

AN ABSTRACT OF THE THESIS OF

ROBERT CLIFFORD BOWEN for the degree of DOCTOR OF PHILOSOPHY
in CHEMISTRY presented on June 12, 1980
Title: OPTICAL AND EPR INVESTIGATIONS OF THE PHOTOCHEMISTRY OF KCl:OH
Abstract Approved: Redacted for Privacy
A. B. Scott

The hydroxide ion as a substitutional defect in KCl can be photo-dissociated at liquid nitrogen temperature by ultraviolet light. The photochemistry of this system was investigated by EPR and optical absorption methods. Theoretical calculations were also performed in an investigation of the KCl:OH system.

The bleaching behavior of photochemically colored KCl:OH was studied by simultaneous visible and EPR spectroscopy, and by broad range optical spectroscopy in the range from 185 nm to 2000 nm. The behavior of the system on warming from liquid nitrogen temperature to room temperature was also studied by the same methods. Pure KCl crystals were colored with x- or gamma-rays at room temperature and studied by EPR and optical methods.

The bleaching rate of photochemically colored KCl:OH was determined to be equivalent when measured by EPR or optical data. This result contradicted data reported previously. The disappearance of the EPR spectrum of ultraviolet irradiated KCl:OH at 250 K was correlated with optical data. This showed that the disappearance of the EPR was simultaneous with the conversion of H_2O^- centers to F centers.

Results were presented and arguments given that the products and mechanism of the bleaching of H_2O^- centers were analogous to the products and mechanism of bleaching F centers. Approximate quantum mechanical calculations were performed which indicated that an exchange interaction of the unpaired F and O^- electrons was not responsible for the disappearance of the EPR spectrum.

Suggestions were made for further investigations which may yield information on the system.

Optical and EPR Investigations of the
Photochemistry of KCl:OH

by

Robert Clifford Bowen

A THESIS
submitted to
Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

June 1980

APPROVED:

Redacted for Privacy

Professor of Chemistry
in charge of major

Redacted for Privacy

Chairperson of the Department of Chemistry

Redacted for Privacy

Dean of Graduate School |

Date thesis is presented June 12, 1980

Typed by CAMPUS PRINTING & COPY CENTER (Mary Syhlman)

for ROBERT CLIFFORD BOWEN

ACKNOWLEDGEMENTS

I would like to give special thanks to my wife, Dr. Colleen McLean-Bowen, for her understanding, patience, support, help, and particularly her encouragement, which kept me going.

I also wish to acknowledge Dr. Scott for everything he did. I am also indebted to Dr. Fredericks for allowing me to use his Perkin-Elmer 450. I am certainly grateful to Dr. Wickman for his helpful discussions, which simplified many of my problems, and for the many hours I was able to spend with the EPR spectrometer.

I would like to acknowledge the National Science Foundation for financial support. Thanks are also due to the O.S.U. Computer Center for their grant of computer time and services, and the Quantum Chemistry Program Exchange for supplying computer programs.

Jerry Zabrowski and Ken Bomben also deserve my gratitude for sharing their computer expertise with me.

Finally, I would like to express thanks to at least a few of my friends and fellow graduate students for their moral support and mental stimulation. Among them, but by no means all, are Emile Firpo, Dr. Larry Fredrickson, Christine Pastorek, Dr. Gerry Robbins, and Dr. Richard Skeeane.

TABLE OF CONTENTS

| | | |
|-----|--|----|
| I | INTRODUCTION | 1 |
| | A. NOTATION AND CHARACTERISTICS OF COLOR CENTERS | 1 |
| | B. OXYGEN-CONTAINING CENTERS | |
| | C. PRODUCTION OF COLOR CENTERS IN PURE CRYSTALS BY IRRADIATION | 8 |
| | D. AIM OF THE PRESENT STUDY | 15 |
| II | EXPERIMENTAL | 19 |
| | A. SAMPLES | 19 |
| | B. SIMULTANEOUS EPR AND VISIBLE SPECTROSCOPY OF KCl:OH | 19 |
| | B-1. Apparatus | 19 |
| | B-2. Procedure | 24 |
| | C. OPTICAL SPECTROSCOPY OF KCl:OH | 25 |
| | 1. Apparatus | 25 |
| | 2. Procedure | 27 |
| | D. IRRADIATIVE COLORATION OF PURE KCl | 28 |
| | 1. Apparatus | 28 |
| | 2. Procedure | 28 |
| | E. CALCULATIONS | 29 |
| III | RESULTS | 31 |
| | A. SIMULTANEOUS EPR AND VISIBLE SPECTROSCOPY | 31 |
| | 1. Bleaching experiment | 32 |
| | 2. Warm-up experiment | 34 |
| | B. OPTICAL SPECTROSCOPY | 35 |
| | 1. Near ultraviolet region, 195 nm to 400 nm (6.70 to 3.10 eV) | 35 |
| | 2. Visible region, 350 nm to 750 nm (3.54 to 1.65 eV) | 40 |
| | 3. Near infrared region, 600 nm to 2000 nm (2.07 to 0.62 eV) | 44 |
| | C. IRRADIATIVE COLORATION OF PURE KCl CRYSTALS | 44 |
| IV | DISCUSSION OF RESULTS | 46 |
| | A. BLEACHING BEHAVIOR | 46 |
| | 1. Bleaching rate of H_2O^- | 46 |
| | 2. Products of bleaching H_2O^- centers | 47 |
| | a. Possibility of H_2O^- formation | 47 |
| | b. Possibilities of other products of H_2O^- bleaching | 50 |
| | B. DISAPPEARANCE OF THE EPR | 53 |
| V | THEORETICAL CALCULATIONS OF AN $F-O^-$ INTERACTION | 55 |
| | A. ESTIMATION OF MEAN F TO O^- DISTANCE | 56 |
| | B. CHOICE OF APPROXIMATE ELECTRONIC WAVE FUNCTIONS | 59 |
| | C. APPROXIMATE QUANTUM MECHANICAL CALCULATIONS | 61 |
| | 1. Molecular orbital calculations | 62 |

| | |
|--|----|
| 2. Exchange calculations | 66 |
| a. Summary of exchange coupling theory | 67 |
| b. Calculations of the exchange energy of the F-0 ⁻ system | 73 |
| VI CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK | 81 |
| A. CONCLUSIONS | 81 |
| B. SUGGESTIONS FOR FURTHER WORK | 82 |
| BIBLIOGRAPHY | 85 |
| APPENDIX I. GLOSSARY OF TERMS AND ABBREVIATIONS | 91 |
| APPENDIX II. COMPARISON OF EXCHANGE APPROXIMATIONS | 92 |

LIST OF ILLUSTRATIONS

| <u>Figure</u> | | <u>Page</u> |
|---------------|--|-------------|
| I-1 | Representation in the [100] plane of the microscopic structure of the defects treated in this work | 4 |
| II-1 | Schematic diagram of apparatus used for simultaneous optical and EPR spectroscopy | 20-21 |
| II-2 | Schematic diagram of a crystal mounted for simultaneous EPR and optical spectra | 22 |
| II-3 | Schematic diagram of cryostat used for optical spectroscopy | 26 |
| III-1 | Change in relative concentration of color centers | 33 |
| III-2 | Average difference between N_t obtained from EPR and optical measurements | 33 |
| III-3 | Average change in relative concentration of color centers, N_t , on warming | 36 |
| III-4 | Change in relative concentration of color centers, N_t , over the entire range of experimental conditions | 37 |
| III-5 | EPR spectra of ultraviolet-irradiated KCl:OH | 38-39 |
| III-6 | Near ultraviolet spectra of ultraviolet-irradiated KCl:OH | 41 |
| III-7 | Visible spectra of ultraviolet-irradiated KCl:OH | 42 |
| III-8 | Visible spectra of ultraviolet-irradiated KCl:OH | 43 |
| IV-1 | Corrected change in relative concentration of color centers, N_t , with bleaching | 48 |
| V-1 | Change in calculated exchange energy, J , between the F and O^- centers with variations of the orbital exponents | 77 |

LIST OF TABLES

| <u>Table</u> | | <u>Page</u> |
|--------------|---|-------------|
| I-1 | Notation and structural models of defects treated in this work | 3 |
| I-2 | Optical absorption maxima of defect centers | 5 |
| V-1 | Results of CNDO molecular orbital calculations | 54-65 |
| V-2 | Calculation of exchange energy between F and O^- centers | 75 |
| V-3 | Results of calculation of singlet to triplet transition energies employing various orbital exponents of the F and O^- centers | 76 |
| V-4 | Results of calculation of M center singlet to triplet energy for varying orbital exponents of F center wave functions | 79 |

OPTICAL AND EPR INVESTIGATION OF THE PHOTOCHEMISTRY OF KCl:OH

I. INTRODUCTION

In 1937 de Boer proposed a model of the F center as an electron trapped on a negative ion vacancy¹. In subsequent years this model has been verified by a large number of optical, electrical, EPR and ENDOR measurements and theoretical treatments and has become almost universally accepted. The simplicity of this model and the amount of information obtained on the behavior and characteristic of the F center make it a valuable tool in the field of solid state research.

In 1971 Papazian² reported the results of experiments on simultaneous EPR and optical measurements on photochemically produced F centers. Whereas the optical absorption band characteristic of the F center was present, no corresponding EPR spectrum was observed. According to the de Boer model, both optical absorption and paramagnetic resonance arise from the same defect, an electron trapped on an anion vacancy. However, Papazian concluded that the defect causing the EPR signal attributed to the F center was not the same as the defect producing color.

In order to understand the subject better, a basic background of the characteristic of the F center, other defect centers and impurity centers and their reactions will be presented first.

A. NOTATION AND CHARACTERISTICS OF COLOR CENTERS

Most of the crystal defect centers discussed in this work have been studied previously and identified in terms of their microscopic

structure in the crystal. The naming of these defects, however, has been described by Morato as "mostly a historical and completely illogical and confusing notation system, understandable only to the insider."³ Therefore, a listing of the historical symbols for these centers, alternate names and symbols and their structural model is given in Table I-1. Likewise in Figure I-1, a representation of the microscopic structure of the defects in the [100] crystal plane is shown. Table I-2 lists these centers and their optical absorption maxima at the stated temperature. When discussing particular centers in the text the historical symbol will generally be used. However, where it will be more descriptive, as in reaction equations, an alternate symbol will be used, such as H_i^0 instead of U_2 for the interstitial hydrogen atom.

The main properties of the F and other trapped electron and hole centers, methods of production and techniques used in this study are covered in several reviews.^{4,5} A knowledge of the following reactions of F centers is necessary to understand many of the processes of color center behavior. In the reaction



the F electron is excited to the conduction band, leaving behind an alpha center. Conversely, an alpha center can trap a conduction band electron to create an F center. An F center may also act as a shallow trap for conduction band electrons, as in the reaction

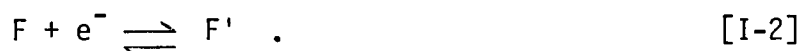


TABLE I-1. NOTATION AND STRUCTURAL MODELS OF DEFECTS TREATED IN THIS WORK.

| Historic symbol | Alternate name or symbol | Structure model |
|-----------------|--------------------------|--|
| F | | electron trapped at an anion vacancy |
| M | F_2 | F centers at adjacent anion sites |
| F' | F^- | two electrons trapped at an anion site |
| α | | anion vacancy |
| H | crowdion | Cl_2^- molecule-ion at an anion site |
| V_k | self trapped hole | Cl_2^- molecule-ion occupying two adjacent anion sites |
| U | $[H^-]$ | substitutional hydride ion |
| U_1 | H_i^- | interstitial hydride ion |
| U_2 | H_i^0 | interstitial hydrogen atom |
| OH^- | | substitutional hydroxide ion |
| O^- | | substitutional oxygen ion |
| $O^{2-\alpha}$ | | substitutional oxide ion adjacent to an alpha center |
| FU_2 | | hydrogen atom at a tetrahedral interstitial site with an F-center at one apex of the tetrahedron |
| H_2O^- | "wet F center" | H_2O molecule embedded in an F center |
| Y | FO^- | F and O^- centers on adjacent anion sites |
| Y' | $F'O^-$ | F' and O^- centers on adjacent anion sites |

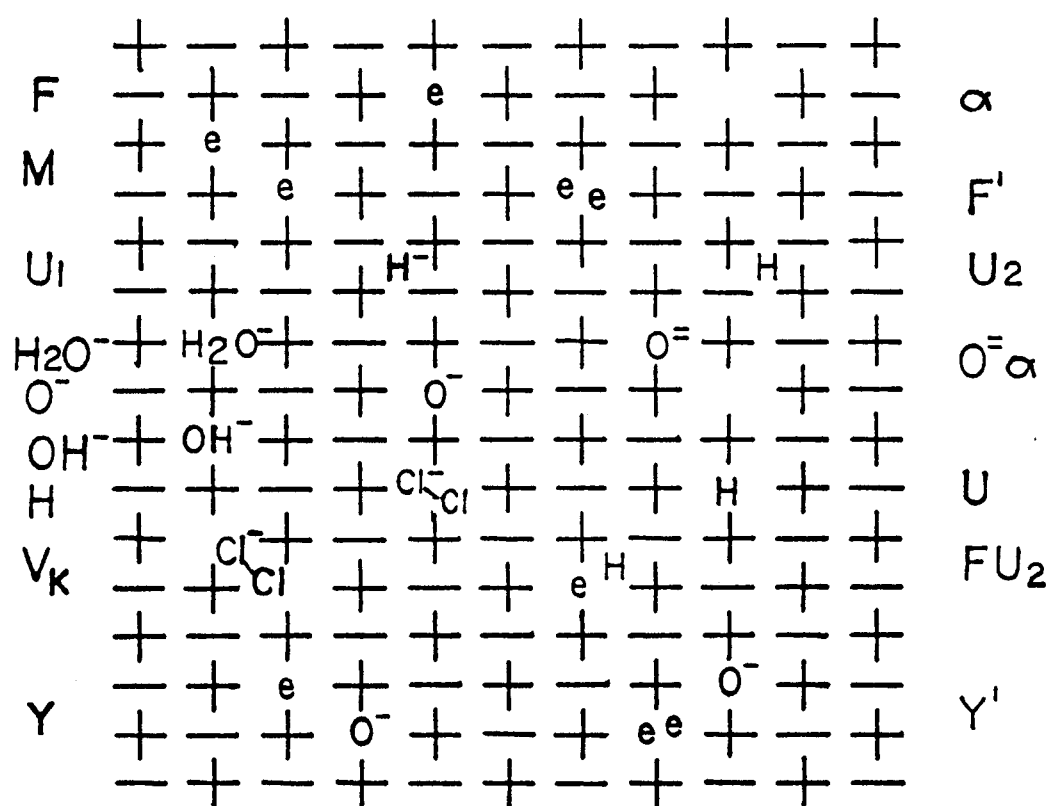


FIGURE I-1. REPRESENTATION IN THE [100] PLANE OF THE MICROSCOPIC STRUCTURE OF THE DEFECTS TREATED IN THIS WORK.

TABLE I-2. OPTICAL ABSORPTION MAXIMA OF DEFECT CENTERS

| Center | λ_{\max} (nm) | temperature | reference |
|-------------------|-----------------------|-------------|-----------|
| F | 540 | 77 K | 4 |
| F | 563 | 298 K | 4 |
| M | 802 | 77 K | 77 |
| α | 177 | 90 K | 5 |
| H | 335 | 4 K | 5 |
| V_k | 365 | 77 K | 5 |
| U | 212 | 77 K | 27 |
| U_1 | 277 | 80 K | 60 |
| U_2 | 235 | 77 K | 27 |
| OH^- | 204 | 298 K | 26 |
| O^- | 185 | 77 K | 15 |
| O^{2-}_{α} | 435 282 212 | 78 K | 78 |
| H_2O^- | 593 517 435 | 4 K | 40 |
| Y | 555 | 77 K | 47 |
| Y' | 625 | 77 K | 47 |
| FU_2 | 630 | 110 K | 49 |

The F' center is thermally unstable at temperatures above 150 K and quickly dissociates back to an F center and a conduction band electron. This reaction is a major process in the optical bleaching of F centers at low temperatures⁵. The aggregation of F centers, described by the reaction.



has been extensively studied^{6,7,8}. Essentially, F centers migrate toward each other, two or more eventually occupying adjacent anion sites to form M centers and higher F aggregate centers with unique characteristics. These aggregate centers can be dissociated optically or thermally to reform isolated F centers.

EPR and ENDOR have been powerful tools widely used in the study of color centers. The EPR signal of F centers in irradiatively colored crystals was first obtained in 1949⁹. Additively colored crystals, in which essentially pure F centers may be obtained, were studied by Hutchison and Noble¹⁰, who noted the seemingly anomalous characteristics of F center EPR. Rather than having the expected Lorentzian lineshape¹¹, the F center EPR signal was Gaussian in shape. In addition, the half-width was approximately 49 gauss, much broader than the theoretical line width of 0.1 gauss¹¹. Finally, the F center had a g-factor of 1.995 ± 0.001 , which is significantly lower than the free electron g-factor of 2.0023. These anomalies were soon clarified and in fact were of value in confirming the de Boer model of the F center. Kip et al.¹² and Portis¹³ performed molecular orbital

calculations based on the overlapping of the F center wave function with the surrounding alkali and halide ions. These calculations show that the observed F center EPR signal is the envelope of hyperfine components arising from interaction of the F electron with the nuclei of the surrounding ions. The Gaussian lineshape arises from the intensity distribution of these components. The negative Δg of the F center was considered by Kahn and Kittel¹⁴ who used molecular orbital calculations to obtain a Δg of the correct order of magnitude. The ENDOR measurement of the hyperfine interactions between the F center electron and its neighbor ions¹⁵ and an improved F center wave function allowed Adrian¹⁶ to refine these calculations and give a more precise explanation of the negative Δg .

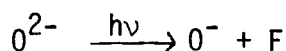
Optical bleaching of F centers, which causes formation of F aggregate centers [equation I-3], causes changes in the optical and EPR spectra of the F center. Bleaching results in a broadening of the optical F band from the accepted half-width of 0.20 eV¹⁷, and a narrowing of the EPR signal to a peak to peak derivative half width, ΔB_w , of 35 gauss¹⁸, as well as changes in the magnetic saturation behavior of the F center. Konitzer and Markham¹⁷ noted that samples of potassium chloride with a very high optical F center absorption, indicative of a high concentration of F centers, gave a larger optical half width than samples with lower concentrations of F centers. The changes in the magnetic properties was investigated by Schwoerer and Wolf¹⁹ who concluded that optical bleaching of the crystal produces a clustering, or loose aggregation, of F centers. The F electron

at a distance of four to six lattice constants can undergo an exchange interaction which causes the narrowing of the EPR signal.

B. OXYGEN-CONTAINING CENTERS

Oxygen-containing impurities in alkali halides were studied in the 1930's by Korth²⁰, who found that the nitrate ion could be reduced by excess electrons to the oxide ion. Similarly, Akpinar²¹ reported oxidation of carbonate ion by oxygen in the air to yield superoxide. Akpinar also characterized many oxygen-containing impurities, including the hydroxide, superoxide and oxide ions in alkali halides.

The photochemical reaction



was reported by Korth²⁰. This reaction is observed in crystals containing oxide ion irradiated with ultraviolet light. This reaction was studied further by Gummer and coworkers^{22,23}, who determined that nearly all O^{2-} impurity centers exist as oxide-alpha pairs. The correct reaction is then



in which an electron from the oxide is transferred to the alpha center, forming an O^- and an F center. The reaction of equation I-4, as well as its back reaction



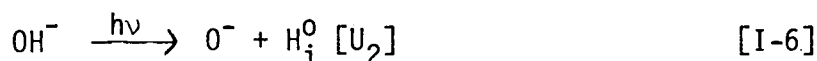
was studied by Staible²⁴. His conclusion was that the O^- and F centers produced by reaction I-4 were separated by several lattice constants. Gummer²³, however, noticed a return of the dielectric loss after reaction I-4 occurred. The O^- and F centers are electrically neutral with respect to the crystal, and if they were separated by a large distance, with no interaction between them, would cause no dielectric loss.

The enhancement of F center production by ultraviolet radiation of crystals containing intentional hydroxide impurity was investigated by Etzel and Patterson²⁵. They found that the F-band produced in such crystals by ultraviolet radiation is directly proportional to the height of the hydroxide band. These results correspond with those of Rolfe²⁶, who studied both doped crystals and commercial crystals exhibiting the hydroxide band as an unintentional impurity. Rolfe also reported that F centers produced photochemically in such crystals were stable in the dark, but were rapidly bleached when illuminated with a tungsten lamp.

