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Title: The Reaction Between O^- Ions and F Centers
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The photochemical reaction between O^- ions and F centers was investigated. The activation energy was determined by the Arrhenius law to be 0.10 ± 0.04 eV for temperature below 180°K. The diffusion of alpha centers towards the oxide ion was eliminated as the rate limiting step and the low trapping rate of O^- ions determined to be responsible for the low temperature dependence of the reaction.

The Reaction Between
O^- Ions and F Centers

by

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# TABLE OF CONTENTS

LIST OF FIGURES

THE REACTION BETWEEN $O^=$ IONS AND F CENTERS

I. INTRODUCTION

In the 1930's a group of workers at Göttingen began investigating the photochemistry of oxygen-containing impurities trapped in alkali halide crystals. The oxide ion was first produced in the crystal by reduction of NO_3^- with excess electrons (14). The reductions were carried out by injecting electrons into the sample by a process known as electrolytic coloration, or by baking the crystal in alkali metal vapor at temperatures around $650^\circ C$. The chemical reaction is

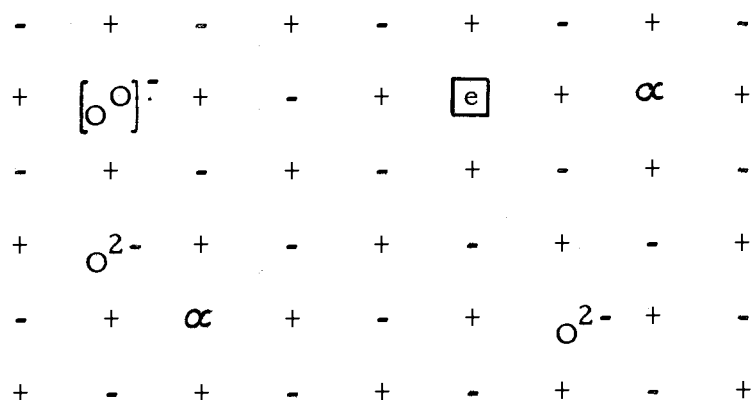$$2NO_3^- + 10e^- = 6O^{2-} + N_2 \qquad (I\text{-}1)$$
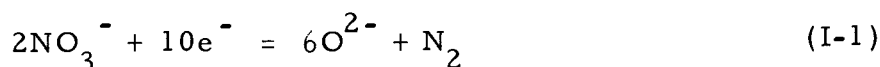
Akpinar (1) reported that oxide was also introduced into alkali halide crystals by the oxidation of carbonate ion by oxygen in the a air to give superoxide (O_2^-). The O_2^- ions were then in turn reduced with F centers to produce oxide in the crystal. Reactions are below.

$$CO_3^{2-} + \frac{3}{2} O_2 = 2O_2^- + CO_2; \qquad (I\text{-}2)$$

$$\text{Then } O_2^- + 3F = 2O^{2-} + 2\alpha \qquad (I\text{-}3)$$
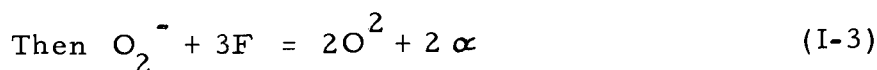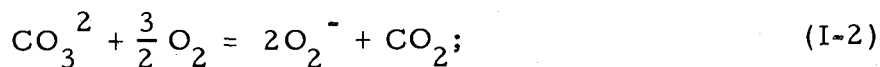
The α in equation I-3 represents an anion vacancy, also commonly

known as an alpha center, which has a net positive charge with re-
spect to the crystal. The alpha center occurs in all alkali halide
crystals from either Schottky pair formation or divalent anion sub-
stitution. A Schottky pair is separated negative-ion vacancy and
positive-ion vacancy, which occur in thermal equilibrium with the
perfect crystal at all temperatures above $O^{\circ}K$ (17). If a divalent
anion is trapped in a crystal then in order to maintain charge neutral-
ity an alpha center must appear. Below is a diagram of the potassium
chloride lattice which has O_2^-, O^{2-}, anion vacancies, oxide-alpha
complexes and F centers trapped in the crystal. The F center is
diagrammed as $\boxed{e}$, i.e. a vacancy with a trapped electron.

```
  -     +     -     +     -     +     -     +     -

  +  [ O ]⁻   +     -     +   [e]   +    α      +

  -     +     -     +     -     +     -     +     -

  +    O²⁻    +     -     +     -     +     -     +

  -     +     α     +     -     +    O²⁻   +     -

  +     -     +     -     +     -     +     -     +
```

Korth (14) reported a method to produce O^- from O^{2-}. This
change was produced by a photochemical treatment which included
irradiation of crystals containing O^{2-} ions by near-ultraviolet light
at room temperature. The chemical equation was given by Korth as

$$O^{2-} = O^- + F \qquad\qquad (I\text{-}4)$$

During the late 1950's Känzig and Cohen (12) began investiga-
ting O_2^- ions in the alkali halides by the method of electron para-
magnetic resonance. W. Sander (20, 21) continued the studies in
the early 1960's utilizing electron paramagnetic resonance to study
the oxygen centers more completely. He was then able to determine
that the products of the photochemical reaction (I-4) were in fact the
O^- ion and the F center. He hypothesized that the ion was situated
on a lattice site and that the spin of the unpaired electrons were
aligned parallel to each of the lattice vectors a, b, c. From this con-
figuration, one would expect a splitting of the g-tensor into parallel
and perpendicular values, which was observed. Later experiments
by Brailsford, Morton and Vannotti (2) were able to verify Sander's
g values; and they gave a quantitative quantum mechanical treatment
for the center. Vannotti and Morton (23) later extended the work by
investigation of an analagous center, S^-, and substantiated the pre-
vious calculations.

