JUL 1 1958

Coo--1054-40

07-7501-000

OPTICAL STUDIES OF F-AGGREGATE COLOR CENTERS
IN IRRADIATED LITHIUM FLUORIDE

by

KAREL L. VANDER LUGT

MASTER

A DISSERTATION

Submitted to the Office for Graduate Studies,
Graduate Division of Wayne State University, Detroit, Michigan,
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

1967

MAJOR: PHYSICS (SOLID STATE)
APPROVED BY

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Advisor

Date

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fla

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ACKNOWLEDGEMENTS

To Professor Y. W. Kim, my thesis advisor, I express my sincere appreciation for his guidance during the past four years, for procuring the needed equipment, and for many suggestions used in writing this manuscript.

I am grateful to Mr. John Van Gemen and to Mr. Milton Shopnick for helping in the design and construction of apparatus; to Dr. R.A. Andrews for discussions on various aspects of color center research; and to Miss Joann Filinger for typing the manuscript.

I am also grateful for financial support from a National Defense Education Act Fellowship and from the Atomic Energy Commission (Contract No. AT(11-1)-1054).

My deepest and heartfelt gratitude goes to my wife, Joyce, for her patience, understanding, and cheerful encouragement during the past three years.

TO MY FATHER

TABLE OF CONTENTS

	Page
Acknowledgements	ii
List of Figures	v
Chapter	
I. Introduction	1
II. Basic Concepts of Color Centers	4
III. Instrumentation	16
Optical Spectrophotometers	16
Arc Lamp and Housing	26
Low Temperature Sample Cell	28
High Temperature Sample Cell	30
IV. Observation of the R_N Band in LiF Near 300°K	33
V. Optical Conversion of the F_3^+ Center in LiF With R Light	38
Introduction	38
Experimental Procedures	42
Results and Discussions	45
Conclusion	53
VI. Photochemical Destruction of the R centers in LiF with R Light	54
Introduction	54
Experimental Procedures	54
Experimental Results	56
Discussions	68
Conclusion	73
Appendix Correction Factor for Kinetic Studies of Photochemical Reactions Involving Color Centers	74
List of References	78
Autobiographical Statement	81

LIST OF FIGURES

Figure	Page
1. Crystal structure for the majority (including LiF) of the alkali halides. The space lattice is fcc with one cation and one anion associated with each lattice point	5
2. Schematic representation of the electron energy band structure for an insulator. A color center may introduce localized levels in the band gap, and optical transitions, which "color" the crystal, are possible between these levels	6
3. Schematic diagram of an F center: three-dimensional array (top) plus a cross-section of a {100} plane (bottom).	8
4. (a) Configuration coordinate diagram of an F center (b) Breathing mode of vibration of the six nearest-neighbor cations of an F center	11
5. Schematic diagram of the current models for F-aggregate centers: (a) a three-dimensional array of the M center and a cross-section of the (100) plane, (b) a three-dimensional array of the R center and a cross-section of the (111) plane, (c) three dimensional arrays of Pick's N_1 and N_2 centers	14
6. Diagram illustrating the geometry used to discuss the attenuation of light by absorbing materials . . .	17
7. Schematic diagram of the Bausch and Lomb model 505 spectrophotometer	19
8. Schematic diagram of the optical system of the Cary model 14 R spectrophotometer	23
9. Simplified schematic diagram of the electronic system of the Cary model 14R spectrophotometer . . .	25
10. Schematic diagram of the arc lamp, lamp housing, and monochromator employed in this investigation . .	27
11. Cross-sectional view of the low temperature sample cell and mount employed in this investigation	29
12. Cross sectional view of the high temperature sample cell and mount constructed for this investigation	31

13. Position of the R, N, and N_R bands of LiF observed in the present work. The solid curve corresponds to a neutron irradiated sample with 1×10^{15} nvt, and the broken curve, to the same sample bleached for 8 hours near 300°K , with a high pressure Hg lamp filtered with a Corning filter #7380 (cutting off the wavelengths less than $340 \text{ m}\mu$) 35
14. The anisotropic optical absorption of a gamma irradiated sample with 100 MR after the sample has been optically bleached with the R light polarized along a $\langle 011 \rangle$ direction for 45 minutes. The anisotropic absorption is obtained by subtracting the "perpendicular" absorption from the "parallel" absorption of the sample 37
15. Absorption spectrum of a gamma-irradiated (40 MR) sample of LiF. (a) before R_1 bleach, (b) after 32 minutes of R_1 bleach 39
16. Uncorrected emission spectrum due to M light ($435 \text{ m}\mu$) excitation of a gamma-irradiated (40 MR) sample of LiF. (a) before R_1 bleach, (b) after 32 minutes of R_1 bleach 41
17. Optical arrangement for measuring emission spectra 44
18. Variation in emission and absorption peaks of a gamma-irradiated (40 MR) sample of LiF with R_1 bleach near 300°K . (a) emission due to M light ($435 \text{ m}\mu$) excitation, (b) absorption 46
19. Plot of $\log [F_3^+]$ against $e^{-k_2 t}$ where t is the time of R bleach.³ The straight lines represent a theoretical plot of Eq. (11), while the circles are experimental points for (a) R_1 bleach ($k_2 = .3$), (b) R_2 bleach ($k_2 = .06$) 50
20. Difference in the absorption spectrum of a gamma-irradiated (100 MR) sample of LiF after 15 seconds of R_1 bleach near 300°K . Solid curve is the observed change; broken curves are decompositions into R bands, an underlying broad band, the M band, and the F_3^+ band. (see Text) 50
21. Absorption spectrum of a gamma-irradiated (100 MR) sample of LiF at room temperature (a) before R_2 bleach, (b) after 13 minutes of R_2 bleach, (c) after 33 minutes of R_2 bleach 57
22. Plot of the increase in the N band against the decrease in the R bands. Region B represents the destruction of the R centers. 59

Figure		Page
23.	Dependence of the ratio $\Delta N_c / \Delta R$ with temperature of sample	60
24.	Change in the absorption peaks when R_2 bleach is applied at 378°K	62
25.	Plot of $\log [R]$ against t' for different intensities of R_2 bleach at room temperature where t' is the effective time of R_2 bleach for constant intensity. (see Text).	64
26.	Plot of the ratio $\Delta N_c / \Delta R$ against the "half-life" of the R centers ($T_{1/2}$) for different intensities of R_2 bleach at room temperature.	66
27.	Change in the absorption peaks when R_1 bleach is applied at room temperature	67
28.	Schematic diagram of the van Doorn model of the R center in LiF. (see Text).	70
29.	Qualitative dependence of light intensity at depth x and at time t , $I_x(t)$, with time t of R bleach. Shaded area represents the total flux at time t	75

CHAPTER 1

INTRODUCTION

The alkali halides are transparent ionic crystals which, except for the cesium halides, have face-centered cubic structures. Various chemical, mechanical, electrical and optical properties of these crystals have been studied for many years. In the 1930's, R.W. Pohl and his co-workers began investigating changes in certain of these properties caused by the presence of point defects in the crystals. The point defects were induced in pure crystals chiefly by two methods, either by exposure to ionizing irradiation or by addition of a stoichiometric excess of one of the constituents. Perhaps the most striking change caused by these point defects was the visible coloration of the crystals; KCl became deep blue, NaCl became pale yellow, etc. For this reason, the point defects were commonly referred to as color centers. Since the initial studies, considerable effort by many investigators has been given to determining the nature of color centers, the mechanisms of their creation and interconversion, and their influence on the various properties of the host crystal. Color centers in alkali halides are not only of interest in themselves, but it is largely from such investigations that the models, theories, and techniques for defects in other classes of insulators have been developed.

Color centers are classified into two general types, depending on whether electrons or electron deficiencies (holes) are trapped at the lattice defects. A large variety of color centers can be produced corresponding to the variety of defects, or combinations of defects,

that can act as electron traps or hole traps. The simplest and most extensively studied color center is the F center (from the German word Farbzentrum). It consists essentially of an electron trapped at the position of a missing halogen ion. A group of color centers known as the F-aggregate centers consist of various combinations of two or more closely associated F centers. The concentration of a particular color center may change when the temperature of the crystal is increased (thermal bleach) or when the crystal is illuminated with intense light of an appropriate wavelength (optical bleach). By careful selection of such bleaching methods, the F and F-aggregate centers can be transformed among themselves.

The purpose of this thesis is to study the nature and interconversion of certain F-aggregate color centers in LiF. F centers and certain of the F-aggregate centers were produced in pure LiF by exposure to gamma-rays, x-rays or neutrons at room temperature. Subsequently, these "colored" crystals were subjected to selective bleaching techniques. Concurrently, optical absorption, luminescence, and photoconductivity measurements were taken to observe the changes induced. In this manner, significant information concerning the nature of F-aggregate centers in LiF and the mechanisms and kinetics of their interconversion were obtained.

In Chapter II some of the basic concepts of color centers are summarized. Particular emphasis is placed on the currently accepted models for the F and F-aggregate centers. The experimental techniques are discussed in Chapter III. Included in this chapter are

descriptions of the optical spectrophotometers, the high intensity arc lamp and housing, the low temperature sample cell, and the high temperature sample cell employed in this investigation. The results and discussions of the observations made are contained in the final three chapters. The appendix gives the derivation of a correction factor needed for accurate kinetic studies of photochemical reactions involving color centers.

CHAPTER II

BASIC CONCEPTS OF COLOR CENTERS

Extensive effort, both experimental and theoretical, has been given to the study of color centers in alkali halides, and several excellent reviews have recently been compiled.¹⁻³ These up-date earlier reviews by Mott and Gurney⁴ and Seitz.^{5,6} The purpose of this chapter is not to summarize all aspects of color centers but only those relevant to the present work.

The majority of the alkali halides (including LiF) crystallize in the well known rock salt structure, shown in Fig. 1. In this structure, each cation (alkali metal ion) is surrounded by six anions (halogen ions) and vice versa. The cations and anions are situated on the sites of separate face-centered cubic lattices.

