quite small. Huber observed that pulse spread velocity with 5 percent O_2 was $\sim 9\times 10^7$ cm/sec and at 40 percent O_2 pulses no longer spread, the velocity in air at 20 percent O_2 being 4×10^7 cm/sec. Thus at 5 percent O_2 with $\mu\sim 2.5$ cm^{-1} the velocity of spread was high, while in air at $\mu\sim 10$ cm^{-1} the velocity was lowered to about half. Thus a change in μ by a factor of 4 reduced v by a factor of 2, and at constant θ this means a factor of 2 change in x_0. When μ increased by a factor of 8 and in theory x_0 was reduced by the same amount, pulses ceased to propagate. Since, however, even with V constant, as V_g varies with p_1 relative to V the constancy of the other variables was not sufficient to warrant accurate quantitative comparison. But it is seen that, as observed for counters, decrease in μ increases v.

Actually it is probable that even at 1 percent O_2 there will be pulses which spread down the wire, but these may require higher potentials than at V_g since r_{0g}/θ at threshold may not be adequate or give the v required. When Huber changed the pressure of the active gas by changing the total pressure of air, the *increase* in μ at higher pressures appeared to *increase* v. However, there were accompanying changes in p, changes in V_g, in r_{0g}, and in drift velocities of electrons, so that the reversal of variation with μ is not significant.

In principle, however, the preceding analysis has given an indication, separate from the very intricate threshold relations, as to physical limitations to be expected on the values of v and x_0, making these quantities more physically significant than the ratio of a fictive distance x_0 and a velocity v.

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F Centers in Pure and Hydride-Containing Alkali Halide Crystals

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Additional evidence regarding the role of imperfections in the gamma-ray coloring and optical bleaching of the alkali halides has been obtained by comparing crystals with and without *U* centers. Parameters varied were gamma-ray exposure rate, crystal temperature, hydride concentration, *F*-band illumination intensity, and thermal history of the crystal. The coloring efficiency increased with temperature, trap depth and vacancy or *U*-center concentration. Under *F*-band illumination, both pure and *U*-centered crystals exhibited an initial period of rapid bleaching, followed by a long slow-bleaching period. Interrupting the bleaching in *U*-centered crystals by storage in the dark restored the higher bleaching rate. The slow bleaching was temperature-dependent, increased slightly with *F*-band illumination intensity, and was essentially independent of the *U*-center concentration. The results support the hypothesis that coloring and bleaching rates are primarily controlled by the availability of suitable holes and vacancies. Crystals containing the hydride color more efficiently than pure crystals because all constituents of the *F* center are present in the parent *U* center; whereas pure crystals bleach faster because of the accessibility of the holes.

I. INTRODUCTION

ALTHOUGH the coloring of alkali halide crystals by ionizing radiations is an old field of study, improvements in experimental technique have continued to yield valuable information concerning the photochemical reactions involved in the coloring process. Interest in the relations between the various crystal imperfections has been stimulated by recent efforts to combine the extensive knowledge of photochemical, photoelectric, and luminescent phenomena into a unified system of defects and reactions.[1]

The object of the current study is to compare the rate, yield and energy requirements for some of the photochemical reactions in pure KBr and in mixed crystals of KBr plus KH in order to gain further insight regarding the effect of the type and concentration of crystal defect on interactions with transient imperfections such as photons. One advantage in the study of *F* centers produced in mixed crystals rests in the fact that both the *F* centers produced and the number of *U* centers destroyed by the transient defects can be measured, thereby providing a check on electrons lost to undetected defects. Although mixed crystals have been used for most of the observations, a sufficient quantity of pure KBr has been included to permit comparison to the extensive data on pure crystals in the literature.

II. EXPERIMENTAL PROCEDURE

Because of the variety of measurements considered, specific experimental details are given in the appropriate section. Crystals grown by the Harshaw Chemical Company were filled with *U* centers by heating the crystals in a mixed atmosphere of potassium vapor and hydrogen. Samples to be compared were split from adjacent positions in the original crystal and given uniform

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[1] F. Seitz, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1950), p. 13; Revs. Modern Phys. **26**, 7 (1954).

thermal histories by simultaneous heat treatment. Uniform temperatures were obtained by heating the crystals in stainless steel chambers either embedded in a large copper block or submerged in a bath of molten aluminum. Radiation sources included x-rays from a 50-kv tungsten target (beryllium-window) tube and a 250-kv tungsten target tube and gamma rays from 0.5- and 10-curie Co^{60} sources. X-ray exposures were measured with air ionization, thimble-type chambers. The 0.5-curie Co source was calibrated by the National Bureau of Standards. All *F*- and *U*-center concentrations were determined from absorption measurements made with a Cary Model 11 recording spectrophotometer.

III. PHOTOCHEMICAL COLORING

A. Pure KBr

In discussing the factors controlling photosensitivity, it is advantageous to begin with crystals before the *U* centers have been added. All crystals contain imperfections in the form of vacancies (lattice positions where ions are missing, called Schottky defects) and dislocations. Equal numbers of positive and negative-ion vacancies are required to maintain electrical neutrality, and vacancies of opposite sign become attached to form pairs. The measurements of Delbecq *et al.*[2] indicate that essentially all Schottky defects are paired at room temperature in crystals of KBr and KI leaving few single vacancies available for *F*-center formation.

When high-energy photons undergo photoelectric, Compton or pair-production interactions in the crystal, the energetic electrons released produce many secondary ionizations and excitations. Some electrons form *F* centers by becoming trapped in vacancies. Others return to neutral bromine atoms (holes left behind in the ionizing process) and are removed from the picture as they reform bromine ions. Part of the absorbed energy presumably goes into the formation of single vacancies either through disruption of Schottky pairs or by interactions between excitons and lattice dislocations. If the *F*-center concentration is plotted as a function of energy absorbed by the crystal, the coloring rate gradually decreases with the total energy until an equilibrium value is reached (Figs. 1 and 2). Presumably the electrons in the conduction band are captured initially by existing or easily formed single vacancies; however, these traps become depleted as the irradiation progresses, and the rate of vacancy formation becomes a governing factor in color center production. The coloring rate is further reduced by thermal bleaching and other forms of *F*-center excitation until at equilibrium, the rate of *F*-center production equals the rate of destruction. Apparently, both the coloring rate and the equilibrium concentration depend on the relative availability of single vacancies and competing holes, the stability of the *F* centers formed, and the rate of energy absorption (see Figs. 1, 2 and 5). Increasing the vacancy concentration and the probability of vacancy creation at dislocations by thermal and mechanical deformation of the lattice has long been known to increase the coloring ability. The most perfect natural alkali halide crystals which have had years to reach thermal equilibrium are difficult to color with x-rays or gamma rays; however, these crystals color easily after they have been heated near to the melting point and quenched.[3] At low coloring rates, it is possible for an *F*-center equilibrium concentration to exist before the scarcity of vacancies dictates a saturated condition. As the ionization rate increases, the loss of *F* centers through thermal bleaching becomes less important, and coloring is limited by the lack of vacancies. In KBr, thermal bleaching at room temperature is appreciable in exposures which last for several days; consequently, the equilibrium *F*-center concentration varies with the rate of energy absorption. In Fig. 1 an eight-fold increase in the x-ray beam current (at 50-kv) raised the equilibrium density by a factor of about 1.3 and similar