In 1966, two German physicists, F. Fischer and G. Gümmer
(8), investigated the quantum efficiency of decomposition of the O^{2-}
center in KCl. In this publication the authors reported that the back
reaction of $O^- + F \longrightarrow O^{2-} + \alpha$ could be caused to occur. However,
they did not report any quantitative data concerning the rates of
reaction or activation energy for the process. The investigation of
these quantities became the basis for this thesis.

There are some aspects of the situation of the O^{2-} ions which need to be discussed. The most important point to recognize is that a high fraction of oxide ions are complexed with anion vacancies to form dipoles. These dipoles are oriented along the $\langle 110 \rangle$ axis. They were studied by Gümmer (11) by means of dielectric relaxation, coupled with optical absorption, to deduce activation energies for reorientation and diffusion processes. Gümmer was able to determine that for concentrations in the neighborhood of 10^{17} center cm^{-3} practically all of the oxide ions are associated with anion vacancies. These dipoles are also able to migrate together to form aggregate double dipoles which reduce the dielectric loss in these crystals. At moderate temperatures, from the rate of dielectric loss as a function of reciprocal temperature, Gümmer calculated the activation energy for migration of the complex to be 0.85eV. He also reported the activation energy for reorientation of the dipole as 0.59eV.

Gümmer also studied the fluorescence spectra of these dipoles and proposed a reasonable model to describe the observed behavior. It is given in the form of an energy level diagram as shown on the following page.
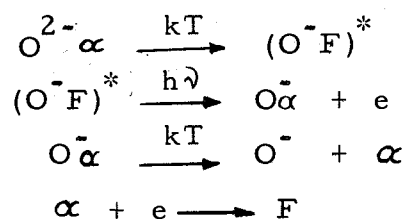
Finally, Gümmer proposed a reasonable mechanism for the production of O^{-} ions and F centers. He considered that each of the dipoles was from time to time in an activated state due to thermal excitation. This state, as described by Gümmer, occurs when the
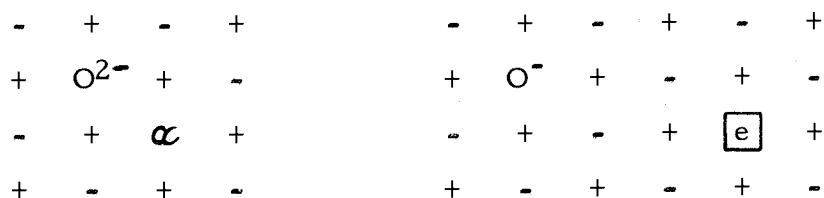
conduction band

1

2

A

B

3

first excited state

4

C

O_α^{2-} ground state
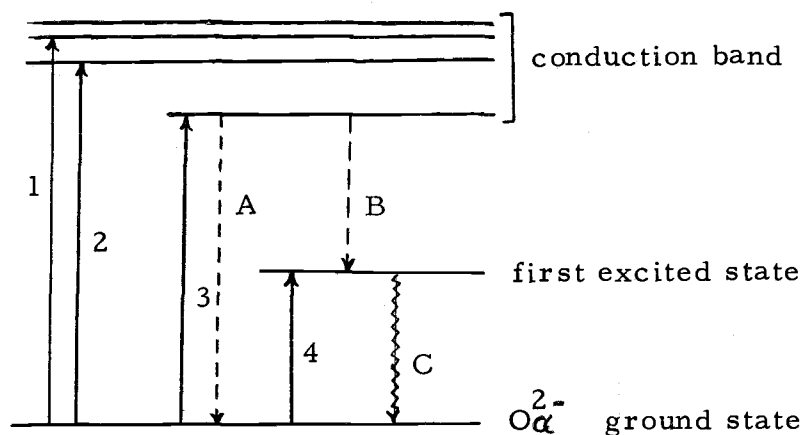
Absorption bands: 1 : 144 nm, 2 : 212 nm, 3 : 283 nm,
4 : 435 nm.
Emission bands: A : 470 nm, B : 1050 nm, C : phonon
emission.

alpha center momentarily traps an electron from the oxide to give

an O^-F complex in an activated state. When the complex is in this

configuration, a photon of proper energy, $h\nu = 4.25$ eV, can ele-

vate the electron into the conduction band. When this occurs, there

is no attraction between the O^- ion and the alpha center, so the

alpha center merely diffuses away aided by thermal energy. If the

alpha center moves to a lattice site out of the range of the O^- ion

then the electron can be trapped to form an F center. Gümmer's

mechanism for the decomposition for the oxide-alpha complex can

be represented by the following set of chemical equations.

$$O^{2-}\alpha \xrightarrow{kT} (O^-F)^*$$

$$(O^-F)^* \xrightarrow{h\nu} O_\alpha^- + e$$

$$O_\alpha^- \xrightarrow{kT} O^- + \alpha$$

$$\alpha + e \longrightarrow F$$

The final products i.e. O^- ions and F centers are individual species which are separated by at least two lattice constants. The diagram below shows the condition of the crystal before and after the reaction.

```
-   +   -   +          -   +   -   +   -   +
+  O²⁻  +   -          +  O⁻   +   -   +   -
-   +   α   +          -   +   -   +  [e]  +
+   -   +   -          +   -   +   -   +   -
```

The crystal is stable in this configuration for at least several days, which lends credibility to the idea that the centers are well separated. When the crystal was in the state of the diagram above then the back reaction could be initiated by irradiation of the crystal with F-light.

II. EXPERIMENTAL

Crystal Preparation

The samples used in this set of experiments were cleaved from larger crystals grown by the Kyropoulos method from reagent grade potassium chloride. The salt was purified by an ion exchange technique developed by Fredericks, Rosztoczy and Hatchett (10). The crystals were grown by James L. Paul and a complete discussion of the apparatus and procedure is reported in his doctoral thesis (18).

The dopant for these crystals was potassium superoxide (KO_2) which was obtained from the Alfa Inorganics Company. The guaranteed purity was 97-99%.