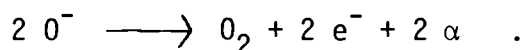
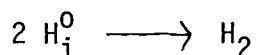
Further research on the subject was done by Cape¹⁵, who irradiated hydroxide doped potassium chloride and potassium bromide crystals at 15 K with a mercury arc lamp. Under these conditions, the optical absorption spectrum produced was similar to that of crystals x-irradiated at the same temperature. Not only were F and O^- centers formed, but also U , U_1 , U_2 , α , and H centers. Kurz²⁷ demonstrated that many of these centers were the result of subsequent reactions caused by long exposure to broad band ultraviolet light at low temperatures.

Experiments on the photochemistry of alkali halides doped with hydroxide and sulphate ion were conducted by Jacobs and Papazian²⁸ in an attempt to ascertain the contribution of oxygen-containing species to the optical spectra of irradiated alkali halides. Their results were clouded by the presence of small amounts of hydroxide in their sulphate doped crystals, but it was still clear that, in the range studied (approximately 200 nm to the near infrared), no absorption from oxygen-containing species was produced on irradiation of hydroxide doped crystals.

The actual photodissociation mechanism of hydroxide was investigated by Kerkhoff et al.^{29,30} using optical and EPR methods. At liquid nitrogen temperature (LNT) they determined the reaction was



where $h\nu$ is light of the frequency absorbed by the hydroxide ion. The presence of O^- was determined by optical absorption; that of U_2 centers by optical absorption and EPR. On warming to 130 K, the EPR and optical spectra of the U_2 center disappeared and a broad, assymmetric absorption band in the approximate position of the F band appeared, while the EPR measurements gave a spectrum very much like that of the F center. On warming to room temperature (RT), the optical absorption band narrowed to a width more nearly that of the F band, while the EPR signal disappeared completely. The loss of the apparent F center EPR signal was attributed to the formation of F aggregate centers and colloidal metal particles. Kerkhoff explained the disappearance of the U_2 centers and the formation of F centers by the following reactions:



The electrons and alpha centers would combine to form F centers by the reverse of reaction I-1. No attempt was made to explain the fate of the hydrogen or oxygen molecules.

Much work on the nature of photochemically produced F centers was done by Papazian. Early work concentrated on the formation of F bands in alkali metal azides by ultraviolet radiation^{31,32,33}. From a study of the relationships of the optical absorption bands in the visible and near infrared regions, the F band in alkali metal azides was thought to arise from a charge-transfer complex in the crystal. Extrapolation of these observations suggested that the F band in alkali halides resulted from a charge-transfer complex also³⁴, rather than originating from the accepted de Boer model.

Papazian also reported on experiments similar to those of Kerkhoff²⁹ and Moran et al.³⁵. As stated previously, Papazian simultaneously measured the EPR and optical behavior, in the region of the F band of ultraviolet irradiated KCl:OH.

In the first part of the experiment, similar to that of Moran et al.³⁵, KCl:OH was irradiated at 93 K, warmed to 133 K and recooled to 93 K, at which time EPR and optical measurements were made. The crystal was then bleached with an unfiltered tungsten lamp. EPR and optical absorbance were measured following bleaching for various amounts of time. The results of this part of the experiment showed that the number of F centers determined from the optical absorption decreased

more rapidly than the number of paramagnetic centers determined from the EPR. Peak heights of the optical absorption band and EPR spectrum were used as measures of the number of centers present.

In the second part of the experiment, the crystal was warmed from 93 K to room temperature, with optical and EPR measurements taken after the crystal had been warmed to various temperatures. During this procedure the height of the optical absorption band increased to more than its original value, while the EPR signal decreased to zero. The anomalous presence of color without an EPR signal led Papazian once again to propose that the optical F band was caused by a charge transfer complex. No attempt was made to explain the EPR spectrum of the F center. It was also noted that pure potassium chloride x-irradiated at room temperature gave an optical absorption band in the region of the F band, but no EPR signal. Continued work by Papazian led to attempts to relate F center color to the absorption of charge transfer complexes in solution^{36,37}, and an interpretation of F center absorptions as related to rotational spectra³⁸.

At about the same time as Papazian's work, the sequence of photochemical reactions was being studied by Rusch and Seidel^{39,40}. They determined from optical, EPR, and ENDOR measurements that the reaction sequence was



Moreover, in the temperature range from 250 K to 360 K, a partial recombination of the products to reform hydroxide ion occurs. The discovery of the H_2O^- , or "wet F" center, clarified a number of differences between the "normal" F center and the centers produced by photochemical dissociation of hydroxide ion. The H_2O^- center yields a broad asymmetric optical absorption band with a peak at 525 nm at LNT, an EPR g-value of 1.996 and a ΔB_w of 40.6 gauss at LNT. The λ_{max} and ΔB_w are significantly different from the normal F center values.

The structure of the "wet F" band was shown to be caused by different alignments of the H_2O molecule on the lattice site. ENDOR measurements indicate that the molecule is situated with its C_2 axis along one of the eight [111] crystal directions. Wave function calculations have shown that the "wet F" electron can still be described by an F type wave function, with a small amount of $4a_1$ H_2O molecular orbital mixed with the F-center wave function. The electron is in an antibonding state of the F- H_2O system and can be described as an F center pushed slightly out of the lattice site by the embedded water molecule.

The role of the O^- ion in the photochemistry of KCl:OH has been elusive. The O^- band at 185 nm is beyond the range investigated by many researchers, and the EPR signal of O^- becomes detectable only below 30 K^{41,42}. It appears, however, that reaction I-5 plays a large part in the instability of F centers produced by reactions I-6 through I-8. Kats et al.⁴³ have presented evidence that the fast bleaching of photochemically produced F centers in KCl:OH and KBr:OH is due to electrons being trapped by the O^- ions. It was also shown⁴⁴ that F

centers in irradiated KBr:OH are stable when kept in the dark. It was concluded that a tunneling recombination of the F electron and the O^- ion is not probable. Conversely, Morato and Luty⁴⁵ have shown that F centers in additively colored KCl:OH exhibit the same stability against permanent bleaching as F centers in pure crystals. This removes OH^- as a participant in any interactions of the F center with other species.

The EPR of O^- centers produced by reactions I-4 and I-6 was studied by Sander^{42,46}. Below 30 K, the O^- ion is displaced in the [100] direction from the center of the lattice site, possibly by the Jahn-Teller effect. The O^- ion then interacts with the nucleus of one neighboring potassium ion (nuclear spin $I = 3/2$) to give four equally intense hyperfine lines. Surprisingly, the presence of what may have been a very weak F center resonance was also noted.

The existence of the Y center, an FO^- complex, was investigated by Kuczynski and coworkers^{47,48}. The existence of this center was previously considered to be impossible, as it was assumed that the F and O^- centers would immediately combine according to equation I-5 if they occupied adjacent lattice sites. The structure of the Y center has not been unequivocally determined, and it may be that the FO^- complex is affected by other impurities or defects in the crystal. A short lived optical absorption band was reported by Gummer²³ at 558 nm when F and O^- centers were produced by reaction I-4. This is at almost the same position as the Y band.

The possibility of the existence of an $F0^-$ complex and other such centers was strengthened by the reported discovery of the FU_2 center⁴⁹. The structure of the FU_2 center is proposed to be a U_2 center, a hydrogen atom in a tetrahedral interstitial lattice site, with an F center at one apex of the tetrahedron instead of an halide ion. In reasoning similar to that used against the Y center, the F and U_2 centers should immediately combine to form a U center. In reality, the FU_2 center appears to be stable at temperatures below 160 K.

C. PRODUCTION OF COLOR CENTERS IN PURE CRYSTALS BY IRRADIATION

The production of color centers by gamma or x-irradiation of pure alkali halides has been extensively reviewed^{4,5}. Only a brief summary of the subject will be given here.

Irradiation of pure alkali halides at 4 K produces only two species of color centers, the F and H centers⁵⁰. The H center has been identified as an X_2^- molecule ion (X = halogen) on an anion site⁵¹.

Coloration at higher temperatures, or warming a crystal colored at 4 K to higher temperatures produces a number of other trapped-hole, or V centers, of which only one, the V_k center, has been definitely identified with a microscopic model. The V_k center, also known as a "self trapped hole", is an X_2^- molecule ion occupying two anion sites in a $[110]$ direction^{52,53}. Other V centers, such as the V_1 , V_2 , V_3 , and V_F centers have not been unequivocally identified in terms of their microscopic structure, but are thought to be molecule ions associated

with other defects or impurities. Most of these centers are unstable at room temperature and bleach rapidly when the crystal is warmed.

The F centers produced by x- or gamma-irradiation are unstable on warming, presumably recombining with hole centers⁵⁴. This is true whether the crystal has been colored at 4 K and warmed to room temperature or colored at room temperature and warmed to a higher temperature.

Coloration at room temperature proceeds initially at a fast rate, then slows to a lesser rate. Irradiation at 4 K produces color centers at a much slower, more constant rate. The initial rapid rate of coloring at room temperature is due to existing vacancies in the crystal being filled with electrons first, after which vacancies must be created in a process similar to that at 4 K^{55,56}.

Molecular orbital calculation on V centers indicate that nearly all can be considered as X_2^- molecule ions with the unpaired electron in a $p\pi_u$ antibonding orbital^{53,57}. This is in contrast to the F center, in which the 1s orbital is spread out over many ions in the lattice.

D. AIM OF THE PRESENT STUDY

The principal purpose of this work was, first, to repeat the experiments of Papazian² on simultaneous EPR and optical investigations of photochemically colored KCl:OH in order to either confirm or refute his results. Secondly, having confirmed Papazian's findings in which an F center apparently yields an optical absorption spectrum without a corresponding EPR spectrum, the author wished to investigate more completely using optical methods the chemical system which gives rise to

these unexpected results. Finally theoretical attempts were made to determine the mechanism by which these phenomena occur, with the intent of reconciling the results with the accepted model of the F center.

Simultaneous optical and EPR measurements made in this laboratory did indeed verify the puzzling observations of Papazian and others^{29,35}. The apparent rate of optical bleaching of the photochemically produced color centers was larger when determined from optical absorption measurements than when obtained from the EPR measurements. Additionally, EPR spectra measured at various temperatures between 77 K and room temperature showed that the paramagnetic resonance of the photochemically produced color centers vanished abruptly and over a very small temperature range. Optical spectra taken over the same range of temperatures indicated little change in the concentration of color centers in the sample.

Further EPR work showed that after its sudden disappearance, the F center EPR signal could not be made to reappear under any circumstances at temperatures between 77 K and room temperature. Optical measurements were made over a broad range of wavelengths to try to discover if any heretofore unsuspected centers which might cause this lack of EPR signal were present in the system. Additionally, the behavior of the optical absorption in the region of the F band was carefully studied and compared with the known characteristics of the F center absorption.

After determining the nature of the system created by the photodissociation of hydroxide ions in potassium chloride, a number of

hypotheses were considered as reasons for the lack of EPR. Those finally considered in detail involved an interaction between the unpaired electrons of the O^- center and the F center. Approximate quantum mechanical calculations were performed to estimate the magnitudes of two types of interactions, the first a weak, long range "molecular bond" between the F and O^- centers, and the second an exchange interaction of the unpaired electrons. The methods and results of these calculations are presented in Chapter IV.

II. EXPERIMENTAL

A. SAMPLES

Hydroxide doped potassium chloride crystals were obtained from the laboratory of Dr. Franz Rosenberg of the University of Utah. The material used was in the form of a large boule grown by the Kryopoulous method. The crystal was grown from ultra-pure potassium chloride with an admixture of 10^{-3} mole fraction of potassium hydroxide. This concentration was verified by titration. Optical spectra of the crystal in the region of 2000 nm to 185 nm showed no noticeable impurities other than the expected hydroxide band at 204 nm. EPR spectra at both room temperature and liquid nitrogen temperature showed no paramagnetic impurities.

Pure potassium chloride crystals were obtained from the University of Stuttgart. Optical spectra in the region of 2000 nm to 185 nm showed no noticeable impurities. EPR spectra at room temperature and liquid nitrogen temperature showed no paramagnetic impurities.

B. SIMULTANEOUS EPR AND VISIBLE SPECTROSCOPY OF KCl:OH

1. Apparatus

Apparatus used for simultaneous EPR and visible spectroscopy was similar to that described by Papazian². Diagrams of the apparatus are shown in Figures II-1 and II-2.

All irradiation, bleaching and measurements were performed with the sample crystal mounted in a Scanco model S-824 EPR quartz dewar

FIGURE II-1. SCHEMATIC DIAGRAM OF APPARATUS USED FOR SIMULTANEOUS OPTICAL AND EPR SPECTROSCOPY. The sample was mounted inside the dewar which was in turn placed within the EPR cavity. The light beam was guided from the monochromator to the sample and thence to the phototube by the fiber optic. The cooling coil was a heat exchanger immersed in a liquid nitrogen bath directly beneath the EPR cavity. Nitrogen gas was passed through the coil into the dewar for cooling of the sample. The gas stream could be split with the bypass valve, allowing temperature control by mixing room temperature gas with the cooled gas. Ultra-violet irradiation of the sample was achieved through a grid in the front of the EPR cavity. A removable cover allowed the EPR cavity to be sealed from extraneous light when the sample was not being bleached or irradiated.

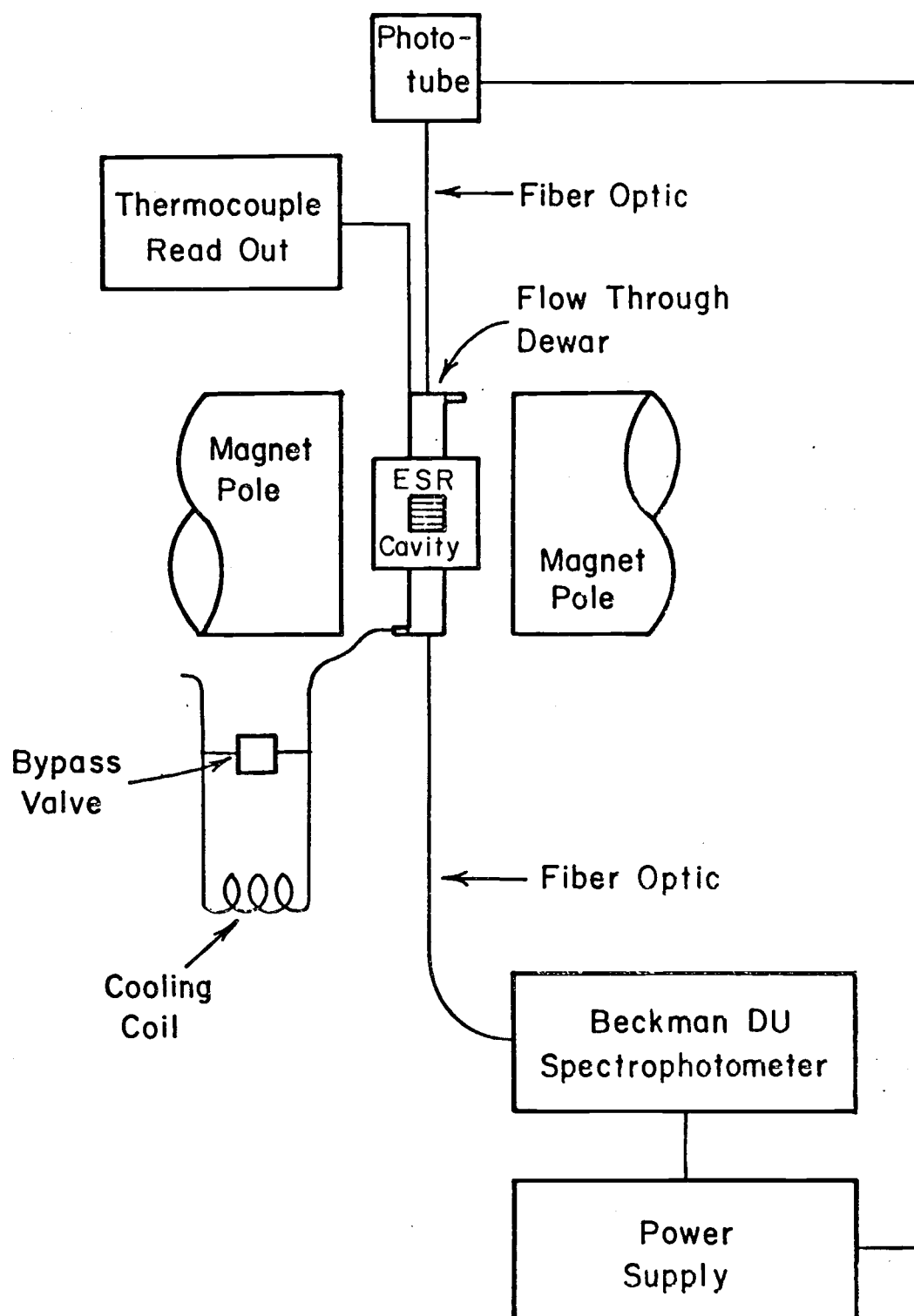


FIGURE II-1.

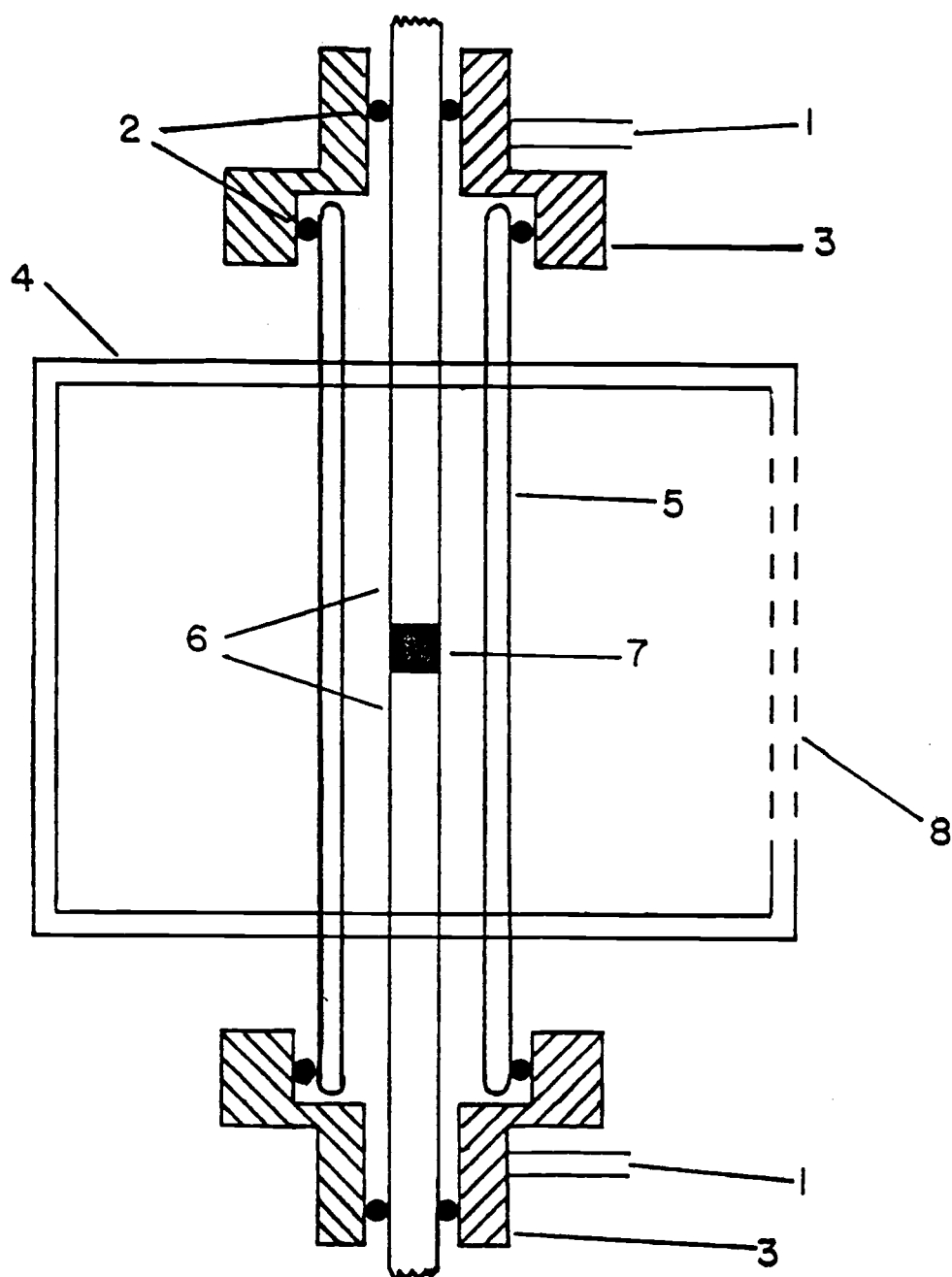


FIGURE II-2. A SCHEMATIC DIAGRAM OF A CRYSTAL MOUNTED FOR SIMULTANEOUS EPR AND OPTICAL SPECTRA.
 1. Cooling gas inlet and outlet. 2. Rubber o-ring seals. 3. End pieces. 4. EPR cavity. 5. Quartz dewar. 6. Quartz light guides. 7. Sample. 8. Grid for irradiation.

mounted vertically through the EPR cavity. Endpieces made in this laboratory allowed optical light guides and cooling gas to pass through the dewar while keeping the interior sealed from condensation and extraneous light.