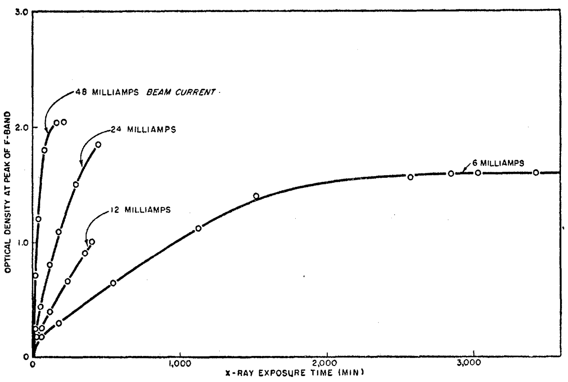

FIG. 1. *F* centers produced in KBr as a function of x-ray energy absorbed for four rates of irradiation.

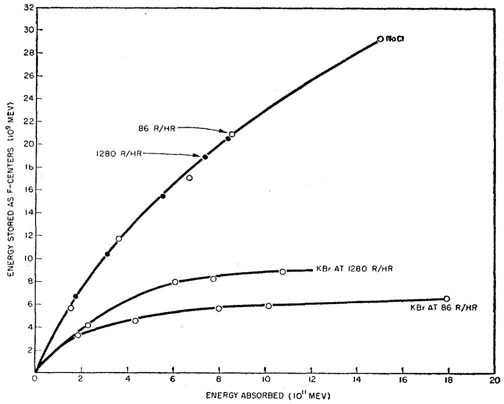

FIG. 2. Influence of energy absorption rate on *F*-center production rate and equilibrium concentration.

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[2] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 577 (1951).

[3] Delbecq, Pringsheim, Vareck, and Yuster, U. S. Atomic Energy Commission Report AECU-1533, 1950 (unpublished).

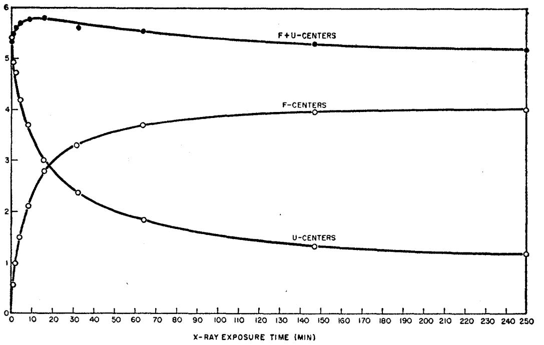

FIG. 3. X-ray-induced U- to F-center reaction in KBr.

results were obtained with Co^{60} for a fifteen-fold increase in energy-absorption rate (see Fig. 2). The initial coloring rate was about the same for all exposure rates used in Figs. 1 and 2; but, during the fairly linear portions of the curves, the lower exposure rates are less efficient for coloring; however, vacancy formation as well as thermal bleaching were probably contributing here. Since thermal bleaching is less severe in more tightly bound F-center electrons, the exposure rate has a smaller effect on NaCl than on KBr (see Fig. 2).

B. $U \rightarrow F$ Reaction

Processes occurring in crystals containing U centers are analogous to those just described; however, the concentration and characteristics of the vacancies and holes formed produce an appreciable enhancement in photosensitivity. If both the U and F bands are measured as a function of x-ray energy absorbed, it becomes apparent that most of the F centers are produced at the expense of U centers.[4] Figure 3 shows the F- and U-center concentrations, as well as their sum, plotted as a function of the x-ray energy absorbed. Initially, the total color-center concentration increases gradually with exposure, presumably because some F centers are created directly from the lattice; however, this contribution is less than ten percent. As the exposure continues, the total concentration decreases as electrons are lost to other centers not measured in the F and U bands. Good evidence exists for the two-step nature of the resonantly excited $U \rightarrow F$-center reaction in which first the electron is excited and second the neutral hydrogen migrates to an interstitial lattice position.[5] With ionizing radiations the hydrogen may lose an electron either through direct excitation or by hole conduction to an adjacent neutral bromine, thereby freeing the neutral hydrogen. Each U center represents a prospective F center, and a large U-center concentration has the same effect on photosensitivity as a large single-vacancy population. Figure 4 shows curves for crystals having varying U-center concentrations, but identical thermal histories produced by heating samples from a single original crystal through an identical thermal cycle. The variation in U-center concentration was obtained by limiting the amount of potassium metal added to the chamber in the coloring process. The reverse reaction of F center$\rightarrow U$ center proceeds slowly; consequently, a further gain in sensitivity results from reduced thermal bleaching, and the equilibrium color-center concentration for crystals containing U centers is much higher than for plain crystals as shown in Figs. 4 and 5.

C. Energy Storage Efficiency

F-center formation can be considered as an energy storage process in which about five electron volts are stored per color center in KCl and KBr. The storage efficiency serves as a figure of merit for photosensitivity. Quantitative energy measurements also can be used to determine the average energy required to convert a U center to an F center. Energy measurements were made on both pure and sensitized crystals, using Co^{60} gamma rays and an exposure rate of about 6.5 r per hour. The energy absorbed in one cm^3 of crystal was calculated on the basis of the following assumptions:

1. At the average gamma-ray energy of 1.27 Mev, the photoelectric absorption contributes only about one percent to the energy absorbed, and pair production is nil; consequently, only Compton interactions are considered.
2. All of the energy transferred to secondary electrons is absorbed in a crystal except for the electrons originating near the crystal surface. A correction factor of 0.87 was included to account for the calculated loss of 13 percent of the energy carried through the crystal surfaces by escaping electrons.

