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Production and Bleaching of Color Centers in X-Rayed Alkali Halide Crystals*

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The x-ray production and optical and thermal bleaching of color centers in NaCl and LiF have been studied quantitatively in regions of substantially uniform concentration, by making optical absorption measurements in a direction perpendicular to the axis along which the crystals were x-rayed. At room temperature F center growth rate for short x-ray exposures is found to be proportional to the rate of absorption of x-rays. For long exposures the rate of growth of the F band increases greatly near the x-rayed surface. Large M band growth accompanies this increased F band growth. The rate of bleaching of F centers by F light in NaCl has been studied at room temperature for low concentrations where the light absorption is nearly uniform along the light path. Differential equations describing the rates of excitation of F center electrons to the conduction band and the trapping of conduction electrons by negative ion vacancies and holes have been integrated under special conditions. The results are found to be consistent with the experimental data. The rate of thermal bleaching of F centers in NaCl has been studied at temperatures up to 150°C. It has not been found possible to analyze the data in terms of a mechanism involving trapping of conduction electrons by negative ion vacancies and holes. The results of several qualitative experiments to investigate the possible formation of vacancies during x-raying are presented.

I. INTRODUCTION

THE nature and interrelation of the various color centers in alkali halide crystals are fairly well established. However, a detailed understanding of the processes of the formation and decay of color centers appears to be lacking. In part, this is a result of insufficient knowledge of such parameters as describe the initial state of the crystal in terms of single and paired vacancies, impurity content, and mechanical strain. In part, the apparent complexity of the processes requires models that cannot be adequately tested by experimental data presently available. The data obtained on x-rayed crystals has been qualitative rather than quantitative, as a consequence of the fact that most of the optical absorption measurements have been made along a path of nonuniform coloration.

This inhomogeneity arises from the attenuation of the x-ray beam with increasing depth in the crystal. The greatest coloration is at the front face of the crystal, and the concentration gradient depends on the energy distribution in the x-ray beam and the stopping power of the crystal. Measurement of color center concentration by optical absorption has generally been made along the same axis as that of the x-ray beam, thereby giving an integrated value of the absorption through the crystal depth. However, quantitative absorption measurements can be obtained by choosing the direction of the optical absorption light path to be perpendicular to the axis of the x-ray beam. If the light beam is sufficiently narrow, the segment of the crystal observed will be essentially homogeneous in color center concentration. This technique has been used to investigate the growth of color centers by x-ray irradiation and their thermal and optical decay. It appears possible to reduce the apparent complexity of these processes by making a quantitative study of segments having a uniform color center concentration.

II. EXPERIMENTAL

The alkali halide crystals were obtained in various lots from the Harshaw Chemical Company. They were cleaved to 1.5 cm×1.5 cm and to various thicknesses. So-called "thick" and "thin" crystals were ∼0.8 cm and less than 0.1 cm, respectively, in the dimension through which the optical absorption was measured. A Picker-Waite diffraction unit with a Machlett tube was employed for the x-ray coloration. The accelerating voltages were in the 30 to 50 kv range, and voltage fluctuations were reduced by a Sola transformer. The x-ray tube had a molybdenum target and beryllium windows 0.5 mm thick, located 2.5 cm from the focal spot. The crystals were mounted ∼4 cm from one Be window. The optical absorption measurements were made on a Beckman Model DU spectrophotometer.

The "thick" crystals were x-rayed and the optical density measured in the same brass holder shown schematically in Fig. 1(a). This simplified the problem of handling the crystal during x-raying and transferring to the spectrophotometer in the dark, a precaution taken to avoid optical bleaching. The "thin" crystals were placed between two thicker crystals of the same alkali halide, and the sandwich was clamped between two brass plates. The purpose of the thicker crystals was to eliminate shadows caused by the brass plates during x-raying. For the optical absorption measurements the "thin" crystals were transferred to the holder employed for the "thick" crystals. The holder and crystal sample were mounted in the Beckman spectrophotometer as shown in Fig. 1(b). The crystal was moved perpendicular to the light path by a micrometer screw and absorption readings were taken about every half millimeter. Reproducibility of positioning was

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* This work was supported by the Bureau of Ordnance, Department of the Navy.

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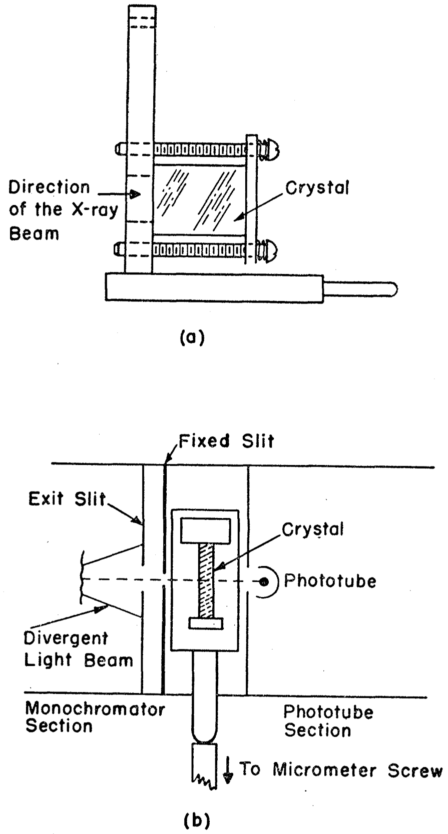

FIG. 1. (a) Crystal holder for x-raying and measuring the optical absorption of alkali halide crystals. (b) Crystal holder mounted in the Beckman spectrophotometer.

assured to ~±0.001 cm by observing the micrometer reading, for which transmission was 50 percent, as the leading edge of the front post passed the optical beam. Since the beam from the exit slit of the Beckman spectrophotometer is divergent, an additional 0.035-cm wide fixed slit was mounted between the variable slit and the crystal. For a Beckman slit of ~0.01 cm the width of the beam passing through the crystal was ~0.04 cm. All absorption values reported here are $\log_{10}$ of the ratio of the transmission before coloration to that after. Crystals used more than once were bleached of all coloration by heating in an oven at 350°C for two hours.

Optical bleaching of NaCl was accomplished in the spectrophotometer at 464 mμ, the frequency of the F band maximum, with the variable slit set at 1 mm, giving a spectral band width of ~35 mμ. After x-raying, and after each bleaching period, about five minutes was allowed for the decay of F' centers before the optical absorption was measured. The total bleaching light flux incident on the crystal was measured with an RCA 929 photocell and found to be ~37 μw/cm^2 or 10^{14} quanta/(cm^2 sec) on the basis of the calibration data of the manufacturer. Various bleaching light intensities were obtained by placing neutral filters in front of the crystal. The measuring light had a spectral band width of ~5 mμ and a flux of ~0.6 μw/cm^2. The bleaching power of the measuring light was negligible, and therefore was neglected in all of the present experiments.

For the study of thermal decay a forced air oven was built around the crystal holder, between the monochromator and detector sections of the spectrophotometer. Oven temperatures were maintained to ±1°C by a Celectray potentiometer type controller with a thermocouple sensing element. A dummy crystal with another thermocouple imbedded in it was clipped to the back plate of the crystal holder to monitor the temperature.

The optical absorption experiments reported here concerning α and β bands in KI crystals were made at 5° and 78°K in a low-temperature cryostat previously described.[1] The optical absorption measurements in this case were made along the same axis as that of the x-ray coloring beam, and the results are therefore only qualitative.

