

Vacancy-Production Efficiencies in KBr at Low Temperatures

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The growth of the prominent absorption bands (α , F , H , 2300 Å) produced by low-energy x-ray and 2.0-MeV electron irradiation has been studied in KBr at temperatures between 5 and 9°K. The growth curves are not, in general, linear when plotted as a function of absorbed dose. The total vacancy production (F plus α centers) is a smooth but nonlinear function of absorbed dose. The α/F ratio is not constant as the irradiation progresses. The ratio is initially 4:1 and reaches a maximum 9:1 at an F -center concentration of 5×10^{16} (F centers)/cm³. Continued irradiation causes the α/F ratio to drop to about 4:1 at 3×10^{17} (F centers)/cm³. This variation in the α/F ratio is the same for all types or "qualities" of radiation when plotted as a function of the F -center concentration. The intensity dependence of vacancy production was investigated by varying the beam current by a factor of 120 for the 2.0-MeV electron irradiations. More energy is required to produce a vacancy at higher intensities, but the α/F ratio is unaffected. The variation of total vacancy production efficiency in KBr with radiation "quality" reported here parallels the F -center efficiencies reported earlier. One is led to the same conclusion reached previously, i.e., the low-temperature coloration process is dominated by mechanisms of the sort proposed by Klick and by Williams which involve the single ionization of two adjacent halide ions.

I. INTRODUCTION

THE simultaneous production of halide-ion vacancies and interstitials in alkali halide crystals exposed to ionizing radiation was first suggested by Varley.¹ Experiments on the high-energy electron irradiation of alkali halides at room temperature led him to the conclusion that a direct-displacement-collision model based on Rutherford scattering was insufficient to account for the permanent F -center coloration produced. He proposed an indirect mechanism in which a halide ion is multiply ionized in a single electron impact to form a positive ion. The strong repulsion caused by the six nearest-neighbor alkali ions then ejects the positive halogen ion to an interstitial site, leaving a halide-ion vacancy which can trap an electron to become an F center. The work of Känzig and Woodruff,² which identified the H center as the equivalent of an interstitial halogen atom, suggested that the Varley mechanism might be operative in the production of color centers by low-energy x rays at liquid-helium temperature. Evidence for the simultaneous formation of Frenkel defect pairs as F and H centers was provided by Rabin and Klick,³ who showed that there is a correlation between the ease of F -center formation and the space available in the lattice for the displacement of a halide ion. The accumulated evidence suggests^{4,5} that one can view the low-temperature coloration process as arising solely from the creation of Frenkel defects and self-trapped holes in the perfect lattice.

Several objections have been raised to the Varley mechanism,⁶⁻⁸ and various authors have proposed alternative mechanisms of Frenkel-defect formation in the alkali halides.⁸⁻¹⁷ In general, these mechanisms involve the transfer of energy to the electronic system of the halogen ion, which is then displaced to an interstitial position as a result of its altered electronic environment. It was pointed out in a previous paper¹⁸ (hereafter referred to as Paper I) that all of the mechanisms may be divided into three groups, characterized by (A) the single ionization of one isolated halide ion, (B) the multiple ionization of one isolated halide ion, or (C) the single ionization of two adjacent halide ions. The reader is referred to paper I for a summary of the details of these mechanisms. Group A includes mechanisms proposed by McLennan¹⁰ and Williams¹³; group B includes the mechanisms of Varley,^{1,15} Platzman,¹¹ Howard *et al.*,¹² Balarin,¹⁶ and Starodubtsev *et al.*¹⁷; group C includes the mechanisms of Klick⁹ and Williams.¹³

The yields of these mechanisms would be expected to vary in different ways as the energy spectrum of the free electrons generated in the material by irradiation

⁶ D. L. Dexter, *Phys. Rev.* **118**, 934 (1960).

⁷ F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1946), Vol. 2, p. 447.

⁸ R. E. Howard and R. Smoluchowski, *Phys. Rev.* **116**, 314 (1959).

⁹ C. C. Klick, *Phys. Rev.* **120**, 760 (1960).

¹⁰ D. E. McLennan, *Can. J. Phys.* **29**, 122 (1951).

¹¹ R. L. Platzman, in *Symposium on Radiobiology*, edited by J. J. Nickson (John Wiley & Sons, Inc., New York, 1952), Chap. 7.

¹² R. E. Howard, S. Vosko, and R. Smoluchowski, *Phys. Rev.* **122**, 1406 (1961).

¹³ F. E. Williams, *Phys. Rev.* **126**, 70 (1962).

¹⁴ F. Seitz, *Phys. Rev. Letters* **7**, 282 (1961).

¹⁵ J. H. O. Varley, *J. Phys. Chem. Solids* **23**, 985 (1962).

¹⁶ M. Balarin, *Kernenergie* **7**, 434 (1964).

¹⁷ S. V. Starodubtsev and A. E. Kiv, *Dokl. Akad. Nauk SSSR* **151**, 550 (1963) [English trans.: *Soviet Phys.—Doklady* **8**, 701 (1964)].

¹⁸ V. H. Ritz, *Phys. Rev.* **133**, A1452 (1964).

¹ J. H. O. Varley, *Nature* **174**, 886 (1954); *J. Nucl. Energy* **1**, 130 (1954).

² W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

³ H. Rabin and C. C. Klick, *Phys. Rev.* **117**, 1005 (1960).

⁴ C. C. Klick and D. A. Patterson, *Phys. Rev.* **130**, 2169 (1963).

