# Formation and Optical Bleaching of F Centers: Impurity Effects\*

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The x-ray darkenability and optical bleaching rate for F centers were measured at room temperature for KCl crystals grown from aqueous solution, and the results compared with crystals of varying purity and method of preparation. The initial rates of formation and bleaching of F centers were lowest for pure KCl grown from solution, highest for melt-grown crystals containing CaCl<sub>2</sub>, and intermediate for Harshaw crystals.

Unfiltered x-rays were used. As with hard x-rays, *F*-center growth consists of two stages; however, with solution-grown crystals the second stage only develops clearly on re-x-irradiation after bleaching and the first stage follows a rate equation second order in the vacancy concentration. One stage is found sufficient to account for optical bleaching.

On re-x-irradiation after bleaching, the same first-stage rate equation is followed. F centers are rapidly formed and the secondary centers are destroyed. The rate depends principally on the concentration of F centers destroyed by the previous bleaching.

The coloration of alkali halides by x-rays is of interest as a means of estimating impurity content. It is believed that F centers are formed at room temperature by two stages<sup>1), 2), 3)</sup>; the first (rapid) stage is supposed to involve the capture of electrons by vacancies already present in the crystal while the second (slow) stage requires creation of vacancies by the x-rays. The effect of impurities is probably chiefly to alter the initial vacancy concentration. The rate of bleaching of F centers by light lying in the F band has been related to impurity concentration; bleaching is also said to occur in two stages.<sup>4)</sup>

Deformation also affects the rate of x-ray coloration<sup>1),2)</sup>, and it has not proved possible to separate completely the effects of deformation from those due to impurities. Part of the difference observed between melt-grown and solution-grown crystals reported here may arise from the fact that the latter are grown under almost equilibrium conditions near room temperature.

Hard x-rays, that is, rays filtered first

\*\* Present address: Laboratories RCA, Inc. C. P. O. Box 219, Tokyo, Japan. through a thin alkali halide crystal, produce uniform volume coloration<sup>5)</sup>, but long exposures are required. Several treatments of the kinetics of this process have been published recently<sup>3)-6)</sup>. The essential features of the two-stage growth curve for F centers are developed in a few minutes by unfiltered xrays under practical conditions; however, there are important differences in the two experiments which must be borne in mind in comparing results. Soft x-rays produce a strong concentration gradient normal to the irradiated surface so that absorbance measurements taken along this direction indicate the concentration of centers averaged over the thickness of the crystal (alternatively the total number of centers per unit area). Unfiltered x-rays were used in these experiments.

The purpose of this investigation was to compare the properties of highly purified KCl crystals grown from aqueous solution with those of various melt-grown and solutiongrown crystals thought to contain impurities. X-ray coloration and bleaching were done at room temperature since at low temperature the impurity- and structure- sensitivity disappears<sup>6</sup>.

#### Experimental

Single crystals were grown from aqueous

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solution in closed polyethylene bottles of 5 cm diameter and 15 cm height. The solution was saturated at 60°C with triply-recrystallized reagent grade KCl and sealed in the bottle: the temperature at the bottom was held at 50°C, while the top was at or near room temperature, which was kept at 25°C. After two weeks, when excess salts and nucleation centers had crystallized and settled, a small addition of warm PbCl<sub>2</sub>, CuCl<sub>2</sub> or KOH solution was made, except for the solutions in which pure crystals were to be grown. The nominal proportion of impurity ions was 10<sup>-2</sup> mole per cent. After four days, four seed crystals of  $1 \times 1 \times 2 \text{ mm}^3$  were suspended in each solution using nylon string. Except in the solution containing lead ions, crystals grown were not single. Usually a crystal grown on a seed was composed of several smaller single crystals grown on each other, and water inclusions were observed in the region where two crystals grew in contact. After two months of growth, several transparent single crystal sections up to  $8 \times 8 \times 5 \text{ mm}^3$  were obtained. The presence of lead ions favored the development of the octahedral habit, as previously reported<sup>7),8)</sup>.

Crystals (referred to hereafter as "pure") were also grown from a melt of specially purified<sup>9)</sup> KCl, using a graphite crucible and an argon atmosphere, or from a melt containing  $10^{-5}$  or  $10^{-3}$  mole fraction of CaCl<sub>2</sub>, by the Kyropoulos method. Some were supplied by the Harshaw Chemical Co.