III. GROWTH OF *F* CENTERS IN NaCl AND LiF

A. Short X-Ray Exposures

The mechanism for the formation of F centers in alkali halides by x-ray irradiation is not clearly understood.[2] In the absence of a clearly defined model upon which to base calculations it seemed worth while to investigate the applicability of simple relationships between the rate of formation of F centers and the rate of x-ray absorption. For short times for which saturation effects can be neglected, the simplest assumption is that the local rate of production of F centers is proportional to the local rate of absorption of x-rays, as given by the equation

$$(dn_F/dt)_x = -a\,dJ(x)/dx, \tag{1}$$

where $J(x)$ is the intensity of the x-ray beam at depth x in the crystal, a is a constant, and n_F is the concentration of F centers at x. To test Eq. (1) the following calculations were made to determine as a function of depth in the crystal the relative energy absorption per cm^3 per sec, which is equal to $-dJ(x)/dx$.

The intensity $J(x,\lambda)$ of a monochromatic x-ray beam of wavelength λ at any depth of penetration x in a crystal is

$$J(x,\lambda) = J_0(\lambda)e^{-\mu x}, \tag{2}$$

where $J_0(\lambda)$ is the energy flux per unit area incident on the crystal face and μ the linear x-ray absorption coefficient of the absorbing crystal.

The unfiltered spectral output of an x-ray tube is not monochromatic but consists of a continuum with characteristic lines superimposed upon it. In this calculation the contribution of the characteristic Mo x-ray lines is neglected. The wavelength distribution of the

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[1] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. 23, 421 (1952).
[2] F. Seitz, Revs. Modern Phys. 26, 7 (1954).

continuous x-rays as given theoretically by Kramers[3] and determined empirically by Kuhlenkampf[4] is of the form

$$J_0(\lambda)=D_0Z\lambda^{-2}(\lambda_0^{-1}-\lambda^{-1}), \tag{3}$$

where $J_0(\lambda)$ is the intensity at wavelength λ, D_0 is a constant related to the efficiency of x-ray production, Z is the atomic number of the x-ray target material, and λ_0 is the short-wavelength cutoff.

The linear x-ray absorption coefficient varies with wavelength as[5]

$$\mu=A\lambda^3+B, \tag{4}$$

where A and B are constants depending on the absorbing material.

The total intensity $J(x)$ at any depth in a crystal irradiated with such a heterogeneous x-ray beam may be derived by combination of Eqs. (2–4) and integration over all λ from the short wavelength cutoff, yielding

$$J(x)=D_0Ze^{-Bx}[(J_1/\lambda_0)-J_2], \tag{5}$$

where

$$J_1=\int_{\lambda_0}^{\infty}\lambda^{-2}\exp(-A\lambda^3x)d\lambda \tag{5a}$$

and

$$J_2=\int_{\lambda_0}^{\infty}\lambda^{-3}\exp(-A\lambda^3x)d\lambda. \tag{5b}$$

The relative energy loss per unit volume, or relative absorption rate of the x-ray energy at any depth in the crystal, is the negative of the derivative of $J(x)$ with respect to the distance x in the crystal, and is given by

$$\begin{aligned}-dJ(x)/dx=-D_0Z\{e^{-Bx}[\lambda_0^{-1}(dJ_1/dx)-(dJ_2/dx)]\\ -Be^{-Bx}[(J_1/\lambda_0)-J_2]\}.\end{aligned} \tag{6}$$

The quantities J_1, J_2, and their derivatives may be evaluated in terms of complete and incomplete gamma functions, Γ_∞ and Γ_{u_0}, respectively, with the change of variable $u_0=A\lambda_0^3x$ as follows:

$$\begin{aligned}J_1=(Ax)^{\frac{1}{3}}\{e^{-u_0}[u_0^{-\frac{1}{3}}+\tfrac{3}{2}u_0^{\frac{2}{3}}]\\ -\tfrac{3}{2}[\Gamma_\infty(5/3)-\Gamma_{u_0}(5/3)]\},\end{aligned} \tag{6a}$$

$$\begin{aligned}J_2=\tfrac{1}{2}(Ax)^{\frac{2}{3}}\{e^{-u_0}[u_0^{-\frac{2}{3}}+3u_0^{\frac{1}{3}}]\\ -3[\Gamma_\infty(4/3)-\Gamma_{u_0}(4/3)]\},\end{aligned} \tag{6b}$$

$$dJ_1/dx=\tfrac{1}{2}A^{\frac{1}{3}}x^{-\frac{2}{3}}\{e^{-u_0}u_0^{\frac{2}{3}}[\Gamma_\infty(5/3)-\Gamma_{u_0}(5/3)]\}, \tag{6c}$$

and

$$dJ_2/dx=A^{\frac{2}{3}}x^{-\frac{1}{3}}\{e^{-u_0}u_0^{\frac{1}{3}}[\Gamma_\infty(4/3)-\Gamma_{u_0}(4/3)]\}. \tag{6d}$$

By using Eqs. (6)–(6d), numerical values of $-dJ(x)/dx$ were calculated for various values of depth x (in cm) for NaCl and LiF. The constants D_0 and Z were arbitrarily taken as unity since the primary interest was in determining the relative energy loss at different depths in a crystal. Values of μ for each alkali halide crystal were computed for various wavelengths from values of the mass absorption coefficient, μ/ρ, for each element, and the density, ρ, of the crystal. From these values of μ, A and B were computed by a least squares fit to be for NaCl, 49.64×10^{24} cm^{-4} and 0.376 cm^{-1}, respectively, and for LiF, 8.953×10^{24} cm^{-4} and 0.435 cm^{-1}. Values of λ_0 in cm were obtained from the equation $\lambda_0=hc/eV$, where V is the x-ray tube peak accelerating voltage.

Computations of $-dJ(x)/dx$ involving the gamma function expressions were quite laborious. A simpler procedure was therefore developed which yielded essentially the same results. The Kramer's energy distribution was divided into half a dozen wavelength segments. The derivative of Eq. (2),

$$dJ(x,\lambda)/dx=-\mu J_0(\lambda)e^{-\mu x}, \tag{7}$$

was computed by using average values of μ and $J_0(\lambda)$ for each segment. These contributions were then summed to give $dJ(x)/dx$. In this case wavelengths greater than ~2 A were neglected. For this reason the segment approximation is not very accurate for $x<0.1$ cm where the long-wavelength x-rays are strongly absorbed.

The x-ray energy absorbed after a given time of irradiation is proportional to the rate of energy absorption, $-dJ(x)/dx$. The results of the calculations of x-ray energy absorption as a function of depth x, based on the segment method of calculating $-dJ(x)/dx$,

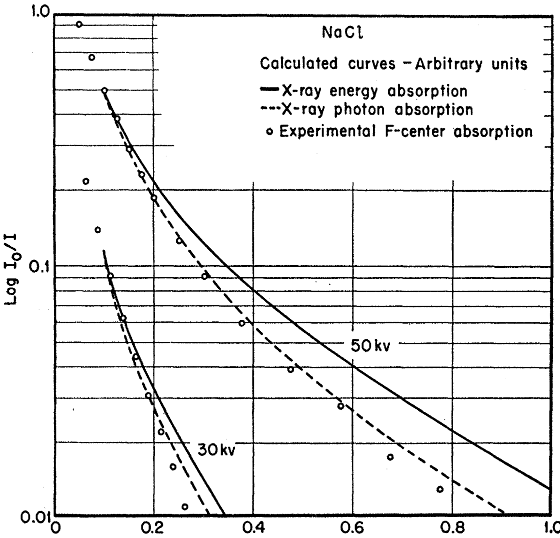

FIG. 2. Comparison of theoretical x-ray absorption and experimental F center concentration as functions of depth in NaCl. The solid line shows the x-ray energy absorbed, the dashed line shows the number of x-ray photons absorbed, and the circles are the observed F center concentrations for short x-ray exposure time (1 minute).

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[3] H. A. Kramers, Phil. Mag. **46**, 836 (1923).

