

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date thesis is presented March 12, 1953

Title CHEMICAL PROPERTIES OF COLOR CENTERS IN ALKALI
HALIDES

Abstract approved Redacted for privacy
(Major Professor)

A discussion of some of the many types of color centers present in additively colored alkali halides is given, with special emphasis being placed on the properties of the centers involved in thermal equilibria. The thermal stability of F-centers in additively colored potassium bromide and potassium iodide was determined over a range of temperatures and concentrations. It was shown that a heterogeneous equilibrium is established in these crystals between F-centers and "colloidal" centers. The equilibrium concentration of F-centers was calculated at several temperatures by means of the Smakula equation and used to determine the ΔH of the process "colloid" \rightarrow F-centers. For K-KBr, $\Delta H = 11.4 \pm 0.4$ kilocalories per mole of F-centers formed at 325°C . For K-KI, $\Delta H = 9.0 \pm 0.3$ kilocalories per mole of F-centers formed at 340°C . These results are similar to those obtained for K-KCl by Scott and Smith.

During the thermal stability measurements on K-KI, a new band was discovered in its absorption spectrum. This band has several properties similar to the "colloidal" band, but the maximum occurs at 650-670 millimicrons, which is about 200 millimicrons less than the "colloidal" band maximum. Exploratory experiments were conducted to ascertain the qualitative behavior of this new band toward light (of wave length corresponding to the band maximum) and heat. No definite conclusions could be drawn as to the structure of the center giving rise to this band.

The position of the "colloidal" band maximum in K-KCl, K-KBr, and K-KI was calculated by means of an equation derived from theoretical considerations by Phol. Agreement between observed values and the calculated

values was very good for K-KCl and K-KI, and fair for K-KBr.

Nonhomogeneously colored potassium chloride and potassium bromide were studied in order to determine the relationship existing between F-centers and M-centers during the coloration process. The results indicated that a rapidly attained thermal equilibrium exists between these two centers and, furthermore, the process involves one F-center per M-center.

Low temperature (-194°C) absorption spectra were obtained for K-KCl, K-KBr, and K-KI in which R_1 -, R_2 -, and M-bands had been developed. Absorption curves for K-KBr and K-KI prepared in this laboratory were measured at 5°K by Dr. J. J. Markham of The Johns Hopkins University Physics Department and are included for completeness.

The energy levels of electrons in F-centers in additively colored NaCl, KCl, KBr, and KI have been calculated by a quantum mechanical method. A variation method was used and generalized equations for the variable parameters obtained. These can be applied to any alkali halide with the NaCl structure. Generalized expressions for the energies of the $1s$ and $2p$ states were derived. The variable parameters were evaluated by successive approximations and were then used in the energy equations to obtain values of W_{1s} and W_{2p} at 20°C . Energy values for the transition $1s \rightarrow 2p$ were calculated and compared to those obtained experimentally, that is, to the energies corresponding to the F-band maxima. The agreement between these calculated values and the observed energies is excellent.

The above method was applied to KCl at -194°C in order to calculate the energy shift of the F-band maximum with temperature. Wave functions for the $1s$ and $2p$ states were obtained with all of the parameters evaluated and used to determine the electron density distribution at 20°C and also at -194°C in the case of KCl. The $2p$ wave functions were used to calculate the thermal energy of activation for the process

$2p \text{ electron} \rightarrow \text{conduction electron}$

in additively colored NaCl, KCl, KBr, and KI.

CHEMICAL PROPERTIES OF COLOR
CENTERS IN ALKALI HALIDES

by

WILLIAM ALTON SMITH, JR.

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1953

APPROVED

Redacted for privacy

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Date thesis is presented March 12, 1953

Typed by Clara Homyer

ACKNOWLEDGMENT

The author wishes to express deep appreciation to Dr. A. B. Scott for his helpful criticism and guidance during the experimental work and preparation of this thesis. His constant interest was a source of inspiration. This work was sponsored in part by the Office of Naval Research, and the support of that agency is gratefully acknowledged.

Dr. R. R. Dempster, of the Department of Physics, made many valuable suggestions during discussions of the theoretical aspects of this work.

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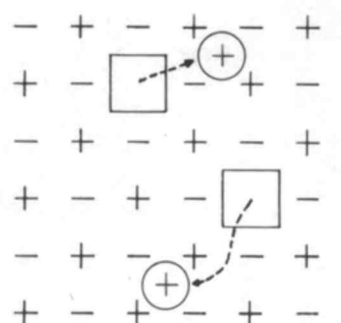
CHEMICAL PROPERTIES OF COLOR CENTERS IN ALKALI HALIDES

CHAPTER I

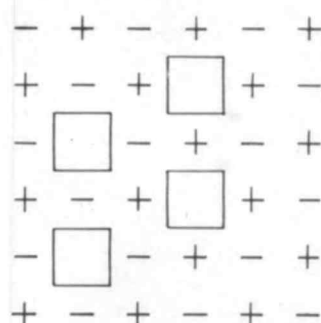
INTRODUCTION

Color Centers

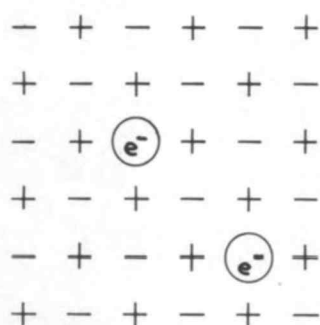
A large body of information has been developed concerning the lattice imperfections of the alkali halides. These crystals have been investigated intensively because of the relative simplicity of their structure as compared to that of other crystals. Some of the most interesting properties of the alkali halides are due to imperfections in the crystal lattice. It was first pointed out by Frenkel that vacant lattice sites and ions in interstitial positions could exist in appreciable concentrations in a crystal in thermal equilibrium at temperatures above absolute zero (4, p.654). However, it was later shown by several investigators that the predominant defect in alkali halides is the so-called Schottky defect which consists of an equal number of positive and negative ion vacancies (11, Chapter 2; 19, pp.497-499; and 28, pp. 339-343). The Frenkel and Schottky defects are shown in a two dimensional representation in Figure 1.



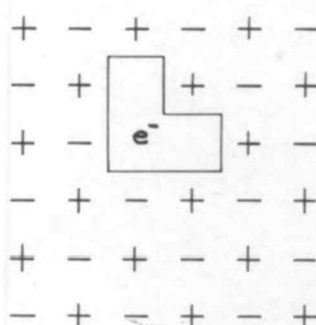
(A) FRENKEL DEFECTS



(B) SCHOTTKY DEFECTS



(C) F-CENTERS



(D) M-CENTER (SEITZ)

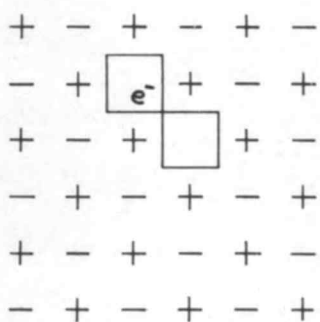
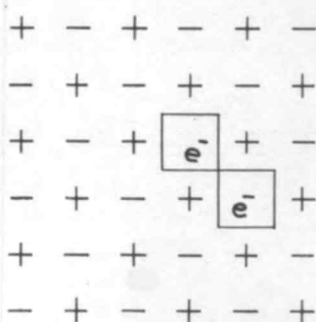
(E) R_1^- OR F_2^{+} -CENTER
(SEITZ)(F) R_2^- OR F_2 -CENTER
(SEITZ)

FIGURE 1. LATTICE IMPERFECTIONS IN ALKALI HALIDES.

Pure alkali halides have no significant optical absorption from the near ultraviolet to the near infrared region of the spectrum. However, these crystals can be colored by several methods, among which are the following:

- (1) Bombardment by cathode rays
- (2) Exposure to x-rays
- (3) Heating the crystal in an atmosphere of alkali metal vapor (additive coloration)
- (4) Electron injection from pointed electrodes

Historically, the first artificially colored alkali halide crystal was observed by Goldstein in some experiments with cathode rays in which he bombarded several of the alkali halides and noticed that each compound assumed a characteristic color (6, p.211). The same coloration can be produced by exposure to x-rays (17, pp.1-82).

The colored alkali halides have optical absorption spectra which are characteristic of the individual crystals and not of the method of preparation (in general). Furthermore, these absorption spectra have many qualitative features in common. Pohl and his co-workers have investigated the colored alkali halides in great detail and a review of this early work was published by Pohl in 1937 (25, pp.3-31).

Pohl called the lattice defects responsible for

the characteristic color of the alkali halides "Farbzentren" or "color centers". The term F-center as now used, refers specifically to the defect pictured in Figure 1(c), that is, an electron trapped at a negative ion vacancy. This model was first proposed by de Boer and has been well supported by the results of many experimental and theoretical investigations (2, p.308). The absorption band associated with this defect is called the F-band. Other absorption bands have been observed in the colored alkali halides and have absorption maxima which lie on both sides of the F-band. Since we shall be concerned primarily with F-bands and bands lying to the long wave length side of the F-bands, no discussion of other bands will be given.

The F-band is very unstable when illuminated with light corresponding to the wave length of the absorption maximum. It has been postulated that the trapped electron in the F-center absorbs a quantum of light and is raised to a 2p level which is still somewhat below the conduction band. In this excited state the electron receives sufficient energy from thermal sources to be raised to the conduction band. The electron then wanders through the lattice until it is again trapped. If the trapping occurs at some defect other than a single negative ion vacancy a new color center results and a band characteristic of the new center appears in the absorption spectrum

of the crystal. In referring to these bands and the centers giving rise to them, we shall use the notation given in Figure 2, wherein the letters identify both the absorption band and the color center.

During the illumination the M-band grows at approximately the same rate as that at which the F-band is diminishing. The M-band can also be reconverted to the F-band by illuminating with light of the M-band wavelength. However, there is a permanent loss of intensity in the F-band in this cycle. The loss has been associated with the appearance of the R_1 - and R_2 - bands which are optically stable (23, p.453, and 25, pp.8-13). Seitz has suggested that the centers responsible for the R_1 - and R_2 - and M-bands are those shown in (e), (f), and (d) of Figure 1 (33, pp.404-407). These centers may be considered to be the first aggregates of F-centers (5, pp.107-108).

When an additively colored alkali halide crystal is prepared at a high temperature and cooled slowly to room temperature the F-centers coagulate and form a "colloid" (which may or may not be colloidal in the usual meaning of the term). This "colloid" gives rise to a band such as that shown in Figure 2 for K-KI. These colloidal centers are in equilibrium with the F-centers over a limited range of temperatures (29, pp.344-345, and 31, pp. 985-986). When a crystal containing F-centers is

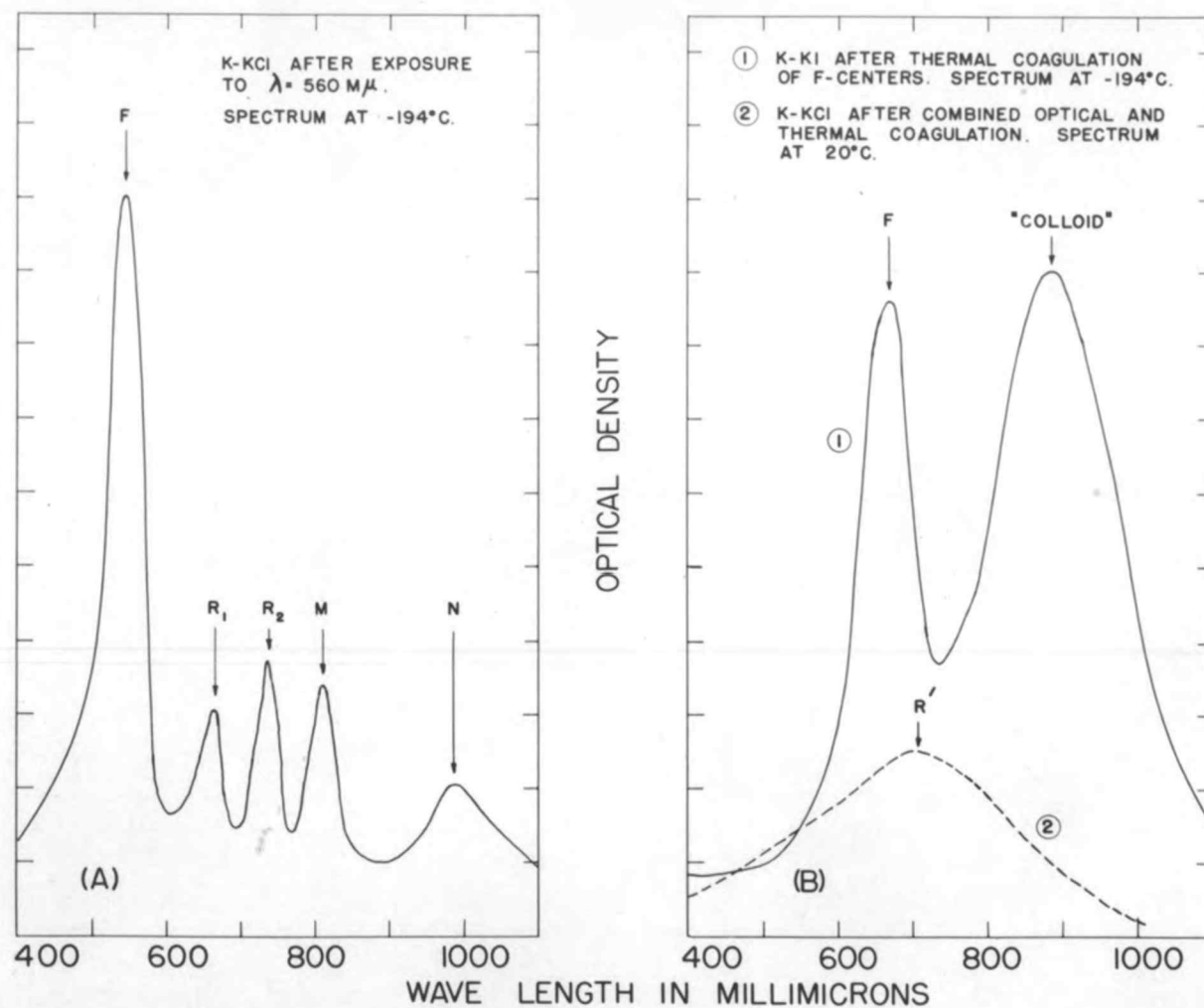


FIGURE 2. TYPICAL ABSORPTION BANDS IN ADDITIVELY COLORED ALKALI HALIDES.

heated and illuminated a broad absorption results which has been designated the R' band (29, p.341). This band has a contour similar to the F'-band reported by Pick (24, p.371).

Ueta has obtained evidence from studying the relative rates of bleaching of the M-band with polarized and nonpolarized light supporting the structure of the M-center given in Figure 1(d) (37, pp.107-109). There is at the present time very little information concerning the structures of the centers responsible for the N, R', and "colloidal" bands (29, p.346; 30, p.349; and 31, p. 986). Some arguments regarding the structure of the "colloid" centers will be presented in Chapter VI.

Properties of F-centers and F-bands of Interest in this Investigation

It has been established that the concentration of F-centers in the additively colored crystals is proportional to the pressure of the alkali metal vapor. Rögener has determined the proportionality constant at several temperatures for potassium chloride and potassium bromide. These results were used to calculate the energy of formation of F-centers (27, p.390). If the concentration of F-centers was not proportional to the vapor pressure of the alkali metal (and therefore to the number of atoms

per unit volume), the deBoer model for the F-center would have to be discarded. It is of interest to note that the model proposed by von Hippel ("self-trapped electron") requires that the excess metal ions and the resulting electrons be present in interstitial positions (38, pp. 680-687). If this model were correct, the concentration of F-centers would be proportional to the square root of the vapor pressure.

F-centers also have the property of existing in equilibrium with the "colloid" centers. This equilibrium is heterogeneous and is easily established for a range of temperatures (31, p.984). If the "colloid" is assumed to be the solid phase and the F-centers to be the dissolved phase, we may treat the equilibrium as a heterogeneous solubility problem. Applying the thermodynamic equation $d \ln K / dT = \Delta H / RT^2$, where K represents the equilibrium concentration of F-centers at the absolute temperature T, and ΔH is the heat of formation of the F-centers in the process "colloid" \rightarrow F-centers. It seems desirable to have information concerning this heat of formation of F-centers for all of the alkali halides. Such information may ultimately lead to a reasonable structure for the "colloid" centers.

Certain characteristics of the F-band are temperature dependent. For example, the width of the band

is directly related to the temperature of observation. This has been shown by Pohl (25, p.7). His results for KBr are shown in Figure 3. According to Mott and Gurney, the temperature broadening is given (theoretically) by $h\Delta\nu = (h\nu/kT)^{\frac{1}{2}}$, where ν is of the same order as the absorption frequency itself (18, p.116). The wave length of the F-band maximum shifts to higher energies as the temperature of observation is lowered. It would be of interest to calculate the magnitude of this energy shift using the de Boer model for an F-center and a suitable quantum mechanical method.

