

Model for F -center production in alkali halides doped with divalent cation impurities that change their valence state by irradiation

S. Ramos B., J. Hernández A., H. Murrieta S., and J. Rubio O.

Instituto de Física, Universidad Nacional Autónoma de México, P.O. Box 20-364, Delegación Alvaro Obregón, 01000 México, Distrito Federal, Mexico

F. Jaque

Departamento de Óptica y Estructura de la Materia C-IV, Universidad Autónoma de Madrid, Madrid 34, Spain

(Received 19 April 1984; revised manuscript received 26 November 1984)

A model for the radiation-induced F -center coloring in alkali halides doped with doubly valent metal impurity ions (M^{2+}) that can change their valence state by irradiation is proposed in the present paper. The primary event is assumed to be the creation of F centers and interstitial halogen (H) pairs. The thermal- and radiation-induced processes associated with the dynamics of H defects and their trapping at defects leading to the stabilization of their counterpart F centers are taken into account during the three stages of the F -coloring curve. The fundamental traps for the interstitials are assumed to be the M^{2+} -cation vacancy dipoles. Therefore, a heterogeneous nucleation process around these complexes is one of the assumptions on which the model is based. It is proposed that stage I of the F -coloring curve is reached with the single process of the capturing of one H defect by a dipole producing an S_1 center. The trapping of one additional interstitial by S_1 generates a less stable center, S_2 . The trapping of one or more interstitials by S_2 gives a stable aggregate center denoted by A , which is responsible for stage III. On the other hand, another way in which these dipoles may vary is through the capture of free electrons during the irradiation process to become either M^+ or M^0 states. It is assumed that these latter states have different capabilities for the trapping of interstitials than those of M^{2+} . The possibility of hole capture by these reduced states, which would allow them to return to the original M^{2+} state, is also included in the model. These basic assumptions are used to postulate a set of ten differential equations which we have solved numerically using a Runge-Kutta iteration program. The numerical solutions of the equations are in good qualitative agreement with the more important features of the experimentally determined effects of room-temperature x-ray irradiation in europium- and lead-doped alkali halides. In some cases, semiquantitative agreement with experiment is obtained.

INTRODUCTION

At the present time, it is well accepted that the radiation-induced production of F centers in the alkali halides involves two mechanisms: (1) a primary event which, through a nonradiative exciton decay process, gives rise to well-separated F and their complementary H centers, and (2) thermal- and radiation-induced process associated with the motion of the halogen interstitials (H) and their subsequent trapping at defects, which leads to the definitive stabilization of the color centers after irradiation. With regard to this last point, it was considered for a long time that in alkali halide crystals doped with doubly valent metal impurities (M^{2+}), the fundamental traps for the mobile halogen defects were the isolated cation vacancies introduced into the crystal in order to preserve its overall charge neutrality.¹⁻³ This idea was arrived at mainly by observing that the experimentally determined amount of first-stage coloration (n_{F0}) was proportional to the square root of the divalent impurity concentration.¹⁻³ In the last few years, however, a large amount of experimental evidence⁴⁻⁷ has been gathered to show that the impurity-vacancy ($I-V$) dipoles, each one consisting of the M^{2+} impurity and a neighboring cation vacancy, act as

the dominant traps for the H defects. Several authors, motivated by this evidence, have recently developed a model^{8,9} for F -center production in alkali halides doped with M^{2+} impurities in which a heterogeneous nucleation process and the present understanding of the nature of the trapped interstitial centers have been incorporated. In the model the isolated $I-V$ dipoles or dipole aggregates are considered to be the fundamental traps for the halogen interstitials. By solving the kinetic equations involved in the model, a large number of experimentally determined effects concerning the radiation-induced production of F centers in alkali halides doped with Sr^{2+} and Ca^{2+} was qualitatively accounted for. In particular, the model predicts that n_{F0} is proportional to the square root of impurity concentration, providing a new explanation for the origin of this relationship. At this point it is important to point out that the model ignores a number of phenomena, such as the formation of F^+ , Z_1 , Z_2 , etc. color centers, as well as complex vacancy centers such as M , R , N , and colloids. Also, the range of validity of the model is restricted to above and about liquid-nitrogen temperatures, where the halogen defects can diffuse through the lattice.