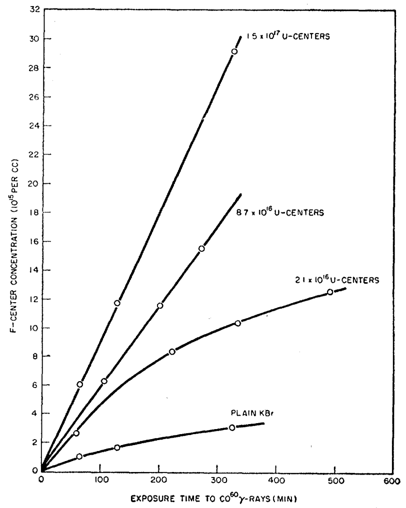

FIG. 4. Effect of U-center concentration on F-center production rate in KBr under gamma-ray bombardment.

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[4] H. Pick, *Photographic Sensitivity* (Butterworths Scientific Publications, London, 1951), p. 9.

[5] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition; Hans Tomine, Ann. Physik **5**, 601 (1949).

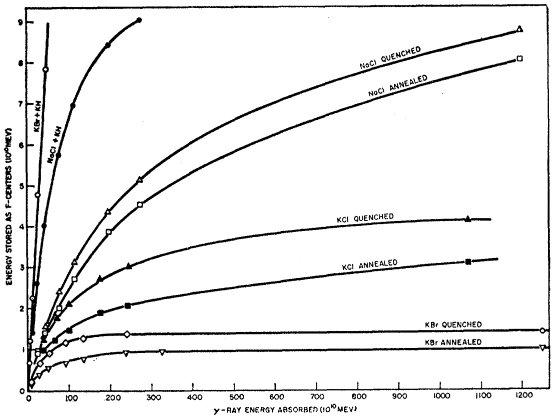

Fig. 5. Effect of crystal material and past thermal history on energy storage efficiency.

3. This correction factor was calculated assuming that all secondary electrons have the average energy of Compton-scattered electrons and the direction of travel corresponds to the average energy. If the correction is made for this surface loss neglecting the small number of electrons originating near the edges, the energy absorbed per gamma ray is 0.075, 0.056, and 0.063 Mev for one cm^3 of KBr, KCl, and NaCl, respectively.

The energy absorbed per unit volume of crystal is

$$E/V = N\sigma\epsilon/V,$$

where ϵ = the average energy of a Compton electron produced by Co^{60} gamma rays = 0.613 Mev, σ = the total Compton cross section for Co^{60} gamma rays, N = number of incident photons, and V = crystal volume = 1 cm^3. Since the Co^{60} source was suspended in mid-air, a reasonably pure spectrum was obtained. Optical measurements were made on the Cary spectrophotometer, and the F-center concentrations calculated using the following equations[6]:

$$N_{\mathrm{NaCl}} = 4.8\times10^{15}\times K,$$
$$N_{\mathrm{KCl}} = 3.7\times10^{15}\times K,$$
$$N_{\mathrm{KBr}} = 3.6\times10^{15}\times K,$$

where K = absorption coefficient at F-band maximum in cm^{-1}, and N_{salt} = number of F centers per cc. From the plot of energy stored as a function of absorbed energy (Fig. 5), it can be seen that the efficiency (energy stored/energy absorbed) at the beginning of irradiation is about four to seven percent for plain crystals, and about 20 percent for sensitized KBr. This efficiency decreases rapidly with increasing F-center concentration in the pure crystals as equilibrium is approached. In a survey of the literature dealing with photochemical reactions involving ionizing radiations, Frerichs[7] found that the average process leads to efficiencies on the order of one to ten percent. For storage of five electron volts per F center, such efficiencies would require energies in excess of 50 electron volts for each F center formed. The reaction energies determined from the data in Fig. 5 lead to values of 92 to 154 electron volts for pure crystals compared to 26 electron volts for sensitized KBr. With plain crystals the curvature in the graph near the origin, combined with the minimum detectable F-center concentration, leads to difficulty in determining accurately the initial slope. Consequently, the 154 electron-volt value is the average for the minimum detectable number of electrons, and the 92 electron volts is for an estimated slope at the origin. These results are somewhat lower than those of Pick who obtained 35 electron volts for sensitized KBr using 50- to 60-kv x-rays. The Co^{60} determination of the reaction energy is probably low due to the assumption made in calculating the energy absorbed. The calculation assumed that six-tenths of the gamma-ray energy absorbed in the Compton process was taken by the Compton electron and the remaining energy was carried out of the crystal by the degraded photons. Many of these degraded photons will undergo additional photoelectric or Compton interactions; thus, the calculated energy will be too low by the amount of energy absorbed in the second collisions. The difficulty in correcting for secondary collisions makes a completely experimental determination of reaction energy more desirable, and such an experiment is in progress utilizing 2-Mev cathode rays from a Van de Graaff generator.

The choice of crystal material offers one method of influencing the energy storage efficiency. When the coloring rates in cubes of NaCl, KCl, and KBr are compared as in Fig. 5, the initial slopes are observed to be about the same for all three pure materials; however, as equilibrium is approached, the curves diverge and the materials having more stable F centers reach a higher equilibrium F-center concentration. The F centers of NaCl, KCl, and KBr require 2.63, 2.20, and 1.96 electron volts, respectively, for excitation at room temperature; consequently, the increased stability of NaCl F centers would contribute to the higher equilibrium value, but it must be remembered that the rate at which vacancies become available, also strongly influences this portion of the curve. By varying the two factors of stability and vacancy availability through the introduction of U centers, it is possible to override the influences of crystal material. Figure 5 also shows the coloring for the KBr and NaCl containing U centers. It will be seen that sensitized KBr, in addition to averaging about ten times the sensitivity of the plain material, rises to a higher equilibrium value than the NaCl. At present the highest U-center concentrations have been obtained in KBr.

D. Temperature Dependence

The thermal effects are negligible for the primary interactions because of the high energies involved; how-

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[6] R. W. Pohl, Proc. Phys. Soc. 49, extra part, 3 (1937).

[7] R. Frerichs, "A Study of the Older Literature Related to the Coloring of Crystals by Irradiation with X-Rays or Nuclear Radiation," Northwestern University report, September, 1950 (unpublished).

ever, the mobilities and diffusions of vacancies and the atoms which control coloring rates vary exponentially with temperature. Measurements at low temperatures are complicated by the appearance of new traps which are thermally unstable at room temperature, e.g., the *F′* and *V* bands; however, certain trends can be detected in the existing data. Harten[8] measured the temperature dependence of the coloring rate in plain KCl over the range from −180°C to 60°C. This measurement showed the following general features: (a) The general coloring ability reached a maximum between −20°C and −75°C; and (b) The initial slope of the curve increased with temperature from −180°C to −20°C and remained constant from that point on to 60°C. The equilibrium *F*-center concentration decreased for all temperatures above 75°C, and since the curves at −110°C and −180°C did not reach equilibrium, the lower temperature limit for this trend cannot be fixed from this data. Duerig[9] measured coloring rates at 5° and 78° Kelvin, and found a higher rate at 5°, which suggests that the higher mobility at 78° Kelvin may cause more *F* centers to be bleached, thus reducing the coloring rate. If the initial slope depends on vacancies that either exist or are readily available, increasing the thermal agitation would assist in production of sites for *F*-center formation; therefore, the initial slope of the coloring curves should increase with temperature until thermal bleaching effects begin to dominate. The equilibrium value on the other hand· would tend to increase as the temperature is lowered until the low temperature traps begin to dominate.