The alkali halides are insulators with a forbidden energy gap on the order of 10 ev. Thus, they are transparent over a large range of wavelengths, generally from the far ultraviolet into the far infrared. The presence of color centers, however, gives rise to localized energy levels in the band gap. Fig. 2 illustrates the band structure for an insulator containing a color center. If transitions between the localized levels correspond in energy to visible light, the crystal can absorb this light (see arrows in Fig. 2). The crystals are then no longer transparent but appear to be colored. In alkali halides colored either by addition of a stoichiometric excess of the alkali metal or by exposure to ionizing radiation at room temperature, the color center produced in greatest

○ Li^+ (CATION)

○ F^- (ANION)

Fig. 1 Crystal structure for the majority (including LiF) of the alkali halides. The space lattice is fcc with one cation and one anion associated with each lattice point.

Fig. 2 Schematic representation of the electron energy band structure for an insulator. A color center may introduce localized levels in the band gap, and optical transitions, which "color" the crystal, are possible between these levels.

concentration is the F center. The accepted model for the F-center is an electron trapped at an anion vacancy⁷ (see Fig. 3). The presence of F centers is easily detected by an optical absorption measurement which reveals a bell-shaped absorption band. This band is called the F band, and its intensity is directly related to the concentration of F centers.^{8,9} The exact spectral position and half-width of the F band depend on the particular alkali halide and on the temperature. Empirically, it is found that at room temperature,¹⁰

$$\lambda_{\max} (\text{\AA}) = 703 d^{1.89} \quad (1)$$

where $\lambda_{\max}$ is the wavelength of the F band peak absorption and d is the interionic lattice distance (both in $\text{\AA}$ units). In each crystal, the temperature affects both the shape and position of the F band. As the temperature is lowered, the band shifts to shorter wavelengths and becomes narrower. The temperature dependence of the half-width is satisfactorily described by the following equation:¹¹

$$W(\text{eV}) = A \left[\coth \left(\frac{h\nu}{2kT} \right) \right]^{1/2} \quad (2)$$

A and ν_g are crystal parameters and h and k are Planck's and Boltzmann's constants, respectively.

The absorption of light in the F band (F light) at low temperatures results in luminescence at a longer wavelength. This shift in energy between the absorption and emission bands is called the Stokes shift. As the temperature is raised, the luminescence efficiency decreases. Typically, F centers do not luminescence at room temperature.

Fig. 3 Schematic diagram of an F center: three-dimensional array (top) plus a cross-section of a {100} plane (bottom).

F centers also exhibit the phenomenon of "concentration quenching"; that is, the luminescence efficiency decreases if the concentration of F centers becomes too great.

The properties of the F center are determined by the interaction of the trapped electron with the lattice. A precise theoretical treatment would have to include the interaction with all of the nuclei and their electrons. The actual calculations are approximations, and so the nature and validity of the approximations become significant factors of all theoretical calculations. The reader is referred to Markham's book (Ref. 3) for an up-to-date discussion of such studies. For the purpose of this thesis, only two theories will be mentioned. In the first (semi-continuum approximation), the periodic nature of the crystal lattice is largely ignored. The anion vacancy is treated as a spherical cavity imbedded in a continuous dielectric medium. The spherical potential problem is then solved by means of the Schrödinger wave equation. Since the model is spherically symmetric, the solution of this problem is analogous to that of the hydrogen atom. The F band absorption corresponds to a $1s \rightarrow 2p$ transition.

While the first approximation replaces the lattice by a continuum and ignores the details of the interaction of the trapped electron with neighboring ions, the second effectively considers only the interaction of the six nearest neighboring alkali ions. This latter approach is called the localized mode approximation and has the advantage of giving an intuitive picture of the general optical properties of the F center. The electron is considered to

be highly localized in the anion vacancy. If one of the six nearest neighboring cations is displaced from equilibrium, the ion will experience a restoring force. To a first approximation, this force is taken to be linear with the displacement. The greatest effect on the electron would occur when all six of its nearest neighbors are vibrating radially and in phase. This mode is commonly referred to as the "breathing mode" and is labelled by a configuration coordinate q . Fig. 4 illustrates a plot of total energy versus q . Two electronic levels, a ground state and an excited, are represented by parabolic curves.

Since the total energy of the center is the sum of electronic energy and vibration energy, horizontal lines are drawn in each parabola to represent the quantized vibrations of the breathing mode. At low temperature, the center will be at its ground state equilibrium position (A). It can make a transition to the excited state (B) by absorbing a photon of energy $E_B - E_A$. The transition is drawn vertically on the assumption (Frank-Condon principle¹²) that the heavy ions do not move during the short transition period. After excitation the center relaxes to the equilibrium position of the excited state (G) by "emitting" several quantized lattice vibrations (phonons) to the lattice.

From (G) the system can return to the ground state (H) by emission of a photon of energy $E_G - E_H$. Finally, equilibrium is again achieved by phonon emission to point (A). It is evident from Fig. 4 that the emitted photon is of less energy than the absorbed photon. This difference in the position of the absorption

Fig. 4 (a) Configuration coordinate diagram of an F center.
 (b) Breathing mode of vibration of the six nearest-neighbor cations of an F center.

band and the emission band is called the Stokes shift. It is quite large for F centers, typically several times the absorption band half-width.

As the temperature is increased, additional vibrational levels of the ground state will become populated, and transitions such as $(E \rightarrow F)$ and $(C \rightarrow D)$ become possible. It is thus seen that as the temperature is raised, the half-width of the absorption band increases.

The decrease in luminescence efficiency with increase in temperature can be illustrated with Fig. 4 by considering transitions such as $(C \rightarrow D)$ which excite the system to an energy greater than that of point (I). At this value of q , the two potential curves "touch", and the possibility of a non-radiative transition to the ground state via (J) exists. A similar argument is used when considering concentration quenching. When the distance between F centers becomes small, their potential curves are influenced by one another and the contact point (I and J) may occur at a smaller value of q . If the temperature is increased sufficiently, the electrons in the excited state may be released into the conduction band. These electrons will no longer be bound to the vacancy and will contribute to photoconductivity.

In addition to the F band, crystals which have been additively colored with excess metal ions or have been exposed to ionizing irradiation may possess weaker bands on the long wavelength side of the F band. In most alkali halides (particularly KCl which has received the greatest amount of experimental study), when these crystals are bleached with F light at room temperature, the F band decreases

and the weaker bands increase. Some new bands, also on the long wavelength side of the F band, may also be developed. Since the color centers responsible for these bands are closely related to the F center, they are called F-aggregate centers.

The first F-aggregate center to be formed both in the initial coloration and upon F bleach is the M center. It consists of a pair of adjacent F centers along a $\langle 110 \rangle$ direction.¹³ There are six equivalent orientations corresponding to the six $\langle 110 \rangle$ crystallographic directions. Longer exposure to ionizing irradiation or longer periods of F bleach also produces R centers. The R center consists of three adjacent F centers forming an equilateral triangle in a $\{111\}$ plane.¹⁴ There are eight equivalent orientations corresponding to the $\{111\}$ planes perpendicular to the eight $\langle 111 \rangle$ directions. Additional F-aggregate centers, called N centers, are developed if the crystal is given prolonged exposure to either ionizing irradiation or F bleach. These centers have not been studied as extensively as have the M and R centers; nevertheless, tentative models, consisting of four closely associated F centers, have been proposed for two N centers.¹⁵ Schematic diagrams of the models for these F-aggregate centers are illustrated in Fig. 5.

The principal transition of the M center is between its ground state and the first excited state and gives rise to the M band. For the R center there are two principal transitions, from the ground state to the R_1 level and from the ground state to the R_2 level. These transitions give rise to two bands, the R_1 and R_2 bands, which lie in the spectral region between the M band and the F band. Two

Fig. 5 Schematic diagram of the current models for F-aggregate centers: (a) a three-dimensional array of the M center and a cross-section of the (100) plane, (b) a three-dimensional array of the R center and a cross-section of the (111) plane, (c) three-dimensional arrays of Pick's N_1 and N_2 centers.

different N centers, N_1 and N_2 , have been observed. Their main absorption bands are on the long wavelength side of the M band.

In addition to the principal absorption bands mentioned above, each F-aggregate center has weaker bands associated with it. These are produced by transitions between the ground state and various "higher" levels. Studies of these additional transitions have been made in KCl. The M center has several weak bands associated with it which lie on the short wavelength side of the M band.¹⁶ In particular, the M_F band lies under the F band. Six additional weak bands associated with the R center have been identified,¹⁷ including bands under the N, M and F bands (R_N , R_M and R_F , respectively). Finally, N centers have been found to have absorption bands (N_R) in the region of the R bands.¹⁸

The study of F-aggregate centers in LiF is made somewhat difficult by the following two facts: (1) LiF cannot be colored by addition of a stoichiometric excess of metallic ions, and (2) bleaching the F band with F light does not result in a conversion of $F \rightarrow F$ -aggregate centers. Therefore, in LiF F-aggregate centers must be produced by exposure of pure crystals to ionizing radiation, and only relatively small concentrations can be obtained. Specifically, the concentration of M centers produced by irradiation is approximately an order of magnitude less than the concentration of F centers produced, and the concentration of R centers is again an order of magnitude less than that of M centers. Only weak absorption bands in the N band region are obtained. The number and spectral positions of additional transitions of the M and R centers in LiF have not yet been established, and the N centers have received only very limited attention.

CHAPTER III

INSTRUMENTATION

Two optical spectrophotometers, a high intensity arc lamp, a low temperature sample cell, and a high temperature sample cell comprise the basic instrumentation employed. These are described separately in the following sections.

Optical Spectrophotometers

Two optical spectrophotometers were employed, a Bausch and Lomb model 505 and a Cary model 14R. Both of these instruments are double-beam recording spectrophotometers. The basic principle of optical absorption is the same for each and will be discussed first. The actual construction and operation differ slightly, however, and will be discussed individually.

Consider a slab of optical material of thickness l with monochromatic light of intensity I_0 , incident on the front face, see Fig. 6. Due to absorption losses, the total intensity of the transmitted light (I) will be less than I_0 . The analytical relation between these two intensities is easily obtained. Let x represent the depth into the material and $I(x)$ the intensity of light at that depth. The loss in intensity per increment of thickness ($-dI(x)/dx$) is assumed to be proportional to the intensity $I(x)$, so that

$$-\frac{dI(x)}{dx} = \alpha I(x) . \quad (3)$$

The proportionality constant α is wavelength dependent and is called the absorption coefficient. Integration of Eq. 3 yields

$$I = I_0 e^{-\alpha l} . \quad (4)$$

Fig. 6 Diagram illustrating the geometry used to discuss the attenuation of light by absorbing materials.

