

Bleaching and Recovery of F Centers in KCl ^{†*}LORETTA E. SILVERMAN[‡] AND L. I. GROSSWEINER*Department of Physics, Illinois Institute of Technology, Technology Center, Chicago, Illinois*

(Received October 12, 1960)

F centers in KCl are optically bleached at room temperature with a minimum light energy of 20.1 ± 1.0 ev per F center. The F band is recovered on further room-temperature x raying with a minimum energy of 69 ± 5 ev per F center. The increase in the M and R bands during optical bleaching of the F band is nullified upon the recovery of the F band by further x raying. The recovery kinetics are of second order in the number of optically bleached F centers with a rate-constant of $(7.9 \pm 0.8) \times 10^{-20}$ cm³/ F center-sec. The rate law requires an energy transfer from the bulk lattice and is consistent with an exciton mechanism.

INTRODUCTION

THERE has been considerable recent interest in the energetics of the production and optical bleaching of F centers.¹⁻⁶ It undoubtedly has been observed by many workers that bleached F centers are recovered on further x raying at a smaller energy expenditure than for initial coloration. It does not appear that the recovery process has been investigated quantitatively. This paper reports experiments in which KCl single crystals were alternately x rayed and optically bleached at room temperature, with the object of evaluating the energetics and kinetics of recovery.

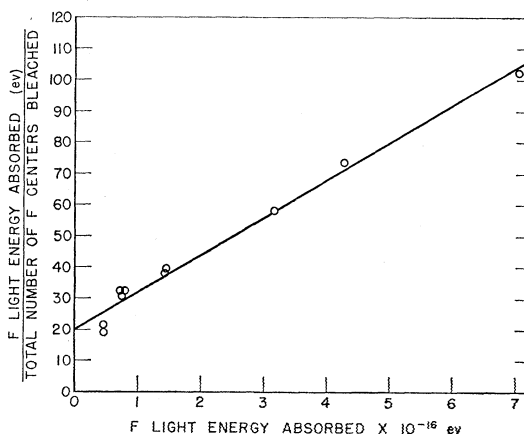
EXPERIMENTAL DETAILS

The experiments were done with Harshaw KCl , cleaved into $1 \text{ cm} \times 1 \text{ cm} \times (0.77 \pm 0.05) \text{ mm}$ samples from several larger blocks. They were x rayed in vacuum at room temperature in a stainless steel sample holder previously described.⁷ The x-ray source was a General Electric CA-6 tube with copper target, operated half-wave rectified at 40 kv. The emergent x rays were filtered by a 0.8 mm beryllium window on the sample holder. The irradiated face area was 0.32 sq cm. Crystals were x rayed at 15 ma to attain a maximum F -band optical density near unity (8×10^{16} F centers per cc), stored in the dark about 12 hours, optically bleached with a tungsten filament lamp, and then x rayed at 5 ma in several stages until the original F -band height was recovered; in some cases a second bleaching and recovery cycle was done. All optical absorption

measurements were made at liquid nitrogen temperature on a Beckman DU spectrophotometer. It was found that prolonged dark storage of bleached crystals induces changes in the color-center bands; therefore, all experiments were completed without interruption after the first bleaching.

The x-ray energy absorbed by the crystal was measured with a Fricke dosimeter consisting of 0.1M $FeSO_4$ in 0.8N H_2SO_4 , using a "G" of 15.1 ion-pairs per 100 ev.⁸ The measurements were made in a lead-shielded polyethylene cell with a 0.003 cm acrylic plastic window, located to intercept the same part of the x-ray beam as the KCl crystal. The solution thickness was 0.94 cm, equivalent to the average x-ray absorption by the crystal. The rate of energy absorption was 2.6×10^{16} ev per minute at 15 ma.

The energy of the bleaching light was measured with the potassium ferrioxalate actinometer as described by Hatchard and Parker.⁹ Light absorption by the actinometer solution above 540 m μ is too low for accurate calibration and the measurements were made with a bandpass filter peaking at 485 m μ . The light energy incident on the filter was calculated from the chemical conversion by integrating the filter transmission, acti-

FIG. 1. Bleaching of KCl F centers at room temperature.