On the other hand, the effects of room-temperature x-ray irradiation on alkali halides doped with M^{2+} impuri-

ties which change their valence state by irradiation have been studied in our laboratories over the last five years.^{5-7,10} It has been ascertained that the effects of x-ray irradiation in NaCl, KCl, KBr, and KI doped with Eu^{2+} or Pb^{2+} are mainly the following: (a) to reduce the number of isolated I - V dipoles, (b) to increase the number of trapped electrons, (c) to change the valence state of the doubly valent impurity ions, and (d) to increase the rate of aggregation of dipoles. In all these experiments the results suggested that the isolated M^{2+} -impurity cation vacancy complexes act as the dominant traps for the radiation-induced interstitials. In fact, in crystals containing a low impurity concentration in which the radiation-induced aggregation of dipoles is an unimportant process, dipole destruction was found to be equal to the sum of the number of F centers produced and the number of converted ions, which is the result expected if the H defects are mainly trapped at the isolated dipoles. However, one of the more interesting results of these investigations^{5,11} was that even for M^{2+} -impurity ions, whose valence state changes under irradiation, the amount of first-stage coloration was found to be proportional to the square root of impurity concentration and dose rate as predicted by the theoretical model mentioned above. This agreement, however, could be very fortuitous in view of the fact that the possibility of the M^{2+} impurities changing valence under irradiation was not taken into consideration in this model.

The main purpose of the present paper is to analyze the influence of the valence change occurring in the M^{2+} ion forming the complex which acts as the fundamental trap for the H defects on the radiation-induced production of F centers in the alkali halides. In order to do this, the possibility that the M^{2+} ion changes to the M^+ and M^0 states through the capture of electrons during the irradiation process has been included in the theoretical model mentioned above. Although the model presented here is oversimplified, it provides an important qualitative view of the more significant features of the experimentally determined effects of room-temperature x-ray irradiation of europium- and lead-doped alkali halides. In some cases semiquantitative agreement with experiment is obtained.

MODEL OF DEFECT GROWTH

The basic assumptions of the model presented here are the same as those employed previously,⁹ i.e., (1) the capture of one halogen interstitial defect (H) by the initially existing I - V dipole traps produces a center S_1 , which is responsible for stage I of the F -center growth, 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 . However, the additional trapping of one or more interstitials by S_2 converts this center into a stable aggregate center A which is the one responsible for stage III.

On the other hand, in order to take into account that the impurity ions may change their valence state by irradiation we assumed (according to the experimental evidence) that the M^{2+} ions may trap free electrons, converting them to the M^+ and M^0 states. The possibility that the impurities in these reduced states may also trap holes

to convert them once again to the M^{2+} initial state has been also considered. However, the conversion $M^{2+} \rightarrow M^{3+}$ by the capture of one hole has not been taken into account in the model since trivalent states of the M impurities in alkali halides produced by irradiation have rarely been found, and in those cases in which they have been detected, large doses of radiation and/or the presence of special types of second-phase precipitates of the doubly valent impurity ions in the crystal have been required.¹² We have also assumed in the model that the halogen interstitial defects are not trapped by the M^+ and M^0 impurities. With regard to this last point, it should be pointed out that the trapping of the interstitial complex by monovalent impurity ions such as Li^+ or Na^+ in the alkali halides has been reported in the literature.¹³ These centers are the so-called H_A centers and they have been observed only at low temperatures (< 50 K), which is not the temperature range (above and about liquid-nitrogen temperatures) of interest for the model proposed in this paper. Moreover, our experimental evidence⁵⁻⁷ in europium- and lead-doped alkali halides indicates that if the H defects are trapped by the impurities in their M^+ and M^0 states, then their number must be quite small in comparison with those which are trapped at the isolated dipoles. This conclusion is equivalent to assuming that in those impurity-vacancy dipoles in which the interstitials have been trapped the M^{2+} ions do not change their valence state as efficiently as when they are not associated with any radiation-induced defect. Therefore, we have also assumed that the M^{2+} impurity ions forming those dipoles associated with centers S_1 , S_2 , and A do not change valence during the irradiation processes and that the M^+ and M^0 ions are not efficient traps for the interstitial halogen defects, at least for the temperature range of interest for the model.