The oxygen in the large boules was in the superoxide form (O_2^-) and it was necessary to reduce superoxide to the oxide (O^{2-}) state. This was done by electrolytic coloration. The technique consists of injecting electrons from a pointed electrode into an alkali halide crystal at an elevated temperature. This was done by placing the crystal between two electrodes, one pointed platinum and the other flat graphite. The temperature of the assembly was raised to 500° C to 750° C. At this point, a field of about 300 V cm^{-1} was imposed. When the potential was applied, a cloud of violet F centers began to appear, migrating from the pointed cathode toward

the flat anode. These conditions were maintained until the cloud had reached its maximum dimensions. The field was then reversed to withdraw the electrons from the crystal through the pointed electrode.

The following equation shows the reaction for describing the effect of this treatment on the oxygen in the crystals.

$$O_2^- + 3e \longrightarrow 2O^{2-}$$
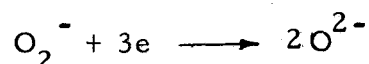
which could also be written as

$$O_2^- + 3F \longrightarrow 2O^{2-} + 2\alpha.$$
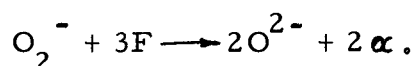
The second equation gives a more accurate representation of the actual conditions of the final state, because each O^{2-} must be balanced with an alpha center in the lattice in order to maintain charge neutrality of the crystal.

From pieces of the crystal which had been electrolytically colored and decolored, slices were cleaved with the approximate dimensions of 10X10X4 mm. These were then wrapped individually in aluminum foil, annealed at 500° C for one minute and quickly quenched into liquid nitrogen. This annealing and quenching was done in order to separate the double dipoles which form if the crystals are heated and cooled slowly or are left for long periods of time at room temperature.

The annealing and quenching was done directly before any optical measurements or other treatment in order to insure the same initial state of the crystal and its constituents. At no time after

quenching was the sample unintentionally subjected to any light.

Optical Treatment of Samples

The freshly quenched samples were mounted in an optical crysotat using Duco cement. The cell was then assembled, attached to a vacuum line and pumped down to 1×10^{-5} mm Hg. The crystals were then cooled to liquid nitrogen temperature in order to take high resolution visible and ultraviolet spectra. These were used to determine the concentration of F-centers and oxide-alpha complexes before any photochemical treatment. The calculation of concentrations was done using the equations given below from Doyle (6) and Fischer (7).

$$n_F = 2.76 \times 10^{16} \cdot A_m \cdot W \qquad \text{and}$$

$$n_C = 1.0 \times 10^{17} \cdot A_m \cdot W$$

where A_m is the absorbance per centimeter at the maximum of the absorption band and W is the half width in eV. At 78° K A_m for the F-band is taken at 540_{nm}; W is 0.22 eV (5). The parameters for the oxide-alpha band: A_m measured at 285_{nm} and W, equal to 0.39 eV (7) both at 78° K.

After the low temperature spectra were taken, the sample was warmed quickly to room temperature. The oxide band was bleached by illumination for five minutes with light from a 100 watt

high-pressure mercury lamp model #C-46-61-1 made by Oriel

Optics, Inc. Due to the fact that the lamp produces light in the F

absorption band, it was necessary to use a Corning Number 7-54

filter. This filter eliminates all wavelengths of light except in the

range 250 nm to 430 nm. In its pass-band the transmittance is at

least 90%.

The sample remained in the cryostat and was placed about 25

centimeters from the lamp. The filter was placed as close to the

sample as possible. This optical bleach was done in a photographic

darkroom to eliminate all light except the output from the mercury

lamp.

The samples were again cooled quickly to liquid nitrogen

temperature or to the temperature of the experiment. The samples

were cooled quickly and never left at room temperature longer

than necessary, in order to keep the aggregation of the dipoles into

double dipoles from taking place. Visible and ultraviolet spectra

were taken in order to calculate the new concentrations of F centers

and oxide-alpha complexes. The concentration of O^-, n_{O^-}, was

calculated by taking the difference between the oxide-alpha complex

concentrations before and after the ultraviolet bleach.

The next step was to allow the sample to come to equilibrium

at the temperature of the experiment. The normal refrigerant was

a slush bath of a substance which melted in the temperature range

which was desired. The temperature of the crystal was monitored with a copper-constantan thermocouple.

The F-light bleaching experiment was then begun. First a spectrum was taken of the ultraviolet region in order to obtain the initial peak heights at the experimental temperature. The crystal was then bleached with F-light. Normally the procedure was to bleach consecutively one minute, three minutes, ten minutes and thirty minutes and to record the spectrum after each bleach. These spectra then provided the data for the growth curves of the oxide-alpha complexes.

To carry out the bleaching by F-light, the cold cell was removed from the spectrophotometer in the dark and placed in front of a projector lamp at a distance of 66 centimeters. Two filters were used; one was a heat filter placed near the projection lamp in the lamp housing, the other was a Corning interference filter with its band-pass center at 533 nm which was placed over the window of the cryostat.

Optical Measurements

All optical measurements were made with a Perkin Elmer model 450 recording spectrophotometer. For measurements made in the far ultraviolet below 200 nm, the sample and reference compartments were purged with prepurified nitrogen.

III. RESULTS

Figure 1 shows the spectrum of sample 1 before and after the ultraviolet bleach at 78° K and the curve for 44 minutes of F-light bleaching at 156°K. The bands at long wavelength are due to N and M centers which are aggregates of the F center. These spectra resemble those shown in Fischer and Gümmer's earlier paper.

The data was extracted from the sets of curves for the growth of the oxide-alpha complexes at five temperatures. The results of these experiments are plotted in Figure 2, which shows the relationship between n_c, the oxide-alpha complex concentration, and the bleaching time in minutes.

The initial rate, R_o, of each growth curve was taken by determining the slope of the line tangent to the growth curve during the first moments of the reaction. To test the adherence to the Arrhenius equation, $\log_{10} R_o$ was plotted versus the reciprocal temperature in K^{-1}. The result is shown as Figure 3. Below approximately 180°K the curve is linear; at higher temperatures the rate was less than that corresponding to the Arrhenius equation.