If common, rather than natural logarithms are used, then Eq. 4 becomes

$$I = I_0 10^{-O.D.} \quad (5)$$

where $O.D. = \alpha l / 2.303$ and is called the optical density.

A single-beam spectrophotometer measures the optical density of a single sample and records $\log(I_0/I) = O.D.$ as a function of wavelength. A double-beam spectrophotometer compares two different samples, (a) and (b), and records $\log(I(b)/I(a))$ as a function of wavelength, where $I(a)$ and $I(b)$ are the intensities of light transmitted through samples (a) and (b) respectively. From Eq. 5 it is seen that

$$\log \frac{I(b)}{I(a)} = O.D.(a) - O.D.(b) + \log \frac{I_0(b)}{I_0(a)} \quad (6)$$

Since the same intensity of light is incident on both samples, $\log(I_0(b)/I_0(a)) = 0$, and it is seen that a double-beam spectrophotometer records the difference in the optical densities of the two materials as a function of wavelength. For convenience, sample (b) is often called the reference material.

A simplified diagram of the optical and photometric system of the Bausch and Lomb model 505 spectrophotometer is shown in Fig. 7. A detailed discussion of the various components is given in the Bausch and Lomb manual.¹⁹ Therefore, only a brief description of the instrument and its operation will be given. A light source, interchangeable between a deuterium lamp for the ultra-violet region (200 mμ to 350 mμ) and a tungsten lamp for the visible region (350 mμ to 800 mμ), is located at (A). The light is collected by a condensing

Fig. 7 Schematic diagram of the Bausch and Lomb model 505 spectrophotometer.

lens (B) and focused onto the entrance slit (C) of the monochromator. The slits operate at a fixed band-width of either 0.5 mμ or 5 mμ. After leaving the exit slit, the light (now monochromatic to within the selected band-width) is split into two beams, a reference beam and a sample beam, by means of a beam splitter (D). The two separated beams are then alternately pulsed using two synchronous rotating mechanical choppers (E). During the first quarter of a cycle the sample beam is directed into the sample chamber and the reference beam is blocked. During the second quarter both beams are blocked. In the third quarter the reference beam is directed into the reference chamber, and the sample beam is blocked. During the last quarter both beams are again blocked. Thus the sample beam and the reference beam are "on" for only one quarter of each cycle. The complete cycle is repeated 60 times per second.

After passing through their respective chambers, the two paths are brought together and focused at (G) onto a photomultiplier (H). If an absorbing material has been placed in the sample chamber, but not in the reference chamber, the output of the photomultiplier consists of alternating square pulses as shown. The first pulse is proportional to the light transmitted through the sample. Following this is a dark period. The second pulse is proportional to the light transmitted through the reference chamber. The reference pulse is larger than the sample pulse since the reference pulse was not attenuated by an absorbing material.

The purpose of the remainder of the system is to record the ratio of the sample-to-reference signals as a function of wavelength.

This is achieved in the following manner. After amplification, the photomultiplier output is separated at (J). The reference signal is applied to a linear potentiometer (K) whose slider is mechanically connected to a recorder pen (L). By means of a servo mechanism, the potentiometer slider is constantly maintained at a position such that the voltage at the slider is equal to the voltage of the sample signal. Hence, the ratio of the distance of the potentiometer slider from the grounded end of the potentiometer to the length of the potentiometer is equal to $I(R)/I(S)$, where $I(S)$ and $I(R)$ are the intensities of light transmitted through the sample and reference material respectively. However, the mechanical connection between the potentiometer and the recorder pen is via logarithmic gears. Thus, the pen records a signal proportional to $\log(I(R)/I(S)) = O.D.(S) - O.D.(R)$, where $O.D.(S)$ and $O.D.(R)$ are the optical densities of the sample and reference respectively. If the reference chamber is left empty, $O.D.(R) = 0$, and the pen records only the optical density of the sample. A continuous curve is obtained by continuously scanning the monochromator.

In order for the electrical system to operate properly, it is necessary to maintain the height of the reference signal approximately constant. This is accomplished by comparing the reference pulse at (K) with a standard pulse (M) and using the difference to regulate the high voltage to the photomultiplier. For example, if the reference signal should decrease due to a decrease in the intensity of the light source, the difference between the two pulses will increase and cause a higher voltage to be applied to the photomultiplier. Since the output of a photomultiplier is proportional to the applied voltage, this will restore the reference signal to its initial value.

In addition to correcting for variations in the light source intensity, a double-beam spectrophotometer can also be used for "differential" absorption measurements. These are obtained by also placing an absorbing material in the reference chamber. The pen now records a signal proportional to the difference in the O.D. of the sample material and that of the reference material. This is a distinct advantage for certain applications.

A diagram of the optical system of the Cary 14R spectrophotometer is shown in Fig. 8. For absorption measurements between 180 $m\mu$ and 350 $m\mu$, a hydrogen lamp (A) is focused by lenses (B,C) onto the entrance slit (D) of the monochromator. For measurements between 350 $m\mu$ and 3000 $m\mu$, mirror (a) is inserted, and a tungsten lamp (c) is focused by lenses (b,C) onto (D). The monochromator consists of a fused silica prism (F) and a grating (J), each with its own collimating mirrors (E,G,J,K) and slit system (D,H,L). After leaving the exit slit, the narrow band of light is focused by lens (M) onto two disks (N and O). These disks are rotated by means of a 30 cps synchronous motor (Q) and are constructed such that the light is separated into a sample beam and a reference beam, each of which is "on" for one-fourth of a cycle. The reference beam is directed through the reference cell (T') and onto the photomultiplier (X) by mirrors (P,R',V',W'). Similarly, the sample beam is directed through the sample cell (T) and onto the detector by mirrors (R,V,W). For operation between 700 $m\mu$ and 3000 $m\mu$, the photomultiplier is replaced with a lead sulfide detector (Y) by means of rod (Z).

Fig. 8 Schematic diagram of the optical system of the Cary model 14R spectrophotometer.

A simplified schematic of the electronic system for the Cary 14R is drawn in Fig. 9. Discussions of the various components are available in a manual provided by the manufacturer.²⁰ So only a brief description will be given. The output of the detector (x) consists of repeated cycles of sample pulse, dark period, reference pulse and dark period. After amplification, two relays (A and B) alternately apply the sample pulse and then some fraction of the reference pulse to a comparison relay (C). The fraction of the reference pulse applied to (C) is determined by the position of the slider of the potentiometer (D). The magnitude and phase of the error signal from (C) controls a servo mechanism which maintains the position of the slider such that the signals on either side of the comparison relay are equal. The potentiometer (D) is logarithmic so that the ratio of the distance of the potentiometer slider from the grounded end of the potentiometer to the length of the potentiometer is equal to $\log (I(R)/I(S))$. Linear gears connect the slider to a recorder pen (E). Thus, the pen records a signal proportional to $\log (I(R)/I(S))$, as in the case of the Bausch and Lomb spectrophotometer.

The height of the reference pulse is kept constant by varying the slit-width which determines the intensity of the light leaving the monochromator. A relay (F) compares the reference pulse to a standard pulse. If, for example, the error signal is positive (reference greater than standard), the width of the slit is decreased by means of the slit motor (M).

The Cary 14R was also employed for luminescence studies. For these measurements, the tungsten lamp (c, Fig. 8) is removed and

Fig. 9 Simplified schematic diagram of the electronic system of the Cary model 14R spectrophotometer.

replaced with the photomultiplier. The luminescent light from the sample travels through the monochromator in the reverse direction to the detector. To obtain linear measurements, the logarithmic potentiometer (D, Fig. 9) is replaced by one which is linear.

High Intensity Arc Lamp and Housing

For optical bleach experiments, a narrow band of high intensity light is required. If the study of kinetics is to be included, the intensity must also be stable for long periods of time. The present work employed a 1000 watt d.c. Hg-Xe arc lamp (model 977B-1) and power supply (model 27801) purchased from E. Hanovia Inc., Newark, New Jersey. The lamp emits the spectra characteristic of both Hg and Xe and thus has major emissions near 248, 253, 313, 365, 435 and 577 m μ . A grating monochromator was used to select the particular wavelength desired.

A cross-sectional view of the lamp and the metal housing constructed to hold it is shown in Fig. 10. Also included is a schematic diagram of the monochromator. (In actual practice, the monochromator is used in a position rotated 90° about the axis shown by the broken line.) The lamp is clamped between heavy copper leads (A,B) which are connected to the power supply through insulators (C,D). The walls of the housing are lined with highly polished aluminum sheeting, and cooling is accomplished by a fan (E) placed at the top of the housing. A spherical reflector (F) is used to increase the solid angle of collected light and adjusted so that the arc image is reflected onto itself. The quartz lens (G) focuses the arc onto the entrance slit (H) of the monochromator. The monochromator consists

Fig. 10 Schematic diagram of the arc lamp, lamp housing, and monochromator employed in this investigation.

of two spherical mirrors (I,J), a grating (K) whose angle is adjustable with dial (L), and a plane mirror (M). Slits corresponding to a bandwidth of 5, 10, or 20 mμ can be selected for both the exit slit (N) and the entrance slit. A quartz lens (O) focuses the beam onto the sample (P).

Low Temperature Sample Cell

In order to carry out optical bleach treatments over a continuous range of temperature, two special sample cells were employed. Each was designed to be used in conjunction with the Cary 14R so that concurrent absorption measurements could be taken. For temperatures between 77°K and room temperature, a miniature Joule-Thomson refrigeration system (Cryo-Tip model AC-1-110) purchased from Air Products and Chemicals, Inc., Allentown, Pennsylvania, was used. Again, details of its operation are contained in a manual provided by the manufacturer.²¹ Therefore, only a brief description is given. A cross-sectional view of the cryostat is illustrated in Fig. 11. Before cooling is begun, the cryostat is pumped out through vacuum port (A). For studies at 77°K nitrogen gas at high pressure (approximately 1500 psi) is allowed to enter through fitting (B). The Joule-Thomson valve is contained in the upper section (C) and cools a "cold finger" (D). The gas exhausts out fitting (E). A copper sample holder (F) was constructed and attached to the cold finger. At its center is a small hole over which the crystal (G) is held by means of a spring mechanism (H) and support (I). Not shown is a thermocouple which was soldered to the sample holder and which entered the cryostat through the lead-in (S). The vacuum jacket (J) can be rotated without breaking the seal. It

Fig. 11 Cross-sectional view of the low temperature sample cell and mount employed in this investigation.

contains four ports which are covered with quartz windows (K, L and two in the plane of the drawing). For studies between 77°K and room temperature, the temperature could be regulated either by adjusting the back pressure of the exhaust gas or by inserting the nitrogen gas at pressure below 1500 psi. The stability at the intermediate temperatures was within a few degrees for periods up to eight hours.