Information Sought in this Investigation

Eventually it is hoped that sufficient data will be accumulated so that exact structures can be assigned to the various color centers. At the present stage of the development of color center theories it seems desirable to have more information concerning the equilibria existing between different color centers in the same crystal. With this in mind, we turned to an investigation of the thermal stability of F-centers in K-KBr and K-KI since there was reason to believe that an equilibrium between F-centers and "colloid" centers existed in these additively colored crystals (31, p.986). More specifically, experiments were designed to obtain the

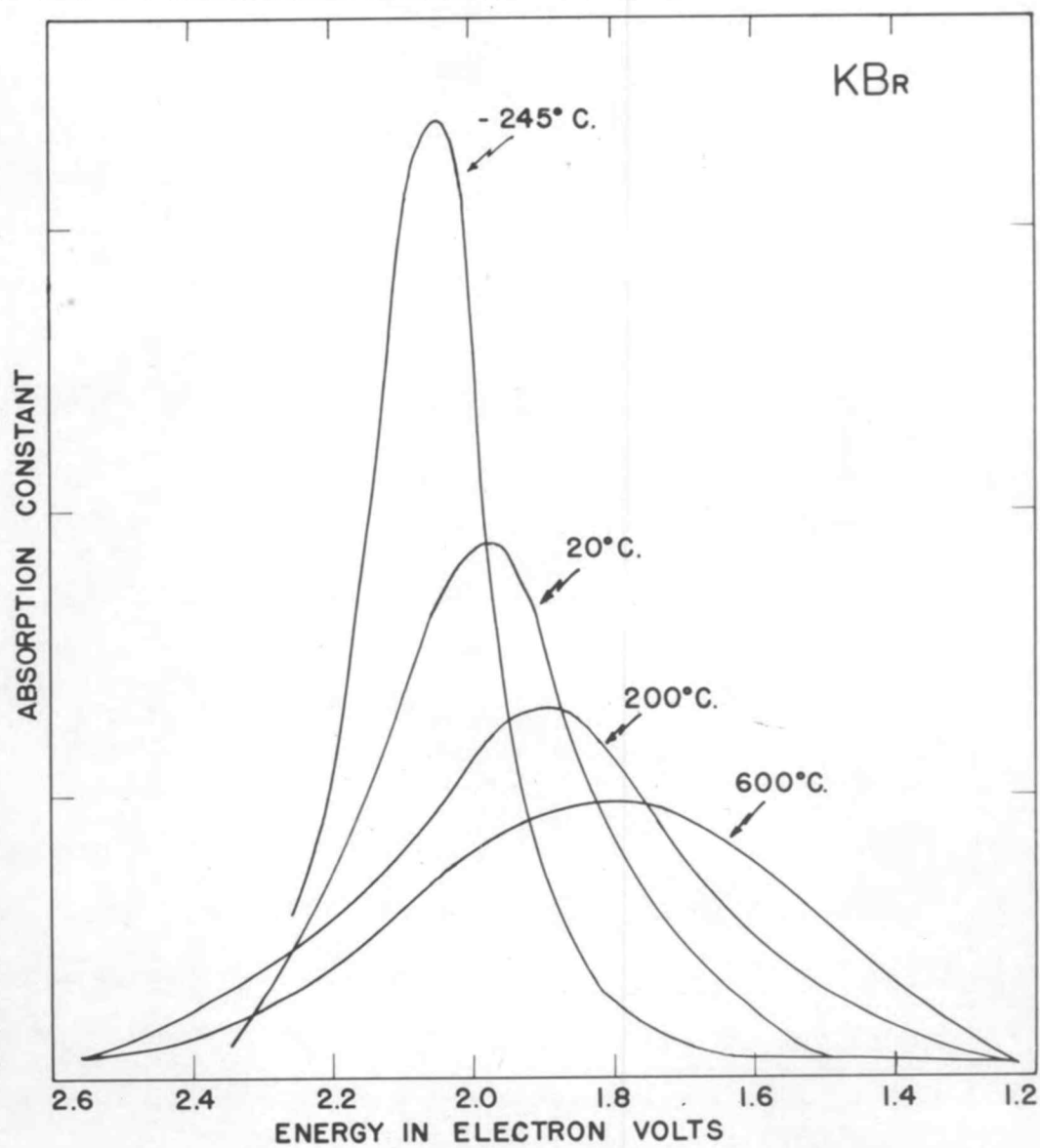


FIGURE 3. INFLUENCE OF TEMPERATURE ON THE ABSORPTION SPECTRUM OF ADDITIVELY COLORED KBr, AFTER POHL.

following information:

- (1) Temperature and concentration ranges for the equilibrium
- (2) F-center concentrations as a function of the temperature
- (3) The heat of formation of F-centers from "colloid" centers

The discovery of a new absorption band in K-KI led to many experiments of an exploratory nature in an effort to characterize the band and to determine some of its properties. These latter experiments are discussed in Chapter III.

Very little information of a quantitative nature is available concerning the relationship of M-centers to F-centers during the coloration process. It has often been reported that M-centers arise only through the optical destruction of F-centers. However, recent experiments indicate that M-centers are formed during the coloration process (31, p.986). More data are needed on this subject.

Experiments were conducted on nonhomogeneously colored KCl and KBr crystals in order to obtain the following information:

- (1) The distribution of F-centers and M-centers as a function of the distance from the crystal exterior
- (2) The relative concentrations of these centers as a function of the distance

(3) The identity of other centers present

Nonhomogeneously colored crystals were chosen in order to have a concentration gradient present. It was thought that if the F-center concentration plays any part in the formation of M-centers, such a role should be revealed by these measurements.

Much of the early theoretical work on color centers was devoted to arguments concerning the validity of the various models proposed for the F-center. The de Boer model survived these arguments and is widely accepted today. An electron trapped in the potential well of a negative ion vacancy should have one or more bound energy levels available to it, depending upon the depth of the well.

There has been considerable interest in the problem of calculating these energy levels using quantum mechanical methods. Mott and Gurney have pointed out that the field acting upon the electron near a lattice defect depends upon the wave function of the electron itself. Therefore, this wave function and the associated potential must be calculated by a self-consistent method (18, p.85).

Tibbs has calculated the energy levels for the F-center in additively colored sodium chloride (36, pp.1478-1484). His results show that the energy of the

1s-2p electronic transition corresponds very closely to the energy of the F-band maximum observed for NaCl. Simpson has used a different method of calculation and has shown that there is good agreement between the 1s-2p energy calculated and that observed for the F-band maximum (34, pp.274-278). Although Simpson used a more refined potential energy function than Tibbs used, his value for the F-band energy did not agree with the observed energy as closely as did Tibbs. In view of this fact, it was thought advisable to repeat Simpson's calculations for NaCl before extending the method to the other alkali halides of interest.

Calculations were carried out with the purpose of obtaining the following information:

- (1) Wave functions for the 1s and 2p states of the F-center in NaCl, KCl, KBr and KI at 20° C.
- (2) Energy values for 1s and 2p levels in the above crystals at 20° C.
- (3) Energy values for 1s and 2p levels in KCl at -194° C.
- (4) Electron density distribution curves
- (5) Thermal activation energies for electrons in the 2p state (to the conduction band)

The data obtained in (2) and (3) would give the theoretical locations of the F-band maxima. The information in (3) was desired for the purpose of calculating the theoretical

energy shift of the F-band maximum as a function of the temperature. These data could be compared with existing experimental values in order to check the accuracy of the method of calculation used. Indirectly the validity of the F-center model is also checked by these results.

Before discussing the experimental work it should be pointed out that quantitative measurements of color center concentrations are quite difficult. The most useful nondestructive method available is that developed by Smakula, and even this method is severely limited in its application. No justification of its use for color centers other than F-centers has been found.

Smakula Equation and Constants

Attempts to determine F-center concentrations in additively colored alkali halides by non-optical methods have been inconclusive (13, p.101 and 31, pp,983-984). Chemical methods cannot be used when the F-center concentration in crystals, which are to be used in subsequent experiments, is desired. In such instances a non-destructive method must be used.

Smakula has derived an equation for calculating F-center concentrations from constants obtained from optical absorption spectra (35, pp.604-607). This

equation is derived in a non-rigorous manner in the Appendix. The derivation shows the origin of the various quantities with which we will be concerned in the discussion which follows. For our purposes the equation may be written

$$n_0 f = 1.31 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{\max} W,$$

where n_0 = number of F-centers cm^{-3}

f = oscillator strength of the trapped electron

n = refractive index of the bulk material in the neighborhood of the F-band maximum

α_{\max} = extinction coefficient in cm^{-1}

W = width of the F-band in electron volts at half-maximum

Since insufficiently reliable values of the oscillator strength, f , (for electrons trapped in the various alkali halides) are not available, it was assumed to be unity in each case. This assumption introduces no complications since we are primarily interested in relative F-center concentrations. Concentrations reported in this thesis may be converted to absolute concentrations when oscillator strength values become available merely by dividing by the accurate f values. Detailed application of the equation to absorption spectra will be discussed later.

It is convenient to rewrite the equation in the form

$$n_0 = A \alpha_{\max} W ,$$

$$\text{where } A = 1.31 \times 10^{17} \frac{n}{(n^2 + 2)^2}$$

Table 1 shows values of A for several alkali halides at 20°C. and at -194°C. It should be pointed out that both α_{\max} and W are temperature dependent as well as the quantity A.

Table 1. Smakula equation constant for
F and M bands in alkali halides.¹

Temperature - 20° C.

| Salt | Band | Band Maximum μμ | Refractive Index n | Smakula Equation Constant $A \times 10^{-16}$ |
|------|------|-----------------------|-----------------------|--|
| KCl | F | 560 | 1.492 | 1.094 |
| | M | 825 | 1.483 | 1.102 |
| KBr | F | 625 | 1.557 | 1.042 |
| | M | 930 | 1.546 | 1.051 |
| KI | F | 700 | 1.654 | 0.966 |
| | M | 1060 | 1.638 | 0.978 |

Temperature -194° C.

| | | | | |
|-----|---|------|-------|-------|
| KCl | F | 540 | 1.500 | 1.088 |
| | M | 805 | 1.491 | 1.095 |
| KBr | F | 605 | 1.566 | 1.035 |
| | M | 905 | 1.553 | 1.045 |
| KI | F | 670 | 1.583 | 1.021 |
| | M | 1030 | 1.545 | 1.052 |

¹The refractive index at -194° C. was obtained by using Harting's values at 20° C. and the temperature coefficient of refractive index dn/dt (8, pp.125-131).

Values of α_{\max} are obtained from the measured optical densities by use of the following equation

$$\alpha_{\max} = 2.303 D_{\max}/d$$

where d = thickness of crystal in cm

D_{\max} = optical density at band maximum

It was observed that the width of the absorption band at half-maximum varied with individual samples of the same crystal. Therefore, for purposes of calculating F-center concentrations it was decided to use an average value for W . By measuring a large number of absorption bands it was possible to reduce the probable error in W to less than one per cent for the 20° C. spectra. These average values for W are given in Table 2. Molnar has obtained values which differ considerably from these (17, p.54).

Table 2. Average values for half-width of F-bands in some alkali halides.

| Crystal | Band Designation (Temperature) | Wave Length mμ | Number of Observations | \bar{W} e.v. | Avg. Dev. | Probable Error in the Mean |
|---------|-----------------------------------|-------------------|---------------------------|-------------------|-----------|-------------------------------------|
| KCl | F 20° | 560 | 30 | 0.359 | 0.013 | 0.002 |
| KBr | F 20° | 625 | 35 | 0.374 | 0.014 | 0.002 |
| KI | F 20° | 700 | 14 | 0.438 | 0.018 | 0.004 |
| KI | F-194° | 670 | 19 | 0.234 | 0.020 | 0.004 |

CHAPTER II

THERMAL STABILITY MEASUREMENTS AND
EXPERIMENTAL TECHNIQUESCrystal Preparation

Additively colored alkali halide crystals were prepared by heating the alkali halide in an atmosphere of potassium vapor. Single crystals of potassium chloride, potassium bromide, and potassium iodide were obtained from the Harshaw Chemical Company. These crystals were of random size and were used without further treatment.

The apparatus used in preparing the additively colored crystals is shown in Figure 4. A Pyrex bomb, having the dimensions shown in (a) of Figure 4, was charged with approximately one and one-half grams of potassium metal and the crystal to be colored. Crystals about 8 x 8 mm in cross-section and up to 2 cm in length were colored satisfactorily in these bombs. The copper strip held the crystal in position in the upper compartment of the furnace shown in Figure 4(b).

This furnace was modeled after one used by Rögener (27, p.387). The two compartments were wound separately with Nichrome wire and their temperatures were controlled independently by Powerstats. An arrangement of this type

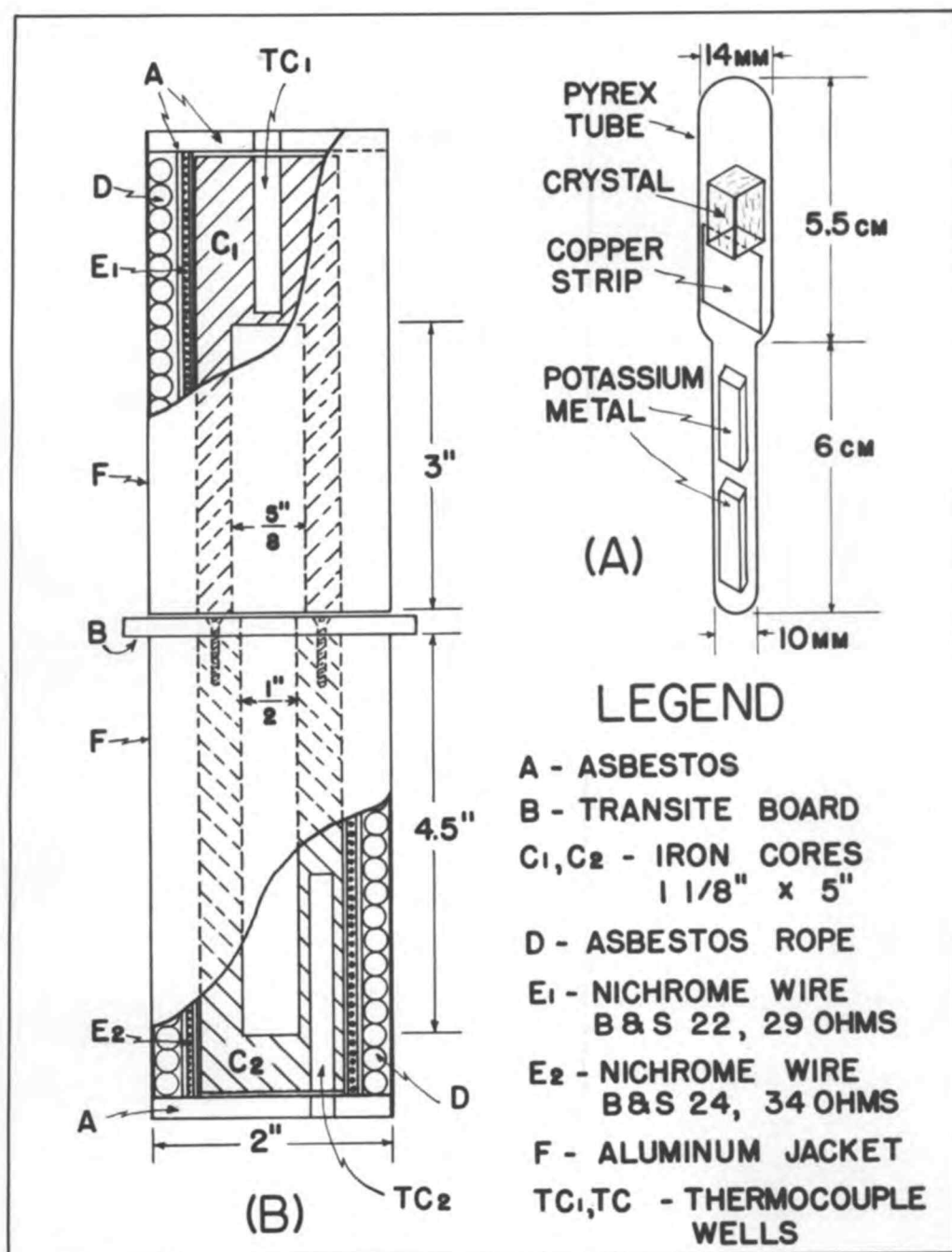


FIGURE 4. APPARATUS USED IN PREPARATION OF ADDITIVELY COLORED CRYSTALS.

was very convenient since it permitted the crystal to be heated to a much higher temperature than the potassium metal. By so doing, the time necessary for establishing an equilibrium concentration of color centers in a given crystal at a specific temperature was reduced. The temperature of the lower compartment determined the vapor pressure of the potassium and therefore the final concentration of color centers since a definite proportionality exists between the concentration of alkali metal atoms in the vapor and color centers in the crystal (15, p.59).

After cooling to room temperature outside the furnace, the bombs were broken and the crystals removed. Fairly rapid cooling was achieved by placing the Pyrex bomb in a copper tube immediately after removing from the furnace. The crystals were washed in absolute ethanol to remove any potassium metal on the surfaces. After drying, the crystals were stored in light-tight containers in a desiccator.

Tables 3 and 4 give details of preparation for additively colored potassium bromide and potassium iodide. Since homogeneously colored crystals were needed for the thermal stability measurements, most of the crystals were heated in the bombs for periods of time much longer than the time necessary for establishing a saturation

Table 3. Preparation details for homogeneously colored potassium bromide. Crystals 1 and 2 were prepared in a copper tube.

| Crystal Number | Original F-center Concentration $\times 10^{-17}$ | Temperature $^{\circ}\text{C.}$ | | Heating Time in Hours |
|----------------|--|---------------------------------|-----------|-----------------------|
| | | Crystal | Potassium | |
| 1 | 3.28 | 420 | 420 | 48 |
| 2 | 2.33 | 430 | 430 | 50 |
| 3 | 0.92 | 595 | 435 | 5 |
| 4 | 1.08 | 596 | 412 | 26 |
| 5 | 0.32 | 598 | 385 | 49.5 |
| 6 | 3.38 | 599 | 414 | 45.5 |
| 7 | 2.10 | 590 | 420 | 14 |
| 8 | 4.78 | 620 | 460 | 42 |
| 9 | 7.01 | 600 | 450 | 33 |
| 10 | 1.95 | 590 | 420 | 39 |
| 11 | 2.34 | 650 | 435 | 76 |
| 30 | 3.29 | 600 | 445 | 86.5 |

Table 4. Preparation details for homogeneously colored potassium iodide.

| Crystal Number | Original F-center Concentration $\times 10^{-17}$ | Temperature $^{\circ}\text{C.}$ | | Heating Time in Hours |
|----------------|--|---------------------------------|-----------|-----------------------|
| | | Crystal | Potassium | |
| 12 | 0.6 | 610 | 400 | 47 |
| 13 | 3.94 | 630 | 445 | 73 |
| 14 | 1.31 | 590 | 415 | 90.5 |
| 15 | 0.6 | 590 | 390 | 78 |
| 16 | 1.67 | 590 | 410 | 169 |
| 17 | 2.25 | 590 | 390 | 260 |
| 18 | 3.88 | 595 | 450 | 118 |
| 19 | 5.21 | 595 | 457 | 129 |
| 20 | 1.96 | 600 | 445 | 86.5 |
| 21 | 0.75 | 600 | 415 | 48 |
| 22 | 1.65 | 600 | 415 | 90.5 |
| 23 | 2.96 | 590 | 390 | 168 |
| 24 | 0.59 | 590 | 390 | 240 |
| 29 | 0.37 | 590 | 415 | 36 |

concentration of color centers. A few crystals displayed homogeneous center sections and more dense edges. These were used after removing the nonhomogeneous part.

Table 5 shows preparation details of nonhomogeneously colored crystals. These crystals were prepared in order to study the relative distribution of the color centers as a function of the distance from an external surface.

Table 5. Preparation details for non-homogeneously colored alkali halides.

| Crystal Number | Original F-center conc. $\times 10^{-17}$ | Temperature $^{\circ}\text{C}$ | | Heating Time |
|----------------|---|--------------------------------|-----------------|--------------|
| | | Crystal | Potassium Metal | |
| KCl 25 | 2.66 to 0.80 | 600 | 445 | 4.5 hrs. |
| KCl 26 | 3.54 to 0.47 | 600 | 445 | 4.0 hrs. |
| KBr 27 | 0.65 to 0.19 | 600 | 445 | 15 min. |
| KBr 28 | 1.91 to 0.36 | 600 | 445 | 30 min. |

Absorption Spectra Measurements at Room Temperature and at -194°C .

All of the absorption spectrum measurements were made with a Beckman quartz spectrophotometer, model DU. Samples were prepared for reading by cleaving thin sections (from 0.2 to about 1 mm. in thickness, depending on the maximum optical density expected) from the particular

crystal under examination. These thin sections were obtained by placing the crystal on a flat surface and using a razor blade as the cleaving instrument. Patience and careful manipulation were necessary to obtain the thinner sections. The colored crystals were handled under red light or under subdued room light.