The activation energy of the reaction was then calculated to be 0.10 ± 0.04 eV. This was done by taking the slope of the best fitting straight line through the three lowest temperature points and setting it equal to $\dfrac{-\Delta E_a}{2.303k}$, where k is the Boltzmann constant.
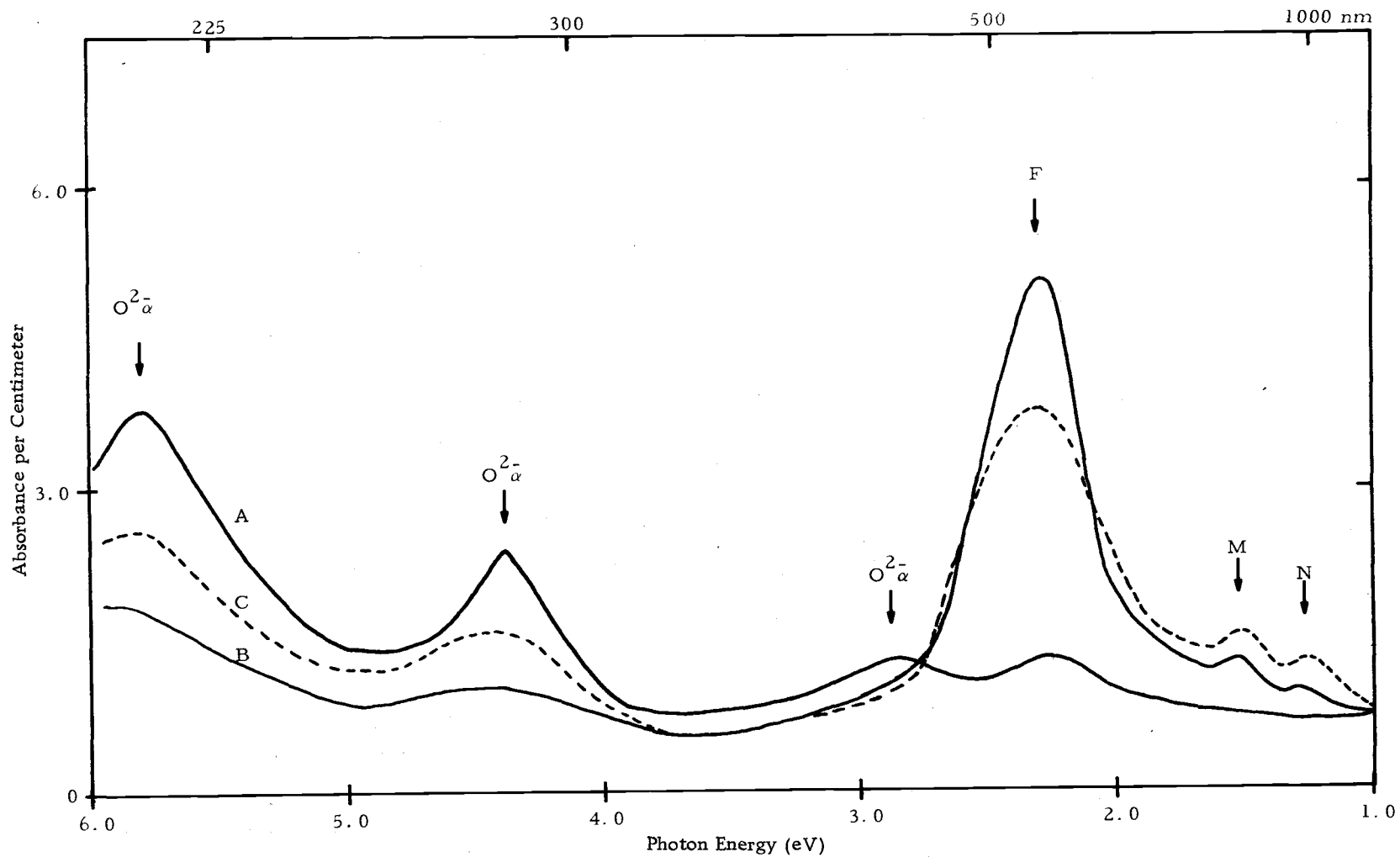