[4] H. Kuhlenkampf, Ann. phys. **69**, 548 (1922).

[5] W. T. Sproull, *X-Rays in Practice* (McGraw-Hill Book Company, Inc., New York, 1946), p. 75.

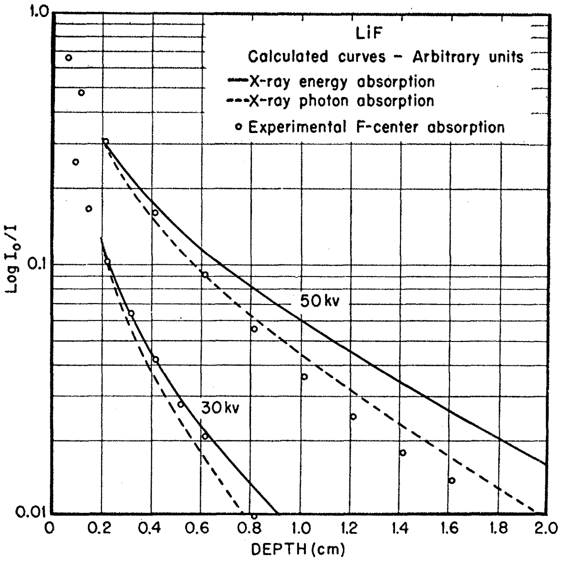

FIG. 3. Comparison of theoretical x-ray absorption and experimental F center concentration as functions of depth for LiF. X-ray exposure times of 2 min (50 kv) and 2.8 min (30 kv).

are shown as solid lines on the semilogarithmic plot in Fig. 2 for NaCl and in Fig. 3 for LiF for 50 and 30 kv x-rays. The intensity incident on the face of the x-rayed crystal, J_0, was assumed to be unknown here. The calculated penetration curves were, therefore, fitted at a depth of 0.1 cm for NaCl and 0.2 cm for LiF to the experimental data for the F center absorption which was measured as a function of depth in the crystal. The experimental points are denoted by circles. Since both the gamma-function method and the segment method of calculation yield very nearly the same depth curve at distances >0.1 cm, only the results from the latter method are shown.

In addition to the calculation for the relative x-ray energy absorption, it was of interest to calculate the relative x-ray photon absorption as a function of depth in the crystal. The rate of absorption of photons with wavelength λ is proportional to $\lambda\mu J_0 e^{-\mu x}$. The total relative photon absorption was calculated by the segment method for different depths in the crystal. The results are plotted in Figs. 2 and 3 as dashed lines.

Figure 2 shows fairly good agreement between calculated x-ray absorption and experimental F center concentrations as functions of depth in NaCl which was x-rayed for one minute at 50 kv and at 30 kv. Figure 3 shows the agreement between calculated and experimental results for LiF x-rayed at 50 kv for 2 minutes and at 30 kv for 2.8 minutes. The slopes of the experimental depth curves do not match the slope of either the calculated energy absorption curve or the calculated photon absorption curve to the exclusion of the other one. We can say that the experimental F center concentrations are approximately proportional to the x-ray absorption as a function of depth through the crystal, but the problem of whether F center formation is more closely related to x-ray energy absorption or photon absorption is unresolved. The reasons for this ambiguity lie partly in experimental error in the determination of the small F center concentrations produced from very short x-ray exposures, and partly in the appearance of saturation effects for exposures long enough to give well-reproducible depth curves. The problem is aggravated by the large range of x-ray energies in the heterogeneous beam available. It is hoped that an experiment can be carried out using monochromatic x-rays with a sufficiently high intensity to allow short times of exposure.

An estimate of the x-ray intensity J_0 at the front face of a crystal is 1.3×10^{16} ev/(cm^2 sec), based on tube operation at 50 kv and 15 ma, and tube efficiency of $\sim1.5\times10^{-9}$. The energy absorbed in the 0.86-cm^3 NaCl crystal in one minute was estimated to be $\sim5\times10^{17}$ ev. The total number of F centers produced in this crystal can be estimated by summing the local concentrations over the depth of the crystal. The local concentration can be found by using Smakula's equation[6]

$$n_F(\mathrm{cm}^{-3})=1.28\times10^{17}\frac{n}{(n^2+2)^2}\frac{\alpha W}{f}, \tag{8}$$

where n is the index of refraction of an uncolored crystal, f is the oscillator strength of the color center,

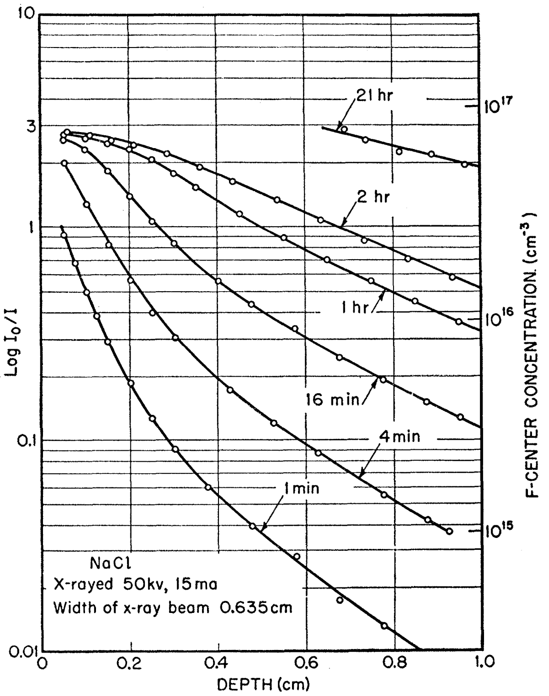

FIG. 4. F center concentration as a function of depth in NaCl for various times of x-ray irradiation.

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[6] A. Smakula, Z. Physik 59, 603 (1930). See also reference 2, footnote 1.

W is the band width in ev at half-maximum, and α is the absorption coefficient at the band maximum given by $\alpha = d_0^{-1}\ln(I_0/I)$, with d_0 taken as the crystal thickness. For NaCl at room temperature $n=1.54$, $f\sim 0.7$, and $W\sim 0.51$ ev. The total number of F centers produced after a one minute x-ray exposure was $\sim 3\times 10^{15}$, so that the average energy for the formation of one F center in NaCl is $\sim 10^2$ ev. This can be compared with the values of 18 and 120 ev reported by Schneider[7] and Harten,[8] respectively, for KCl x-rayed at room temperature.

B. Growth for Long X-Ray Exposures

F center concentrations as a function of depth in the crystal are shown in Fig. 4 for NaCl x-rayed for various times at 50 kv. The concentrations range from less than 10^{15} to $\sim 10^{17}$ cm^{-3}. For a particular crystal, absolute values of $\log(I_0/I)$ for a given depth and length of x-ray exposure could be reproduced to $\sim\pm 10$ percent, under the experimental conditions employed. Variations between crystals were somewhat larger than this. The slope of the depth curve at a given depth for a given length of exposure for all crystals of the same alkali halide could be reproduced to ± 1 percent. Variations in the x-ray tube current as well as differences in the treatment of the crystals were responsible for the large scatter in absolute determinations of the concentrations. Changes in the x-ray voltage and slight instability in the Beckman spectrophotometer blank determinations affected the depth curve slope reproducibility.

