PHYSICAL REVIEW VOLUME 137, NUMBER 1A 4 JANUARY 1965

# Role of Multiple Ionization in the Generation of Defects in Alkali Halides by Soft X Rays*

J. Sharma and R. Smoluchowski
*Princeton University, Princeton, New Jersey*

(Received 24 July 1964)

*F* coloration in KCl and KBr has been studied at liquid-nitrogen temperature as a function of wavelength of monochromatic x rays on either side of the *K* edges of Cl and Br. The coloration on the high-energy side of the edge is higher than the coloration on the low-energy side by a factor of 2.5 for KCl and 1.1 for KBr. This is interpreted as evidence for the importance of multiple ionization in the process of vacancy formation as required by a Varley-type mechanism based on an Auger effect. In KBr, the *K*-edge coloration discontinuity was studied as a function of radiation dose at 78, 195, and 300°K. At 78°K the discontinuity becomes more pronounced as irradiation proceeds and generation of new vacancies takes place. The discontinuity does not show up at 195 and 300°K, presumably because at these temperatures the coloration of existing vacancies is the dominating phenomenon.

## INTRODUCTION

The mechanism of defect production in alkali halides by soft x rays is not yet clearly understood. When the energy of the x rays is less than 30–50 kV, the photoelectrons are not capable of displacing the ions by direct collision; therefore, an ionization mechanism has to be invoked for generating vacancies. Seitz[1] was first to suggest that the recombination of electrons and holes or excitons at dislocation jogs can provide enough energy to produce pairs of vacancies at these sites. Later Varley[2] suggested that multiple ionization of the anion, for instance through an Auger effect, would leave it in a highly unstable position because of the highly perturbed electrostatic potential. If the time required for the anion to recover at least one electron is long enough, say $10^{-13}$ sec, to permit displacement, it will be forced out of its equilibrium position into an interstitial site, whence it can diffuse somewhat through the crystal. The anion vacancy can pick up an electron and form an *F* center. A modified version of the Varley mechanism has been suggested by Howard *et al.*[3] who used the idea that an Auger effect and thus a multiple ionization is followed by a de-excitation collision. This process provides a specific mechanism and enough energy to explain the observed large separation between the vacancy and the interstitial near 4°K. Klick[4] and Williams[5] have suggested that two adjoining singly ionized anions can lead to the formation of a vacancy and an interstitial, although these will be rather closely associated at low temperatures. A series of recent studies of x-ray coloration at various temperatures[6–8] suggests that the structure-sensitive part of coloration at or near room temperature cannot be accounted for by a simple evaporation of vacancies from dislocations, while, at low temperatures, a Varley-type mechanism has to be invoked. Studies of the generation of interstitials by Känzig,[9] Gebhardt,[10] Wiegand,[11] and Nadeau[12] confirm this view.

Dexter[13] has pointed out that x rays in the vicinity of the *K* edge of the anion provide a vantage point for testing the role of the Varley mechanism. On the high-energy side of the halogen *K* edge, most of the x rays are absorbed in its *K* shell and a major part of *K* ionization (90% for Cl; 50% for Br) is followed by an Auger effect, which leads to multiple ionization in the *L* shells. If multiple ionization of the anion is instrumental in the generation of *F* centers, more *F* centers should be produced on the high-energy side of the *K* edge than on the low-energy side per unit absorbed energy. Since the background contribution from photoelectrons and excitation of *L* and *M* shells remains approximately the same on either side of the *K* edge, an increase in the *F*-center colorability on the high-energy side of the *K* edge would provide clear evidence that multiple ionization and thus a Varley mechanism does play a vital role in the generation of *F* centers.

In the present work, preliminary experiments were performed on KCl and NaCl using total radiation from an x-ray tube whose anode potential was varied through the *K*-excitation potential of chlorine. Final experiments were performed using monochromatic radiations near the *K* edges of chlorine and of bromine.

## EXPERIMENTAL

In view of the fact that the *K* edge of chlorine is at 4.3851 Å (2.826 kV), it was necessary for the preliminary white-spectrum studies to install a small

---

* Work supported by the Atomic Energy Commission and National Science Foundation research contracts.