All crystals were irradiated with the same x-ray flux from a copper-target tube, operated at 35 KVp and 15 ma. The crystals were reproducibly positioned 4.5 cm from the beryllium window of the tube. Absorbance measurements over the range 200 to 1,500 m $\mu$  were made by means of a Beckman Model DK1 recording spectrophotometer. *F*-band peak height measurements were made by means of a Beckman Model DU spectrophotometer, with wavelength 560 m $\mu$  and slit width 0.04 mm. For bleaching the slit width was 2.0 mm, the light being incident on the face opposite that which received the x-ray irradiation.

*F*-center concentrations were computed from Smakula's formula. Assuming an oscillator strength of 0.85, one obtains

## $n_F \cong 10^{16} (A/b)$

where  $n_F$  is the concentration of F centers

per cm<sup>3</sup> and (A/b) is the absorbance per cm at the maximum of the *F* band. The *F*-center concentrations are averages over the crystal thickness of 0.40–0.42 mm. From the data of Mador *et al.*,<sup>5)</sup> for NaCl, the surface concentration is estimated to be about three times the average for this thickness.

Optical absorption spectra were taken before x-ray irradiation in the wavelength range from 200 to 1,500 m $\mu$ . Crystals grown from solutions containing lead ions showed two prominent absorption bands in the ultraviolet whose peak locations agreed with those observed in melt-grown crystals containing lead ions.<sup>10)</sup> The absorbance of crystals grown from solutions containing Cu<sup>++</sup> or OH<sup>-</sup> ions was indistinguishable from that of crystals grown from pure KCl solutions; the incorporation of these ions from aqueous solution is therefore slight.

## **Results and Discussion**

### X-ray Coloration

A typical experiment, performed on a Harshaw KCl crystal, is shown in Fig. 1.



Fig. 1. *F*-center growth curves for initial and re-x-ray irradiations and optical bleaching curves of *F* centers for *F*-light irradiation in Harshaw KCl (H 3).

The crystal was x-ray irradiated 80 minutes, bleached with 560 m $\mu$  light for 50 minutes, then x-ray irradiated and bleached through two additional cycles. Particularly to be noted is the rapid re-attainment of the second-stage (linear) portion of the growth curve on each successive x-ray irradiation, and the increase in *F*-center concentration (points B, D, and F) after each successive bleaching period. Fig. 2 shows the results of a similar experiment (without curves for bleaching) performed on a variety of crystals. In general, the linear stage was not clearly developed in crystals other than Harshaw, during the first irradiation. Fig. 3 illustrates the initial stages of coloration. It is clear that significant differences exist between samples, not only in the initial rate, but in the distinctness of onset of the linear stage. The crystals grown from solution, even those containing Pb<sup>++</sup> ions, display the lowest initial rate, the "pure" melt-grown crystals next, followed by the Harshaw samples, and finally by crystals containing Ca<sup>++</sup>.



Fig. 2. F-center growth curves for initial and re-x-ray irradiations in various KCl crystals. (Crystal designation as in Table I.)



Fig. 3. Initial stages of *F*-center growth for various KCl crystals.

The energy to form an initial F center is proportional to the reciprocal of the slope of growth curve. The solution-grown crystals exhibit the highest value and the calciumdoped crystals the lowest.

Etzel and Allard<sup>11)</sup> gave an equation for the initial stages of coloration of synthetic NaCl by unfiltered x-rays which can be written as

$$\frac{t}{n_F^I} = \frac{t}{n_H^0} + B$$
, (1)

where t is the time (proportional to the energy absorbed),  $n_F^I$  is the concentration of F centers produced by the first-stage process,  $n_H^0$  is the (constant) value of  $n_F^I$  at  $t=\infty$ , and B is a constant proportional to the energy required to form an F center at t=0. We identify  $n_H^0$  with the concentration of halide ion vacancies originally present in the crystal.

If the second stage growth curve is linear with time, having slope a.

$$n_F^I = n_F - at$$
,

and  $t/(n_F - at)$  should then be linear with time according to Eq. (1). In Fig. 4,  $t/(n_F - at)$ is plotted against t for several representative experiments. Harshaw crystals and the calcium-doped crystals follow the relations well on both original and re-x-irradiation. Solution-grown and "pure" melt-grown crystals show marked deviations near the time origin for the first x-irradiation but not generally for the re-x-irradiation. The curve was not linear for the solution-grown crystal containing lead in any case.