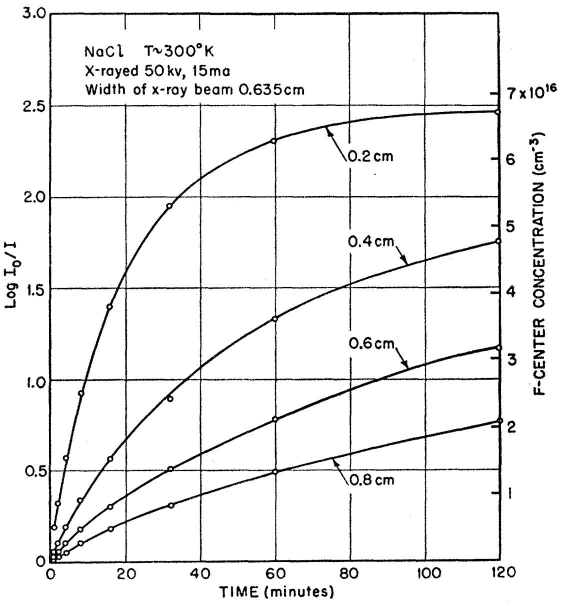

FIG. 5. F center concentration as a function of x-ray exposure time for several depths in NaCl.

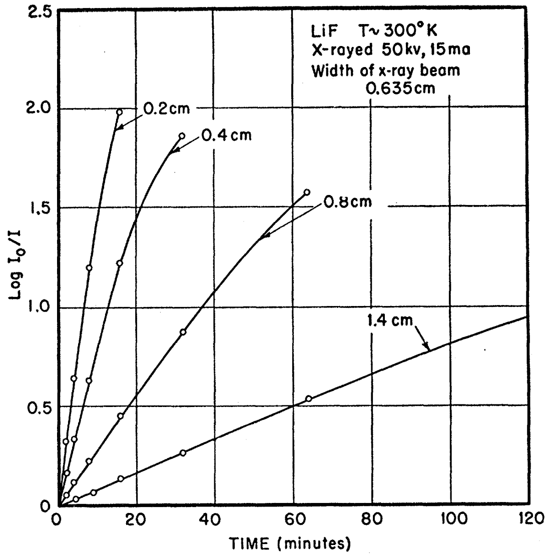

FIG. 6. F center concentration as a function of x-ray exposure time for several depths in LiF.

Figure 5 is a cross plot of data for Fig. 4 and shows F center growth up to two hours of x-ray exposure for several depths in the same NaCl crystal. The growth rate varies markedly through the crystal for the early exposures, and a trend toward saturation soon appears near the x-rayed face. Platt and Markham,[9] Schneider,[7] and Harten[8] have reported qualitatively similar growth curves, although their absorption measurements were taken in the same direction as that of the x-ray beam, and did not show the quantitative differences apparent at various depths in the crystal.

The trend toward saturation appears in the concentration range of $\sim 4\text{–}6\times 10^{16}$ cm^{-3} as shown in the curves taken at depths of 0.2 and 0.4 cm from the x-rayed face of the NaCl. At greater depths the growth rates are not constant, but they vary much more slowly with time than those at the smaller depths. The x-ray intensity incident on the crystal was varied by changing the x-ray tube filament current. The depth curve for a given current and length of exposure was the same within 2 percent as that for one-half the current and twice the length of exposure.

F center growth curves at various depths are shown in Fig. 6 for LiF. In contrast to the behavior of NaCl, the growth rates for LiF are very nearly constant close to the x-rayed face. At optical densities about the same as those for which NaCl showed a trend to saturation, luminescence in the LiF during and following x-ray irradiation had become sufficiently intense to decrease the accuracy of the optical absorption measurements.

Figure 7 shows color center concentration with depth after a thin NaCl crystal had been x-rayed for 2 hours

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[7] See E. E. Schneider in J. W. Mitchell, *Fundamental Mechanisms of Photographic Sensitivity* (Academic Press, New York, 1951), p. 13.

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

[9] R. T. Platt, Jr., and J. J. Markham, Phys. Rev. **92**, 40 (1953).

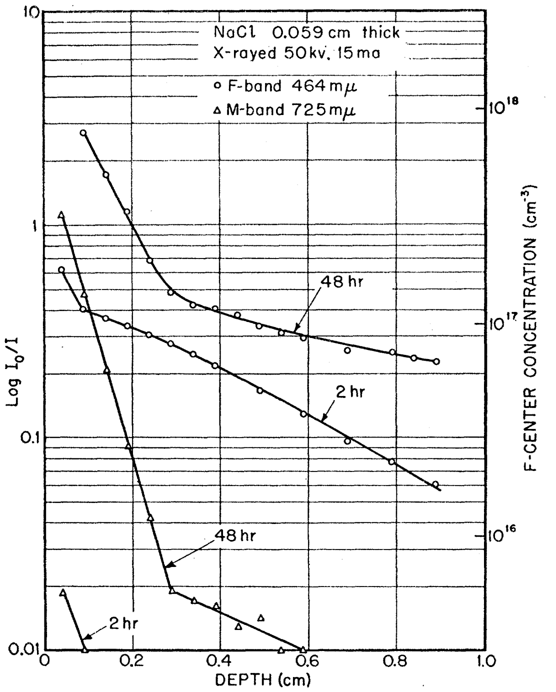

FIG. 7. Color center concentrations as a function of depth in NaCl for 2- and 48-hr x-ray exposure for F band (○) and M band (△).

and 48 hours. For the shorter time the F center curve shows appreciable coloration extending through the crystal. Within 0.1 cm of the x-rayed face there is unexpected increase in F center concentration, greater than the apparent saturation value of $\sim 10^{17}$ cm^{-3}. For the same length of exposure and for depths up to 0.1 cm a small but significant amount of M band is observed.

After 48 hours the F center concentration through the back portion of the crystal is $\sim 10^{17}$ cm^{-3}. Near the front, however, a large increase of F band growth results in concentrations of $\sim 10^{18}$ cm^{-3}. The M band for this exposure is very large in the front and decreases rapidly within the front 0.3-cm region where the F center concentration is $> 10^{17}$ cm^{-3}.

Measurements on other thin NaCl crystals have confirmed the fact that under continued irradiation, and for F center concentrations of $\sim 10^{17}$ cm^{-3}, the growth rate of the F band breaks from the trend toward saturation and rises rapidly. Under these conditions the growth rate of the M band, and also possibly the R and V bands, increase rapidly. The break visible in the depth curves moves into the crystal from the x-rayed face, up to an apparent limiting value which is reached after about 24 hours' exposure to this type of radiation. For NaCl this limiting depth appears to be ~ 0.3 cm for the x-ray intensity employed.

Estermann, Leivo, and Stern[10] reported measurable decreases in crystal density for KCl after x-ray irradiation for several hours with an intensity having the same order of magnitude as was used in the present experiments. This fact leads us to suggest that the large increase in F center growth near the x-rayed surface and the accompanying increase in M center growth are associated with the production of vacancies by the x-rays.

The NaCl crystals x-rayed for long times appear "black" in the portion near the x-rayed face, and yellow in the remaining portion. In Fig. 8 are given three absorption spectra for 35-hour x-rayed NaCl; one was taken in the black portion, one at the diffuse boundary between the black and yellow portions, and one in the yellow portion, at 0.09, 0.29, and 0.49 cm, respectively, from the x-rayed face. Only at the 0.09-cm depth are there indications of appreciable band structure other than the F band. At this depth there is a well defined M band, and indications of two V bands, as well as a long tail on either side of the F band which could include K and R bands.