Optical measurements were made with a Beckman model DU-2 spectrophotometer. As shown in Figure II-1, the monochromator and detector were separated and measurements were made along the axis of the dewar. An Ealing model 22-0301 fiber light guide, 36 inches long with a 1/8 inch bundle diameter, guided light to an optically clear quartz rod, 3 mm in diameter, which passed through an o-ring seal in the endpiece into the dewar and EPR cavity. A delrin connector provided steady alignment between the fiber optic light guide and the quartz light guide, as well as excluding extraneous light.

EPR measurements were made on a Varian E-line EPR spectrometer with no special modification.

Cooling of the sample in the range from liquid nitrogen temperature to room temperature was done with nitrogen gas flowing through a coil of 1/4 inch copper tubing immersed in liquid nitrogen. Temperatures were varied using a valve which diverted room temperature gas around the cooling coil and mixed it with the cooled gas. The temperature could also be controlled by varying the flow rate of the cooling gas. The mixing valve allowed temperatures to be maintained within two degrees of the desired temperature.

Temperatures were measured upstream of the sample with a copper-constantan thermocouple made from five mil teflon coated wire obtained from Omega Engineering. An ice-water slush served as a reference.

Thermocouple voltages were measured with a Keithley Instruments model 148 nanovoltmeter attached to the thermocouple with special copper connectors. Calibration tables for the thermocouple were checked against liquid nitrogen, dry ice and ice water.

A problem with excessive vibration in the EPR cavity developed early in the experiments. This appeared to be caused by a small amount of the cooling nitrogen condensing in the exchange coil. Small droplets of liquid nitrogen were carried along with the gas stream up into the dewar where the motion of the droplet caused enough vibration to render the EPR spectra unusable. The problem was solved by using Swagelok 1/4 inch bulkhead connectors to attach a small can into the system upstream of the exchange coil. This allowed the condensed liquid to collect in the can while the cold gas continued on through the system.

2. Procedure

The sample of KCl:OH were cleaved to approximately $1 \times 2.5 \times 2.5$ mm³ in size.

Initial EPR and optical scans were done at room temperature and liquid nitrogen temperature. The crystal was then irradiated with a Hanovia model 30620, 140 watt hydrogen lamp for one hour at liquid nitrogen temperature through a grid in the EPR cavity. Optical and EPR spectra were done at liquid nitrogen temperature immediately following the irradiation and at every subsequent step in the experiment.

Following irradiation, the crystal was warmed to 130 K for five minutes and re-cooled to liquid nitrogen temperature. The crystal was then bleached with a 100 watt tungsten lamp through the grid in the

EPR cavity for periods of up to twelve minutes. The bleaching was stopped at intervals for EPR and optical measurements. After the bleaching segment of the experiment, the crystal was warmed from liquid nitrogen temperature to room temperature. As the crystal reached various temperatures, the warming was halted and the crystal held at that temperature for several minutes. The crystal was recooled to liquid nitrogen temperature and EPR and optical measurements were made.

C. OPTICAL SPECTROSCOPY OF KCl:OH

1. Apparatus

The samples were mounted in a cryostat constructed in this laboratory (Figure II-3). The outer case of the cryostat was an aluminum cylinder with two quartz windows set at the proper height for the spectrophotometer beam. A valve was screwed through the cryostat case to allow evacuation of the sample chamber. A stainless steel flange was bolted onto the top of the case and sealed with an o-ring. A cold finger welded to the flange was made of one inch diameter stainless steel tubing to which was attached a one and one half by one inch solid copper cylinder. A brass radiation shield was attached to the copper cylinder and also served as the sample mount.

Optical spectroscopy was performed with a Perkin-Elmer model 450 UV-Vis-IR spectrophotometer. The only modification was a sample compartment door which allowed the sample mounted in the cryostat to be placed in the light beam while the body of the cryostat remained outside of the sample compartment.

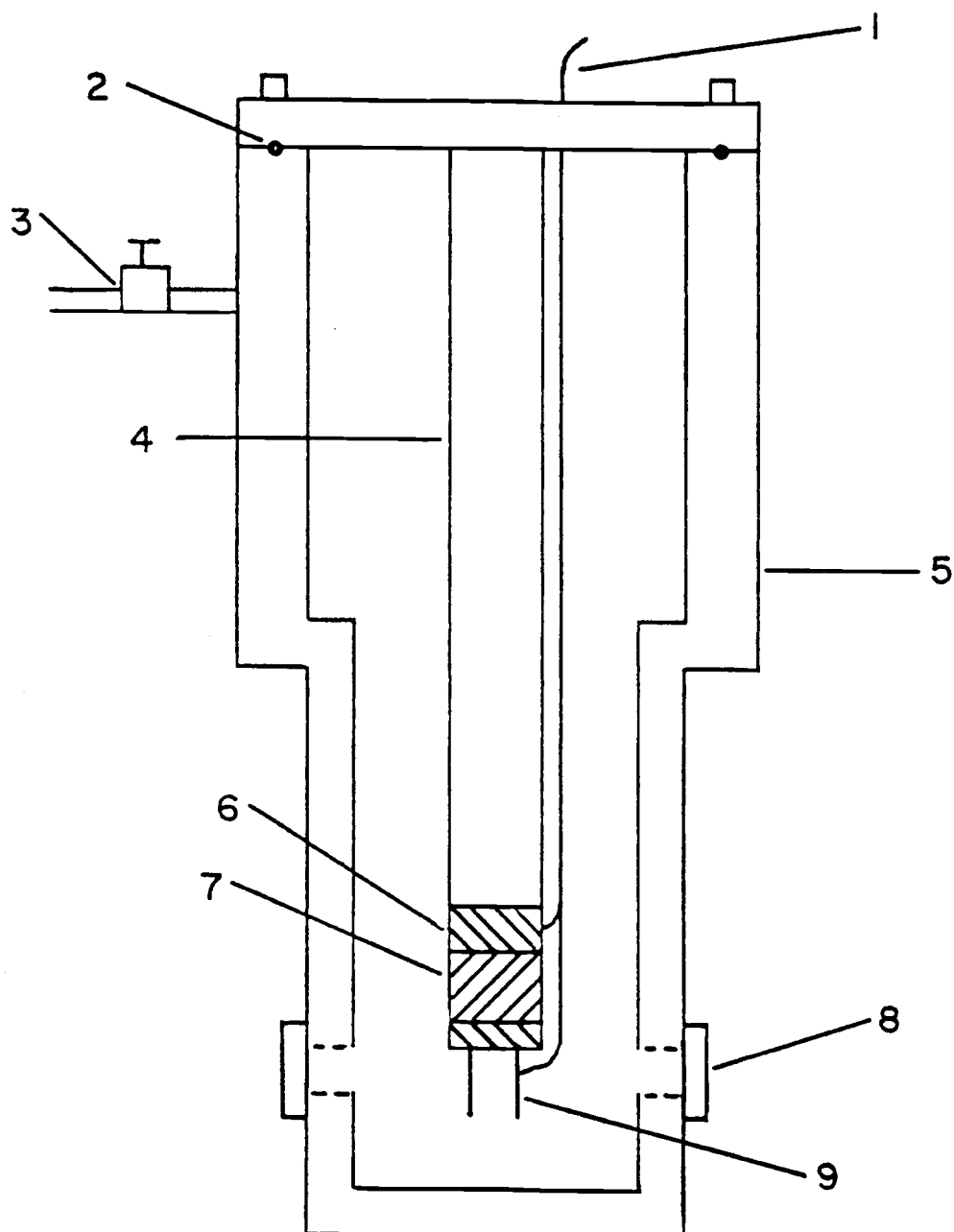


FIGURE II-3. SCHEMATIC DIAGRAM OF CRYOSTAT USED FOR OPTICAL SPECTROSCOPY. 1. Thermocouple and heater wire. 2. Rubber o-ring. 3. Valve for pumping out cryostat. 4. Stainless steel liquid nitrogen reservoir. 5. Outer case. 6. Copper cold finger. 7. Thermofoil heater. 8. Quartz windows. 9. Radiation shield and crystal mount.

To attain temperatures between liquid nitrogen temperature and room temperature a Minco Products model HK-913N, 120 ohm thermofoil heater was cemented to the copper cold finger. The heater was powered by a Variac transformer. Temperatures were measured with a copper-constantan thermocouple as described in Section II-B-1.

2. Procedure

The procedure for the optical experiments generally followed that of the EPR-optical experiments, in that crystals were irradiated at liquid nitrogen temperature and spectra were taken after various bleaching times as well as after the crystals had been warmed to temperatures above liquid nitrogen temperature. Crystal samples were cleaved to a thickness of 0.8 to 1.2 mm. The samples were cemented directly onto the brass radiation shield, which gave good thermal contact. The thermocouple was cemented to an edge of the crystal.

Because of uncertainties introduced in switching the spectrophotometer from one range to another, separate sets of experiments were done for the ranges 2000 nm to 700 nm, 750 nm to 350 nm, and 400 nm to 185 nm. Spectra were taken at room temperature and liquid nitrogen temperature of the untreated crystals and at liquid nitrogen temperature at each subsequent step of the experiment.

Samples were irradiated for one hour as previously described in Section II-B-2. Bleaching was done with a 100 watt tungsten lamp and Optics Technology Spectracoat Monopass filters. Filter number 533 (transmission maximum 533 nm) was used for bleaching of H_2O^- and F centers at liquid nitrogen temperature and filter number 566 (transmission maximum 566 nm) was used for bleaching F centers at room

temperature. To utilize the full intensity of the hydrogen and tungsten lamps the sample was irradiated and bleached outside the spectrophotometer with dry air blowing around the cryostat to prevent the formation of frost on the windows.

D. IRRADIATIVE COLORATION OF PURE KCl

1. Apparatus

KCl crystals were x-irradiated using a General Electric model CA-7 Coolidge Tube with a copper target. The tube was operated at a voltage of 35 kV and a current of 18 mA. Coloration of crystals by gamma-rays was performed with the ^{60}Co source at the Oregon State University Radiation Center. Optical measurements were made on the Perkin-Elmer model 450 spectrophotometer and EPR measurements were made on the Varian E-Line spectrophotometer previously described.

2. Procedure

Separate samples of x-irradiated KCl were used for optical and EPR measurements. These were cleaved from the same material and x-irradiated simultaneously. Crystals destined for optical measurements were 1.2 mm to 1.4 mm thick and were mounted on the cryostat described in Section II-C-1. Crystals destined for EPR measurements were mounted on a quartz rod. Samples were irradiated for 16 hours and transferred to the optical and EPR spectrometers in the dark.

Crystals colored by gamma-rays were cleaved to dimensions of approximately $5 \times 5 \times 5 \text{ mm}^3$ and wrapped in aluminum foil. They were then irradiated for 40 hours at room temperature. Following exposure,

samples were cleaved for EPR and optical spectra and mounted as previously described.

Once in place in the measuring instruments the samples were treated as previously described. Initial spectra were taken at room temperature, liquid nitrogen temperature and at various temperatures in between.

E. CALCULATIONS

Relative concentrations of color centers were determined by graphic integration of the area under the EPR and optical spectra. A method described by Alger⁵⁸ for graphic integration of derivative EPR spectra was used for those measurements.

Concentrations of F centers obtained were calculated from the optical spectra using a form of the Smakula equation,

$$Nf = 1.68 \times 10^{16} A_m W \quad [II-1]$$

where N is the concentration of F centers per cm^3 , f is the oscillator strength of the F center, W is the half width of the optical absorption band in eV and A_m is the absorbance per cm at λ_{max} . The oscillator strength reported by Silsbee⁵⁹ from EPR measurements, $f = 0.85$, was used.

EPR and optical measurements described in section III-A were compared by the following method. Immediately after color center formation, the areas under the EPR and optical spectra were evaluated as a measure of color center concentration at zero time. The relative concentrations

of color centers in the samples during the course of the experiment were then obtained as a ratio of the area under the subsequent spectra to the area under the curves measured at zero time. This is expressed by the simple relation.

$$A_t/A_0 = N_t \quad [II-2]$$

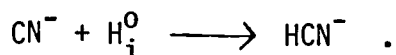
where A_0 is the area under the spectrum at zero time, A_t is the area after treatment of the crystal by bleaching or warming, and N_t is the fraction of color centers remaining. The quantity N_t is thus a relative concentration of color centers in the sample after it has been bleached for various times or warmed to a temperature above 77 K.

III. RESULTS

A. SIMULTANEOUS EPR AND VISIBLE SPECTROSCOPY

EPR and visible spectra of the samples were taken immediately after ultraviolet irradiation. Optical spectra in the region from 700 nm to 400 nm showed no absorption. EPR spectra gave a pair of multiplets identified as arising from the U_2 center^{10,60,61}. When the crystal was warmed to approximately 140 K, the U_2 center resonance disappeared and the appearance of the "wet" F center EPR and optical spectra^{39,40} was noted.

A pair of triplets which appeared in the tails of the H_2O^- EPR spectrum was identified as the spectrum of an HCN^- impurity center⁶². This impurity center consists of an HCN^- molecule ion occupying an anion lattice site and is formed by a reaction analagous to reaction I-7. This is given by the equation



The HCN^- center appears to be a common impurity produced in photochemically colored alkali halides doped with hydroxide ion, having been previously noted by Rusch and Seidel³⁹. It has also been observed in the EPR spectra of photochemically colored crystals doped with hydrosulfide ion, SH^- , and hydroselenide, SeH^- ⁶². No reason has been proposed for the presence of cyanide ion in doped alkali halides.

Because the EPR signal of the HCN^- center disappeared at about the same temperature as the H_2O^- EPR signal, it was assumed that this

species behaved similarly to the H_2O^- center, forming an F center and an interstitial HCN molecule on warming to 250 K. Accordingly the area of the HCN^- EPR spectrum was included in the comparison of optical and EPR measurements.

1. Bleaching experiment

Bleaching of photochemically produced color centers in hydroxide doped potassium chloride gave results essentially the same as those of Papazian² and Moral *et al.*³⁵. In Figure III-1, the change in the relative area under the EPR and optical absorption curves is shown. The data points are the average of values obtained from eight independent experiments. The error bars represent one standard deviation.

Taken individually, the sets of data in Figure III-1 show normal color center behavior if the area under the spectrum is taken to be a measure of the concentration of the color centers. After bleaching the sample for various times with white light, the concentration of color centers decreased proportionally with time. Comparing the sets of data, however, it is seen that the relative concentration of centers measured by optical absorption decreased much more than did the relative concentration as measured by EPR.

Closer inspection of the results revealed that the difference between the relative concentration measured by optical absorption and EPR remains almost constant during bleaching. Figure III-2 shows the average difference between the relative concentrations measured by optical absorption and EPR. The data points are averaged over eight

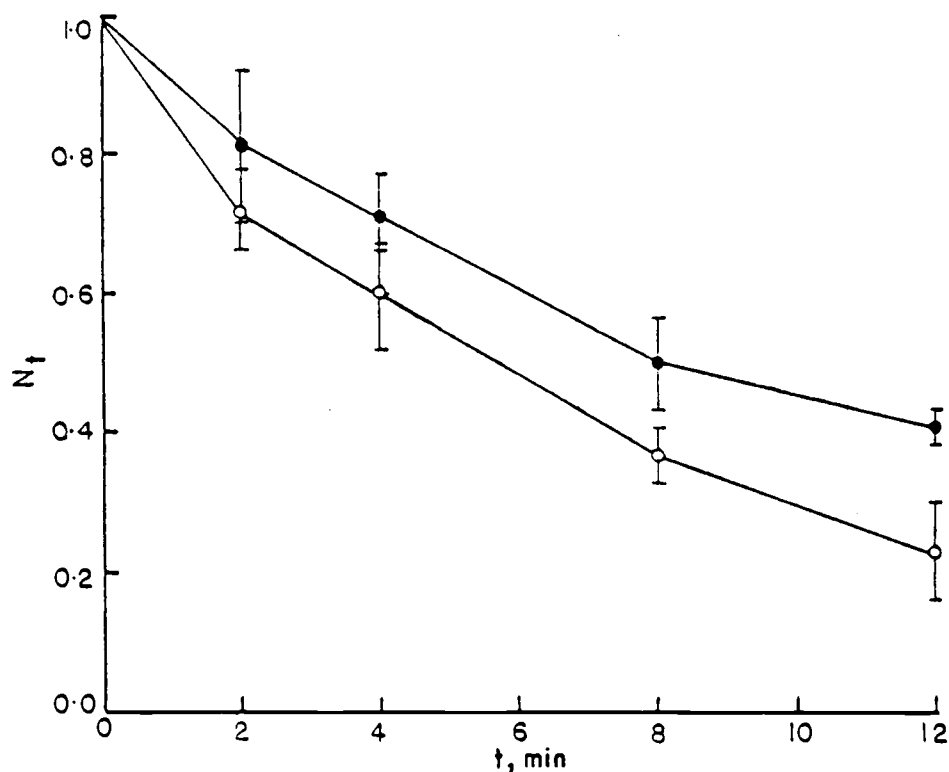


FIGURE III-1. CHANGE IN RELATIVE CONCENTRATION OF COLOR CELTERS, N_t , WITH BLEACHING TIME, t . N_t was determined as in equation II-2. The upper set of data points given as solid circles, represent N_t obtained from EPR measurements and the lower points, open circles, represent N_t obtained from the optical measurements. Samples were treated as explained in the text. All measurements were made at liquid nitrogen temperature. Samples were bleached with white light through the grid in the EPR cavity.

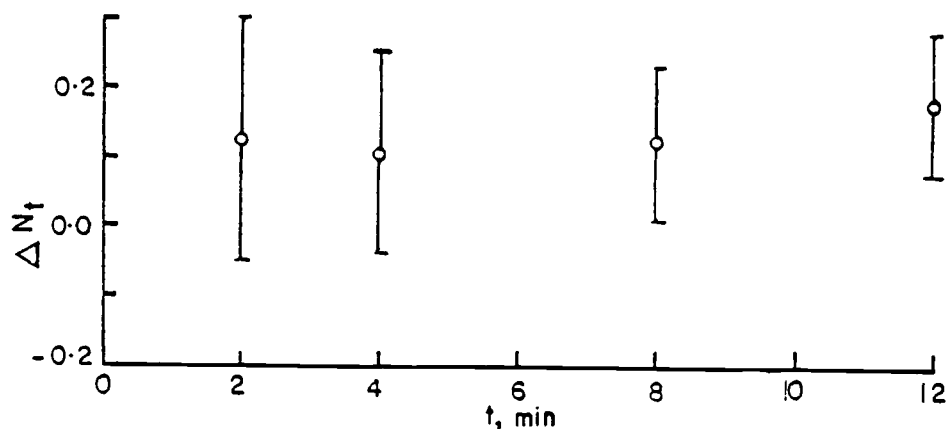


FIGURE III-2. AVERAGE DIFFERENCE BETWEEN N_t OBTAINED FROM EPR AND OPTICAL MEASUREMENTS. $\Delta N_t = N_{t(\text{EPR})} - N_{t(\text{optical})}$.

independent experiments, with error bars indicating one standard deviation. The difference between measured concentrations at zero bleaching time is given as zero because the initial concentrations determined from both measurement techniques were normalized to unity. The significance of this will be discussed in the following chapter.

The EPR spectrum of the HCN^- impurity was unaffected by bleaching with white light. The area under the HCN^- triplets was 0.19 ± 0.04 of the initial EPR spectrum throughout the bleaching experiment.

2. Warm-up experiment

After bleaching, the sample was warmed from liquid nitrogen temperature to various higher temperatures and EPR and optical spectra were taken. A comparison of the areas under the EPR and optical curves made during warming is shown in Figure III-3. The curves were obtained by plotting the data for five independent experiments, drawing the best curve for each set of points and averaging the values of the curves at several temperatures. The error bars indicate the spread between the highest and lowest values of the curves drawn for the individual experiments. The graphs show that the relative concentration of color centers as measured by EPR and optical measurements increases significantly when the crystal is warmed after bleaching, reaching a maximum when warmed to about 140 K. As the sample is warmed to higher temperatures, the optical absorption curve decreases slightly then increases to approximately its original value. The EPR curve decreases slowly until the crystal is warmed to 250 K, at which point it drops sharply, disappearing completely by the time the sample is warmed to 270 K, within the limits of the measurements.