[†] Presented at the American Physical Society, Washington, D. C., April 25-28 (1960).

^{*} Supported in part by the U. S. Atomic Energy Commission.

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¹ L. I. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, Phys. Rev. **96**, 617 (1954).

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

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

⁵ R. D. Jordan and R. S. Alger, J. Appl. Phys. **31**, 747 (1960).

⁶ W. E. Bron and A. S. Nowick, Phys. Rev. **119**, 114 (1960).

⁷ A. R. Reinberg, thesis, Illinois Institute of Technology, June, 1959 (unpublished).

⁸ M. Frilley and M. Lefort, J. phys. radium **20**, 516 (1959).

⁹ C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. (London) **A235**, 518 (1956).

TABLE I. Effect of alternate x raying and optical bleaching at room temperature on the optical densities of the *M*, *R*₁, and *R*₂ bands.

Bleach time (min)	<i>M</i> band (800 mμ)				<i>R</i> ₁ band (650 mμ)				<i>R</i> ₂ band (725 mμ)			
	Initial x ray	Bleach 1	Recovery	Bleach 2	Initial x ray	Bleach 1	Recovery	Bleach 2	Initial x ray	Bleach 1	Recovery	Bleach 2
0.5	0.061	0.157	0.062	0.147	0.007	0.020	0.016	0.017	0.007	0.019	0.013	0.019
1.0	0.045	0.151	0.057	0.132	0.019	0.030	0.027	0.026	0.002	0.014	0.021	0.021
2.0	0.045	0.145	0.018	0.155	0.008	0.043	0.020	0.044	0.006	0.044	0.000	0.045
4.0	0.060	0.162	0.058	...	0.015	0.082	0.013	...	0.015	0.095	0.016	...
5.0	0.068	0.118	0.067	0.087	0.033	0.128	0.041	0.120	0.017	0.137	0.031	0.126
10.0	0.064	0.106	0.083	0.105	0.007	0.094	0.019	0.098	0.013	0.133	0.029	0.136
60.0	0.054	0.118	0.049	0.110	0.017	0.150	0.011	0.153	0.000	0.169	0.000	0.174
mean	0.057		0.056		0.015		0.021		0.009		0.016	
	±0.003		±0.004		±0.003		±0.003		±0.003		±0.003	

nometer absorption, and quantum yield. The relative bleaching lamp output was calculated from its measured color temperature (2725°K) with Wien's law, corrected for the spectral emissivity of tungsten.¹⁰ From the 485-mμ calibration point, the spectral energy incident on the crystal was calculated. This was integrated over the 78°K *F* band for a maximum optical density of unity. Although the area under the KCl *F* band is almost independent of temperature,¹¹ a correction was made to account for the spectral distribution of the bleaching lamp. The ratio of the room temperature *F*-band light absorption to that at 78°K was 1.44 for the *F*-center concentrations used. Corrections for small changes in height from run to run were made by assuming that the light absorption is proportional to the product of the band maximum and half-width. In a typical experiment the light absorbed in the room temperature *F* band, from 480 to 640 mμ, was 2.39×10^{14} ev per sec.

RESULTS

The energy efficiency for optical bleaching of the *F* band at room temperature was determined for crystals bleached for various short times. The *F*-center concentration was determined with Smakula's formula for an oscillator strength of 0.81. Figure 1 shows the number of bleached *F* centers as a function of the absorbed light energy—each point is a separate run. The ordinate is the total energy absorbed per total number of *F* centers bleached at that energy, and was chosen only for convenience in giving a linear plot over this region. The intercept of the "least squares" best line is 20.1 ± 1.0 ev per *F* center. This corresponds to an average quantum yield of 0.11 *F* centers bleached per photon, which is in fair agreement with the value of 0.14 to 0.17 obtained by Bron and Nowick.⁶

Figure 2 illustrates a typical recovery experiment. A crystal was x rayed to a maximum *F*-band optical density near 1.0, bleached for 60 minutes, x rayed to recover the *F* band, and bleached again for 60 minutes.