The half-width of the F band in the yellow portion of this crystal x-rayed for 35 hours is ~ 0.49–0.50 ev, which is about what is observed after short x-ray exposures at any depth. Near the front of the crystal the half-width has grown to ~ 0.61 ev. This variation in half-width is larger than that reported by Mador, Markham, and Platt[11] who included in their study of KBr half-widths at 78°K F bands made by additive coloration as well as x-ray coloration. There may be two reasons for this large half width near the x-rayed face: (1) if the K, V, and R bands in the F band tails are growing faster than the F band, there could be an increase in apparent half-width; (2) the high concen-

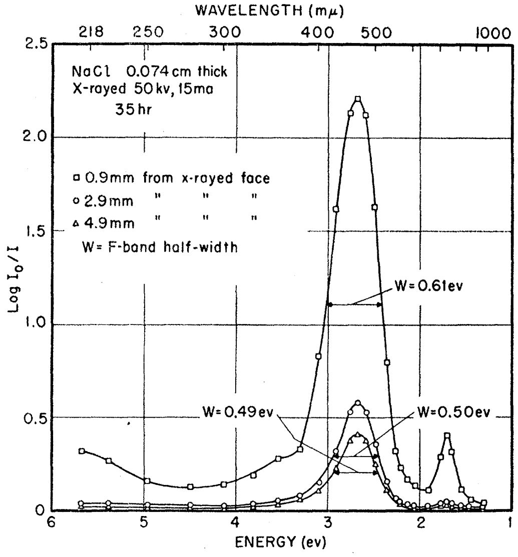

FIG. 8. Absorption spectra of NaCl x-rayed for 35 hr. □ in the black portion; ○ at the boundary between the yellow and black portions; △ in the yellow portion.

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[10] Estermann, Leivo, and Stern, Phys. Rev. 75, 627 (1949).

[11] Mador, Markham, and Platt, Phys. Rev. 91, 1277 (1953).

tration of imperfections at this depth in the crystal might cause interactions which could increase the true half-width.

Figure 9 shows a large amount of *F* and *M* bands extending through the whole depth of an LiF crystal x-rayed for 24 hours. No break similar to that found at 0.3 cm for NaCl is observed for this crystal, but preliminary experiments on a larger LiF sample indicate that a break may occur for this length of exposure at a depth of ~1.8 cm. Another experiment indicates that a similar break occurs in KCl at ~0.15 cm.

An attempt was made to test the hypothesis that vacancy diffusion from a surface is rate determining in *F* center formation. A NaCl crystal was partially cleaved in the direction perpendicular to that of the x-ray beam, and the whole crystal was x-rayed for 16 minutes. The *F* center concentration decreased somewhat more rapidly with depth beyond the cleavage plane than in an uncleaved crystal, but it showed no discontinuity at the cleavage plane to indicate anomalous *F* center growth at the boundary. Absorption measurements were made every 0.25 mm through the cleavage region with a light beam width of ~0.04 cm. For this period of exposure no effect on the rate of growth of *F* centers caused by proximity to a crystal surface was observed.

On the basis of this study, *F* center growth at room temperature appears to be divided into three parts. First, there is an early fast growth which is proportional to the relative x-ray absorption through the whole crystal. Secondly, there is a slower growth tending to a saturation concentration through the whole crystal, which for various NaCl samples ranges between $\sim 6\times 10^{16}$ and $\sim 2\times 10^{17}$ *F* centers per cm^3. Thirdly, there is an increased growth in the very heavily x-rayed front portion of these relatively large crystals, which is accompanied by growth of other centers.

IV. OPTICAL BLEACHING OF *F* CENTERS IN NaCl

The analysis of the optical bleaching of *F* centers is simplified if the crystal is uniformly colored so that the local and average concentrations are equal. In actual practice the nonuniform absorption of x-rays and of bleaching light lead to gradients in the *F* center concentration.

The technique of orienting the bleaching light path perpendicular to the axis of x-ray permits one to study substantially uniform initial concentrations provided the light beam is sufficiently narrow. A condition of uniform light absorption throughout the region of bleaching may be approximated by choosing *F* center concentrations and crystal thicknesses so that only a small fraction of the incident light is absorbed.

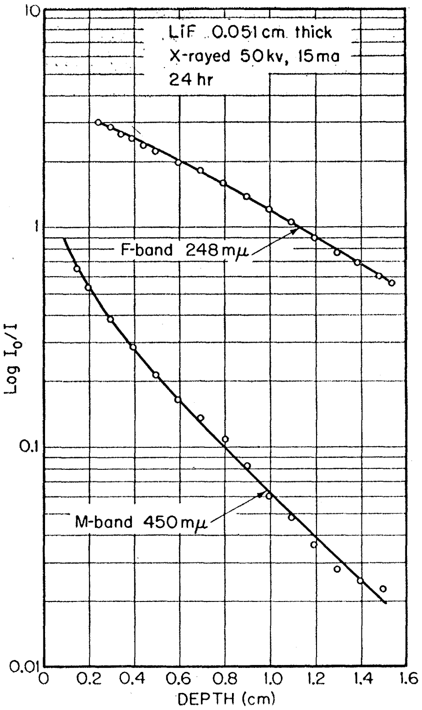

FIG. 9. Color center concentrations as a function of depth in LiF after 24-hr x-ray exposure.

Observations[12] of photocurrents in x-rayed crystals during irradiation with *F* light at room temperature indicate that electrons are transferred to the conduction band in optical bleaching. The conduction electrons may then be captured either by positive holes or by negative ion vacancies. The nonlinear kinetic equations for these processes may be written as

$$dn_F/dt=-\sigma_F I n_F+k_1 n_c n_v, \tag{9}$$

$$dn_c/dt=\sigma_F I n_F-k_1 n_c n_v-k_2 n_c n_h, \tag{9a}$$

$$dn_v/dt=\sigma_F I n_F-k_1 n_c n_v, \tag{9b}$$

$$dn_h/dt=-k_2 n_c n_h, \tag{9c}$$

where I is the local intensity of the bleaching *F* light, n_F, n_c, n_h, and n_v are the local concentrations of *F* centers, conduction electrons, holes, and negative-ion vacancies, respectively, σ_F is the cross section for the optical decomposition of *F* centers, and k_1 and k_2 are rate constants. Conservation of charge and of negative-ion vacancies lead to the equations

$$n_h=n_c+n_F, \tag{10}$$

and

$$n_v^0+n_F^0=n_v+n_F=N, \tag{10a}$$

where n_v^0 and n_F^0 are the respective initial concentrations.

A simple limiting case arises if the capture cross section of a vacancy for a conduction electron is negligible, i.e., $k_1=0$. Then

$$dn_F/dt=-\sigma_F I n_F. \tag{11}$$

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[12] J. J. Oberly and E. Burstein, Phys. Rev. **79**, 217 (1950).

The rate of optical bleaching of F centers in KCl has been investigated by Grant[13] and by Hesketh.[14] Their results are consistent with the first-order decay law given by Eq. (11) only at the start of the bleaching period. Hesketh then considered the possibility of capture of conduction electrons by vacancies. He assumed that n_c is a constant in time and is negligible compared with n_F and that $k_1=k_2$. Hesketh expressed the rate equation involving these assumptions in terms of the average F center concentration and average light absorption throughout the crystal. It was found that the experimental data were not consistent with this rate equation.

Before rejecting the above mechanism it is worthwhile to investigate whether the discrepancy found by Hesketh is due to the nonvalidity of the special assumptions made or to F center concentration gradients and nonuniform light absorption in the crystal.