[1] F. Seitz, Rev. Mod. Phys. **26**, 7 (1954).

[2] J. H. O. Varley, Nature **174**, 886 (1954); J. Nucl. Energy **1**, 130 (1954); Phys. Chem. Solids **23**, 985 (1962).

[3] R. E. Howard, S. Vosko, and R. Smoluchowski, Phys. Rev. **122**, 1406 (1961).

[4] C. C. Klick, Phys. Rev. **120**, 760 (1960).

[5] F. E. Williams, Phys. Rev. **126**, 70 (1962).

[6] D. A. Wiegand and R. Smoluchowski, Phys. Rev. **109**, 220 (1958).

[7] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[8] V. H. Ritz, Phys. Rev. **133**, A1452 (1964).

[9] M. H. Cohen, W. Känzig, and T. O. Woodruff, Phys. Rev. **108**, 1096 (1954); Phys. Chem. Solids **9**, 70 (1958).

[10] W. Gebhardt, Phys. Chem. Solids **23**, 1123 (1962).

[11] D. A. Wiegand, Phys. Rev. Letters **9**, 201 (1962).

[12] J. S. Nadeau, J. Appl. Phys. **33**, 3480 (1962).

[13] D. L. Dexter, Phys. Rev. **118**, 934 (1960).

x-ray tube right in the Dewar. This arrangement permitted the elimination of windows between the x-ray target and the sample. The tube was operated alternately for $\frac{1}{2}$ h at 3.3 and 2.8 kV, keeping the current constant at 25 mA. The build-up of coloration was measured with a Cary 14R spectrophotometer after each exposure. In order to take into account the difference in x-ray intensity for the two voltages, the photon output was checked using a Bendix M3 photon detector. The usual 1.14 power law was confirmed. Further control experiments were made using NaF which has no absorption edge in this region.

For studies with monochromatic x rays near the *K* edge of chlorine, a bent crystal vacuum monochromator was constructed using a quartz crystal $20\times10\times0.3$ mm with reflection occurring on the $(10\bar{1}0)$ plane. The crystal was ground to a cylindrical radius of 40 cm and then bent to a radius of 20 cm giving a dispersion of 0.02 Å/mm in the region of interest. The x-ray tube, the monochromator, and the crystal-holding Dewar were part of the same vacuum system. A small region of the white spectrum, centered about the *K* edge of chrorine ($\theta=31°9'$) was displayed on a KCl crystal, set at the proper angle on the Rowland circle. After 25 h of exposure with 50–75 mA, 4.2 kVp x rays, the coloration produced on the crystal was scanned transversely using a Cary spectrophotometer with a slide wire covering the 0–0.1 range of optical density. The scanning was done at 5400 Å, which is the maximum of the *F* band for KCl at liquid-nitrogen temperature. The low-temperature Dewar, the monochromator and the x-ray tube assembly was mounted on rails, so that the crystal could be moved across the Cary beam by means of a micrometer. The intensity distribution in the spectrum was obtained by substituting an x-ray film in place of the crystal. In these experiments, the principal difficulty was the low intensity of the monochromatic x rays. Extremely long exposures could not be given, because the surface of the crystal progressively deteriorated as a result of degassing of the x-ray tube. This difficulty prevented a study of the discontinuity observed in KCl as a function of dose and temperature.

The coloration of KBr crystals with monochromatic x rays in the vicinity of the *K* edge of bromine (0.918 Å, 13.475 kV) was studied using a Siemens bent-and-ground crystal monochromator, having a dispersion of 0.03 Å/mm in the region of interest. The reflection at about 7° was taken from the $(10\bar{1}0)$ plane of quartz bent to a radius of 25 cm. The monochromator was held at such an angle that a well focused spectrum peaked about the *K* edge of bromine was obtained on the KBr crystal which straddled the *K* edge position on the Rowland circle. The x rays illuminated the crystal at an angle of about 15° which had no measurable defocusing effect for the narrow spectral region displayed on the crystal. After giving an exposure of 80–100 h at 50 mA and 50 kV, the *F* coloration on the crystal was measured in the Cary beam in a direction normal to the crystal surface. Scanning gave the *F* coloration as a function of the wavelength of x rays. The intensity distribution in the x-ray spectrum was obtained by making similar measurements on LiF since LiF has no absorption edge in this region of the spectrum. An unperturbed intensity distribution could not be obtained with x-ray film due to the presence of bromine in the photographic emulsion.