The sample was then cemented to the aperture plate, shown in Figure 5(a), with Duco cement. These plates had apertures about 0.7 by 2.0 mm. in size and were made from thin brass. In Figure 5(b) is shown the holder which supported the plate (a) in the Beckman DU cell carrier. These holders were made from Bakelite and had the dimensions shown. It was found convenient to use three of these holders in the cell carrier simultaneously thus making it possible to read the optical densities of three crystals with only one setting for 100 per cent transmission. The phosphor-bronze clip was cemented to the holder and permitted easy mounting and manipulation of the aperture plate. In order to obtain a correct measurement of the absorption beyond the F-band maximum, it was found necessary to make the measurements from 1100 millimicrons toward 400 millimicrons. If the measurements had been made in the opposite direction, some of the F-centers would have been converted to R_1 -, R_2 -, and M-centers and the resulting absorption spectrum would

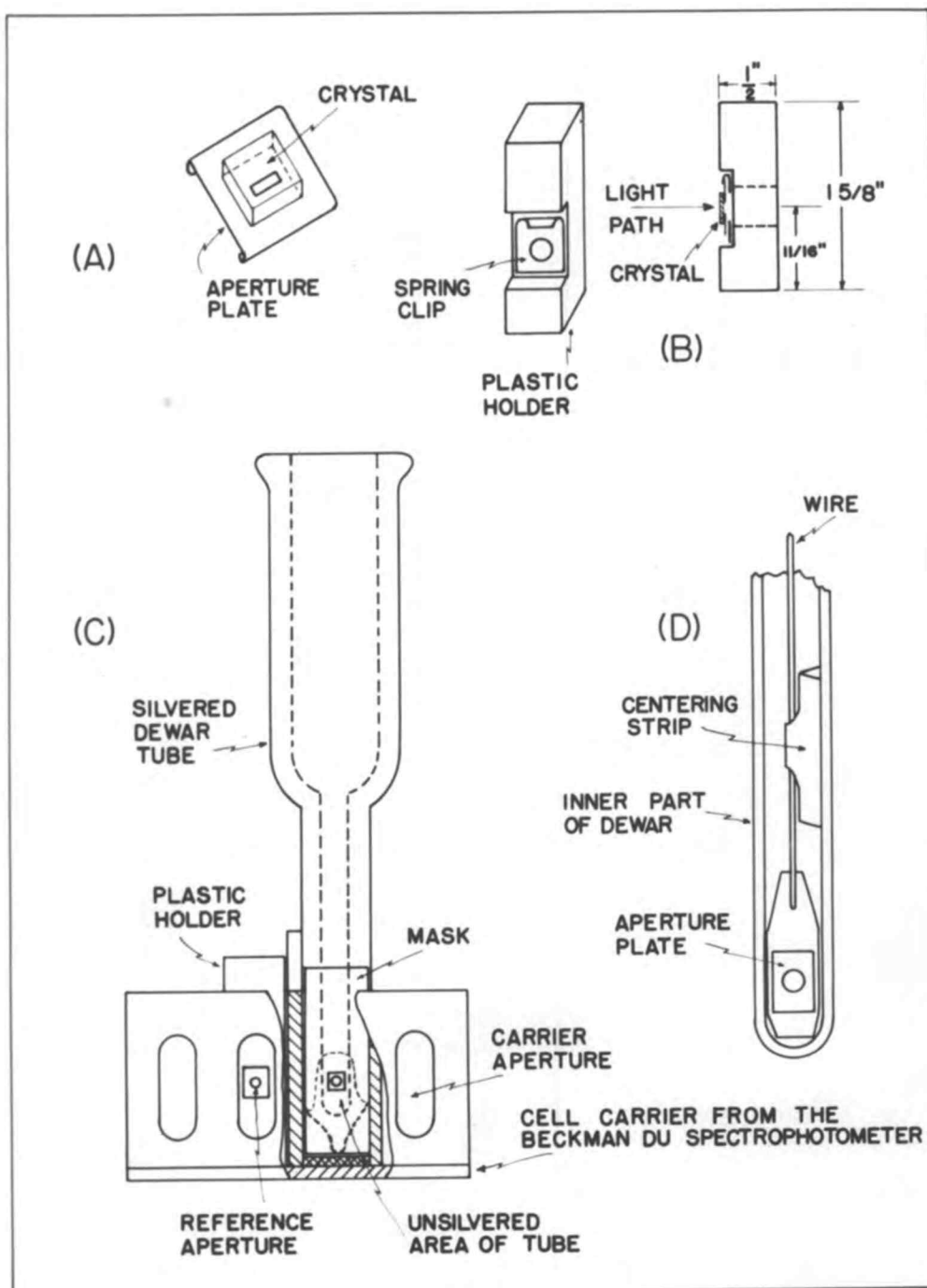


FIGURE 5. CRYSTAL HOLDERS AND APPARATUS FOR DETERMINING ABSORPTION SPECTRA OF CRYSTALS IN AIR AND IN LIQUID NITROGEN.

have represented the absorption due to the initial centers present plus the centers produced by optical destruction of the F-band.

In order to measure absorption spectra at the temperature of liquid nitrogen (-194°C.), it was necessary to employ a crystal mount which could be immersed in liquid nitrogen contained in a Dewar type tube (29, p.343). This tube was made to fit snugly into the cell-carrier supplied with the Beckman DU spectrophotometer. That portion of the tube in the light path was unsilvered. A light-tight box was provided to cover the cell-carrier compartment and the Dewar tube, which protruded from the compartment some four inches. The box was $7\frac{1}{2}$ inches high, $5\frac{1}{2}$ inches wide, and 3 inches deep. A mask as shown in Figure 5(c) was used to confine the light beam to a definite area in the cell holder aperture. Immediately behind the square aperture in this mask the crystal holder (d) of Figure 5 was positioned by means of the wire. The reference aperture plate was adjusted to occupy the same relative position when shifted into the light beam.

Samples were prepared as described above and cemented to the aperture plate of (d), Figure 5. The Dewar tube was cleaned and dried, then filled with liquid nitrogen previously filtered through cotton to remove solid carbon dioxide and ice. Streams of small

bubbles rose from the bottom of the tube and were eliminated by scrubbing the inside of the tube with a cotton swab. The holder, bearing the crystal, was immediately placed in position for reading. Very little trouble was experienced from bubbles after using this procedure. Optical density values were read from 1100 to 400 millimicrons in 25 millimicron steps except in regions of the spectrum near absorption maxima. Near these maxima, readings were taken every 10 millimicrons.

Method Used to Calculate F-Center Concentrations

In order to calculate F-center concentrations it was necessary to know the thickness of the absorbing medium. Thicknesses were measured by means of a microscope provided with a calibrated micrometer eyepiece and a 10 X objective. The crystal sample was cleaved along a plane parallel to the light path and at a point in the center of the beam. Measurements of the thickness were made at three different positions and the average value taken.

Optical density values were plotted against corresponding wave lengths in millimicrons. See Figure 6 for a typical example. The following procedure was used in determining the F-center concentration from the absorption curve and the appropriate Smakula equation:

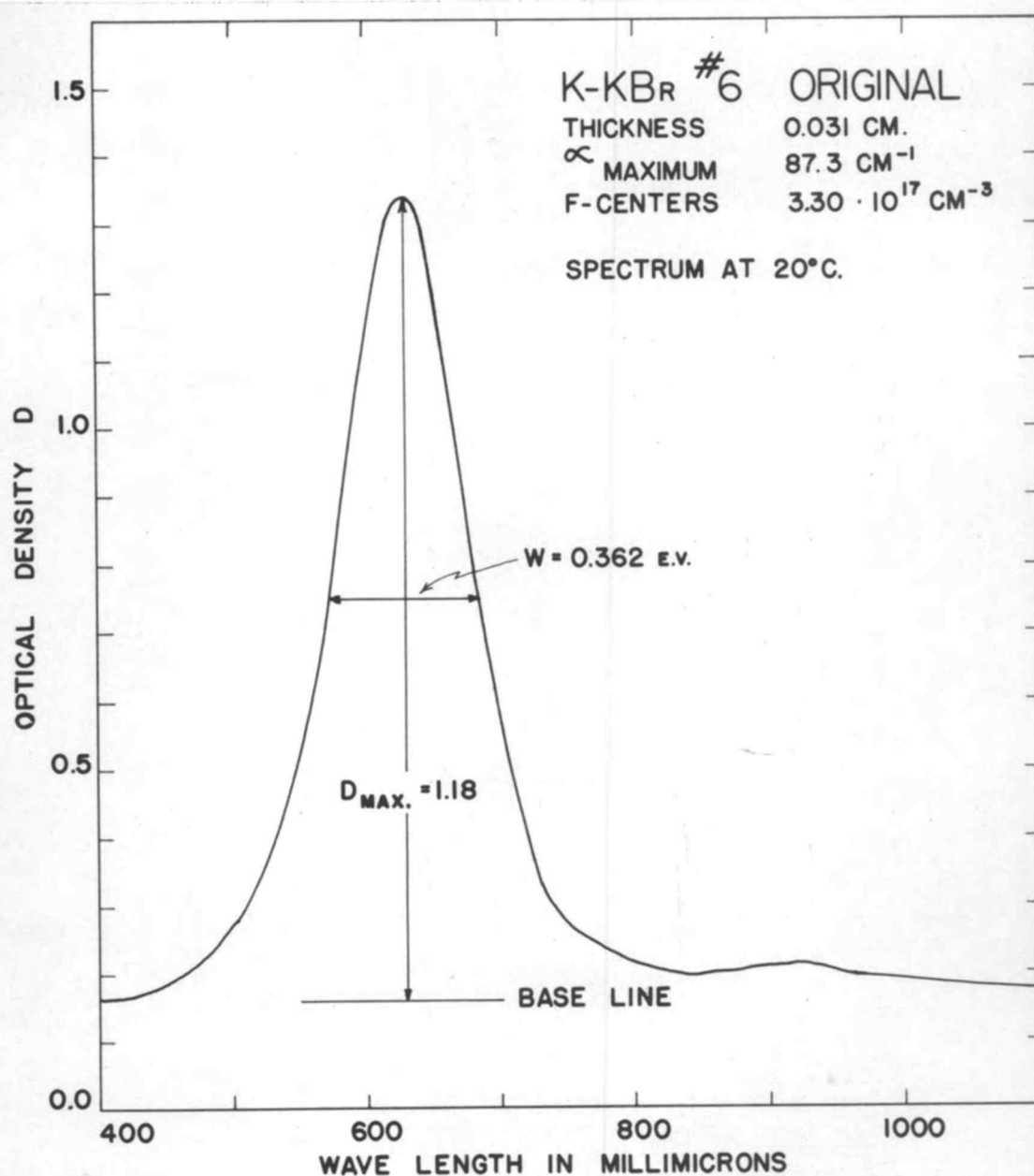


FIGURE 6. TYPICAL F-CENTER ABSORPTION BAND.

- (1) A base line, representing no absorption, was determined and drawn on the plot of optical density against wave length. Figure 7 shows the results of several measurements, which were made in order to determine the behavior of the various apertures and the effect of several materials on the optical density readings. It was observed in some previously reported experiments on potassium chloride that a reliable base line could be established by examining the spectrum in the region near 1000 millimicrons (31, p.984). This procedure holds only in the case where the F-band is not seriously distorted by the colloidal band. In cases where distortion occurred, the base line for the F-bands was determined by (a) assuming the colloidal band to be symmetrical, (b) drawing a vertical line through the center of the colloidal band, (c) constructing a mirror image of the long wave length portion of the band about this center line, and (d) taking the intersection of this constructed curve with the vertical line through the F-band maximum as the F-band base line. Reference to Figure 8 should make this procedure clear.
- (2) The value of D_m was obtained by subtracting the D value at the base line from the maximum D value, that is, at the center of the F-band. Using the equation $\epsilon_m = 2.303 \frac{D_m}{d}$, where d = thickness of the crystal in centimeters, gave the correct value of the extinction coefficient to be used in the Smakula equation.
- (3) Since the width of the absorption band at half its maximum height should be a constant at a given temperature, an average value for W was employed. These widths have been tabulated previously.
- (4) Insufficient reliable data are available concerning oscillator strength values; hence, f was assumed to be unity in each case.

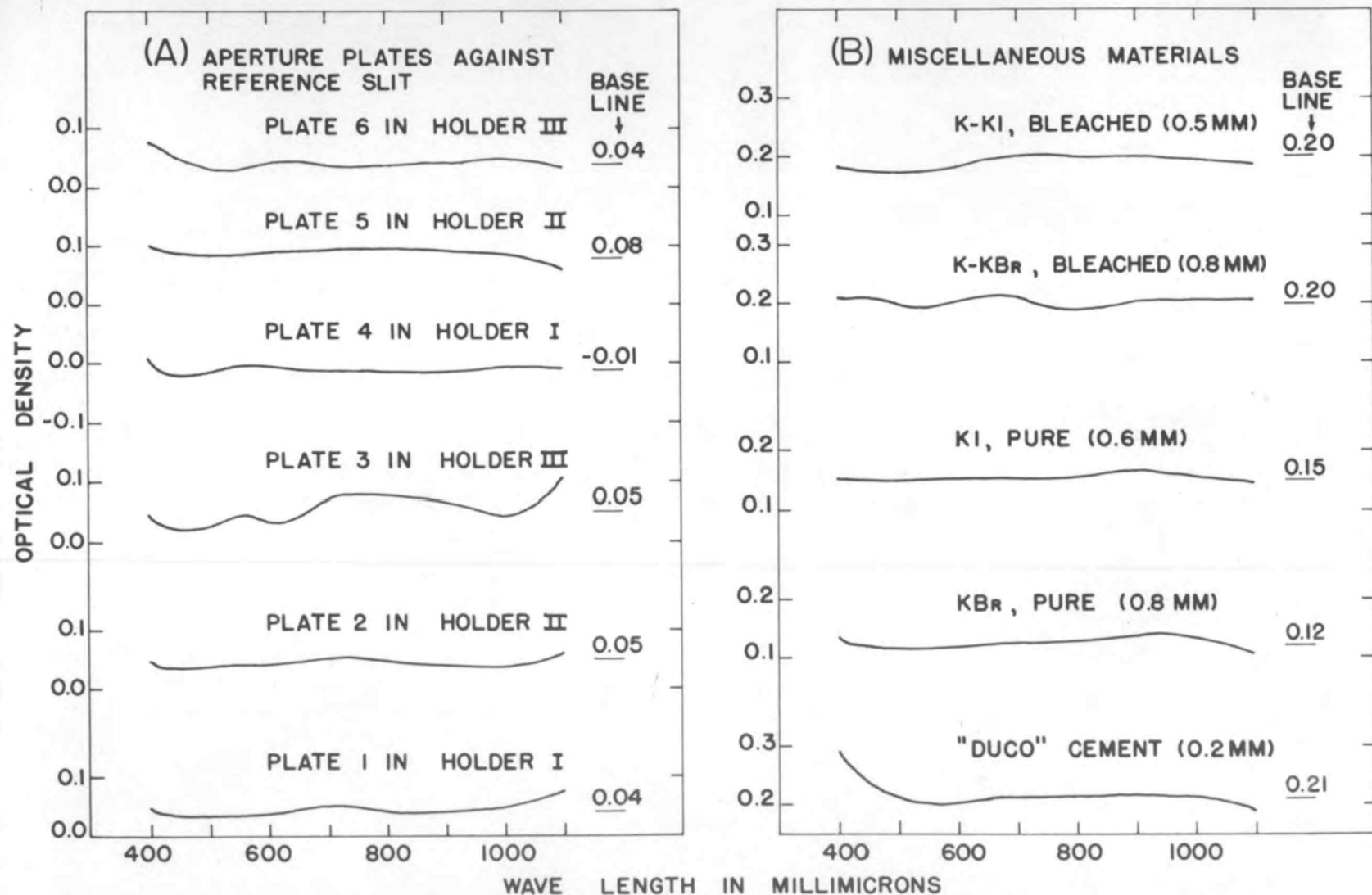


FIGURE 7. OPTICAL DENSITY CURVES FOR VARIOUS APERTURE PLATES AND OTHER MATERIALS.

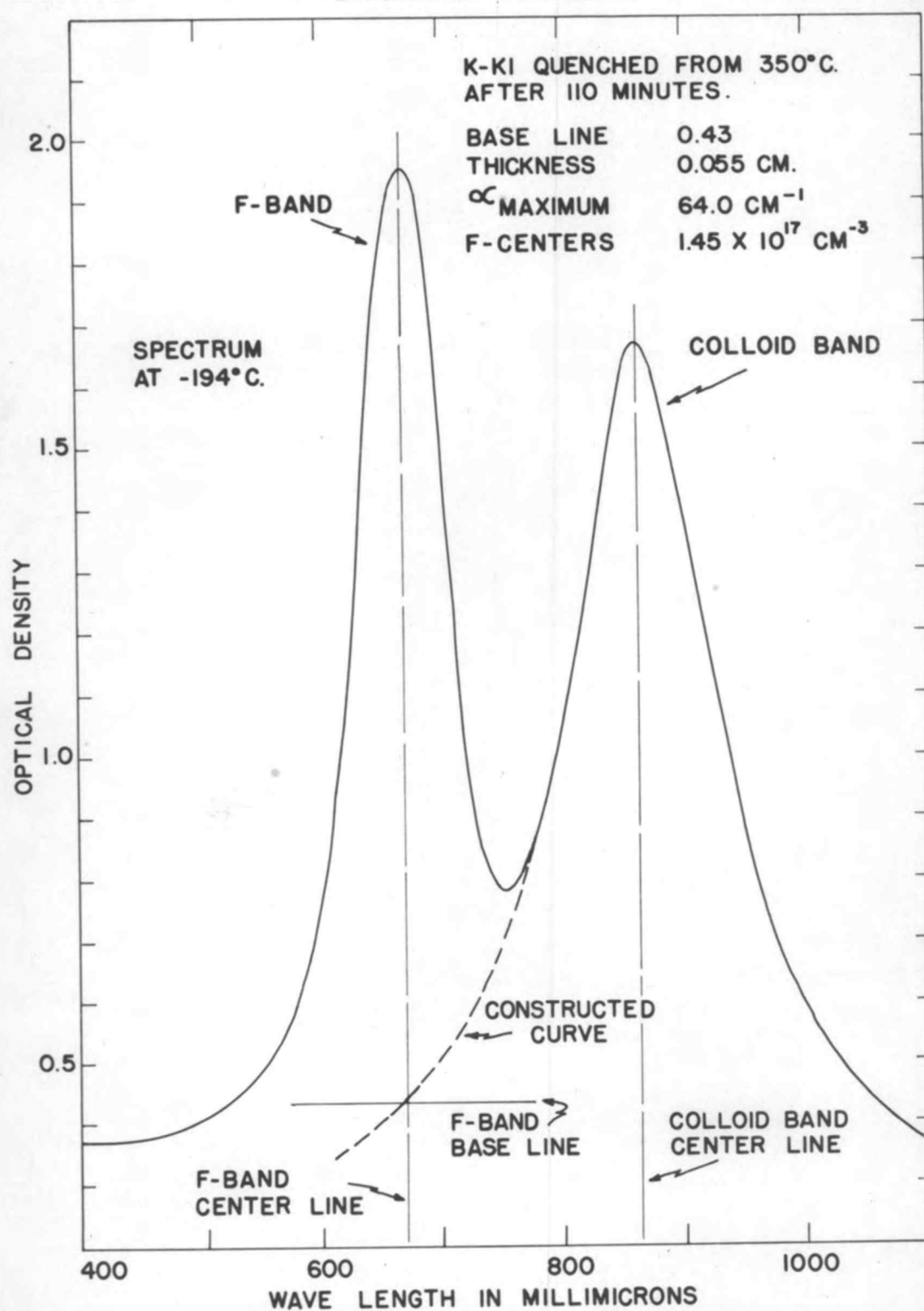


FIGURE 8. TYPICAL ABSORPTION CURVE SHOWING F-BAND AND COLLOID BAND OVERLAP.

