PHYSICAL REVIEW VOLUME 137, NUMBER 1A 4 JANUARY 1965

X-Ray Generation of Color Centers in Zone-Refined KCl and KBr†

T. M. SRINIVASAN AND W. D. COMPTON
Department of Physics, University of Illinois, Urbana, Illinois

(Received 3 August 1964)

The techniques of zone purification of KCl and KBr crystals are described, and the success of this technique in removing impurities such as hydroxyl ions and divalent cations is demonstrated. A comparison of the defects introduced into zone-purified salts and commercial salts by x irradiation at room temperature and at liquid-helium temperature is given. Studies of the optical bleaching of F, H, and V_K centers by F-band light at liquid-helium temperature gives evidence of the spatial proximity of these centers.

INTRODUCTION

ALTHOUGH there is ample evidence that defects are generated in the alkali halides by irradiation with x rays, the mechanism by which the energy of the incident x ray is used in displacing the ions has not been firmly established.[1] The energy that must be absorbed from an x-ray beam to form an F center at room temperature is characteristically less than 100 eV during the initial stages of coloration.[2,3] For longer irradiation times, the efficiency decreases to a point where several thousand electron volts are required to produce an F center. Approximately the same energy is required to form an F center at helium temperature. It has been suggested that this approximate agreement between the efficiencies at these two temperatures may indicate that the mechanism of vacancy formation is the same at the two temperatures.[4]

Impurities significantly affect the efficiency for forming color centers at room temperature. Impurities such as Ca^{++}, OH^-, and H^- greatly reduce the energy required to form an F center during the initial stages of coloration. It has been suggested that this "first-stage" coloration results from putting electrons into vacancies which exist as a consequence of the impurities.[5] An extension of these ideas would suggest that the more pure the crystal, the less significant would be the "first stage" of coloration.

At liquid-helium temperature, impurities do not significantly affect the efficiency for F-center production. The same result seems to hold true for the production of H centers,[6] at least for reasonable irradiation times. This is demonstrated by a linear relationship between the intensity of the F and H bands. At low coloration intensities, this relationship is not valid and the concentration of F centers seems to exceed that which would be predicted from the concentration of H centers. The shape of the absorption band that peaks in the vicinity of the H band also changes as the concentration of H centers is built up by continued irradiation. This might suggest that some F centers are being formed, even at helium temperature, from vacancies which already exist in the crystal. Alternatively, this might suggest the presence of two overlapping bands which grow at different rates.[7,8] Since the purity of the crystal seems to determine the concentration of vacancies in the crystal, it seemed desirable to examine this effect in zone-refined crystals.

This paper describes the technique of zone purifying KCl and KBr.[9] The ionic conductivity at the knee of the conductivity curve is used as an indication of the level of purity. A comparison is made between the zone purified crystals and single crystals purchased from Harshaw Chemical Company. Samples of each of these materials were irradiated with x rays at liquid-helium and at room temperature. A comparison of the growth of the F bands as a function of time is given for the room-temperature irradiation of the commercial and zone purified crystals. A comparison between the F and H bands is made for the helium irradiations. The bleaching of the F and H bands by optical irradiation with F light at liquid-helium temperature is studied. The significance of these studies in relation to the mechanism of color-center formation is discussed.

EXPERIMENTAL PROCEDURE

The zone purification apparatus for KCl and KBr consisted of a MRC Manufacturing Corporation zone refining apparatus, model Z-83, with the heater driving mechanism operated from a stabilized power supply.[10] The zone heater consisted of a Kanthal ribbon 0.25 in. wide and 0.06 in. thick which was supported inside a short ceramic tube by its current leads. Approximately 550 W of power were dissipated in the heater. Radiation losses were reduced by platinum reflectors attached to the inner wall and ends of the ceramic tube.

---

† Supported in part by U. S. Air Force Contract AF 49 (638)-529.

[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1962).

[2] H. W. Etzel and J. Allard, Phys. Rev. Letters **2**, 452 (1959).

[3] W. Martienssen, Z. Physik **131**, 488 (1952); Nachr. Akad. Wiss. Göttingen Math. Physik. Kl, IIa **111** (1952).

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

[5] See Ref. 1, p. 219.

[6] B. Faraday, Ph.D. thesis, Catholic University of America, 1963 (unpublished).

[7] W. D. Compton and C. C. Klick, Phys. Rev. **110**, 349 (1958).

[8] J. A. Cape, Phys. Rev. **122**, 18 (1961).

[9] See H. Gründig, Z. Physik **158**, 577 (1960) for a similar study of the ionic conductivity of zone-refined KCl.

[10] For a more extensive discussion of the zone purification techniques see Tech. Rept No. 3, AF 49(638)-529, Directorate of Solid State Sciences, Air Force Office of Scientific Research, Washington, D. C. (unpublished).

Half-round fused silica crucibles of length 25 cm and diameter 2.5 cm were used for the majority of the experiments. The ingot and the crucible were contained in a fused silica tube of 2.7-cm internal diameter. The clearance between this silica tube and the external Kanthal heater loop was about 1 mm.

Two zones, produced by a pair of heaters, were simultaneously passed through the ingot. The zone left at the center of the ingot by the first heater at the end of a pass was maintained by the second heater starting the next pass.

Refining of KBr was also done in a sealed silica tube of 1 cm internal diameter which was held vertically. The zone was moved slowly from top to bottom followed by a rapid return of the heater to the top.