In terms of our notation involving local concentrations, Hesketh's assumptions lead to the rate equation

$$dn_F/dt=-(\sigma_F I/N)n_F^2, \tag{12}$$

which, on integration with respect to time, gives

$$n_F^0/n_F=1+(n_F^0/N)\sigma_F It. \tag{13}$$

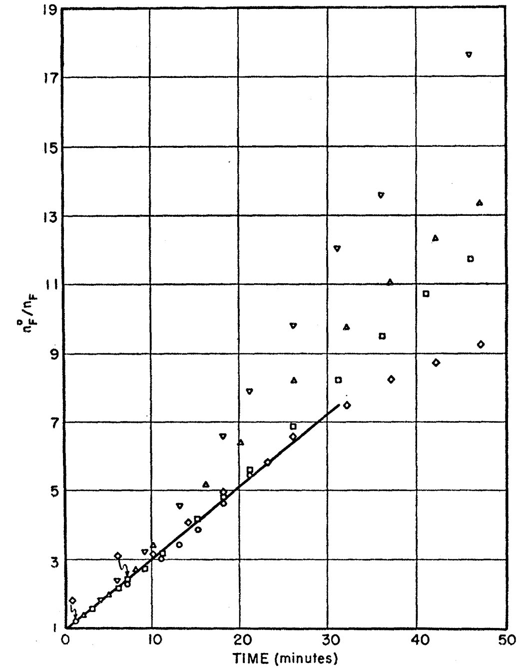

FIG. 10. Reciprocal of the fraction of F centers optically bleached *vs* time in a "thin" NaCl crystal. Initial F center concentrations (cm^{-3}): ○—3.2×10^{16}; ◇—4.3×10^{16}; □—6.7×10^{16}; △—8.7×10^{16}; ▽—1.4×10^{17}.

The system of Eqs. (9)–(10a) may be integrated exactly[15] for the case $k_1=k_2$ without placing restrictions on n_c. One obtains

$$\frac{N}{n_F}=\frac{(N/n_F^0)+\alpha[\tau-\beta^{-1}(1-e^{-\beta\tau})]}{1-\alpha(1-e^{-\beta\tau})}, \tag{14}$$

where

$$\tau=k_2Nt, \tag{14a}$$

$$\gamma=\sigma_F I/(k_2N), \tag{14b}$$

$$\beta=1+\gamma, \tag{14c}$$

$$\alpha=\gamma/\beta. \tag{14d}$$

The quantity k_2N may be expected[15] to be $\sim10^8$ sec^{-1}. For times long compared with 10^{-8} sec, neglect of the exponential terms is justified and leads to the approximation

$$\frac{n_F^0}{n_F}=1+\gamma-\left(\frac{n_F^0}{N}\right)\left(\frac{\gamma}{1+\gamma}\right)+\left(\frac{n_F^0}{N}\right)\sigma_F It. \tag{15}$$

For ordinary light intensities γ may be expected[15] to be a small number $\sim10^{-8}$ and may be neglected compared with unity. Equation (15) then becomes identical with Eq. (13) derived for a stationary state in the conduction electrons. The special assumptions concerning n_c made by Hesketh appear to be quite well justified for the interpretation of the optical bleaching data. According to Eqs. (13) and (15), a plot of n_F^0/n_F *vs* t is linear.

Experimental data for the optical bleaching of a "thin" crystal are plotted in Fig. 10. The optical density $\log(I_0/I)$ at the F band maximum is taken to be proportional to the average F center concentration along the light path. For uniform concentrations,

$$\left(\log\frac{I_0}{I}\right)_{t=0}\bigg/\left(\log\frac{I_0}{I}\right)_{t=t}=\frac{n_F^0}{n_F}. \tag{16}$$

The curves for the three lowest initial F center concentrations are quite linear over the major portion of the bleaching period. The curves for the two highest concentrations are not linear. After several minutes of bleaching, the slopes are appreciably larger than those for the low concentrations. Although it is not evident in Fig. 10, the experimental data indicate that the initial slopes are somewhat smaller than the low concentration slopes.

In Fig. 11 are plotted optical bleaching data for a "thick" crystal in which the x-rayed region was 6.3 mm thick. The two lower concentrations yield plots of n_F^0/n_F *vs* t which are fairly linear. The highest concentration shows a smaller slope than the low concentrations in the region $n_F^0/n_F<3$ while at larger values of n_F^0/n_F the slope increases.

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[13] D. F. Grant, thesis, University of Durham, Durham, England, 1950 (unpublished). We are indebted to Dr. E. E. Schneider for copies of this thesis and that referred to in reference 14.

[14] R. V. Hesketh, thesis, University of Durham, Durham, England, 1953 (unpublished).

[15] Herman, Meyer, and Hopfield, J. Opt. Soc. Am. **38**, 999 (1948).

Since the optical density is proportional to the product of F center concentration and thickness of the x-rayed region, the linear relation between n_F^0/n_F and t has been observed over a tenfold range of n_F^0 values for the two thicknesses employed. The explanation for the results at the high concentrations is not completely clear. At high concentrations the light absorption is not uniform and concentration gradients develop during bleaching. To take into account this effect as well the recapture of electrons by vacancies would require the solution of a nonlinear partial differential equation and has not been attempted as yet.

Some qualitative observations may, however, be made. For uniform initial F center concentrations Eq. (12) may be integrated over the thickness of the crystal. The initial rate of change of the average F center concentration is then found to be proportional to the average light intensity along the light path. The average intensity is smaller for high concentrations than for low concentrations. The initial slopes in the plot of n_F^0/n_F vs t may then be expected to be smaller in the former case than in the latter.

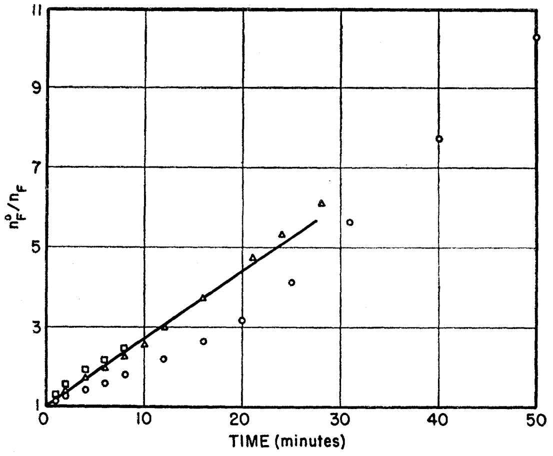

FIG. 11. Reciprocal of the fraction of F centers optically bleached *vs* time in a "thick" NaCl crystal. Initial F center concentrations (cm^{-3}): □—6.7×10^{15}; △—1.7×10^{16}; ○—4.6×10^{16}.

The effect of concentration gradients on the rate may be investigated for the case of a constant gradient and uniform light intensity. If the gradient is g, integration of Eq. (12) over the thickness d_0 of the crystal yields

$$dN_F/dt = -(\sigma_F I/N)[(N_F^2/d_0)+(g^2d_0^3/12)], \quad (17)$$

where

$$N_F = \int_0^{d_0} n_F dy. \quad (17a)$$

For $g=0$,

$$dN_F/dt = -(\sigma_F I/N)(N_F^2/d_0). \quad (17b)$$

A constant concentration gradient, therefore, leads to an increased rate over that for a zero gradient and the same average concentration. This effect offers a possible explanation for the relatively large slopes found at high concentrations and long bleaching times.

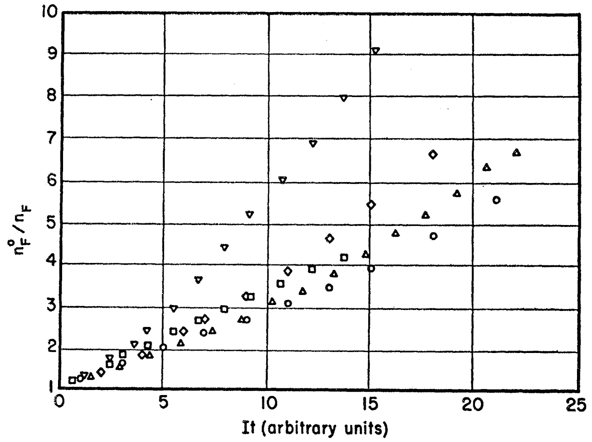

FIG. 12. Reciprocal of the fraction of F centers optically bleached with light of intensity $I=fI_i$ in a "thin" NaCl crystal as a function of It. Initial F center concentrations (cm^{-3}) and relative intensity, f: □—3.2×10^{16}, 0.305; △—3.1×10^{16}, 0.734; ○—3.2×10^{16}, 1.00; ▽—1.39×10^{17}, 0.305; ◇—1.44×10^{17}, 1.00. $I_i=37$ μwatt/cm^2.