For comparison, optical and EPR data for a single representative experiment over the entire set of experimental conditions is shown in Figure III-4.

Figure III-5 shows the change in the EPR spectrum over the course of the experiment. The measured ΔB_w of the major band of the EPR spectrum was 40 ± 1 gauss and the measured g value was 1.995 ± 0.002 . These values did not change during the course of the experiment and their lack of change indicates that the strong EPR signal is due solely to the presence of H_2O^\cdot centers with no measurable contribution from F centers.

B. OPTICAL SPECTROSCOPY

Optical spectra were taken over the range from 2000 nm to 185 nm to determine if any centers other than those previously noted in equations I-6 through I-8 were involved. The behavior of the photochemically colored KCl:OH was investigated under a variety of bleaching and temperature conditions. As in the previous experiments, all measurements were made at liquid nitrogen temperature.

1. Near ultraviolet region, 185 nm to 400 nm (6.70 to 3.10 eV)

The prominent feature of the near ultraviolet region is the strong hydroxide band at 240 nm. Due to the high concentration of hydroxide ion in the crystal, no significant change in the band was observed during any part of the experiment.

Immediately after ultraviolet irradiation of the sample at liquid nitrogen temperature a strong U_2 band appeared at 236 nm, as well as

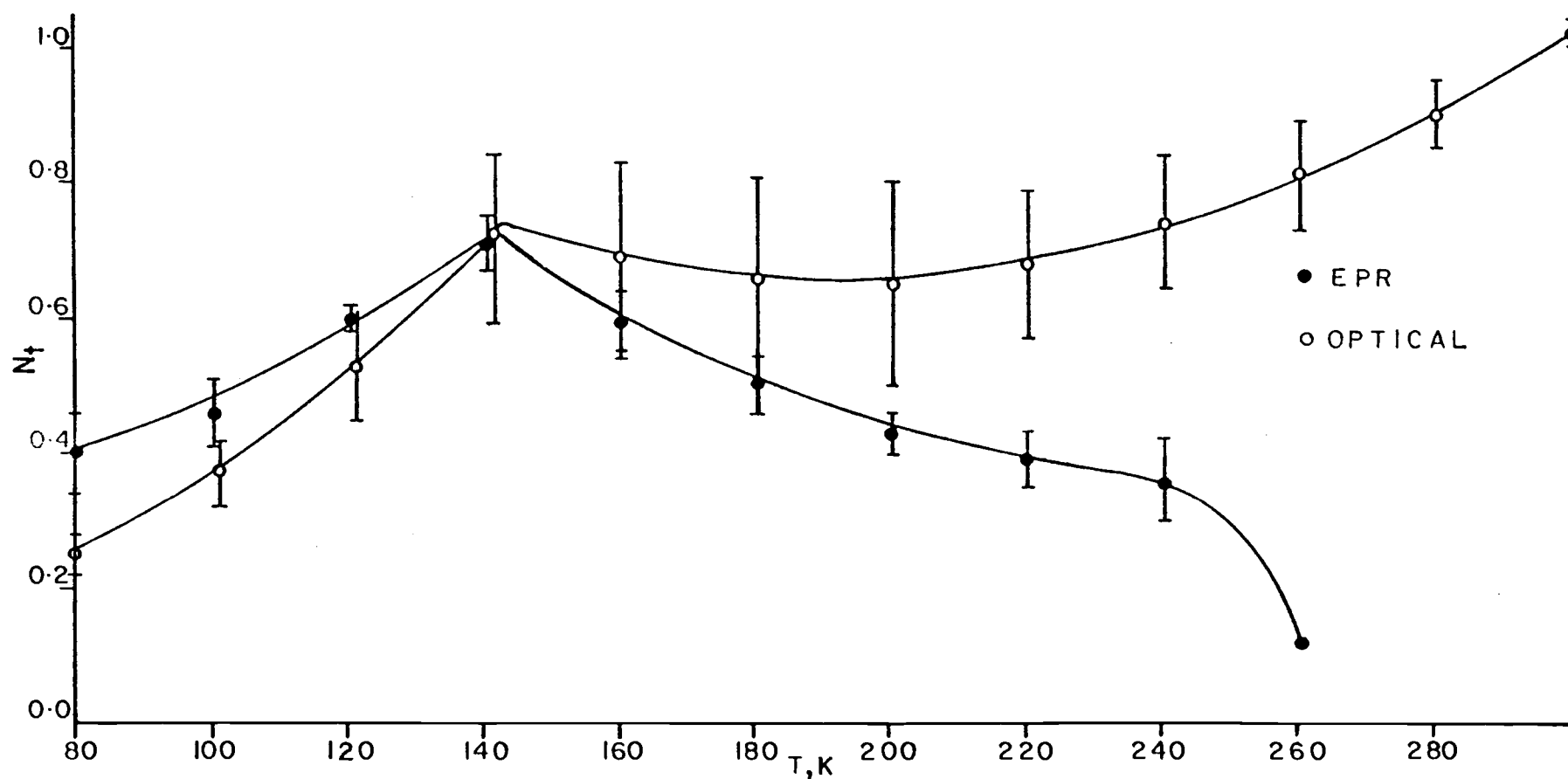


FIGURE III-3. AVERAGE CHANGE IN RELATIVE CONCENTRATION OF COLOR CENTERS, N_t , ON WARMING. Samples were colored by ultraviolet irradiation and bleached for twelve minutes with white light before warming. The curves were obtained by plotting the data from five experiments and drawing the best curve to fit the points. The error bars represent the extreme range of values obtained in the data of individual experiments.

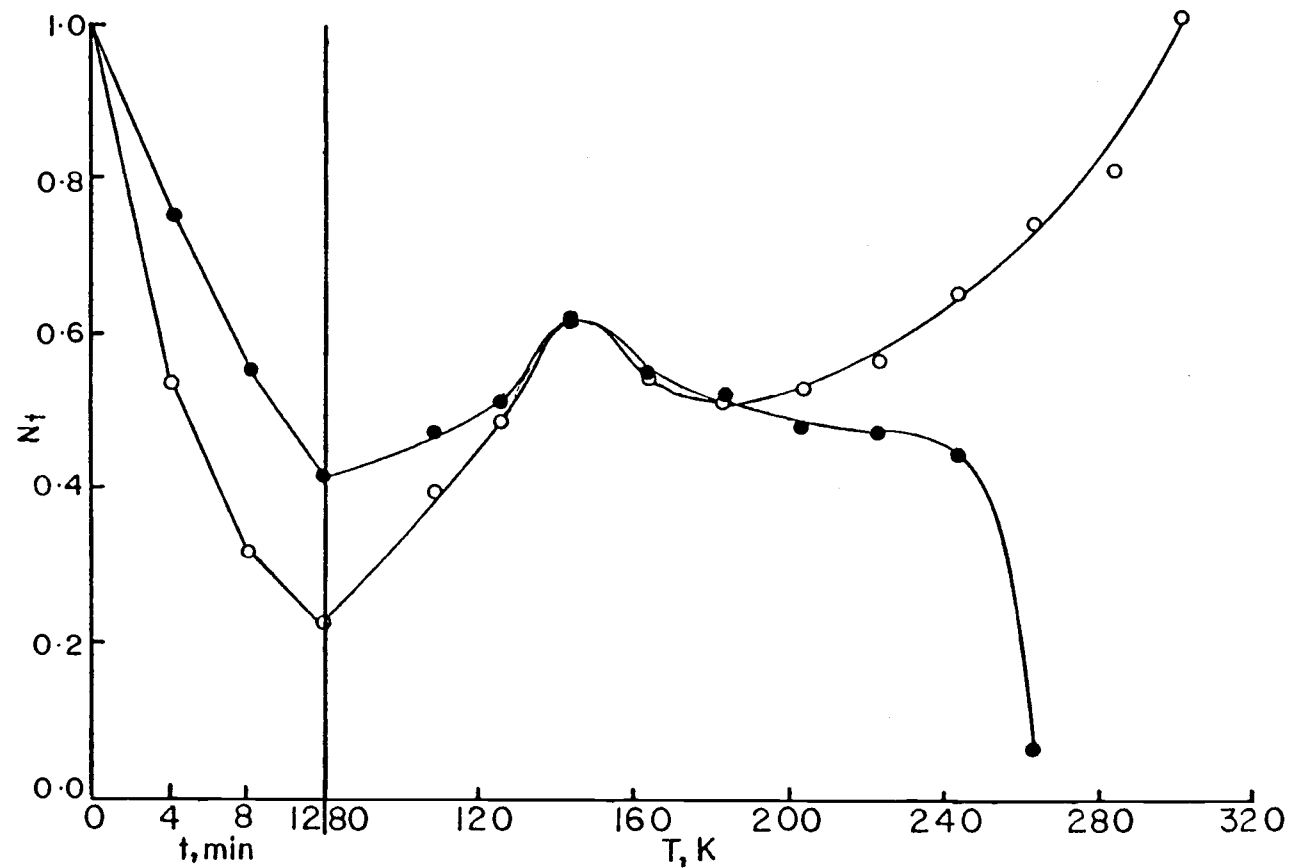


FIGURE III-4. CHANGE IN RELATIVE CONCENTRATION OF COLOR CENTERS, N_t , OVER THE ENTIRE RANGE OF EXPERIMENTAL CONDITIONS. Data presented are for a single representative experiment. Solid circles represent data points obtained from EPR measurements, and the open circles data points obtained from the optical measurements.

FIGURE III-5. EPR SPECTRA OF ULTRAVIOLET-IRRADIATED KCl:OH . All spectra were measured at liquid nitrogen temperature. The scale at the top of the figure (2750 G to 3750 G) relates to Curve 1, the EPR spectrum of the U_2 center. The scale at the bottom (3050 G to 3450 G) relates to the remaining curves, the spectra of the H_2O^- center and the HCN^- center. The asymmetric resonance in the center of several of the curves is caused by paramagnetic centers in the quartz dewar created by ultraviolet irradiation. Curve 1 shows the spectrum immediately after ultraviolet irradiation of KCl:OH at liquid nitrogen temperature. Curve 2 was obtained after warming the same to 140 K. Curves 3 and 4 are the spectra obtained after bleaching the sample with white light for four and twelve minutes respectively. Spectra 5, 6, 7, and 8, were obtained after warming the sample to 170 K, 210 K, 245 K, and room temperature, respectively.

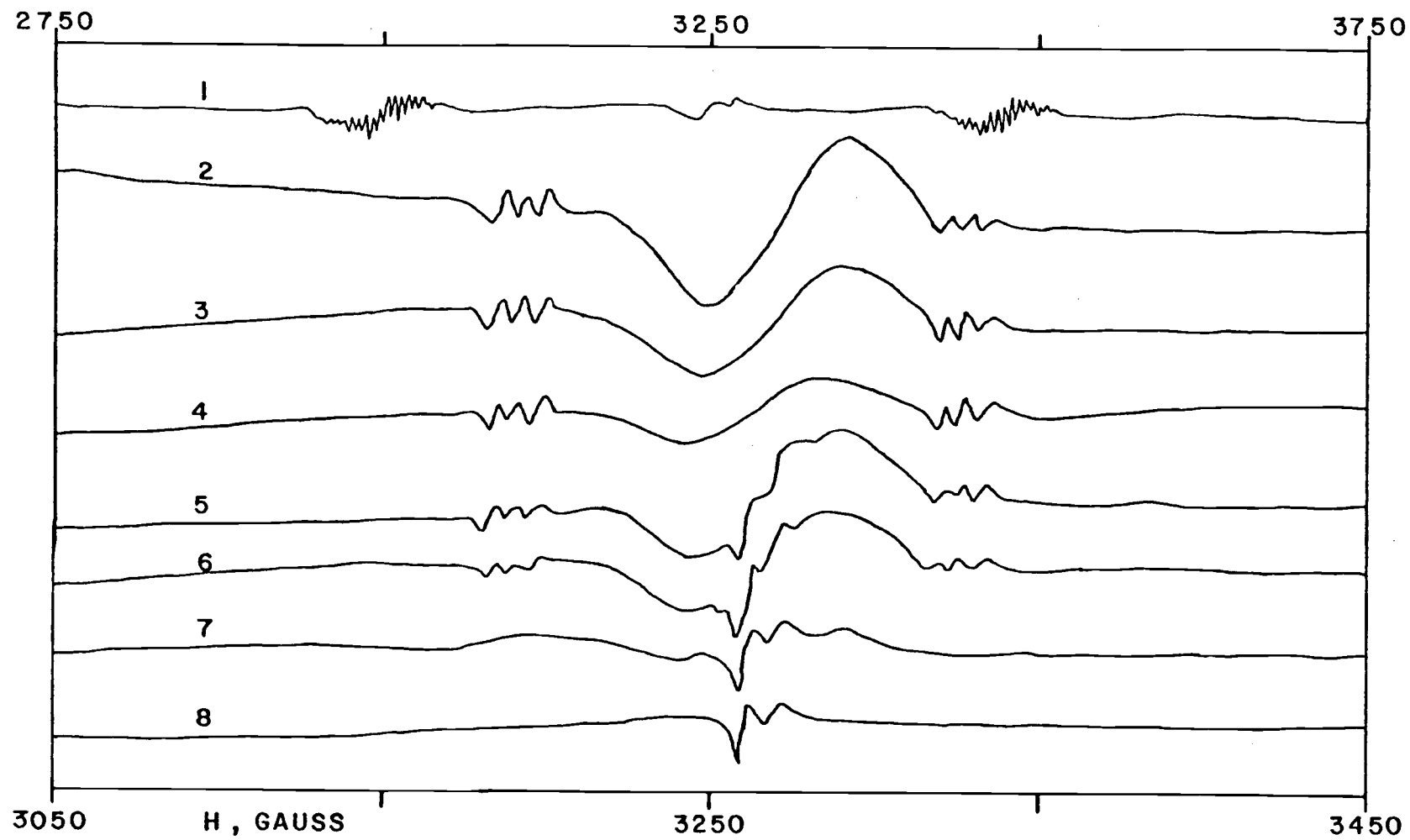


FIGURE III-5.

the long wavelength tail of the O^- band. On warming the crystal to 140 K, the U_2 band disappeared and a slight decrease in the tail of the O^- band was observed. Bleaching the sample with white or 533 nm light or further warming from 140 K to higher temperatures had no further effect on the spectrum in this region.

Figure III-6 shows the spectra observed in the near ultraviolet region. The tail of the O^- band is at the left end of the figure.

2. Visible region, 350 nm to 750 nm (3.54 to 1.65 eV)

No absorption bands were observed in this region immediately after irradiation of the crystal. After warming to 140 K only the H_2O^- band appeared, identified by its characteristic shape and λ_{\max} at 525 nm. The H_2O^- band exhibited bleaching behavior similar to that of the F band. Bleaching at liquid nitrogen temperature with 533 nm light produced a decrease in the height of the H_2O^- band which was proportional to bleaching time. Warming the crystal to 140 K after bleaching resulted in a partial regeneration of the H_2O^- band. No other bands were observed during bleaching of the H_2O^- band at liquid nitrogen temperature. On warming the crystal no change in the H_2O^- band was observed until the temperature reached 250 K. At that temperature the transition from "wet" F to "normal" F center occurred.

In Figure III-7 the bleaching behavior of the H_2O^- center is presented. Figure III-8 shows the effect of warming the sample from liquid nitrogen temperature to room temperature on the optical absorption band. Warming the crystal to 243 K produced no change in the shape of the H_2O^- band. When the crystal was warmed to 258 K, the band narrowed to a shape approximating that of the F band. In this

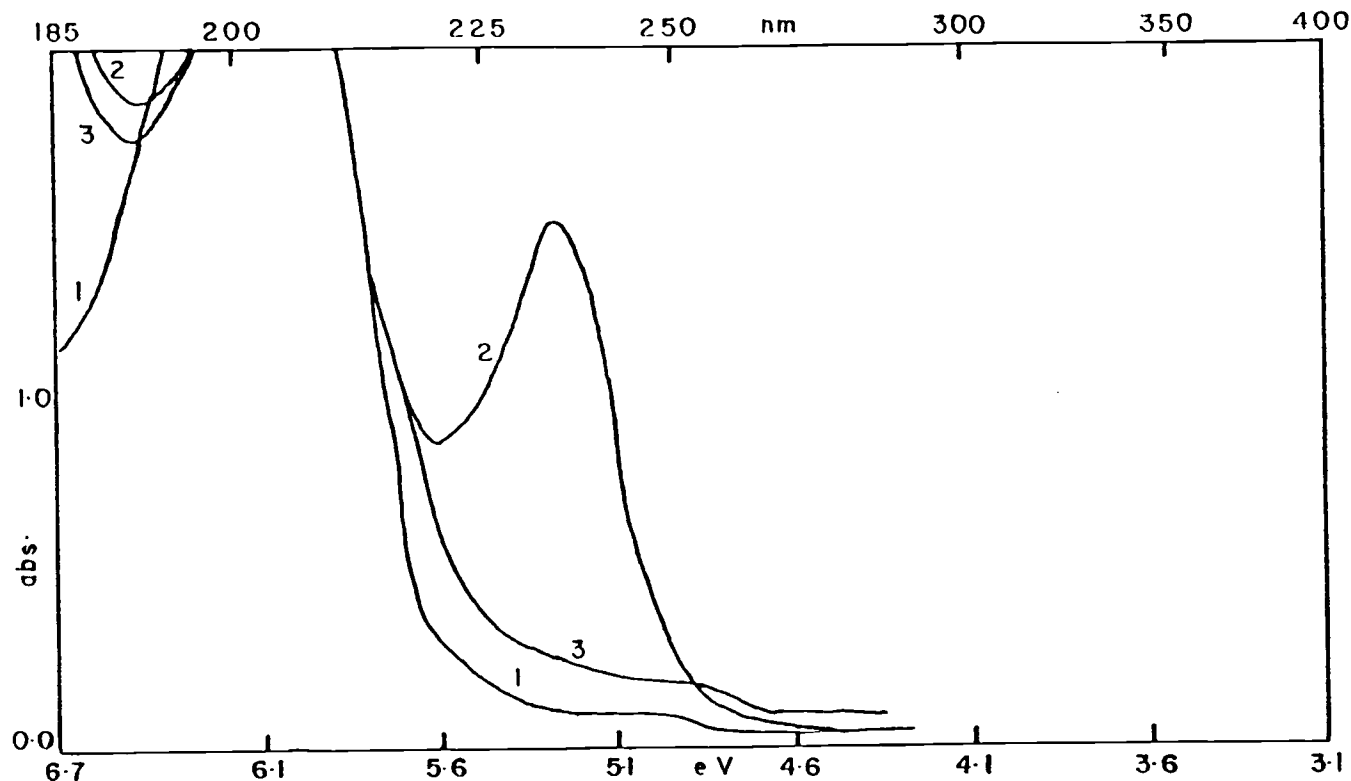


FIGURE III-6. NEAR ULTRAVIOLET SPECTRA OF ULTRAVIOLET IRRADIATED KCl:OH. All spectra were measured at liquid nitrogen temperature. Samples were mounted in the cryostat as described in Chapter II. The very large optical absorption centered at 204 nm is the hydroxide band. The band centered at 236 nm in curve two is the U_2 optical absorption. The long wavelength tail of the O^- band is seen at the extreme left in curves two and three. Curve one shows the ultraviolet spectrum of KCl:OH prior to irradiation with ultraviolet light; Curve 2 the spectrum following irradiation for 60 minutes, and curve 3 the spectrum after warming the sample to 140 K.