Since molten alkali halides have a tendency to wet silica and adhere to it upon freezing, it is difficult to prevent the fracture of the crucibles upon cooling to room temperature. This was satisfactorily prevented by the following treatment of the silica crucibles and the salts.

The silica crucibles were cleaned with dichromic acid, washed with deionized water, dried, and then heated to 1000°C in a silica tube containing chlorine gas at about one atmosphere pressure. The crucible was filled with reagent-grade potassium chloride powder that had been dried for about ten hours at 80°C. The crucible and salt were then placed in an evacuated silica tube, heated to 700°C, and filled with chlorine gas at one atmosphere pressure. The temperature was raised until the salt melted. After about three hours, the crucible was cooled to room temperature, the chlorine gas was replaced by fresh chlorine prior to the zone purification. Although this treatment was effective in preventing the sticking of powdered reagent-grade potassium chloride to the crucible, ingots prepared from Harshaw single crystals occasionally stuck to the crucible.

The chlorine gas was purified as in Fig. 1. Tank chlorine was condensed with liquid nitrogen at A or B. Uncondensed gases were pumped off. The liquid nitrogen was replaced by melting toluene (−95°C) and the chlorine distilled slowly into C. The chlorine gas from tube C was then condensed into Appendix H. The treatment for the potassium bromide was similar except that bromine gas was used.

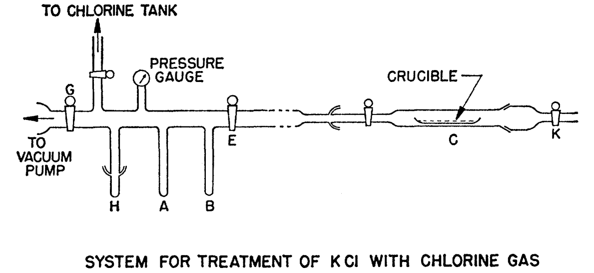

FIG. 1. Schematic representation of halogenation treatment system used in preparing salts for zone purification.

Since potassium chloride and bromide expand on melting, mass transport of the salt occurs during horizontal zone refining in a direction opposite to that of the zone motion. This transport was prevented by progressive tilting of the crucible after each pass of the zone. A total of eight degrees was adequate for compensation of mass transport during 25 passes.

The dc electrical conductivity of the crystals was measured with a vibrating reed electrometer. Currents less than 10^{-12} A were used. Colloidal graphite electrodes were painted on the larger faces of crystals with dimensions 3 mm×3 mm×0.1 mm. The samples were held between platinum electrodes in a helium-filled oven. Temperatures were measured with Pt−Pt+10% Rh thermocouples.

Optical absorption measurements before and after x irradiation were made with a Cary Model 14R spectrophotometer. The crystals were mounted in a helium cryostat, x irradiated through a beryllium window and optically measured through fused silica windows. The crystal holder was a thin-walled copper can with liquid helium maintained in it. The temperature, as measured with a germanium thermometer substituted for the crystal, was 7°K. Samples of thickness between 0.007 and 0.015 in. were cleaved from a polycrystalline zone purified ingot or from a single crystal of Harshaw material and were irradiated with x rays from a Philips x-ray machine operating at 100-kV constant potential and 25-mA filament current. Filtration of 0.004 in. of copper was used to ensure uniform coloration of these thin samples.

RESULTS AND CONCLUSIONS

Zone Refining

The ionic conductivity of a few of the purest potassium chloride and bromide crystals prepared by zone refining is shown as a function of temperature in Figs. 2 and 3. The curves labeled "starting material" were obtained from single crystals that were grown by Kyropoulos method from reagent-grade salts. The curves labeled "Harshaw" are typical of data obtained from single crystals purchased from the Harshaw Chemical Company. The high-temperature intrinsic conductivity of Figs. 2 and 3 may be represented by the equation

$$\sigma=(A/T)\exp(-Q/kT), \tag{1}$$

where the activation energy $Q=1.90$ eV for KCl and 1.65 eV for KBr. T is the absolute temperature in °K, k is Boltzmann's constant, and A is a constant.

The impurity content of KCl crystals may be roughly estimated by using the data of Kelting and Witt.[11] According to these authors the concentration of cation vacancies in a pure crystal depends upon temperature

---

[11] H. Kelting and H. Witt, Z. Physik **126**, 697 (1949).

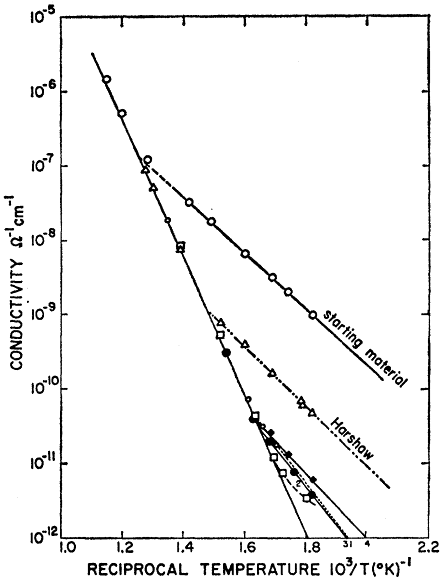

FIG. 2. Ionic conductivity of KCl as a function of reciprocal absolute temperature. The curves labeled 1–4 correspond to the data given in Table I.

