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Optical Bleaching of *F* Centers in X-Rayed Alkali Halide Crystals*

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When *F* light is absorbed by *F* centers it is assumed that electrons leave negative-ion vacancies and are transferred to the conduction band. Conduction electrons may be captured by holes and by negative ion vacancies. It is assumed that the cross sections for the latter two processes are equal and that the conduction electron concentration is small and stationary. Under these conditions the local *F*-center concentration, n, is specified by the equation $\partial n/\partial t=-bIn^2$, where I is the local *F*-light intensity assumed to be given by the Beer-Lambert law and b is a constant. Exact expressions for n and I have been obtained for the case of a uniform initial *F*-center distribution. The theoretical results are compared with quantitative measurements of the *F*-center concentration as a function of *F*-light irradiation time in x-rayed NaCl for a range of incident light intensities and initial *F*-center concentrations. It is found that the behavior of the model is consistent with experimental data in lightly x-rayed crystals having initial concentrations in the range $\sim 10^{16}$–$\sim 10^{17}$ cm^{-3}. In more heavily x-rayed crystals, appreciable growth of M and R bands occurs during the bleaching and deviations from the behavior of the model are observed.

I. INTRODUCTION

DURING the course of a recent investigation on the production and bleaching of color centers in x-rayed alkali halide crystals,[1] we became interested in the possibility of describing the optical bleaching process by means of a model. Such a model should take into account the spatial distribution of the centers produced by the x-rays and the nonuniformity of the bleaching light intensity throughout the crystal. The model should also be consistent with the fact that photoconductivity[2] is associated with optical bleaching at temperatures that are not too low and with the possibility that there is an appreciable concentration of unfilled negative ion vacancies in an x-rayed alkali halide crystal. Mathematical descriptions of this kind have been studied in connection with the luminescence and conductivity of phosphors.[3] Similar models have been applied to the case of electronic conductivity in semiconductors.[4]

Relatively little work on the above type of models has been done for color center phenomena in the alkali halide crystals. We feel that the investigation of the properties of theoretical models is important as a means of interpreting quantitative experimental data. Even the study of simple models may yield some understanding of the gross features of the data and provide a basis for more "realistic" models.

The present paper deals specifically with the bleaching by *F* light of *F* centers produced by x-rays in crystals of various thicknesses. A range of bleaching light intensities and initial color-center concentrations was employed.

II. EXPERIMENTAL

All of the experimental work described in this paper concerns single crystals of NaCl obtained in various lots from the Harshaw Chemical Company. The x-ray coloration was done at room temperature using a Picker-Waite diffraction unit with a Machlett x-ray tube and an accelerating voltage of 50 kv. The optical absorption measurements and bleaching were carried out at room temperature with a Beckman Model DU spectrophotometer having a 2-volt and 6-volt Sorensen power supply.

The *F*-center concentration in an x-rayed crystal is nonuniform in the direction of the x-ray beam. For this reason the direction of the bleaching *F* light as well as the light used for the optical absorption measurements was taken perpendicular to the x-ray beam direction. In this way the bleaching process was initiated in a portion of crystal containing an essentially uniform distribution of *F* centers. The details concerning experimental arrangements and techniques are discussed fully in reference 1.

III. THEORETICAL MODEL

In a previous paper,[1] a discussion was given for the optical bleaching of an initially uniform distribution of *F* centers with the restriction that only a small fraction of the incident light is absorbed and that, consequently, negligible concentration gradients develop during the bleaching process. The present work extends this treatment by removing this restriction.

The electron transfer processes during bleaching involve the elevation of an electron from an *F* center into the conduction band by the absorption of a quantum of radiation and a phonon, and the capture of conduction electrons either by positive holes or by negative ion vacancies.[5] The nonlinear kinetic equations

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

[1] Mador, Wallis, Williams, and Herman, Phys. Rev. **96**, 617 (1954).

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

[3] See, for example, Herman, Meyer, and Hopfield, J. Opt. Soc. Am. **38**, 999 (1948) as well as numerous other references in *Bibliography on Physical Electronics* prepared by W. B. Nottingham and staff (Massachusetts Institute of Technology, Cambridge, 1954).

[4] See report of Conference on Photoconductivity held at Atlantic City, November 4–6, 1954 (to be published).

[5] It should be noted that the *F*-center concentration after optical bleaching was determined after the thermally unstable F'

for these processes may be written as follows,[1] remembering that all dependent variables are both space- and time-dependent:

$$\partial n_F/\partial t = -\sigma_F I n_F + k_1 n_c n_v, \tag{1a}$$

$$\partial n_c/\partial t = \sigma_F I n_F - k_1 n_c n_v - k_2 n_c n_h, \tag{1b}$$

$$\partial n_v/\partial t = \sigma_F I n_F - k_1 n_c n_v, \tag{1c}$$

and

$$\partial n_h/\partial t = -k_2 n_c n_h, \tag{1d}$$

where I is the local intensity of the bleaching F light; n_F, n_c, n_v, and n_h are the local concentrations of F centers, conduction electrons, negative-ion vacancies, and holes, respectively; σ_F is the cross section for the optical decomposition of F centers and k_1 and k_2 are rate constants.[6] The conservation of negative-ion vacancies, filled or unfilled, and the balance between holes and electrons lead to the following equations of condition:

$$n_v^0 + n_F^0 = n_v + n_F = N, \tag{2a}$$

and

$$n_h = n_c + n_F, \tag{2b}$$

where n_v^0 and n_F^0 represent the initial concentrations of unfilled single negative-ion vacancies and of F centers, respectively.