The *M* and *R* band changes induced by bleaching the *F* band are nullified on recovery of the *F* band. Table I summarizes data for various bleaching times. In each case the *F* band maximum after initial x raying and recovery was the same and near unity. Within the limits of precision, the *M* and *R* band changes are reversible for all runs. The ratio of the *R*₂ to *R*₁ band maxima for all points is 1.062 ± 0.020 . The constant value is in agreement with the results of Herman, Wallis, and Wallis.¹²

The kinetic data for recovery of the *F* band show a linear dependence of (E/N) against *E*, where *N* is the number of *F* centers recovered at energy *E*(ev)—Fig. 3. If the linear relationship is followed exactly, i.e.,

$$(E/N) = mE + b, \quad (1)$$

then the reciprocal of the slope *m* is the maximum number of *F* centers that can be recovered and the intercept *b* is the minimum differential recovery energy. Table II shows that the product of the measured slope of Eq. (1) and the number of *F* centers optically

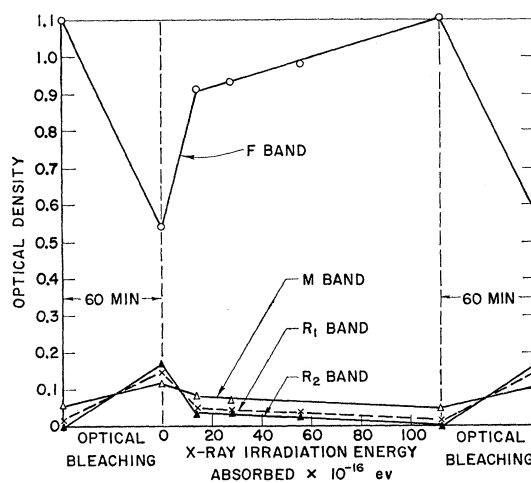


FIG. 2. Optical densities of the *F*, *M*, *R*₁, and *R*₂ band maxima during optical bleaching and recovery.

¹⁰ P. S. Shurrager, Armed Services Technical Information Agency Report ASTIA-207460 (unpublished).

¹¹ J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

¹² R. Herman, M. C. Wallis, and R. F. Wallis, Phys. Rev. **103**, 87 (1956).

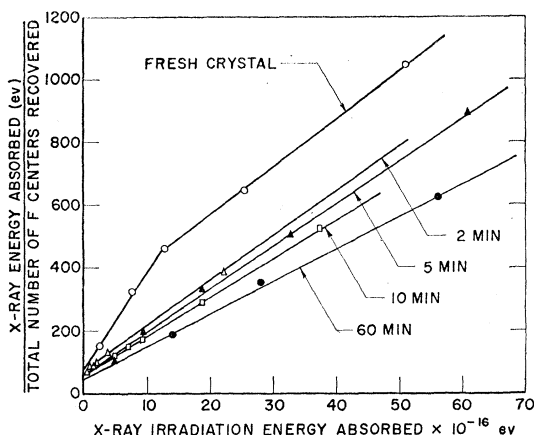


FIG. 3. Recovery of the F band as a function of absorbed x-ray energy and optical bleaching time.

bleached, as measured with the spectrophotometer, is close to unity for various bleaching times. Thus, the calculated number of F centers ultimately recovered can be identified with the number optically bleached. This indicates that the x-ray energy absorbed during recovery is predominantly used for conversion of bleached F centers and not for the production of new ones, and strongly suggests an energy transfer process. The average value of the intercept gives a minimum differential recovery energy of 69 ± 5 ev per F center—there appears to be only a random variation with the number of F centers bleached. (The choice of experiments in Fig. 3 gives the appearance of a systematic variation of intercept with optical bleaching time, which is not shown by the data in Table II.)

A plot for fresh crystal is shown on the same figure. The growth clearly displays the two-stage process described by Mitchell, Wiegand, and Smoluchowski.³ It should be noted that Etzel and Allard² analyzed growth of the NaCl F band in this way and did not report an abrupt change in slope. The minimum energy required to darken fresh KCl is 80 ev per F center, which is in fair agreement with other measurements.⁵ The small difference between the minimum energies for recovery and initial darkening is consistent with the suggestion of Rabin¹³ and others that initial coloration utilizes negative ion vacancies already in the crystal.