in a manner described by the equation

$$\ln N = 26.24 - 8\times10^3/T, \qquad (2)$$

where N is the number of vacancies per cubic centimeter and T is the absolute temperature. It has been assumed that the knee of a conductivity curve as shown in Fig. 2, where the slope of the curve deviates from the value characteristic of the pure crystal, marks the temperature T^* at which the concentration of cation vacancies in a pure crystal is equal to the concentration of divalent cation impurities in the crystal. If this assumption is correct, insertion of T^* into Eq. (2) yields a number N which is the concentration of cation impurities in the crystal. Table I contains such an estimate of the impurity content of KCl crystals used in obtaining the conductivity data of Fig. 2. Since much less data are available on the temperature dependence of the number of cation vacancies in KBr, a similar analysis of the impurity content is not possible. Curves 1 and 2 of Fig. 3 were obtained on the samples used in the x-ray irradiation experiment. It must be emphasized that Eq. (2) can only be used to give an order of magnitude estimate of the cation vacancy concentration. The use of somewhat different values for A and Q in Eq. (1) would alter the constants in Eq. (2) such that the estimate of N might be several times larger than that given in Table I.

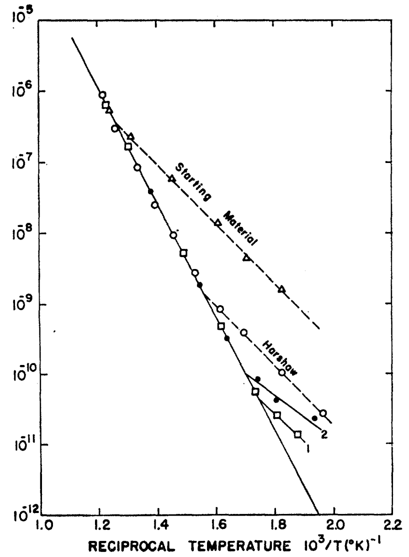

Figure 3

FIG. 3. Ionic conductivity of KBr as a function of reciprocal absolute temperature.

TABLE I. Summary of zone purification of KCl samples.

Sample number	Starting material	Number of zones passed through the samples	Estimated divalent cation impurity concentration	Fig. 2 curve
1	Reagent-grade powder	27	9×10^{12}	3
2[a]	Reagent-grade powder	27	1×10^{13}	4
3	Reagent-grade powder	10	1×10^{13}	1
4[b]	Sample 3	11	6×10^{12}	2

[a] Sample 2 is a section of the same ingot as Sample 1.

[b] The ends of the ingot which furnished Sample 3 were removed and the ingot subjected to 11 additional passes.

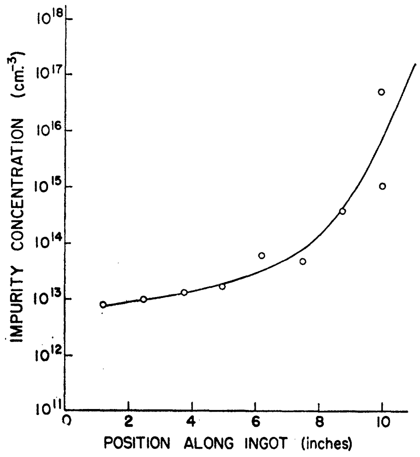

FIG. 4. Impurity concentration as a function of position in a zone refined ingot of KCl. Impurity concentrations were determined by Eq. (2).

Figure 4 illustrates the approximate divalent cation impurity content of eight sections of an ingot of KCl as

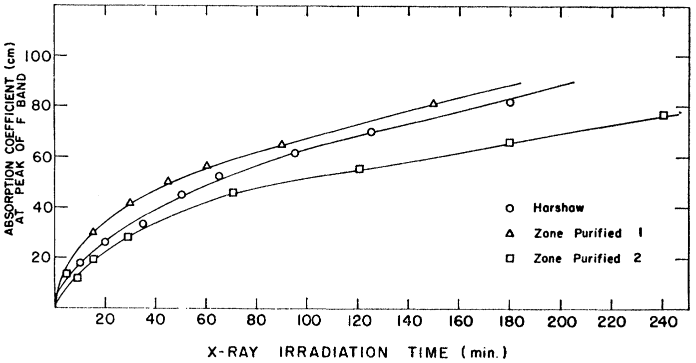

FIG. 5. Absorption coefficient at the peak of the *F* band versus x-irradiation time at room temperature for a Harshaw sample and two samples of zone refined KBr. Zone refined samples 1 and 2 correspond to samples whose conductivity is given by curves 1 and 2 in Fig. 3. Measured at 77°K. *F*-center concentration is found by multiplying the absorption coefficient by 2.3×10^{15}.

a function of position along the ingot. The end of the ingot where the zone was started is the purest.

The ionic conductivity indicates that a significant reduction has been made in the concentration of divalent cations in the zone-refined KCl. The improvement in the KBr is substantial, but to a lesser degree than for the KCl. Optical absorption measurements in the ultraviolet and infrared indicated that the halogen treatment significantly reduced the content of hydroxyl ions in the crystal. It is therefore believed that a substantial reduction has been made in the concentration of impurities which are important in sensitizing a crystal for coloration by x rays. These results are complementary to those published by Gründig.[9]

X Irradiation at Room Temperature

Room-temperature x irradiation of KBr produced the results shown in Fig. 5. No significant difference seems to exist between the coloration of crystals from Harshaw Chemical Company and those which have been zone refined. Similar effects were found for KCl. It therefore appears that the initial stage of easy coloration in these pure crystals cannot be attributed to those impurities which can be removed by zone purification or halogen gas treatment.