Fig. 4. Test of Eq. (1) for initial and re-x-ray irradiation of various KCl crystals.

The differential form of Eq. (1) is

$$\frac{dn_F^{I}}{dt} = \frac{1}{B(n_H^0)^2} (n_H^0 - n_F^{I})^2 \,.$$

Thus the rate varies with the square of the unfilled vacancy concentration,  $n_{H}^{0} - n_{F}^{I}$ , a marked difference from the rate dependence given by Mitchell, Wiegand, and Smoluchowski<sup>12)</sup> for coloration by hard x-rays. In that case, the first stage is (neglecting a small bleaching constant) first order in the unfilled vacancy concentration. Neither Eq. (1) nor a firstorder equation applies satisfactorily to the behavior of solution-grown or "pure" meltgrown crystals during the first irradiation. Superficially, at least, these crystals resemble natural halite.<sup>11</sup>

From curves such as those of Fig. 4,  $n_{H}^{0}$ , a, and B were found, for those cases in which linearity occurred. B was about  $1.0 \text{ cm}^3 \text{ min}$ for Harshaw crystals and less than 0.5 cm<sup>3</sup> min for the calcium doped crystals for the first irradiation. For all crystals on re-xirradiation B was between 0.22 and  $0.35 \,\mathrm{cm}^3$ min with no correlation observable between B and impurity content. Clearly, less energy is required to generate F centers initially from secondary centers than from virgin crystal, in agreement with the results of Silverman and Grossweiner.<sup>13)</sup> Table I gives a and  $n_{H}^{0}$ , along with the decrease of F-center concentration during the bleaching step, for the original irradiation of Harshaw and calciumdoped crystals, and for the re-irradiation of these and other crystals.

Note that  $n_{H}^{0}$  for the re-irradiation is about equal to  $dn_{F}$  for the Harshaw crystals, indicat-

ing that vacancies are produced in amount equal to the number of F centers destroyed by bleaching. For the calcium-doped crystals, which were not irradiated fully into the second stage  $n_H^0$  for the re-irradiation is, as expected, still somewhat greater than  $\Delta n_F$ . For the remaining crystals, it appears that part of the vacancies produced on bleaching are not available for forming F centers, as  $n_H^0$  is less than  $\Delta n_F$ . Further, the growth curve for reirradiation does not form a continuation of the original, but is in all cases lower.

The results on solution-grown and "pure" melt-grown crystals bear a similarity to those of Rabin and Klick<sup>6)</sup> concerning the coloration of NaCl at liquid helium temperature. In that case, the original x-irradiation produced an almost linear growth of F-center concentration. On re-x-irradiation after bleaching the original curve was rapidly reattained. Rabin and Klick assumed that free vacancies were not available to form F centers originally but were produced during bleaching. Here we may likewise take the view that these crystals contain originally very few available negative ion vacancies.

It is of interest to note also that the formation of F centers from U centers by x-rays, as reported by Martienssen and Pick<sup>14)</sup> follows an equation similar to Eq. (1), with  $n_H^0$  replaced

	Original irradiation		Re-irradiation $I=$ First re-irrad. II=Second re-irrad.			
Crystal	$a \times 10^{-16}$ cm <sup>-3</sup> min <sup>-1</sup>	$n_{H}^{0}  imes 10^{-16} \ { m cm}^{-3}$		$\Delta n_F \times 10^{-16} { m cm}^{-3}$	$a \times 10^{-16} \mathrm{cm^{-3}}_{min^{-1}}$	$n_{H}^{0}  imes 10^{-16} \ { m cm^{-3}}$
H 1	0.032	2.64				
H 2	0.033	1.85	I	3.58	0.033	3.83
			II	4.20	0.033	4.35
H 3	0.031	2.49	Ι	4.05	0.031	4.20
			II	4.60	0.031	4.47
M(0.001Ca)	0.033	5.53		6.57	0.033	6.88
M(0.1Ca)	0.016	17.24	Ι	10.35	0.016	18.80
			II	17.85	0.016	19.09
W 2			I	4.35	0.040	3.32
			II	4.48	0.028	4.21
W 3				4.16	0.045	3.54
W(OH)				4.53	0.049	2.95
W(Cu)				4.38	0.048	3.30
				1	1	

Table I. Constants of Eq. (1) for X-ray irradiation.