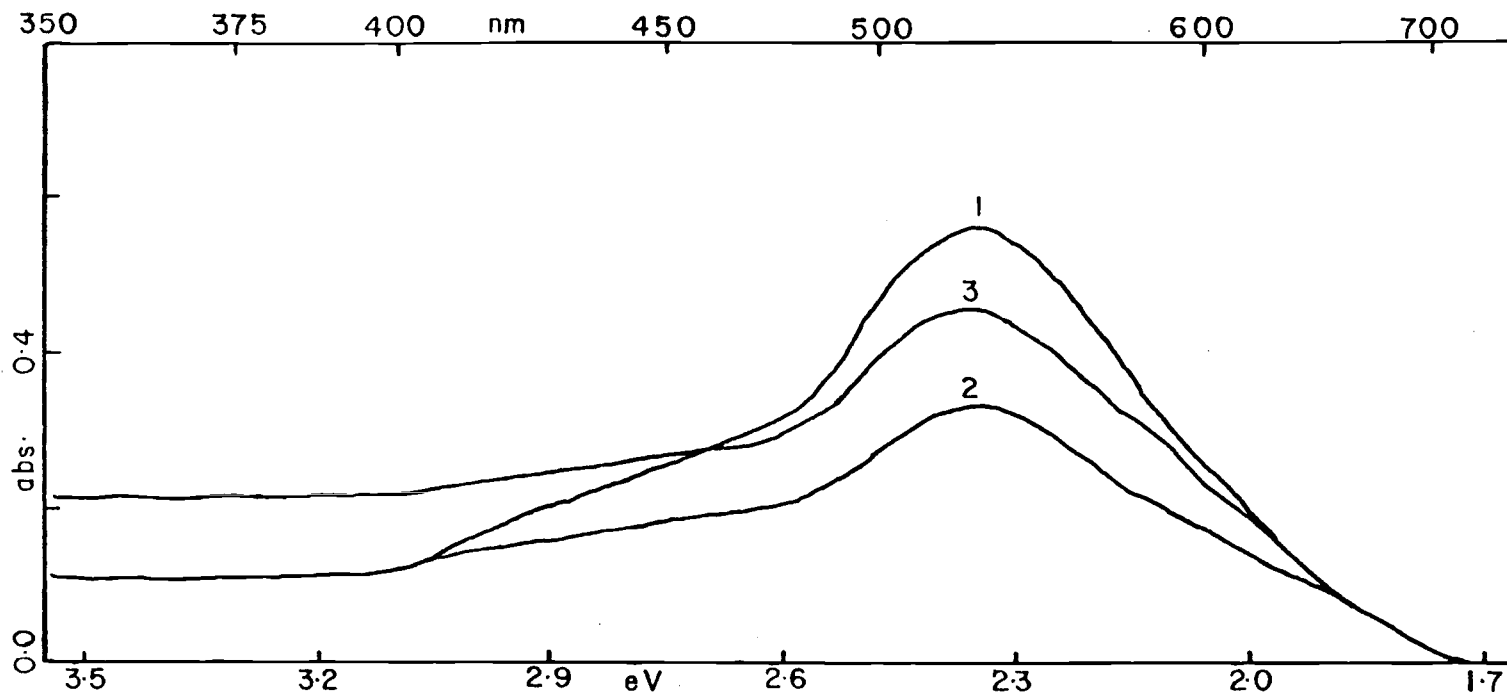


FIGURE III-7. VISIBLE SPECTRA OF ULTRAVIOLET-IRRADIATED KCl:OH. All spectra were measured at liquid nitrogen temperature. Curve 1 is the visible spectrum of KCl:OH after ultraviolet irradiation for 30 minutes and warming to 140 K. The visible spectrum Curve 2. Curve 3 shows the visible spectrum of the sample after rewarming to 140 K. The correction of the baseline shift seen in curve 3 is described in the test. The regeneration of the bleached H_2O^- band on warming is shown by curves 2 and 3.

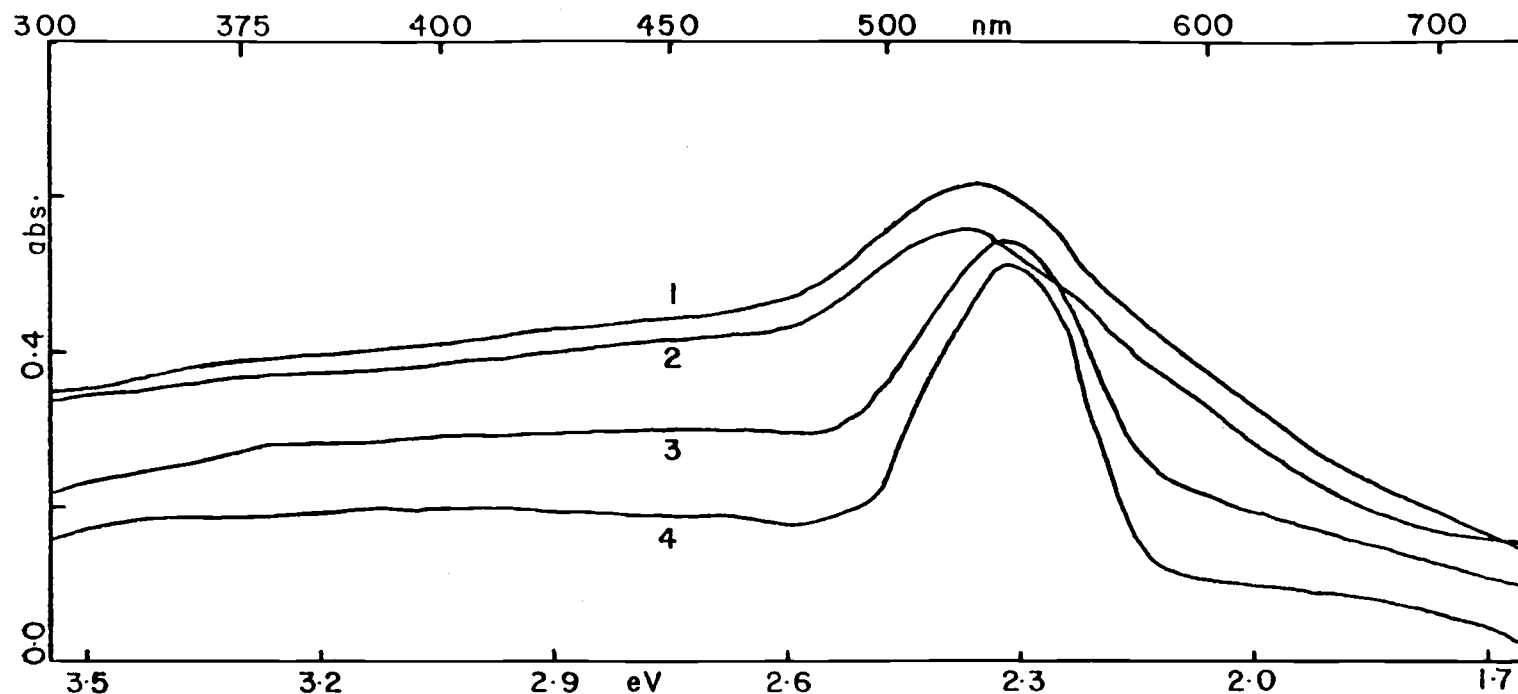


FIGURE III-8. VISIBLE SPECTRA OF ULTRAVIOLET-IRRADIATED KCl:OH. All spectra were measured at liquid nitrogen temperature. Curve 1 was obtained after ultraviolet irradiation for 60 minutes and warming to 130 K. Curve 2 was obtained following warming to 243 K. Curve 3 and curve 4 were obtained after warming to 258 and room temperature, respectively. These spectra illustrate the transition from H_2O^- center to F center described in Chapter I. Curves 1 and 2 are spectra of the H_2O^- center and curve 4 is virtually a pure F center band. Curve 3 is essentially the F band broadened and shifted slightly by a small concentration of remaining H_2O^- centers. The difference in width and λ_{max} of the H_2O^- band and the F-band is well illustrated. The shift in the baseline was corrected for calculations as described in the text.

case a half width of 0.25 ± 0.01 eV and a λ_{max} at 533 nm were noted. Further warming to room temperature gave an absorption band nearly identical to the "normal" F band. The F band obtained in this way had a λ_{max} at 540 nm at liquid nitrogen temperature and was broadened slightly, having a half width of 0.225 ± 0.008 eV. Final concentrations of F centers obtained in the several repetitions of the experiment were between 1.5×10^{16} and 2.5×10^{16} F centers per cm^3 .

When the F band obtained in this way was bleached with 566 nm light at room temperature, the optical absorption disappeared completely and irreversibly within a few minutes. No indication of other centers was observed.

The shift of the absorption baseline seen in Figures III-7 and III-8 is apparently due to minute amounts of condensation on the quartz windows of the sample cell. These shifts were compensated for in the determination of color center concentration by measuring a number of shifted baselines with no sample in the cell. The best fitting baseline was then used in the measurement of the area under the spectrum.

3. Near infrared region, 600 nm to 2000 nm (2.07 to 0.62 eV)

Spectra in the near infrared region were featureless under all conditions, except for the tail of the H_2O^- band. No indication of F aggregate centers or any other centers was observed.

C. IRRADIATIVE COLORATION OF PURE KCl CRYSTALS

Nominally pure potassium chloride crystals were colored by gamma or x-rays at room temperature. Optical measurements of these crystals

showed only an F band in the range from 2000 nm to 185 nm. The very weak V_2 and V_3 bands were not observed within the limits of detection. The half width of the F band so obtained, measured at liquid nitrogen temperatures, varied over several samples from 0.21 to 0.229 eV in a manner apparently unrelated to irradiation time or any other experimental parameter. Concentrations of F centers obtained were from 11.1×10^{16} to 3.38×10^{16} F centers per cubic centimeter.

EPR spectra of pure crystals colored by gamma or x-rays at room temperature showed no F center resonance under any conditions.

IV. DISCUSSION OF RESULTS

A. BLEACHING BEHAVIOR

A discussion of the bleaching behavior of photochemically colored KCl:OH will be considered in two parts: The difference between the bleaching rates measured by EPR and optical absorption methods and the products and mechanism of the bleaching of the H_2O^- center.

1. Bleaching rate of H_2O^-

The results in section III-A were obtained by calculating the relative concentration of color centers, N_t , as defined by equation II-2. As shown in Figure III-1, N_t as determined from EPR measurements decreases less rapidly during bleaching than N_t obtained from optical measurements. However, the difference between the two rates is nearly constant after the second minute of bleaching. As was noted previously, the two rates coincide at zero time because the relative concentrations were normalized to unity. It was also noted in Chapter III that the portion of the EPR spectrum attributed to the HCN^- center did not decrease in area during bleaching.

Because the HCN^- center does not bleach with white light, we may assume that it does not absorb visible light and therefore does not contribute to optical absorption in the region of the F band. In addition, the EPR spectrum of the HCN^- center does not show the inhomogeneous broadening that would indicate hyperfine interactions between the unpaired electron and the crystal. Thus the unpaired electron must be localized on the HCN molecule, in contrast to the H_2O^- center, which is essentially an F center perturbed by a water molecule. Therefore

the HCN^- center is not expected to contribute to the optical absorption measurements during the bleaching experiment.

The EPR measurements, then, give a relative concentration of color centers that is too large by the amount of HCN^- centers present. Because the concentration of HCN^- centers remains constant during bleaching, this error can be corrected as follows:

$$A_{tF} = A_t - A_{t\text{HCN}} \quad [\text{IV-1}]$$

In this relation A_{tF} and $A_{t\text{HCN}}$ are the areas under the EPR spectra arising from "wet" F and HCN^- centers, respectively. The quantity $A_{t\text{HCN}}$ has been determined to be $0.19 A_0$. So, to find the relative concentration of "wet" F centers, equations IV-1 and II-2 are combined, and we obtain

$$\frac{A_{tF}}{A_{oF}} = \frac{A_t - 0.19 A_0}{A_0 - 0.19 A_0} \quad [\text{IV-2}]$$

The corrected results, presented in Figure IV-1, show that the relative concentrations of H_2O^- centers determined from EPR and optical measurements decrease equally, within the limits of error, when bleached with white light.

2. Products of bleaching H_2O^- centers

a. Possibility of H_2O^- formation

The fate of the unpaired electron excited from the H_2O^- center during bleaching is not clear, since no optical absorption arose which could be definitely attributed to the ejected electron. If we consider that reactions analogous to reactions I-1 and I-2 occur, we

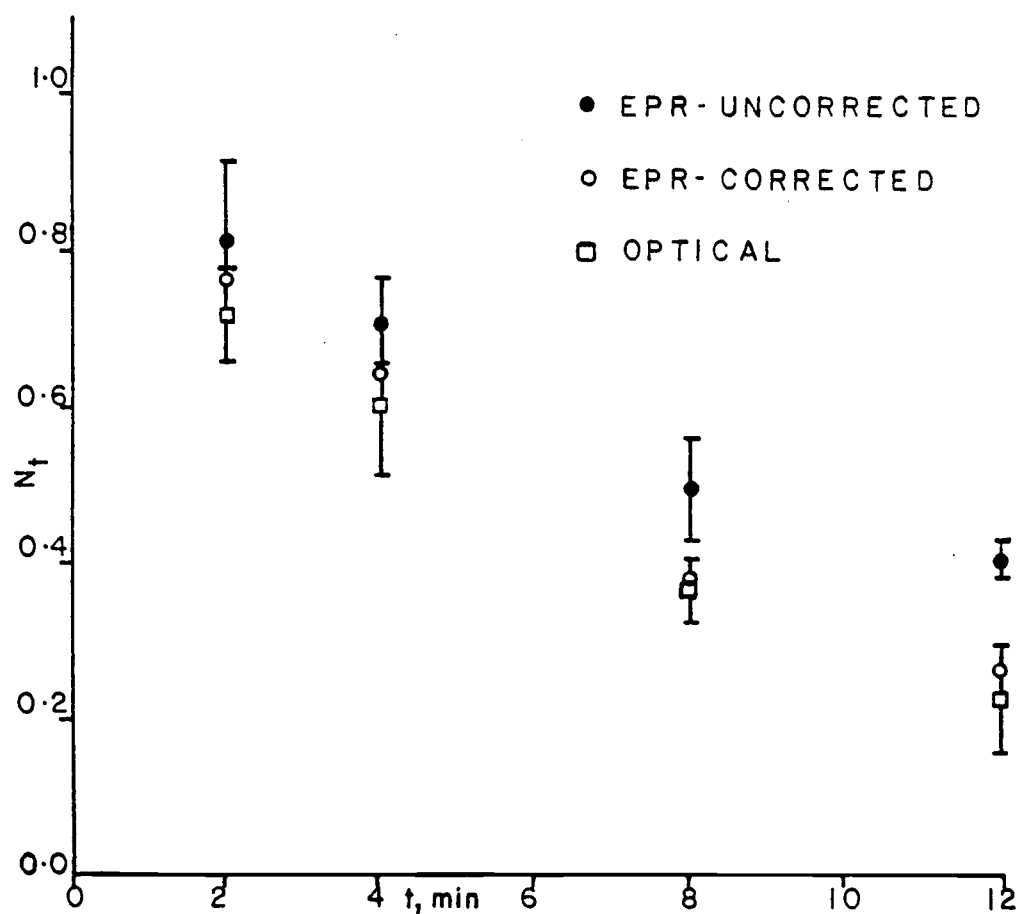
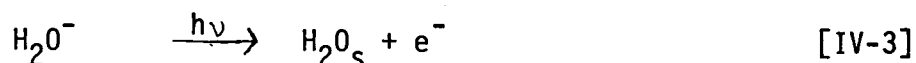


FIGURE IV-1. CORRECTED CHANGE IN RELATIVE CONCENTRATION OF COLOR CENTERS, N_t , WITH BLEACHING. N_t was determined as in equation II-2 from optical and EPR measurements. N_t obtained from EPR measurements was corrected according to equation IV-2 for the presence of HCN^- centers. The values of the corrected N_t 's show that the bleaching rates of the H_2O^- center are the same, within the limits of error, whether it is determined from EPR or optical measurements.

would expect them to be



Here H_2O_s is equivalent to an alpha center with a neutral water molecule embedded in it, and H_2O^{2-} is equivalent to an F' center with an embedded water molecule. On consideration of the possibilities, the formation of "wet" F and "wet" alpha centers are the most likely products of bleaching the H_2O^- centers with visible light.

The unpaired electron of the H_2O^- center has been shown to be in an antibonding orbital of the F- H_2O system⁴⁰. Without taking the potential of the surrounding lattice into account, the introduction of a second electron into the antibonding orbital would make the system energetically unstable. However, the Madelung potential of potassium chloride is about 7.4 electron volts and the water molecule is a small perturbation on the state of the unpaired electron. In the crystal lattice then, the H_2O^- center would be in a shallow potential well in the same way that the F center is. That being the case, an H_2O^{2-} center should be relatively stable at liquid nitrogen temperature.

The F' optical absorption is a very weak, broad band with an estimated half width of 2 eV^4 , which underlies the F band. The F' optical absorption is often observed as a slight broadening of the F band and a small shift of the absorption baseline. Since the H_2O^-

band is much broader and slightly weaker than the F band, an H_2O^{2-} band would be shallower and broader than the F' band and could easily pass unnoticed. Figure III-7 shows that after bleaching, the height of the H_2O^- band is greatly reduced, but no sign of an H_2O^{2-} absorption could be detected within the limits of measurement.

As can be seen from Figures III-3,4,5, and 7, the bleaching and regeneration of both the EPR and optical absorption spectra of the "wet" F centers are nearly identical to the behavior of the F center spectra under the same conditions. These results support the argument that reactions IV-3 and IV-4 occur. The lack of an H_2O^{2-} optical absorption, which should be nearly undetectable, is not a serious weakness in the arguments in favor of a "wet" F' center as a main product of the bleaching of H_2O^- centers.

b. Possibilities of other products of H_2O^- bleaching

The other possible fates for the electron produced by reaction IV-3 are combination with other impurity centers in the crystal. It has been established from EPR and optical absorption investigation that the only other impurities present in measurable amounts are O^- , OH^- and HCN^- . The OH^- center is diamagnetic and an OH^{2-} center formed by trapping a conduction band electron would be paramagnetic and detectable by EPR. The EPR spectrum of the HCN^- center remains unchanged during bleaching and thus the formation of a diamagnetic HCN^{2-} center can also be ruled out as a possible fate for a conduction band electron produced by reaction IV-3.

An alternate fate for an electron from reaction IV-3 is entrapment by an O^- center to form a substitutional oxide ion, O^{2-} , by the reaction



Combining reactions I-6 and I-7 we obtain

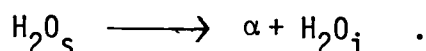


which shows that equal amounts of O^- and H_2O^- centers are formed when KCl:OH is photochemically colored. A comparison of the electron trapping cross sections of the H_2O^- and O^- centers, however, leads us to expect that reaction IV-4 is much more likely to occur than reaction IV-5. Staible²⁴ has established that the trapping cross section of the O^- center is of the order of the cross section of the 2p orbitals, about $4 \times 10^{-16} \text{ cm}^2$. The trapping cross section of the F center is $4 \times 10^{-15} \text{ cm}^2$ ⁶³, an order of magnitude greater than that of the O^- center. It was previously noted that the H_2O^- molecule perturbs the F center electron by pushing it slightly out of the vacancy^{39,40}. Therefore the trapping cross section of the "wet" F center should be slightly larger than that of the F center. The likelihood of a conduction band electron being trapped by an O^- center is thus much less than the probability of it being trapped by an H_2O^- center.

No doubt a small amount of oxide ion is formed by reaction IV-5, but the quantity of electrons trapped by O^- centers must be very small compared to the number reacting with centers containing

water molecules. This conclusion is supported by the results showing that H_2O^- centers are regenerated when the crystal is warmed after bleaching. We would not expect an oxide ion formed by reaction IV-5 to dissociate back to an O^- center and a conduction band electron on being warmed only a few degrees.

From reaction IV-3, the other product of bleaching H_2O^- centers is an $\text{H}_2\text{O}_\text{s}$ center. We would expect the neutral water molecule to remain in its substitutional site rather than move to an interstitial site. By the reverse of reaction IV-4, when an H_2O^{2-} center dissociates thermally, the conduction band electron can then be trapped by another H_2O^- center to reform a "wet" F' center, by an O^- center to form an oxide ion, or by an $\text{H}_2\text{O}_\text{s}$ center to form an H_2O^- center. If an appreciable number of neutral water molecules had moved from substitutional to interstitial sites, alpha centers would be left behind, the reaction being



These alpha centers would then trap conduction band electrons to become "normal" F centers. The F band is much narrower than the H_2O^- band and has a λ_{max} at a longer wavelength. Any substantial number of F centers would cause a definite change in the shape of the optical absorption band. No such change was observed.

B. DISAPPEARANCE OF THE EPR

The sudden and complete disappearance of the EPR signal of the F center is the most perplexing aspect of the KCl:OH system. As was noted previously, when an ultraviolet irradiated crystal of KCl:OH is warmed to temperatures higher than 250 K the EPR signal suddenly decreases to zero, while the optical absorption, presumably caused by the same center, increases slightly. The temperature at which the EPR signal vanishes was also shown to be the temperature at which a marked change in the shape of the optical absorption spectrum occurred. This change was the result of the transition from H_2O^- to F center, as shown in reaction I-8.

The optical spectrum obtained by warming a sample containing "wet" F centers leaves little doubt that "normal" F centers are produced. The shape and position of the optical absorption band are the same as in additively colored crystals which contain "pure" F centers. The broadening of the absorption band and the shift of λ_{max} with increasing temperature are also the same as in additively colored crystals.