To adapt the cryostat to the Cary 14R an adjustable mount was constructed. This consists of a cylindrical sleeve (M) held to the cryostat by means of several Allen screws (N). The sleeve is fastened to a rectangular plate (O) with a flange. A second rectangular plate (P) fits the top of the spectrophotometer sample chamber. The cryostat can be horizontally positioned by loosening screws (Q,R) and moving plate (O), and thereby the cryostat, relative to plate (P). Vertical adjustment can be accomplished by loosening the Allen screws and sliding the cryostat up or down.

Absorption measurements were taken with the sample in the position shown. To optically bleach the crystal, the top section (C), and thereby the attached sample holder (F), was rotated 90° relative to the jacket and mount. The bleaching light entered in a direction perpendicular to the plane of the paper.

High Temperature Sample Cell

For studies above 300°K a high temperature cell was constructed. A cross-sectional view is illustrated in Fig. 12. A brass cylindrical shell (A) and end plate (B) are fastened to a rectangular copper plate (C). Together, (A), (B), and (C) form an enclosure for the heating element. Several turns of high resistance wire are wound around a

Fig. 12 Cross-sectional view of the high temperature sample cell and mount constructed for this investigation.

copper sleeve (D). To prevent an electrical short a thin layer of asbestos is inserted between the wires and the sleeve. Attached to the sleeve is a copper disk (E) with a small hole in the center. The sample (F) is held over this aperture with a spring and mounting support. To prevent tarnishing of the disk (E) and thus poor heat transfer to the sample, the disk was gold plated. To reduce heat loss by conduction, the sleeve assembly is held by means of stainless steel screws from plate (C). To reduce heat loss from convection, additional asbestos is packed in the space around the sleeve, and quartz windows (G,H) are added. This "oven" assembly is fastened to a mount (I) which fits into the sample compartment of the Cary 14R. The sample can be accurately positioned in the light beam by loosening screws (J,K) and sliding the "oven" relative to the bracket (I). To protect the optical system of the spectrophotometer from excessive heat, the entire assembly is cooled by running water through the copper plate (C). The hose connections for this are not shown. Also now shown is a thermocouple which enters via feed-through (L) and is soldered to the sample disk (E).

The resistance wire is connected to a variac, and the temperature is regulated by varying the voltage. Temperatures up to 700°K are easily obtained, and the stability is within a degree for periods up to several hours.

CHAPTER IV

OBSERVATION OF THE R_N BAND IN LiF NEAR 300°K

This chapter investigates whether R centers in LiF possess associated bands in the N band region. Such a determination is necessary before more detailed investigations can be made with regard to the conversion mechanisms of R centers, which involve absorption changes in the N band region.

Recently, Silsbee²² has investigated the stress-induced dichroism of the R center in KCl near 2°K, and observed a broad (optical absorption) band in the region of the N bands (N_1 near 960 mμ and N_2 near 1028 mμ)²³, which Silsbee has attributed to an optical transition of the R center from the ground state to the first excited state. It is designated the R_N band. The R center exhibits two prominent bands: R_1 (680 mμ) and R_2 (740 mμ).²⁴ The dichroism of the R_N band is directly associated with the dichroism of the R_1 and R_2 bands. This chapter presents experimental evidence of a broad band in LiF near 300°K, which is similar to the R_N band of KCl. A summary of this work has recently been published by this author and Y.W. Kim in Physics Letters.²⁵

In the case of LiF, the R_1 and R_2 bands are centered at approximately 310 mμ and 378 mμ respectively,²⁶ while the N_1 and N_2 bands are reported to be centered near 520 mμ and 540 mμ respectively.^{27,28} In order to identify the R_N band of LiF, it is necessary first to distinguish the optical bands (N for convenience) expected in the region of the N bands, and their associated "higher" bands (N_R), which are in the region of the R bands. Secondly, one has to examine possible

dichroism of these N and N_R bands due to optical bleaching by polarized R light,²⁹ so that the dichroism of the R_N band can be distinguished from that of the N bands.

Thermal annealing and/or optical bleaching of samples of neutron or gamma irradiated single crystals of LiF have yielded three distinct bands in the region of the N bands. For convenience they are labeled the N_a , N_b and N_c bands, and the color centers responsible for them as the N_a , N_b and N_c centers respectively. The N_a band is centered at approximately 500 $m\mu$ and can be produced only by thermal annealing of samples above 300°K. Thus, it is of no concern in the present work. The N_b band (525 $m\mu$) and N_c band (550 $m\mu$) are present in heavily irradiated samples. The latter band can be greatly enhanced by optical bleaching of the R bands with R light. The N_b and N_c centers possess associated N_R bands at 365 $m\mu$ and 415 $m\mu$ respectively. In order to maintain a consistent notation, these associated bands are labeled N_{b_1} and N_{c_1} respectively. Fig. 13 illustrates a typical optical absorption spectrum exhibiting the R_1 and R_2 bands, the N bands and their weaker associated bands, and the M band (445 $m\mu$). The solid curve corresponds to a sample exposed to neutron irradiation for a dose of 10^{15} nvt, and the broken curve, to the same sample subsequently bleached for eight hours near 300°K with a high pressure Hg lamp filtered with a Corning filter #7380 (cutting off the light of wavelength less than 340 $m\mu$). The location of the N_b and N_c bands is fairly close to that of the N_1 and N_2 bands previously reported.

When samples exhibiting predominant N_b and N_c bands and their higher bands are optically bleached with the R light polarized along

Fig. 13 Position of the R, N, and N_R bands of LiF observed in the present work. The solid curve corresponds to a neutron irradiated sample with 1×10^{15} nvt, and the broken curve, to the same sample bleached for 8 hours near 300°K, with a high pressure Hg lamp filtered with a Corning filter #7380 (cutting off the wavelengths less than 340 mμ).

a $\langle 011 \rangle$ direction, subsequent optical absorption studies have yielded no noticeable dichroism in the region of the N bands. This indicates that the centers responsible for the N and N_R bands are not involved in the dichroism of the R center in the region of the N bands.

When samples containing the R centers are bleached with the R light polarized along a $\langle 011 \rangle$ direction, dichroism is definitely induced. Fig. 14 illustrates the dichroic absorption obtained by subtraction of the "perpendicular" absorption from the "parallel" absorption of a gamma irradiated sample, which was previously bleached by the polarized R light for 45 minutes near 300°K. The dichroism of a broad band ranging from 480 mμ to 600 mμ, and the growth and decay of the band have been found to be associated with the dichroism of the R bands and their growth and decay. No noticeable dichroism could be induced in the R bands or in the region of the N bands with the R light polarized along a $\langle 001 \rangle$ direction. This is expected since the symmetry axis of the R center is known to be along the $\langle 111 \rangle$ direction.³⁰ The results indicate that the observed dichroism of the broad band in the region of the N bands is similar to that of the R_N band of KCl, and thus the broad band is attributed to the R_N band of LiF.

Fig. 14 The anisotropic optical absorption of a gamma irradiated sample with 100 MR after the sample has been optically bleached with the R light polarized along a $\langle 011 \rangle$ direction for 45 minutes. The anisotropic absorption is obtained by subtracting the "perpendicular" absorption from the "parallel" absorption of the sample.

CHAPTER V

OPTICAL CONVERSION OF THE F_3^+ CENTER IN LiF WITH R LIGHT*

Introduction

The work described in this chapter is concerned with the effect of R bleach on the interconversion among F and F-aggregate centers. The results of the last chapter play an important role in this determination.

Single crystals of LiF, when exposed to ionizing radiation at room temperature, develop stable F, M, F_3^+ , and R (color) centers.³¹⁻³⁸ A typical absorption spectrum is illustrated by the solid curve (a) of Fig. 15. The peak of the large F (center) band is near 245 mμ.³⁹ The M center, consisting of a pair of F centers,⁴⁰ has its principal band near 445 mμ. The R center consists of a cluster of three F centers,⁴¹⁻⁴⁶ and thus can also be designated as the F_3 center. This center has two principal bands, the R_1 and R_2 bands centered at 313 mμ and 378 mμ respectively. Another band (R_N) resulting from a lower energy transition of the R center has been discussed in the previous chapter.

Under the M band there is a weak band whose peak is almost coincident with that of the M band. This weaker band is ascribed to the F_3^+ center,^{47,48} an ionized R center. Although the half-width of this band is .318 ev. while that of the M band is .19 ev.,⁴⁹ the weaker band is often masked by the more intense M band. However, the

* The content of this chapter is based on a manuscript submitted to the Physical Review by this author and Y.W. Kim..

Fig. 15 Absorption spectrum of a gamma-irradiated (40 MR) sample of LiF.

(a) before R₁ bleach

(b) after 32 minutes of R₁ bleach

existence of F_3^+ centers in irradiated LiF can be demonstrated and investigated by measuring the luminescence induced with an M light excitation.⁵⁰ The observed spectrum of the luminescence exhibits two prominent emission bands. When the spectral response of the detector is linearized, the peak of one band is near 540 mμ and that of the other near 670 mμ.⁵¹⁻⁵³ A typical uncorrected emission spectrum is shown by the solid curve (a) of Fig. 16. The 540 mμ emission band has been assigned to the F_3^+ center,^{54,55} while the 670 mμ emission band is tentatively assigned to the M center.⁵⁶ This latter assignment, however, does not seem to be well established, since there has been a claim that another weak band underlying the large M band may be responsible for all or part of the 670 mμ emission band.⁵⁷ In any case, the 540 mμ emission band facilitates the investigation of the F_3^+ center under controlled optical treatments, which will be discussed in the present paper.