Tomine[5] studied the *U*-band absorption of KBr+KH throughout the temperature range from −253°C to 500°C and found that the quantum yield, i.e. (*F* centers produced)/(uv light quantum absorbed), had a value of unity at 500° and decreased to 20 percent at 20°, becoming zero at −120°C. Since *U*-band photons are resonantly absorbed by *U* centers, the thermal behavior presumably results from changes in the hydrogen atom mobility; therefore, Tomine's results substantiate the previously discussed two-step nature of the *U*-to-*F* conversion process as suggested by Mott and Gurney.[5] The possibility of *F*-center formation then becomes a temperature-dependent reaction which is quite sensitive to changes in the hydrogen mobility. At low temperatures, i.e., below −120°C, the details of the coloring picture are complicated by the formation of *U′* and *U″* centers. In sensitized crystals colored with x-rays, the thermal effects have a possibility of modifying several stages in the process. The probabilities for Compton and photoelectric interaction processes are proportional to the first and fifth powers of the atomic number, respectively; consequently, Br^- with 36 electrons, compared to 2 for H^-, will monopolize the initial interactions. If direct ionizations or excitations by photoelectrons involve primarily the valence electrons, the fraction of the energy absorbed by the *U* centers would not account for the number destroyed. Crystals containing 10^{18} *U* centers per cm^3 have 10^4 Br ions present for each H^-; consequently, less than 0.01 percent of the absorbed energy is available for the $U \rightarrow F$ reaction instead of the 15 to 20 percent observed stored as *F* centers. Some mechanism such as migrating holes or excitons is required for transferring absorbed energy from Br^- to the *U* centers. This additional step offers another opportunity for the temperature dependence although the reduced hydrogen mobility is still probably the predominant thermal effect. Once the *U* center has received sufficient energy to excite the electron or the electron has been captured by a near-by hole, it is necessary for the hydrogen to depart as in the case of resonance absorption before a vacancy is available for *F*-center formation.

Figure 6 shows the result of measurements made on both plain and sensitized KBr samples exposed to x-rays over the temperature range from −180°C to 89°C. Sensitized crystals containing 10^{17} *U* centers per cm^3 exhibited the same temperature dependence as those containing more than 10^{18} *U* centers. The crystal temperature was maintained throughout the x-ray exposure by enclosing the samples in a copper chamber which in turn was immersed in the heating or cooling liquid. The filtration of the x-ray tube, plus that due to the crystal holder and Dewar flask, produced an effective x-ray energy of about 170 kv. The maximum color-center yield for plain crystals occurred between −60°C and 20°C, decreasing at both higher and lower temperatures in agreement with the work of Harten.[8] At elevated temperatures, the drop for plain crystals is due presumably to thermal bleaching; whereas the increased stability of sensitized crystals permits the yield to continue increasing throughout the temperature range covered. The reduction in the *U* band shown at

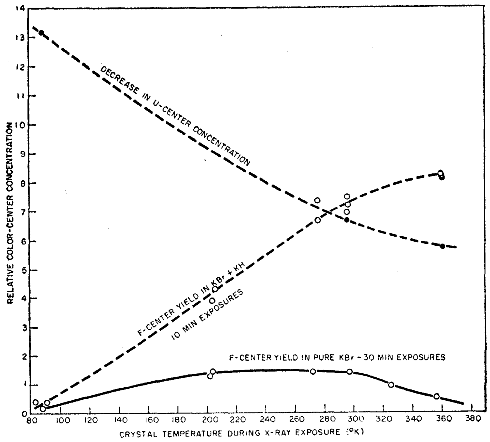

FIG. 6. Color-center yield in plain and sensitized KBr as a function of exposure temperature for x-ray exposures of 10 and 30 minutes, respectively.

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[8] H. Harten, Z. Physik **126**, 619 (1949).

[9] W. H. Duerig, Ph.D. Thesis at University of Maryland, 1952 (unpublished).

the top of the graph agrees with the F-center production. All crystals were measured at room temperature after exposure to the x-rays.

E. Luminescence

When both pure and sensitized KBr, colored at liquid nitrogen temperature, are heated to room temperature, a small fraction of the stored energy is released as thermoluminescence; however, the magnitude and temperature location of the emission peaks do not coincide in the two materials. Table I lists the temperature location and relative intensity of the peaks between $-196°C$ and 250°C observed at a constant heating rate of 21°C per minute. No emission between 2000 and 8000 A could be detected with 1P28 photomultiplier tubes for KBr+KH heated from 20°C to 350°C although complete bleaching occurred at the highest temperature. Since all of the crystals tabulated in Table I received the same x-ray exposure, the F-center concentration was an order of magnitude higher in the sensitized salt; therefore, radiationless transitions in KBr+KH account for a larger fraction of the thermal bleaching than in pure KBr. The extremely low quantum yield in pure KBr (approximately one photon per 100 F centers destroyed)[10] leads to the assumption that defects other than F centers and neutral bromine atoms are involved in the transition. The absence of thermoluminescence above room temperature and the low relative yield at low temperatures would suggest that KBr+KH either bleaches by a different process or cannot utilize the defects responsible for thermoluminescence in the pure crystals. The bleaching process will be discussed in subsequent paragraphs.

F. Effect of Past History

Previous mention has been made of the increase in sensitivity that can be obtained by mechanically or thermally increasing the vacancy concentration in plain crystals. Figure 5 shows coloring curves for KBr, KCl, and NaCl crystals both annealed and thermally shocked by quenching in air from 700°C to room temperature. The initial coloring rate is higher for all quenched crystals, and the knee marking the onset of equilibrium occurs later, indicating that a larger number of single or prospective vacancies are available in the heat-treated crystals. The effects of mechanical strain are usually apparent in crystals which have been split from larger chunks since the coloration is noticeably darker where some straining and cracking has accompanied the splitting. This effect of mechanical strain was not found in the sensitized materials, apparently due to the predominance of the U- to F-center transition which completely masked any additional sensitivity arising from mechanical factors.