(Crystal designation: H=Harshaw, M=melt grown, W=solution grown. Impurities and indication of level given in parentheses. Arabic numerals indicate replicate crystals.)

by  $n_U^0$ , the initial concentration of U centers. The U centers presumably serve in this case not only as one source of electrons, but as the source of vacancies, if, after ionization of the hydride ion by x-rays, the proton diffuses away.

## Bleaching of F Centers

During the optical bleaching of F centers the absorption at the short wavelength tail of the F band, which is called the K band, increased continuously. The M band grew during the early stage of F-light irradiation and decreased after reaching a maximum.  $R_1$ ,  $R_2$ , and N bands grew continuously, approaching saturation. The absorption in the region of the  $V_2$  and  $V_3$  bands remained constant or decreased very slightly. As a whole, the bleaching process observed in the present experiment is very similar to that of additively colored crystals. This kind of bleaching process is usually observed in heavily x-rayed crystals.4)

It was found in most cases that the concentration of F centers,  $n_F$ , was related to the time of F-light irradiation, t, by an equation analogous to that for the first stage of formation of F centers by x-rays, namely

$$\frac{t}{n_F^0 - n_F} = \frac{t}{n_T^0} + \frac{1}{K}, \qquad (2)$$

 $n_F^0$  is the initial concentration of F centers,  $n_T^0$  and K are constants. The physical significance of  $n_T^0$  cannot be inferred from this experiment alone, but, since it is the value of  $n_F^0 - n_F$  at large t, we choose to identify  $n_T^0$  with the number of stable traps for electrons (other than negative ion vacancies) originally present in the crystal.

Fig. 5, in which  $t/(n_F^o - n_F)$  is plotted against t, illustrates the application of Eq. (2) to several crystals, including data given by Bron.<sup>4)</sup> It was also found to apply to data of other investigators.<sup>15),16)</sup> With the exception of our crystals grown from pure aqueous KCl solution, which show some deviation near the time origin, the agreement with Eq. (2) is very good. There appears to be no necessity to assume a second stage in bleaching, as long as one simple rate expression is adequate over the whole range. The increase in the residual *F*-center concentration on successive bleaching, alternated with x-irradiation (locations B, D, and F, Fig. 1) is easily

accounted for on this basis.  $n_{\tau}^{0}$  is apparently about the same at the start of each bleaching period so that as  $n_F$  increases, the final value of  $n_F^0 - n_F$  is about the same. Actually, continued x-raying seems to increase  $n_T^0$  somewhat, which is not surprising if these traps are principally vacancy clusters. Bron<sup>4)</sup> found that the residual F center concentration was equal to the total concentration of F centers formed by the second stage of x-irradiation up to the start of bleaching. This is not true of the experiment illustrated in Fig. 1; however, the two experiments were not strictly comparable. While  $n_T^0$  appears to be constant on the basis of data presented here, other information, particularly on the variation of rate of M center formation with temperature,<sup>16)</sup> make it appear that traps which form secondary centers are also produced by migrational processes during bleaching.



Fig. 5. *F*-center bleaching curves and test of Eq. (2) for various KCl crystals.

The importance of concentration gradients developed during bleaching should not be overlooked. In crystals of medium absorbance ( $\sim 0.5$ ) these can be sufficient to obscure seriously the actual bleaching curve at any point in the crystal, and data obtained in this way should not be unduly weighted. Current bleaching experiments in this laboratory are made in such a way that the concentration

of centers is maintained essentially uniform during bleaching.

The constants of Eq. (2) were found graphically.  $n_T^0$  was found to increase with increasing  $n_F^0$  for all crystals, but  $n_T^0/n_F^0$ decreased with increasing  $n_F^0$ . K also varied with  $n_F^0$ , but  $K/n_F^0$  was nearly a constant for each class of crystal. The ratio  $K/n_F^0$ , averaged over two to six bleaching measurements, is given in Table II. This ratio appears to give a good index of impurity content.

Table II.  $K/n_F^0$ , from bleaching, for various KCl crystals

Crystal designation (see Table I)	Average $K/n_F^0$ , min <sup>-1</sup>			
W	0.34			
W(OH)	0.42			
W(Cu)	0.48			
Μ	0.70			
Η	1.86			
W(Pb)	2.0			
M(Ca)	3-9			

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### DISCUSSION

**Kanzaki**, **H**.: Our conclusions on the state of defects in NaCl crystals grown from aqueous solution containing Pb<sup>++</sup> are as follows; (1) The crystals are as imperfect as those grown from the melt (for example Harshaw crystals). There is no difference between etch pits count of these two kinds of crystals. (2) Experiments on heat treatment of water-grown crystals led us to the following conclusions.