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

$$\frac{df}{dt} = g - \sigma_0 f i, \quad (1)$$

$$\frac{di}{dt} = g - \sigma_0 i (f + s_0 + s_1 + s_2 + n_a^{2/3} a) + \beta s_1 + \alpha s_2, \quad (2)$$

$$\frac{ds_0}{dt} = -\sigma_0 i s_0 + \beta s_1 - b_2 + s_0 e + b h m^+, \quad (3)$$

$$\frac{ds_1}{dt} = -\sigma_0 i s_1 + \sigma_0 i s_0 - \beta s_1 + \alpha s_2, \quad (4)$$

$$\frac{ds_2}{dt} = \sigma_0 i s_1 - \sigma_0 i s_2 - \alpha s_2, \quad (5)$$

$$\frac{da}{dt} = \sigma_0 i s_2, \quad (6)$$

$$\frac{dm^+}{dt} = e(b_2 + s_0 - b_+ m^+) + b h (m^0 - m^+), \quad (7)$$

$$\frac{dm^0}{dt} = b_+ e m^+ - b h m^0, \quad (8)$$

$$\frac{de}{dt} = p - e(b_2 + s_0 + b_+ m^+ + \sigma_0 h), \quad (9)$$

$$\frac{dh}{dt} = p - h[b(m^+ + m^0) + \sigma_0 e], \quad (10)$$

where f , i , and s_0 represent the concentration of F centers, free interstitials, and empty traps, respectively. s_1 , s_2 , and a denote the concentration of interstitial centers mentioned above.

In these equations it is considered that the ionizing radiation creates electron-hole pairs at a rate p , while F and H centers are created at a rate g , where in general $g \ll p$. 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 (I - V dipoles), S_1 , S_2 , and A centers. This equation also includes the halogen detrapping terms βs_1 and αs_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 as a function of time. The reduction in this concentration is the result of halogen trapping, as well as of the possible capture of one electron by the doubly valent impurity ion forming the dipolar complex. In this equation the detrapping terms βs_1 as well as the transformation $M^+ \rightarrow M^{2+}$ by the capture of one hole have been included. The latter process has been accounted for by means of the term, $b = \sigma_0 DR$, where $D = D_0 e^{-E/k_B T}$ is the diffusion coefficient of the V_k center and R is a "critical distance" within which it is possible that the hole may be captured by the M^+ impurity. The value employed^{14,15} for R was 10^{-7} cm which corresponds approximately to three times the lattice parameter of any of the alkali halides, while those for $D_0 = 0.03$ cm² and $E = 0.37$ eV were obtained from the analyses of the decay of the V_k centers as a function of temperature, as well as from the analysis of thermoluminescence peaks previously reported in the literature.¹⁵⁻¹⁷ The set of equations (4)–(6) gives the evolution of the interstitial centers S_1 , S_2 , and A respectively, while Eqs. (7) and (8) express the concentration of the M^+ - and M^0 -impurity states as a function of the irradiation time. Finally, Eqs. (9) and (10) give the production of electron and holes, respectively. At this point it is important to notice that one of the most important assumptions implicitly accepted in these equations is that the capture rates for interstitial trapping by empty traps S_0 , F centers, S_1 , and S_2 , except for the capture by the aggregate center A , have been considered following Aguilar *et al.*,⁹ to be equal ($\sigma_0 = 10^{-14}$ cm³ sec⁻¹). For the aggregate center A the capture rate σ_a was assumed to be proportional to the surface of the interstitial cluster, i.e., $\sigma_a = n_a^{2/3} \sigma_0$, where n_a is the mean number of interstitials per cluster. On the other hand, we have also assumed that the capture rate for electron-hole recombination is equal to that for interstitial F -center recombination (σ_0). These are obviously very rough approximations but do not essentially alter the physical picture. Moreover, they are not essential to the model, and if necessary can be easily removed. Moreover, the capture rate for electron trapping by M^{2+} ions has been considered ($b_{2+} = 10^{-17}$ cm³ sec⁻¹) to be 10 times larger than that ($b_+ = 10^{-18}$ cm³ sec⁻¹) for the M^+ -impurity ions. The latter was obtained by calculating the electron affinity of some M^{2+} and M^+ ions from the electronegativity concept as established by Campbell.¹⁸ Similar computer results, such as