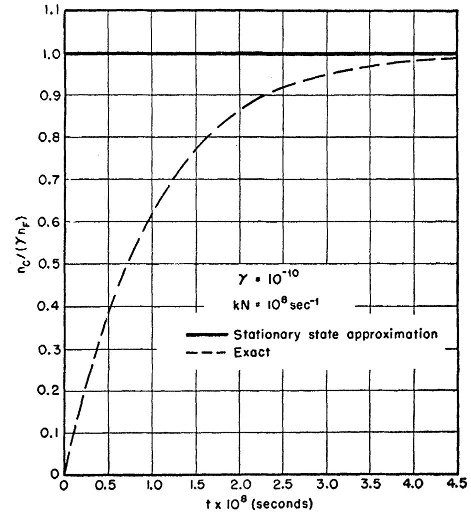

FIG. 1. Comparison of the exact and stationary state solutions for the conduction electron concentration, n_c, as a function of time of bleaching.

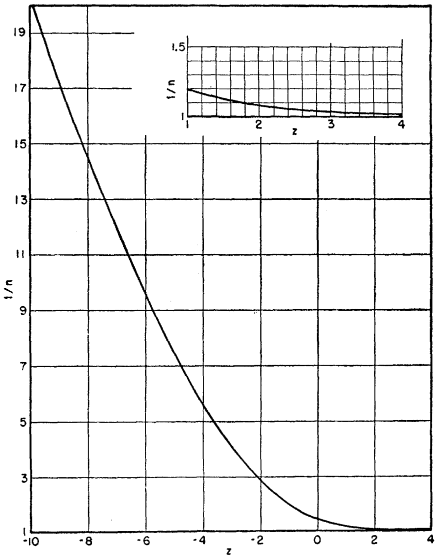

FIG. 2. Exact solution of Eqs. (4) and (6) giving the F-center concentration as a function of z which depends on the depth and time of optical bleaching.

As in previous work,[1,7] we again make certain simplifying assumptions, namely, that the conduction electron concentration is stationary in time, $dn_c/dt=0$, the rate constants k_1 and k_2 are equal, $k_1=k_2=k$, and that $n_F \gg n_c$. From these assumptions and Eqs. (2a) and (2b), it follows from Eq. (1b) that

$$n_c \cong (\sigma_F I/kN) n_F. \tag{3}$$

An exact expression for n_c for the case $k_1=k_2$ with the initial condition $n_c=0$ for $t=0$ is given by[3]

$$n_c = \frac{\gamma\{1-\exp[-(1+\gamma)kNt]\}}{1+\gamma\exp[-(1+\gamma)kNt]} n_F, \tag{3a}$$

where

$$\gamma = \sigma_F I/(kN). \tag{3b}$$

For $\sigma_F \sim 10^{-16}$ cm^2, $I \sim 10^{14}$ quanta cm^{-2} sec^{-1}, $k \sim 10^{-9}$ cm^3/sec, and $N \sim 10^{17}$ cm^{-3}, $\gamma \sim 10^{-10}$ and may be neglected compared with unity. The exponentials in Eq. (3a) may then be neglected for times $t \gg 1/(kN) \sim 10^{-8}$ sec and the approximation given in Eq. (3) is obtained. These results are presented graphically in Fig. 1. It is clear that for physically interesting values of γ and kN the stationary state solution is a very good approximation except for the initial rise time.

Using Eqs. (2a) and (3), Eq. (1a) may be transformed to the simplified form

$$\partial n_F(x,t)/\partial t = -bIn_F^2, \tag{4}$$

where

$$b = \sigma_F/N, \tag{4a}$$

and x is distance measured from the illuminated face

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centers were allowed sufficient time to decay. In the theoretical treatment the influence of the F' center has been neglected. See reference 1. The small thermal decay of F centers in NaCl at room temperature has also been neglected.

[6] Note that if σ_p is the cross section for the absorption of a photon by the F center yielding an excited F center, then $\sigma_F = q_1\sigma_p$ where q_1 is the primary quantum efficiency for the destruction of F centers, i.e., the fraction of the electrons elevated into the excited state which are then transferred to the conduction band by the absorption of a phonon. The constants k_1 and k_2 may be written as $\sigma_1 v$ and $\sigma_2 v$, respectively, where σ_1 and σ_2 are the corresponding cross sections and v is the average speed of the conduction electrons. For orders of magnitude, $\sigma_1 \sim \sigma_2 \sim 10^{-16}$ cm^2, $v \sim 10^7$ cm/sec, and $k_1 \sim k_2 \sim 10^{-9}$ cm^3/sec.

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

of a crystal of thickness x_0 in the direction of the bleaching light beam. In the limiting case where the initial optical density is very low the light intensity I can be assumed to be a constant I_i. Equation (4) then yields upon integration[1]

$$n_F^0/n_F=1+n_F^0 bI_i t. \tag{5}$$

In the more general case, we assume that the Beer-Lambert law is obeyed so that one may write

$$\partial I(x,t)/\partial x=-\sigma_p n_F I, \tag{6}$$

where σ_p is the cross section for the absorption of a photon by an F center.