Another variable which affects the slope of the n_F^0/n_F vs t plot is the ratio n_v^0/n_F^0. The near coincidence of the plots at low concentrations indicates that in these cases this ratio is nearly constant. The changes in slope found in passing to higher concentrations may involve a variation in n_v^0/n_F^0.

The above discussion indicates that the discrepancy found by Hesketh is not due to the special assumptions concerning n_c and the rate constants, but may be attributed to F center concentration gradients and nonuniform light absorption in the crystal.

Equation (13) predicts that n_F^0/n_F is a function of the product It. In Fig. 12 are plotted experimental data for optical bleaching of a thin crystal for various intensities of the incident light. For the low initial concentrations the curves nearly coincide. This result is consistent with a dependence of n_F^0/n_F on It, and with a nearly constant value of the ratio n_F^0/N for the three examples at low concentrations.

The two curves for high concentrations, on the other hand, show a considerable deviation from one another. This indicates that n_F^0/n_F is a function not only of It but also of some variable such as n_v^0/n_F^0 or of I alone which differs in the two cases.

The initial rate of destruction of F centers specified by Eq. (13) is given by

$$\left(\frac{dn_F}{dt}\right)_{t=0} = -\frac{n_F^0}{N}\sigma_F I n_F^0. \quad (18)$$

If σ_P is the cross section for the absorption of photons, then $\sigma_F = q_1\sigma_P$ where q_1 is the primary quantum efficiency for the destruction of F centers. The local rate of

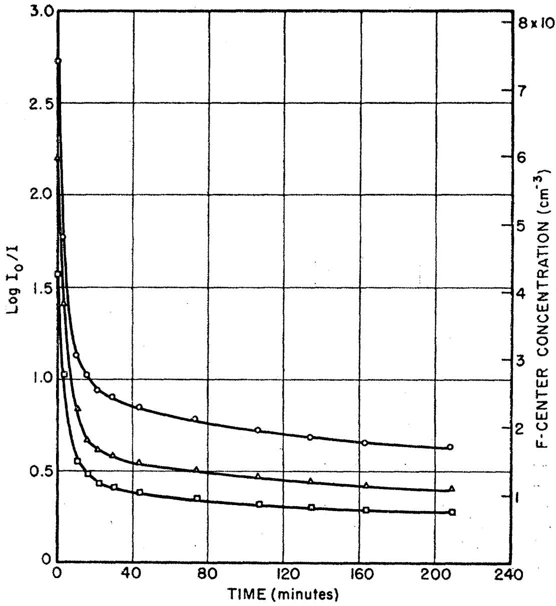

FIG. 13. Thermal bleaching of F centers in a "thick" NaCl crystal at 150°C *vs* time. Initial F center concentrations (cm^{-3}): □—4.3×10^{16}; △—6.0×10^{16}; ○—7.4×10^{16}.

absorption of photons is initially equal to $\sigma_P I n_F^0$. The net quantum efficiency q is defined as the net rate of destruction of F centers divided by the rate of absorption of photons. At $t=0$,

$$q=(n_F^0/N)q_1=[n_F^0/(n_v^0+n_F^0)]q_1. \tag{19}$$

Initial rates of destruction of F centers in the optical bleaching of NaCl were determined from the experimental data by using Smakula's formula given in Eq. (8). The bleaching light intensity was measured as described in Sec. II. The net quantum efficiency q was then calculated to be $\sim$0.3. Within the limit of experimental error the value of q was found to be the same for the various values of n_F^0 considered. The present result is nearly equal to the value 0.23 found by Camagni and Chiarotti[16] for the initial net quantum yield for the optical bleaching of F centers in x-rayed KCl containing strontium impurity.

A value of q less than unity follows from Eq. (19) if q_1 is less than unity, or if $n_v^0\neq0$, or both. If n_v^0 is proportional to n_F^0, then Eq. (19) indicates a lack of dependence of q on n_F^0. The assumptions that q_1 is unity at room temperature and that $n_v^0>0$ are consistent with the present data, and with the quantum yields obtained by Pick[17] for the transformation of F centers to F' centers in additively colored KCl and NaCl.

V. THERMAL BLEACHING OF F CENTERS IN NaCl

Thermal decay of F centers in "thick" NaCl crystals was studied at various depths through the crystals in the temperature range 29° to 150°C. Prior to a thermal bleaching experiment the F center concentration of a freshly x-rayed NaCl crystal was determined at room temperature. The crystal and holder were then removed from the spectrophotometer while the oven was heated to the desired temperature. Zero time for the run was taken when the crystal was replaced in the hot oven, although it took 5 to 10 minutes for the sample to reach thermal equilibrium. Because the F band $\lambda_{\max}$ shifted towards longer wavelengths as the crystal temperature increased, measurements for the three highest temperature runs were taken at 470 mμ instead of 464 mμ. The room temperature determinations of the initial concentrations were corrected to account for the decrease of the absorption at the band maximum with increasing temperature at constant concentration. This was observed in a separate run, and found to be 0.06 percent per degree.

Figure 13 shows the F center concentration as a function of time for 150°C bleaching at three depths in the crystal. There is rapid bleaching at first, followed by a long period of slow bleaching, typical of all the bleaching curves. The break from fast to slow bleaching is more gradual for the depth with the highest initial concentration.

Figure 14 shows decay curves for different temperatures taken at about the same depth in the crystal, and hence for almost the same original concentration. The initial fast decay accounts for most of the bleaching observed, representing approximately 60 to 80 percent for the 140° and 150°C runs, respectively. In this

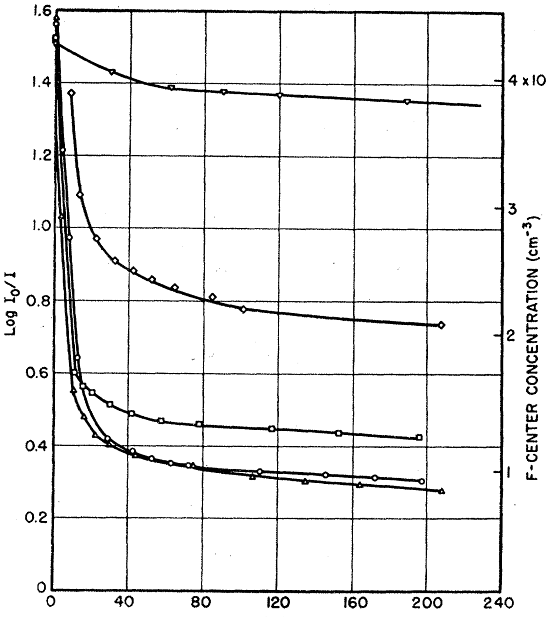

FIG. 14. Thermal bleaching of F centers in a "thick" NaCl crystal *vs* time at various temperatures. Initial F center concentrations $\sim4.5\times10^{16}$ cm^{-3}. ▽—29°C; ◇—98°C; □—120°C; ○—140°C; △—150°C.

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[16] P. Camagni and G. Chiarotti, Nuovo cimento **XI**, 1 (1954).
[17] H. Pick, Ann. Physik **31**, 365 (1938).

temperature range the bleaching rates in the slow portion are the same within experimental error. All the curves decrease continuously with no leveling off, even in the very slow decay just above room temperature. Bleaching was 99 percent complete at 150°C after 92 hours; it was only 86 percent complete at 120° after 120 hours.