It has been hoped that optical absorption spectra over a wide range of wavelengths would yield information about new, unsuspected centers, or perturbations affecting the known centers, which would give a clue as to the reason for the total lack of EPR. Only the centers previously described, the OH^- , O^- and F centers, were detected after the crystal had been warmed to temperatures above 250 K. The only difference between the F center optical band recorded in these

experiments and the F band obtained from additively colored pure crystals was a slightly larger half width. The half width measured in these experiments was 0.225 ± 0.0008 eV, as compared to an accepted half width of 0.20 eV¹⁷ for the "pure" F band. This broadening of the half width was explained by previous work showing that the F band is widened by the presence of impurity centers^{64,65}.

Since optical and EPR spectra gave no clue about the reason for the total lack of EPR from apparently normal F centers, it was hypothesized that perhaps an interaction between the unpaired electrons of the F center and the O^- center caused an alignment of the electrons, leading to a diamagnetic $F-O^-$ complex of some sort. Theoretical arguments and calculations based on this hypothesis are presented in the following chapter.

V. THEORETICAL CALCULATIONS OF AN F- O^- INTERACTION

It has been shown that before warming the sample to 250 K, the only species present in photochemically colored KCl:OH are the OH^- , O^- , and H_2O^- centers. From reaction I-8 it is seen that after warming to above 250 K, the species present are OH^- , O^- , H_2O_i and F centers. It was already established that there is no interaction between OH^- and F centers⁴⁵. Since the water molecule has a quasi-neon electronic structure it was likewise not expected to interact significantly with the F center.

The O^- center, however, has a $2s^2 2p^5$ electronic structure and it was considered that an interaction between the unpaired O^- 2p electron and the F center electron could lead to a state wherein the electron spins were align antiparallel to one another. This spin alignment would, of course, be diamagnetic and not yield any EPR signal.

The hypothesis was thought to be strengthened by the discovery of the FU_2 center and the "perturbed" F center⁴⁹. The "perturbed" F center was reported to be an F center perturbed by a U_2 center several lattice constants away. The main feature of the perturbed F band is a half width that is broadened to 0.24 eV. Unfortunately, no EPR spectroscopy was done on the FU_2 system.

Additionally, the reported discovery of the Y center^{47,48} seemed to indicate that F and O^- centers could exist in close proximity without immediately reacting to form an oxide-alpha pair. Apparently, no EPR spectroscopy was attempted on the Y center system, either.

Proceeding with the hypothesis that the F center is perturbed by an O^- center at some distance, several decisions must be made. First, a mean F to O^- distance must be estimated in order to decide what range of separate ions should be considered. Then appropriate electronic wave functions must be chosen. Finally, the type of interactions to investigate must be decided.

A. ESTIMATION OF MEAN F TO O^- DISTANCE

The mean F to O^- separation in the samples studied can be estimated in a fairly straightforward fashion. The hydroxide dopant in the crystal is present in a concentration of approximately 10^{-3} mole fraction. This means that one anion site in every thousand is occupied by a hydroxide ion. If the hydroxide ions were evenly distributed in the lattice, a cube of volume containing one thousand anion sites would contain one hydroxide ion. The edge length of such a cube is ten anion to anion distances, or $10\sqrt{2}$ lattice constants, about 44 angstroms. Thus, if the hydroxide ions were evenly spaced, the hydroxide to hydroxide separation would be about fourteen lattice constants. Since, in reality, the hydroxide ions are randomly situated, fourteen lattice constants can be taken to be the mean distance between two neighboring hydroxide ions.

From reactions I-6 and I-7, when a hydroxide ion is dissociated by ultraviolet light it forms a U_2 center and an O^- center. The U_2 center then migrates randomly through the crystal until it is trapped by an O^- center to reform a hydroxide ion, or by a hydroxide ion to form an H_2O^- center. Since all three centers are electrically neutral

with respect to the crystal environment, there is no coulombic attraction or repulsion between the U_2 center and the O^- or OH^- center. Because of this, the probability of the U_2 center being trapped by either the O^- or OH^- center is approximately equal.

It has been determined that only about ten percent of the hydroxide ions are dissociated by ultraviolet irradiation⁴⁰. Of the U_2 centers produced, only 25 to 50 percent react further to form H_2O^- centers. From this data, one may make several assumptions. First, since only a small percentage of the hydroxide ions are dissociated, the resultant O^- centers can be presumed to be effectively isolated from one another. Second, since only a fraction of the U_2 centers are trapped by hydroxide ions to form H_2O^- centers, the rest are presumably trapped by O^- centers to reform hydroxide ions. This is supported by optical data which indicates that when the crystal is warmed to 140 K, the U_2 center absorption disappears and the O^- absorption decreases, as can be seen in Figure III-6. Now, inasmuch as the O^- centers are presumed to be isolated from one another, the large fraction of U_2 centers that are trapped by O^- centers to reform hydroxide ions are most likely to do so at the lattice site from whence they came. Since a large fraction, 50 to 75 percent, of the U_2 centers recombine with O^- centers, and most probably do so at the original lattice site, one may conclude that most of the U_2 centers reside within a few lattice constants of the O^- center. That is, on the average, U_2 centers are distributed in the lattice so as to be closer to their "parent" O^- centers than to the nearest hydroxide ion.

Now, on warming the crystal the U_2 centers migrate through the lattice in a three-dimensional random walk. If we consider the probability that a U_2 center will migrate to a site within an arbitrary distance, R , we obtain a spherical probability distribution around the U_2 center. There is a finite probability that the U_2 center, during its random walk, will react with a center within a sphere of radius R around the original U_2 site. A hydroxide ion that, by random arrangement, lies closer to an O^- center than the mean O^- to OH^- distance will also, on the average, be closer to the U_2 center than hydroxide ions farther from the O^- . Therefore, hydroxide ions close to an O^- center will have a greater probability of capturing a U_2 center to form an H_2O^- center. From this we can see that the mean O^- to H_2O^- distance will be less than the mean hydroxide to hydroxide separation. Likewise, after warming the sample to above 250 K, the mean F to O^- distance will be somewhat less than fourteen lattice constants.

Having estimated that the mean F to O^- separation is less than fourteen lattice constants, a range of distances may be chosen over which to investigate a possible F- O^- interaction. The minimum separation is $\sqrt{2}$ lattice constants, 4.44 angstroms, at which distance the two centers occupy adjacent anion sites. The maximum distance considered was twenty lattice constants, about 63 angstroms. At such a large separation, any direct interaction between the F and O^- centers would be expected to be vanishingly small.

B. CHOICE OF APPROXIMATE ELECTRONIC WAVE FUNCTIONS

In order to arrive at a reasonable approximation of the extent of an interaction between the F and O^- centers, approximate electronic wave functions must be chosen. These wave functions will then serve as a basis set for approximate quantum mechanical calculations. As a first approximation, Slater-type orbitals^{66,67} were chosen for the F and O^- center electronic wave functions. Slater orbitals are widely accepted as a basis set for approximate calculations and computer programs employing them are readily available.

For the F center, the wave function designated as type I by Gourary and Adrian⁵⁵ was chosen. The type I function approximates the F center electronic function as a 1s Slater-type orbital of the form

$$\psi_F = (\xi_F/\pi)^{1/2} \exp(-\xi_F r) \quad [V-1]$$

The orbital exponent, ξ_F , was determined as a variational parameter. In potassium chloride, Gourary and Adrian found ξ_F to be approximately equal to 0.39 when atomic units were employed.

For the O^- center, the wave function employed was a suitable linear combination of Slater orbitals formed from a valence basis set. That is, the 2s, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals were used in the calculations. The computations discussed in the following sections indicated that the unpaired electron on the O^- center was essentially a $2p_z$ oxygen Slater orbital represented by

$$\psi_O = \left(\frac{1}{\pi}\right)^{1/2} \xi_O^{5/2} r \exp(-\xi_O r) \cos\theta \quad [V-2]$$

The $2p_z$ orbital was employed as an approximate wave function for the unpaired O^- electron in the calculation of exchange integrals, discussed in a following section.

The orbital exponent, ξ_0 , of the $2p_z$ electron of the O^- ion was determined to be approximately 1.4. This value for ξ_0 was chosen by assuming that the radial expectation value, $\langle r \rangle$, was approximately equal to the radius of the lattice site occupied by the O^- ion, about 1.8 angstroms. This is not very different from the crystal radius of the O^- ion, 1.76 angstroms⁶⁸. Solving the equation

$$\langle \psi_0 / r / \psi_0 \rangle = 1.8 \text{ \AA}$$

for ξ_0 yielded a value of 1.4. As a check, the equation

$$\langle \psi_0 / r^2 / \psi_0 \rangle = (1.8 \text{ \AA})^2$$

was also solved for ξ_0 and also gave a value very close to 1.4. The rules given by Slater⁶⁷ for determining orbital exponents as a result of the screening of nuclear charge by other electrons in the atom give the value $\xi_0 = 2.1$. This value is for an O^- ion in vacuum, however, and if the Madelung potential of the potassium chloride lattice is considered, $\xi_0 = 1.4$ appears to be a good choice for a starting approximation.

It should be noted once again that the functions given for ψ_F and ψ_0 are only first approximations. They are not intended to be taken as accurate wave functions, but rather as a starting point which will yield an indication of the magnitude of an $F-O^-$ interaction.

C. APPROXIMATE QUANTUM MECHANICAL CALCULATIONS

The F center wave function is diffuse, spread out over several lattice constants around the central vacancy. It seemed possible that there could be a significant interaction between the F and O^- centers, even though they are separated by several lattice constants. Experimental evidence has been reported that there is significant exchange interaction between F centers several lattice constants apart¹⁹. Based on the hypothesis of a long range F- O^- interaction, two types of interaction were investigated.

Approximate molecular orbital calculations were performed to investigate the possibility of a weak, long range "bond" forming between the centers. An F- O^- molecule should be isoelectronic with the hydroxide ion and the hydrogen fluoride molecule. If an appreciable amount of molecular orbital formation was shown to be possible over the relatively large distances, that would be evidence that the F and O^- centers might exist as a loose diamagnetic molecule-complex in the crystal. Additionally, it was considered that the molecular orbital calculations would yield information about the choice of electronic wave functions.

Exchange calculations were done to determine the magnitude of such an interaction between the unpaired electrons on the F and O^- centers. If the exchange energy was found to be of significant magnitude, arguments could be presented to explain the lack of F center EPR in crystals containing O^- centers.

1. Molecular orbital calculations

Calculations were performed using the complete neglect of differential overlap (CNDO) method. The crystal environment was approximated as a continuous dielectric medium in which the centers were embedded. The CNDO calculations were done using a computer program detailed by Pople and Beveridge⁶⁷, altered slightly to introduce the F center wave function and the approximation of the crystal as a dielectric medium. Computations were performed on the Oregon State University CYBER computer.

The program employed a valence basis set of Slater orbitals in the calculation of molecular orbitals. That is, the 1s orbital is used for hydrogen, the 2s and 2p orbitals for oxygen and so forth. The only difference between the 1s hydrogen orbital and the type I F center orbital given in equation V-1 is the value of the orbital exponent. Since the 1s orbital would not be used as part of the oxygen atom basis set, it was a simple matter to substitute the value of ξ_F for the orbital exponent of the hydrogen atom. Likewise, the value of ξ_0 in the crystal was substituted for the orbital exponent of an oxygen atom in vacuum.

To introduce the approximation of the crystal as a dielectric medium, a dielectric constant was inserted into the potential energy operator terms of the Hamiltonian operator. The potential energy terms concerning coulombic forces on an electron are inversely proportional to r , the distance from an electron to another charged particle. If the coulombic forces are considered to be acting through

a dielectric continuum, then the potential energy terms are divided by the dielectric constant of the medium. This gives terms of the form

$$V \propto 1/\epsilon r \quad [V-3]$$

where ϵ is the dielectric constant and the operator V includes both attractive and repulsive terms. The high frequency dielectric constant of potassium chloride, $\epsilon = 2.22$, was chosen over the static dielectric constant on the basis of arguments given by Knox and Teegarden⁶⁹.

When the above changes had been made, it became possible to run the program for a variety of F and O^- distances. Calculations were performed for F and O^- separations varying from twenty lattice constants (62.8 angstroms) to $\sqrt{2}$ lattice constants (4.44 angstroms). The results of the computations were the eigenvalues and eigenvectors of molecular orbitals formed between the F and O^- centers over the range of distances.

The eigenvalues and eigenvectors obtained from the calculations are presented in Table V-1. Results are given for F to O^- separations of $\sqrt{18}$ lattice constants (13.3 angstroms) and less. At distances greater than $\sqrt{18}$ lattice constants the calculations indicated that the F and O^- centers exist as isolated species, with no interaction between the two. Unfortunately, the CNDO program apparently did not allow for configurations in which there were unpaired electrons. For F to O^- distances larger than $\sqrt{18}$ lattice constants, the results

TABLE V-1. RESULTS OF CNDO MOLECULAR ORBITAL CALCULATIONS.

$R = \sqrt{18}$ lattice constants - 13.3 Angstroms

| Eigenvectors ^a | Eigenvalues ^b |
|----------------------------------|--------------------------|
| 1 $\sigma = 2s$ | $e_1 = -1.3060$ |
| 1 $\pi = 0.0001 \ 2p_x + 2p_y$ | $e_2 = -0.7083$ |
| 2 $\pi = 2p_x + 0.0001 \ 2p_y$ | $e_3 = -0.7083$ |
| 2 $\sigma = -0.0001 \ 2p_z + 1s$ | $e_4 = 0.0017$ |
| 3 $\sigma = -2p_z - 0.0001 \ 1s$ | $e_5 = 0.1181$ |

$R = 4$ lattice constants = 12.6 Angstroms

| Eigenvectors ^a | Eigenvalues ^b |
|----------------------------------|--------------------------|
| 1 $\sigma = 2s$ | $e_1 = -1.3042$ |
| 1 $\pi = 0.0001 \ 2p_x + 2p_y$ | $e_2 = -0.7059$ |
| 2 $\pi = -2p_x + 0.0001 \ 2p_y$ | $e_3 = -0.7059$ |
| 2 $\sigma = -0.0002 \ 2p_z + 1s$ | $e_4 = 0.0017$ |
| 3 $\sigma = -2p_z - 0.0002 \ 1s$ | $e_5 = 0.1205$ |

$R = \sqrt{12}$ lattice constants = 10.9 Angstroms

| Eigenvectors ^a | Eigenvalues ^b |
|----------------------------------|--------------------------|
| 1 $\sigma = 2s + 0.0001 \ 1s$ | $e_1 = -1.2977$ |
| 1 $\pi = 0.0005 \ 2p_x + 2p_y$ | $e_2 = -0.6994$ |
| 2 $\pi = 2p_x + 0.0005 \ 2p_y$ | $e_3 = -0.6994$ |
| 2 $\sigma = -0.0005 \ 2p_z + 1s$ | $e_4 = 0.0017$ |
| 3 $\sigma = -2p_z - 0.0005 \ 1s$ | $e_5 = 0.1270$ |

$R = \sqrt{8}$ lattice constants = 8.9 Angstroms

| Eigenvectors ^a | Eigenvalues ^b |
|--|--------------------------|
| 1 $\sigma = 2s + 0.0004 \ 1s$ | $e_1 = -1.2868$ |
| 1 $\pi = -0.0014 \ 2p_x + 2p_y$ | $e_2 = -0.6885$ |
| 2 $\pi = -2p_x - 0.0014 \ 2p_y$ | $e_3 = -0.6885$ |
| 2 $\sigma = -0.0004 \ 2s + 0.0021 \ 2p_z + 1s$ | $e_4 = 0.0017$ |
| 3 $\sigma = -2p_z - 0.0021 \ 1s$ | $e_5 = 0.1380$ |

$R = \sqrt{6}$ lattice constants = 7.7 Angstroms

| Eigenvectors ^a | Eigenvalues ^b |
|--|--------------------------|
| 1 $\sigma = 2s + 0.0009 \ 1s$ | $e_1 = -1.2775$ |
| 1 $\pi = -0.9763 \ 2p_x + 0.2163 \ 2p_y$ | $e_2 = -0.6792$ |
| 2 $\pi = 0.2163 \ 2p_x + 0.9763 \ 2p_y$ | $e_3 = -0.6792$ |
| 2 $\sigma = -0.0055 \ 2p_z + 1s$ | $e_4 = 0.0017$ |
| 3 $\sigma = -2p_z - 0.0055 \ 1s$ | $e_5 = 0.1472$ |

TABLE V-1. RESULTS OF CNDO MOLECULAR ORBITAL CALCULATIONS(Continued).

| R = 2 lattice constants = 6.28 Angstroms | |
|---|--------------------------|
| Eigenvectors ^a | Eigenvalues ^b |
| 1 $\sigma = 2s + 0.0027 \ 1s$ | $e_1 = -1.2618$ |
| 1 $\pi = -2p_x + 0.0016 \ 2p_y$ | $e_2 = -0.6635$ |
| 2 $\pi = 0.0016 \ 2p_x + 2p_y$ | $e_3 = -0.6635$ |
| 2 $\sigma = -0.0027 \ 2s - 0.0165 \ 2p_z + 0.999 \ 1s$ | $e_4 = 0.0016$ |
| 3 $\sigma = 0.0001 \ 2s - 0.9999 \ 2p_z - 0.0165 \ 1s$ | $e_5 = 0.1628$ |
| R = $\sqrt{2}$ lattice constants = 4.44 Angstroms | |
| Eigenvectors ^a | Eigenvalues ^b |
| 1 $\sigma = 0.9999 \ 2s + 0.0006 \ 2p_z + 0.0105 \ 1s$ | $e_1 = -1.2229$ |
| 1 $\pi = 0.9990 \ 2p_x - 0.0449 \ 2p_y$ | $e_2 = -0.6245$ |
| 2 $\pi = 0.0449 \ 2p_x + 0.9990 \ 2p_y$ | $e_3 = -0.6245$ |
| 2 $\sigma = -0.0104 \ 2s - 0.0613 \ 2p_z + 0.9981 \ 1s$ | $e_4 = 0.0011$ |
| 3 $\sigma = 0.0013 \ 2s - 0.9981 \ 2p_z - 0.0613 \ 1s$ | $e_5 = 0.1997$ |

^a $2s$, $2p_x$, $2p_y$, $2p_z$ signify the valence orbitals of the oxygen atom

^b eigenvalues are in units of Hartrees. 1 Hartree = 27.21 eV

indicated that the two electrons were localized on the F center site and six were localized on the oxygen site. This yielded the unacceptable situation in which an F' center and a neutral substitutional oxygen atom are the ground state of the system.

From the calculated orbital energies of a loose $F-O^-$ 'molecule', the electronic configuration is $1\sigma^2 1\pi^4 2\sigma^2$. However, from the coefficients of the Slater orbitals making up the molecular orbitals, it is evident that the orbitals are virtually identical to single atomic orbitals with only a minute amount of other orbitals mixed in, even at the minimum separation. The 1σ and 3σ molecular orbitals are essentially 2s and $2p_x$ atomic oxygen orbitals, respectively, and the 2σ molecular orbital is virtually identical to the 1s F center orbital. These results were useful, however, in justifying some of the approximations made in the following section.

The CNDO calculations give a picture of the $F-O^-$ system that is far from correct. However, that the calculations showed any amount of interaction at all between the centers was somewhat encouraging, considering the approximations used and the shortcomings of the CNDO method as it was interpreted in the program.

2. Exchange calculations

Calculations were performed to determine the amount of exchange interaction between the unpaired electrons of the F and O^- centers. As noted previously, experimental evidence for a significant exchange energy between F centers separated by several lattice constants¹⁹ led to the hypothesis that an exchange interaction between the F and O^-

centers might cause a spontaneous coupling of the unpaired electrons. If the calculated exchange energy was sufficiently large and negative it would indicate that the electron spins were aligned antiparallel to one another. This would lead to a diamagnetic $F-O^-$ complex by a mechanism similar to that of antiferromagnetism. Additionally, it was considered that superexchange, or indirect exchange, might play a part in the lack of EPR of the F center. The theory of these types of exchange coupling is described in several works⁷⁰⁻⁷³. A brief summary of the theory, its approximations and methods will be presented.

In the approximation used here only the interaction between the unpaired electrons is considered. Thus the problem is one of finding the exchange energy of a two electron system. For the purposes of discussion, the F center may be considered to be an atom, with the potential well created by the anion vacancy equivalent to its nucleus.

a. Summary of exchange coupling theory

Two methods useful in calculating an exchange interaction are the molecular orbital approximation and the Heitler-London approximation. These methods differ in the construction of ground state one electron wave functions and the way the Hamiltonian operator is subdivided in treating different aspects of the electronic energy.

