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Influence of Impurities on the Room-Temperature Coloration Processes in Alkali Halides

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The *F*-center growth curves for undoped KCl and KCl crystals doped with Ba, Co, and Cd have been obtained by x irradiation at room temperature. These growth curves are fitted to an equation with two exponential terms and a linear term, and the parameters occurring in the equation are evaluated. Two exponential terms have been found to be adequate to describe the first-stage coloration, with which this paper is mainly concerned. The analysis shows that the slower exponential component is strongly influenced by the presence of impurities; specifically, the rate of coloration during the process responsible for this component decreases, and the saturation level for the process increases, on account of the impurities. The faster exponential component appears to be relatively insensitive to the presence of impurities. These results are discussed with reference to certain mechanisms that have been put forward to account for the first stage.

I. INTRODUCTION

There has been considerable interest in recent years in the mechanisms of color center production

by ionizing radiation in alkali halides.¹ Among other methods employed, the analysis of the plots of *F*-center growth versus time of irradiation (or radiation dose) has yielded useful information regarding

these mechanisms.²⁻⁴ These growth curves indicate that the room-temperature *F*-center production consists of at least two stages. The first of these stages, which is known to be highly structure sensitive, is generally associated with the rapid filling in of anion vacancies already present in the crystal, while the subsequent stages are believed to arise from the generation of new vacancies by the radiation. Rivas and Levy³ have studied the influence of radiation intensity, plastic deformation, and optical bleaching on the first-stage coloration in x-irradiated NaCl at room temperature. They have analyzed the *F*-center growth curves in terms of an equation of the form

$$\alpha_F = \alpha_L t + \sum_i^n A_i (1 - e^{-a_i t}), \quad (1)$$

where α_F is the absorption coefficient at the peak of the *F* band and n is the number of "exponential" components in the coloring curve. Their analysis shows that the so-called first stage of coloration consists of at least two distinct substages. This confirms the conclusions obtained by Harrison⁵ and Agullo-Lopez^{6,7} from their studies on *F*-center production characteristics. It has been suggested that the first substage, a fast exponential one, is due to an "electronic" process^{6,7} involving the trapping of electrons by anion vacancies released with little expenditure of energy, competing with a bleaching process induced by the radiation. The second, a relatively slow exponential component, is attributed^{6,7} to an unspecified process involving the release of vacancies from aggregates or other lattice defects, competing with thermally activated vacancy trapping. This vacancy process is different from the vacancy-generation mechanisms responsible for the linear term in (1).

There is also a growing interest⁸⁻¹³ in the role of impurities in the coloration processes in alkali halides. Divalent cation impurities in the crystal require that extra cation vacancies be also present in the crystal, and such vacancies are held responsible for the observed enhancement in coloration in doped crystals.¹⁰⁻¹² In the mechanism proposed by Crawford and Nelson,¹⁰ there is a radiation-induced conversion of cation vacancies to anion vacancies, resulting in an enhancement in coloration. Alternatively, the cation vacancies can trap halogen interstitials^{14,15} and reduce the recombination rate between the *F* centers and interstitials. The resulting stabilization of the defects¹⁶ can then lead to enhanced *F*-center production. Recent evidence¹³ shows, however, that impurities may be involved in more complicated secondary reactions. A third process suggested in connection with the role of impurities in room-temperature coloration is the one proposed by Pooley,¹⁷ in which the impurities reduce

the forward creation process by acting as electron-hole recombination centers.