Figure 1. Absorption spectrum A. after quenching, B. after ultraviolet bleaching, C. after 44 minutes of F-light bleaching.
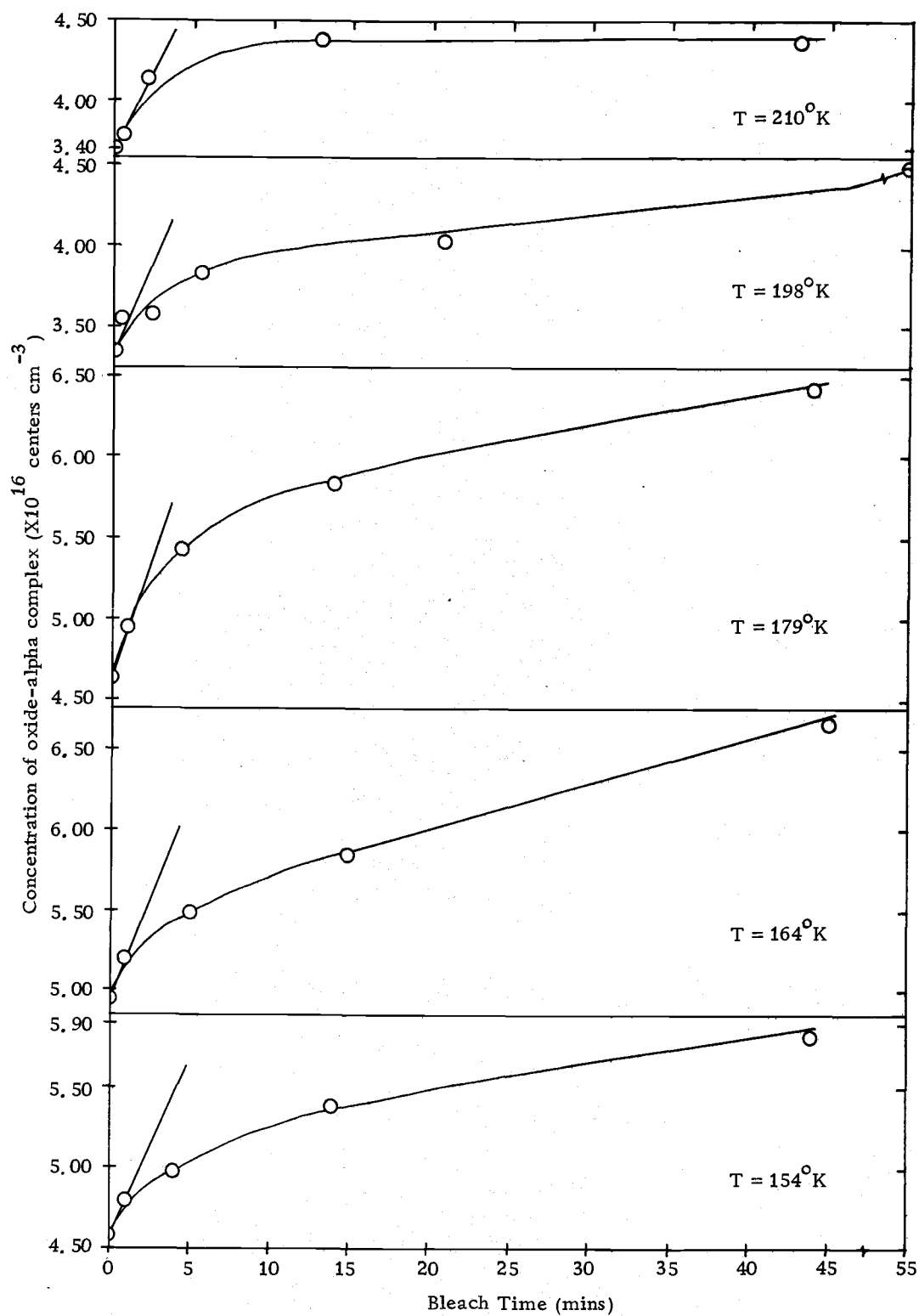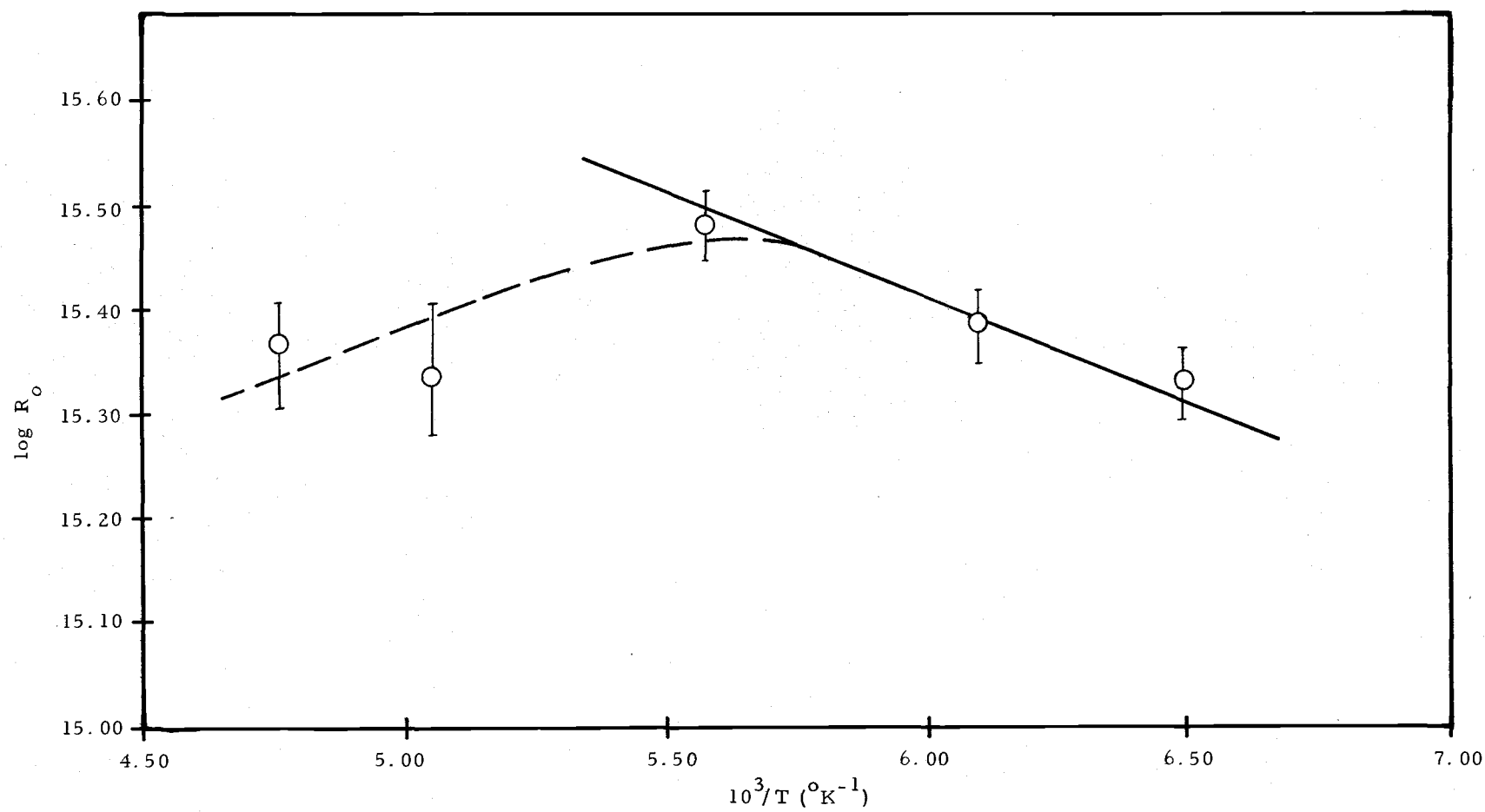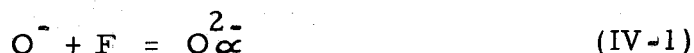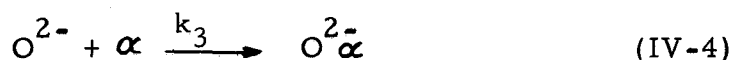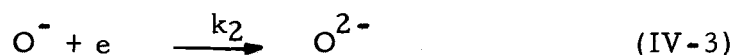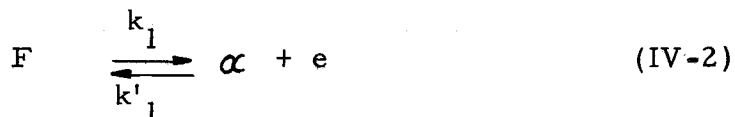
Figure 2. n_c vs Bleaching Time

