown" and "well-aged"

samples. The existence of these complexes at the start of irradiation will decrease the rate of F-center coloring even more than in the cases discussed above especially if the aggregates and/or precipitates are not efficient traps for the mobile H defects. Therefore, the crossing of the coloring curve corresponding to a heavily doped crystal with that of a slightly doped one is expected to occur at a shorter irradiation time. Also, the amount of coloring should decrease as impurity concentration increases.

On the other hand, it should be mentioned that the effects due to valence changes induced by irradiation on Mn^{2+} and Pb^{2+} have not been considered in the model. It is expected, however, according to our previous results, that these effects only change the saturation level of F coloring, keeping the crossover of the coloration curves.

Finally, the model presented here provides a quite useful scheme to explain qualitatively the effects of x- or γ-ray irradiation in alkali halides systems doped with M^{2+} impurities for which the coloring curves for heavily doped samples are found to cross those for slightly doped ones in such a way that more coloring is achieved in slightly than in heavily doped crystals. The analyses of the experimental data may allow us to establish the correctness of the assumption on which the model is based, which possibly reflect the main physical processes occurring during F-center production in alkali halides doped with M^{2+} ions which aggregate during the irradiation process. Moreover, this model together with those previously reported gives a quite good and complete theoretical basis to explain the production of F centers in alkali halides doped with M^{2+} impurities under different experimental conditions.

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