Auxiliary experiments were performed to check that the coloration observed in the experiment corresponded to the linear part of the growth curve in which the generation of new vacancies is the main effect and that the reciprocity law is obeyed at liquid-nitrogen temperature. In order to avoid the intensity problem, these experiments were performed using the total radiation from an x-ray tube operated in such a manner that the peak of the white spectrum occurred at 13.5 kV or 0.918 Å. During the experiment on growth of coloration, reciprocity tests were performed by decreasing the tube current by a factor of five and correspondingly increasing the exposure periods. These tests were monitored using a proportional counter in a Bragg spectrograph attached to another window of the x-ray tube.

The crystals used in these experiments were cleaved from "as received" crystals from the Harshaw Chemical Company. They were 2–3 mm thick which assured that the radiation incident on the crystal was completely absorbed. The linear absorption coefficients for KBr on the shorter and longer side of the *K* edge of bromine are 310 and 75.6 $\text{cm}^{-1}$, respectively. The corresponding values for KCl at the *K* edge of chlorine are 1875 and 425 $\text{cm}^{-1}$, respectively.

## RESULTS

The results obtained using white x-ray radiation from a tube operated below and above the *K*-excitation potential of Cl are shown in Fig. 1. Alternate equal exposures show that more *F* centers are produced when *K* excitation takes place. Similar zig-zags were obtained with NaCl but the coloration change was smaller by a factor of 5 in this case. The zig-zags show up better at higher dose, beyond the initial structure-sensitive range. One might suspect that this difference in coloration is not related to an onset of a new defect formation process, but to the slightly higher efficiency of x-ray generation at the higher voltages. That this is not the case was checked by measuring directly the photon intensity for both voltages and by noting that a smooth growth curve i.e., no zig-zags was observed for NaF which has no absorption edge in this region of wavelengths.

The results obtained with KC1 at 78° using monochromatic radiation in the vicinity of the *K* edge of chlorine are shown in Fig. 2(b), which gives *F* coloration as a function of wavelength. Figure 2(a) gives an

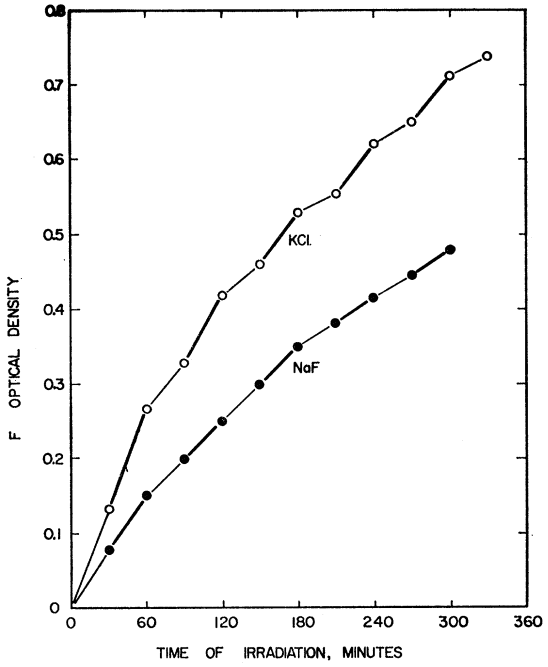

FIG. 1. $F$-band coloration in KCl and NaF produced by alternate 30 min, 25-mA irradiation with 2.8 kV (thin line) and 3.3-kV (thick line) x rays at 78°K.

indication of the intensity distribution of the x-ray spectrum as obtained with an x-ray film. Figure 2(c) is a calculated curve, drawn for comparison, based on the known slit resolving power and assuming a step of colorability at the $K$ edge in the ratio of 1:2.5. It is seen from Fig. 2 that the $F$-coloration discontinuity at the edge is in reasonable agreement with this ratio.