Recent investigations^{58,59} have demonstrated that F_3^+ centers can be converted into R centers either by bleaching with F light near 300°K or by x-irradiation near 77°K. The reaction mechanism is as follows:

The electron (e) participating in the above mechanism is presumably provided by the photoionization of the F center in the case of F bleach, and by the photoelectric effect in the case of the x-irradiation.

The present chapter presents experimental evidence pertaining to the transformation of F_3^+ centers into R centers by means of R bleach. The existing knowledge of the electronic structure of M and R centers

Fig. 16 Uncorrected emission spectrum due to M light (435 mμ) excitation of a gamma-irradiated (40 MR) sample of LiF.

(a) before R_1 bleach

(b) after 32 minutes of R_1 bleach

indicates that it is not possible to photoionize these centers by means of R bleach. Accordingly, any observable conversion of F_3^+ centers into R centers by R bleach should be attributed to a new band which lies in the region of the R bands and which can be easily photoionized by R light, thereby yielding free electrons. These photoelectrons can combine with the existing F_3^+ centers to form R centers according to Eq. (7).

Experimental Procedures

Single crystals of LiF were purchased from Harshaw Chemical Company, Cleveland, Ohio, and also from Optovac, Inc., North Brookfield, Massachusetts. Samples approximately $10 \times 7 \times 1 \text{ mm}^3$ were cleaved along the cubic axes and subsequently irradiated with gamma-rays, x-rays, or neutrons at room temperature. The x-rays were generated from a molybdenum target operated at 50 kV and 20 mA for periods up to 20 hours. The thermal neutron irradiation was performed at the Phoenix Memorial Laboratory, Ann Arbor, Michigan, for doses of 10^{15} nvt. The gamma-irradiation was carried out at the Phoenix Memorial Laboratory and also at the Naval Research Laboratory, Washington, D.C., for doses of from 1 to 100 MR. Care was taken during irradiation and storage to prevent any accidental exposure of the samples to room light.

Subsequently, the irradiated samples were subjected to optical absorption and emission studies as well as photoconductivity measurements. The absorption measurements were made with a Bausch & Lomb model 550 double beam spectrophotometer (200 mμ to 800 mμ). The concentration of R centers was conveniently measured by the peak height of the R_2 band, because of the following two reasons. First, the R_1

and R_2 bands arise from transitions of the same center and thus retain a constant relative peak height ratio. Secondly, the R_1 band was somewhat masked by the low energy side of the intense F band. Usually the F center concentration was so large that accurate measurements of the F band could not be made. N centers, which have absorption bands on the long wavelength side of the M band, were not present in the samples used in this investigation.

As described in the Introduction, the concentration of F_3^+ centers was measured in terms of the emission band of the F_3^+ centers. The emission spectra were obtained using a Cary model 14 R spectrophotometer in the arrangement shown in Fig. 17. A 150 watt tungsten lamp was focused onto the sample by means of a condensing lens. A copper sulfate solution (f_1) was used to reduce heat. The M light was obtained by means of an interference filter (f_2) with λ_0 at 435 m μ and a band-width of 10 m μ . To eliminate the background light in the region of the emission bands, a Corning glass filter #5113 (f_3) was inserted. The photomultiplier had an S-20 spectral response.

In order to observe possible generation of free electrons by bleaching with R light, photoconductivity measurements were taken. These were made by placing the sample between two electrodes, one a small copper plate and the other a nickel screen, in series with a 300 volt d.c. potential difference. The exciting light entered through the screen and produced a current of the order of 10^{-13} amperes. The current was measured with an electrometer (General Radio Company type 1230-A) using an input resistance of 10^{10} ohms.

Fig. 17 Optical arrangement for measuring emission spectra.

The R light used for the bleaching was obtained from a 1000 watt d.c. Hg-Xe arc in conjunction with a grating monochromator. For R_1 bleach the monochromator was set at 313 m μ with a slit-width of 10 m μ . For R_2 bleach the monochromator was set at 365 m μ with a slit-width of 20 m μ . The larger slit-width in the latter case was used to gain intensity since the rates of the reactions induced by R_2 bleach were considerably slower than those induced by R_1 bleach.

Results and Discussions

Figure 18 illustrates the effect on both the emission (a) and absorption (b) spectra of an irradiated sample of LiF with increasing time of R_1 bleach. It is seen that after a slight initial increase, the R bands (measured by the peak height of the R_2 band) slowly decrease and are completely destroyed after 25 minutes. The peak height of the M band increases slowly and saturates at about a 15% increase when the R centers are destroyed. It appears that the 670 m μ emission band increases slightly, but small changes in this band are difficult to measure accurately due to the overlap of the 540 m μ emission band. The 540 m μ emission band decreases rapidly to about half its initial intensity. The broken curves (b) of Figs. 15 and 16 show the absorption and emission spectra, respectively, at the termination (after 32 minutes for this sample) of the R_1 bleach. A comparison of the two curves in Fig. 15 reveals that the R centers have been destroyed and the M band has grown. The broken curve (b) of Fig. 16 indicates that the 540 m μ emission band decreased approximately 50% whereas the 670 m μ emission band changed only slightly. The early stages of R_2 bleach (365 m μ) also reveals a rapid partial decrease of the 540 m μ

Fig. 18 Variation in emission and absorption peaks of a gamma-irradiated (40 MR) sample of LiF with R_1 bleach near 300°K.

(a) emission due to M light (435 m μ) excitation

(b) absorption

emission band and a slight increase of R centers. Thus using either R_1 or R_2 light, the behavior of the R bands and the 540 m μ emission band during the early stages of bleaching is the same: the R bands increase slightly and the 540 m μ emission band decreases to about half its initial intensity. Since the 540 m μ emission band is due to the F_3^+ center, this suggests that during the early stages of bleaching, F_3^+ centers are converted into R centers.

Concurrently with observing changes induced in the emission and absorption spectra, photoconductivity measurements were taken. Using either R_1 or R_2 light as the source of excitation, a photocurrent was observed. Moreover, this photocurrent decreased rapidly with time of R bleach. The decay in the photocurrent followed the decrease of the 540 m μ emission band. It ceased when the 540 m μ emission band ceased decreasing. These measurements indicate the generation of free electrons by the R bleach, which participate in the conversion of F_3^+ centers into R centers during the early stages of R bleach. The fact that the photocurrent ceased early in the bleaching process while a considerable concentration of R centers still remained is consistent with the reported observation that R centers are not photoionized by R light.⁶⁰ Thus, the free electrons must originate from the photoionization of a new kind of color center (designated X for convenience), whose main absorption band (the X band) lies in the region covering the two R bands.

Additional supporting evidence on the conversion of F_3^+ centers into R centers by means of the X center can be obtained from studying the kinetics of the decrease of F_3^+ centers. The reaction, Eq. (7),

would be expected to be governed by an equation for a second order process:

$$\frac{d[F_3^+]}{dt} = -k [F_3^+][e] \quad (8)$$

where $[F_3^+]$ and $[e]$ are the concentrations of F_3^+ centers and electrons, respectively, present at time t . If the electrons are furnished by the photoionization of the X centers, the concentration of X centers would be expected to be described by a first order reaction:

$$[X] = [X]_0 e^{-k_2 t} \quad (9)$$

where $[X]_0$ is the initial concentration. The concentration of electrons present at time t is then taken to be

$$[e] = \gamma[X] = \gamma[X]_0 e^{-k_2 t} \quad (10)$$

where γ is a proportionality factor. From Eqs. (8) and (10) one obtains

$$\ln \frac{[F_3^+]}{[F_3^+]_0} = 2.303 \log \frac{[F_3^+]}{[F_3^+]_0} = \frac{k_1}{k_2} (e^{-k_2 t} - 1) \quad (11)$$

where $k_1 \equiv k\gamma[X]_0$ and $[F_3^+]_0$ is the initial concentration of F_3^+ centers. Thus Eq. (11) indicates that a plot of $\log [F_3^+]$ against $\exp(-k_2 t)$ should be linear, the slope being $k_1/2.303k_2$. Let $[F_3^+]_\infty$ be the concentration of F_3^+ centers in the limit as $t \rightarrow \infty$, or $\exp(-k_2 t) \rightarrow 0$. In the sample used for R_1 bleach, 48% of the F_3^+ centers remained even after prolonged bleach, and thus $[F_3^+]_\infty/[F_3^+]_0 = .48$. For convenience, the initial concentration $[F_3^+]_0$ is normalized to 1. Then the concentration of F_3^+ centers decreased from 1 to .48. The "theoretical"

plot (using the observed value of $[F_3^+]_\infty$) of Eq. (11) is shown by the straight line in Fig. 19(a). In the sample used for R_2 bleach, 37% of the F_3^+ centers remained for $t \rightarrow \infty$. The theoretical plot in this case is shown by the straight line in Fig. 19(b). Since the experimental data of $\log [F_3^+]$ is taken as a function of time t , the comparison of the experimental data with the theoretical straight line can be made by searching for an optimum value of k_2 . The best fit was obtained using $k_2 = .3$ for the case of R_1 bleach, and $k_2 = .06$ for the case of R_2 bleach. The results are illustrated by the circles of Fig. 19. It should be noted here that the above procedure is based on several simplifying assumptions: (a) that the intensity of the 540 mμ emission band is proportional to the concentration of F_3^+ centers, (b) that the intensity of the bleaching light is constant and uniform throughout the sample, (c) that the proportionality factor γ remains constant, (d) that the X center is destroyed by a first order reaction, and (e) that all the photoelectrons released are captured by F_3^+ centers. Considering these simplifications, the agreement between the experiment and theory is satisfactory.