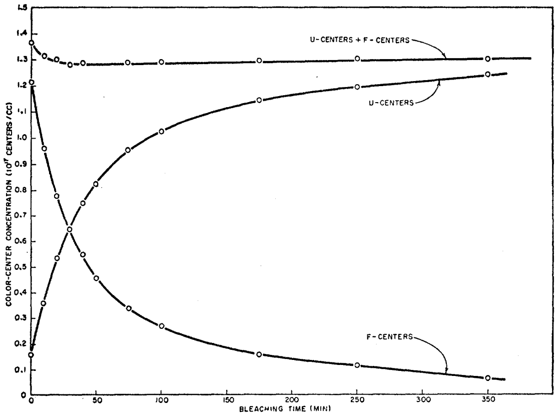

FIG. 7. Conversion of F to U centers in KBr by illumination in the F band.

TABLE I. Thermoluminescent peaks in pure and sensitized KBr.

Material	Temp. location of peak	Relative intensity
Pure KBr	$-120°C$	200
	$-80°C$	50
	$-40°C$	50
	0°C	50
	20°C	100
	60°C	50
Sensitized KBr	$-140°C$	1¼
	$-130°C$	1
	$-60°C$	25

IV. PHOTOCHEMICAL BLEACHING

A. Pure KBr

Once again some insight into the mechanisms occurring in sensitized crystals can be obtained from the examination of data available for pure alkali halides. F centers can be destroyed and the crystal returned to its original colorless condition by optical, thermal or mechanical bleaching. During the bleaching process, some of the stored energy is liberated either as a direct consequence of the bleaching or as a byproduct in the form of luminescent radiation which has been termed photoluminescence, thermoluminescence, and triboluminescence, depending on the method of bleaching. The most outstanding feature of the bleaching process is the apparent difference in stability of the various color centers in a single crystal. Under constant illumination in the F band, the initial bleaching is rapid; whereas the final bleaching proceeds slowly and is sensitive to the origin, past history, and impurity condition of the crystal. Casler, Pringsheim, and Yuster[11] have observed that both the type of irradiation used and the coloring rate influence the F-center stability. For example, stability increased in going from beta-ray to soft x-ray to gamma-ray exposures, and decreased

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[10] M. L. Katz, Izvest. Akad. Nauk (S.S.R.R.) **13**, 149 (1949).

[11] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 887 (1950).

with increasing coloring rate. Alexander and Schneider[12] observed an increase in F-center stability with time between coloring and bleaching. In the bleaching process, F centers escape from vacancies and return to holes, reforming the halogen ions; consequently, the V centers which result from the presence of neutral halogen atoms in the lattice are destroyed along with the F centers. The type of deficiency center, i.e., V_1, V_2, V_3, V_4, or alpha or beta, depends strongly on the irradiation temperature, and a corresponding temperature dependence of the F-center stability is observed.

Since the F bands do not change with the shifts in stability, the bleaching mechanisms proposed generally control the rate by availability of the holes.[11–13] Schneider[13] suggests that electrons and positive holes formed in the photochemical process remain in the same vicinity in the crystal, the electron as an F center and the hole either free or trapped as a V center. Rapid bleaching results from the recombination of electrons and holes that are close at hand; whereas the slow bleaching requires a disruption of more stable V centers or involves more remote holes and electrons. It will be observed that all of the bleaching-rate factors control in part the availability of receptors. For example, soft x-rays and beta rays produce very intense local ionization; consequently, the distance between F centers and holes will be less than in a crystal irradiated with higher energy gamma rays. Similarly, a storage period after irradiation or a low irradiation rate permits time for the more stable V-center complexes to form.

B. $F \rightarrow U$ Reaction

The distinguishing difference between the bleaching process in pure and sensitized crystals is the high stability of the F centers formed from U centers, which presumably is due to the difference in the behavior of the holes formed in the two processes. Figure 7 shows the typical behavior of the F and U bands under constant illumination from a tungsten filament lamp. The F band bleaches rapidly at first as in the case of pure crystals and the sum of $U+F$ centers decreases slightly, indicating that some electrons are returning to halogen neutrals. If bleaching is interrupted with periods of storage in the dark, the bleaching rate is observed to increase after each dark period as shown in Fig. 8. In some crystals the absorption increases on the long wavelength side of the F band, presumably due to F' or other centers which bleach out thermally during the dark storage period, giving rise to additional U centers. Although this increase in the bleaching rate is most pronounced during the initial rapid change in slope, the increase can be observed after each dark storage as long as F centers remain in the crystal.

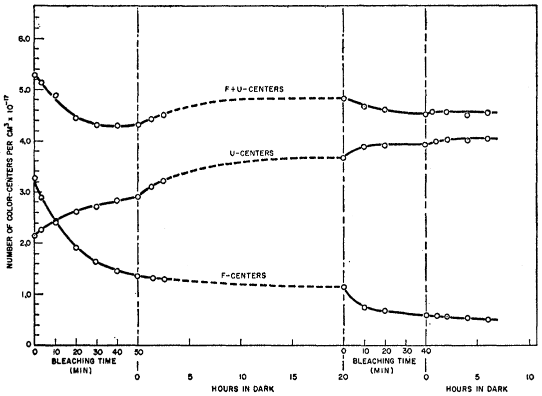

FIG. 8. Restoration of rapid bleaching rate in KBr+KH by periods of storage in the dark. The bleaching light intensity was approximately 5000 ft candles of white light. (Note the difference in time scales.)

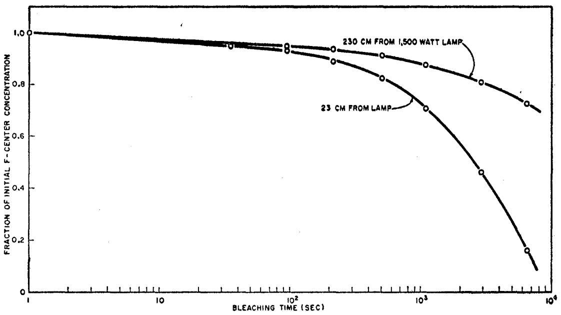

FIG. 9. Bleaching of F band in KBr+KH for a 100-fold variation in illumination intensity.