Figure 15 is a plot of the reciprocal of the fraction of *F* centers bleached *vs* time. The initial slopes of the 120°–150° runs are comparable with those observed for the 10^{14} quanta/(cm^2 sec) *F* light optical bleaching, but the subsequent lower slopes, representing the break from fast to slow thermal decay, are a departure from the behavior of the optical decay slopes. The room temperature thermal decay shows the same qualitative behavior as that of the higher temperatures.

In a separate experiment a crystal was bleached at 140°C for two hours and then bleached optically at room temperature. The optical decay proceeded at nearly the same rate for the remaining concentration as in a freshly x-rayed crystal, and was not changed by the prior removal of those *F* centers involved in the initial fast thermal decay.

Luminescence at room temperature was observed from the heavily x-rayed region of a NaCl crystal. Thermoluminescence had been reported in KCl by Grant[13] and Hesketh[14] to accompany thermal bleaching, and was attributed to direct recombination of the *F* center electron and a positive hole. Heating an x-rayed NaCl crystal on a hot plate produced a substantial amount of blue-white thermoluminescence, particularly during the first several minutes while the crystal was warming up.

The thermal bleaching curves such as in Figs. 14 and 15 are not amenable to analysis in terms of one or two independent monomolecular processes,[13,14] nor can they be explained by the model developed for the optical bleaching involving electron excitation to the conduction band and retrapping.

Thermal bleaching has been considered[14] to involve a tunneling process with a very small activation energy in which the *F* center electron recombines with a positive hole without entering the conduction band. No activation energy could be determined from the present experiments, though this may be due only to the small temperature range covered. The break from fast to slow bleaching would probably have to be explained in terms of a spatial arrangement of nearby and faraway holes if tunneling were the only process involved.

It is possible that tunneling at the onset of thermal decay might cause sufficient luminescence to produce some optical bleaching, the cessation of which, shortly after the sample attains thermal equilibrium, might contribute to the relatively sharp break back to a purely thermal decay process.

The present experiments on the thermal bleaching of *F* centers in NaCl have shown a fast decay followed by a slow decay, which, in the absence of knowledge concerning conductivity and luminescence effects are very difficult to analyze to yield an understanding of the mechanisms involved.

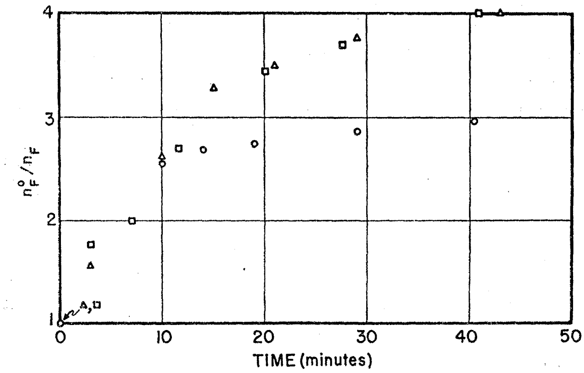

FIG. 15. Reciprocal of the fraction of *F* centers thermally bleached in a "thick" NaCl crystal *vs* time with initial concentrations ~6.5×10^{16} cm^{-3}. ○—120°C; □—140°C; △—150°C.

VI. VACANCIES

To obtain evidence concerning the role of negative ion vacancies in the growth and decay of *F* centers, several qualitative experiments were carried out by investigating the relationship of the α and β bands to the *F* band in KI. The α band is ascribed[18] to the excitation of an ion adjacent to a negative ion vacancy, and the β band to that of an ion adjacent to an *F* center. Both bands lie in the ultraviolet and are obscured by the tail of the first fundamental except at low temperatures. Even at low temperatures the quantitative determination of their intensities is difficult.

The intensity of the β band is roughly proportional to that of the *F* band, both during growth by x-raying and bleaching by *F* light, at 78° and 5°K.[18] The α band can be developed to some extent by x-raying. However, it is also observed in some KI crystals additively colored[19] with excess K and in some KI crystals prior to x-raying. Partial emptying of *F* centers during the quenching of the additively colored crystals could account for the former case, and divalent negative-ion impurities could account for the latter case. It is also possible that the appearance of the α band at these low temperatures indicates that some single negative-ion vacancies have been frozen in from a higher temperature equilibrium vacancy concentration. For an x-rayed crystal, the largest amounts of α band are observed after *F* band optical bleaching.

To study the possible formation of negative-ion vacancies during x-ray irradiation a KI crystal was x-rayed and optically bleached at 78°K. This crystal was then cooled to 5°K and x-rayed again. A second KI crystal was x-rayed at 5°K for the first time. The

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[18] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952).

[19] R. T. Platt, Jr. and J. J. Markham (private communication).

rate of growth of the *F* band for the reirradiation of the first crystal was much larger than that for the initial irradiation of the second crystal. This result indicates that negative ion vacancies may be formed by x-raying at low temperatures, and that their concentration may be rate determining in the growth of *F* centers. On the basis of this, then, one would expect that the concentration of unfilled negative ion vacancies during irradiation would be negligible compared with the *F* center concentration. However, the simultaneous formation of an *F* band and an α band indicates that the concentration of unfilled negative ion vacancies is not negligible. The destruction of *F* centers during x-raying may be a possible explanation for the presence of these unfilled vacancies.

During the α- and β-band studies of KI several other observations were made. As with KBr,[20] a large fraction of the *F* centers bleach when irradiated with *F* light at 78° and 5°K, and after bleaching there is partial dark recovery. A low, wide band at 275 mμ[18] grows at low temperatures independent of any x-raying or bleaching, and seems to be caused not by an impurity in the crystal, but possibly by a surface deposit condensed on the crystal.

It appeared likely that vacancies could be involved in the addition and removal of water from natural rock salt crystals as reported by Barnes.[21] We found that water was readily removed from such crystals by heating, as measured by the intensity of absorption at $\sim 3\ \mu$, but all of our attempts to introduce H_2O into natural or synthetic crystals were unsuccessful. The addition was tried by immersion in liquid H_2O under various conditions of *p*H, temperature, and mechanical deformation, and by heating in steam in a high-pressure bomb.

VII. CONCLUSION

It has been possible to minimize the difficulties due to nonuniform color center concentrations inherent in x-ray colored crystals by making optical absorption measurements perpendicular to the direction of x-ray penetration.

It appears that there is approximate proportionality between the number of *F* centers produced and the amount of x-ray radiation absorbed for short times of exposure. The production of large concentrations of both *F* and *M* centers after prolonged irradiation as well as the low-temperature rate of growth of *F* centers in a crystal previously x-rayed and optically bleached indicate that vacancies are created by the x-rays.

Experimental rates of optical bleaching of *F* centers at low concentrations may be explained on the basis of a set of nonlinear differential equations describing the transfer of *F* center electrons to the conduction band and trapping of the conduction electrons by holes and vacancies. Observations on thermal bleaching, however, may not be so interpreted at present.

We believe that additional understanding of the mechanisms involved in the formation and bleaching of color centers could be achieved by electrical conductivity measurements in conjunction with determinations of growth and bleaching rates.

VIII. ACKNOWLEDGMENTS

We wish to express our appreciation to Mr. Joel Selbin for his assistance in calculating x-ray penetration curves and Mr. F. Harler, of the Naval Research Laboratory for assistance in cryogenics. We also wish to thank Miss Doris Rubenfeld for her untiring cooperation in the preparation of the illustrations as well as Miss Shirley Thomas and Miss Agnes Fogelgren for typing the manuscript.

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[20] Markham, Platt, and Mador, Phys. Rev. **92**, 597 (1953).

[21] R. B. Barnes, Phys. Rev. **43**, 82 (1933); **44**, 898 (1933).