In order to consolidate further the existence of this new X band, changes in the absorption spectrum during the early stages of the bleaching were more carefully examined by means of a "difference" spectrum. This is obtained by placing an identical irradiated crystal in the reference beam of the spectrophotometer. Using this difference spectrum, small changes induced by short periods of bleaching are no longer masked by the large absorption bands, but appear as deviations from a "flat" spectrum of zero optical density. A difference spectrum

Fig. 19 Plot of $\log [F_3^+]$ against $\exp(-k_2 t)$ where t is the time of R bleach. The straight lines represent a theoretical plot of Eq. (11), while the circles are experimental points for

(a) R_1 bleach ($k_2 = .3$)

(b) R_2 bleach ($k_2 = .06$)

obtained after 15 seconds of R_1 bleach is illustrated by the solid curve in Fig. 20. Similar results have also been obtained by means of R_2 bleach. Three points of interest should be mentioned in connection with the solid curve (difference spectrum) of Fig. 20. First, the relatively large dip below zero in the region between 300 m μ and 380 m μ indicates a decrease in the corresponding region of the absorption spectrum (not the difference spectrum) during the early stage of R_1 bleach. The maximum dip region does not belong properly to either the R_1 band or the R_2 band. Secondly, the region of the R_N band has increased, indicating an increase of the R center concentration. This should account for the two "peaks" near the centers of the R_1 and R_2 bands. Thirdly, in the region of the M band, there is a positive peak and two negative dips. The former is located at the center of the M band. This pattern can be most easily accounted for as a result of two simultaneous, but distinct, changes: one, an increase in the M band absorption, and the other a decrease in the F_3^+ absorption. These observations are consistent with the proposed mechanism for the participation of the X center in the conversion of F_3^+ centers into R centers. The broken curves in Fig. 20 represent an optimum graphical decomposition of the solid curve in accordance with the conversion mechanism operating in the early stages of R bleach. It shows that the new X band is fairly broad.

The X band is not present in unirradiated samples, but appears when samples obtained from different manufacturers are irradiated with x-rays, gamma-rays, or neutrons. This indicates that the X band

Fig. 20 Difference in the absorption spectrum of a gamma-irradiated (100 MR) sample of LiF after 15 seconds of R_1 bleach near 300°K. Solid curve is the observed change; broken curves are decompositions into R bands, an underlying broad band, the M band, and the F_3^+ band. (see Text)

is a general characteristic of LiF irradiated at room temperature and not something particular to a few samples. It is not a transition associated with either the M center or the R center, since these increase, not decrease, during the early stages of R bleach. It is unlikely that the X band is a transition associated with the F_3^+ center, since the conversion ceased while nearly half of the F_3^+ centers still remained. Thus the broad X band is not associated with any of these centers currently known to exist in the irradiated sample. However, no definitive model of the X center is easily available at the moment. This is mainly due to the very small concentration of the X center and its thermal instability above room temperature.

Conclusion

R_1 and R_2 bleach of irradiated LiF near 300°K have revealed the existence of a new color center whose main absorption band covers the region of the R_1 and R_2 bands. The new center is not related with any of the known color centers, and facilitates the conversion of F_3^+ centers into R centers according to the mechanism:

where the electron is provided by the photoionization of the new color center by the R bleach. Additional supporting evidence is provided by photoconductivity measurements and reaction kinetics studies.

CHAPTER VI

PHOTOCHEMICAL DESTRUCTION OF THE R CENTER IN LiF^{*}

Introduction

The previous chapter demonstrated the existence of a new broad band in irradiated LiF underlying both the R_1 and R_2 bands and its involvement in the conversion of F_3^+ centers into R centers by R bleach. The R bleach photoionizes the defect responsible for the broad band, leading to the reaction: $F_3^+ + e \rightarrow R$. Experimentally, this reaction is found to be of the second order. Simultaneously, but at a slower rate, R bleach also destroys the R centers. Therefore, the concentration of R centers with time of R bleach can be represented by a consecutive photochemical reaction of the form:

The present work was undertaken to determine the specific kinetics and mechanisms involved in the optical destruction of R centers with R bleach, the second reaction of Eq. (12).

Experimental Procedures

Single crystals of LiF were purchased from Harshaw Chemical Company, Cleveland, Ohio. Samples about $10 \times 10 \times 1 \text{ mm}^3$ were cleaved along the cubic axes and subsequently irradiated at room temperature with gamma-rays for doses of from 1 to 100 MR. Care was taken during irradiation and storage to prevent any accidental exposure of the samples to room light. The irradiated samples were subjected to

^{*} The content of this chapter is based on a manuscript submitted to the Physical Review by this author and Y.W. Kim.

either R_1 light (313 m μ) or R_2 light (365 m μ) at temperatures ranging from 77°K to 380°K. In order to observe the effects of the R bleach, the absorption spectrum was taken periodically until the R centers were completely destroyed. In all cases, the absorption measurements were taken with the sample at the same temperature at which it was bleached. The spectra were recorded with a Cary 14R spectrophotometer. For measurements above room temperature a high temperature cell was constructed, which could hold the sample at a constant temperature ($\pm 1^\circ$ K) of from 300°K to 675°K. The cell contained two quartz windows and could be rotated 90° such that the sample could be alternated between the bleaching light and the measuring beam of the spectrophotometer. For measurements below room temperature down to 77°K, a miniature Joule-Thomson refrigeration system (Cryo-Tip, model AC-1-110) purchased from Air Products and Chemical, Inc., Allentown, Pennsylvania, was used. The vacuum jacket of this cell contained three quartz windows and the inner sample holder could be rotated 90°, again permitting a convenient alternation between the bleaching position and the measuring position.

The R light used for the bleaching was obtained from a 1000 watt d.c. Hg-Xe arc lamp (model 9778-1) and its power supply (model 27801) purchased from E. Hanovia, Inc., Newark, New Jersey, in conjunction with a grating monochromator. For R_1 bleach the monochromator was set at 313 m μ with a slit-width of 10 m μ . For R_2 bleach the monochromator was set at 365 m μ with a slit-width of 20 m μ . The larger slit-width in the latter case was used to gain intensity since the rates of the reactions induced by R_2 bleach were considerably slower

than those induced by R_1 bleach. The intensity of the bleaching light was measured by means of a calibrated thermopile (model RBL 500) purchased from Charles M. Reeder Company, Detroit, Michigan

Experimental Results

A. R_2 Bleach

Figure 21 illustrates the absorption spectrum of an irradiated sample of LiF (a) before R_2 bleach, (b) after 13 minutes of R_2 bleach, and (c) after 33 minutes of R_2 bleach. The decrease of the R_1 and R_2 bands and the appearance of a band at 550 $m\mu$ are evident. Since the F-aggregate bands on the long wavelength side of the M band are commonly referred to as N bands, the band at 550 $m\mu$ to be discussed in this paper will be designated as the N_c band for convenience and the color center responsible for it as the N_c center. This notation is consistent with that used in Chapter IV. This notation, however, does not necessarily imply that the N_c center actually corresponds to Pick's model of N centers (see Discussion). As Chapter IV demonstrated, the decrease on the long wavelength side of the M band (445 $m\mu$) is due to a decrease of the R_N band. This band is due to a low lying transition of the R center and extends from approximately 460 $m\mu$ to 600 $m\mu$. Whenever the N_c band is produced, two smaller bands, one on the short wavelength side of the M band and the other under the R_2 band, also increase. These are labeled N_{c_1} and N_{c_2} , respectively, and are ascribed to higher transitions of the N_c center. The N_{c_1} band is masked by the larger M band, but the N_{c_2} band was determined to have a peak height one-sixth that of the N_c band. The peak of the M band in Fig. 21 extends to an optical density of 2.2. It changed only slightly

Fig. 21 Absorption spectrum of a gamma-irradiated (100 MR) sample of LiF at room temperature

- (a) before R_2 bleach
- (b) after 13 minutes of R_2 bleach
- (c) after 33 minutes of R_2 bleach

during the bleaching process. The F band (245 mμ) was too large to observe accurately.

To determine whether the N_c band increased in a direct relation to the decrease of the R bands, a plot of the increase in the optical density (O.D.) of the peak of the N_c band (ΔN_c) versus the decrease in the O.D. of the peak of the R_2 band (ΔR) is shown in Fig. 22. ΔR was measured at the peak of the R_2 band since the R_1 band is rather masked by the much larger F band. The graph is divided into two regions by a broken line: region A is to the left and region B, as shown, is to the right. The region A represents the first few minutes of bleach. As discussed in Chapter V, during the early stages of bleach, R centers are created as well as destroyed due to the conversion of F_3^+ centers. In the region B, the creation process (the first reaction of equation (12)) has nearly ceased, and the destruction process dominates. It is seen that in the region B the relation between ΔR and ΔN_c is linear. This indicates that the growth of the N_c band is directly related to the decay of the R bands. The slope of the linear region in Fig. 22 is 1.25.

When the R_2 bleach is applied at a controlled temperature, above or below room temperature, the N_c band is again produced. The resulting plots of ΔN_c versus ΔR are similar to Fig. 22; however, the slope of the linear portion (region B) decreases as the temperature is increased. This variation of slope with temperature is illustrated in Fig. 23. The fact that the slope decreases as the temperature increases indicates that for a given number of R centers destroyed, more N_c centers are produced at lower temperatures than at higher temperatures.

Fig. 22 Plot of the increase in the N band against the decrease in the R bands. Region B represents the destruction of the R centers.

Fig. 23 Dependence of the ratio $\Delta N_c / \Delta R$ with temperature of sample.

This suggests that in addition to the $R \rightarrow N_c$ conversion there is at least one other mechanism whereby R_2 bleach destroys R centers. The latter mechanism necessarily becomes more efficient as the temperature increases.

The existence of simultaneous modes of destruction is illustrated in Fig. 24, where the R_2 bleach is applied at 378°K. The F band was measured by means of a "difference" spectrum, with the reference sample necessarily at room temperature. The observed change in the F band was not as accurate as those in the R, M, or N_c bands, and thus is shown by a broken curve. It is seen in Fig. 24 that the M, F and N_c bands all increase in direct relation to the decrease of the R bands. The results indicate that the destruction of R centers by R_2 bleach occurs by two concurrent mechanisms: qualitatively speaking, (a) an individual R center is destroyed either by decomposition into an F center and an M center or (b) it is destroyed by conversion into an N_c center. The latter mode is permanent; that is, no decrease in the N_c band occurs when a bleached sample is stored in the dark at room temperature for several months. The former mode, however, is not entirely permanent, for some regrowth of the R bands and decrease in the M and F bands are observed after storage in the dark for several months. Therefore, the second stage of Eq. (12) is replaced explicitly by a pair of concurrent processes:

The proposed mechanism of Eq. (13) is consistent with the observed kinetics for the R_2 bleach. Let $[R]$ be the concentration of R centers

Fig. 24 Change in the absorption peaks when R_2 bleach is applied at 378°K.

present at time t . The decrease of R centers should be of the first order, since Eq. (13) implies that⁶¹

$$\frac{d[R]}{dt} = -k_a[R] - k_b[R] = -k[R] \quad (14)$$

where the specific reaction rate k is the sum of the individual rates. Upon integration, it is seen that a plot of $\ln[R]$ against t should be linear, the slope being equal to $-k$. Using common logarithms a plot of $\log [R]$ against t is also linear, the slope being $-k/2.303$.