C. Effect of Illumination Intensity

The availability of electrons for U-center formation depends on the electron concentration in the conduction band, which in turn is determined by the intensity of illumination in the F band. At sufficiently low light levels, the bleaching rate is controlled by the rate of electron release; however, at intensities corresponding to room light or brighter, swarms of electrons are available in the conduction band and other factors limit the bleaching rate. Figures 9 and 10 are typical examples of bleaching as a function of light intensity for continuous and chopped irradiation, respectively. In all cases, the samples compared were split from a single sensitized crystal and the illumination came from a 1500-watt tungsten lamp filtered to remove the infrared and supplying approximately 2000 ft candles at the 23-cm position. A one hundred-fold decrease in intensity for continuous illumination (Fig. 9) reduced the bleaching rate by a factor of 3 to 10. Similar curves for the average light transmitted by rotating sector disks show little change in slope after the first 100 minutes for a 20 to 1 variation in the number of holes in the chopper disk. The transition of electrons from one vacancy to another as a result of F-center destruction, plus re-

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[12] J. Alexander and E. Schneider, Nature **164**, 653 (1949).

[13] E. Schneider, *Photographic Sensitivity* (Butterworths Scientific Publication, London, 1952), p. 21.

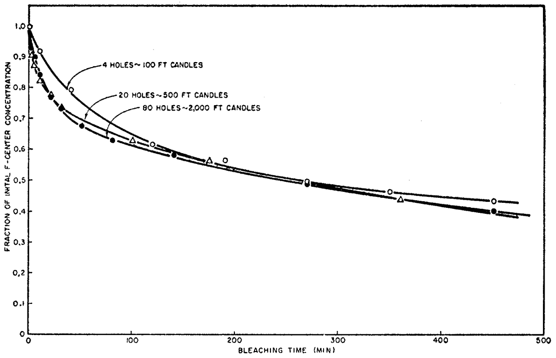

FIG. 10. Bleaching of F band in KBr+KH for three different average light intensities as obtained with sector disks.

capture of an electron from the conduction band, can be looked upon as a form of temporary vacancy migration which could assist the bleaching process by bringing an unoccupied vacancy within reach of a hydrogen atom; consequently, the illumination effects are not solely tied to electronic transitions.

D. Thermal Effects

The F centers in sensitized crystals are quite stable up to temperatures of 100°C; however, the optical bleaching rate is strongly temperature-dependent even below this value. Figure 11 shows typical bleaching curves for three adjacent samples from a single sensitized crystal bleached at −196°C, 20°C, and 100°C. The −196°C and 20°C temperatures were maintained throughout the six hours of measurement while the 100°C crystal was cooled to room temperature for each F-center determination. At −196°C the F-center concentration dropped eight percent during the first 25 minutes and then remained constant. The crystal at 100°C was completely bleached in 50 minutes. Since the light intensity (approximately 2000 foot candles of white light) was the same as the maximum in Fig. 9, a large surplus of electrons was present in the conduction band at all temperatures. Consequently, the thermal effect must involve other components of the U centers.

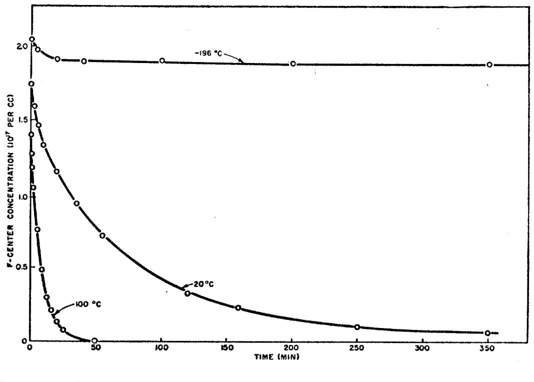

FIG. 11. Optical bleaching of F centers in KBr as a function of crystal temperature—adjacent pieces from a single crystal sensitized with KH and bleached with white light (intensity approximately 2000 ft candles).

E. Effects of U-Center Concentration

Other factors which influence the bleaching process are U-center concentration, crystal thermal history, foreign ions, and crystal material. The study of U-center concentration effects is complicated by the difficulty in holding all other factors constant in preparing and bleaching the crystal. In order to assure a uniform past thermal history, all crystals compared here were heated simultaneously in the molten aluminum temperature bath using stainless steel chambers. Variations in U-center concentration were achieved by limiting the amount of alkali metal added to the containers. The pure crystals used in the comparison were put through the same heating and quenching cycles. Figure 12 shows the bleaching characteristics of crystals containing 0, 10^{16}, and 10^{18} U centers per cm^3 prior to the x-ray exposure. The abscissa has been related to the energy absorbed in bleaching the F band by graphically integrating the area under the time bleaching curve, allowing for the change in energy absorbed from the bleaching light as the absorption coefficient decreases with the reduction in F-center concentration. The pronounced difference in the bleaching rate between pure and mixed crystals is indicative of the relative ease with which F-center electrons can recombine with bromine and hydrogen atoms. In the pure crystal, bleaching occurs through capture by bromine atoms, while in crystals containing large U-center concentrations, essentially all of the F centers are formed through the disruption of U centers, and bleaching necessitates the recombination of the F-center electron with a hydrogen atom. Between these extremes are crystals containing small U-center concentrations in which case F centers will be formed from both H^- and Br^-; consequently, the bleaching curve would be expected to indicate an initial rapid bleaching until the neutral bromines are used up, followed by a slow bleaching as recombination with hydrogen atoms occurs. Increasing the number of U centers beyond the concentration required for 100 percent production of the F centers would have little effect on the bleaching rate, because two crystals with different U-center concentrations but the same number of F centers would appear identical during the bleaching process, assuming that the H^- play no part in the bleaching. If both crystals had the same thermal and impurity background and had been irradiated to produce the same F-center concentration, then the number of F centers and neutral hydrogen atoms would be identical and the recombination process should be identical. The experimental evidence lends qualitative support to this picture and the bleaching time is found to be of the same order of magnitude for all crystals starting with the same F-center concentration, but ranging in U-center concentrations from 10^{17} to 10^{18}

U centers per cm^3. However, the difficulty in obtaining finer agreement would indicate that all of the other variables are not being held constant during the observation. Crystals containing 10^{16} or less *U* centers exhibit the initial rapid bleaching for a time comparable to that required to bleach the pure KBr followed by long, slow bleaching as shown in Fig. 12. Previous mention has been made of the fact that pure crystals that are hard to color are also difficult to bleach. Similarly in the mixed crystals, the more easily colored samples bleach faster.