This paper describes the results of experiments in which *F*-center growth curves for undoped and doped KCl crystals have been obtained at room temperature and analyzed in terms of an equation of the form of (1) with two exponential terms. It was hoped that such an analysis would enable one to isolate, and if possible identify, a coloration process which is strongly influenced by the presence of impurities. Crystals doped with three divalent impurities were studied: barium, representative of the alkaline-earth elements; cobalt, from the iron group of elements; and cadmium, from the group-II B elements. Of these, Co²⁺ is believed to occupy interstitial positions in KCl,¹⁸ and a brief report on cobalt-doped KCl has been published earlier.¹⁹

II. EXPERIMENTAL

The "pure" KCl [designated as KCl(I)] and the KCl crystals doped with Ba and Cd were grown at the National Physical Laboratory, New Delhi, and were kindly supplied by S. Radhakrishna. The KCl(I) crystal was grown from "specpure" grade salt procured from J. Matthey and Co., London. The other nominally pure KCl crystal, designated as KCl(II), as well as the Co:KCl crystals were grown in our laboratory by the Bridgman-Stockbarger method, from reagent grade material. All crystals were analyzed for some selected impurities by semi-quantitative spectrographic analysis at the Bhabha Atomic Research Center, Bombay, and the dopant concentrations are shown in Table I. The analysis also showed that all the crystals had varying amounts of Ca, Ba, Sr, and Na in them. The Co:KCl crystals showed, in addition, the presence of Fe, Mn, and Ni, and the Cd:KCl crystal showed the presence of Zn. From the analysis, it was apparent that the KCl(I) crystal was the purest of the samples studied.²⁰ The doped crystals were heated at about 400 °C for 20 min and quenched to room temperature before irradiation, to distribute the impurity-vacancy dipoles.²¹ Freshly cleaved samples were used for each run, the thicknesses along the direction of irradiation being as shown in Table I.

X irradiation of the samples was performed with a General Electric EA-75 type x-ray tube with a tungsten target and beryllium window. The tube was operated at 60-kV peak and 30 mA on a XRD-6 diffractometer assembly, under which conditions the x-ray intensity at the sample site is about 30 000 R/sec.²² However, an aluminium filter, 0.25 mm thick, was interposed to cut down the soft x rays. It was assumed, without any separate measurements, that the coloration was uniform because of the filtration.² Optical-absorption measurements were made with a Cary Model 14R spectrophotom-

TABLE I. *F*-center growth-curve parameters giving the best fit with experimental data.

Sample number	Sample	Dopant concentration (ppm)	Sample thickness (mm)	a_L ($\text{cm}^{-1}/\text{min}$)	a_2 (min^{-1})	A_2 (cm^{-1})	a_3 (min^{-1})	A_3 (cm^{-1})
1	KCl (I)	...	0.58	0.255	1.45	22.0	0.259	19.25
2	KCl (II)	...	0.40	0.256	1.27	17.4	0.162	12.1
3	Co : KCl (I)	200	0.28	0.348	0.952	26.1	0.0886	27.5
4	Co : KCl (II)	25	0.44	0.355	1.39	18.6	0.117	25.5
5	Ba : KCl	100	0.68	0.253	1.49	21.5	0.144	25.8
6	Cd : KCl	50	0.34	0.244	1.55	22.8	0.115	23.4

eter by periodically interrupting the x irradiation. The samples were kept in darkness during irradiation and transfer to the spectrophotometer. All irradiations and optical measurements were done at room temperature, which, at the time of the experiments, was about 22 °C.

III. RESULTS AND ANALYSIS

The *F*-center growth curves for six crystals are shown in Fig. 1, in which the *F*-band absorption coefficient α_F has been plotted against the time of x irradiation. The growth curves have been fitted to the expression

$$\alpha_F = A_2(1 - e^{-a_2 t}) + A_3(1 - e^{-a_3 t}) + a_L t. \quad (2)$$

Two exponential terms have been found to be sufficient to describe the first-stage coloration. We did not observe the small "fastest" component $A_1(t)$ observed by Rivas and Levy^{3,23} in NaCl and more recently by Levy *et al.*²⁴ in KCl. It may be mentioned here that Jaque *et al.*²⁵ have also found two exponential terms to be sufficient to describe the first-stage *F*-center growth in undoped KCl. In any case, $A_1(t)$ seems to be observable only under special experimental conditions,²⁴ and when observed, is small enough to be neglected.³ For the two exponential components observed by us, we have used the same notation as that of Rivas and Levy,³ for the sake of uniformity.