In the as-grown state,  $Pb^{++}$  ions are dispersed in crystals as the state combined strongly with water molecules or  $OH^-$  ions. During annealing, water molecules or  $OH^-$  ions escape to outside through diffusion path along dislocation walls. As the results,  $PbCl_2$  phase starts to precipitate.

**Scott**, **A. B.**: It would be valuable to know also if the crystals grown in the absence of lead show a degree of imperfection equal to that of melt grown crystals. Lead incorporates readily, as is well known, and, as was true of our experiments, affects colorability more than  $OH^-$  or  $Cu^{++}$ .

Frequently, acid is added to facilitate the growth of alkali halide crystals containing lead; this may eliminate the incorporation of  $OH^-$ . Since  $PbCl_2$  and KCl form the double salt  $K_2PbCl_4$ , a possible mode of incorporation of lead is as the complex ions  $PbCl_4^{--}$ .

**Pick, H.**: Prof. Scott, what do you think are the main impurities still present in your water grown crystals? Did you do any work to analyse the water grown crystals?

**Scott, A. B.**: I believe lead and iron are two likely impurities still present in crystals grown from KCl solution, as the starting material contained traces of these elements and they are not easily removed by recrystallization. Ultraviolet absorption spectra showed no definite indications of these elements, so that it is my opinion that they were present at concentrations well below the limits of conventional analysis.

Nowick, A. S.: I should like to point out that there were several reasons which led

Bron to the conclusion that bleaching occurs in two stages. Perhaps the strongest argument was the fact that the initial bleaching rate depends on the F-center density produced in the first stage of coloration, rather than the total F-center concentration. The mere fact that one equation fits the bleaching data does not necessarily imply a single process. For example, one can write a single equation made up of a transient term plus a linear term, which usually is regarded as suggestive of two processes.

Scott, A. B.: A second of Bron's reasons was the fact that in his experiment the residual F-center concentration after bleaching was equal to the concentration of F-centers produced in the second stage of the preceding X-irradiation. This is not true of the present experiment. However, the two experiments are not strictly comparable.

In contrast to the example you cite of a single equation containing a transient term and a linear term, the differential form of our equation contains only a single term, the rate being second order in the concentration  $n_+^0 - (n_F^0 - n_F)$ , which certainly does not suggest two processes. Precise measurements of *F*-center concentration at long exposures, by a method in which concentration gradients are completely avoided would be useful in settling this point.

**Howard, R.**: It seems surprising that the number of initial halide-ion vacancies is larger in the  $Ca^{++}$  doped crystal than in the pure crystal. From mass-action considerations, doping with  $Ca^{++}$  ions should reduce the number of negative ion vacancies.

Scott, A. B.: It is true that the action of  $Ca^{++}$  is opposite to that expected upon the basis of the mass action principle, a result that has not yet, to my knowledge, been satisfactorily explained. One possibility is the following: the high positive-ion vacancy concentration increases the probability of hole-trapping so that electron-hole recombination is reduced and *F*-center formation is promoted. Special assumptions would be required to account for the observed coloration rate or the high saturation vacancies in the neighborhood of positive-ion vacancies may require considerably less energy than in the ideal lattice, so that we have two stages in vacancy generation, one easy and one difficult. Until this problem is settled, it may be best to consider  $n_{H}^{0}$  only as the first-stage saturation parameter, without attaching physical meaning, in the case of crystals containing divalent cations.

**Crawford, J. H.**: In work to be described in our paper\* later in the program, we have observed similar behavior in the growth of F-coloration in  $\gamma$ -irradiated KCI: Calcium doped crystals show a very linear second stage, whereas high purity melt grown crystals show marked curvature in the second stage. In this regard there is a danger in using unfiltered X-rays which lead to a strong gradient in ionization intensity in the crystals. Sonder and Sibley have shown that the number of F-centers produced per unit absorbed energy increases markedly with increasing ionization intensity. Therefore, coloration curves obtained in the direction of the X-ray beam in the crystal represent a composite coloration curve for a wide range of ionization intensities, a factor which might make stage II coloration appear more linear with increasing X-irradiation than it really is.

\* Proc. Int. Conf. Cryst. Latt. Def. (1962): J. Phys. Soc. Japan 18 Suppl. III (1963).