⁵ T. M. Srinivasan and W. D. Compton, *Phys. Rev.* **137**, A264 (1965).

is varied. In Paper I the efficiencies for F -center production [$eV/(F \text{ center})$] were measured at liquid-helium temperature for KBr, KCl, LiF, and NaCl irradiated with 2.0-MeV electrons from a Van de Graaff generator and with low-energy x rays from a tungsten-target beryllium-window x-ray tube. It was found that the F -center production efficiency is a strong function of the energy distribution of the free electrons generated by irradiation, i.e., a strong function of radiation "quality." Various quantitative and qualitative arguments indicate that inner-shell ionization does not adequately account for either the magnitude of the observed F -center production or the direction of its energy dependence. A correlation can be made between the coloration efficiency and the ionization density along the tracks of the free electrons generated by irradiation. The mechanisms of group C involving the single ionization of two adjacent halide ions appear to be the only group in which the spatial distribution of the ionized halide ions would influence the coloration efficiency. Thus, the F -center production efficiencies measured in paper I strongly suggest that mechanisms of the sort proposed by Klick⁹ and by Williams¹³ are dominant in the low-temperature coloration process.

Since more vacancies are created in the form of alpha centers^{19,4} than in the form of F centers at low temperature, the above conclusion rests on the assumption that the F -center production is related in some consistent way to the total vacancy production (F plus alpha centers) in the crystal. This paper will describe an extension of Paper I in which the alpha, F , and total vacancy production efficiencies have been measured in KBr at temperatures between 5 and 9°K.

II. EXPERIMENTAL TECHNIQUES

A. General

Single crystals of KBr obtained from the Harshaw Chemical Company were cleaved along their principal planes with a razor blade. The crystal thicknesses for particular x-ray or electron irradiations were the same as those used in Paper I. The energy absorbed by the crystals during irradiation was measured with the glass block dosimeters described elsewhere.^{18,20}

Optical absorption measurements of the alpha band at high optical densities were complicated by the normal scattered light in the spectrophotometer, a Cary Model 14 MR. This was evident from the marked saturation of the alpha band when the optical density of the Dewar and crystal exceeded 3 relative to a stop in the reference beam. This effect was investigated in some detail by comparing the shape of the alpha band as it grew under several successive irradiations. The optical density of the band was tabulated after subtraction of the baseline due to the Dewar and unirradiated crystal.

The net optical density resulting from the first irradiation was divided into the net optical density measured in subsequent irradiations. This ratio was taken at 10-Å intervals between 2300 and 1900 Å. When the peak height was small (o.d. <1), one obtained a constant ratio in this region. As the band grew larger the ratio began to drop at the peak of the alpha band at 2020 Å and at wavelengths below about 1950 Å. At the same time the optical density of the shoulder of the gamma band approached that of the peak of the alpha band. This indicated that some extraneous light was perturbing the measurements at high optical densities, so that the peak height was no longer an accurate measure of the band strength. A common technique used in such a situation is to make an extrapolation from the tail of the absorption band. This makes the important assumption that no smaller bands exist under the main band which grow at a different rate. The ratios tabulated as described above showed no evidence for such an effect between the peak of the alpha band and 2300 Å. This result is consistent with the work of Kurz and Gebhardt,²¹ in which a linear relation was found between the alpha band and the smaller 2300-Å band attributed to the interstitial ion. The alpha-band optical densities to be reported in the present paper were accordingly extrapolated from the optical density in the 2020–2300-Å region whenever the peak optical density exceeded 1.0.

B. X Irradiations

Measurements were made in a temperature-variable Dewar similar to the one described by Swenson and Stahl.²² The sample holder was thermally isolated from the helium reservoir. Heat was removed from the sample holder by a heat exchanger which consisted of a tube wound around the sample holder. Liquid helium was drawn through the tube from the helium reservoir, vaporized and expanded at the sample holder, and was removed through tubing to a vacuum pump. The refrigeration rate was controlled by a needle valve between the Dewar and vacuum pump. A small electric heater was imbedded in the sample holder to provide additional temperature variation at a constant refrigeration rate by varying the heat influx to the sample holder. The sample could be held at a constant temperature by balancing the refrigeration rate against the heat influx from the heater. This Dewar was capable of continuous variations of sample temperature from 5 to 300°K, in either direction. The temperature could be maintained to $\pm 0.2^\circ\text{K}$ at any temperature between these limits.

Temperatures between 5 and 100°K were measured with a germanium resistance thermometer waxed into a hole in the base of the sample holder with vacuum grease. The thermometer was calibrated to $\pm 0.1^\circ\text{K}$

¹⁹ H. Ruchardt, Phys. Rev. **103**, 873 (1956); Z. Physik **140**, 547 (1955).

²⁰ V. H. Ritz and C. H. Cheek, Radiation Res. **25**, 537 (1965).

²¹ G. Kurz and W. Gebhardt, Phys. Status Solidi **7**, 351 (1964).