The Hamiltonian operator for a two electron system can be written as

$$H = \frac{1}{2} \nabla_1^2 + \frac{1}{2} \nabla_2^2 + \frac{1}{r_{12}} - \left(\frac{1}{r_{F1}} + \frac{1}{r_{O2}} \right) - \left(\frac{1}{r_{F2}} + \frac{1}{r_{O1}} \right)$$

where the subscripts denote the part of the system on which a term operates. That is, r_{12} denotes the distance between electrons one and

two, r_{F2} denotes the distance from electron two to the F center and so forth. The Hamiltonian can then be subdivided into one electron and two electron parts.

$$H = H_1 + H_2 + H_{12} \quad [V-4]$$

where H_1 and H_2 depend only on the spatial coordinates of electrons one and two respectively. The two electron terms, H_{12} , is treated as a perturbation which contains the interelectronic repulsion term, $1/r_{12}$, and terms in r_1 and r_2 sufficient to make H_{12} small compared to H_1 and H_2 . The exact form of H_{12} depends on the viewpoint of the particular approximation being used.

In the molecular orbital approximation, an electron is not thought of as having a definite affinity for a single nucleus. It may move equally around all the nuclei and be affected equally by all of them. The coulombic repulsion between electrons is treated as a small perturbation between electrons, the two electron Hamiltonian being

$$H_{12} = 1/r_{12} \quad [V-5]$$

The electron wave functions are delocalized over the entire molecule, and since the electrons are assumed to move freely about the molecule, the correlation of motion arising from interelectronic repulsion is under emphasized.

The Heitler-London approximation, on the other hand, treats electron repulsion as very important, and assumes that the electrons tend to spend most of their time at opposite ends of the molecule.

In this case, each one electron wave function is considered to be essentially localized upon one of the nuclei. Thus the secondary perturbation is taken to be an interaction between atoms rather than between electrons. The two electron Hamiltonian then becomes

$$H_{12} = 1/r_{12} \sim (1/r_{F2} + 1/r_{O1}) \quad [V-6]$$

Treating the unperturbed states as noninteracting atoms on which the electrons are localized introduces a large degree of correlation, and thus over emphasizes the coulombic repulsion between electrons.

In the case of an $F-O^-$ interaction, the Heitler-London approach was well suited as an approximation on which to base calculations. The F and O^- centers are separated by relatively large distances, on an atomic scale. The results of the CNDO calculations given in Table IV-1 indicate that each electron is indeed essentially localized on one nucleus. The degree of delocalization is small, as can be seen from the amount of mixing between the oxygen orbitals and the F center orbital. This allows us to approximate the F center wave function as the 1s orbital given by equation V-1. Also, since the orbital which would be occupied by the O^- electron is almost a pure $2p_z$ function, the wave function for this center is approximated as the 2p orbital given in equation V-2.

From these one electron functions, two electron product wave functions, ϕ , can be written to satisfy the approximate two electron Schroedinger equation

$$(H_1 + H_2) \phi = (E_1 + E_2) \phi \quad [V-7]$$

where E_1 and E_2 are the unperturbed one electron orbital energies. When properly symmetrized, the product wave functions form spatial functions of the form

$$\varnothing_+ = N_+ [\psi_F(r_1)\psi_0(r_2) + \psi_F(r_2)\psi_0(r_1)] \quad [V-8]$$

$$\varnothing_- = N_- [\psi_F(r_1)\psi_0(r_2) - \psi_F(r_2)\psi_0(r_1)]$$

The function \varnothing_+ is a symmetric spatial function, \varnothing_- an antisymmetric function, and r_1 and r_2 are the coordinates of electrons one and two respectively. From the results of calculations performed for the $F-0^-$ system, N_+ and N_- differed negligibly from $1/\sqrt{2}$. These spatial functions are then multiplied by the spin functions of the electrons to obtain the total wave function of the system.

Now, only certain combinations of spatial and spin functions are allowed because the total wave function of the system must be antisymmetric. That is, \varnothing_+ must be multiplied by an antisymmetric spin function and \varnothing_- must be multiplied by a symmetric function to produce a properly antisymmetrized total wave function. Employing the standard notations of α and β for spin up and spin down functions, the allowed combinations are

$$\varnothing_+[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

$$\varnothing_- \alpha(1)\alpha(2), \varnothing_- \beta(1)\beta(2), \varnothing_- [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

Thus the symmetric spatial function, when multiplied by the one antisymmetric spin function, gives rise to the singlet state, wherein the electron spins are aligned antiparallel. The antisymmetric spatial

function can be multiplied by any of the three symmetric spin functions, giving rise to the triplet state.

The difference in energy between the states is a result of the perturbation represented by the Hamiltonian H_{12} given in equation V-6. In the unperturbed ground state the atoms are assumed to be non-interacting species with a random orientation of the spins of the unpaired electrons. The perturbation brings about an increase or decrease in the ground state energy depending on the nature of the spatial wave function, and therefore on the direction of spin alignment. This perturbation energy can be found from the equation for the expectation value of H_{12} ,

$$\langle \phi / H_{12} / \phi \rangle = E_{12} \quad [V-9]$$

If the functions for ϕ_+ and ϕ_- from equation V-8 are used, we find

$$E_{12} = 2N_{\pm}^2 (Q \pm J) \quad [V-10]$$

where the sign alternative indicates the perturbation energy of the singlet or triplet state. Q and J are the well known coulomb and exchange integrals

$$Q = \iint \psi_F(r_1) \psi_O(r_2) H_{12} \psi_F(r_1) \psi_O(r_2) d\tau_1 d\tau_2 \quad [V-11]$$

$$J = \iint \psi_F(r_1) \psi_O(r_2) H_{12} \psi_F(r_2) \psi_O(r_1) d\tau_1 d\tau_2 \quad [V-12]$$

Since the normalization constants were both almost equal to $1/\sqrt{2}$, equation V-10 reduces to

$$E_{12} = (Q \pm J) \quad [V-13]$$

from which we see that the energy difference between the triplet and the singlet state is

$$E = E_{\text{singlet}} - E_{\text{triplet}} = 2J \quad [\text{V-14}]$$

From this relation one can also determine which state is lower in energy. If

$$J < 0, E_{\text{singlet}} < E_{\text{triplet}}; J > 0, E_{\text{singlet}} > E_{\text{triplet}} \quad [\text{V-15}]$$

so that the sign of the exchange integral J indicates whether the singlet or triplet state is the ground state.

The problem now is one of determining the value of the exchange integral shown in equation V-12. Recalling the form of H_{12} from equation V-6, all of the terms are inversely proportional to distance. As was done for relation V-3, the approximation of the potassium chloride host lattice as a dielectric continuum can be introduced by dividing terms in $1/r$ by the dielectric constant, $\epsilon = 2.22$. The dielectric constant may be factored out of H_{12} as a constant divisor and then factored out of the exchange integral J so that

$$J_{\text{crystal}} = J_{\text{vacuum}} / 2.22 \quad [\text{V-16}]$$

This approximation has been used previously in the calculation of exchange energies between F center pairs¹⁹. Combining equations V-6 and V-12, we finally obtain

$$J = \iint \psi_F(r_1) \psi_O(r_2) \frac{1}{r_{12}} \psi_F(r_2) \psi_O(r_1) d\tau_1 d\tau_2 - \iint \psi_F(r_1) 1/r_{O1} \psi_O(r_1) d\tau_1 - \alpha \iint \psi_F(r_2) 1/r_{F2} \psi_O(r_2) d\tau_2 \quad [\text{V-17}]$$

as the final form of the exchange integral which must be evaluated.

The symbol α denotes the overlap integral, defined as

$$\alpha = \int \psi_F(r) \psi_O(r) d\tau \quad [\text{V-18}]$$

The exchange integral represented by equation V-17 will yield information on the state of the $F-0^-$ system. From the sign of the calculated value of J we can determine whether the singlet or triplet state is the ground state. The magnitude of the exchange energy will allow us to determine whether or not a spontaneous alignment of electron spins occurs at the temperature at which the EPR was measured. A comparison of the exchange energy, J , and the thermal energy, kT , will show the temperature where thermal agitation will be sufficient to destroy the alignment of the electrons caused by the exchange interaction^{70,72}. This temperature would be interpreted to be similar to the Néel temperature in antiferromagnetic materials. If J was determined to be larger than kT over the temperature range studied, it would mean that the exchange interaction does result in a spontaneous ordering of the electron spins in the $F-0^-$ system. Conversely, if J was much less than kT , thermal agitation would destroy any alignment of electron spins.

It should be kept in mind that the approximations employed mean that the calculated value of J will not be an exact result. The values are intended only to supply an estimate of the spin dependent energy from which qualitative conclusions may be made.

b. Calculations of the exchange energy of the $F-0^-$ system

The integrals making up equation V-17 were evaluated on the Oregon State University CYBER computer using programs supplied by the Quantum Chemistry Program Exchange^{74,75}. The program for evaluation of the interelectronic repulsion integral followed the method of Rudenberg⁷⁶. The program to evaluate the overlap and attractive

potential integrals followed the Roothaan method⁷⁷. These programs employ Slater orbitals as a basis set and allowed the variation of the orbital exponents of the chosen functions as well as the center to center distance.

The results of calculations using the initial choices of orbital exponents are presented in Table V-2. The sign of J is positive, which indicates that the triplet state is the ground state. However, the magnitude of the exchange energies are not significantly different from zero when compared with the thermal energy. At 77 K, the temperature at which the EPR was measured, $kT = 6.6 \times 10^{-3}$ eV. This is an order of magnitude greater than the largest calculated value of the spin dependent energy. Any alignment of electron spins would be obliterated by thermal agitation at 77 K and the spins would be randomly oriented. It therefore seems that an exchange interaction does not contribute to the lack of EPR in the system.

Further calculations for the $F-O^-$ system were performed by substituting a variety of orbital exponents into the wave functions. A center to center distance of two lattice constants was chosen, which would have the two centers separated by a single potassium ion. The results are given in Table V-3 and Figure V-1. It is evident from these results that for most combinations of orbital exponents the exchange energy is small compared to the thermal energy. Only for small orbital exponents did the exchange energy approach the magnitude of the thermal energy at 77 K. Exponents smaller than the original choices were deemed to be unrealistic as they would allow too large

TABLE V-2. CALCULATION OF EXCHANGE ENERGY BETWEEN F AND O⁻ CENTERS. Column I indicates the separation between centers, lattice constants. Column II shows the calculated value of interelectronic repulsion energy integral,

$$\iint \psi_F(r_1) \psi_O(r_2) 1/r_{12} \psi_F(r_2) \psi_O(r_1) d\tau_1 d\tau_2 ,$$

atomic units. Column III shows the calculated value of the product of the overlap integral and the sum of the attractive potential integrals,

$$\alpha \int \psi_F(r_1) 1/r_{O1} \psi_O(r_1) d\tau_1 + \alpha \int \psi_F(r_2) 1/r_{F2} \psi_O(r_2) d\tau_2 ,$$

atomic units. Column IV indicates the calculated value of the total exchange integral, equation IV-18, atomic units. The calculated value of singlet to triplet transition energy, $2J_{\text{crystal}}$, in electron volts is listed in Column V.

| I | II | III | IV | V |
|-------------|--------------------------|--------------------------|--------------------------|------------------------|
| $\sqrt{2}$ | 1.3562×10^{-3} | 1.3551×10^{-3} | 1.1748×10^{-6} | 2.88×10^{-5} |
| 2 | 1.0350×10^{-4} | 9.2448×10^{-5} | 1.1049×10^{-5} | 2.70×10^{-4} |
| $\sqrt{6}$ | 1.3447×10^{-5} | 1.1545×10^{-5} | 1.9019×10^{-6} | 4.66×10^{-5} |
| $\sqrt{8}$ | 2.3980×10^{-6} | 2.0022×10^{-6} | 3.9580×10^{-7} | 9.70×10^{-6} |
| $\sqrt{12}$ | 1.3802×10^{-7} | 1.0572×10^{-7} | 2.5101×10^{-8} | 6.16×10^{-7} |
| 4 | 1.1250×10^{-8} | 9.0572×10^{-9} | 2.1927×10^{-9} | 5.38×10^{-8} |
| $\sqrt{18}$ | 3.6994×10^{-9} | 2.9114×10^{-9} | 7.8799×10^{-10} | 1.93×10^{-8} |
| $\sqrt{22}$ | 4.7348×10^{-10} | 3.6838×10^{-10} | 1.0510×10^{-10} | 2.58×10^{-9} |
| $\sqrt{26}$ | 7.2310×10^{-11} | 5.5756×10^{-11} | 1.6554×10^{-11} | 4.06×10^{-10} |
| $\sqrt{32}$ | 5.5854×10^{-12} | 4.2619×10^{-12} | 1.3235×10^{-12} | 3.24×10^{-11} |
| 6 | 1.1519×10^{-12} | 8.9447×10^{-13} | 2.5643×10^{-13} | 6.28×10^{-12} |
| $\sqrt{46}$ | 3.1494×10^{-14} | 2.3611×10^{-14} | 7.8829×10^{-15} | 1.93×10^{-13} |
| 8 | 1.1679×10^{-16} | 8.8139×10^{-17} | 2.8652×10^{-17} | 7.02×10^{-16} |

TABLE V-3. RESULTS OF CALCULATIONS OF SINGLET TO TRIPLET TRANSITION ENERGIES EMPLOYING VARYING ORBITAL EXPONENTS OF THE F AND O^- CENTERS. Center to center separation is 2 lattice constants. The F center orbital exponent is listed in Column I. Column II shows the O^- center orbital exponent. The calculated value of the interelectronic repulsion integral,

$$\iint \psi_F(r_1) \psi_O(r_2) \frac{1}{r_{12}} \psi_F(r_2) \psi_O(r_1) d\tau_1 d\tau_2$$

in atomic units is given in Column III. Column IV shows the calculated value of the product of the overlap integral and the sum of the attractive potential integrals,

$$\alpha \int \psi_F(r_1) \frac{1}{r_{O1}} \psi_O(r_1) d\tau_1 + \alpha \int \psi_F(r_2) \frac{1}{r_{F2}} \psi_O(r_2) d\tau_2$$

using atomic units. The calculated value of the total exchange integral in atomic units is given in Column V. Column VI lists the calculated value of singlet to triplet transition energy $2J_{\text{crystal}}$, in electron volts.

| I | II | III | IV | V | VI |
|-----|-----|-------------------------|-------------------------|--------------------------|------------------------|
| 0.6 | 2.1 | 1.2505×10^{-6} | 1.0538×10^{-6} | 1.9676×10^{-7} | 4.82×10^{-6} |
| 0.6 | 1.7 | 3.0592×10^{-6} | 3.0063×10^{-6} | 5.2924×10^{-8} | 1.30×10^{-6} |
| 0.6 | 1.4 | 7.7174×10^{-6} | 8.5934×10^{-6} | -8.7594×10^{-7} | -2.14×10^{-5} |
| 0.6 | 1.2 | 1.7468×10^{-5} | 2.1419×10^{-5} | -3.9509×10^{-6} | -9.68×10^{-5} |
| 0.5 | 2.1 | 5.5103×10^{-6} | 4.1441×10^{-6} | 1.3662×10^{-6} | 3.14×10^{-5} |
| 0.5 | 1.7 | 1.2241×10^{-5} | 1.1032×10^{-5} | 1.2091×10^{-6} | 2.96×10^{-5} |
| 0.5 | 1.4 | 2.7524×10^{-5} | 2.8497×10^{-5} | -9.7313×10^{-7} | -2.38×10^{-5} |
| 0.5 | 1.2 | 5.5548×10^{-5} | 6.4735×10^{-5} | -9.1877×10^{-6} | -2.27×10^{-5} |
| 0.4 | 2.1 | 2.1890×10^{-5} | 1.3358×10^{-5} | 8.5318×10^{-6} | 2.10×10^{-4} |
| 0.4 | 1.7 | 4.4294×10^{-5} | 3.4093×10^{-5} | 1.0201×10^{-5} | 2.50×10^{-4} |
| 0.4 | 1.4 | 8.9914×10^{-5} | 8.2524×10^{-5} | 7.3899×10^{-6} | 1.81×10^{-4} |
| 0.4 | 1.2 | 1.6462×10^{-4} | 1.7361×10^{-4} | -8.9848×10^{-6} | -2.20×10^{-4} |
| 0.3 | 2.1 | 7.3722×10^{-5} | 3.2251×10^{-5} | 4.1471×10^{-5} | 1.02×10^{-3} |
| 0.3 | 1.7 | 1.3601×10^{-4} | 7.9679×10^{-5} | 5.6330×10^{-5} | 1.38×10^{-3} |
| 0.3 | 1.4 | 2.5009×10^{-4} | 1.8464×10^{-4} | 6.5454×10^{-5} | 1.60×10^{-3} |
| 0.3 | 1.2 | 4.1895×10^{-4} | 3.6864×10^{-4} | 5.0490×10^{-5} | 1.24×10^{-3} |
| 0.2 | 2.1 | 1.8306×10^{-4} | 4.4660×10^{-5} | 1.3840×10^{-4} | 3.40×10^{-3} |
| 0.2 | 1.7 | 3.0857×10^{-4} | 1.0839×10^{-4} | 2.0018×10^{-4} | 4.90×10^{-3} |
| 0.2 | 1.4 | 5.1378×10^{-4} | 2.4533×10^{-4} | 2.6847×10^{-4} | 6.58×10^{-3} |
| 0.2 | 1.2 | 7.8775×10^{-4} | 4.7474×10^{-4} | 3.1301×10^{-4} | 7.68×10^{-3} |

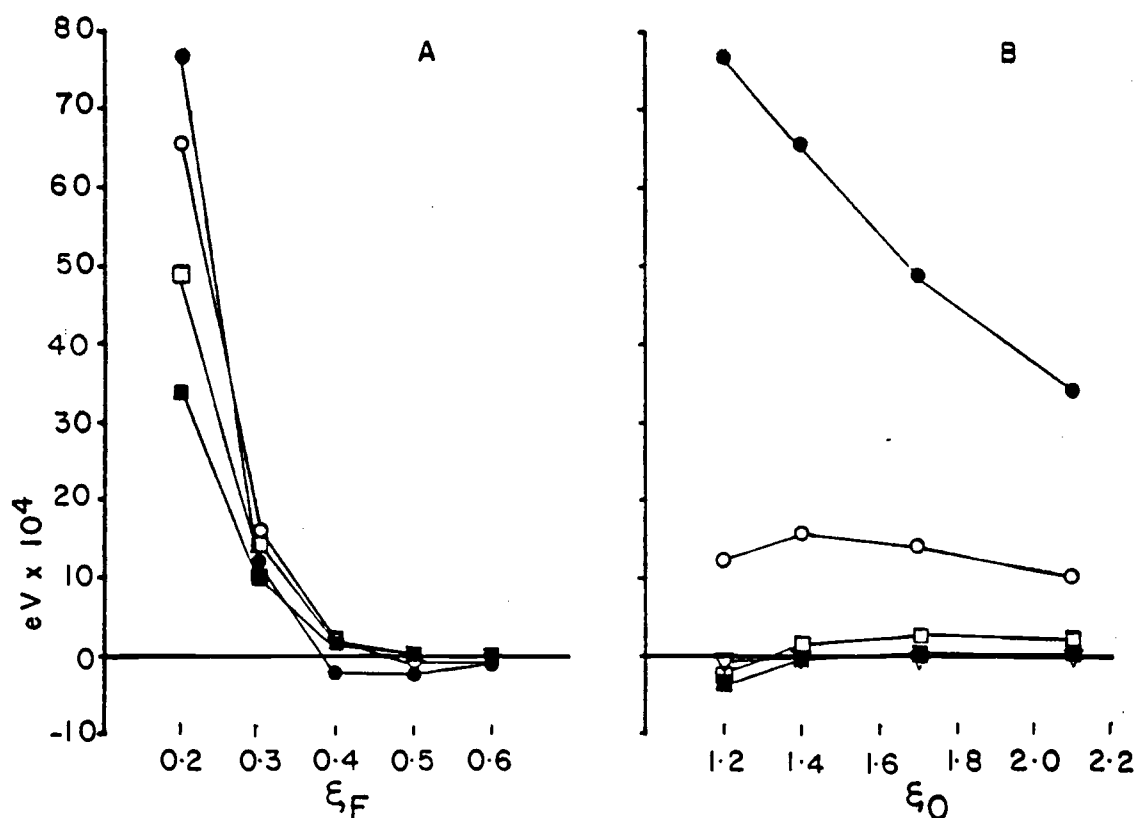


FIGURE V-I. CHANGE IN CALCULATED EXCHANGE ENERGY, J , BETWEEN THE F AND O^- CENTERS WITH VARIATIONS OF THE ORBITAL EXPONENTS. In Figure A, the change in J with ξ_F while ξ_0 remains constant is shown, with the solid circles representing $\xi_0 = 1.2$, the open circles $\xi_0 = 1.4$, the open squares $\xi_0 = 1.7$, and the solid squares $\xi_0 = 2.1$. In Figure B, the change in J with ξ_0 while holding ξ_F constant is shown with the solid circles representing $\xi_F = 0.2$, the open circles $\xi_F = 0.3$, the open squares $\xi_F = 0.6$. The exchange integral J , given in equation V-17 was calculated for the $F-O^-$ system using a variety of orbital exponents. In A is shown the change in J when ξ_F is varied and ξ_0 is held constant. B shows the change in J when ξ_0 is varied and ξ_F held constant.

a portion of the electronic charge to be found outside of the anion vacancy.