An exact solution to Eqs. (4) and (6) has been found for the case that $n_F(x,t)$ and $I(x,t)$ satisfy the boundary conditions:

$$n_F(x,t)=n_F^0 \text{ at } t=0 \text{ for all } x, \tag{7a}$$

and

$$I(x,t)=I_i \text{ at } x=0 \text{ for all } t. \tag{7b}$$

If one introduces the dimensionless variables

$$n=n_F/n_F^0, \tag{8a}$$

$$\mathscr{I}=I/I_i, \tag{8b}$$

$$y=\sigma_p n_F^0 x, \tag{8c}$$

$$\tau=s_0 t, \tag{8d}$$

where

$$s_0=n_F^0 bI_i, \tag{8e}$$

then the exact solution may be written as

$$z=-\mathrm{Ei}[\ln(1/n)], \tag{9}$$

where

$$z=y-\mathrm{Ei}[\ln(1+\tau)] \tag{9a}$$

and $\mathrm{Ei}(\xi)$ is the exponential integral function[8] defined by

$$\mathrm{Ei}(\xi)=\int_{-\infty}^{\xi}\frac{\exp\phi}{\phi}d\phi \tag{9b}$$

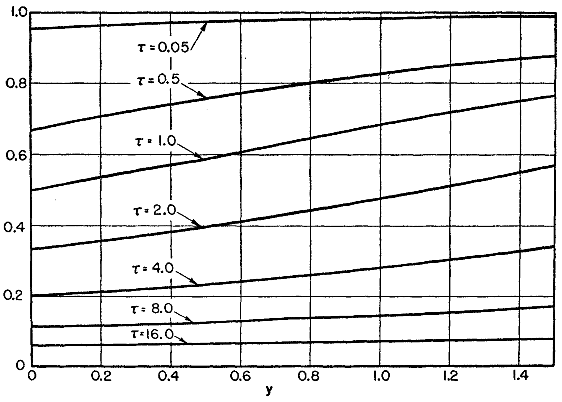

FIG. 3. The F-center concentration as a function of depth in the crystal for various times of optical bleaching according to the exact solution.

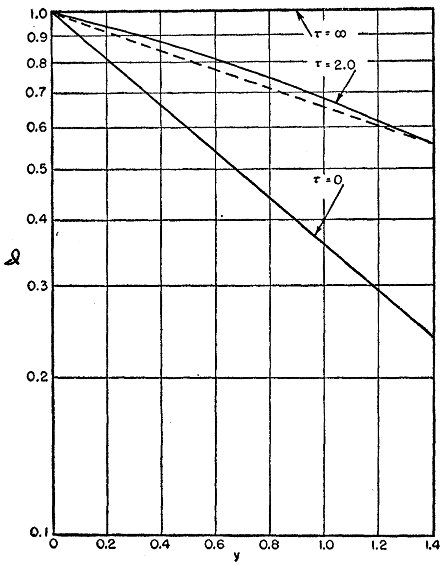

FIG. 4. The bleaching light intensity as a function of depth in the crystal for various times of optical bleaching. The dashed curve shows $\mathscr{I}=f(y)$ for a uniform distribution of F centers having the same average concentration as the solid curve at $\tau=2.0$.

where the principal value of the integral is to be taken. A derivation of Eq. (9) is given in Appendix A.

The local light intensity $\mathscr{I}$ is shown in Appendix A to be given by

$$\mathscr{I}=\ln(1/n)/\ln(1+\tau). \tag{9c}$$

In Fig. 2, is given a plot of $1/n$ *vs* z as obtained from Eq. (9). The value of n for any given depth y and time τ is readily found by first computing z using Eq. (9a) and then determining $1/n$ from Fig. 2.

Equations (4) and (6) may also be integrated numerically by using the finite difference equations,

$$\Delta n_F=-bIn_F^2\Delta t, \tag{10a}$$

$$\Delta I=-\sigma_p n_F I\Delta x, \tag{10b}$$

and the boundary conditions on n_F and I given in Eq. (7). Some of the calculations reported in this paper were made by numerical integration prior to the finding of the exact analytical solution. Spot checks indicated that the numerical results are within ~10 percent of the exact values.

The nonuniformity of the bleaching light in the crystal leads to the formation of concentration gradients during the bleaching. The effect of a concentration gradient has been shown[1] to increase the average bleaching rate compared with the rate for a uniform concentration of the same average value. The variation of n with distance y at various times τ is shown in Fig. 3. It may be seen that for $\tau=2$ the concentration is ~40 percent higher at $y=1$ than at $y=0$.

The variation of light intensity, $\mathscr{I}$, with y at various values of τ is shown in Fig. 4. The presence of a positive F center concentration gradient for $\tau=2$ causes $\mathscr{I}$ to be

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[8] See *Tables of Sine, Cosine, and Exponential Integrals* (Works Projects Administration, Mathematical Tables Project, New York, 1940).

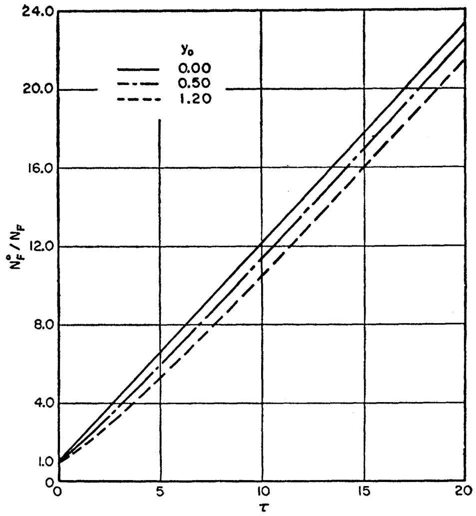

FIG. 5. The reciprocal of the average value of the F-center concentration *versus* the duration of optical bleaching for various crystal thicknesses according to the exact solution.

somewhat larger at interior points of the crystal than the values corresponding to a uniform concentration of the same average value.