DISCUSSION

Table II shows that the F -band recovery process is in quantitative agreement with Eq. (1) if the maximum number of recoverable F centers is identified with N_0 , the number optically bleached. The differential equation integrating to Eq. (1) is

$$(dN/dE) = k(N_0 - N)^2, \quad (2)$$

¹³ H. Rabin, Phys. Rev. **116**, 1381 (1959).

TABLE II. Comparison of the number of optically bleached F centers with the calculated maximum number of F centers recovered.

Bleach time (min)	No. of F centers ^a bleached, N_0	From (E/N) vs E graph		Intercept (ev per F center)
		Slope	Slope $\times N_0$	
2.0	5.35×10^{14}	1.41×10^{-15}	0.754	72.73
4.0	7.81×10^{14}	0.98×10^{-15}	0.766	105.86
5.0	8.33×10^{14}	1.38×10^{-15}	1.148	60.54
8.0	9.85×10^{14}	1.29×10^{-15}	1.266	54.93
10.0	8.08×10^{14}	1.23×10^{-15}	0.998	60.45
30.0	10.40×10^{14}	0.99×10^{-15}	1.031	81.04
60.0	11.48×10^{14}	1.03×10^{-15}	1.188	48.60
		Mean	1.02 ± 0.05	69 ± 5

^a As measured at F -band maximum with spectrophotometer.

where $b = (kN_0)^{-1}$. Equation (2) can be written as

$$(dN/dt) = k(dE/dt)(N_0 - N)^2, \quad (2')$$

for constant rate of energy absorption. This represents a process which is of second order in the number of unrecovered F centers. A simple physical model is applicable. Consider a volume-kinetic recombination of free electrons with negative-ion vacancies:

$$(dN/dt) = k'n(N_0 - N), \quad (3)$$

where n is the number of free electrons and $(N_0 - N)$ is the number of bleached F centers. A comparison of Eq. (2') and (3) shows that the number of free electrons must be

$$n = (k/k')(dE/dt)(N_0 - N). \quad (4)$$

The constant k is given by (m^2/b) of Eq. (1). From the data of Table II, a best value of $(2.25 \pm 0.22) \times 10^{-32}$ (ev- F center)⁻¹ is obtained. The conventional rate-constant in concentration units is obtained by multiplying by the volume of irradiated crystal, 0.0246 cc, and the rate of energy absorption, 1.42×10^{14} ev per sec, giving a second-order recovery rate-constant of $(7.9 \pm 0.8) \times 10^{-20}$ cc per F center-sec.

Equation (4) shows that the steady-state number of free electrons is of first order in the number of negative-ion vacancies. This cannot be the case if the electrons utilized in recovery are generated directly in the bulk lattice. Since the M and R bands show reversibility with the F band during recovery, it is reasonable to assume that they are the predominant source of the free electrons, although other traps may also contribute. A plausible mechanism for the energy transfer process is the ionization of trapping centers by excitons generated in the bulk lattice. We can discuss the rate processes which might occur and make rough estimates of the magnitudes. For a linear dependence of n on x-ray intensity, excitons must be generated at a rate far from saturation and disappear by a fast first-order process. At steady state:

$$q = (\tau_q/\epsilon)(dE/dt), \quad (5)$$

where q is the number of excitons, τ_q is the exciton lifetime, and ϵ is the minimum energy to produce an exciton. If it is assumed that the collisions between excitons and trapping centers obey classical kinetic theory, the number of free electrons during x raying is given by

$$n = \tau_n \sigma v_q (N_0 - N) q, \quad (6)$$

where τ_n is the lifetime of a conduction electron, σ is the cross section for ionization of a trapping center by an exciton, and v_q is the thermal velocity of the exciton. Substitution of Eq. (5) into Eq. (6) gives the dependence required by Eq. (4).

For a numerical estimate, ϵ may be taken as 10 eV, τ_q as the optical exciton lifetime of 10^{-8} second, and σ as 10^{-15} sq cm. The mean lifetime of a conduction electron against trapping by an *F* center has been calculated by Redfield¹⁴ as 7×10^{-10} sec at 200°K. If it is assumed that this is the predominant process establishing a steady-state electron concentration at 300°K,

¹⁴ A. G. Redfield, Phys. Rev. **94**, 537 (1954).