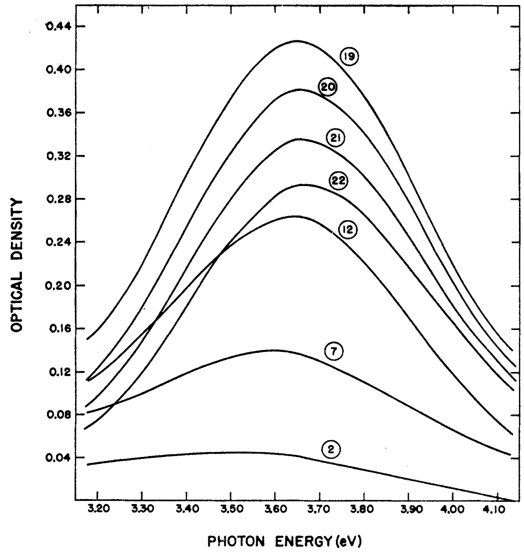

FIG. 6. Optical density in the neighborhood of the *H* band as a function of photon energy for zone refined KCl. X irradiation and measurements were made at 7°K. The treatment utilized in arriving at a given curve is given by the same number in Table III.

X Irradiation at 7°K

X irradiation at 7°K generated the same optical absorption bands in zone-refined KCl and KBr that have been extensively studied in material which was not zone refined. As first reported by Duerig and Markham,[12] the *F* and *H* bands are quite prominent. Absorption bands are also found at 230 mμ in KBr and 194 mμ in KCl. Figure 6 presents data taken on zone refined KCl in the vicinity of the *H* band in KCl. Curves 2, 7, 12, and 19 represent progressively greater irradiation times. It is clearly seen that the spectral shape and peak position of these curves vary as the irradiation progresses. It therefore appears that this change in shape cannot be ascribed to those impurities which are readily removed by halogen treatment or zone purification. No significant change in position or peak position was found for the *H* band in KBr.

Figure 7 presents data which were obtained on the α band in zone refined KBr. The absorption coefficient at the peak of the *F* band is plotted as a function of the absorption coefficient at the peak of the α band. As has been reported by Martienssen,[3] and by Klick and Patterson,[13] the absorption coefficient at the peak of the α band greatly exceeds that at the peak of the *F* band. The zone purification and halogenation appear to produce no significant change in the ratio of *F* to α centers.

Since the change in the shape of the *H* band with length of irradiation and the relative concentration of *F* and α centers appear to be quite general phenomena, it seems likely that these arise from processes which are fundamental to an understanding of the mechanism of defect formation.

---

[12] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1034 (1952).

[13] C. C. Klick and D. A. Patterson, Phys. Rev. **130**, 2169 (1963).

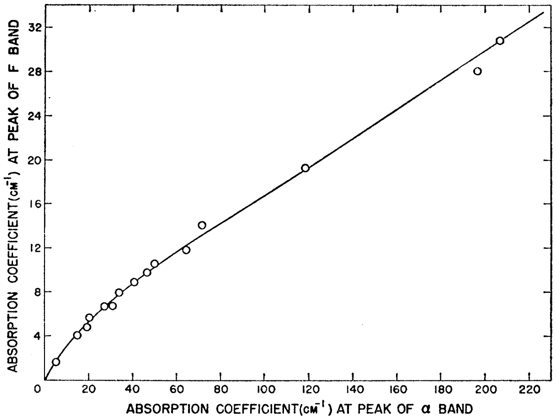

FIG. 7. Absorption coefficient at the peak of the F band versus absorption coefficient at the peak of the α band following x irradiation at 7°K of a zone refined crystal of KBr. Measured at 7°K.

Känzig and Woodruff[14] have reported that electron spin resonance measurements indicate that a significant number of V_K centers are generated by x irradiation at 20°K. The relative concentration of V_K to H centers decreases with increasing irradiation time. Compton and Klick[7] have observed that bleaching with H-band light results in a shift in the peak position of the H band in KCl but not in KBr. Kingsley[15] has suggested that this resulted from V_K centers in the crystals.

Table II gives the peak positions and positions of the half-maxima of the V_K and H bands in KCl and KBr. These values are taken from results in which the influence of nearly overlapping absorption bands has been minimized.[7,8,16] It is seen in Table II that the V_K and H bands in KBr have nearly the same peak positions and half-maxima positions. Since this is not true in KCl, it follows that as the concentration of V_K centers decreases in proportion to H centers, the peak of a composite band would shift toward shorter wavelengths. This suggests that curve 2 of Fig. 6 arises predominantly from V_K centers whereas curve 19 arises from a much larger proportion of H centers. A change in the relative proportion of H and V_K centers in KBr will not result in an appreciable alteration in the peak position of the composite band. This is in agreement with observation.

TABLE II. Position of H and V_K bands in KCl and KBr.

	KCl Position (in eV) of the			KBr Position (in eV) of the		
	peak	half-maxima		peak	half-maxima	
V_K	3.40	3.80	2.99	3.22	3.59	2.86
H	3.70	4.06	3.42	3.26	3.49	3.04

Figure 8 represents a plot of the absorption coefficient at the peak of the composite H band versus the absorption coefficient at the peak of the F band for a sample of zone refined KCl. The sample was maintained at 7°K throughout these measurements. The treatment used in going from any point on the curve to the next point is indicated in Table III. The solid line in Fig. 8 describes the growth of the F band and composite H bands with x irradiation while the dashed line indicates the bleaching with F-band light. The optical bleaching was done at 5600 A with the measuring light of the Cary spectrophotometer. A slitwidth of 3 mm was used.

TABLE III. Sample treatment of Fig. 8.