It should be noted here that in studying the kinetics of the R -bleach, care must be taken to insure that a constant intensity of light be incident on all parts of the sample. In all cases reported in this work, as the R bleach progresses, the optical density of the R bands gradually decreased since the R centers were gradually being destroyed. Therefore, as the bleach continued, the samples became more transparent to R light, and the intensity of the bleaching light at any given depth in the sample (except the front face) gradually increased. This required a correction factor to be applied to the observed data. This correction factor is derived in the Appendix. In short, it amounts to using an effective time of bleach t' , which, except for $t=0$, is slightly less than t . For accurate studies of the kinetics, $\log [R]$ should be plotted against t' rather than against t . The corrections are small unless the difference in the initial and final optical density at the wavelength of the bleaching light is more than 0.1.

The data, dots and circles, in Fig. 25 represent three sets (a), (b) and (c) of experimental plots of $\log [R]$ versus t' for R_2 bleach at room temperature. The (a), (b) and (c) sets correspond to different

Fig. 25 Plot of $\log [R]$ against t' for different intensities of R_2 bleach at room temperature where t' is the effective time of R_2 bleach for constant intensity. (see Text)

intensities of R_2 light: 2×10^{15} photons/cm²/sec for set (a) to 1×10^{16} photons/cm²/sec for set (c). The initial R center concentrations are normalized to 1, and the first few data points (for small t') are omitted for reasons discussed following Fig. 22. The straight lines fitting the experimental points are each obtained from Eq. (14) with $k = 0.0063$, 0.033 and 0.067 , respectively for the sets (a), (b) and (c). In each case the data points are well represented by a straight line and are thus consistent with Eqs. (13) and (14).

From comparison of plots (a), (b) and (c) in Fig. 25 it is seen that the reaction proceeds faster as the intensity of the bleaching light is increased. By defining $T_{1/2}$ as the time required for half of the R centers to be destroyed, it is evident that $T_{1/2}$ decreases as the intensity increases. It was also observed that the intensity affected the number of N_c centers to be produced from a given number of destroyed R centers ($\Delta N_c / \Delta R$). This dependence at room temperature is shown in Fig. 26 as a plot of $\Delta N_c / \Delta R$ against $T_{1/2}$. The relation is linear and indicates that at a given temperature relatively more N_c centers are produced as the intensity of the bleaching light is increased.

B. R_1 Bleach

The changes induced in the absorption spectrum of an irradiated sample of LiF with time of R_1 bleach at room temperature are illustrated in Fig. 27. The initial O.D. at the peak of the R_2 band was 0.085. The R bands decrease steadily and are completely destroyed after 17 minutes of bleach for this sample. An experimental plot of $\log [R]$ against t' is well represented by a straight line indicating that the destruction of R centers by R_1 bleach is also of the first order. Both the M band

Fig. 26. Plot of the ratio $\Delta N_c / \Delta R$ against the "half-life" of the R centers ($T_{1/2}$) for different intensities of R_2 bleach at room temperature.

Fig. 27 Change in the absorption peaks when R_1 bleach is applied at room temperature.

and the F band increase steadily until the R centers are destroyed, and then remain constant. The ratio of the increase in the O.D. of the F band to that of the M band is 7:4, the same as for the case of R_2 bleach in Fig. 24. No formation of N_c centers is observed. This indicates that at room temperature R_1 bleach destroys R centers only by decomposition into F centers and M centers (the mode (a) of Eq. (13)). However, when similar R_1 bleach is conducted at 77°K, a large N_c band is produced, and the increase in the F and M bands is small. These results indicate that the destruction of R centers by bleaching with either R_1 or R_2 light occurs by the same two concurrent mechanisms of Eq. (13). However, R_1 bleach differs from R_2 bleach in that the temperature range where each of the two mechanisms is effective differs. For the case of R_2 light (365 mμ) at room temperature, most of the R centers are converted into N_c centers. As the temperature is increased, more of the excited R centers have an energy sufficient to decompose. Using R_1 light (313 mμ), which is .56 eV higher in energy than R_2 light, the excited R centers possess sufficient energy to decompose at room temperature. At lower temperatures fewer R centers can decompose, and more are converted into N_c centers.

Discussions

The present results confirm Okuda's suggestion that an R center can be decomposed into an M center plus some other defect nearby.⁶² This latter defect is clearly identified as an F center in the present work. Furthermore, the results of the present work have established definitely that the N_c band (550 mμ) can be produced with R bleach only, without any need of simultaneous M bleach. According to Okuda,

however, a similar band centered at 550 mμ was obtained by a simultaneous application of M bleach and R bleach.

The R to N_c conversion does not involve any capture of one or more additional defects by the R center. Two major reasons in support of this reasoning may be given. First, such a capture conversion would not yield the observed first order kinetics but a higher order kinetics. Furthermore, the capture conversion would be more efficient generally as the temperature increases, since the mobility of the participating defects is then enhanced. Experimentally, however, the observed R to N_c conversion is relatively less noticeable at elevated temperatures. Secondly, the location of the N_c band (550 mμ) differs definitely from the locations of known charged R center configurations such as R^+ (458 mμ)⁶³ or R' (820 mμ to 960 mμ).⁶⁴ Thus, a rearrangement of the R center into the N_c center is most favorable.

In order to facilitate the discussion of the rearrangement mechanism, Fig. 28 illustrates the van Doorn model of an R center in LiF. The closed circles represent cations (Li^+ ions), and the open circles represent anions (F^- ions). The R center is represented by the three broken circles (numbered 1, 2 and 3) lying in a {111} plane and forming an equilateral triangle. Consider the anion sub-lattice and the F center at site 1. Its nearest-neighbors (neglecting the cation sub-lattice) consist of twelve anion sites (sites 2 through 13). Of these, two sites (2 and 3) are also occupied by F centers. There are thus ten sites available for a near-neighbor jump of the F center at 1. When, for example, the ion at site 7 and the F center at site 1 are interchanged, the F center at site 1 is said to jump to site 7.

Fig. 28 Schematic diagram of the van Doorn model of the R center in LiF. (see Text)

If the F center at site 1 jumps to one of the sites 8, 10, 11, 12, and 13, the result is a decomposition of the R center into an M center (2 and 3) separated from an F center. If the F center at site 1 jumps to site 6, the result corresponds to merely another R center. However, if the F center jumps to sites 7 or 9, the result is a new configuration consisting of three F centers forming an isosceles triangle still in a $\{111\}$ plane. If the F center jumps to sites 4 or 5, the result is a new configuration consisting of three F centers forming a right isosceles triangle in a $\{100\}$ plane. Thus of the ten sites available for the F center at site 1, jumping to five of them results in the destruction of the R center by decomposition, jumping to one results in a reorientation only, and jumping to the remaining four results in the destruction of the R center by rearrangement into a new configuration consisting of an isosceles triangle in either a $\{111\}$ or $\{100\}$ plane. The same division of possible jumps exists for all three of the F centers comprising the R center regardless of the original orientation of the R center.

Now when an R center absorbs an "R" photon and is excited, there is a non-zero probability that one of the three F centers comprising the R-center will jump to one of those five sites that lead to the destruction of the R center into an M center and an F center. Energy considerations indicate that, at a given temperature, this probability is higher for R_1 light (313 mμ) than for R_2 light (365 mμ) and increases in both cases as the temperature is raised. This is consistent with the mode a of Eq. (13) and its observed characteristics. If the energy of the excited R center is not sufficient for this type of jump to occur, it is still possible that the R center may be destroyed by

having one of the three F centers jump to one of the four sites, thereby resulting in the rearrangement of the R center in a {111} or a {100} plane. Rearrangement is favored over decomposition at lower temperatures since the decomposition jump is more inhibited energywise at the lower temperatures. This rearrangement mechanism is consistent with the observed properties of the mode b of Eq. (13). Thus the N_c center is highly likely to be a rearrangement of the R center into an isosceles triangle in either a {111} or {100} plane.

The N_c band observed in the present work is probably not related to the I band reported by Farge et al.,⁶⁵ whose peak absorption at 77°K is at 550 mμ, for at 77°K the peak of the N_c band is shifted to 542 mμ. Moreover, the I band is produced by neutron or heavy electron irradiation at low temperatures, while the N_c band is produced by optical bleach of R centers. The relation of the N_c band to the so-called N bands is uncertain. N bands in LiF have their absorption peaks near 550 mμ.⁶⁶⁻⁶⁸ Models for these N centers have not yet been well established, though current Pick's models of the N centers consist of two distinct combinations of four closely associated F centers.⁶⁹ They are produced either by prolonged irradiation or by raising the temperature of a moderately colored sample to above 450°K. It is also known that N centers have higher absorption bands (N_R) in the region of the R_1 and R_2 bands,⁷⁰ as does the N_c center (see Fig. 21). If an N band near 550 mμ is to be identified with the N_c band observed in the present work, the present work would favor the rearranged F_3 model for the N center over Pick's F_4 model. It is interesting to note here that a similar proposal has recently been made for the N_1 center in KCl.⁷¹

Conclusion

The destruction of R centers in LiF by R_1 or R_2 bleach has been found to occur by two concurrent mechanisms: (a) decomposition of an R center into an M center and an F center, and (b) conversion of an R center into another color center whose absorption band (550 m μ) is in the N band region. This mechanism is governed by a first order kinetics. This rules out any capture process involving other defects. Relatively speaking, the conversion destruction is more predominant over the decomposition at lower temperatures. If an N band in LiF is to be identified with the 550 m μ band, the present work favors a rearranged F_3 model for the N center over the current Pick's model of an F_4 complex. A discussion based on the van Doorn model of the R center strongly indicates that the color center responsible for the 550 m μ band is a rearrangement of the R center into an isosceles triangle configuration in either a {111} or a {100} plane.