those described below, are obtained, however, if $b_{2+} = kb_+$, where k is a constant in the range 5–10. Finally, the values used in the numerical calculations for the detrapping constants β and α are the same as those considered by Aguilar *et al.*,⁹ i.e., $\beta = 10^{-2}$ sec⁻¹ and $\alpha = 5$ sec⁻¹. With these 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, and a comparison with the experimental data can be carried out. At this point it is important to note that there is a considerable amount of experimentally determined data dealing with the effects of room-temperature x-ray irradiation in europium- and lead-doped alkali halides. Unfortunately, they have been obtained with a broad band x-ray spectrum and energy deposition rates have not been reported. This fact prevents a quantitative comparison with the theoretical predictions of the model. However, in order to make a meaningful comparison between experiment and model, we were able at least to calculate the energy deposition rates with which our original data on the system KI:Eu²⁺ and NaCl:Pb²⁺ were obtained. Therefore, we shall concentrate on the effects of room-temperature x-ray irradiation in the latter two systems and determine whether or not the predictions of the model can account for the experimental data.

RESULTS AND DISCUSSION

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

Figure 1 shows the computer-simulated F -coloring curves as a function of the initial concentration of empty dipole traps and for a value of $p/g = 500$. The latter value was selected following Williams,¹⁹ who has discussed that the yield of electron-hole recombination is ~ 0.1 of the total production of electron-hole pairs and that only approximately 10^{-1} – 10^{-2} of these recombinations give rise to F and H centers. Accordingly, these results indicate that the experimentally determined average ratio of $p/g \sim 500$. In all cases the value of g has been

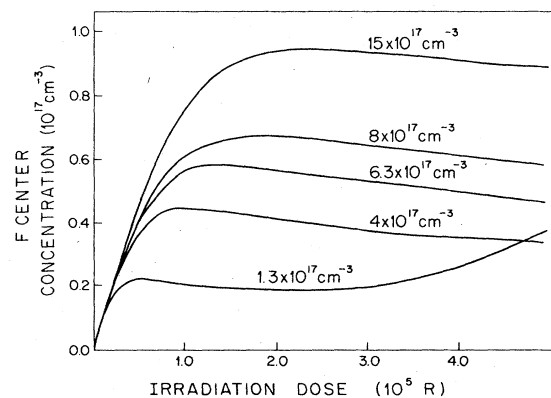


FIG. 1. Computer-simulated F -coloring curves for the ratio $p/g = 500$ as a function of impurity concentration and irradiation dose.

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 that the creation of each F - H pair requires of $\sim 100 \text{ eV}$.⁹ Reference to Fig. 1 shows that the three stages normally observed in the experimentally determined curves are clearly apparent in our computer-simulated curves. Also, the F -coloring height of stage I and the lengthening of stage II increases as a function of concentration of the preexisting traps in agreement with the experimental data. It is also obtained that for a given impurity concentration the efficiency for coloring during stage I decreases as p/g increases. This result is to be expected if one considers that increasing the value of p , while maintaining g constant, simulates the effect of more M^{2+} impurities trapping electrons, short circuiting the electron-hole recombination, and therefore inhibiting the production of F and H centers. Also, the number of available interstitial traps is reduced by this effect.

Figure 2 displays the corresponding evolution of the interstitial centers S_1 , S_2 , and A as a function of the irradiation time for two selected impurity concentrations (4×10^{17} and $15 \times 10^{17} \text{ cm}^{-3}$). In the same figure the average number (n_d) of halogen interstitials forming the aggregate center A as well as the number of free interstitials as a function of irradiation time are also plotted for the sake of comparison. The curves obtained are quite similar to those reported by Aguilar *et al.*⁹ In particular it is observed that the growth of the F -coloring curve during stage I correlates with the growth of the S_1 -interstitial center and a maximum in the concentration of this center is reached at the end of that stage. During stage II a slow transformation $S_1 \rightarrow S_2 \rightarrow A$ takes place in such a way that the concentration of S_2 goes through a maximum and then decreases in favor of the stable aggregates A , which are responsible for the growth of the F -center concentration during stage III.