- (5) Finally, these experimentally determined quantities were used in the Smakula equation,

$$n_0 = A \alpha_m W, \text{ to get F-center concentrations.}$$

Thermal Stability of F-centers in Potassium Bromide

Additively colored potassium bromide samples were prepared by the method previously described. These stock samples were stored in light-tight containers in a desiccator. The method used for determining the thermal stability of F-centers in alkali halides was developed in experiments on potassium chloride (31, p.985). Briefly, this method may be outlined as follows:

- (1) Additively colored crystals of potassium bromide were selected which had color center densities within the limits imposed by the cleaving technique and the spectrophotometer.
- (2) Samples of these crystals were wrapped in copper or aluminum foil and placed in a muffle furnace, previously brought to the temperature required for the experiment. After a suitable time interval, these samples were removed and immediately dropped into carbon tetrachloride, usually at room temperature. The time interval was long enough to insure that equilibrium had been established.
- (3) These quenched samples were stored in light-tight containers and sections were used for absorption spectrum measurements.
- (4) The absorption spectra yielded values of α_{\max} , which were then used in the Smakula equation to give F-center concentrations.

This would appear to be a straightforward procedure. However, many exploratory experiments were performed in order to establish its reliability. Below are listed some of the factors which were given consideration:

- (a) The possible effect of the metallic foil. Platinum, copper, and aluminum foils were used and no change in the absorption spectrum was observed.
- (b) The possible effect of the quenching medium. Several quenching media were investigated among which were mercury, a saturated solution of the halide being used, and carbon tetrachloride. The mercury and saturated salt solutions caused excessive shattering of the crystal. However, samples quenched in these media had spectra which were identical with the spectrum obtained from samples quenched in carbon tetrachloride. Since carbon tetrachloride did not cause the crystals to shatter and had no apparent effect on the spectrum, it was used in preference to the other media.
- (c) The possible effect of the rate of cooling on the final F-center concentration. At the higher temperatures this effect may be important since the heating periods are not long compared to the time required for cooling to room temperature. At lower temperatures, the heating time is so much longer than the cooling time that any change in F-center concentration resulting from slow cooling would be negligible.
- (d) The effect of bleaching on F-center concentration. This effect was minimized by using interior sections of the crystals which showed no visible bleaching, and, if bleached areas were observed in the crystals while making thickness measurements with the microscope, the resulting values for F-center concentration were discarded.

The muffle furnace was controlled automatically by means of a TEMCO control unit. Temperatures were measured by a Chromel-Alumel thermocouple and microvoltmeter. The lower temperatures were checked with a mercury-in-glass thermometer. Temperatures reported are correct within 5° C.

In order to be sure that a true equilibrium between F-centers and colloidal centers was established at any given temperature, it was found necessary to run a series of experiments in which the heating time was increased until the F-center concentration showed no further change. The equilibrium for a given temperature was approached from opposite directions by using crystals containing F-centers for one series of samples and crystals containing colloidal centers for another series. The F-center concentrations determined in this manner were the same within experimental error.

The values of F-center concentration listed in Table 6 are those obtained from crystals which showed no nonhomogeneous areas and were free from cracks and bubbles. No colloidal band was formed at 400° C. but the results are included for completeness. The average of the eighteen values at 309° C. was taken since there was no significant difference for the various heating times.

Table 6. Equilibrium concentration of F-centers in potassium bromide at various temperatures and for various heating times.

| Temperature °C. | Heating Time-- Minutes | F-Center Concentration $\times 10^{-17} \text{ cm}^{-3}$ | | | Average F-Center Concentration $\times 10^{-17} \text{ cm}^{-3}$ |
|--------------------|------------------------------|--|-------|-------|---|
| 400 | 15 | 0.945 | 0.504 | 0.667 | No colloidal band present. |
| | | 1.480 | 0.484 | 5.570 | |
| | | 2.860 | 1.170 | | |
| 350 | 100 | 2.743 | 3.200 | | |
| | 120 | 3.046 | 3.225 | | 3.053 |
| 340 | 120 | 2.54 | 2.29 | 2.68 | |
| | | 2.41 | 2.20 | | 2.42 |
| | 180 | 2.51 | 2.63 | 2.69 | 2.61 |
| 325 | 180 | 2.01 | 1.92 | 2.42 | |
| | | 1.92 | 2.06 | 1.82 | |
| | | 1.64 | | | 1.97 |
| 318 | 180 | 1.76 | 1.72 | 1.88 | |
| | | 1.62 | 1.70 | | 1.74 |
| 309 | 90 | 1.503 | | | |
| | 120 | 1.477 | 1.292 | 1.550 | |
| | | 1.477 | 1.370 | 1.580 | |
| | | 1.344 | | | 1.441 |
| | 180 | 1.762 | 1.829 | 1.599 | |
| | | 1.508 | 1.755 | 1.386 | 1.640 |
| 283 | 500 | 1.344 | 1.480 | 1.230 | |
| | | 1.577 | | | 1.408 |
| | | | | | |
| 230 | 1035 | 0.97 | 1.07 | 0.93 | |
| | | 1.27 | | | 1.06 |
| 230 | 1035 | 0.512 | 0.523 | 0.466 | |
| | | 0.473 | 0.527 | 0.562 | |
| | | 0.689 | 0.512 | 0.639 | 0.545 |

Table 7 shows the average values of F-center concentration for the temperature range 230° - 350° C. The error listed in the last column is the mean probable error given by $\frac{0.845 \text{ (Average Deviation)}}{(N-1)^2}$ where N is the number of observations. A plot of $\log_{10} [F] - 16$ against $1/T$ is shown in Figure 12 where $[F]$ is the average F-center concentration $\times 10^{-17}$ and T is the absolute temperature. The slope of the curve gives the heat absorbed for the process "colloid" \rightarrow F-centers by use of the equation

$$\Delta H = 2.303 R \times 10^3 (\text{Slope}) \text{ Kcal/mole, where } R \text{ is } 1.987 \text{ cal/deg mole.}$$

Table 7. Equilibrium concentrations of F-centers in potassium bromide as a function of temperature.

| Temperature °C | Number of Values | Average F-center Concentration $\times 10^{-17} \text{ cm}^{-3}$ | Average Devia- tion | Probable Error in the Mean |
|-------------------|---------------------|---|---------------------------|----------------------------------|
| 350 | 4 | 3.05 | ± 0.16 | ± 0.08 |
| 340 | 8 | 2.49 | ± 0.14 | ± 0.05 |
| 325 | 7 | 1.97 | 0.17 | 0.06 |
| 318 | 5 | 1.74 | 0.07 | 0.03 |
| 309 | 18 | 1.50 | 0.15 | 0.03 |
| 283 | 4 | 1.06 | 0.11 | 0.05 |
| 230 | 9 | 0.545 | 0.06 | 0.018 |

In Figure 9 are shown absorption curves for a series of additively colored potassium bromide crystals of varying initial concentration. These crystals were quenched from 309° C. The curves in Figure 10 are those

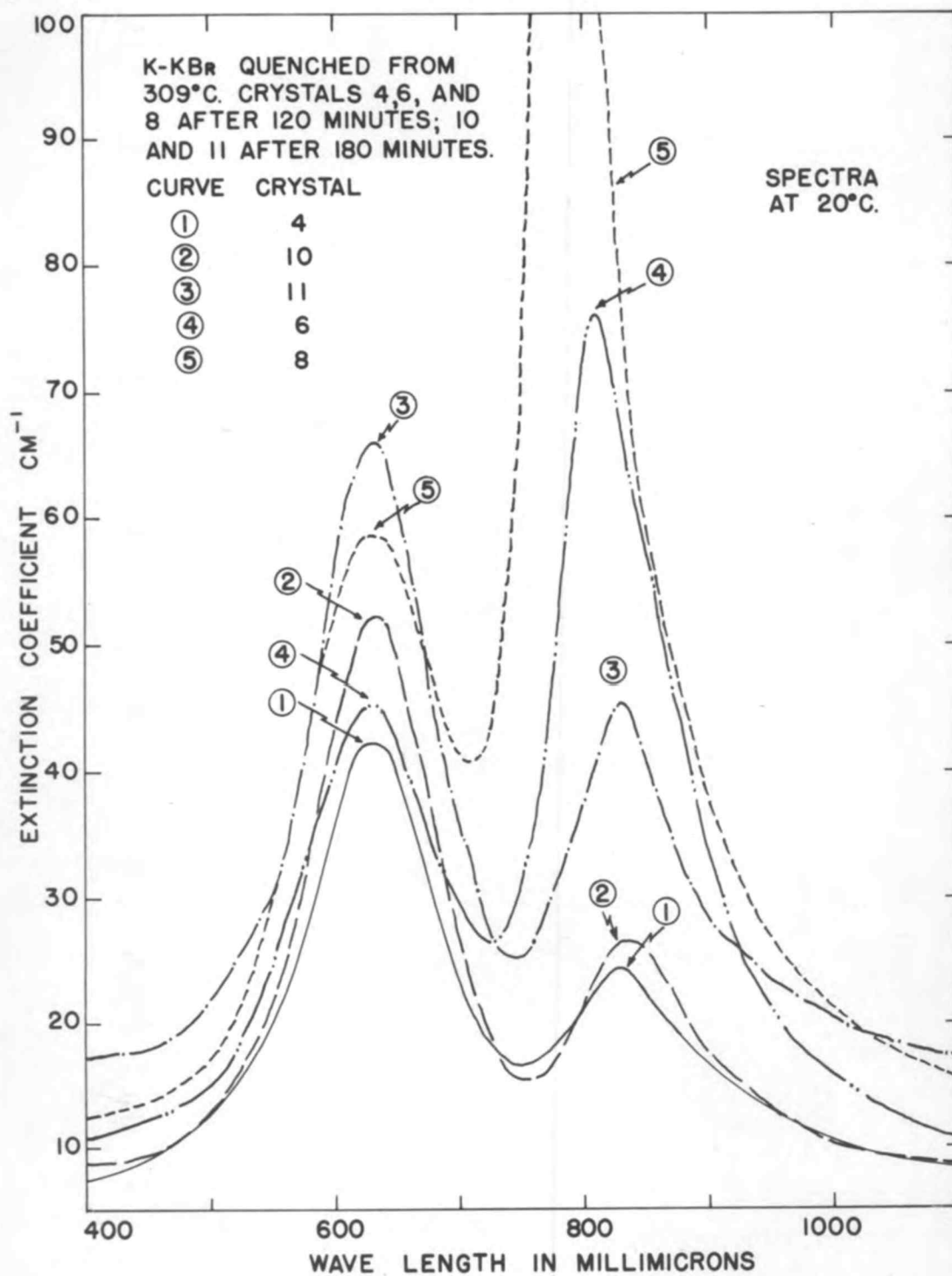


FIGURE 9. ABSORPTION CURVES FOR A SERIES OF K-KBr CRYSTALS OF VARYING INITIAL CONCENTRATION.

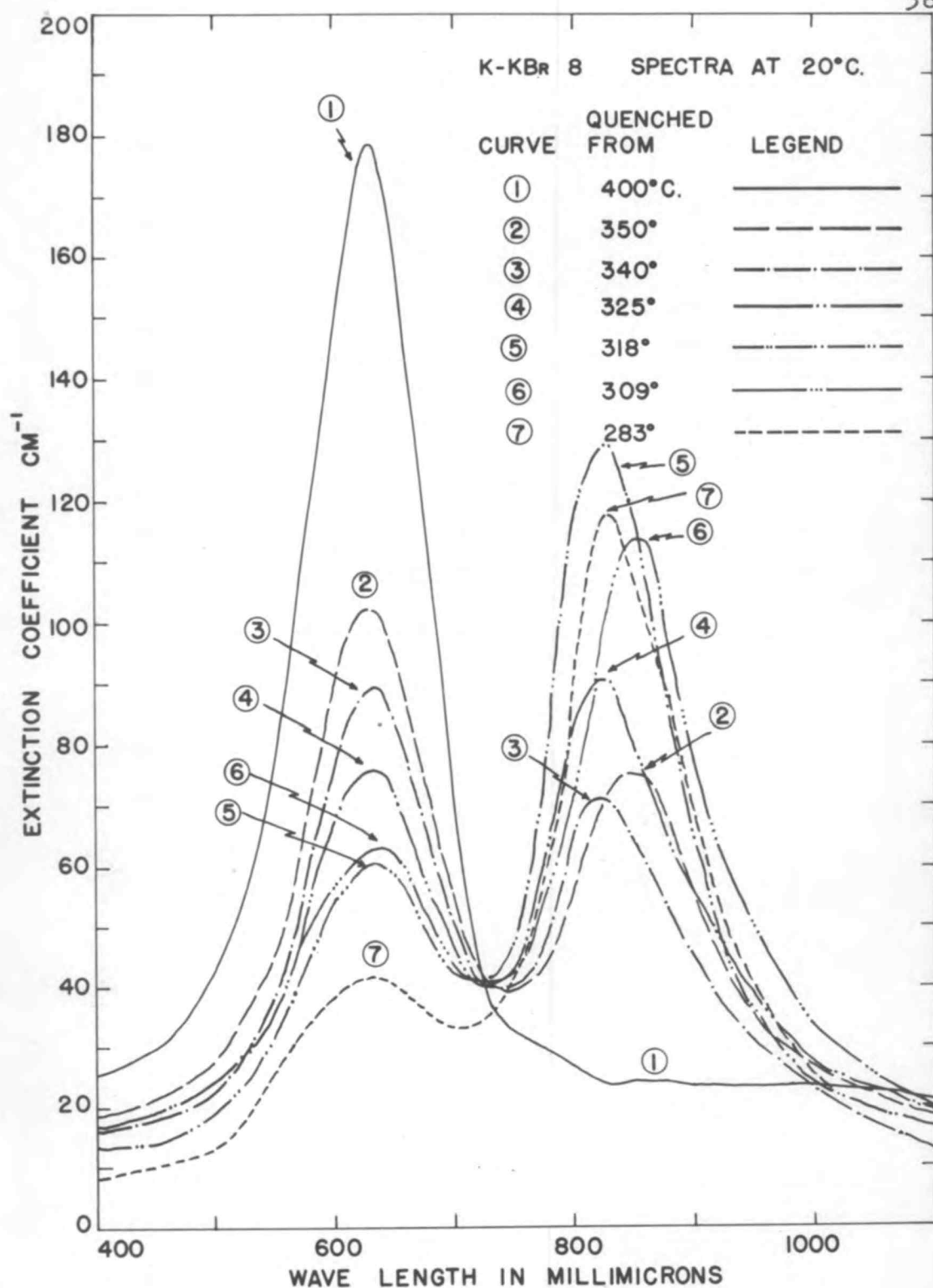


FIGURE 10. VARIATION OF F-CENTER STABILITY WITH THE TEMPERATURE FOR A SERIES OF K-KBr CRYSTALS OF THE SAME INITIAL CONCENTRATION.

for one crystal (K-KBr #8) quenched from the temperatures indicated.

Thermal Stability of F-centers in Potassium Iodide

Preliminary experiments were conducted on crystals 12, 13, 14, 15, 16, and 17 in order to determine temperature and concentration limits for the equilibrium. It soon became apparent that the 20° C. absorption spectra could not be used because of the overlapping of the colloidal band and the F-band. This overlapping prevented an accurate determination of the F-center concentration. Typical spectra taken at 20° C. are shown in Figure 11. The low temperature (-194° C.) spectra were examined and found to be suitable for determining F-center concentrations. These spectra are also shown in Figure 11. Of the six crystals listed above, three were found to have original concentrations much too low to be used in the equilibrium measurements. These were replaced with crystals having higher initial concentrations, that is by 18, 19, and 20.

Interpretation of absorption curves of some of the additively colored potassium iodide crystals was further complicated by the appearance of an unexpected band between 650 and 670 millimicrons. Several of these bands are shown in Figure 11 (f). At first these bands were

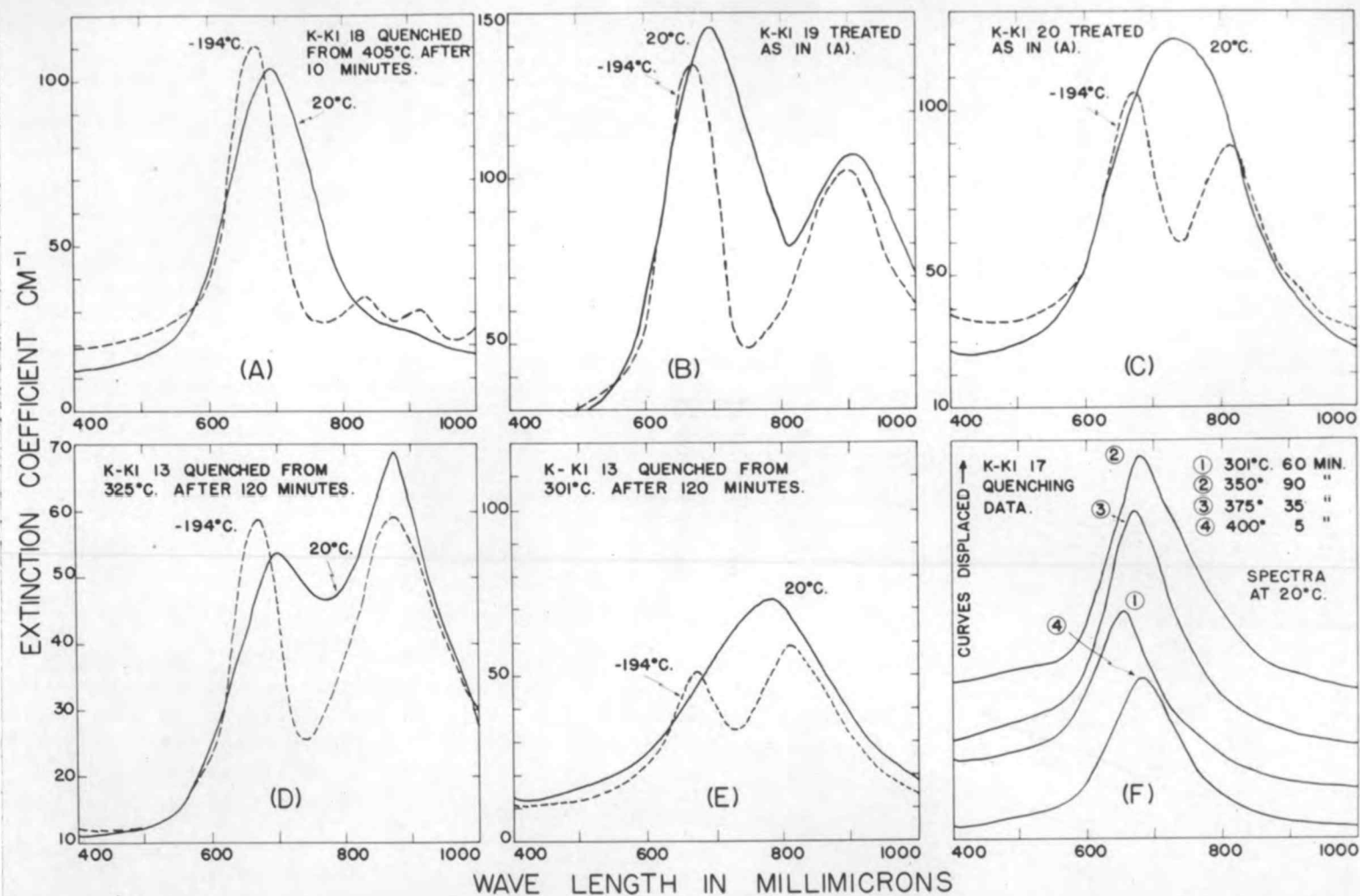


FIGURE 11. ABSORPTION CURVES FOR ADDITIVELY COLORED POTASSIUM IODIDE CRYSTALS.

thought to be a type of F-band but subsequent experiments did not support this view. These experiments will be discussed later.