²² C. A. Swenson and R. H. Stahl, Rev. Sci. Instr. **25**, 608 (1954).

by the manufacturer.²³ A constant current supply was employed with the resistance thermometer so that the temperature could be monitored continuously on a potentiometric strip chart recorder. Small-diameter manganin lead wire was used to minimize the heat influx to the sample holder. It was found that ordinary copper-constantan thermocouples installed in the Dewar for routine temperature measurements in the 100–300°K range raised the temperature of the sample holder at low temperatures. The use of very fine copper-constantan thermocouple wire (0.002 in. diam) eliminated this problem.²⁴

The copper-constantan thermocouple installed in the Dewar was used in an attempt to determine the temperature difference, if any, between alkali halide crystals and the copper cold finger on which they were mounted with vacuum grease. The thermocouple was calibrated against the germanium thermometer in the 6–100°K range by placing its junction next to the resistance thermometer in the hole in the base of the sample holder. The tip of the thermocouple was then moved around to measure the equilibrium temperature of the alkali halide crystal as a function of the temperature of the copper sample holder measured with the resistance thermometer. The measurements indicated that the dominant heat leak was the room temperature infrared radiation impinging on the sample through the holes for the x-ray and spectrophotometer beams in the thermal shields. A thermocouple placed on a KBr crystal registered 20°K when the block was at 6°K under the condition that the holes in the thermal shields were unobstructed.²⁵ When the holes were closed by covering them with greased aluminum foil, the thermocouple indicated 6°K, i.e., the same temperature as the block. This experiment does not measure the actual crystal temperature, however, since the thermocouple absorbs all of the room-temperature infrared radiation while the alkali halide crystal is transparent to that radiation. Thus, the thermocouple may be much warmer than the crystal. A run in which physical contact between the thermocouple and crystal was broken indicated that the room-temperature radiation raised the thermocouple temperature to 30°K. Thus it would appear that the crystal actually cooled the thermocouple in the measurement described previously. It was concluded that the alkali halide crystals were probably not warmed by room-temperature radiation in view of their transparency in that region and the good conductivity of the vacuum grease used to mount them on the sample holder. It should be noted, however, that samples which are opaque in the infrared may be 10–20°K warmer than the temperature of the copper sample holder at liquid-helium temperature.

The above measurements indicated that precau-

tionary measures might be taken to prevent room-temperature infrared radiation from impinging on the sample. The holes in the thermal shields used for x irradiation were closed with 0.001-in. beryllium foils which were in good thermal contact with the shields. The holes used for the spectrophotometer beam were closed with 0.030-in.-thick fused silica (Corning No. 7940) windows. With this arrangement the transmission was less than 0.1% from 4 to 40 μ , so almost all of the room-temperature infrared radiation was excluded.

It was difficult to move the Dewar from the x-ray machine to the spectrophotometer without sudden excursions in temperature, and therefore an arrangement was devised which allowed the Dewar to be x rayed in the sample compartment of the spectrophotometer. A hole was drilled in the sample compartment to accommodate the x-ray tube so that the x-ray beam was perpendicular to the spectrophotometer light beam. The sample holder was oriented at 45° to both the light and x-ray beams so that it could be x rayed and scanned in the spectrophotometer without movement of the Dewar. A lead box inserted in the sample compartment reduced the external x-ray field to a negligible level. The box was provided with two lead shutters which were closed during x irradiations to protect the spectrophotometer optics. An external shutter placed between the x-ray tube and the Dewar made it possible to obtain short irradiations (0.1 min) with an accuracy of better than 1%.²⁶

The dependence of the coloration efficiency upon the intensity of the radiation field (eV/cm² sec) was investigated in Paper I by reducing the emission current of the x-ray tube. A practical limitation on this procedure is the accuracy with which the x-ray emission current meter can be read. An alternative procedure is to monitor the x-ray emission with an ionization chamber using an accurate current-measuring system. An air-filled transmission monitor chamber²⁷ was designed for low-energy x-ray beams which was similar in general configuration to the Van de Graaff monitor chamber described in Paper I. It consisted of three parallel beryllium electrodes in the form of discs (0.071 cm thick) with an electrode separation of 0.01 cm. The very narrow air gap between the collector and high-voltage plates insured almost complete collection (>99%) of the ions produced in the chamber even in radiation fields as high as 5×10^9 R/h. The radiation field in the present experiment was orders of magnitude smaller, so that any error from inadequate ion collection was negligible. Complete ion collection is important because the current from a poorly designed chamber may drop to a fraction of its true value at high radiation intensities. The current from the monitor chamber was measured by means of a vibrating-reed electrometer employed in a Townsend null circuit. The voltage

²³ Minneapolis-Honeywell Inc., Philadelphia, Pennsylvania.

²⁴ Omega Engineering Inc., Springdale, Connecticut.

²⁵ A similar measurement at liquid-nitrogen temperature indicated that the crystal was 4 deg warmer than the block.

²⁶ V. H. Ritz, *Rev. Sci. Instr.* **36**, 862 (1965).

²⁷ V. H. Ritz (to be published).

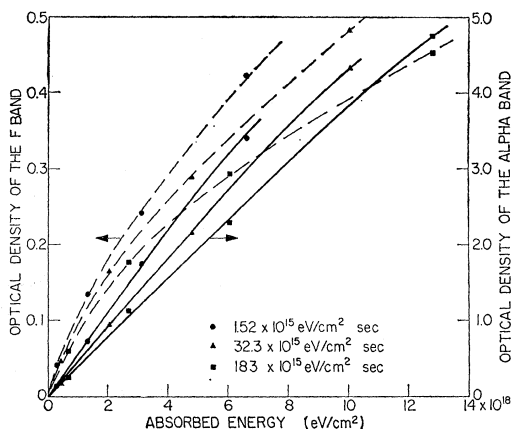


FIG. 1. Growth of the F and alpha bands in KBr for various incident radiation intensities ($\text{eV}/\text{cm}^2 \text{ sec}$). The crystals were irradiated with 1.9-MeV electrons at 5°K . Arrows point to the relevant ordinates.

produced on a calibrated resistor was measured to $\pm 0.1\%$ by a precision voltage divider and potentiometer. The maximum x-ray output available was 40 mA at 50 kV. It was found possible to run the tube at as little as 0.1 mA, thus permitting variations of intensity by a factor of 400. The ratio of these intensities could be determined with an accuracy of about 1%. At low voltages, the reduced output of the tube and the consequent slow crystal coloration severely limited the practical intensity variation that could be made.