Figure 3. $\log_{10} R_o$ vs $10^3 T^{-1}$.

IV. DISCUSSION

The photochemical reaction between F centers and O^- ions can be expressed simply as

$$O^- + F = O^{2-}_\alpha \tag{IV-1}$$

However, the process is probably not as uncomplicated as the equation might suggest. A more complete set of equations below outlines the likely mechanism for the reaction as a three-step process.

$$F \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} \alpha + e \tag{IV-2}$$

$$O^- + e \xrightarrow{k_2} O^{2-} \tag{IV-3}$$

$$O^{2-} + \alpha \xrightarrow{k_3} O^{2-}_\alpha \tag{IV-4}$$

This investigation was begun under the assumptions that the last step of the reaction (IV-4) would most likely be the rate determining step. Under this assumption the activation energy derived from the temperature dependence would then be the same as the activation energy for alpha center migration.

The modern value for ΔE_a for alpha center migration, as derived from high temperature conductivity and diffusion work, is generally around 1 eV. Chandra and Rolfe (4) reported a value of 0.97 eV for KCl which was calculated from careful conductivity

measurements. However, there is substantial disagreement between the high temperature value and the low temperature value. Lüty, et al. (16) reported a value around 0.6 eV for alpha migration at low temperatures. This result was calculated from some experiments involving reorientation of F_A centers.
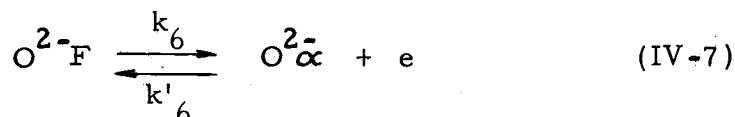
The initial step of the reaction requires a photon to be absorbed to ionize the F center into equal numbers of alpha centers and free electrons. The number of F centers that are ionized during any period is proportional to the number of photons which are absorbed by the crystal. This step is fast and reversible so that alpha centers can retrap the electrons to form F centers again. The retrapping, which is due to the coulombic attraction between alpha centers and electrons, is also fast.

In order for the reaction to proceed, an electron must be captured by an O^- ion to produce an oxide ion. Following this step an alpha center will become attracted to the oxide ion due to coulombic forces and migrate towards the O^{2-} in order to form the complex. The data in Figure 2 comprise the growth curves for the product of the last reaction, i.e. for the formation of the complex from O^{2-} and an alpha center.

The method of integration as outlined by Laidler (15) was then applied to test for the order of the reaction with respect to the reactant concentrations n_F and n_{O^-}. Reaction orders of one,

one-half, two, three-halves and three were tested. However, there were no positive results. Part of the reason for the failure may arise from lack of constancy, both in time and space, of the F-center ionization rate. Even though the intensity of F light remained constant, a decrease in n_F (most pronounced at the surface nearer to the source), causes a decrease in the fraction of light absorbed. A second cause may be the occurrence of complicated competing reactions.

Listed below are the plausible competing reactions which are active under the conditions of the experiments.

$$F + e \underset{k'_4}{\overset{k_4}{\rightleftharpoons}} F' \tag{IV-5}$$

$$F + \alpha \underset{k'_5}{\overset{k_5}{\rightleftharpoons}} F_2^+ \tag{IV-6}$$

$$O^{2-}F \underset{k'_6}{\overset{k_6}{\rightleftharpoons}} O^{2-}\alpha + e \tag{IV-7}$$

$$F_2^+ + e \overset{k_7}{\longrightarrow} M \tag{IV-8}$$

The species on the left in equation IV-7 is a complex composed of an oxide ion and an F center at adjacent anion sites.

One can now write kinetic equations in order to express the rate of the overall reaction as a function of the concentrations of the

initial and intermediate reactants. The assumption is made that the concentration of electrons attains a steady state, where

$$\frac{dn_e}{dt} = 0.$$ This is a reasonable assumption to make. The lifetime of the electron in the conduction band maybe estimated from the data of Chapple, Lehmann and Scott (3) to be on the order of 10^{-6} sec. Because the lifetime is so short and the rate of production is large, the concentration of electrons must reach a steady state quickly.