The initial choice of $\xi_F = 0.39$, for example, places about 90 percent of the F-electron's charge within the vacancy, which agrees with the calculations of Gourary and Adrian⁵⁵. Likewise, a ξ_0 smaller than 1.4 would give an O^- wave function more diffuse than is realistically probable based on the observed crystal radius⁶⁸.

Calculations to find the singlet to triplet transition energy of the M center were also done with a variety of F center orbital exponents. These were done to check the validity of the chosen F center wave functions. Results are shown in Table V-4. The initial choice of $\xi_F = 0.39$ gave a value fairly close to the estimated transition energy of about -0.4 eV ⁷⁸. This agreement implies that the approximations made yield energies that are close enough to the true values of J to make qualitative conclusions.

Direct exchange between the unpaired electrons of the F and O^- centers does not appear to be of sufficient magnitude to account for the lack of EPR in photochemically colored KCl:OH. It had been hoped that the exchange interaction would prove to be large enough to cause spontaneous alignment of the electron spins at least at the minimum F- O^- separation, $\sqrt{2}$ lattice constants, even if it were shown to be a small perturbation at large distances. If that had been the case, the theory of superexchange⁷⁹ would have been used to try to explain the lack of EPR of an F center in proximity to an O^- center.

TABLE V-4. RESULTS OF CALCULATION OF M CENTER SINGLET TO TRIPLET ENERGY FOR VARYING ORBITAL EXPONENTS OF F CENTER WAVE FUNCTION. Column I indicates the F center orbital exponent. The calculated value for the interelectronic repulsion integral, $\iint \psi_F(r_1) \psi_F(r_2) 1/r_{12} \psi_F(r_2) \psi_F(r_1) d\tau_1 d\tau_2$ in atomic units is in Column II. Column III shows the calculated value of the product of the overlap integral and the sum of the attractive potential integral, $2 \alpha \iint \psi_F(r_1) 1/r_F \psi_F(r_1) d\tau_1$, in atomic units. Column IV indicates the calculated value of the total exchange integral in atomic units. The calculated value of singlet to triplet transition energy, $2J_{\text{crystal}}$, in electron volts is listed in Column V.

| I | II | III | IV | V |
|------|-------------------------|-------------------------|--------------------------|--------|
| 0.50 | 5.7863×10^{-3} | 1.2674×10^{-2} | -6.8879×10^{-3} | -0.169 |
| 0.40 | 1.4559×10^{-2} | 3.3627×10^{-2} | -1.9068×10^{-2} | -0.468 |
| 0.39 | 1.6102×10^{-2} | 3.7455×10^{-2} | -2.1352×10^{-2} | -0.524 |
| 0.30 | 3.0934×10^{-2} | 7.6213×10^{-2} | -4.5279×10^{-2} | -1.11 |
| 0.20 | 5.0172×10^{-2} | 1.3398×10^{-1} | -8.3812×10^{-2} | -2.06 |

Calculations on the "wet" $F-O^-$ system would also have been done, using a wave function of the H_2O^- center given by Rusch and Seidel⁴⁰. This calculation would have been to determine if the H_2O molecule was a sufficient perturbation on the wave function of the electron to make the exchange energy of the $H_2O^-O^-$ system small when compared with the thermal energy.

VI. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A. CONCLUSIONS

The bleaching mechanism of the "wet" F center appears to be essentially the same as that of the F center at low temperature. The bleaching behavior of the H_2O^- center was found to be nearly identical to that of the F center, and no sign of other centers as "storage sites" of the photoelectrons was seen. The similarity between F and H_2O^- center behavior indicates that the embedded water molecule is indeed only a small perturbation on the state of the F center and thus the "wet" analogs of the F' and alpha centers are formed during bleaching at 77 K.

The difference in rate of bleaching of the H_2O^- center as measured by EPR and optical methods was not significant when compared to the disparity reported previously^{2,35}. When the bleaching rate measured from EPR data was corrected for errors caused by small amounts of impurities, the dissimilarity between the rates decreased to well within the limits of error. The rate of bleaching of the center causing optical absorption is the same as that of the center causing EPR. This leads to the conclusion that the same center causes both EPR and optical spectra.

The reason for the disappearance of the EPR signal when the transition from H_2O^- to F center takes place remains unknown. It is clear that the sudden fading of the EPR is definitely associated with the conversion of "wet" F to F centers. However, the hypothesis

as to why an apparently "normal" F center would yield no EPR was found to be in error. It had been proposed that an exchange interaction between the unpaired electrons of the F and O^- centers could be demonstrated to be a possible cause for the lack of F center EPR. Calculations of the extent of the interaction, however, have shown it to be inconsequential.

Had an exchange interaction proved to be a possible cause of the nonexistence of the EPR in the F- O^- system, a similar interaction would have been suggested to be responsible for the nonexistence of EPR in alkali halides colored at room temperature by x- or gamma-rays. The nature of the hole centers in crystals irradiatively colored at room temperature is not known and thus calculations on this system could not be done.

B. SUGGESTIONS FOR FURTHER WORK

Obviously, if the reason for the lack of the expected F center EPR is to be found, further investigation will be necessary. It was noted by Sander⁴² that what seemed to be a weak F center EPR signal appeared in crystals containing F and O^- centers at temperatures below 30 K. If this were confirmed, then EPR spectra of F centers in crystals containing O^- centers should be compared with those of "pure" F centers. Useful information obtained in this way might include deviations in the half-width and g value of the spectrum and relaxation times, T_1 and T_2 of the F center. A broadening or narrowing of the half-width could indicate a change in the hyperfine structure (HFS)

or an exchange coupling with another center. A shift in the g factor and the presence of anisotropy would also be valuable in determining any perturbation in the state of the F center.

If the F center in O^- -containing samples should prove to be paramagnetic at low temperature, then electron nuclear double resonance (ENDOR) would provide much more information than EPR. The ENDOR spectrum of the F center is well known and hyperfine interaction constants of the F center have been measured as far as the thirteenth shell of neighboring ions⁸⁰. Extensive ENDOR measurements have also been made on the H_2O^- center^{39,40}, but no investigation of the F centers produced by warming "wet" F centers has been done. It would certainly be of interest to determine the hyperfine interaction between the F center and the protons of the H_2O_i center.

Crystals doped with $O^{17}H^-$ would be of considerable value in an investigation of interactions between F centers and oxygen-containing centers. Hyperfine structure arising from the O^{17} nucleus ($I = 5/2$) would yield more information about the role of oxygen-containing centers than is possible from the nonmagnetic oxygen isotopes. Additionally, the relatively large, negative nuclear g values of O^{17} ($g = -0.76$) would set the O^{17} part of the ENDOR spectrum apart from that of the alkali and halide ions.

The ENDOR spectrum would be of particular interest. By finding the hyperfine interaction between centers, one might determine a range of distances between centers, or at least that the centers were effectively isolated from one another. In any case, one would hope

to find some indication of the nature of the perturbation which causes the F centers to exhibit no EPR.

BIBLIOGRAPHY

- 1 De Boer, J. H. 1937. Über die natur der farbzentren in alkali-halogenid kristallen. Recueil des Travaux Chimiques des Pays-Bas 56:301-309.
- 2 Papazian, H. A. 1971. On the electron spin resonance and color in KCl and KCl(OH). Canadian Journal of Physics 49:2202-2206.
3. Morato, S. P. 1973. Photodecomposition and reactions of hydroxyl ions and hydrogen defects in potassium chloride crystals. Ph.D. Thesis, University of Utah, Salt Lake City.
- 4 Markham, J. J. 1966. F Centers in Alkali Halides. Academic Press, New York.
- 5 Schulman, J. H., and W. D. Compton. 1962. Color Centers in Solids. The MacMillan Company, New York.
- 6 Hirai, M., and A. B. Scott. 1966. Formation of M centers from "stored" photoelectrons. The Journal of Chemical Physics 46: 2896-2904.
- 7 Paul, J. L., and A. B. Scott. 1972. The mechanism of F center aggregation. Physica Status Solidi (b) 52:581-590.
- 8 Scott, A. B., and L. P. Bupp. 1950. The equilibrium between F centers and higher aggregates in KCl. The Physical Review 79: 341-346.
- 9 Hutchison, C. A. 1949. Paramagnetic resonance absorption in crystals colored by irradiation. The Physical Review 75:1769-1772.
- 10 Hutchison, C. A., and G. A. Noble. 1952. Paramagnetic resonance absorption in additively colored crystals of alkali halides. The Physical Review 87:1125-1126.
- 11 Kittel, C., and E. Abrahams. 1953. Dipolar broadening of magnetic resonance lines in magnetically dilute crystals. The Physical Review 90:238-243.
- 12 Kip, A. F., C. Kittel, R. A. Levy, and A. M. Portis. 1953. Electronic structure of F centers: Hyperfine interactions in electron spin resonance. The Physical Review 91:1066-1071.
- 13 Portis, A. M. 1953. Electronic structure of F centers: Saturation of the electron spin resonance. The Physical Review 91: 1071-1078.

- 14 Kahn, A. H., and C. Kittel. 1953. F center wave functions and electronic g-values in KCl crystals. The Physical Review 89:315-320.
- 15 Cape, J. A. 1961. Photochemically produced color centers in KCl and KBr. The Physical Review 122:18-25.
- 16 Adrian, F. J. 1957. Electronic g-factor and the structure of F centers. The Physical Review 107:488-490.
- 17 Konitzer, J. D., and J. J. Markham. 1959. Experimental study of the shape of the F band absorption in KCl. Journal of the Physics and Chemistry of Solids 32:843-849.
- 18 Noble, G. A. 1960. Saturation and recovery of a portion of the electron spin resonance of F centers in KCl at 4° K. The Physical Review 118:1028-1034.
- 19 Schwoerer, M., and H. C. Wolf. 1963. Elektronen spin resonanz untersuchungen zur aggregation von F-zentren in KCl. Zeitschrift fur Physik 175:457-479.
- 20 Korth, K. 1935. Ultrarote absorption spektra photochemischen sensibilisierter alkalihalogenid kristallen. Akademie der Wissenschaften Gottingen. Mathematisch Physikalische Klasse. Nachrichten, neuefolge 2:221-227.
- 21 Akpinar, S. 1940. Uber den einbau chemisch definierter zusatze in alkalihalogenid kristallen. Annalen der Physik 37:429-441.
- 22 Fischer, F., and G. Gummer. 1966. Quantenausbeute fur den photochemischen abbau von O^{--} -zentren in KCl. Zeitschrift fur Physik 184:97-112.
- 23 Gummer, G. 1968. O^{--} -lucken-dipole in alkalihalogenid kristallen. Zeitschrift fur Physik 215:256-278.
- 24 Staible, T. F. 1972. The reaction between O^- and F centers. Masters Thesis, Oregon State University, Corvallis.
- 25 Etzel, H. W., and D. A. Patterson. 1958. Optical properties of alkali halides containing hydroxyl ions. The Physical Review 112:1112-1116.
- 26 Rolfe, J. 1958. Hydroxide absorption band in alkali halide crystals. Physical Review Letters 1:56-59.
- 27 Kurz, G. 1969. OH^- dissociation and U_2 decomposition in hydroxide-doped KCl and KBr crystals. Physica Status Solids 31:93-105.

- 28 Jacobs, P. W. M., and H. A. Papazian. 1962. Photochemical behavior of alkali halide crystals containing OH^- and SO_4^{2-} ions. The Physical Review 127:1567-1571.
- 29 Kerkhoff, F. 1960. Zum photochemischen verhalten sauerstoffhaltiger komplex in alkalihalogenid kristallen. Zeitschrift fur Physik 158:595-606.
- 30 Kerkhoff, F., W. Martienssen, and W. Sander. 1962. Elektronen spin-resonanz and photochemie des U_2 -zentrums in alkalihalogenid kristallen. Zeitschrift fur Physik 173:185-202.
- 31 Papazian, H. A. 1961. Color centers in the alkali metal azides. The Journal of the Physics and Chemistry of Solids 21:81-86.
- 32 Papazian, H. A. 1966. Color centers in alkali metal azides. The Journal of the Physics and Chemistry of Solids 27:906-907.
- 33 Papazian, H. A. 1968. On the Irradiation of alkali metal azides. The Journal of Physics and Chemistry of Solids 30:462-463.
- 34 Papazian, H. A. 1961. The optical F absorption band. Nature 192:1286-1287.
- 35 Moran, P. R., S. H. Christensen, and R. H. Silsbee. 1961. Electron spin resonance and optical absorption of electron excess centers in KCl. The Physical Review 124:442-449.
- 36 Papazian, H. A. 1973. Color center analogs. Physica Status Solidi (b) 59:K89-K91.
- 37 Papazian, H. A. 1973. On the nature of color center absorptions. Physica Status Solidi (b) 59:621-627.
- 38 Papazian, H. A. 1975. Color centers as rotational spectra. Chemical Physics Letters 37:365-369.
- 39 Rusch, W., and H. Seidel. 1971. The F center containing a water molecule. Solid State Communications 9:231-234.
- 40 Rusch, W., and H. Seidel. 1974. The H_2O^- center in KCl: An F like paramagnetic and paraelectric defect. Physica Status Solidi 63:183-195.
- 41 Brailsford, J. R., and J. R. Morton. 1969. Paramagnetic resonance spectrum of O^- trapped in KCl, RbCl, and KBr. The Journal of Chemical Review 51:4794-4798.

- 42 Sander, W. 1962. Elektronen spin resonanz von kaliumchlorid mit sauerstoffhaltigen zusatzen. Zeitschrift fur Physik 169:353-363.
- 43 Kats, M. L., K. E. Gyunsberg, L. I. Golubentseva, and N. P. Zverdova. 1973. Influence of oxygen ions on the photo-conductivity of KCl and KBr single crystals. Soviet Physics-Solid State translated from Fizika Tverdogo Tela 15:221-222.
- 44 Kats, M. L., L. I. Golubentseva. and K. E. Gyunsberg. 1971. Low Temperature Optical Destruction of F Center in KCl-KOH and KBr-KOH. Soviet Physics-Solid State translated from Fizika Tverdogo Tela 13:3151-3152.
- 45 Morato, S., and F. Luty. 1974. Photoreactions between F centers and OH⁻ impurities and their significance for information storage and U_a center formation. Proceedings of the 1974 International Conference on Color Centers in Ionic Crystals, Sendai, Japan Paper H186.
- 46 Sander, W. 1964. Elektronen spin resonanz von sauerstoffzentren in KCl and KBr. Naturwissenschaften 51:404.
- 47 Kuczynski, G. C., P. E. Dietz, W. H. Hamill, and J. H. Jischke. 1978. H₂O related centers in potassium chloride. Physica Status Solidi (b) 87:581-588.
- 48 Matsumura, G., and G. C. Kuczynski. 1974. New color centers in KCl crystals. Physical Status Solidi (b) 55:324-334.
- 49 Dumke, V. R., and M. de Souza. 1974. Interaction between F centers and interstitial H atoms in KCl crystals. The Physical Review 10:1617-1622.
- 50 Duerig, W. H., and J. J. Markham. 1952. Color centers in alkali halides at 5° K. The Physical Review 88:1043-1047.
- 51 Kanzig, W., and T. O. Woodruff. 1958. The electronic structure of an H center. The Journal of Physics and Chemistry of Solids 9:70-92.
- 52 Castner, T. G., and W. Kanzig. 1957. The electronic structure of V centers. The Journal of Physics and Chemistry of Solids 3:178-196.
- 53 Castner, T. G., W. Kanzig, and T. O. Woodruff. 1958. The electronic structure of a V center. Supplemento al Volume VIII. Serie X del Nuovo Cimento: 612-620.
- 54 Hersh, H. 1956. Color centers in x-rayed potassium iodide. The Physical Review 105:1158-1166.

- 69 Knox, R. S., and K. J. Teegarden. 1965. Electronic excitations of perfect alkali halide crystals. In: Physics of Color Centers, ed. E. Beall. Academic Press, New York.
- 70 Martin, D. H. 1967. Magnetism in Solids. The M.I.T. Press, Cambridge, Massachusetts.
- 71 Anderson, P. W. 1963. Exchange in insulators: Superexchange, direct exchange, and double exchange. In: Magnetism, eds. G. T. Rado and H. Suhl. 1:25-83. Academic Press, New York.
- 72 Mattis, D. C. 1965. The Theory of Magnetism. Harper and Row, New York.
- 73 Herring, C. 1966. Direct exchange between well-separated atoms. In: Magnetism, eds. G. T. Rado and H. Suhl. 28:2-181. Academic Press, New York.
- 74 Offenhartz, P. O. 1968. One electron integrals between Slater-type orbitals. Quantum Chemistry Program Exchange 11:117.
- 75 Bernardi, F., and G. Painsco. 1967. Program to Evaluate two-center exchange integrals occurring in molecular problems. Quantum Chemistry Program Exchange 11:106.
- 76 Rudenberg, K. 1951. A study of two-center integrals useful in calculations on molecular structure. II. The two center exchange integral. Journal of Chemical Physics 19:1459-1477.
- 77 Roothaan, C. C. J. 1951. A study of two-center integrals useful in calculations on molecular structure. I. Journal of Chemical Physics 19:1445-1458.
- 78 Meyer, A., and R. F. Wood. 1964. Electronic structure of the M-center in LiCl and LiF. The Physical Review 133: A1436-A1442.
- 79 Ginsberg, A. P. 1971. Magnetic exchange in transition metal complexes VI. Aspects of exchange coupling in magnetic cluster complexes. Inorganica Chimica Acta Reviews 5:45-68.
- 80 Seidel, H., and H. C. Wolf. 1968. ESR and ENDOR spectroscopy of color centers in alkali halide crystals. In: Physics of Color Centers, ed. W. B. Fowler. Academic Press, New York.
- 81 Sugiura, Y. 1927. Über die Eigenschaften des Wasserstoffmoleküle im grundzustande. Zeitschrift für Physik 45:484-492.

APPENDICES

APPENDIX I

GLOSSARY OF TERMS AND ABBREVIATIONS

| | |
|------------------|---|
| bleach | refers to a decrease in the optical absorption of a sample and is frequently applied to a decrease in a single absorption band |
| ΔB_w | peak to peak half-width of a derivative EPR spectrum |
| Doping | refers to the intentional addition of known amounts of specific impurities to a nominally pure crystal |
| ENDOR | electron nuclear double resonance |
| EPR | electron paramagnetic resonance |
| KCl:OH | potassium chloride doped with hydroxide ion |
| lattice constant | the distance, in the [100] direction, from the center of an anion (cation) lattice site to the nearest neighbor anion (cation) site. In KCl, 3.14 Angstroms |
| λ_{\max} | position of the peak height of an optical absorption band |

APPENDIX II

COMPARISON OF EXCHANGE ENERGIES CALCULATED BY DIFFERENT METHODS.

Exchange energies between two F centers were calculated by different methods. The energies, J, were calculated using the approximations and computer programs described in this work with a variety of orbital exponents. The energies A^F were calculated using a formula derived by Schworer and Wolf¹⁹ from the hydrogen molecule calculation of Sugiura⁸¹. Results of these calculations are given in the table below for a variety of F to F center distances. Distances, R, are given in lattice constants.

| R | A^F | ξ_F | J |
|------------|---------------------------|---------|---------------------------|
| $\sqrt{2}$ | -6.7805×10^{-4} | 0.3 | -2.0396×10^{-2} |
| | | 0.39 | -9.6180×10^{-3} |
| | | 0.4 | -8.5892×10^{-3} |
| | | 0.5 | -3.1027×10^{-3} |
| 2 | -1.3298×10^{-4} | 0.3 | -4.8881×10^{-3} |
| | | 0.39 | -1.2751×10^{-3} |
| | | 0.4 | -1.0874×10^{-3} |
| | | 0.5 | -2.0377×10^{-4} |
| 4 | -2.1185×10^{-7} | 0.3 | -1.7010×10^{-6} |
| | | 0.39 | -5.5733×10^{-7} |
| | | 0.4 | -3.7673×10^{-7} |
| | | 0.5 | -6.8211×10^{-9} |
| 6 | -1.8180×10^{-10} | 0.3 | -3.4473×10^{-8} |
| | | 0.39 | -1.3521×10^{-10} |
| | | 0.4 | -7.2135×10^{-11} |
| | | 0.5 | -1.2187×10^{-13} |