The results for KB4 at 78°K are shown in Fig. 3(b) where again the $F$ coloration is plotted as a function of wavelength. Figure 3(a) gives the x-ray spectrum as indicated by $F$ coloration in a LiF crystal, which does not have any absorption edge in this part of the x-ray spectrum. The discontinuity in the coloration at the $K$ edge of bromine is approximately 10:11 which is much less than in KCl. The densities of $F$ centers produced were approximately $7\times10^{17}$ per cc and $1.8\times10^{17}$ per cc on the higher and lower energy sides of the $K$ edge, respectively. As Fig. 3(c) shows there is no definite $K$-edge effect in the coloration curve at 195°K. Similarly, at 300°K no coloration discontinuity is observed because of an early saturation which makes the curve rather flat on the longer wavelength side. This saturation is a characteristic effect at these temperatures.

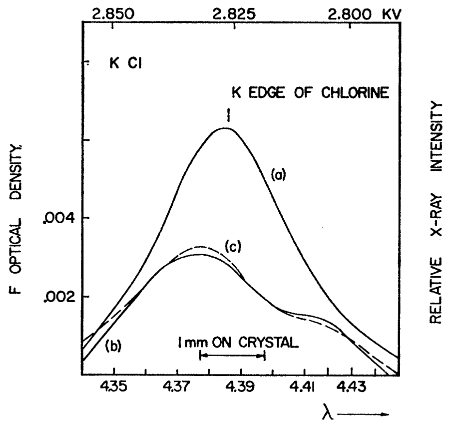

FIG. 2. (a) White x-ray spectrum in the vicinity of the $K$ edge of chlorine as obtained by the bent crystal monochromator with an x-ray film. (b) $F$ coloration in KCl as a function of wavelength of x rays. (c) Calculated coloration curve based on the assumption of a rectangular step at the $K$ edge in the ratio of 1:2.5.

Figure 4 shows coloration at 78°K as a function of irradiation dose for the longer and shorter wavelength side of the $K$ edge. The initial variation in coloration is due to the fact that the penetration of x rays on the shorter wavelength side is about one fourth of that on the longer wavelength side. Therefore after an initial structure-sensitive part the saturation takes place earlier on the short wavelength side and it is displaced towards longer times on the longer wavelength side.

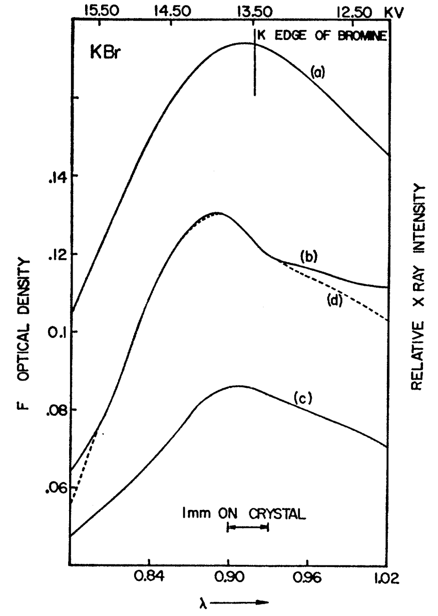

FIG. 3. (a) White x-ray spectrum in the vicinity of the $K$ edge of Br, as obtained with $F$ coloration of a LiF crystal at room temperature exposed for 58 h. (b) $F$ coloration of KBr crystal at 78°K as a function of wavelength of x rays, exposed for 93 h. (c) $F$ coloration of KBr at 195°K, exposed for 63.5 h. (d) Calculated coloration curve, based on the assumption of a rectangular step at the $K$ edge in the ratio of 1:1.1.