From equations IV-1 through IV-8 we may write

$$\frac{dn_e}{dt} = k_1 n_F + k_6 n_{O^{2-}F} + k'_4 n_{F'} - k_4 n_F \cdot n_e - k_2 n_{O^{-}} \cdot n_e - k'_6 n_c \cdot n_e - k_7 n_{F_2^+} n_e$$

(IV-9)

If one assumes a steady state, then $\frac{dn_e}{dt} = 0$, so that

$$n_e = \frac{k_1 n_F + k_6 n_{O^{2-}F} + k'_4 n_{F'}}{k_4 n_F + k_2 n_{O^-} + k'_6 n_c + k_7 n_{F_2^+}}$$

(IV-10)

Then from reactions IV-3 and IV-4 the rate as a function of specific rate constants and concentrations can be expressed by means of the following

$$\frac{dn_{O^{2-}}}{dt} = k_2 n_{O^-} n_c = \frac{k_2 n_{O^-}(k_1 n_F + k_6 O^{2-}F + k'_4 F}{k_4 n_F + k_2 n_{O^-} + k'_6 n_c + k_7 n_{F_2^+}}$$

(IV-11)

so that

$$n_{O^{2-}} = \int_o^{n_{O^{2-}}} dn_{O^{2-}} = \int_o^t \frac{k_2 n_{O^-}(k_1 n_F + k_6 n_{O^{2-}F} + k'_4 n_{F'}) \, dt}{k_4 n_F + k_2 n_{O^-} + k_6 n_c + k_7 (n_{F_2^+})}$$

(IV-12)

Then the rate of production of oxide-alpha complexes is given by

$$\frac{dn_c}{dt} = k_3 n_{O^{2-}} n_\alpha = k_3 k_2 n_\alpha \int \frac{n_{O^-} (k_1 n_F + k_6 n_{O^{2-}F} + k'_4 n_F) \, dt}{k_4 n_F + k_2 n_{O^-} + k'_6 n_c + k_7 (n_{F_2^+})} \qquad \text{(IV-13)}$$

This equation is intractable in its present form; the best

chance one can have to reduce its complexity is to establish a hierar-

chy of rate constants. Then by using these relative rates one can

determine whether the equation produces the results on a qualitative

basis. The only concentration which is well defined at different times

is n_c but the other concentration variables i. e. n_α, n_{O^-}, n_F, and

$n_{O^{2-}}$ are generally unknown. The values of n_{O^-} and n_α are known

initially.

First consider the very fast reactions IV-2 and IV-5. The

ionization of F centers and retrapping of the electrons by alpha

centers are fast processes; this forms the basis for considering the

concentration of electrons to reach the steady state quickly. There

is another fast photochemical reaction which occurs, namely the

conversion of F centers into F' centers. F' centers are produced at

low temperatures in colored crystals by irradiation in the F band.

The electrons which are liberated are trapped by other F centers

to produce the F' center. The F' centers are thermally unstable and

dissociate slowly. The half life of the F' center in KCl at 170°K

is on the order of 10^3 seconds (19). In order to take the

concentration effects into account, one must have some knowledge of the relative concentrations. n_F is large initially and remains quite large throughout the experiment; n_α and n_e are small and nearly constant throughout the course of the experiment. The concentration of F' centers is increased from zero initially to about 10^{-3} times n_F after a few seconds of irradiation then reaches a steady value. One can list the order of the products of specific rate constant times concentration, so that

$$k_1 n_F \approx k'_1 n_\alpha n_e > k_4 n_F n_e \approx k'_4 n_{F'}$$

Consider equations IV-6 and IV-8. These equations represent the common reactions used in the mechanism for M center production. An M center is an aggregate consisting of two F centers which are situated on adjacent sites. The first step of the reaction is trapping of an alpha center by a F center to form F_2^+. This step is limited by alpha-center diffusion and is slow at temperatures below $250^\circ K$. The second step is trapping of an electron by F_2^+ to form M. These reactions do not compete significantly with the oxide-alpha complex reactions but are necessary to explain the growth of the M band, which is observed at 850 nm in Figure 1.

Consider the following reaction.

$$O^{2-}F \underset{k'_6}{\overset{k_6}{\rightleftharpoons}} O\alpha^{2-} + e$$
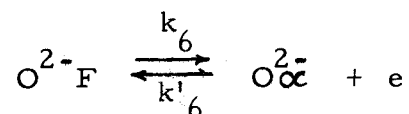
The species on the left consists of an oxide ion and an F center at adjacent sites. This complex has not been investigated; however, it is reasonable to suppose that it would be reasonably stable. A photochemical reaction can occur if a photon is absorbed by the complex and a conduction electron is produced along with an oxide-alpha complex. One would expect the rate constant to be large, but would expect the concentration of the $O^{2-}F$ complex to be relatively small. The reaction to the left appears to be potentially significant also. This supposition arises from the results of unpublished photoconductivity work which was done in this laboratory. The results show that the free electron lifetime is extraordinarily low in oxide doped, additively colored KCl. The hypothesis is that the O^{2-}_α complex acts as an efficient trap for the electrons even at room temperature. On this basis, one would expect that both reactions are active in this experiment.

Now one is able to apply some new approximations to IV-12, other than the steady state electron concentration approximation. Recognizing that $k_7(n_{F_2}+)$, $k'_4 n_{F'}$ and $k_6 n_{O^{2-}F}$ are small with respect to the other terms equation IV-12 can be simplified to

$$\frac{dn_c}{dt} = k_1 k_2 k_3 n_\alpha \int_0^t \frac{(n_F n_{O^-})\, dt}{k_2 n_{O^-} + k'_6 n_c} \qquad \text{(IV-16)}$$

While n_c is known during the course of the reaction, only a rough estimate of n_{O^-} is possible. Further, n_α is unknown at all stages of the reaction. Consequently, even with this much simplified form of the rate equation, integration of IV-16 to predict the time dependence of n_c is not feasible.