τ_n can be taken as 10^{-9} sec. Finally, v_q from the exciton effective mass¹⁵ is about 10^7 cm/sec. Substitution of these quantities gives a value for n of $\approx 10^{-26} (dE/dt) (N_0 - N)$. This may be compared to the experimental recovery rate if a value is assumed for k' , the rate-constant for the reaction between free electrons and negative-ion vacancies. Again from kinetic theory, for a capture cross section of 10^{-14} sq cm and an electron velocity of 10^7 cm/sec, k' equals 10^{-7} cc per electron-sec. Thus, (k/k') equals $\approx 10^{-26}$. Although the agreement is fortuitous, these calculations show that an exciton transfer mechanism is consistent with the observed recovery process.

A final point is that the energy required to recover *F* centers is independent of the extent of optical bleaching. This suggests that the recovered *F* centers are isolated and not clustered, which is consistent with the conclusion of Konitzer and Markham¹¹ that "the *F* center is in a perfect lattice, no matter how it is made."

¹⁵ W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

Ultrasonic Attenuation in Normal Metals at Low Temperatures

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(Received September 6, 1960; revised manuscript received October 24, 1960)

Expressions for the attenuation α_d and α_t of plane dilatational and shear sound waves are obtained by solving the Boltzmann transport equation for the electron distribution function f without assuming the existence of a relaxation time τ for the collision term in this equation. Instead the collision integral is considered to arise explicitly from the interaction of electrons with thermal phonons and impurities. Making the usual "ideal metal" assumptions, it is found that the attenuation in general depends on a set of effective relaxation times τ_{LM} which are associated with the various terms in the expansion of f in a series of spherical harmonics $Y_{LM}(\theta, \varphi)$; the τ_{LM} are independent of the subscript M , and hence the same set $\{\tau_L\}$ determines both α_d and α_t . Explicit expressions for τ_L are derived.

For the case in which all the τ_L equal to one another and equal to τ say, the analytical expressions for α_d and α_t obtained here are

the same as those of Pippard. However, usually τ_L are not equal to one another. It is then found that when $\lambda \gg l$ (λ is the wavelength of the sound wave and l a mean free path of the electrons), τ in Pippard's expressions must be replaced by τ_2 and, contrary to what is usually assumed, α would not be in general proportional to the electrical conductivity σ ($\sigma \propto \tau_1$). When $\lambda \ll l$, the attenuation, with one exception, is independent of $\{\tau_L\}$ and is the same as that given by Pippard. For $\lambda \sim l$, and τ_L not equal to one another, α may be calculated numerically if the ratios τ_L/τ_1 are known; the results of one such calculation show that the deviations from Pippard's analytical expressions are at most about 20%, provided τ in the latter is identified as τ_2 .

Lastly, the possible influence of electron-electron collisions on attenuation is briefly discussed.

INTRODUCTION

BELOW about 20°K, the attenuation of ultrasonic waves in metals arises primarily from their interaction with the conduction electrons. Pippard¹ gave an extensive *kinetic* treatment of this phenomenon in terms of the free-electron model of a metal. His basic idea is that the steady-state distribution of the electrons, determined under the combined influence of the electric field set up by the sound wave passing through the metal and the collisions of the electrons with lattice

vibrations and other defects in the metal, is not identical with that which the electrons would have if they were locally in thermal equilibrium. Hence there is a dissipation of sound energy into heat energy. Steinberg,² using Pippard's model, formulated the problem in terms of the Boltzmann transport equation. In both these treatments the existence of a relaxation time τ for collisions is assumed. In the Boltzmann formulation this assumption is expressed by the equation

$$[\partial f / \partial t]_{\text{coll}} = -(f - \bar{f}) / \tau, \quad (1)$$

¹ A. B. Pippard, Phil. Mag. **41**, 1104 (1955).

² M. S. Steinberg, Phys. Rev. **111**, 425 (1958).