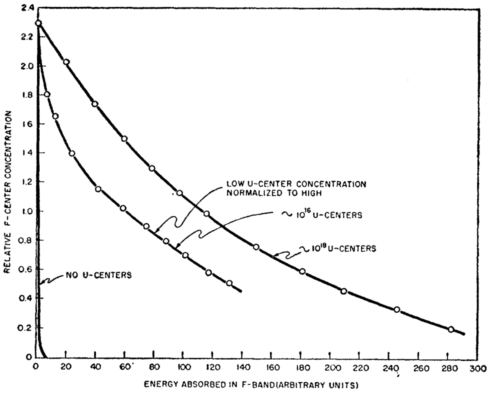

FIG. 12. Influence of *U*-center concentration on bleaching rate. Initial *F*-center concentrations in the ratio of 1 to 0.22 to 0.13 have been normalized. Crystals with low *U*-center concentrations received longer x-ray exposures.

F. Hydrogen Mobility Effects

If, as has been suggested, the bleaching rate in sensitized crystals is ultimately controlled by the behavior of the hydrogen, it might be possible to reduce the bleaching rate by forming *U* centers from deuterium. The quantum efficiencies for the photochemical decomposition of KH and KD molecules have been measured in KBr over the region from −100°C to 50°C. Throughout this region the quantum yield is about five percent lower for KD, suggesting that the deuterium has a lower diffusion coefficient.[14]

The crystals for this study were prepared by both the one- and two-step process. In the one-step process, samples split from adjacent portions of a single crystal were heated in identical chambers containing the same amount of potassium metal but under hydrogen and deuterium atmospheres. In the two-step process, the crystals were colored additively, then split and hydrogenated and deuteriumated in identical chambers. All heating was carried out in the molten aluminum bath.

Typical bleaching curves for crystals, sensitized with hydrogen and deuterium, are shown in Fig. 13. In all cases where comparable amounts of KH and KD were present and where similar *F*-center concentrations resulted from a given x-ray exposure, the over-all bleaching rate was higher in the crystals containing hydrogen. The initial rate in Fig. 13 was higher for KBr+KH; however, in other cases where both crystals had the same initial rate, the total bleaching time was longer in KBr+KD. The results lend qualitative support to the dependence of bleaching rate on hydrogen mobility, but improved crystal-preparation techniques are needed for a quantitative determination.

V. DISCUSSION AND CONCLUSION

In presenting the results on photochemical coloring, considerable attention has been given to the role played by holes and vacancies in the coloring process. The comparison between pure and sensitized KBr indicates two primary reasons for the enhanced photosensitivity in the mixed crystals; first, the *U* centers represent the storage of a large number of prospective vacancies which can be utilized in *F*-center formation; secondly, the neutral atoms formed in the disruption of *U* centers offer little competition to the vacancies for the available electrons. Consequently, the color centers formed are more stable. If only the constituents involved in the coloring reaction are considered, the process in pure and sensitized KBr, respectively, can be symbolized as follows:

(a) *Pure* KBr:

$$\mathrm{Br}^- + h\nu \rightarrow \mathrm{Br} + e,$$

$$e + \text{vacancy} \rightarrow F \text{ center}.$$

(b) KBr+KH:

$$U \text{ center} + h\nu \rightarrow \mathrm{H} + e + \text{vacancy},$$

$$e + \text{vacancy} \rightarrow F \text{ center},$$

where Br$^-$ and Br represent the halogen ion and neutral atom, respectively; $h\nu$ = photon energy; e = the electron; and, H = neutral hydrogen. In the pure crystal, the deionization of Br$^-$ provides an electron plus a neutral atom. The vacancy required for *F*-center formation must either exist as a defect in the crystal or be created by another ionizing or exciting event.[15] The

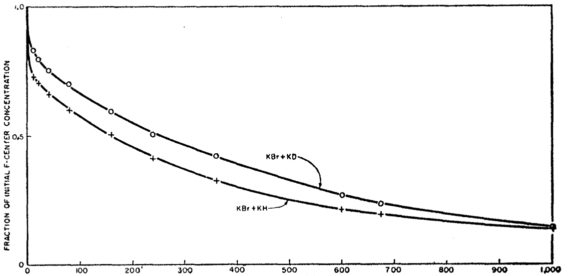

FIG. 13. Comparison of *F*-center bleaching in mixed crystals of KBr+KH and KBr+KD.

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[14] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, p. 149.

[15] F. Seitz, reference 1, p. 57.

bromine neutral atoms left behind in the ionizing process have a strong affinity for electrons in the conduction band and many electrons are lost through recombination with holes before a vacancy can be found for F-center formation. The ease with which pure crystals can be completely bleached by F-band illumination demonstrates this strong affinity between electrons and bromine atoms. The equation for KBr+KH shows that all of the F-center components are present in the parent U center; consequently, the initial high coloring rate continues as long as sufficient U centers are present in the crystal. The neutral hydrogen atoms left after F-center formation do not occupy the same position or play the same role as the bromine atoms produced in the pure crystals. The hydrogen occupies interstitial lattice positions and produces no potential disturbance that has been detected by the optical absorption bands; whereas the bromine atoms are confined to lattice sites and give rise to the various V bands. Initially, both pure and mixed crystals contain a concentration of vacancies which is determined by the past thermal history of the crystal. As coloring continues, these vacancies are used up by F-center production in pure crystals; but, when the F centers are produced from U centers, no change in vacancy concentration is required. The stability of F centers in the absence of F-band illumination gives some indication of the ease with which hydrogen and bromine atoms can recombine directly with F centers. Pure KBr crystals stored in complete darkness have been observed to lose one-third of the F centers because of thermal bleaching at room temperature over a period of a week's time; whereas mixed KBr+KH exhibited no detectable change in F-center concentration during the same time under identical storage conditions. A phosphorescence which can be observed visually in pure KBr continues for hours after extensive coloring by x-rays. KBr+KH shows no phosphorescence under identical conditions. Since the luminescence in the alkali halides accompanies the destruction of F-centers, this phosphorescent behavior of pure and mixed crystals is in accord with the observed stability of the F centers of the two materials in the absence of illumination. A neutral bromine atom located at a lattice site results in a hole in the filled band. This hole can migrate through the crystal by electronic transitions in which an electron jumping from a neighboring negative ion to the neutral atom appears as a hole migrating in the reverse direction. When through hole migration, a Br atom is formed in the vicinity of an F center, it is conceivable that the F-center electron could tunnel through the potential barrier to recombine with the bromine. Schneider[14] has concluded from data on the maximum F-center concentrations obtainable by the photochemical method that recombination by this tunneling process occurs for separations of about 10 to 30 lattice spacings. The high F-center concentrations and the stability of the centers formed in KBr+KH indicate a very low probability for the combination of F-center electrons and hydrogen atoms located at interstitial lattice positions.