C. Van de Graaff Irradiations

The vertical electron beam from the Naval Research Laboratory 2.0-MeV Van de Graaff accelerator was deflected into a horizontal direction by a magnetic beam bender and directed to a conventional fixed-temperature Dewar with a 0.005-in.-thick aluminum

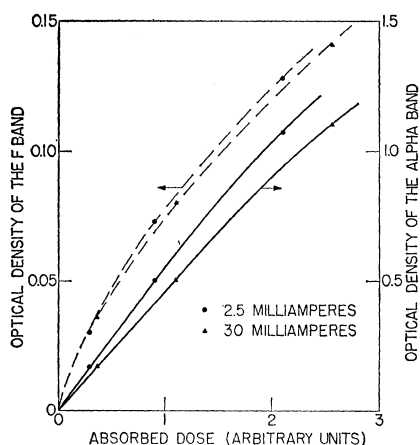


FIG. 2. Growth of the F and alpha bands for two different x-ray tube emission currents. The crystals were irradiated with 15-kV unfiltered x rays at 5°K .

window. The Dewar was moved to the spectrophotometer during periodic interruptions in the irradiation. The sample holder was perpendicular to both the x-ray and spectrophotometer beams. The outer shell of the Dewar was rotated to place the aluminum window or fused silica windows in position. The precautions taken in the variable-temperature Dewar to exclude room-temperature infrared radiation were not introduced into this particular arrangement. The electron beam was monitored during the irradiations with the ionization chamber and integrating system described in Paper I.

The addition of a beam-stabilizing pentode circuit in the high-voltage terminal of the Van de Graaff accelerator made it possible to use beam currents that were an order of magnitude smaller than those used previously. The lowest current used in the present experiment corresponded to $7 \times 10^{-10} \text{ A}/\text{cm}^2$ with a stability of $\pm 10\%$. It was possible to raise the current by a factor of 100 for an intensity-dependence study without undue heating of the sample during irradiation.

III. EXPERIMENTAL RESULTS

A. Intensity, Temperature, and Orientation Dependence

The dependence of the coloration efficiency upon the intensity of the radiation field ($\text{eV}/\text{cm}^2 \text{ sec}$) was investigated over a wide range of dose rates with 1.90-MeV electrons. Thin KBr crystals (0.015 in. thick) were irradiated in the fixed-temperature Dewar at 5°K . The growth of the F and alpha bands is shown in Fig. 1. Both the F - and alpha-production rates are depressed slightly as one goes to higher intensities. A similar trend is shown in Fig. 2 for crystals irradiated at 5°K with 15 kV unfiltered x rays. The dose rate was held constant to $\pm 0.5\%$ in the latter experiment. Figure 1 indicates that an increase of the dose rate by a factor of 120 decreases the coloration rate to about 0.7 of its original value. The small magnitude of this

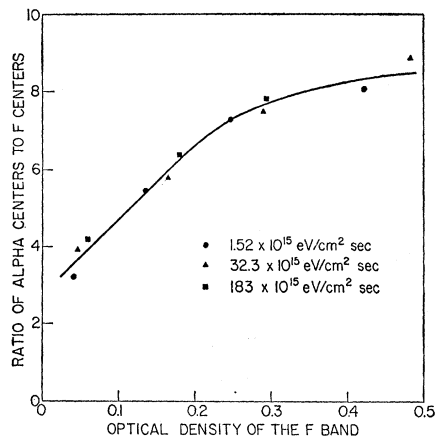


FIG. 3. Electron-irradiation data of Fig. 1 replotted to show variation of α/F peak optical-density ratio with F optical density.

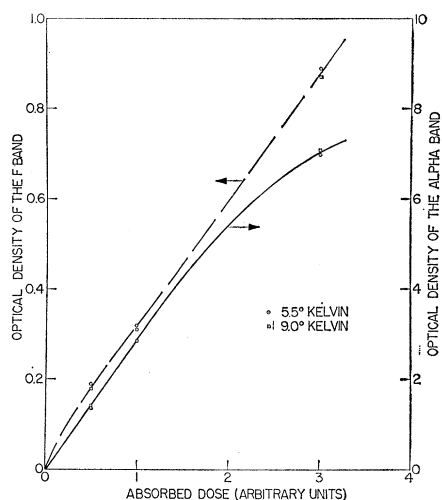


Fig. 4. Growth of the F and alpha bands at 5.5 and 9.0°K under 15-kV unfiltered x irradiation.

effect accounts for the fact that it was not detected in Paper I, in which the intensity was varied by only a factor of 5.

It is of interest to see if the F - and alpha-production rates change in the same way as a function of intensity. The electron irradiation data of Fig. 1 is replotted in Fig. 3 to show the variation in the α/F peak optical-density ratio as a function of the optical density of the F band for the different radiation intensities. One sees that the α/F ratio changes as the irradiation progresses, but that it is independent of the incident-radiation intensity.

One would expect from previous experiments^{19,28} that the coloration efficiency would be independent of temperature below the first major annealing step of the alpha band at 11°K. The data of Fig. 4 at 5.5 and 9.0°K confirm this expectation. Figures 3 and 4 also indicate that the samples were not heated above 11°K during the Van de Graaff irradiations. If they had been warmed during irradiation, one would expect the data for the higher dose rates to fall on different curves in Fig. 3.