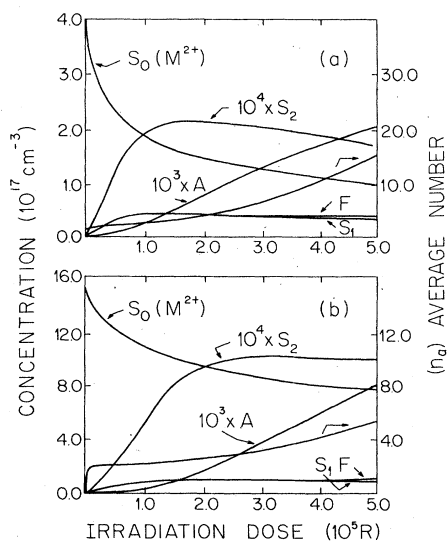


FIG. 2. Computer-simulated evolution of the concentration of the various traps with irradiation dose for the ratio $p/g=500$ for a selected impurity concentration: (a) $s_0=4 \times 10^{17} \text{ cm}^{-3}$ and (b) $s_0=15 \times 10^{17} \text{ cm}^{-3}$.

Figure 3 outlines the corresponding evolution of the concentration of free electrons, free holes, and M^{+} - and M^0 -impurity states for the same two impurity concentrations employed to obtain the data given in Fig. 2. In the same figure the decrease in the concentration of empty dipole traps (M^{2+}) as a result of interstitial trapping and/or electron capture is also given for the sake of comparison. The results obtained indicate that the number of free electrons grows very rapidly at the beginning of the irradiation process, reaches a maximum value, and then decreases as the irradiation time increases while the concentration of free holes increases monotonically. The latter behavior was also found in the evolution of the number of M^{+} and M^0 impurities produced by irradiation. This finding may be a qualitative explanation of the physical processes going on in the only experimental data available dealing with the evolution of the M^{+} and M^0 states of manganese ions in NaCl as a function of irradiation time.¹⁰ Again, the deposition energy during irradiation was not reported in this investigation and therefore a more quantitative comparison with the theoretical predictions is not possible. However, the important point to be stressed is the overall qualitative behavior which is well reproduced by the model by using only a few physical arguments.

The computed relationship among dipole destruction (ΔN_d), M^{2+} reduction (ΔN_o), and F -center creation (F) is portrayed in Figs. 4 and 5 for two selected initial dipole trap concentrations. As was expected, dipole destruction is equal to the sum of the number of F centers produced and the number of M^{2+} impurities which have changed their valence state during the irradiation processes. The computed results shown in these figures may be compared with those we have experimentally determined⁵⁻⁷ in alkali halides doped with a low concentration of Eu^{2+} or Pb^{2+} ,

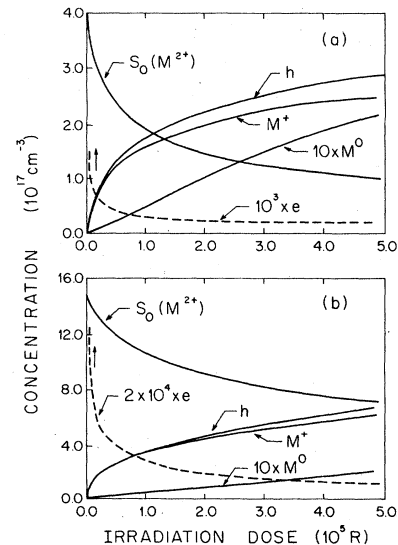


FIG. 3. Computer-simulated evolution of the concentration of M^{2+} , M^{+} , and M^0 valence states as well as that of free holes and electrons as a function of irradiation time for the ratio $p/g=500$ for a selected impurity concentration: (a) $s_0=4 \times 10^{17} \text{ cm}^{-3}$ and (b) $s_0=15 \times 10^{17} \text{ cm}^{-3}$.