For simplicity the coloring reactions were represented by direct interaction of photons with Br ions and U centers; however, most of the actual excitations occur by secondary processes, and a majority of the absorbed energy is dissipated in the crystal as heat, or lost through photoemission and is not stored in the form of color centers. A comparison of the energies required to produce the average F center in pure and sensitized crystals provides a more quantitative measurement of the efficiency of the reaction. Unfortunately, a wide variation in the conversion energy has been reported by the various investigators. Martienssen and Pick[16] found the initial rate to be constant in KBr+KH for all U-center concentrations above 10^{17} per cm^3, indicating that good energy transfer could occur up to distances of the order of 50 lattice spacings. Using 50- to 60-kv x-rays on crystals containing more than 10^{17} U centers per cm^3, Pick found that initially 35 electron volts were required per F center formed as compared with something in excess of 150 electron volts for pure crystals under similar conditions. Schneider[14] colored pure NaCl crystals with 40- to 50-kv filtered x-rays, obtaining an energy of less than 18 electron volts per F center formed, while Harten[8] found 120 electron volts were required per F center produced by x-rays in pure KCl. The initial coloring rates in pure KBr, KCl, and NaCl are quite similar as shown by Fig. 5. Consequently, the ionization energies found by Schneider and Harten should be comparable to the determination for pure KBr. The results discussed in Sec. III for coloring with Co^{60} gamma rays gave 26 electron volts per F center in sensitized KBr, compared to 92 to 154 electron volts in the pure crystal. Although the ionization energy determined with Co^{60} is probably on the low side, the initial ratio of about 4 between pure and sensitized crystals is valid and provides a comparison of reaction rates. Experiments now in progress, using 2-Mev monoenergetic cathode rays, should provide shortly a better figure for the reaction energy for irradiation in the Mev region.

The bleaching reactions in pure and mixed KBr crystals can be analyzed with reference to the following equations:

(a) *Pure* KBr:

$$F\text{ center}+h\nu\rightarrow e+\text{vacancy},$$

$$e+\text{hole}\rightarrow \text{Br}^-;$$

(b) KBr+KH:

$$F\text{ center}+h\nu\rightarrow e+\text{vacancy},$$

$$e+\text{vacancy}+\text{H}\rightarrow U\text{ center}.$$

In the coloring process one hole was produced for each F center formed in the pure crystal while one neutral

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[16] W. Martienssen and H. Pick, Z. Physik **135**, 309 (1953).

hydrogen was formed for each F center in the sensitized KBr. Since the action of F-band illumination on an F center is identical in the two materials, any difference in the bleaching reaction must result from the processes represented by the second lines in the above equations. Schneider[14] has analyzed bleaching curves for pure salt in terms of exponentials and finds that a satisfactory fit can be obtained with two exponentials having decay constants of the order of 1.7×10^{-3} seconds^{-1} and 2.5×10^{-4} seconds^{-1}, respectively. He accounts for the two bleaching rates by the configuration of the hole involved in the reaction. In the fast decay, electrons released from F centers combine with nearby available single holes; whereas the slow decay is attributed to F centers which lose their electrons to bound holes such as V centers. About 50 to 70 percent of the centers were of the slow-bleaching variety. An analysis of bleaching data associated with Sec. IV shows qualitative agreement with Schneider's results although the experimental conditions were quite different, i.e., the F-center concentration was lower by a factor of two and the bleaching rate higher by an order of magnitude than reported by Schneider's experiment. The fast components decay at similar rates; whereas the various slopes obtained for the slow decays indicate more dependence on the past history of the crystal. The initial number of slow centers was never observed to exceed 40 percent and not all the bleaching curves for the pure crystals could be fitted by the above analysis, although there was no known significant difference in past history of the crystals.

The bleaching process in sensitized KBr involves the combination of three components to form the U center. There are four conceivable modes of the combination; first, a three-body collision; second, a direct recombination between the F center and a hydrogen atom; third, a hydrogen atom becomes trapped in a vacancy and electron capture follows; and fourth, an F-center electron attaches itself to a hydrogen atom producing an H^- which is captured by a vacancy. Mode 1 is statistically unlikely and Mode 2 has been ruled out by the stability of the color centers in the dark. The other modes depend on the rate at which the hydrogen ions and the vacancies come together. Qualitatively, all the sensitized crystals exhibit an initial period of fast decay followed by long, slow recombination. However, quantitatively the difference between the crystals has precluded a satisfactory analysis of the bleaching curves. On occasion, exponential bleaching has occurred similar to that observed in pure crystals, but with a much longer decay constant. However, the large majority do not follow the simple bleaching process. The third bleaching mechanism is of the bimolecular type. MacDonald[17] has analyzed some decay curves in the light of diffusion theory and has found that at room temperature $N=(A+Bt)^{-1}$, where N is the number of F centers and t=bleaching time. Unfortunately, all curves do not follow this bimolecular form of bleaching and the effect of crystal temperature and light intensity do not follow the predictions of the diffusion process.

Qualitatively, the difference between F centers in pure and sensitized salt follows from the nature of the holes and the complexity of the bleaching reaction, but quantitative explanations in both pure and sensitized salts require further work. Apparently, two types of hole configuration are required to account for the fast and slow bleaching of sensitized KBr in addition to possible recombinations between electrons and neutral bromine atoms because both bleaching rates are observed in crystals which have been previously irradiated in the F band to remove the holes. The recovery of the rapid bleaching rate during storage in the absence of F-band illumination requires that the configuration responsible for fast bleaching be capable of forming at room temperature in the absence of both ionizing and visible irradiation. Following the reasoning applied to plain crystals, it can be assumed that some of the hydrogen atoms will be located near or perhaps slightly attached to vacancies. These favorably located atoms readily trap electrons to reform the U centers and give rise to rapid bleaching. As these prospective U centers are used up, the bleaching rate slows down and depends on the rate with which hydrogen atoms and vacancies can come together. Interrupting the bleaching process with storage in the dark allows time for other hydrogens to reach favorable locations; consequently, rapid bleaching ensues when electrons are released by light. The limited number of prospective U-centers and the low rate with which they form would lead to an initial exponential type of decay. Unfortunately, many of the unexplained features observed with variations in light intensity, temperature, and color-center concentration result from unknown differences between crystals. Improved control is needed in the crystal preparation process for better quantitative results.

The authors wish to acknowledge the assistance of Miss Mary Denham who prepared many of the crystals and carried out the measurements, Lt. B. W. Downs who calculated the energy absorbed from Co^{60} gamma rays, Mr. Robert A. Levy who made the thermoluminescent measurements, and Professor F. Seitz who suggested the hydrogen-deuterium experiment.

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[17] J. R. MacDonald, "Radiac detector DT-50 dosimeter reader and comparison scale" (unpublished report).