A number of recent experiments involving heavy-particle bombardment of materials other than the alkali halides have demonstrated that the range of the incident particles is strongly affected by the crystallographic orientation of the sample.²⁹ In addition, many atomic displacement processes are known to depend upon the crystallographic direction in which the atom begins to move.³⁰ The possibility that the coloration efficiency was dependent upon the relative orientation

²⁸ N. Itoh, B. S. H. Royce, and R. Smoluchowski, *Phys. Rev.* **137**, A1010 (1965).

²⁹ D. K. Holmes, in *The Interaction of Radiation with Solids*, edited by R. Strumane *et al.* (John Wiley & Sons, Inc., New York, 1964), p. 33 ff.

³⁰ M. W. Thompson, in *The Interaction of Radiation with Solids*, edited by R. Strumane *et al.* (John Wiley & Sons, Inc., New York, 1964), p. 84 ff.

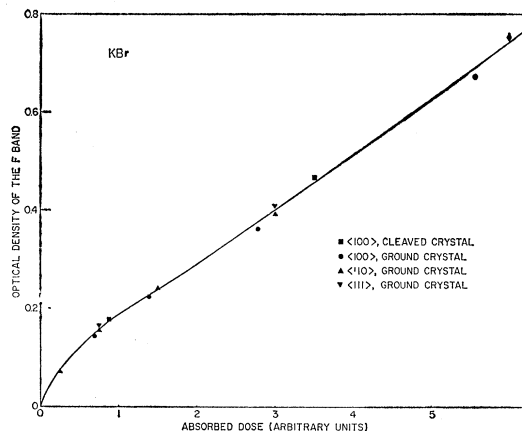


Fig. 5. Growth of the F band in KBr irradiated along various crystallographic axes at 5°K with 1.9-MeV electrons.

of the electron beam and sample has been investigated³¹ in this laboratory briefly, although none of the currently held theories of Frenkel defect formation in the alkali halides would seem to predict such behavior. Crystals were cut parallel to the (100), (110), and (111) planes with a string saw, ground to a thickness of 0.010 in., and irradiated at 5°K with 1.9-MeV electrons. A crystal was also cleaved to the same thickness along the normal (100) cleavage plane. The growth of the F band is plotted in Fig. 5 and is seen to be the same to within $\pm 4\%$ for all of the samples. Some difficulty was encountered in measuring the alpha-band height in the ground crystals because their surfaces were not of good optical quality. An erratic depression of alpha-band growth was observed in all of the ground crystals relative to the cleaved crystal. This was attributed to the larger errors inherent in the extrapolation technique when used with crystals which had a high initial optical density because of the grinding process. The maximum

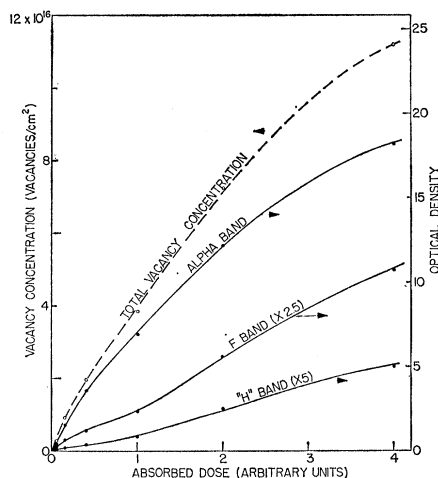


Fig. 6. Growth of the prominent absorption bands produced in KBr at 5°K after 600-keV electron irradiation.

³¹ H. Rabin and V. H. Ritz (unpublished data).

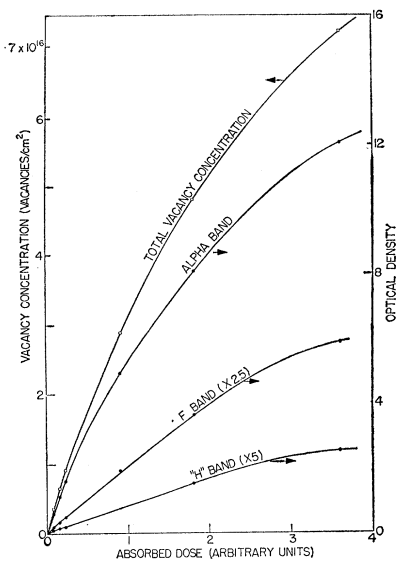


Fig. 7. Growth of the prominent absorption bands produced in KBr at 5°K after 15-kV unfiltered x irradiation.

difference in alpha-band growth between the cleaved and ground crystals was, however, less than 20%. This result indicates that the coloration is not dependent upon crystallographic orientation under the conditions of most electron irradiations. It does not preclude the possibility of such an effect in very thin crystals irradiated with a well-collimated electron beam or in crystals irradiated with heavy particles.

B. Growth Curves

The variation in the α/F ratio shown in Fig. 3 suggested that it might be valuable to investigate the growth curves out to very high color-center concentrations. Growth curves were obtained for all of the radiation qualities used in Paper I as well as for a few additional qualities. Figure 6 is typical of high-energy electron irradiations which produced a uniform coloration. Figure 7 illustrates a low-energy x irradiation in which the crystal was nonuniformly colored. The growth curves are, in general, not linear when plotted as a function of absorbed dose. The alpha band begins to grow linearly and then continues to grow at a gradually decreasing rate. The F band grows fairly rapidly at first, slows down, and then rises at an increased rate before decreasing again at very high concentrations. Note that the inflection points evident in Fig. 6 are masked in Fig. 7 when the crystal is nonuniformly colored. The composite " H " band at 3800 Å, which consists of H - and V_K -center absorption, generally follows the same behavior as the F band, although the F / H ratio seems to decrease somewhat as the irradiation progresses. The band at 2300 Å, which has been attributed to the interstitial ion,^{21,28} is not plotted, but it is directly proportional to the alpha band at all points on the growth curve. Finally, the total vacancy

concentration (F plus alpha centers) is a smooth but nonlinear function of absorbed dose.