Since the band described above appeared only in certain crystals having an initial concentration below about $3 \times 10^{17} \text{ cm}^{-3}$ these crystals were not used in determining equilibrium concentrations of F-centers at various temperatures. Absorption spectra were measured in liquid nitrogen using the method outlined in the section on experimental techniques.

The data in Tables 8 and 9 were calculated by the method described previously using the constants for -194° C . Thermal stability curves for KI, KBr, and KCl are shown in Figure 12. The diameter of the circles indicates the magnitude of the probable error in the F-center concentration value. Horizontal lines through the circles represent the magnitude of the uncertainty in the temperature, that is $\pm 5^{\circ} \text{ C}$.

Table 8. Equilibrium concentration of F-centers in potassium iodide at various temperatures. Values were calculated from absorption curves measured at -194°C .

| Temperature $^{\circ}\text{C}$ | Heating Time-- Minutes | F-Center Concentration $\times 10^{-17} \text{ cm}^{-3}$ | | |
|-----------------------------------|------------------------------|--|-------|--|
| 375 | 130 | 1.83 | 2.00 |) Combined under 372.5° below. |
| | | 2.25 | 2.08 | |
| | | 1.79 | | |
| 370 | 100 | 2.08 | 2.13 | |
| | | 1.96 | 2.33 | |
| | | 1.95 | | |
| 350 | 200 | 1.46 | 1.93 | |
| | | 1.51 | 1.76 | |
| | | 1.75 | | |
| 323 | 180 | 1.14 | 1.19 | |
| | | 1.06 | 1.45 | |
| | | 1.14 | 1.25 | |
| | | 0.94 | 1.08 | |
| | | 1.21 | | |
| 303 | 120 | 0.956 | 0.980 | |
| | | 0.930 | 1.023 | |
| | | 0.971 | | |
| | 180 | 0.938 | 0.775 | |
| | | 0.919 | 0.942 | |
| | | 0.919 | | |

Table 9. Data used to determine heat of formation of F-centers in potassium iodide

| Temperature °C. | Number of Values | Average F-center Concentration $\times 10^{-17} \text{ cm}^{-3}$ | Average Deviation | Probable Error in the Mean |
|--------------------|---------------------|---|----------------------|----------------------------------|
| 372.5 | 10 | 2.04 | ± 0.13 | ± 0.04 |
| 350 | 5 | 1.68 | 0.16 | 0.06 |
| 323 | 9 | 1.16 | 0.10 | 0.03 |
| 303 | 5 | 0.90 | 0.05 | 0.02 |

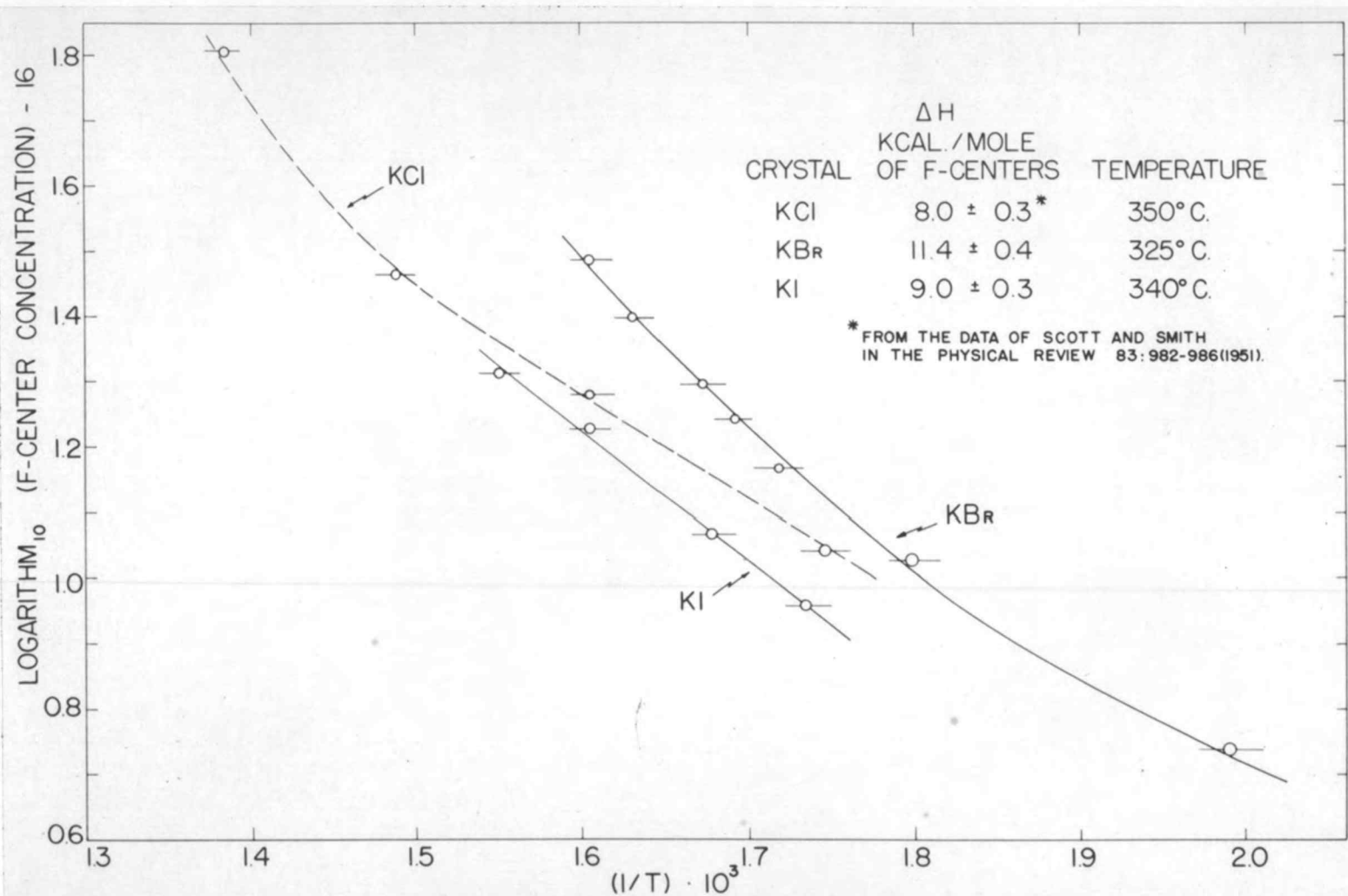


FIGURE 12. VARIATION OF THE SATURATION CONCENTRATION OF F-CENTERS WITH THE TEMPERATURE IN K-KCl, K-KBr, AND K-KI.

Figure 13 shows absorption curves for a series of potassium iodide crystals of varying initial concentration quenched from 350° C. after 120 minutes. Figure 14 shows absorption curves for one crystal (K-K1 #18) quenched from four different temperatures. All of the curves were obtained with the crystals in liquid nitrogen.

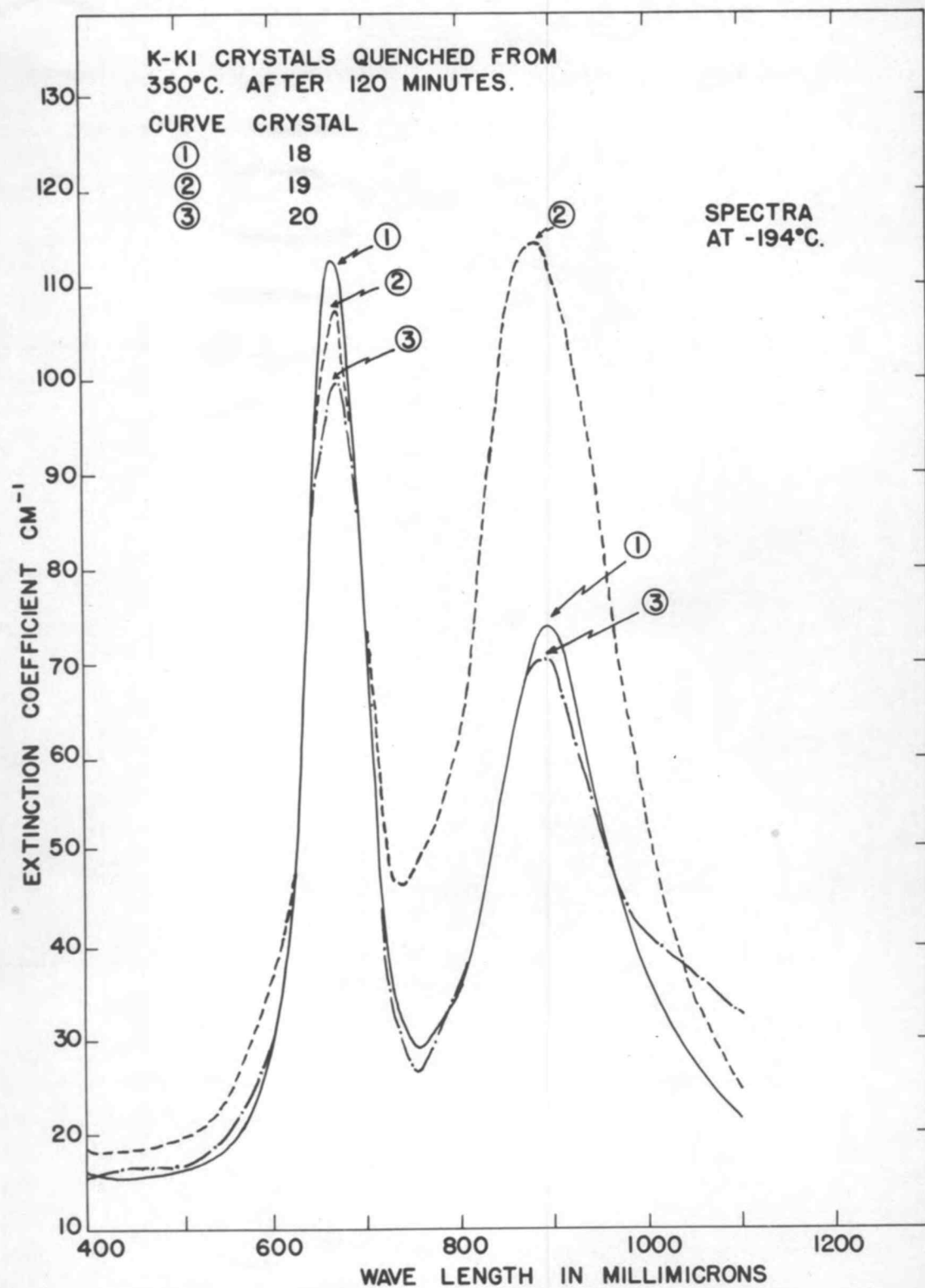


FIGURE 13. ABSORPTION CURVES FOR A SERIES OF K-KI CRYSTALS OF VARYING INITIAL CONCENTRATION.

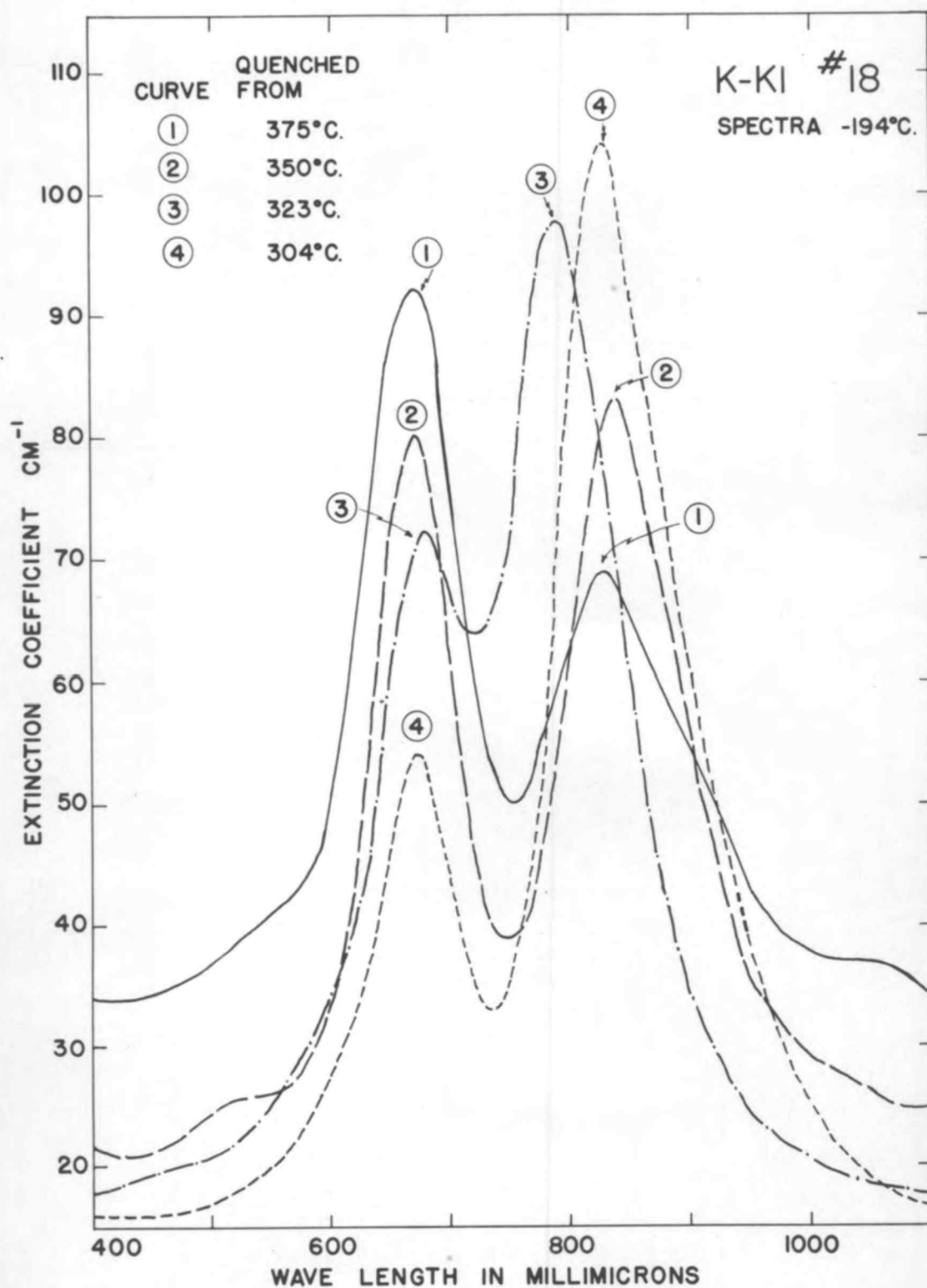


FIGURE 14. VARIATION OF F-CENTER STABILITY WITH THE TEMPERATURE FOR A SERIES OF K-KI CRYSTALS OF THE SAME INITIAL CONCENTRATION.

CHAPTER III

NEW BAND IN ABSORPTION SPECTRUM OF
ADDITIVELY COLORED POTASSIUM IODIDELow Temperature Behavior of New Band

During the preliminary experiments on the thermal stability of F-centers in potassium iodide it was found that unexpected absorption bands were produced in four of the crystals. These bands had absorption maxima lying between 650 and 670 millimicrons. In Figure 11 (f) are shown absorption curves for different samples of one crystal quenched from four different temperatures between 300° and 400° C.

At first it was thought that these bands might be some type of F-band. It was reasoned that if they were actually F-bands, they should display the following characteristics typical of F-bands:

- (a) An absorption maximum which shifts to lower wave length (higher energy) as the temperature of observation is lowered
- (b) A decrease in band width as the temperature is lowered, and
- (c) Rapid destruction of the band by light of wave length corresponding to the band maximum and a simultaneous growth of bands having maxima at wave lengths greater than the F-band maximum.

The low temperature behavior of these bands (maxima from 650 to 670 millimicrons) was studied in liquid nitrogen. Absorption spectra were measured in air and in liquid nitrogen using the techniques described previously. Some of the resulting absorption curves are shown in Figure 15. Examination of these and other curves revealed no significant change in the position of the band maximum or in the width of the band at half its maximum height.

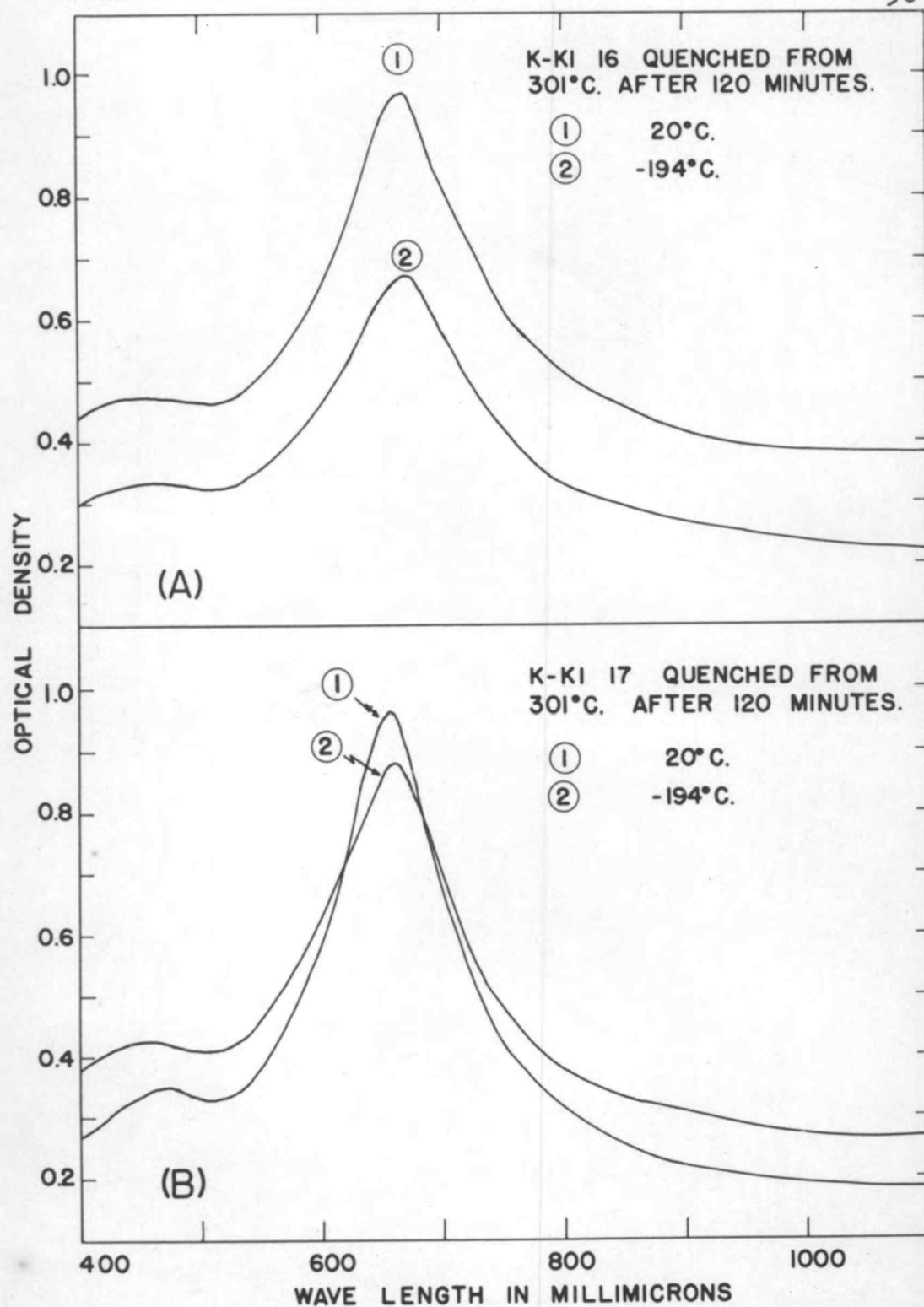


FIGURE 15. ABSORPTION CURVES FOR ADDITIVELY COLORED KI SHOWING THE 650 MILLIMICRON BAND.