The measurement of the optical density yields the average value N_F of the F-center concentration over the thickness of the crystal. In Fig. 5 are plotted theoretical values of N_F^0/N_F against τ for various values of the crystal thickness y_0. In the limit $y_0 \to 0$, the curve is a straight line in agreement with Eq. (5). For any y_0, the initial slope of the curve is proportional to the average initial bleaching light intensity. As y_0 increases, the initial slope accordingly decreases. For given $y_0 > 0$, as τ increases, the slope increases and approaches that of the limiting case $y_0 = 0$.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The optical bleaching experiments on NaCl described below were carried out on both thin ($\sim$0.1 cm) and thick ($\sim$1.0 cm) crystals covering an initial F-center concentration range of $\sim 10^{15}$–$\sim 4\times 10^{17}$ cm^{-3}. The theoretical model discussed in Sec. III appears to agree rather well with the results for initial F-center concentrations of $\sim 10^{16}$–$\sim 10^{17}$ cm^{-3}. Outside this range of concentrations deviations were observed which will be discussed later.

It should be emphasized that there does not appear to be a general theoretical treatment for the optical bleaching of a crystal containing an arbitrary nonuniform initial concentration distribution of F centers. The theory discussed above treats the case of a uniform initial distribution. For this reason the experiments were carried out by bleaching x-rayed crystals in the direction perpendicular to the x-ray beam. The bleaching light beam was sufficiently narrow so that the change in F-center concentration over the beam width was small. Various initial F-center concentrations were obtained by bleaching at various distances from the x-rayed crystal face. The experimental and theoretical results were compared in the following manner. The experimentally measured optical density, $\log_{10}(I_i/I_{x0})$, for a crystal of thickness x_0, can be directly related to the average F-center concentration along the light path, N_F, if the Beer-Lambert law is assumed. The relation is

$$\left(\frac{\ln 10}{\sigma_p x_0}\right)\log_{10}\left(\frac{I_i}{I_{x0}}\right)=\int_0^{x_0} n_F dx \Big/ \int_0^{x_0} dx = N_F, \quad (11)$$

where I_{x0} is the transmitted bleaching light intensity. The cross section for the absorption of photons, σ_p, can be determined assuming Smakula's equation relating the absorption coefficient to the F-center concentration.[9] By using an oscillator strength $f=0.7$ and an F-band half-width of 0.51 ev, σ_p for NaCl was computed to be 1.32×10^{-16} cm^2.

The theoretical value of N_F at any time t is obtained by evaluating the integral in Eq. (11) using the values of n_F *vs* x given by Eqs. (9) and (9a). This result depends on the value of the quantity $s_0 = n_F^0 b I_i$ which defines the dimensionless time coordinate in Eq. (8d). The quantity s_0 was adjusted to secure the best agreement between theory and experiment. If one assumes that the quantum yield $q_1 = 1$ (see footnote 6) then $\sigma_F = \sigma_p$. Since I_i and σ_p are known and since n_F^0 can be determined by using Eq. (11), the adjustment of s_0 yields the value of N which is the total number of filled and unfilled single negative-ion vacancies.

The values of N_F^0/N_F derived from experiment on an NaCl crystal are plotted against the time of bleaching t in Fig. 6 for initial F-center concentrations between 0.34×10^{16} and 1.42×10^{16} cm^{-3}. The incident bleaching light intensity was maintained constant at 0.87×10^{14} quanta cm^{-2} sec^{-1}. The theoretical values of N_F^0/N_F

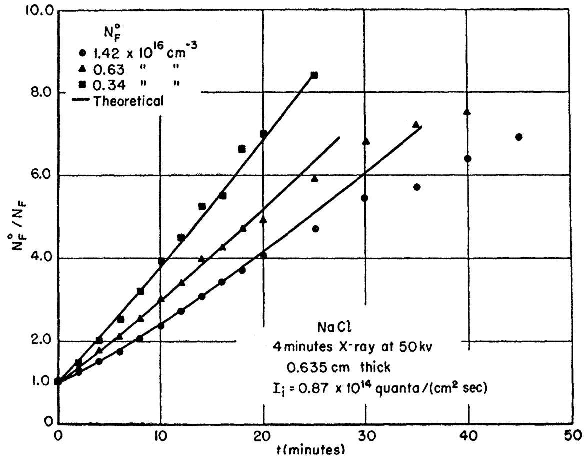

FIG. 6. A comparison of theory with experiment for the optical bleaching of F centers in x-rayed NaCl for initial F-center concentrations in the range $\sim 10^{15}$–$\sim 10^{16}$ cm^{-3}.

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[9] A. Smakula, Z. Physik **59**, 603 (1930).

with s_0 chosen to give the best fit to experiment are indicated by the solid lines. The agreement between theory and experiment is quite good except for the bleaching of the last 25 percent of the *F* centers in the case of the two highest initial concentrations. The origin of this discrepancy is not clear.

Experimental data and theoretical curves for the bleaching of an NaCl crystal at initial concentrations between 0.32×10^{17} and 1.44×10^{17} cm^{-3} are presented in Fig. 7. The intensity of the bleaching *F* light was the same as in the former case. The experimental results are seen to be consistent with the behavior of the model.