C. Variation of the α/F Ratio

The α/F concentration ratio is plotted as a function of the optical density of the F band in Fig. 8 for a variety of radiations. The concentration ratios were obtained from the optical density ratios using Onaka and Fujita's oscillator-strength ratio of 1.31³² and a half-width ratio of 1.42. The α/F ratio is initially 4:1 and rises in a fairly rapid linear fashion to reach a maximum of 8:1 or 9:1. Continued irradiation causes the α/F ratio to drop more slowly to at least 4:1. All of the different radiation qualities seem to follow the same trend and reach approximately the same maximum and minimum values of the α/F ratio. The 7-kV x-ray data were not taken at low enough optical densities to show the initial rise in the α/F ratio.

It is useful to plot the data of Fig. 8 as a function of the F -center concentration instead of the F -center optical density. In this way one can compare the α/F ratio for the different radiations at points on the growth curves which correspond to the same F -center concentrations in the crystal. Two Van de Graaff runs with thick and thin crystals at different electron energies were made, the crystal thicknesses and electron energies were chosen so that the energy absorbed at the front and back surfaces of the crystals were the same. This insured that the energy deposition distribution in the two crystals was identical, although slightly non-uniform.³³ The average color-center concentrations in the two crystals were then simply derived from the measured crystal thicknesses. The results are plotted in

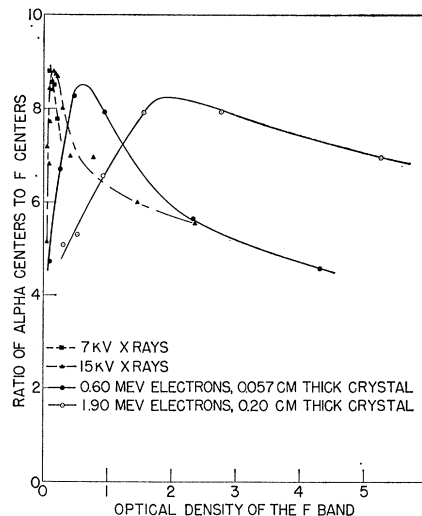


Fig. 8. α/F concentration ratio as a function of the optical density of the F band for various radiation qualities.

³² R. Onaka and J. Fujita, *J. Quant. Spectry. Radiative Transfer* 2, 599 (1962).

³³ C. H. Cheek and V. Linnebon, National Radiation Laboratory Report 5448, 1960 (unpublished).

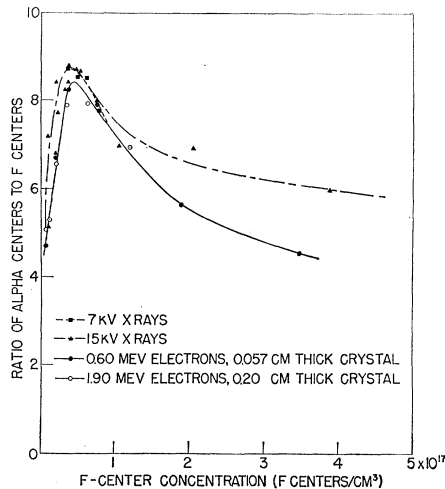


FIG. 9. α/F concentration ratio as a function of F -center concentration. The F -center concentrations were derived from the crystal thicknesses for the electron runs and by the method described in the text for the other radiations.

Fig. 9. The agreement between the two Van de Graaff runs is very good and they have been plotted as a single curve. It should be emphasized that the Van de Graaff data in Fig. 8 have simply been divided by the crystal thicknesses. No other normalization of the data with relation to the vertical or horizontal scales has been performed.

It is rather difficult to calculate meaningful average concentrations for the low-energy x-ray irradiations because of the nonuniform coloration caused by strong x-ray absorption at the front face of the crystal. Thus the 7 and 15 kV x-ray data of Fig. 8 have simply been normalized along the horizontal axis so that they fit best with the Van de Graaff data in Fig. 9. This normalization determined an effective thickness, or coloration depth, which was 0.017 cm for 15-kV x rays. For comparison, an approximate calculation was made of the F -center coloration gradient in KBr irradiated with 15-kV x rays at 5°K. The energy deposition gradient was obtained from a knowledge of the incident x-ray spectrum and the energy transfer coefficients of KBr.¹⁸ The coloration gradient was estimated by modifying the energy deposition gradient for the following: 1, the variation in F -center production efficiency at low x-ray energies; and 2, the shape of the F -center growth curve. This gradient could not be described by a simple exponential function and corresponding $1/e$ depth. The crystal depth which contained 90% of the total coloration in the crystal was found to be 0.015 cm. This close agreement is perhaps fortuitous in view of the uncertainties in the coloration-gradient calculation.

D. Vacancy-Production Efficiencies

The α/F ratio was measured for x rays generated at 10 and 50 kV exciting potentials with inherent filtration (1.5-mm beryllium), and 50 kV with an added 1 mm of

TABLE I. Energies (eV) which a KBr crystal at 5°K must absorb in order to produce one F center or one vacancy (either F or α center), for various radiation qualities.