Point	Time of x irradiation (min) differential	Total	Time of optical bleaching (min) differential
2	15	15	
3			2
4			13
5	15	30	
6	15	45	
7	30	75	
8			2
9			5
10			15
11	70	145	
12	30	175	
13			2
14			7
15			22
16	3	178	
17	30	208	
18	20	228	
19	45	273	
20			2
21			5
22			15
23	3	276	

Several very interesting facts emerge from these data. The initial nonlinear portion of the curve suggests that the V_K and H centers have different oscillator strengths. If, as suggested above, the proportion of V_K centers to H centers decreases as the irradiation progresses, it follows that the oscillator strength of the V_K center is less than that of the H center. Bleaching of the F and H bands with F light decreases the ratio of F to H from that which was present following irradiation; i.e., the bleaching curve does not follow the growth curve. This can be understood if the bleaching results in the removal of more V_K centers than H centers and the oscillator strength of the V_K center is smaller than that of the H center. Such a bleaching would, therefore, result in a further shift of the composite H band toward that of the pure H band. Curves 20, 21, and 22 of Fig. 6 correspond to the points having the same numbers of Fig. 8. It is seen in Fig. 6 that the peak of the curve indeed shifts to shorter wavelengths upon bleaching.

---

[14] W. Känzig and T. O. Woodruff, Phys. Chem. Solids **9**, 70 (1959).

[15] J. Kingsley, Phys. Rev. **122**, 772 (1961).

[16] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961); C. J. Delbecq, B. Smaller, and P. H. Yuster, *ibid.* **111**, 1235 (1958).

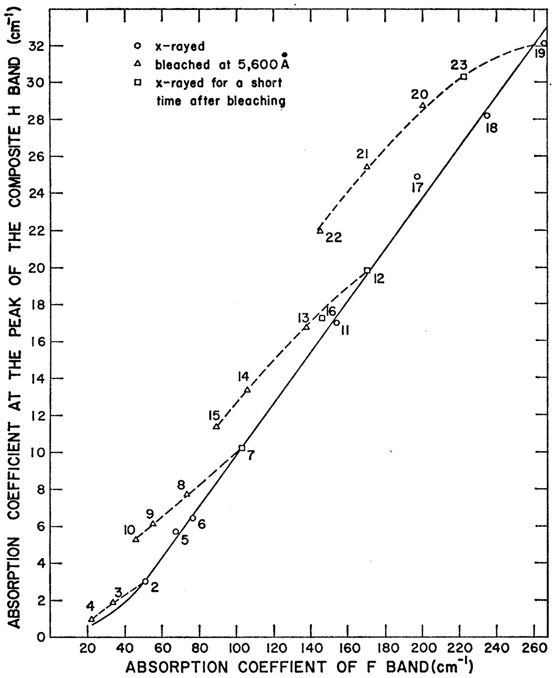

FIG. 8. Absorption coefficient measured at the peak of the composite *H* band versus the absorption coefficient at the peak of the *F* band for zone refined KCl. X irradiation and measurements were made at 7°K. The treatment utilized in arriving at a given point is given by the same number in Table III.

A three-minute x irradiation (point 15 to 16) recovered a large fraction of the *F* centers lost by the optical bleach. The number of *F* centers regenerated by this short irradiation is about three times the number produced by the original 30 min irradiation in going from point 11 to 12. Thus, very little energy is expended in generating the *F* center after the optical bleach. It has been suggested that the optical bleach merely results in a redistribution of electrons with the vacancy being left behind in the lattice.[7] An *F* center can then be reformed by merely trapping an electron at the vacancy. Since it is unnecessary to form the vacancy, the energy required is smaller than would be required to form the vacancy and then trap an electron. This interpretation has been strengthened by the observation that the optical bleaching of x irradiated KBr at 7°K with *F* light increases the concentration of α centers. The increase in the absorption of the α band agrees quantitatively with the observed decrease in *F* centers. The x irradiation after the bleaching decreases the α band. Although the α band was not observable in KCl in this experiment, it seems reasonable to expect that the results on KBr are an accurate description of the situation in KCl. Thus, the bleaching of the *F* center is accomplished by removing the electron from the vacancy, leaving the vacancy isolated in the lattice.

The results obtained on KBr were essentially the same as shown in Fig. 8 with the curve of coloration not following the curve for optical bleaching. It appears that the V_K center has a lower oscillator strength than the *H* center in both KBr and KCl.

The band at 230 mμ in KBr and 194 mμ in KCl were not affected by bleaching with *F* light or by x irradiation following the bleaching.

Past measurements of the low-temperature photoconductivity of crystals containing *F* centers indicate that excited *F* centers are *not* ionized at 7°K by illumination with *F* light. Since *F* centers can be bleached in irradiated crystals by *F*-light illumination, the means by which the electron is removed from the vacancy and the subsequent fate of that electron must be determined. Markham, Platt, and Mador[17] have suggested that the *F* center is bleached as a result of the tunneling of the electron from the excited *F* center to a trap. Since no F' centers are observed to be produced by the bleach and since the region of the *H* band decreases, it is reasonable to assume that the electron disappears as a result of recombination with a hole. If tunneling is important, it seems likely that this takes place over a relatively short distance. Thus, a knowledge of the defects which are bleached should provide some information about the distribution of these defects relative to the *F* centers.