In analyzing the curves also, we have followed their procedure by first extrapolating the linear portions of the curves back to $t = 0$. This gives a_L , the rate of the second-stage coloration process, as well as the amount of total first-stage coloration. The first-stage coloration is then decomposed into two exponential components, labeled a_3 and a_2 , which are shown in semilog plots in Figs. 2 and 3, respectively. From Fig. 2 one obtains the parameters a_3 and A_3 , which describe the slower exponential component (henceforth called "the second substage"), while Fig. 3 gives a_2 and A_2 , the parameters corresponding to the faster exponential component ("the first substage"). However, this

graphical procedure could lead to errors; hence a least-squares calculation was performed on an IBM 7044 computer, by varying the parameters about the graphically determined values. The values of the parameters a_L , a_2 , A_2 , a_3 , and A_3 which give the best fit with experimental curves are tabulated in Table I. These values have been used to compute the solid curves in Fig. 1, where the experimental points are shown as open and filled circles. As can be seen, the fit is fairly good, with the mean deviation being less than 2% in all

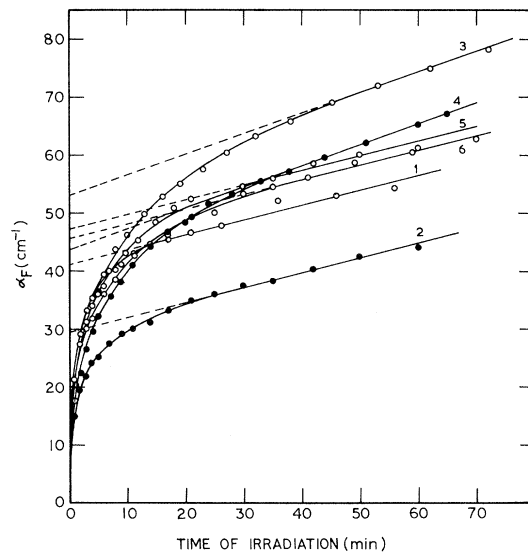


FIG. 1. *F*-center growth curves for doped and undoped KCl crystals, x irradiated at room temperature with the *F*-band absorption coefficient α_F plotted against the time of irradiation. The curves are numbered as follows: 1: KCl(I); 2: KCl(II); 3: Co:KCl(I); 4: Co:KCl(II); 5: Ba:KCl; 6: Cd:KCl. The solid curves have been computed from Eq. (2), using the parameters listed in Table I. The intercepts on the ordinate of the extrapolation of the linear portions of the curves give the amounts of first-stage coloration.

cases. The growth curves for samples taken from the same larger crystal were generally reproducible to within 10%, but in some cases the variation was as much as 20%.

A few significant features emerge from this analysis. Firstly, the values of a_2 and A_2 are not very dissimilar for the different crystals studied, suggesting that the process responsible for the first substage is relatively insensitive to the presence of impurities. Only for the Co: KCl(I) sample, a_2 is somewhat smaller and A_2 is somewhat larger, than for the other samples. In contrast, the values of a_3 for all the doped crystals are about half or less than half of that for the undoped crystal KCl(I). The KCl(II) crystal, grown from reagent grade material, may be considered as an intermediate case²⁰ between the KCl(I) crystal and the doped ones, and as can be expected, its a_3 value lies in between those for the doped crystals and KCl(I) crystal. Next, the saturation levels for the process, represented by the parameter A_3 , are invariably more in the doped crystals than in the undoped ones. The ratio A_3/A_2 is greater than 1 in all the doped crystals and less than 1 in the undoped ones. Thus, in impurity-doped crystals, the second substage seems to contribute a major portion of the net first-stage coloration. The fact that such diverse impurities as Ba, Co, and Cd all produce a uniform effect on the slower process is striking. These results are