The auxiliary experiments performed on the growth curve and the reciprocity tests are represented in Fig. 5. They show that the coloration measurements of the coloration discontinuity have been done in the so-called linear portion of the growth curve (this is also evident from Fig. 4), and that the coloration follows the

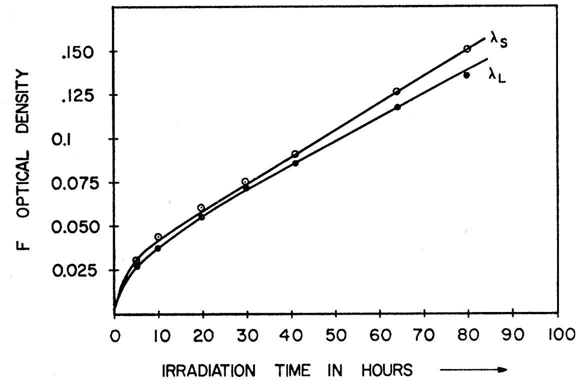

FIG. 4. $F$ coloration as a function of irradiation time for x rays at 0.90 and 0.93 Å on the high and low side of the $K$ edge of Br.

reciprocity law. The latter point is also confirmed by the observations of Harrison,[14] Ritz,[8] and Pretzel.[15] This is an important point, since otherwise one might conclude that the discontinuity observed at the $K$ edge is just a result of different absorption rates on the two sides of the $K$ edge. On the high-energy side, the absorption coefficient being larger, the density of the absorbed x rays would be higher by a factor of 4, and if reciprocity were not obeyed this would result in discontinuities similar to those observed.

## DISCUSSION

The $K$-edge discontinuity in coloration is an evidence in support of the role of multiple ionization in defect formation. When the $K$ edge is crossed to the high-energy side most of the x rays cause $K$ ionization which leads to an Auger effect and to a multiple ionization of the anion. On the low-energy side of the $K$ edge, the same amount of energy is being dissipated in the crystal, but none of it goes to the $K$ shell of the anion. The background coloration, which may be caused by an excitation of higher shells and by photoelectrons, should remain approximately the same on either side of the $K$ edge. Therefore the increase in coloration shown at the $K$ edge indicates that multiple ionization makes an important contribution to the generation of vacancies and $F$ centers, although other mechanisms[4,5] may also play a role.

The $K$-edge discontinuity is larger for KCl than for KBr because $K$ ionization is not a necessary prerequisite for vacancy generation. Even when the $K$ electron is not ejected, multiple ionization in the higher shells, photoelectrons or a Klick-type mechanism could cause $F$ centers to be generated. These effects would be more important for KBr than KCl because of a larger number of outer electrons in bromine.

A rough estimate of the expected $K$-edge coloration discontinuity can be made by considering that according to Rabin and Klick[7] about 1300 eV of energy is required for the generation of an $F$ center at low temperature. In KCl, on the low-energy side of the $K$ edge about 2.3 $F$ centers would be produced by the dissipation of a 3-kV photon. If, on the high-energy side, one extra center is produced through $K$ ionization and a Varley mechanism, the coloration will increase by an amount comparable to the background coloration. In KBr, on the other hand, the $K$ edge of bromine occurs at 13.45 kV and a similar argument leads to the conclusion that the F coloration per photon would increase by less than 10%. Both these rough estimates are not far off from the experimental results.

These colorability values will be further modified by other factors. In bromine, the efficiency of an Auger effect after $K$ ionization is 50%,[16] whereas in chlorine it is 90%.[16,17] Related to this is the fact that in KBr on the shorter wavelength side of the $K$ edge in bromine 15 to 20% of the incident energy escapes from the front surface of the crystal as fluorescence. For KCl, however, the comparable loss is only 3 to 4%. Another factor that may reduce the $K$-coloration discontinuity is the contribution of photoelectrons. On the low-energy side of the $K$ edge, the energy of the primary photoelectrons will be about $(K-L)$, whereas on the high-energy side, by the Auger process, it will be $(K-2L)$. Thus the degradation of the energy of the photoelectrons will be somewhat higher in the latter case. This may tend to reduce background coloration on the high-energy side of the $K$ edge. Since, however, the $K$-excitation energy is large compared to $L$, the effect will be small.