In order to determine whether the *F*-band light bleached V_K, *H*, or both of these defects, the difference between curves 19 and 22 of Fig. 6 is plotted as the upper curve of Fig. 9. The peak of the bleached spectrum does not coincide with the peak of either the V_K band, *H* band, or the peak of curve 19 of Fig. 6. Using the peak positions and half-widths of the V_K and *H* bands as given in Table II, it is possible to graphically decompose the upper curve in Fig. 9 into a V_K and *H* band. The points shown on the upper curve are the sum

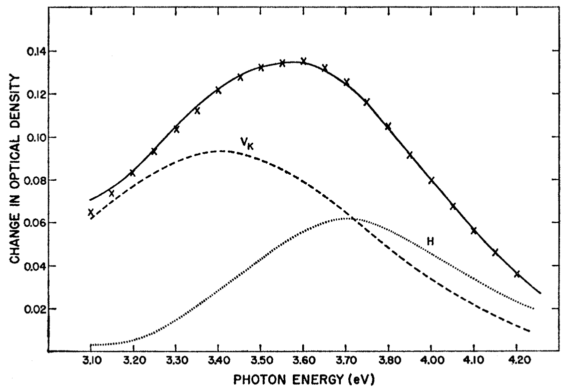

FIG. 9. Bleached spectrum in the region of the composite *H* band resulting from *F*-light irradiation at 7°K. Upper curve is the difference between curves 19 and 22 of Fig. 6. Curves labeled V_K and *H* correspond to the best graphical separation of the upper curve into composite V_K and *H* curves. The graphical sum of the two lower curves is shown by the points on the upper curve.

---

[17] J. J. Markham, R. T. Platt, and I. L. Mador, Phys. Rev. **92**, 597 (1953).

of the V_K and H bands which are shown. The agreement is sufficiently good that it may be argued that the bleaching with F-band light has resulted in the destruction of *both* H and V_K centers. A similar conclusion was obtained for the other bleaching cycles such as for points 7 to 10, etc.

The short x irradiation after the optical bleach has been shown to reform the F centers with a small expenditure of energy. The same appears to be true of the H-band region since Fig. 8 indicates the bleaching curve is retraced as a result of the x irradiation. This cycle was retraceable with the difference curve, as plotted in Fig. 9, indicating that the bleaching of a number of F centers resulted in the bleaching of the same number of H *and* V_K centers. In addition, the ratio of H centers to V_K centers that were bleached was not affected by the cycling. In all cases the efficiency for bleaching seemed to approach a very small value; i.e., it became very hard to bleach more than a certain fraction of the centers.

It seems necessary to conclude from all of this that some F centers have H centers close, others have V_K centers close, and still others have neither close to them. The rather surprising fact is that after bleaching, the x rays reform V_K centers close to the F centers. If the formation of V_K centers is a process of trapping a hole at any random halide ion, one would expect that the number of V_K centers which are close to F centers would decrease with each cycle of bleaching and irradiation.

Mechanism of Defect Formation

The above results may be briefly summarized as showing that F, H, V_K, and α centers are formed by x irradiation at 7°K and that some F centers have H centers as close neighbors, others have V_K centers as close neighbors, and some are isolated. Much attention has recently been given the mechanism by which defects are formed by x rays. The present results seem pertinent to these discussions

Seitz,[18] Varley,[19] Klick,[20] Howard *et al.*,[21] and Williams[22] have suggested various mechanisms of defect formation. Seitz has suggested that dislocations, impurities, and other extrinsic properties of the crystal determine the formation of defects. Results of Rabin and Klick[4] and Faraday[6] indicate that this is not valid for irradiation at these low temperatures. Varley suggested that there is a reasonably high probability of producing a doubly ionized halide ion which, as a result of electrostatic repulsions, will be ejected into the lattice to form a positive interstitial halogen ion. Dexter[23] has objected to this mechanism on the grounds that an electron may be attracted from a neighboring halide ion to neutralize the positive charge before the positive halide ion can be ejected from its lattice site. Klick has suggested that although the electrostatic forces are nullified by such a charge transfer, the energy that is released may be used in stimulating the diffusion of the halogen molecule through the lattice. Howard, Vosko, and Smoluchowski[21] suggest that a de-excitation collision between the positive halide ion and a neighboring negative halide ion may produce a series of focused collisions. An interstitial atom would thus be formed several lattice spaces away from the vacancy.

Although these mechanisms exhibit many differences, all of them lead to the formation of a negative ion vacancy and a positive interstitial ion separated by some number of lattice spaces. The trapping of an electron by each of these defects would give the F and H centers. None of these mechanisms would appear to generate V_K and α centers directly.

Lüty[24] has suggested that an α center will not trap an electron to form an F center if a negative interstitial halide ion is within six lattice sites of the vacancy. This suggestion is supported by studies of the field ionization of *excited* F centers. The electric field of the interstitial ion is sufficient to ionize an electron that might be trapped by the vacancy before the center can relax into its ground state to form a stable F center. This influence of the electric field requires that the radiative lifetime of an excited F center be long.[25,26] The formation of the vacancy and interstitial negative halide ion might proceed by any of the above mechanisms if the interstitial positive ion traps both of the electrons which were freed by the double ionization of the halide ion.

The generation of V_K centers which are close to F centers can occur by a mechanism proposed by Williams as a modification of the mechanism of Klick. Two halogen atoms are formed as nearest neighbors by the irradiation. As a result of an ion-induced dipole force, each atom will tend to move toward a neighboring halide ion. Changes in the Coulomb energy result from the formation of a negative halogen molecule. This energy appears as a kinetic energy which is believed to impart sufficient momentum to the halogen molecule to lead to a series of "billiard ball" collisions of the ion cores. This process leads to a separation of the negative halogen molecule, and the vacancy, with the negative halogen molecule occupying a single halide ion site removed from the halide vacancy. The second ionized atom moves away from the vacancy by hole motion. An α, H, and V_K center are thereby generated.