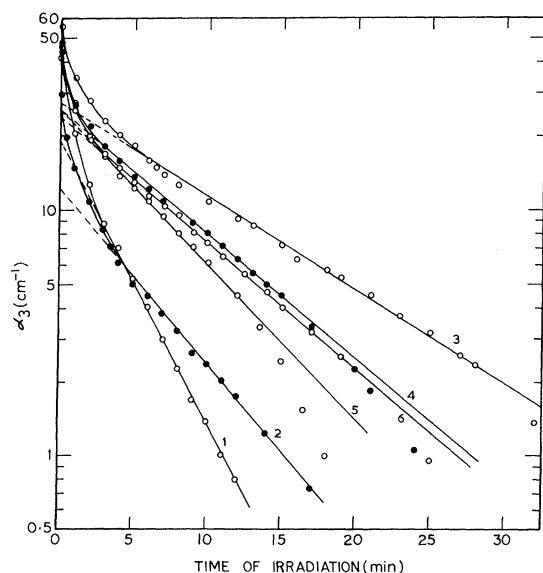


FIG. 2. Slow exponential component α_3 of the first-stage coloration, plotted on a logarithmic scale. α_3 is the difference of the linear extrapolation of Fig. 1 and the actual growth curve (see Ref. 3). Curves are numbered as in Fig. 1.

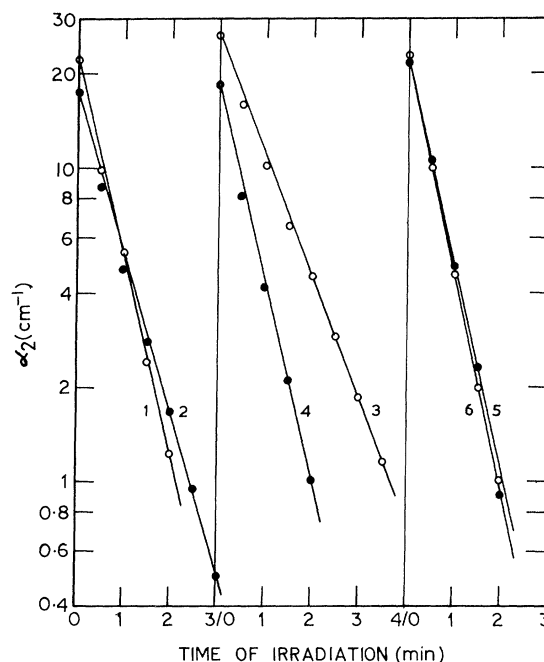


FIG. 3. Fast exponential component α_2 of the first-stage coloration, plotted on a logarithmic scale. α_2 is the difference between the α_3 curve and the linear extrapolation of Fig. 2 (see Ref. 3). Lines are numbered as in Fig. 1.

supported by those of Rivas and Levy³ on Korth and Harshaw NaCl crystals. Their Korth crystals contain a greater amount of trace impurities, and show a decreased a_3 and an increased A_3 when compared with the Harshaw samples. It is then reasonable to conclude that, primarily, impurities reduce the rate of coloration (i.e., the rate of approach to saturation) in the second substage and increase the saturation level for the process responsible for this component.

Figure 2 reveals another feature: There is a small but steady deviation from exponential behavior as the second substage saturates in some of the doped crystals. This departure, indicating an increased rate of coloration, does not seem to be describable by a simple expression, nor is it clear why it occurs. However, since the maximum deviation did not exceed 3% of the net first-stage coloration in all cases, this aspect will not be considered in Sec. IV.

IV. DISCUSSION

Before examining any specific processes that can be invoked to explain the results given above, it is worthwhile to consider the validity of Eq. (1) for the description of F -center growth curves. We feel

that there is now sufficient evidence^{3,6,23-25} to believe that an equation of the form of (1) constitutes a valid description of the F -center growth curves for NaCl and KCl, provided the number of exponential components is reasonably small. Levy *et al.*²⁴ recently found that Eq. (1) with three exponential terms gives an excellent fit with growth curves obtained by making optical measurements *during* irradiation. It was also observed³ that changing the experimental conditions alters one or two of the parameters, leaving the others unchanged. This suggests that each component in Eq. (1) arises out of a separate physical process which is affected in a specific way by any change in the experimental conditions. However, it is not possible, on the basis of the present as well as previous data, to pinpoint any specific processes and to construct a complete model for Eqs. (1) or (2). This is because a number of kinetic processes may be constructed, which have the saturating exponential behavior that is observed. In what follows, our experimental results along with those of others will be discussed in relation to some mechanisms which have been put forward earlier.