Consequently, the data was treated in a less elegant but justifiable manner. If the F-light intensity and the initial concentrations n_{O^-}, n_c, and n_F were constant for all experiments, and provided that n_α attains its steady value in a time short compared with the time scale of the measurements, then the initial slope of the growth curve would be a function of temperature only. According to the Arrhenius Law at fixed initial concentrations, the initial rate, R_O, is given by:

$$\ln R_O = - \frac{\Delta E_a}{kT} + \text{constant}$$

The temperature dependence of the initial rate, the above concentrations and the F-light intensity being held approximately constant, is shown in Figure 3. The activation energy, 0.10eV, is not only surprisingly small, but in fact hardly differs significantly from zero.
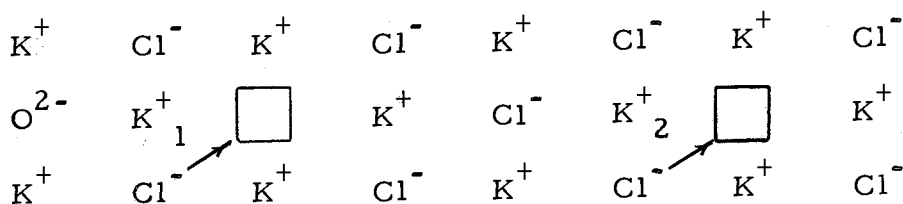
Above $180°K$, the law is not followed, perhaps due to an increased rate of competing reactions or a change of reaction mechanism.

The resulting activation energy was incompatible with the

alpha-center migration activation energy previously determined.
One cause may be that the alpha center is in close proximity to the
oxide ion rather than being well separated. In this case the coulomb-
ic attractive energy could be on the order of the activation energy for
migration, thus producing an increase in the rate of migration.

Two situations can be analyzed to determine the effect of the
coulombic interactions on the activation energy for alpha center
migration. The migration process can be visualized in terms of a
chloride ion jumping into the adjacent anion vacancy so that the
vacancy appears to have migrated. Consequently, the coulombic
interaction that pushes the migration is a negative-negative repulsion
between the oxide ion and chloride ion. The two cases which will be
discussed are illustrated below: case 1 is for the chloride ion jump-
ing close to the oxide ion and case 2 is for chloride ion jumping at a
large separation distance.

$$K^+ \quad Cl^- \quad K^+ \quad Cl^- \quad K^+ \quad Cl^- \quad K^+ \quad Cl^-$$

$$O^{2-} \quad K^+_1 \quad \square \quad K^+ \quad Cl^- \quad K^+_2 \quad \square \quad K^+$$

$$K^+ \quad Cl^- \quad K^+ \quad Cl^- \quad K^+ \quad Cl^- \quad K^+ \quad Cl^-$$

The boxes in the diagram above depict an anion vacancy.

The quantity one must calculate is the decrease in the zero
field barrier for the chloride ion migration in the field due to the
oxide ion. This correction is made by subtracting the energy dif-
ference which comes about due to the fact that as the chloride moves

away to the top of the barrier, it experiences a lower potential energy due to the oxide.

In case 1 the chloride ion is adjacent to the oxide and is moved to a position two interionic spacings from the oxide. Assume that the barrier is half way between the chloride ion and the vacancy and that the zero field barrier is 1.00eV.

Taking the geometry of the cubic crystal into account, the chloride ion is initially a distance $a \cdot \sqrt{2}$ from the O^{2-} ion and then moves to the top of the energy barrier at $a \cdot \sqrt{2.25}$ from the O^{2-} ion. The letter $\underline{a}$ represents the interionic distance for KCl. Then by calculation of the electrostatic energy at both points, the effective activation energy is given by

$$E_a = 1.00 - \frac{e_o^2}{b \varepsilon} \left[1 - \frac{1}{1.13} \right]$$

where $b = a\sqrt{2}$, $a = 3.10 \overset{\circ}{A}$, $\varepsilon = 1.00$, and $e_o = 4.8 \times 10^{-10}$ esu,

So

$$E_a = 1.00 - 0.36 = 0.64eV$$

The dielectric constant here is taken as that of vacuum, since no material occupies the space between the Cl^- ion in question and the oxide ion. The result is much larger than the experimentally determined activation energy, so that it is unreasonable to deduce that the low activation energy is due to the coulombic interactions at short distances. This calculation was made using the extreme case of the

alpha center being trapped initially only two lattice spacings from the

oxide. This assumption is not a plausible one because the O^- ions

and F centers are thought to be initially well separated due to the

stability of the crystal in the O^- + F state.

The situation for case 2 assumes the oxide ion and anion

vacancy are well separated initially. The distances between the

oxide ion and the chloride ion in the initial position is 5a and the top

of the barrier is 5.5a. The effective activation energy can be cal-

culated in the same manner as for case 1.

$$E_a = 1.00 - \frac{e_o^2}{\epsilon a} \left[\frac{1}{5} - \frac{1}{5.5} \right]$$

where $a = 3.10 \, \overset{o}{A}$ and $\epsilon = 4.6$ so

$$E_a = 1.00 - 0.02 = 0.98 eV$$

Here it is logical to take the ordinary static dielectric constant as the

appropriate value of ϵ. In the second case the effective activation

energy is essentially the same as the zero field activation energy.

Consequently the anion vacancy migration would be quite slow when

the centers are well separated.

The result of these calculations is that for both extreme cases

the activation energy for alpha center migration is much higher than

that which was measured experimentally. Due to this fact one can

eliminate the coulombic interactions as the cause of the extremely

low activation energy.

Another plausible reason for the low temperature dependence of the reaction rate is a low trapping rate of electrons by O^- ions (eq. IV-3). It is reasonable to expect this reaction to be slow. A substitutional O^- ion exerts no coulombic attraction for a distant electron so that the trapping cross section cannot be much greater than the cross-section of the 2p orbitals, or about $2 \times 10^{-16} cm^2$. This is less, by a factor of about two orders of magnitude than reported cross sections, for example, of singly charged positive centers. Further, if the rate is determined by electron-trapping by O^- ions, the rate should depend on temperature only through the electronic thermal velocity which increases as $T^{\frac{1}{2}}$. The low activation energy is consistent with this interpretation.

V. CONCLUSION

This study of the reaction between O^- ions and F centers has revealed that the reaction rate is not limited by diffusion of the alpha center towards the oxide ion. This is surprising due to the low diffusion rates of anion vacancies at temperatures below $200^\circ K$. It now seems most likely that the process of electron trapping by the O^- ion is responsible for the low rate and the low temperature dependence.

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