Illumination Experiments on New Band

Illumination experiments were conducted on several of the crystals in order to determine the stability of the new band toward light. The criterion of stability was arbitrarily chosen to be the rate of destruction of the F-band (by light of wave length corresponding to the F-band maximum) appearing at 700 millimicrons. Crystals were illuminated by means of the Beckman DU spectrophotometer light source. Optical density readings were made after each illumination without removing the crystal from the holder. A typical result is shown in Figure 16.

A plot of the logarithm of the ratio of initial F-center concentration to the concentration after each illumination against the time should result in a straight line if the destruction of the F-band follows a first order rate law. It is not necessary to know F-center concentration since this is proportional to the optical density. Hence, the optical density ratios can be used instead of the concentration ratios. Data in Table 10 were computed from Figure 16. The base line was taken at $D = 0.20$ and $D_0 = D$ maximum for the original spectrum.

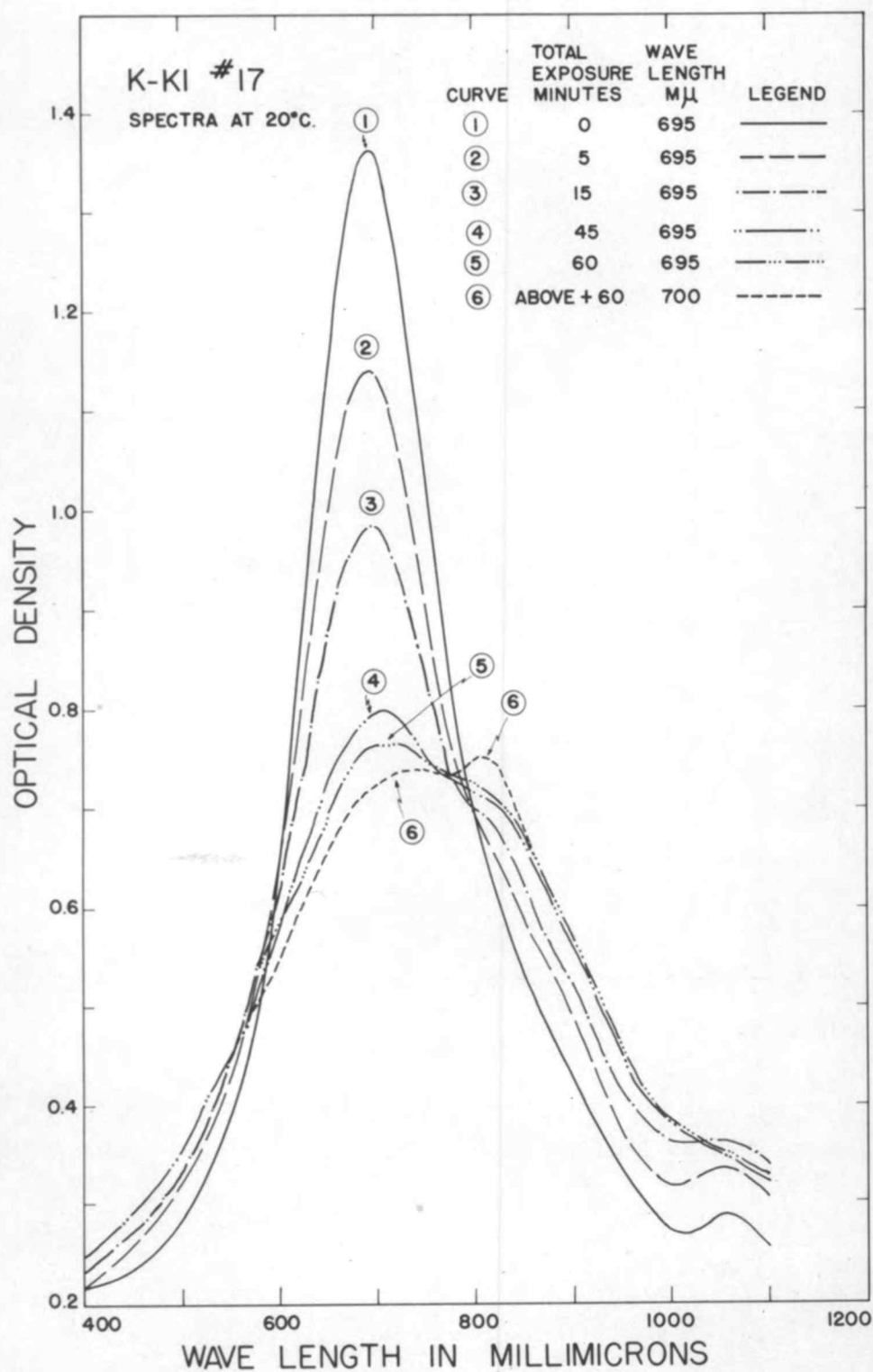


FIGURE 16. ABSORPTION SPECTRUM OF AN ILLUMINATED K-KI CRYSTAL AT 20°C.

Table 10. Illumination study in K-K1
#17 (original)

| <u>Curve</u> | <u>Time Minutes</u> | <u>D_{max}</u> | <u>$\frac{D_o}{D_t}$</u> | <u>Log D_o/D_t</u> |
|--------------|-------------------------|------------------------|-------------------------------------|--|
| 1 | 0 | 1.165 | 1.000 | 0.000 |
| 2 | 5 | 0.940 | 1.240 | 0.093 |
| 3 | 15 | 0.785 | 1.485 | 0.171 |
| 4 | 45 | 0.595 | 1.959 | 0.292 |
| 5 | 60 | 0.565 | 2.063 | 0.314 |

Table 11. Illumination study on K-K1 #17
quenched from 301°C. after 120
minutes heating. (Slit = 1.5 mm
 $\lambda = 650$ mμ.)

| <u>Curve</u> | <u>Time Minutes</u> | <u>D_{max}</u> | <u>$\frac{D_o}{D_t}$</u> | <u>Log D_o/D_t</u> |
|--------------|-------------------------|------------------------|-------------------------------------|--|
| 1 | 0 | 0.650 | 1.000 | 0.000 |
| 2 | 5 | 0.635 | 1.022 | 0.009 |
| 3 | 15 | 0.630 | 1.032 | 0.013 |
| 4 | 30 | 0.610 | 1.065 | 0.027 |
| 5 | 45* | 0.610 | 1.065 | 0.027 |

* Slit increased to 2.0 mm.

Table 12. Illumination study on K-K1 #16 quenched from 301° C. after 120 minutes heating. (Slit = 2.0 mm $\lambda = 675$ m μ .)

| Curve | Time Minutes | D_{\max} | $\frac{D_o}{D_t}$ | $\text{Log } D_o/D_t$ |
|-------|-----------------|------------|-------------------|-----------------------|
| 1 | 0 | 0.650 | 1.000 | 0.000 |
| 2 | 10 | 0.607 | 1.070 | 0.029 |
| 3 | 30 | 0.575 | 1.130 | 0.053 |
| 4 | 50 | 0.562 | 1.156 | 0.063 |

Figure 17 shows a plot of $\log D_o/D_t$ against time. It should be noted that the initial rate of destruction is quite fast but falls off rapidly and slowly approaches a saturation value, that is, illumination beyond a certain time produces no appreciable change in the F-band. This behavior has been observed for F-bands in additively colored potassium bromide and potassium chloride.

Experiments in which a more intense light source was used gave substantially the same results, that is, a slow initial rate of destruction compared to that observed in crystals containing the 700 millimicron F-band. Another point of interest in these illumination experiments on crystals having bands between 650 and 670 millimicrons was the absence of the R_1 , R_2 and M-bands after illumination. These bands are developed very rapidly, particularly the M-band, in crystals in which the F-band appears at 700 millimicrons. This may be seen clearly

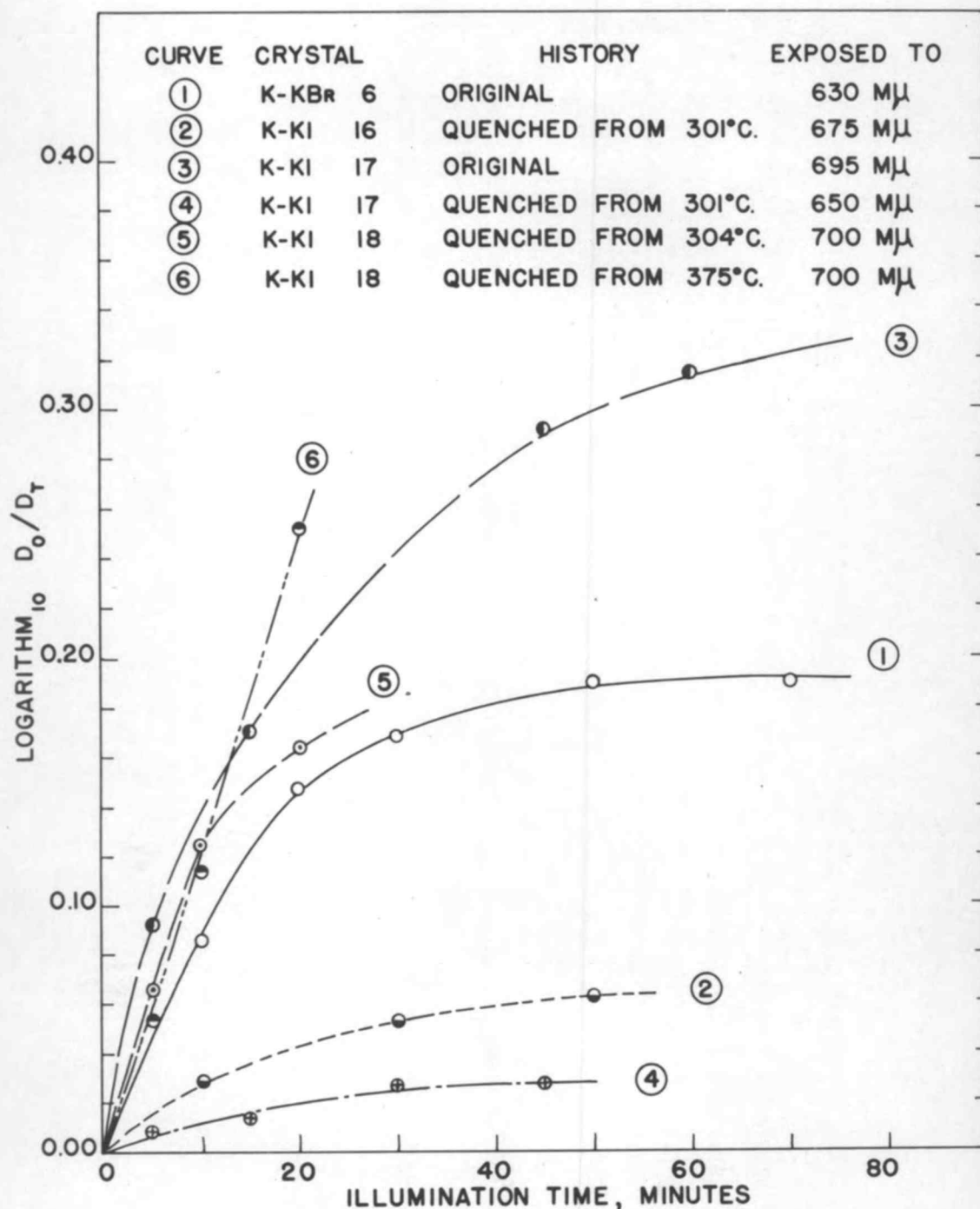


FIGURE 17. DESTRUCTION OF F-BANDS BY LIGHT.
FIRST ORDER RATE LAW PLOT.

in Figure 16.

The results from the illumination experiments and those from the low temperature absorption spectra measurements on the new band may be summarized as follows:

- (1) No apparent shift in the band maximum was observed as the temperature was lowered
- (2) No appreciable change in the band width at half-maximum height was noticed
- (3) The rate of conversion or destruction of the band was very slow compared to that observed for the 700 millimicron band
- (4) Growth of R_1 , R_2 , and M-bands was not observed as a result of illumination.

These facts led to the conclusion that this new band, in all probability, was not an F-band. The behavior of this band was very much the same as the "colloidal" band appearing between 800 and 950 millimicrons in K-KI. A series of experiments to test the thermal stability of the new band was performed on crystals in which the band had been developed by heating at 300°C . The results are shown graphically in Figure 18.

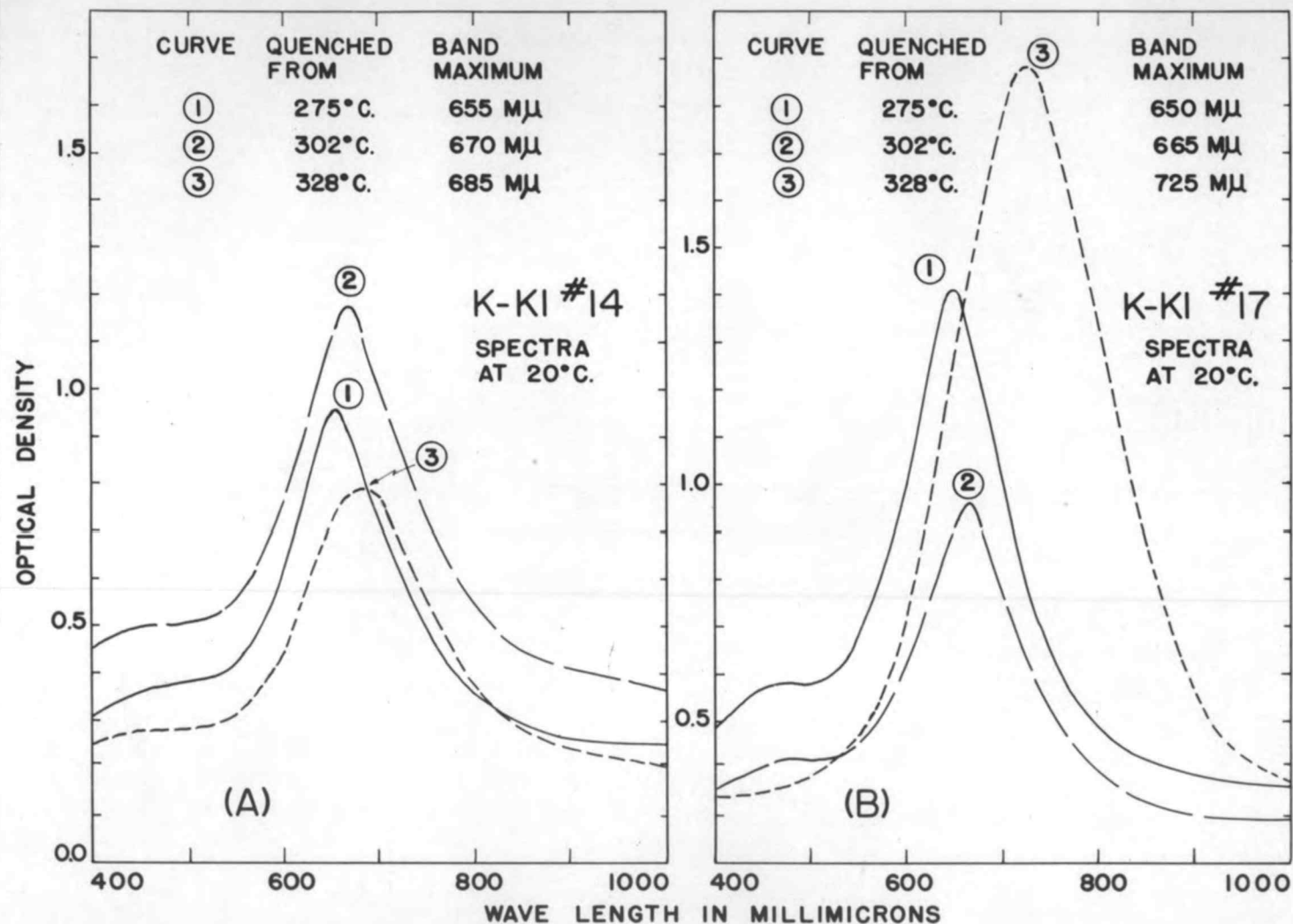


FIGURE 18. THERMAL STABILITY OF THE 650 MILLIMICRON BAND IN K-KI.

Thermal Stability of New Band

Samples of K-KI #14 and #17 were wrapped in aluminum foil and heated at 302° C. for 60 minutes and then quenched in carbon tetrachloride. Sections were cleaved and their absorption curves determined. These curves are labeled 2 in Figure 18. Samples of the above treated crystals were wrapped in foil and heated at 275° C. for 60 minutes before being requenched. Absorption curves were again obtained at 20° C. and these curves are labeled 1 in Figure 18. Two additional samples of #14 and #17 were heated at 299° C. for 70 minutes, in order to develop the 650 millimicron band, and quenched. These were then heated at 328° C. for 60 minutes, requenched, and absorption curves obtained. These curves are labeled 3 in Figure 18.

In the work on the thermal stability of F-centers in potassium iodide it was assumed that the new band (at 650 millimicrons) was not present. Evidence upon which this assumption was based appears in part in Figure 17. The curves for K-KI #18 quenched from 304° C. (120 minutes) and quenched from 375° C. (130 minutes) show a rapid initial rate of destruction of F-centers by light of 700 millimicrons wave length. This behavior is typical of the F-band with band maximum at 700 millimicrons. Another fact supporting this assumption was that

under no conditions did the new band appear in the crystals used for the measurements of thermal stability of F-centers, nor was there any qualitative indication that the new band might have been present.