The color centers that are found depend upon which

---

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

[19] J. H. O. Varley, Nature **174**, 886 (1954); J. Nucl. Energy **1**, 30 (1954).

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

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

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

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

[24] F. Lüty, in *Hableiter Probleme* (Vieweg and Sohms, Braunschweig, 1961), Vol. VI, p. 238.

[25] R. Swank and F. C. Brown, Phys. Rev. Letters **8**, 10 (1962); Phys. Rev. **130**, 34 (1963).

[26] R. N. Euwema and R. Smoluchowski, Phys. Rev. **133**, A1724 (1964).

of these centers capture the two electrons released by the ionization. These two electrons may be distributed among the three defects in three ways, if it is assumed that any defect can accept at most one electron. These combinations are (a) F and H with the V_K being annihilated, (b) α and interstitial halide ion with the V_K being annihilated, and (c) F, V_K, and interstitial halide ion. It is suggested that the distribution of these *groups* of defects is random, but that the separation of the α, H, and V_K centers which are formed by one event determines whether group (a), (b), or (c) will result from the trapping of the electrons. The separation of the defects would seem to be about as follows: (a) The F and H centers are separated by more than six lattice spaces, but are sufficiently close to permit the optical bleaching. Following bleaching, the F and H centers become an α center and interstitial ion, respectively. If they were closer than six lattice spaces, the α center could not trap an electron to reform the F center. The H centers are also re-formed in the same concentration as prior to bleaching, but without making additional interstitials. (b) The α and interstitial halide ion are closer than six lattice spacings. Thus, the electron is prevented from being trapped by the α center. Optical bleaching with F light does not influence these defects. (c) The F and V_K centers are sufficiently close to allow optical bleaching of the two centers when the F center is excited. The interstitial ion is presumably greater than six lattice sites away from the α center. Optical bleaching destroys the V_K center, forms an α center, and leaves the interstitial ion unaffected. X irradiation after bleaching allows an electron to be trapped at the α center with the hole being trapped to form a V_K center. Since it is known that the hole has a very small mobility at these temperatures,[16] the hole cannot move far from where it is formed. A hole trapped far from any defect, thus forming a V_K center isolated in the lattice, would likely be annihilated by electron capture. A stable V_K center could be formed in a region in which there was a stable electron trap—namely, an F center. The x irradiation following the bleaching generates many electron-hole pairs; however, only those formed near an α center form an F and V_K center. Thus, the F and V_K centers are re-formed close together.

All of the trapped electrons and holes can be accounted for by assuming that only F, H, α, V_K, and interstitial halide ions are formed by the irradiation, if it is assumed that an interstitial ion *or* atom must be formed in order to produce each F and each α center.

It must be emphasized that an F center need not be formed in order to form a V_K center. The role of impurities in the formation of V_K centers for x irradiation at 77°K is well known.[16] These impurities—Tl^+, Ag^+, and Pb^{++}—act as effective electron traps which allow the hole to be trapped to form a V_K center. It is also known that such impurities enhance the formation of V_K centers for irradiation near helium temperature.[7] According to the arguments presented above, the bleaching with F light should remove *only* those V_K centers near to F centers and leave unaffected the other V_K centers formed near impurities. Since the concentration of F centers is insensitive to the Pb^{++} for irradiation at 7°K, it follows that the bleaching of a given concentration of F centers would bleach the same concentration of V_K centers as in a pure crystal. Comparison of Fig. 10 for the bleaching of a $KCl+PbCl_2$ (0.01 $M\%$ in melt) with that of Fig. 9 for zone purified KCl, indicates that the fraction of H centers bleached by the F light was even greater than in the zone purified crystal. Since this particular curve was taken for longer x irradiation than was used for Fig. 9, this is not particularly surprising.

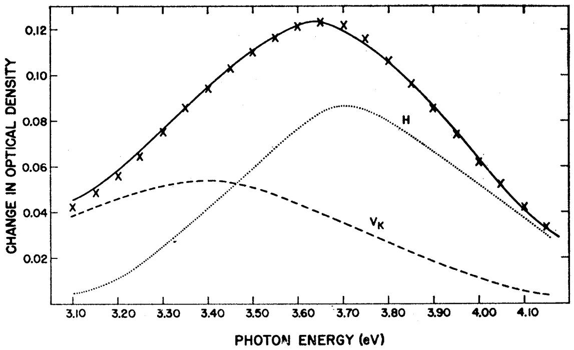

FIG. 10. Bleached spectrum in the region of the composite H band resulting from F-light irradiation at 7°K of KCl doped with 0.01 $M\%$ $PbCl_2$ (in the melt). Curves labeled V_K and H correspond to the best graphical separation of the upper curve into its composite V_K and H. The graphical sum of the two lower curves is shown by the points on the upper curve.

It is of interest to note that x irradiation of a silver-doped crystal of KBr at helium temperature did not generate F centers for a short irradiation time. Large absorption was found in the ultraviolet region. The F centers appeared for a longer irradiation time in essentially the same concentration as would have been produced in a pure crystal. This suggests that the defects are generated by the x rays, but that the silver ions act as such good electron traps that the α center cannot trap an electron until the silver traps have been exhausted. Unfortunately, it is not possible to conclusively test this suggestion by observing the magnitude of the α band. The presence of large absorption bands arising from the silver in the same spectral region makes such a measurement uncertain. It is clear, however, that a significant α band is produced during this initial irradiation.