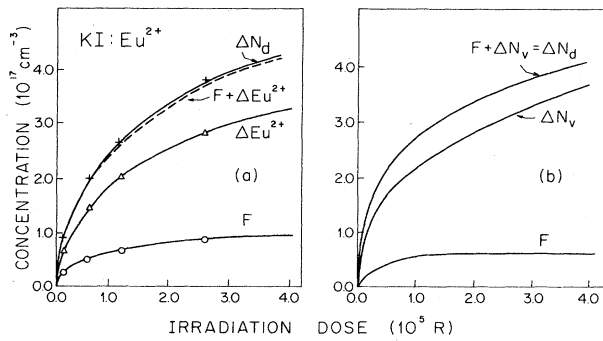


FIG. 4. (a) Experimentally determined evolution of the number of F centers produced, the number of doubly valent impurity ions which have changed valence by irradiation (ΔN_v) and dipole destruction (ΔN_d) for the system KI:Eu²⁺ for $s_0 = 6.3 \times 10^{17} \text{ cm}^{-3}$ (after Rubio *et al.*, Ref. 5). (b) Computer-simulated evolution for the ratio $p/g = 500$ for the same impurity concentration.

where the radiation-induced aggregation of dipoles is an unimportant process. In order to do this our original data on KI:Eu and NaCl:Pb were replotted as a function of radiation dose to make the comparison with the computer-simulated curves more meaningful. These results are also given in Figs. 4 and 5. Reference to these figures shows that the quantitative concordance between the experimental and theoretical curves for dipole destruction and valence change and F -center growth curves is reasonably good for the system KI:Eu²⁺, although the exact matching is of no special significance. In this respect, it should be pointed out that probably different values of the rate coefficient σ_0 should be used for the various stabilization

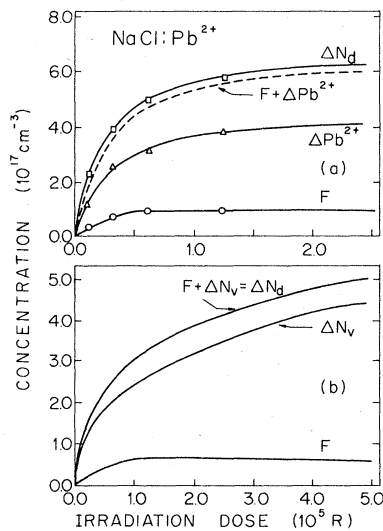


FIG. 5. (a) Experimentally determined evolution of the number of F centers produced, the number of doubly valent impurity ions which have changed valence by irradiation, and dipole destruction for the system NaCl:Pb²⁺ for $s_0 = 8 \times 10^{17} \text{ cm}^{-3}$ (after García *et al.*, Ref. 7). (b) Computer-simulated evolution for the ratio $p/g = 500$ for the same impurity concentration.

processes that are dominant at the various stages of the F -center growth curve. 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. On the other hand, it should be mentioned that although the semiquantitative agreement between experimental and theoretical curves in the system NaCl:Pb²⁺ is not as good as in the KI:Eu²⁺ case, the overall experimental features for ΔN_d , ΔN_v , and F -center growth are also reasonably well reproduced. The larger discrepancy in this case might be due to the fact that the value employed to perform the calculations for the electron cross sections for both europium and lead ions were taken to be equal. However, it appears from the available data that the lead ion is a more efficient electron trap than the europium ion. In fact, if the value for this parameter is increased, then the agreement between experimental and theoretical curves for dipole destruction and valence change is much better. In any case, we would like to emphasize that the main value of the model is that it provides a general scheme to qualitatively account for the major features of ΔN_d , ΔN_v , and F -center growth curves for alkali halides doped with any kind of doubly valent impurity which can change its valence state under irradiation.

Considering that the $I-V$ dipoles are the fundamental traps for the halogen interstitials, it is expected that dipole destruction correlates with F -center creation. Figure 6