Development of the 650-670 millimicron band in certain of the colored potassium iodide crystals was a reproducible phenomenon at several temperatures. After some of the properties of the new band had been established the question arose as to the possibility of reproducing the conditions under which the crystals were colored initially and thereby producing crystals having the same properties as K-KI #14, 16, and 17.

It was noticed that all three of these crystals were heated for very long periods of time (from 90 to 260 hours) while coloring. Since the temperature of the crystal in the upper compartment was the same for the three crystals and other conditions were comparable, it appeared that the heating time might be a determining factor.

Three crystals were colored under the same conditions as #14, except for heating times of 36, 48, and 90.5 hours. These crystals were then heated at various temperatures between 266° and 325° C. and quenched in carbon tetrachloride. Absorption curves gave no evidence of a band at 650 to 670 millimicrons.

Two crystals (#23 and 24) were prepared under the same conditions as #17 except for heating times of 168 and 240 hours. Subsequent heating at 300° C. produced the band at 650 millimicrons in the crystal heated for 240 hours (K-KI #24) but not in the one heated for 168 hours. Figure 19 shows absorption curves for several of the crystals prepared in attempting to reproduce K-KI 14. and K-KI 17.

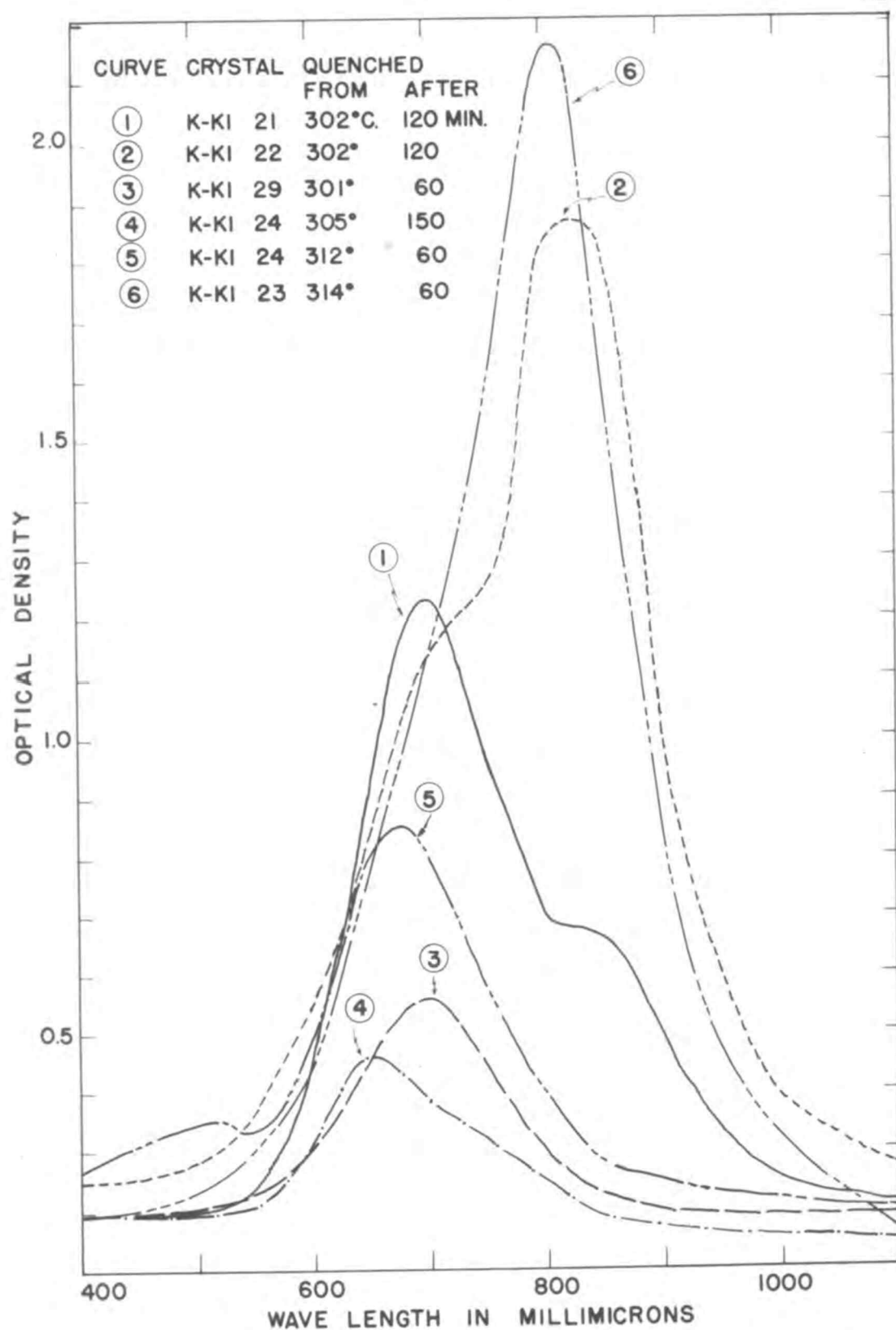


FIGURE 19. ABSORPTION CURVES FOR VARIOUS K-KI CRYSTALS.

CHAPTER IV

MISCELLANEOUS OBSERVATIONS

Information Obtained from Spectra Measured in Liquid Nitrogen

Much useful information was obtained from spectra of the additively colored alkali halides measured in liquid nitrogen. In the chapter on energy level calculations, use will be made of the F-band wave length shifts listed in Table 13.

Table 13. Temperature dependence of F-band maximum.

| Crystal | F-band Maxima in Millimicrons | | $\Delta\lambda$ Observed m. μ . | $\Delta\lambda$ in e.v. | $\Delta\lambda$ e.v. (Molnar) |
|---------|----------------------------------|----------|---|----------------------------|----------------------------------|
| | 20° C. | -194° C. | | | |
| KCl | 560 | 540 | 20 | 0.082 | 0.074 |
| KBr | 625 | 605 | 20 | 0.066 | 0.061 |
| KI | 700 | 670 | 30 | 0.079 | 0.037 |

Examination of the low temperature spectra of the crystals in Table 13 revealed the locations of the R_1 , R_2 , and M-band maxima. From these and other absorption curves, Table 14 was prepared. Typical spectra are shown in Figure 20.

Table 14. Location of optically produced bands in additively colored alkali halides.

| Crystal | Temperature °C. | Location of Band Maximum (mμ.) | | | |
|---------|--------------------|--------------------------------|----------------|------|------|
| | | R ₁ | R ₂ | M | N |
| KCl | 20 | 670 | 735 | 830 | 1000 |
| | -194 | 660 | 735 | 805 | 975 |
| KBr | 20 | --- | 810 | 930 | --- |
| | -194 | 740 | 810 | 905 | --- |
| KI | 20 | --- | --- | 1060 | --- |
| | -194 | 835 | 915 | 1030 | --- |

The location of the R₁-band in KBr and KI at 20°C. was obscured by overlapping of the F-band, and the 670 millimicron value for KCl is probably too high for the same reason. Potassium iodide absorption curves at 20°C. were so poorly defined in the region from 750 to 1000 millimicrons that it was not possible to determine the R₂-band maximum. However, from the behavior of the R₂-band in KCl and KBr the maximum in KI may be inferred to be at 915 millimicrons.

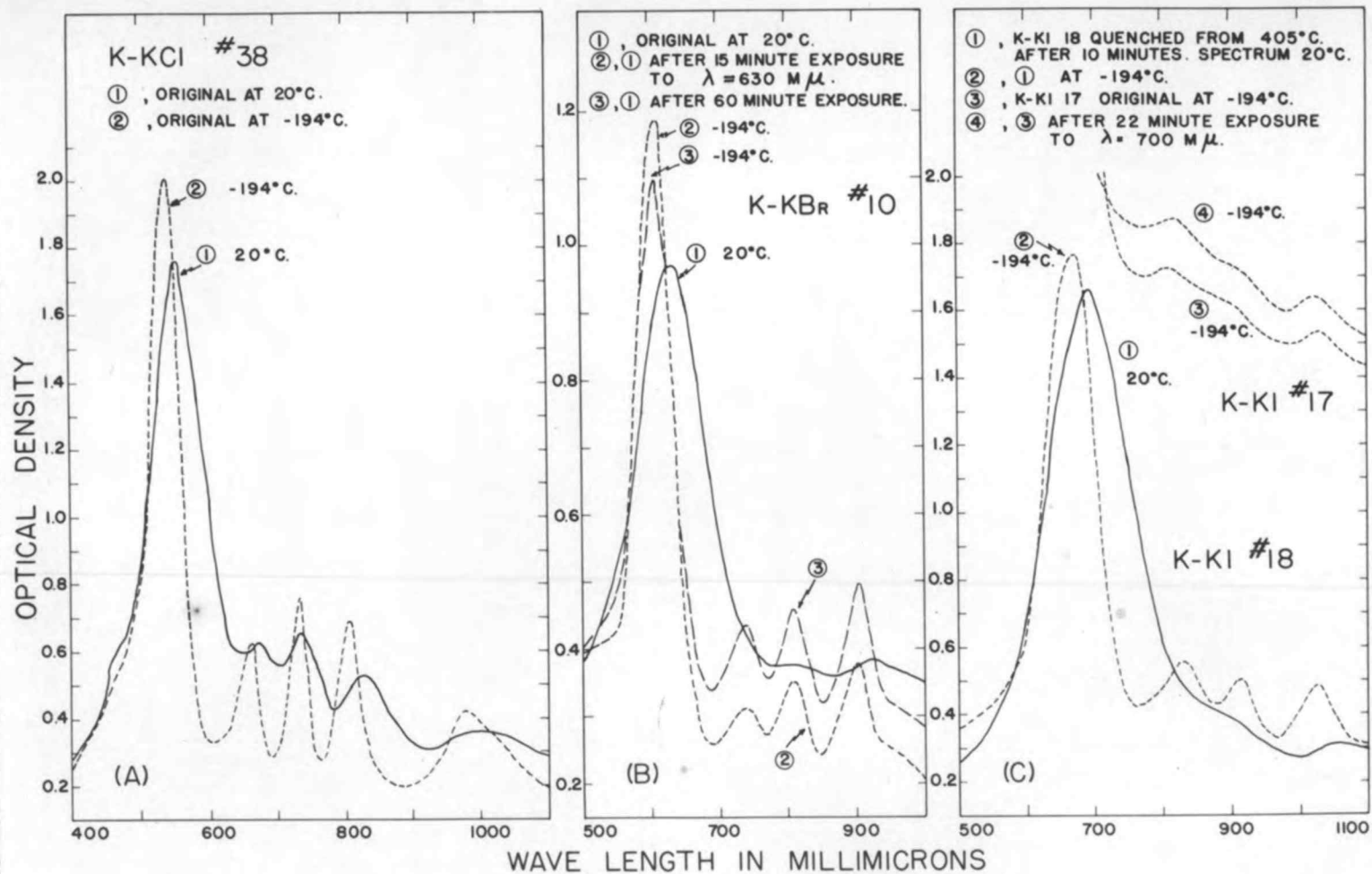


FIGURE 20. TYPICAL ABSORPTION SPECTRA OF SOME ADDITIVELY COLORED ALKALI HALIDES AFTER VARIOUS TREATMENTS.

Measurements on Nonhomogeneously Colored Alkali Halides

Information concerning the distribution of color centers in non-uniformly colored crystals was desired. Of particular interest was the relative concentration of F-centers and M-centers at varying distances from the outer surfaces of a crystal.

Crystals were prepared in the furnace described in Chapter II by heating for periods of time less than those required for equilibrium to be established. The crystals were handled in subdued light and stored in light-tight containers. Cross sections were obtained by cleaving with a razor blade. The sections were of such a thickness as to permit optical density readings to be made very close to the outer face of the original crystal.

A crystal holder was constructed to fit into the Beckman DU cell carrier. This holder is shown in detail in Figure 21. The essential features of this holder are (a) a fixed slit, (b) a movable crystal mount which passes behind the slit, and (c) a screw for moving the crystal mount without removing the holder from the cell carrier. The screw had a 4-36 NC thread and was turned by means of a slotted plastic rod. A series of measurements was made on the displacement of the movable mount caused by turning the screw. The entire holder was placed on a

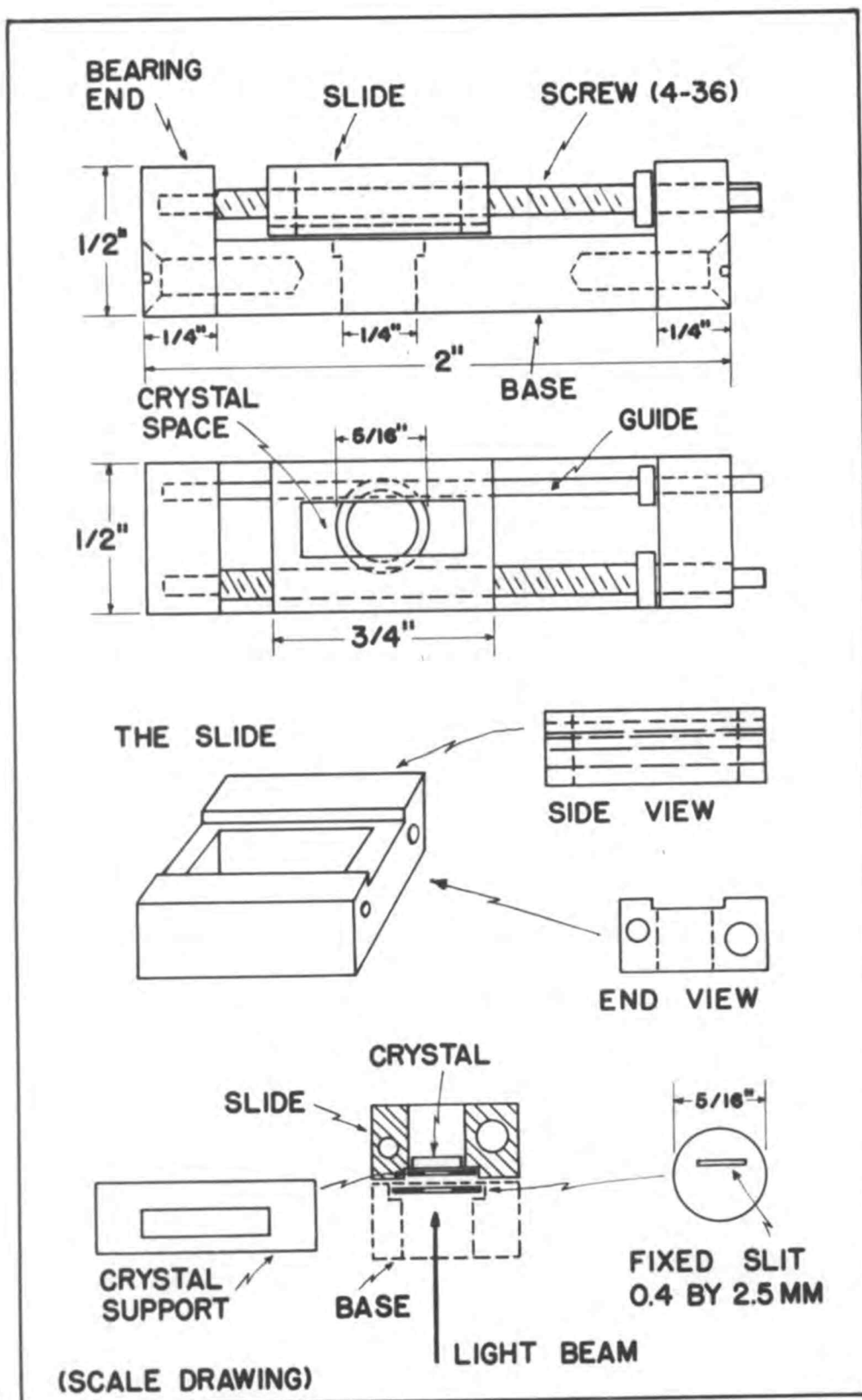


FIGURE 21. CRYSTAL HOLDER WITH MOVABLE MOUNT.

microscope stage and clamped in position. A micrometer eyepiece and 10X objective served to measure the movement of the crystal mount as the screw was turned.

Table 15. Calibration of the movable crystal mount as function of number of turns of the screw.

| Trial | Displacement of mount by | | |
|----------------|--------------------------------|--------------------------------|--------------------|
| | $\frac{1}{4}$ turn of screw | $\frac{1}{2}$ turn of screw | 1 turn of screw |
| 1 | 0.147 mm | 0.332 | 0.715 |
| 2 | 0.184 | 0.343 | 0.703 |
| 3 | 0.170 | 0.352 | 0.716 |
| 4 | 0.195 | 0.349 | 0.707 |
| 5 | 0.157 | 0.366 | 0.713 |
| Average | 0.171 | 0.348 | 0.711 |
| Ave.dev. \pm | 0.015 | \pm 0.008 | \pm 0.004 |

The samples were mounted on the movable holder with Duco cement and the holder placed in the Beckman DU so that the crystal was behind the slit, thus exposing only that portion of the crystal directly behind the slit to the light beam. This prevented growth of R_1, R_2 , and M bands in other parts of the crystal as the absorption spectrum was being measured at 20°C. Measurements were from the dense surface toward the interior of the crystal.

No samples of potassium iodide were studied because of the poorly defined bands in the absorption spectrum at 20°C. Typical curves for potassium chloride and potassium

bromide are shown in Figures 22 and 23, respectively. These curves were used to obtain the data in Table 16.

The constancy of the α_F/α_M values for a specific crystal indicates that there is no appreciable difference between the relative concentration of F-centers to M-centers at different points in a nonhomogeneously colored crystal of potassium chloride or potassium bromide. Figure 24 shows a logarithmic plot of F-center concentration against slit position for the three crystals in Table 16.