Our results on the first substage are in agreement with earlier conclusions^{3,6} that a rapid "electronic" process is dominant during this substage, in which initial vacancies in the crystal are filled in. Most of these initial anion vacancies are perhaps bound in small clusters, and are released under the action of the radiation. Equations developed by Mitchell *et al.*² for this case are valid here, and a saturating exponential growth is readily obtained. As mentioned earlier, impurities do not appear to influence this process strongly, at least at the x-ray intensity used in the present work. The work of Rivas and Levy³ indicates, however, that there is a small difference in the saturation level A_2 for Harshaw and Korth crystals, and that this difference increases with increasing x-ray intensity.

A simple process, however, does not seem to be responsible for the second substage, which is evidently the most important one when considering impurity effects. A saturating exponential can again be obtained if a process similar to the one mentioned above is operative, with perhaps a different rate constant for the release of vacancies and a different electron capture cross section for these vacancies.² However, there is evidence⁷ that certain secondary reactions take place at room temperature which affect this process. Sanchez and Agullo-Lopez⁷ suggest a process consisting of the release of anion vacancies from certain "sources" with a simultaneous removal of these vacancies by certain "traps." Since the present work shows that this process must be influenced by impurities, it would appear likely that the sources and/or traps in question are as-

sociated with the presence of impurities. Excess positive ion vacancies, present on account of impurities, can act as sources if they are converted to anion vacancies through the Crawford-Nelson mechanism. Such a forward reaction, along with the enhanced number of sources, could conceivably account for the increase in A_3 in the doped crystals. If A_3 is determined primarily by the cation vacancy concentration, it would not be expected to vary with the radiation intensity. That this is the case is shown by the work of Rivas and Levy.³ However, to account for the decrease in a_3 , one would have to postulate that impurities also enhance the concentration of traps and/or increase the trapping efficiency. Except that the trapping process is characterized by an activation energy of 0.39 eV in NaCl,⁷ not much is known about it to enable one to establish the exact effect of impurities on it.

A major objection that may be raised against the model described above is the rather large activation energy that would be required by the Crawford-Nelson process - of the order of 1 eV.¹⁵ Recent results obtained by Rivas and Levy²³ indicate that an energy of about 0.1 eV is associated with the process responsible for the second substage. Ikeya *et al.*¹¹ have also obtained a value of 0.08 eV for the initial F -center formation in calcium-doped NaCl. Using the fact that halogen interstitials are mobile with rather low activation energies, Farge and co-workers^{15,26} have developed a model for F -center growth, in which the mobile interstitials can recombine with F centers or other traps. According to Farge,¹⁵ the presence of divalent impurities introduces a certain number of "saturable" traps for the interstitials, in addition to the "nonsaturable" ones which are supposed to be related to defects other than impurities. Theoretical growth curves obtained by him from his equations show that (a) the approach to the second stage is exponential, and (b) increased numbers of saturable traps result in higher saturation levels for the first-stage production. Thus, if excess cation vacancies trap interstitials, the increase in A_3 in the doped crystals is understandable. However, Sonder^{13,27} has shown that this model is an oversimplification, and that it does not always represent the situation correctly.

Thus, while a complete model is yet to emerge, our results emphasize the need to consider the precise effects of impurities on room-temperature coloration processes before constructing such a model. The discussion given above has been restricted to a consideration of the general effects of divalent impurities, without regard for any possible individual effects of each impurity. For instance, it will be seen from Table I that the slope a_L in the linear-stage coloration is nearly the same for all

the samples, except for the two cobalt-doped samples. It is not clear, at present, whether this peculiar difference is because the Co^{2+} ions occupy interstitial sites or because of some other properties of the Co^{2+} ion.

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