Radiation	eV/(F center)	eV/vacancy
2-MeV electrons	4700	540
50-kV x rays, 1 mm Al	2740	290
50-kV x rays	1700	190
15-kV x rays	3300	320
10-kV x rays	4600	480

aluminum filtration, as well as for the radiations shown in Fig. 9. The numbers of F centers per unit area were calculated using the Lorentzian form of Smakula's equation as described in Paper I. The numbers of alpha centers per unit area were calculated in a similar fashion, again using Onaka and Fujita's value of the oscillator strength.³² The results are shown in Fig. 10 where the total vacancy production (F plus alpha centers) is plotted as a function of the absorbed energy (eV/cm²) for various radiations. One gets the same general variation for the total vacancy production as was reported in paper I for the F -center production, even out to very high concentrations. KBr is hard to color with 2.0-MeV electrons, becomes easier to color with moderate energy x rays, and then becomes difficult to color at very low energies. The intensity dependence shown in Fig. 1 has only a slight effect on these data, and no correction for it has been made.

One can compare the vacancy production efficiencies of Fig. 10 at points where the α/F ratio is the same. This is most conveniently done at the maximum value of the α/F ratio. Table I lists the F -center production efficiencies reported earlier and the vacancy-production efficiencies determined in the present experiment.

IV. DISCUSSION

A. Vacancy-Production Mechanisms

The parallel trend of the production efficiencies for F centers and for total vacancies, shown in Table I,

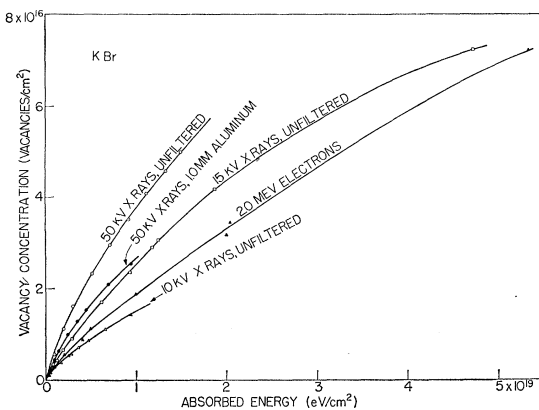


FIG. 10. Vacancy production in KBr at low temperature (5–9°K) as a function of absorbed energy for various radiation qualities.

leads one to the same conclusions that were reached in Paper I. The direction of the energy dependence of the vacancy production efficiency for radiation qualities in the 50-kV x-ray to 2.0-MeV electron region can be explained only by mechanisms of the sort proposed by Klick⁹ and by Williams,¹³ which involve the single ionization of two adjacent halide ions. The vacancy-production efficiency for these mechanisms was calculated in Paper I according to a simple model. The calculation involved two yield functions, n_3 and n_1 , which represented the three-dimensional and one-dimensional probabilities for the formation of a vacancy along the path of a free electron generated by the irradiation. The experimental values would be expected to lie between these two limiting cases. For KBr the calculated values are 650–3500 eV/vacancy for the 2.0-MeV electron region and 270–580 eV/vacancy for the 50-kV x-ray region. The experimental vacancy-production efficiencies of Table I are seen to be in fairly good agreement with these predictions. It was pointed out in Paper I that agreement between this simple model and experiment was not as good in the very low energy x-ray region (10–15 kV). The recombination of centers along the densely ionizing particle tracks at low energies was suggested as a possible reason for the increase in the energy required to make an F center as one went to x-ray energies below 50 kV. The same sort of possibility would seem to apply to the vacancy production efficiency results reported here.

The F coloration in various alkali halides has been studied at liquid nitrogen temperature as a function of energy of very low-energy monochromatic x rays on either side of the K edge.^{34,35} As the edge is crossed discontinuities are observed which may be due either to the formation of F centers from the multiple ionization of one isolated halide ion or to a change in the probability for a Klick-Williams event because of the modified photoelectron spectrum. The unscrambling of these two possibilities at low x-ray energies would appear to be very difficult in the absence of well-known cross sections for the processes involved. These discontinuities at the x-ray absorption edges would seem to have little effect on the 50-kV x-ray to 2.0-MeV electron energy region in which a good comparison can be made between theory and experiment.^{36,37}

The results reported here indicate that mechanisms of the sort suggested by Klick and by Williams are the dominant ones at low temperature. It has been pointed out⁵ that William's mechanism may be the more likely one, because it produces widely separated F and H

centers as well as V_K centers. It should be kept in mind that other mechanisms may be devised in the future which also fit the quality dependence of coloration at low temperature. Indeed, several papers have indicated that quite different processes may be operative at higher temperatures.^{38,39}

B. Track Effects

It was pointed out in Paper I that the coloration efficiency depends upon the probability of ionization along the individual electron tracks rather than on the average probability for the whole bulk of the crystal. Thus, the coloration is not produced uniformly at random sites in the crystal but is concentrated along the electron tracks.⁴⁰ It is interesting to note that room-temperature measurements of the thermal conductivity of irradiated alkali halides have been interpreted in terms of nonuniform F -center formation.⁴¹ Spin resonance has also given a fairly detailed picture which suggests that there are clusters of F centers in irradiated crystals.^{42,43} In addition, recent experiments⁴⁴ have suggested that the relation between F - and M -center formation at low temperature may be quality-dependent, a result consistent with the model of F -center formation discussed in paper I.