A series of bleaching experiments were carried out at the same initial *F*-center concentration but different incident bleaching light intensities. The results are given in Fig. 8 for $n_F{}^0=0.31\times10^{17}$ cm^{-3} and in Fig. 9 for $n_F{}^0=1.4\times10^{17}$ cm^{-3}. In this series of experiments the bleaching light intensity varied from $\sim3\times10^{13}$–$\sim9\times10^{13}$ quanta cm^{-2} sec^{-1}.

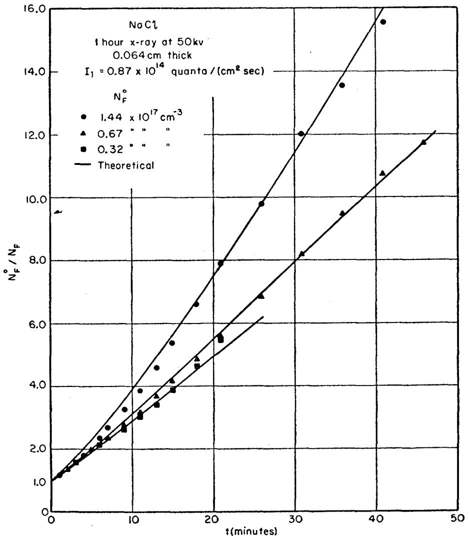

FIG. 7. A comparison of theory with experiment for the optical bleaching of *F* centers in x-rayed NaCl for initial *F*-center concentrations in the range $\sim10^{16}$–$\sim10^{17}$ cm^{-3}.

Values of the parameter $N=n_F{}^0+n_V{}^0$ were computed from the values of s_0 obtained by the fitting of the theoretical curves to the experimental data. The results are given in Table I. The quantity $n_F{}^0+n_V{}^0$ is plotted against $n_F{}^0$ in Fig. 10. Now an increase in $n_F{}^0$ unaccompanied by an increase in the total number of filled or unfilled single negative ion vacancies, i.e., $n_F{}^0+n_V{}^0$, would imply that the x-ray process fills but does not produce negative ion vacancies. The fact that $n_F{}^0+n_V{}^0$ is roughly proportional to $n_F{}^0$, as can be seen in Fig. 10, is evidence that the x-ray process produces single negative ion vacancies.

Reference to Table I shows that for a given value of $n_F{}^0$ the value of $n_F{}^0+n_V{}^0$ determined by a bleaching experiment is essentially independent of the bleaching light intensity, I_i. This result is consistent with the foregoing theoretical model in that I_i occurs only in the product s_0t as shown in Eqs. (8d) and (8e).

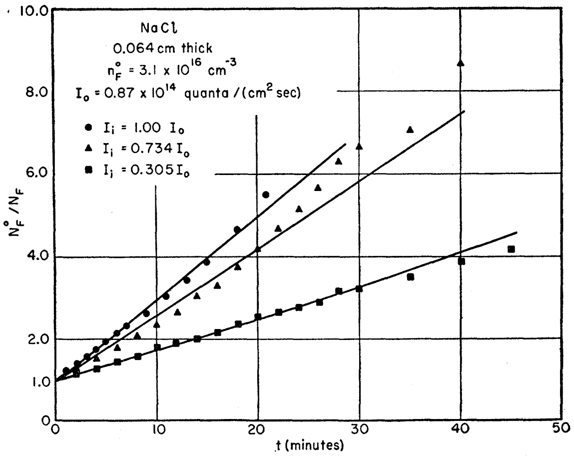

FIG. 8. A comparison of theory with experiment for the optical bleaching of *F* centers in x-rayed NaCl for various bleaching light intensities at an initial *F*-center concentration of $\sim3\times10^{16}$ cm^{-3}.

For initial *F*-center concentrations outside the range $\sim10^{16}$–$\sim10^{17}$ cm^{-3} we consider first the case of crystals x-rayed for a prolonged period and having initial concentrations between $\sim1\times10^{17}$ and $\sim4\times10^{17}$ cm^{-3}. In Fig. 11 is shown $N_F{}^0/N_F$ *vs* t for a NaCl crystal x-rayed for $\sim$40 hr at 50 kv. Two features of the curves should be noted, namely, that the rate of bleaching is considerably lower than for lower initial *F*-center concentrations and that the curvature is different than in the former cases and is not in agreement with the proposed model for the case $k_1=k_2$.[11] During these optical bleaching experiments it was noted that the *R* and *M* bands grew to a significant extent as the *F* band was bleached. However, this was not observed for crystals having shorter x-ray irradiation times.

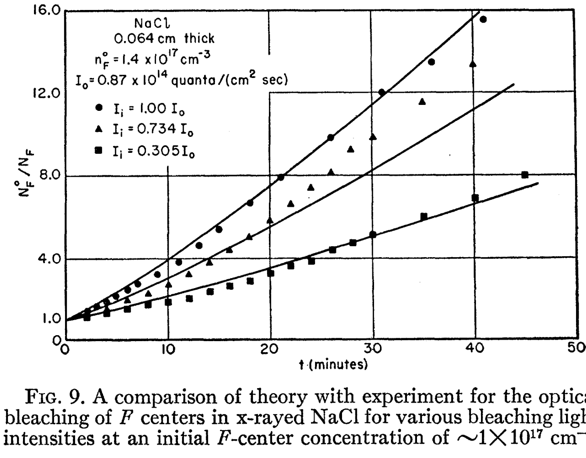

FIG. 9. A comparison of theory with experiment for the optical bleaching of *F* centers in x-rayed NaCl for various bleaching light intensities at an initial *F*-center concentration of $\sim1\times10^{17}$ cm^{-3}.