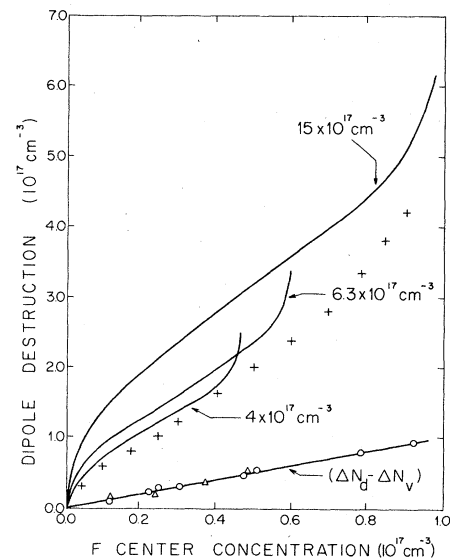


FIG. 6. Computer-simulated relationship between dipole destruction and F -center production for the ratio $p/g = 500$ and three different initial trap concentrations. The + symbols represent experimental data for the system KI:Eu²⁺ for $s_0 = 6.3 \times 10^{17} \text{ cm}^{-3}$. The straight line represents the same theoretical data after subtracting those dipoles which changed their valence state after irradiation. The symbols o and Δ represent experimental data on KI:Eu²⁺ for $s_0 = 6.3 \times 10^{17}$ and $s_0 = 1.3 \times 10^{17} \text{ cm}^{-3}$ [after Rubio *et al.* (Ref. 5)].

shows the computed plot of ΔN_d vs F for three different initial dipole concentrations. It is observed that there exists, except for short irradiation times, a linear relationship between dipole destruction and F -center production which holds during stage I of the F -coloring curve. During stage II, however, a deviation from this linear behavior is obtained. The same results as those given in Fig. 6 are obtained for other values of s_0 , as well as for other ratios of p/g . It is important to notice, however, that dipole destruction in this case occurs not only by means of possible interstitial trapping but also because the doubly valent impurity ions change their valence state during the irradiation process. Therefore, if the dipole destruction is corrected by the number of dipoles which were destroyed as a result of the fact that the M^{2+} ions forming the complex were converted to the M^+ and M^0 states, then a linear relationship between $\Delta N_d - \Delta N_v$ and F -center production is found. If we compare all these computed results with our experimental observations in europium-doped KI and KBr, which are also shown in Fig. 6, one arrives at the conclusion that the semiquantitative agreement between the theoretical predictions and experiment is once again quite reasonable.

The dependence of yield of the first-stage coloration n_{F0} on an initial trap concentration (C) is portrayed in Fig. 7 in a logarithmic plot. It is found that the slope of the computed plot is not very sensitive to the value employed in the calculations for the ratio p/g . In fact, the value obtained for the slope is close to 0.5 for p/g in the range 100–500. This result is in very good agreement with the experimental findings in europium-doped NaCl and KCl, which established that n_{F0} is proportional to $C^{1/2}$.

The dependence of the amount of first-stage coloration on the dose rate is also portrayed in Fig. 7 for a selected concentration of preexisting traps ($s_0 = 4 \times 10^{17} \text{ cm}^{-3}$). Similar results are obtained using other values of s_0 . Reference to this figure shows that n_{F0} is proportional to $g^{1/2}$. This result is in very good agreement with our previous data¹¹ on the system NaCl:Eu²⁺.

From all the results given above, it might be concluded that the major features of room-temperature x-ray irradiation in europium-, lead-, and manganese-doped alkali halides can be qualitatively reproduced by the model presented in this paper. In some cases, however, semiquantitative agreement between model and experiment was also achieved. In particular, the experimental finding in the sense that the amount of first-state coloration is proportional to the square root of dose rate and preexisting impurity concentration is well reproduced by the theoretical model. Moreover, the predictions of the model dealing with dipole destruction, valence change, and F -center growth compare reasonably well with those reported in the system KI:Eu²⁺ and NaCl:Pb²⁺, for which a meaningful comparison between model and experiment

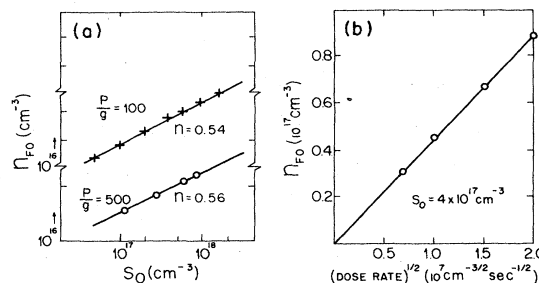


FIG. 7. (a) Computer-simulated relationship between the first-stage coloration (n_{F0}) and the impurity concentration (C) for different p/g ratios; the n values are the slopes of the log-log plot. (b) The first-stage coloration versus the square root of dose rate (g) is shown to be linear in this computer-simulated relationship as it was experimentally determined by Ramos *et al.* in NaCl:Eu²⁺ (Ref. 11).