It was mentioned before that the $K$-edge discontinuity does not show up at 195 and 300°K. This is presumably so because in this temperature range the coloration of existing vacancies dominates. Since the generation of

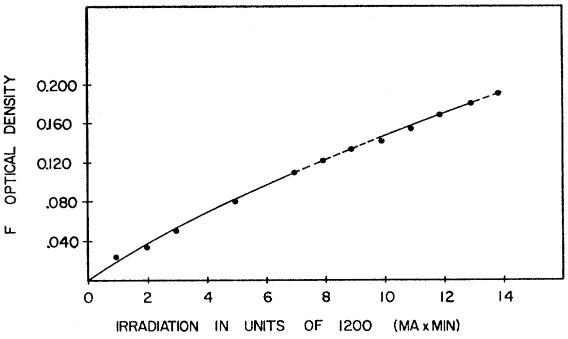

FIG. 5. $F$-center growth curve of KBr with white radiation peaked at 13.5 kV. In the dashed part, the intensity was reduced by a factor of 5 and the time of exposure was correspondingly increased.

---

[14] G. Harrison, Phys. Rev. **131**, 2505 (1963).

[15] F. E. Pretzel (private communication).

[16] E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, London, 1952).

[17] F. Bertrand, G. Champak, F. Suzar, J. Phys. Radium **20**, 956 (1959).

new vacancies is not required, a Varley-type mechanism does not show up. This conclusion is also evident from Fig. 1(a) where the zig-zags do not appear in the early part of the curve, as long as the structure-sensitive part of coloration dominates.

It is clear that if the formation of all new $F$ centers at low temperatures were the result of $K$ ionization then the jump in coloration at the $K$ edge would be huge. The fact that it is relatively small indicates that many centers are formed through ionization of the $L$ shell in chlorine and $L$ and $M$ shells in bromine. This conclusion agrees also with the average expenditure of about 1300 eV per $F$ center as compared to the ionization energy for the $K$ edges (2.8 and 13.5 kV for Cl and Br), $L$ edges (215 and 1650 eV), and $M$ edge (250 eV for Br). Since the Auger effect is more probable for the outer shells than for the $K$ shell, all these initial single ionizations lead to multiply ionized halogens which are then available for a Varley-type mechanism. It should be stressed, however, that the simultaneous production of vacancies through various kinds of ionizations and the often unknown ratio of alpha to $F$ centers remove much significance from the often quoted absolute magnitude of the energy expenditure per $F$ center. Similar uncertainties exist on the theoretical side[18] in the treatment of the ionization efficiency in the low-energy range. The present tests of reciprocity and those of Harrison,[14] Pretzel,[15] and Ritz[8] confirm that $F$-center generation at low temperatures is linear and not proportional to the square of the x-ray intensity. It thus seems that truly random multiple ionization is rather unimportant, at least in the range of intensity employed in the present and similar experiments.

Ritz's results[8] indicate that when coloration is performed with x rays much more energetic than the $K$ edge then the variation of colorability with energy is small. This is understandable since then the differences in the ionization probability are not strongly wavelength dependent. When comparing colorability of different alkali halides, other factors such as the above mentioned fluorescence need to be taken into account. It is known that alkali halides requiring higher energy per $F$ center fluoresce more than those which are easily colored. For instance Bose and Sharma[19] noted that the fluorescence of KCl and KBr is least because they color readily. Similarly Klick[20] observed that in going to liquid-helium temperature fluorescence of alkali halides increases a few orders of magnitude.

## ACKNOWLEDGMENT

The authors wish to thank Professor B. S. H. Royce for his stimulating discussions and counsel throughout this investigation.

---

[18] J. Durup and R. L. Platzman, Discussions Faraday Soc. **31**, 156 (1961).

[19] H. N. Bose and J. Sharma, Proc. Natl. Inst. Sci. India **16**, 47 (1950).

[20] C. C. Klick (private communication).