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[11] See Fig. 5 which shows the curvature predicted by the model for $k_1=k_2$.

TABLE I. Parameters $n_V{}^0$ and $n_V{}^0+n_F{}^0$ for various initial F-center concentrations and incident bleaching light intensities.

$n_F{}^0$ cm^{-3}	I_i quanta cm^{-2} sec^{-1}	$n_V{}^0+n_F{}^0$ cm^{-3}	$n_V{}^0$ cm^{-3}
0.34×10^{16}	0.87×10^{14}	0.82×10^{16}	0.48×10^{16}
0.63×10^{16}	0.87×10^{14}	2.0×10^{16}	1.4×10^{16}
1.4×10^{16}	0.87×10^{14}	5.1×10^{16}	3.7×10^{16}
3.2×10^{16}	0.87×10^{14}	1.13×10^{17}	8.1×10^{16}
3.1×10^{16}	0.64×10^{14}	1.00×10^{17}	6.9×10^{16}
3.2×10^{16}	0.27×10^{14}	0.89×10^{17}	5.7×10^{16}
6.7×10^{16}	0.87×10^{14}	2.0×10^{17}	1.3×10^{17}
1.4×10^{17}	0.87×10^{14}	2.8×10^{17}	1.3×10^{17}
1.4×10^{17}	0.64×10^{14}	2.8×10^{17}	1.3×10^{17}
1.4×10^{17}	0.27×10^{14}	1.9×10^{17}	0.5×10^{17}

It may be seen from Fig. 7 and Fig. 11 that the bleaching rate for the concentration $n_F{}^0=\sim1\times10^{17}$ cm^{-3} was considerably slower in the crystals x-rayed for a prolonged period (heavily x-rayed crystals) than in those x-rayed for a short time (lightly x-rayed crystals). This difference may be due only to a difference in the particular crystals or it may be due to the difference in the intensity and hardness of the x-rays at different depths in the crystal. To attempt to clarify this point, two specimens cleaved from the same crystal were x-rayed, one for one hour and the other for $\sim$40 hours. They were then re-x-rayed in a direction perpendicular to the original direction of x-ray at depths for which the F-center concentration was $\sim5.5\times10^{16}$ cm^{-3} in each case. It was found that the rate of production of F centers during the second irradiation was significantly larger in the crystal initially irradiated for 40 hours than in that irradiated for one hour. This result and the difference in the optical bleaching rates appear to be consistent with a larger value of $n_V{}^0/n_F{}^0$ at a given value of $n_F{}^0$ in a crystal irradiated for a prolonged period at low x-ray intensity than in a crystal irradiated for a short period at a high intensity of somewhat softer x-rays.

Another possible explanation for the slowness of bleaching in heavily x-rayed crystals and for the shape of the curves in Fig. 11 is that some of the holes are trapped in an aggregate of positive-ion vacancies such that the resulting V center has a small cross section for capture of conduction electrons. It has been observed by Casler, Pringsheim, and Yuster[12] that the so-called V_3 band is present in a KCl crystal x-rayed for two hours at room temperature, that this band does not bleach appreciably when the F band is bleached by F light, and that it is difficult to bleach the F band completely. Seitz[13] has suggested that the V_3 center consists of a hole trapped at a pair of positive-ion vacancies. Such a model would have a net negative charge and would repel conduction electrons. Further experimental work on lightly and heavily x-rayed crystals is required to clarify the role of the V bands during the F-light bleaching of the F band.

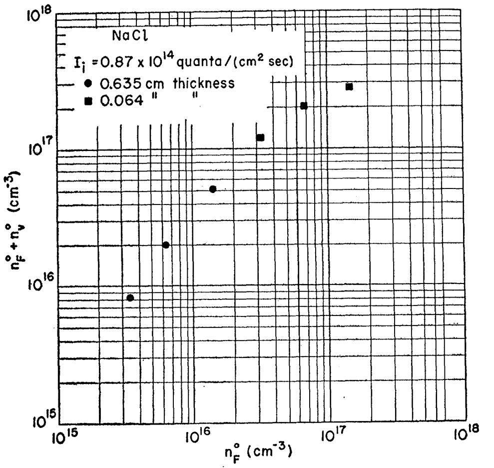

FIG. 10. The total concentration of filled and unfilled negative ion vacancies *versus* the initial F-center concentration.

For initial concentrations in the range 1.0×10^{15}–7.0×10^{15} cm^{-3} optical bleaching rates of the F band were studied using a very thick (1.67 cm) NaCl crystal and short x-ray irradiation times ($\sim$3 min). The results were qualitatively similar to those obtained for the heavily x-rayed crystals (Fig. 11) rather than those for $n_F{}^0$ values in the range 10^{16}–10^{17} cm^{-3} (Fig. 7). No explanation has been established for the deviation of the results for very thick crystals from the behavior of the model. It is possible that impurities are playing a significant role in the concentration range under 10^{16} cm^{-3}.