was possible. Although the exact matching between model and experiment was not achieved, this could be done in principle by varying the values of some of the parameters involved in the rate equations until the experimental curves are fitted. With this procedure, however, a different set of parameters would be needed for each crystal system to explain the experimental observations, and the model will be of little general use. We preferred to calculate the values for the major part of these parameters from a physical basis without varying them from system to system and to compare the theoretical predictions with the experimental determinations. In this way, the model will provide a quite useful scheme to *qualitatively* explain the major features of the room-temperature x-ray irradiation of alkali halides doped with any kind of doubly valent impurity ion which can change its valence state by irradiation. Moreover, the analysis of the data allows us to establish that the principal conclusion is the correctness of the assumptions on which the model is based, which possibly reflects the main physical processes occurring during F -center production in alkali halides doped with doubly valent impurity ions that change valence by irradiation. Moreover, the assumed capabilities of trapping and detrapping of the different center created are qualitatively correct. This also applies to the roughly calculated values of the parameters involved in the rate equations which might be very representative of the real physical values of the chosen systems.

ACKNOWLEDGMENTS

This work was partially supported by Consejo Nacional de Ciencia y Tecnología (México) and Consejo Superior de Investigaciones Científicas (Spain) and was performed under sabbatical leave of S. Ramos from Centro de Estudios Nucleares, Universidad Nacional Autónoma de México.

¹J. H. Crawford, Jr., *Adv. Phys.* **17**, 93 (1968).

²M. Ikeya, K. Kusau, T. Okada, N. Itoh, and T. Suita, *J. Phys. Soc. Jpn.* **20**, 289 (1965).

³M. Ikeya, N. Itoh, T. Okada, and T. Suita, *J. Phys. Soc. Jpn.*

21, 1304 (1966).

⁴J. N. Marat-Mendes and J. D. Comins, *Cryst. Lattice Defects* **6**, 141 (1975); *J. Phys. Chem. Solids* **38**, 1003 (1977).

⁵J. Rubio O., M. G. Aguilar, F. J. López, M. Galán, J. García

- Solé, and H. S. Murrieta, *J. Phys. C* **15**, 6113 (1982); J. Rubio O., C. M. Flores, H. Murrieta S., J. Hernandez A., F. Jaque, and F. J. López, *Phys. Rev. B* **26**, 2199 (1982).
- ⁶J. Rubio O., F. J. López, J. García M., and H. Murrieta S., *Solid State Commun.* **49**, 127 (1984).
- ⁷J. García M., J. Hernandez A., H. Murrieta S., and J. Rubio O., *Solid State Commun.* **47**, 515 (1983).
- ⁸J. D. Comins and B. O. Carragher, *J. Phys. (Paris)* **41**, 166 (1980); *Phys. Rev. B* **24**, 283 (1981).
- ⁹M. Aguilar, F. Jaque, and F. Agulló-López, *J. Phys. (Paris)* **41**, 341 (1980); *Radiat. Effects* **61**, 215 (1982).
- ¹⁰F. J. López, J. M. Cabrera, and F. Agulló-López, *J. Phys. C* **12**, 1221 (1979).
- ¹¹S. Ramos B., H. Murrieta S., M. Aguilar, and J. Rubio O., *Radiat. Effects Lett.* **68**, 173 (1983).
- ¹²M. Aguilar G., J. García Solé, H. Murrieta S., and J. Rubio O., *Phys. Rev. B* **26**, 4507 (1982).
- ¹³D. Schoemaker, *J. Phys. (Paris) Colloq.* **37**, C7-63 (1976); in *Defects and Their Structure in Non-Metallic Solids*, edited by B. Henderson and A. E. Hughes (Plenum, New York, 1976).
- ¹⁴M. Aguilar G., Ph.D. thesis, University of Madrid, 1980.
- ¹⁵D. Pooley, *Proc. Phys. Soc. London* **89**, 723 (1966).
- ¹⁶K. Teegarden and R. Weeks, *J. Phys. Chem. Solids* **10**, 211 (1959).
- ¹⁷F. J. López, Ph.D. thesis, University of Madrid, 1979.
- ¹⁸J. A. Campbell, *Chemical Systems* (W. H. Freeman and Company, San Francisco, 1970).
- ¹⁹R. T. Williams, *Semicond. Insul.* **3**, 251 (1978).