Appendix

From Eq. (14) it is seen that to determine if the photochemical destruction of R centers is of the first order, $\log [R]$ is plotted against time (t). If a constant intensity of light is incident on all parts of the system and if the reaction is indeed of the first order, the experimental points will lie on a straight line. However, in the experiments reported in this paper, the intensity of light incident on all parts of the system was not constant due to the fact that the optical density at the wavelength of the bleaching light decreased as the reaction proceeded.

To determine the necessary correction factor consider a thin slab of sample at a depth x, refer to Fig. 6, Chapter III. Let the intensity of light at the depth x and at time t be $I_x(t)$. $I_x(t)$ is qualitatively illustrated by the solid curve in Fig. 29. I_0 is the intensity incident on the front face ($x = 0$). I_x is initially less than I_0 , but gradually approached I_0 as t increases, since the sample becomes more transparent as the bleach continues. The total flux having passed through the slab between $t = 0$ and $t = t$ is represented by the shaded area under the curve. An effective time of bleach (t'') is now defined for the slab by the relation

$$\text{Total Flux} = I_0 t'' = \int_0^t I_x(t) dt \quad (\text{A-1})$$

so that the same total flux passes, but the intensity of light at the slab is considered constant and equal to I_0 .

For any x, let $I_x(t)$ be related to I_0 by the relation

$$I_x(t) = I_0 e^{-\alpha(t)x} \quad (\text{A-2})$$

Fig. 29 Qualitative dependence of light intensity at depth x and at time t , $I_x(t)$, with time t of R bleach. Shaded area represents the total flux at time t .

where $\alpha(t)$ is not constant, but decreases with time of bleach. The explicit form of $\alpha(t)$ is yet to be determined. After substitution, Eq. (A-1) takes the form

$$t'' = \int_0^t e^{-\alpha(t)x} dt. \quad (A-3)$$

This must be averaged over x and becomes

$$\langle t'' \rangle = t' = \frac{1}{l} \int_0^t \int_0^l e^{-\alpha(t)x} dx dt \quad (A-4)$$

where l is the thickness of the sample. To obtain t' the right hand side must be integrated, and so an analytic expression for $\alpha(t)$ is needed.

Experimentally, it was found that despite the change in the internal intensity, a plot of $\log [R]$ against t was fairly well represented by a straight line. This is because the change in the optical density (O.D.) at the wavelength of the bleaching light was not great (typically 0.2) so that the correction is relatively small (typically 10%). It was therefore assumed that $\alpha(t)$ decayed by first order, so that

$$\alpha(t) = \alpha_0 e^{-\beta t} \quad (A-5)$$

where β is obtained from the best straight line drawn through the experimental points from the plot of $\log [R]$ against t . Eq. (A-4) then becomes

$$t' = \frac{1}{l} \int_0^t \int_0^l e^{-\alpha_0 x} e^{-\beta t} dx dt. \quad (A-6)$$

After expansion of the exponentials, integration yields

$$t' = t - \frac{\alpha_0 l}{2} \left(\frac{e^{-\beta t} - 1}{-\beta} \right) + \frac{\alpha_0^2 l^2}{6} \left(\frac{e^{-2\beta t} - 1}{-2\beta} \right) + \dots \quad (A-7)$$

where $\alpha_0 l = 2.303 (O.D._0)$ and $O.D._0$ is the total decrease in the optical density of the sample at the wavelength of the bleaching light (the total decrease in the R bands at 313 m μ or 365 m μ for R_1 and R_2 bleach respectively). The magnitude of the higher order terms decrease rapidly, and so only the first two need be retained. Using Eq. (A-7) the effective time of bleach t' can easily be obtained from the experimental data. A plot of $\log [R]$ against t' is linear and gives the correct slope for the reaction.

LIST OF REFERENCES

1. J.H. Schulman and W.D. Compton, Color Centers in Solids (MacMillan Co., New York, 1962).
2. W.D. Compton and H. Rabin, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16.
3. J. Markham, F Centers in Alkali Halides (Academic Press Inc., New York, 1966).
4. N.F. Mott and R.W. Gurney, Electronic Processes in Ionic Crystals (Clarendon Press, Oxford, 1940).
5. F. Seitz, Rev. Mod. Physics 18, 348 (1946).
6. Ibid., 26, 7 (1954).
7. J. Markham, loc. cit.
8. A. Smakula, Zeits. f. Physik 59, 603 (1930).
9. D.L. Dexter, Phys. Rev. 101, 48 (1956).
10. H. Ivey, Phys. Rev. 72, 341 (1947).
11. J.H. Schulman and W.D. Compton, loc. cit., p. 53.
12. M. Lax, J. Chem. Phys. 20, 1752 (1952).
13. W.D. Compton and H. Rabin, loc.cit., p. 136.
14. W.D. Compton and H. Rabin, loc.cit.
15. W.D. Compton and H. Rabin, loc.cit.
16. F. Okamoto, Phys. Rev. 124, 1090 (1961).
17. R.H. Silsbee, Phys. Rev. 138, 180 (1965).
18. S. Hattori, J. Phys. Soc. Japan 17, 1454 (1962).
19. Bausch and Lomb Reference Manual #33-28-20 (Bausch and Lomb, Inc., Rochester, New York).
20. Instruction Manual for Cary 14 (Applied Physics Corp., Monrovia, California).
21. Cryo-Tip Instruction and Operating Manual (Air Products and Chemicals, Inc., Allentown, Pennsylvania).
22. R.H. Silsbee, loc.cit.

23. W.D. Compton and H. Rabin, loc. cit. p. 127.
24. W.D. Compton and H. Rabin, loc. cit.
25. K.L. Vander Lugt and Y.W. Kim, Physics Letters 22, 50 (1966).
26. W.D. Compton and H. Rabin, loc. cit., p. 126.
27. K. Kubo, J. Phys. Soc. Japan 16, 2294 (1961).
28. S. Hattori, J. Phys. Soc. Japan 15, 2117 (1960).
29. Light absorbed by the R_1 band is designated simply as R_1 light, and similarly for R_2 light. R light refers to either R_1 or R_2 light.
30. A. Okuda, J. Phys. Soc. Japan 16, 1746 (1961).
31. C.C. Klick, Phys. Rev. 79, 894 (1950).
32. C.J. Delbecq and P. Pringsheim, J. Chem. Phys. 21, 794 (1953).
33. K. Kubo, loc. cit.
34. A. Okuda, loc. cit.
35. J.V.R. Kaufman and C.D. Clark, J. Chem. Phys. 38, 1388 (1963).
36. Y. Farge, M. Lambert, and R. Smoluchowski, Solid State Comm. 4, 333 (1966).
37. J. Nahum and D.A. Wiegand, Phys. Rev. 154, 817 (1967).
38. J. Nahum, Phys. Rev. 158, 814 (1967).
39. J. Markham, loc. cit.
40. W.D. Compton and H. Rabin, loc. cit. p. 121.
41. C.Z. van Doorn, Philips Res. Repts. 12, 309 (1957).
42. Ibid., Suppl. #4 (1962).
43. H. Pick, Z. Physik 159, 69 (1960).
44. R.H. Silsbee, loc. cit.
45. C.B. Pierce, Phys. Rev. 148, 797 (1966).
46. A. Okuda, loc. cit.
47. Y. Farge, G. Toulouse, and M. Lambert, J. de Physique 27, 287 (1966).

48. J. Nahum and D.A. Wiegand, loc. cit.
49. J. Nahum and D.A. Wiegand, loc. cit.
50. Light absorbed by the M band is designated M light.
51. A. Okuda, loc. cit.
52. Y. Farge, G. Toulouse, and M. Lambert, loc. cit.
53. P. Görlich, H. Karras, and G. Kötitz, Phys. Stat. Sol. 3, 1803 (1963).
54. J. Nahum and D.A. Wiegand, loc. cit.
55. Y. Farge, G. Toulouse, and M. Lambert, loc. cit.
56. A. Okuda, loc. cit.
57. J. Nahum and D.A. Wiegand, loc. cit.
58. J. Nahum and D.A. Wiegand, loc. cit.
59. Y. Farge, G. Toulouse, and M. Lambert, loc. cit.
60. J. Nahum and D.A. Wiegand, loc. cit.
61. S. Glasstone, Textbook of Physical Chemistry (D. Van Nostrand Co., New York, 1946) p. 1085.
62. A. Okuda, loc. cit.
63. J. Nahum and D.A. Wiegand, loc. cit.
64. A.E. Hughes, Solid State Comm. 4, 337 (1966).
65. Y. Farge, M. Lambert, and A. Guinier, J. Phys. Chem. Solids 27, 499 (1966).
66. K. Kubo, loc. cit.
67. T. Kamikawa et al., Phys. Stat. Sol. 14, 435 (1966).
68. W. von der Osten, Z. Physik 174, 423 (1963).
69. H. Pick, loc. cit.
70. S. Hattori, J. Phys. Soc. Japan 17, 1454 (1962).
71. I. Schneider and M.N. Kabler, J. Phys. Chem. Solids 27, 805 (1966).

AUTOBIOGRAPHICAL STATEMENT

NAME: Karel Leo Vander Lugt

BIRTH: April 25, 1940; Pella, Iowa

EDUCATION: High School Diploma, Holland High School, Holland, Michigan, 1958;
Bachelor of Arts, Hope College, 1962

RECOGNITIONS: Blue Key National Honorary Fraternity, 1961
Bachelor of Arts, cum laude with Faculty Honors, 1962
The Society of the Sigma Xi, 1965
National Defense Education Act Fellowship (1962-1965)

PROFESSIONAL MEMBERSHIPS: The Society of Sigma Xi

PUBLICATIONS: "Observation of the R_N Band in LiF Near 300°K," K.L. Vander Lugt and Y.W. Kim, Phys. Letters 22, 50 (1966).
"Optical Conversion of the F_3^+ Center in LiF with R light," K.L. Vander Lugt and Y.W. Kim, submitted to the Physical Review (1967).
"Photochemical Destruction of the R Center in LiF with R Light," K.L. Vander Lugt and Y.W. Kim, submitted to the Physical Review (1967).