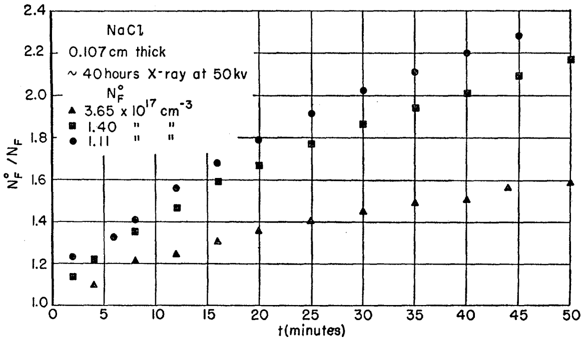

FIG. 11. Experimental values of the reciprocal of the average F-center concentration *versus* time of optical bleaching in a heavily x-rayed NaCl crystal. The bleaching light intensity $I_i=0.87\times10^{14}$ quanta/(cm^2 sec).

The work of Etzel and Maurer[14] on the electrical conductivity of NaCl indicates that positive-ion vacancies diffuse at an appreciable rate at room temperature. It is possible that association of positive- and negative-ion vacancies may occur with the result that the effective capture cross section of negative-ion vacancies for conduction electrons does not remain constant

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[12] Casler, Pringsheim, and Yuster, J. Chem. Phys. 18, 1564 (1950).

[13] F. Seitz, Revs. Modern Phys. 26, 57 (1954).

[14] H. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

during the bleaching. This possible association of positive and negative ion vacancies was investigated by optically bleaching a NaCl crystal ~22 hours after x-raying and comparing the results with those for a specimen cleaved from the same crystal and x-rayed in the same manner but optically bleached ~1 hour after x-raying. The values of n_V^0 calculated for runs at the same value of n_F^0 were 15–30 percent lower in the former case than in the latter. This result indicates that during the course of a bleaching experiment (<3 hours duration) effects arising from association of positive and negative ion vacancies are probably negligible.

A number of experiments were performed to test the effect of the initial state of the crystal on the optical bleaching rate. A given crystal was found to give reproducible results if it was heated to 350°C for two hours between runs. Different batches of Harshaw NaCl crystals, when treated in the above manner, gave qualitatively the same results. Various batches differed somewhat in the largest value of n_F^0 for which the behavior of the model agreed with experiment and in the value of $n_V^0+n_F^0$ which gave the best fit to the data for a given n_F^0 value.

Several experiments were carried out using lead-free ($<0.0001\%$ Pb) NaCl single crystals prepared by Mrs. E. W. Claffy at the Naval Research Laboratory and kindly supplied to us by Dr. H. W. Etzel. For n_F^0 values in the range 3.1×10^{16}–1.3×10^{17} cm^{-3} the experimental results agree rather well with the behavior of the model. The values of n_V^0/n_F^0 were roughly double those obtained from the data given in Fig. 7. For n_F^0 values in the range 3.5×10^{15}–1.7×10^{16} cm^{-3} the experimental values of N_F^0/N_F are significantly lower during the last one-third of the bleaching than the values given by the theoretical curves fitted to the data for the first two-thirds of the bleaching. This effect is shown in a somewhat less pronounced manner in Fig. 6.

A cursory investigation was made of the effect of various heat treatments prior to x-ray irradiation on the optical bleaching rate of *F* centers. Two crystals cleaved from the same source were heated to 750°C for two hours. One crystal was cooled quickly (~2 min) to room temperature while the second was cooled slowly to room temperature over a period of ~18 hours. The crystals were then x-rayed and the rates of optical bleaching of the *F* band determined. The bleaching rate for the slowly cooled crystal was more rapid than for the rapidly cooled crystal. Both rates were more rapid than for a crystal (Fig. 7) heated to 350°C before x-raying and bleaching. Typical values of n_V^0/n_F^0 calculated from the data are tabulated in Table II. For the crystals heated to 750°C the quantity n_V^0/n_F^0 was found to be considerably smaller in the crystal cooled slowly than in that cooled rapidly. The n_V^0/n_F^0 values for the latter case were smaller than those for the crystal heated to 350°C. Optical bleaching rates for a crystal heated to 600°C and cooled quickly before x-raying gave values of n_V^0/n_F^0 somewhat smaller than those for the crystal heated to 350°C. The crystals heated to 600°C and 750°C showed more rapid bleaching of the last one-third of the *F* band than is predicted by the theoretical model. It is possible that besides single negative-ion vacancies other imperfections which act as traps for conduction electrons are present in the crystals heated to the higher temperatures.

TABLE II. Effect of heat treatment on optical bleaching rates.

Heat treatment	Cooling period	n_F^0 (cm^{-3})	n_V^0/n_F^0
2 hr at 750°C	18 hr	5.4×10^{16}	0.15
2 hr at 750°C	2 min	6.6×10^{16}	0.61
4 hr at 600°C	20 min	5.9×10^{16}	1.3
2 hr at 350°C	20 min	6.7×10^{16}	1.9

V. ACKNOWLEDGMENTS

We are greatly indebted to Dr. James W. Follin, Jr., who obtained the exact solution to Eqs. (4) and (6). We are also indebted to Dr. Bernard Fleishman who pointed out the possibility of numerically integrating these equations. We wish to thank Professor F. Seitz for a profitable discussion. We should like to express our appreciation to Dr. H. W. Etzel of the Naval Research Laboratory for supplying us with lead-free NaCl crystals prepared by Mrs. E. W. Claffy. We wish to thank Miss M. C. Williams for carrying out the experimental measurements and Miss Jacquelyn Siler for performing the numerical calculations. Finally we thank Miss Doris Rubenfeld who prepared the figures and Miss Shirley Thomas for assistance with the manuscript.