C. Variation of the α/F Ratio

Figure 9 shows that, for uniform coloration with electrons, there exists a unique relationship between the α/F ratio and the F -center concentration. Furthermore, there are indications that, if one knew how to specify the proper average concentrations, this same relationship would hold for the nonuniform x-ray coloration. None of the vacancy-production mechanisms discussed here would seem to predict a variation in the α/F ratio. They all concern themselves with an isolated Frenkel pair creation event which would, in the first approximation, be independent of the F -center concentration. It has been suggested by Kabler⁴⁵ that the intense electron-hole recombination luminescence generated during low-temperature irradiation may influence the relation between alpha centers and F

³⁸ T. P. P. Hall, D. Pooley, W. A. Runciman, and P. T. Wedepohl, Proc. Phys. Soc. (London) **84**, 719 (1964).

³⁹ L. S. Goldberg and H. Mahr, Bull. Am. Phys. Soc. **10**, 373 (1965).

⁴⁰ A comprehensive discussion of "track effects" in radiation physics and chemistry is given by R. L. Platzman, in *Radiation Biology and Medicine*, edited by W. D. Claus (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), Chap. 1.

⁴¹ C. T. Walker, Phys. Rev. **132**, 1963 (1963).

⁴² R. Kaplan and P. J. Bray, Phys. Rev. **129**, 1919 (1963).

⁴³ R. W. Warren, D. W. Feldman, and J. G. Castle, Phys. Rev. **135**, A1347 (1964).

⁴⁴ E. Sonder and W. A. Sibley (private communication).

⁴⁵ M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

³⁴ J. Sharma and R. Smoluchowski, Phys. Rev. **137**, A259 (1965).

³⁵ J. Sharma and R. Smoluchowski, Bull. Am. Phys. Soc. **10**, 308 (1965).

³⁶ J. Durup and R. L. Platzman, Discussions Faraday Soc. **31**, 156 (1961).

³⁷ W. J. McConnell, H. H. Hubbell, Jr., R. N. Hamm, R. H. Ritchie, and R. D. Birkhoff, Phys. Rev. **138**, A1377 (1965).

centers. A forthcoming paper⁴⁶ will discuss the variation in α/F ratio shown in Fig. 9 and show that it is possible to account for this variation in terms of the competing processes of F -center bleaching by the luminescence and electron trapping by alpha centers.

V. SUMMARY

The principal results of this investigation may be summarized as follows:

1. The growth curves (α , F , "H," 2300-Å band and total vacancies) are not linear with dose.
2. The vacancy-production efficiency is slightly dose-rate dependent, but the α/F ratio is not.

⁴⁶ V. H. Ritz and M. N. Kabler (to be published).

3. The α/F ratio is not constant as the irradiation progresses, but it varies in the same way for all types or "qualities" of radiation.

4. The quality dependence of vacancy production follows the same trend reported previously for F centers.

5. Mechanisms involving the single ionization of two adjacent halide ions are the most probable cause of low-temperature vacancy production.

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V_K Center in NH_4Br and NH_4Cl Single Crystals

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The EPR spectrum of Br_2^- in NH_4Br single crystals has been observed and fitted with an axial spin Hamiltonian. Optical transitions of the V_K center in NH_4Br and NH_4Cl have been identified and an interpretation of the radiation-induced 380-m μ absorption band, first observed by R \ddot{u} chardt in both ammonium halides, is presented. These measurements show that the V_K center in the ammonium halides is essentially the same as in the alkali halides. A description is given of a procedure for determining the polarization of the two observed Br_2^- optical transitions, and they are both found to be largely σ -polarized. These polarizations can be explained by the generally accepted energy-level scheme.

INTRODUCTION

THE ammonium halides offer the possibility of an interesting extension of the work done on radiation-induced defect centers in the alkali halides. Structural investigations have been performed on single crystals of NH_4Cl , NH_4Br , and NH_4I using the techniques of x-ray diffraction, infrared absorption, and nuclear magnetic resonance.¹ Each of these materials has three structure modifications in different temperature intervals²: a high-temperature phase in which the crystal structure is of the NaCl type, an intermediate-temperature phase within which the crystal structure is of the CsCl type, and a low-temperature phase resulting from an order-disorder transition due to re-orientation of the ammonium ion.³ At liquid-nitrogen temperature the ammonium ions are ordered in each material. The NH_4Cl crystal is of the CsCl structure,

while NH_4Br and NH_4I have a distortion along one axis which makes the space lattice tetragonal.

R \ddot{u} chardt⁴ first observed radiation-induced optical absorption bands in pure and doped single crystals of NH_4Cl and NH_4Br at temperatures below 200°K. He ascribed an intense band occurring at 380 m μ (3.26 eV) in both the chloride and bromide to the NH_4^0 ion, which could result from an electron being stripped from a Cl^- ion and trapped by NH_4^+ . Another small absorption band in the uv was not identified.

Zeller, Vannotti, and K \ddot{a} nzig⁵ have reported observing the electron paramagnetic resonance (EPR) absorption of Cl_2^- (termed the V_K center) in single crystals of NH_4Cl irradiated at liquid-nitrogen temperature. They found that the ground-state wave function for the unpaired electron of the Cl_2^- molecule ion differed little from NH_4Cl to NaCl. The local symmetry is higher in the ammonium halides because the Cl_2^- molecules are oriented along the $\langle 100 \rangle$, as opposed to

¹ References to this work are contained in the two papers by Itoh, R. Kusaka, and Y. Saito, *J. Phys. Soc. Japan* **17**, 463, 481 (1962).

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³ H. A. Levy and S. W. Peterson, *Phys. Rev.* **86**, 766 (1952).

⁴ H. R \ddot{u} chardt, *Z. Physik* **134**, 554 (1953).

⁵ H. R. Zeller, L. Vannotti, and W. K \ddot{a} nzig, *Phys. Kondens. Materie* **2**, 133 (1964).