It should be noted that the electron-spin resonance[14] indicates that the F, V_K, and H are not sufficiently close to alter the resonance spectra of these centers. It is unclear what separation is necessary to ensure this absence of interaction. The present results suggest that six lattice distances are sufficient.

The mechanism of the optical bleaching of the V_K

and H centers by excited F centers is not well understood. Although a tunneling of the excited electron may occur, it is possible that the process is simply one in which the spatial extent of the excited electron wavefunction is sufficiently great that significant overlap occurs with the trapped hole. Recent calculations by Fowler[27] indicate that the extent of the wavefunction of the excited state is significantly greater than previously thought.

SUMMARY

(1) Zone purification of KBr and KCl in a halogen atmosphere is an effective technique for removing OH^- impurity and positive divalent ion impurities.

(2) The initial stage of easy coloration at room temperature appears to be insensitive to those impurities that can be removed from KCl and KBr by zone purification and halogenation.

(3) The large α-center concentration and the formation of V_K centers by x irradiation at helium temperature is essentially the same in zone purified and commercial crystals, indicating that impurities removed by this treatment are not responsible for these defects.

(4) X irradiation at helium temperatures generates F, H, α, V_K. It is suggested that interstitial halide ions are also generated. Studies of the optical bleaching with F-band light followed by short x irradiations indicate that the following groupings of centers occur:

(a) F and H centers. These centers are separated by more than about six lattice spaces, but are sufficiently close to permit optical bleaching of both centers.

(b) α and interstitial halide ions. These centers are located within about six lattice spaces.

(c) F, V_K, and interstitial halide ion. The F and V_K centers are sufficiently close to allow optical bleaching of the two centers. The interstitial halide ion is presumably located at a distance greater than six lattice sites from the F center.

(5) The mechanism of optical bleaching of F and V_K or H centers with F-band light without the production of free electrons is not well understood.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the keen interest of Professor Robert J. Maurer and the assistance of Dr. E. A. Davis in this work.

---

[27] W. B. Fowler, Phys. Rev. **135**, A1725 (1964).

PHYSICAL REVIEW VOLUME 137, NUMBER 1A 4 JANUARY 1965

Effects of Diffusion on Double Injection in Insulators

R. Baron
Hughes Research Laboratories, Malibu, California

(Received 20 July 1964)

The theoretical treatment of double injection in insulators has been extended to include both diffusion and field terms. The effect of diffusion is shown to influence strongly both the form and the magnitude of the current-voltage characteristics, even for the case where the sample length L is much greater than the ambipolar diffusion length L_a. The effects of diffusion showed themselves primarily in the shape of the density distribution $n(x)$ and in the necessity of assuming more realistic boundary conditions. A family of numerical and approximate solutions have been found for the reduced carrier and potential distributions which depend on only one parameter, the minimum reduced carrier density η_0. For $\eta_0<1$, the carrier distributions are characterized by an exponentially decreasing region from the boundaries in which $n\propto e^{|x/L_a|}$, merging into a more slowly varying, Lampert-like distribution. For this case $\eta_0^{-3/2}$ is approximately proportional to the length of the Lampert-like region measured in units of L_a. For $\eta_0>1$, the carrier distributions approach rapidly that found for the pure diffusion case, $n\propto\cosh x/L_a$. The appropriate boundary conditions are given by $n\propto JL_a$, which allows the current-voltage characteristics to be determined with L/L_a appearing as a parameter. It was found that J rises at least as fast as V^m, where $m=3/(1-10L_a/3L)$, compared with $J\propto V^3$ predicted by Lampert. It was also found that J was increased by an approximate factor of $(L/L_{\mathrm{eff}})^5$, where $L_{\mathrm{eff}}=L-Q\times(2L_a)$ and Q is a slowly varying function of J with values normally between 1.7 and 3.8. Even in the extreme case of $L/L_a=100$, the magnitude of J is increased by a factor of ≈ 1.25 and J is rising at least as fast as $V^{3.1}$. Experimental results described in the second paper of this series confirm most of the conclusions of this work.

1. INTRODUCTION

In this paper, the theoretical treatment of double injection in insulators has been extended to include the effects of both electric field and carrier diffusion. Previous theoretical work on double injection in both insulators and semiconductors[1–10] has been confined to the consideration of the more restricted limiting cases where the effects either of field or of diffusion have been

---

[1] R. N. Hall, Proc. IRE **40**, 1512 (1952).

[2] A. Herlet and E. Spenke, Z. Angew. Phys. **7**, 99, 149 (1955); A. Herlet, Z. Physik **141**, 335 (1955).

[3] D. A. Kleinman, Bell System Tech. J. **35**, 685 (1956).

[4] V. I. Stafeev, Fiz. Tverd. Tela **1**, 841, 848 (1959) [English transl.: Soviet Phys.—Solid State **1**, 763, 769 (1959)].

[5] R. H. Parmenter and W. Ruppel, J. Appl. Phys. **30**, 1548 (1959).

[6] M. A. Lampert, RCA Rev. **20**, 682 (1959).

[7] M. A. Lampert and A. Rose, Phys. Rev. **121**, 26 (1961).

[8] M. A. Lampert, Phys. Rev. **125**, 126 (1962).

[9] M. A. Lampert, Proc. IRE **50**, 1781 (1962).

[10] K. L. Ashley and A. G. Milnes, J. Appl. Phys. **35**, 369 (1964).