APPENDIX A

Equations (4) and (6) may be written in terms of the dimensionless quantities defined in Eq. (8) as follows:

$$\partial n/\partial\tau=-\mathcal{I}n^2, \tag{A1}$$

$$\partial\mathcal{I}/\partial y=-\mathcal{I}n. \tag{A2}$$

This pair of equations may be written as

$$\partial\eta/\partial\tau=\mathcal{I}, \tag{A3}$$

$$\partial\mathcal{I}/\partial y=-\mathcal{I}/\eta, \tag{A4}$$

where

$$\eta=1/n. \tag{A5}$$

Differentiating Eq. (A3) with respect to y and making use of Eq. (A4), one obtains

$$\partial^2\eta/\partial\tau\partial y=-\partial\ \ln\eta/\partial\tau. \tag{A6}$$

Integrating with respect to τ,

$$\partial\eta/\partial y=-\ln\eta+f(y). \tag{A7}$$

Making use of the boundary condition given by Eq. (7a), we have for $\tau=0$, $\eta=1$ for all y so that $\ln\eta=0$,

$\partial\eta/\partial y=0$, and finally $f(y)=0$. Thus

$$\partial\eta/\partial y=-\ln\eta, \tag{A8}$$

which becomes

$$e^u\partial u/\partial y=-u \tag{A9}$$

if

$$u=\ln\eta.$$

Integrating Eq. (A9) yields

$$y=-\int_1^u \frac{e^\phi}{\phi}d\phi+g(\tau). \tag{A10}$$

Equation (5) may be written as

$$u=\ln(1+\tau) \tag{A11}$$

and specifies u for $y=0$. Evaluating $g(\tau)$ yields

$$y=-\int_1^u \frac{e^\phi}{\phi}d\phi+\int_1^{\ln(1+\tau)} \frac{e^\phi}{\phi}d\phi, \tag{A12}$$

or

$$y=-\mathrm{Ei}(u)+\mathrm{Ei}[\ln(1+\tau)], \tag{A13}$$

which is equivalent to the result stated in Eqs. (9), (9a), and (9b).

By differentiating Eq. (A13) with respect to τ and making use of Eq. (A3), one may show that

$$\mathcal{J}=\ln\eta/\ln(1+\tau). \tag{A14}$$

By using the series expansion for $\mathrm{Ei}(u)$ given by

$$\mathrm{Ei}(u)\simeq\gamma+\ln u+\sum_{p=1}^{\infty}\frac{u^p}{p\cdot p!},$$

where γ is Euler's constant defined by

$$\gamma=\lim_{\epsilon\to 0}\int_{-\infty}^{\epsilon}\frac{\exp\varphi}{\varphi}d\varphi+\int_{\epsilon}^{1}\frac{d\varphi}{\varphi}=0.577216\cdots,$$

one can show that Eq. (A13) is consistent with the boundary condition $\eta=1$ for all y at $\tau=0$. By eliminating η from Eqs. (A13) and (A14), one may verify that these equations are consistent with the boundary condition $\mathcal{J}=1$ for all τ at $y=0$.

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Specific Heat of Bismuth at Liquid Helium Temperatures

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The specific heat of bismuth has been investigated in the liquid helium region down to 1.3°K by means of a new vacuum calorimeter. The Debye θ is found to increase from 103.5 to 120 in the range 4.1 to 2°K and appears to attain a constant value at lower temperatures. Evidence is obtained for an electronic contribution of $0.114\times10^{-4}T$ calories/°K to the atomic heat of bismuth.

1. INTRODUCTION

THE specific heat of bismuth does not seem to have been investigated accurately at very low temperatures.[1] The measurements of Keesom and van den Ende[2] appear to be the only work that has extended down to liquid helium temperatures. From these they concluded that the atomic heat obeys a T^3 law to a first approximation in the entire range covered by them (3 to 20°K). However, the results they obtained at temperatures below 4°K are not claimed to be very accurate. Since this happens to be the region where the electronic contribution to the specific heat becomes appreciable, it was decided to obtain fresh data with an improved calorimetry technique.

2. EXPERIMENTAL DETAILS

The results described below were obtained with a new vacuum calorimeter[3] which was recently developed in this laboratory, capable of an accuracy better than 3 percent in the range 4.2 to 1.3°K. In this apparatus the specimen is suspended inside a hermetically sealed can, the air in which is frozen out while cooling with liquid helium. The use of an exchange gas and the operation of high-vacuum equipment which are essential in conventional methods, are avoided by means of a mechanism which can make or break a thermal contact of the specimen with the bath as necessary. The heat capacities are measured by thermally isolating the specimen and dissipating a known amount of electrical energy through a heating coil wound around it. The temperature rise (this is always kept below 0.04°K) is then measured with a carbon resistance thermometer (a $\frac{1}{2}$-watt 100-ohm resistor manufactured by Speer Resistor Corpora-

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[1] Since this work was completed, we have come across the recent measurements of P. H. Keesom and N. Pearlman [Phys. Rev. **96**, 897 (1954)], with which our results show good agreement.

[2] W. H. Keesom and J. N. van den Ende, Communs. Kamerlingh Onnes Lab. Univ. Leiden, No. 203d: Proc. Koninkl. Ned. Akad. Wetenschap. **33**, 243 (1930); Leiden Communs. 213c, Proc. Koninkl. Ned. Akad. Wetenschap. **34**, 210 (1931).

[3] K. G. Ramanathan and T. M. Srinivasan, Phil. Mag. **46**, 338 (1955).