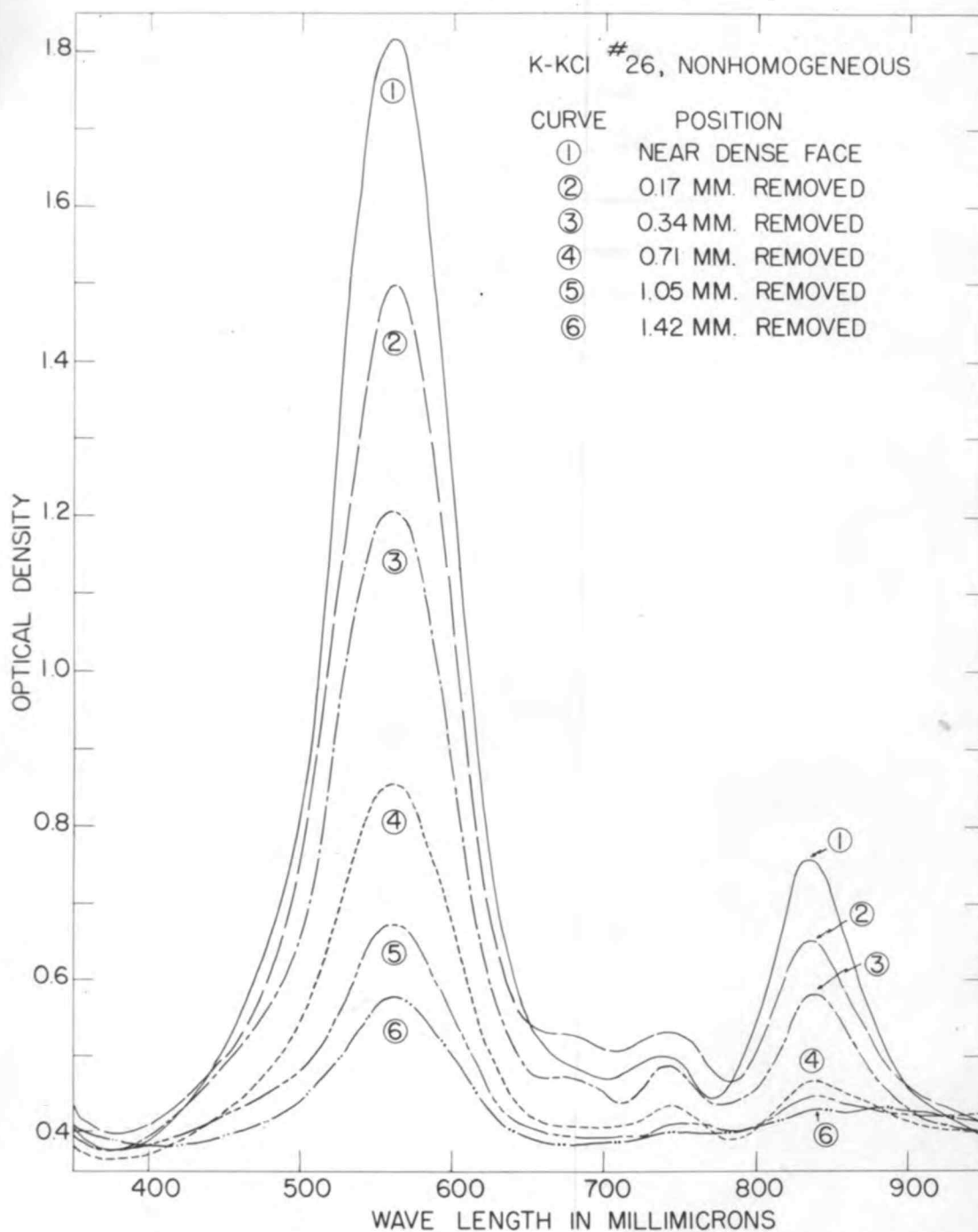


FIGURE 22. ABSORPTION SPECTRUM OF NONHOMOGENEOUS, COLORED KCl.

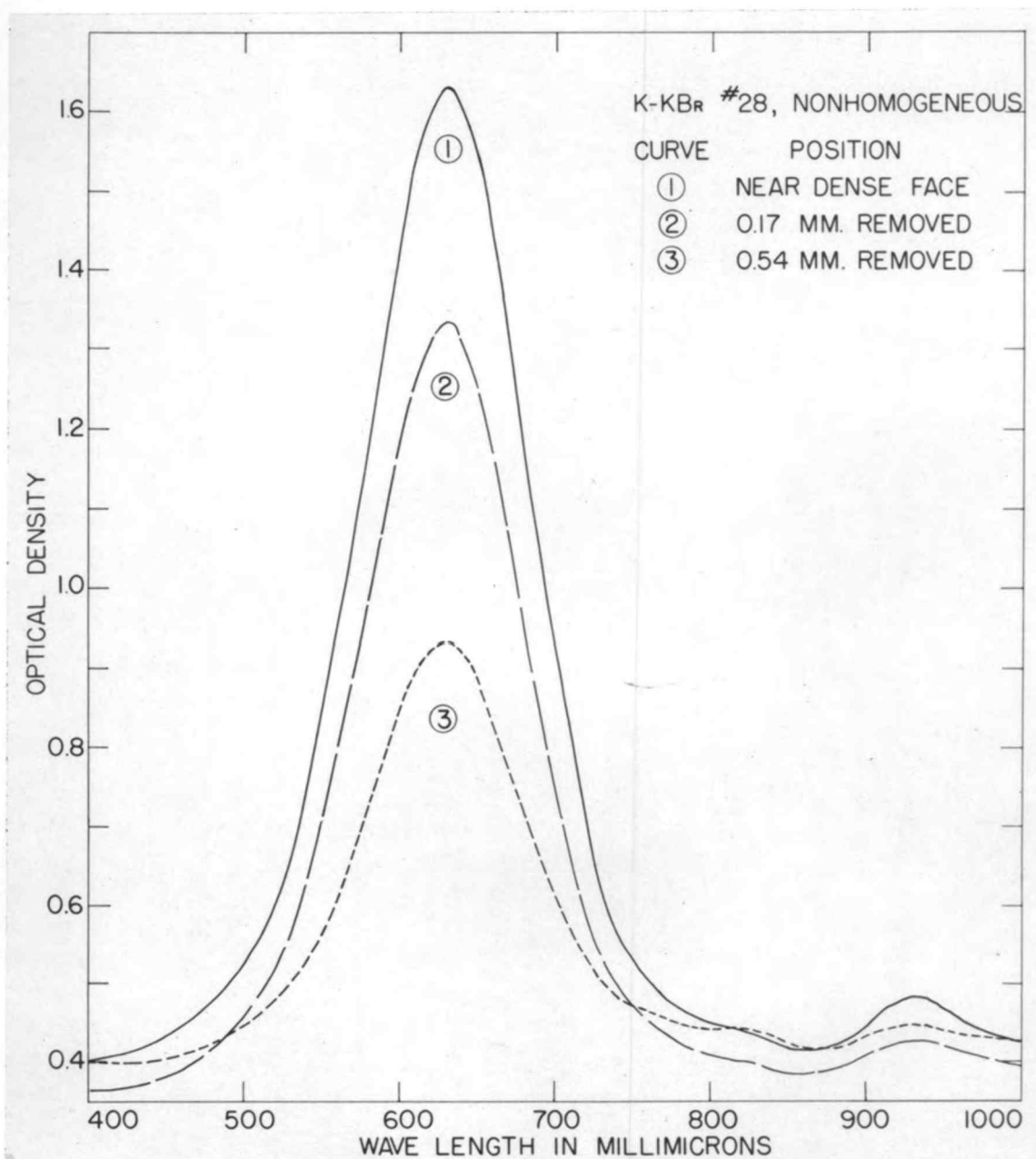


FIGURE 23. ABSORPTION SPECTRUM OF NONHOMOGENEOUS, COLORED KBr.

Table 16. Relative distribution of color centers as a function of distance from an exterior face of the original nonhomogeneously colored crystal.

| Crystal | Curve Number | Position of slit in mm. | F-band $\alpha_{\text{max.}}$ | M-band $\alpha_{\text{max.}}$ | $\frac{\alpha_F}{\alpha_M}$ | M-centers $\times 10^{-16} \text{ cm}^{-3}$ | F-centers $\times 10^{-17} \text{ cm}^{-3}$ | $K' = \frac{(M)}{(F)}^*$ |
|--------------|--------------|-------------------------|-------------------------------|-------------------------------|-----------------------------|---|---|--------------------------|
| K-KCl #25 | 1 | 0 | 67.9 | 14.8 | 4.58 | 1.99 | 2.66 | 0.075 |
| | 2 | 0.17 | 44.5 | 8.44 | 5.27 | 1.13 | 1.75 | 0.065 |
| | 3 | 0.35 | 32.8 | 6.45 | 5.08 | 0.87 | 1.29 | 0.067 |
| | 4 | 0.52 | 26.4 | 5.36 | 4.93 | 0.72 | 1.04 | 0.069 |
| | 5 | 0.71 | 20.5 | 3.87 | 5.30 | 0.52 | 0.80 | 0.065 |
| K-KCl #26 | 1 | 0 | 90.3 | 22.9 | 3.94 | 3.08 | 3.54 | 0.087 |
| | 2 | 0.17 | 68.9 | 15.3 | 4.50 | 2.06 | 2.70 | 0.076 |
| | 3 | 0.35 | 52.0 | 11.9 | 4.37 | 1.60 | 2.04 | 0.078 |
| | 4 | 0.71 | 30.7 | 6.26 | 4.90 | 0.84 | 1.20 | 0.070 |
| | 5 | 1.06 | 18.4 | 4.26 | 4.32 | 0.57 | 0.72 | 0.079 |
| | 6 | 1.42 | 11.9 | 2.82 | 4.22 | 0.38 | 0.47 | 0.081 |
| K-KBr #28 | 1 | 0 | 48.8 | 3.37 | 14.5 | 0.49 | 1.91 | 0.026 |
| | 2 | 0.17 | 38.6 | 2.74 | 14.1 | 0.39 | 1.51 | 0.026 |
| | 3 | 0.52 | 20.9 | 1.27 | 16.4 | 0.18 | 0.82 | 0.022 |

* (M) denotes M-centers per cm^3 and (F) = F-centers per cm^3 .

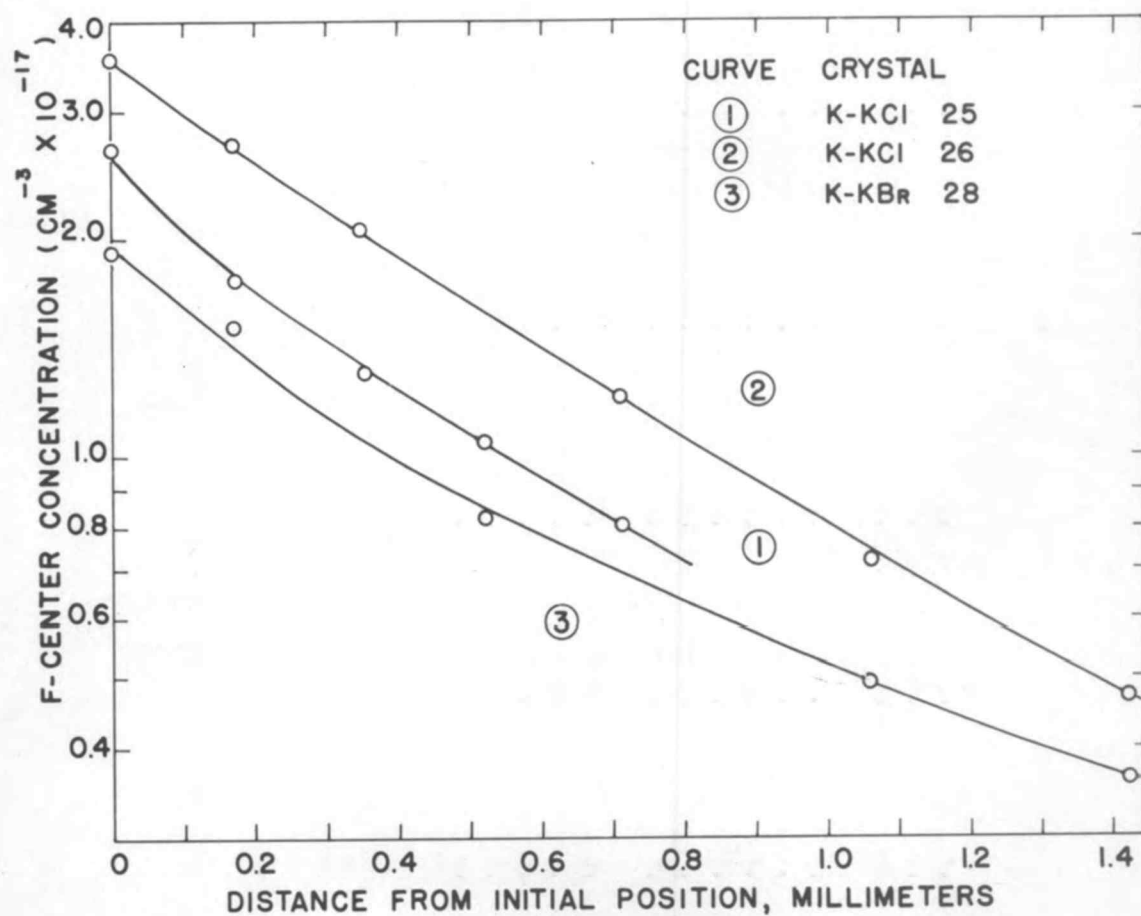


FIGURE 24. DISTRIBUTION OF F-CENTERS IN SOME NONHOMOGENEOUSLY COLORED ALKALI HALIDES.

CHAPTER V

ENERGY LEVELS OF ELECTRONS IN F-CENTERS
IN ALKALI HALIDESTheoretical Considerations

In order to calculate energy levels of electrons trapped in polar crystals we must first construct a mechanical model and from this model deduce certain parameters needed in setting up suitable wave equations for these electrons. As mentioned before, the field acting upon an electron near a lattice defect depends upon the wave function of the electron itself and, therefore, a self-consistent method must be used in determining the energy levels.

The model chosen to represent the F-center was the same as that used by Tibbs and by Simpson (34,p.275 and 36,p.1479). A two dimensional representation is shown in Figure 25. The plus signs denote alkali metal ions and minus signs denote halide ions. When a negative ion is removed from the lattice an effective positive charge is left at the lattice point. This positive charge causes a polarization of the medium. Therefore, in determining the form of the potential field in which the trapped electron moves it is necessary to consider (a) the field

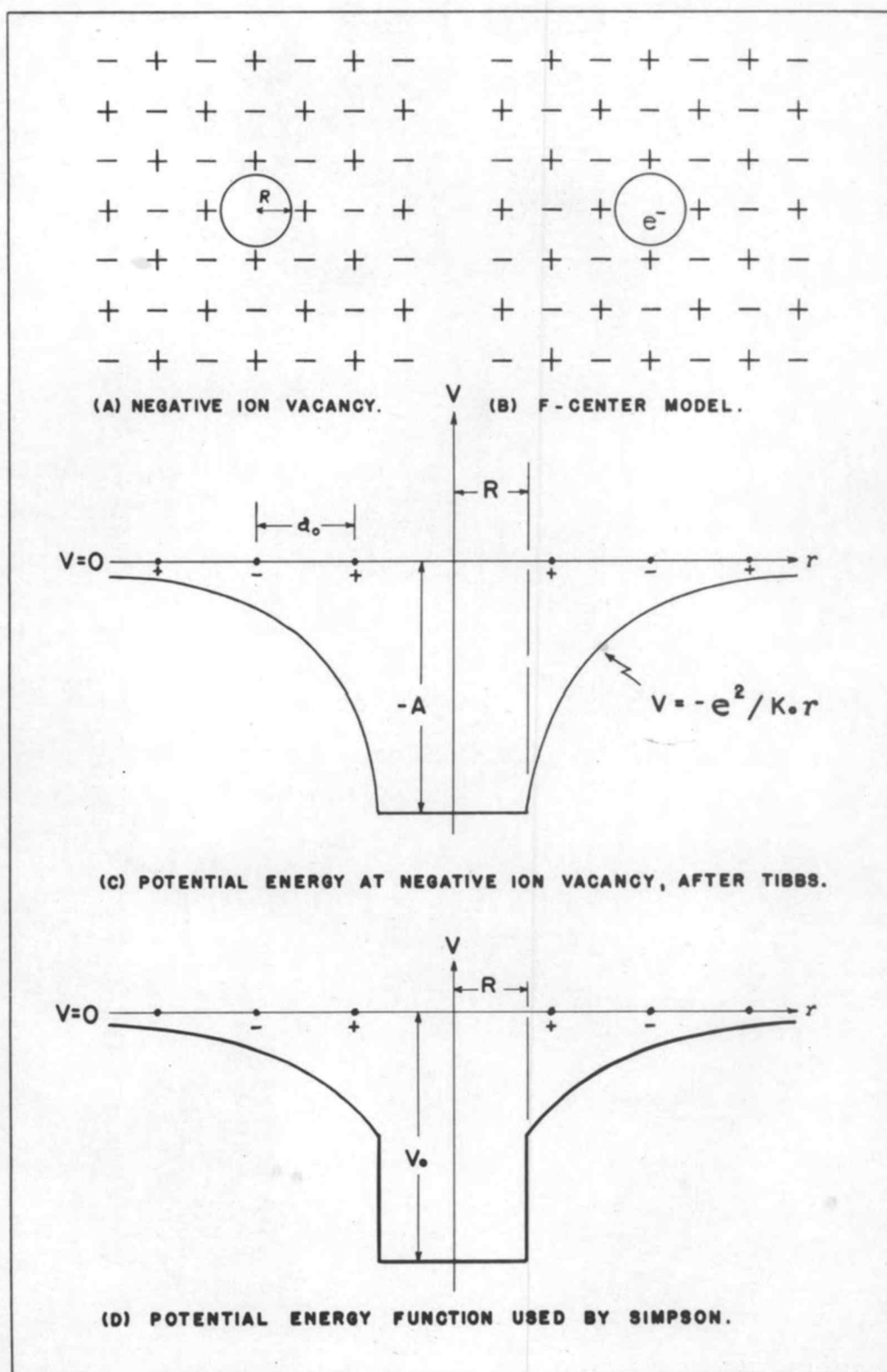


FIGURE 25. F-CENTER MODELS USED BY TIBBS AND SIMPSON.

due to the effective positive charge at the negative ion site, and (b) the field due to that part of the polarization of the medium that remains constant when the electron moves.

Tibbs made the following assumptions in his calculations:

- (a) The potential energy of the electron for $r > R$ is $\frac{-e^2}{K_0 r}$, where K_0 is the high frequency ($> 5 \times 10^{12} \text{ sec}^{-1}$) dielectric constant.
- (b) The potential energy in the region $0 < r < R$ was taken to be constant and given by the equation

$$A = -\frac{\alpha e^2}{2a} + \frac{e^2}{R} \left(1 - 1/K_0\right).$$

The last term is the energy gained from polarization of the medium.

- (c) The bottom of the potential well was assumed flat with a value $-A$ at $r = 0$. The intersection of the line $-A$ with the curve $V = -e^2/K_0 r$ (of Figure 25 (c)) determined the value of R (the radius of the hole in the dielectric continuum left upon removal of a negative

ion). That is, at $r = R$ we have $V = -e^2/K_0R$ and $R = -e^2/K_0V = e^2/K_0A$.

- (d) The potential hole was spherically symmetrical.

Simpson used a more refined method in estimating the shape of the potential field near the negative ion vacancy (34, p.270 and pp.274-277). His arguments follow those of Mott and Gurney and are given below in outline form (18, p.85).

That part of the polarization of the medium due to displacement of the ions remains constant during the short time of an electronic transition. The field acting on the electron consists of two parts when the electron is at a radius r from the vacant negative ion lattice point. These two parts are:

- (1) The field e/K_0r^2 due to the positive charge, where K_0 is the dielectric constant when the ions are held in their normal positions.
- (2) The low-frequency part of the polarization, which is due to motion of the ions, is produced by the positive charge at the vacant lattice point and the fraction of the electronic charge, $-ep(r)$, that is normally within radius r . If Ψ is the wave function of the electron,

$$p(r) = \int_0^r |\Psi|^2 4\pi r'^2 dr'.$$

Hence the field due to this part of the polarization is

$$-(e/r^2)[1 - f_{c+}](1/K_0 - 1/K)$$

where K is the static dielectric constant.

Finally, the field acting on the electron at radius r is

$$F_{(r)} = (e/K_0 r^2) - (e/r^2)[1 - f_{c+}](1/K_0 - 1/K)$$

$$F_{(r)} = (e/K r^2)[1 - f_{c+}] + (e/K_0 r^2) f_{c+} .$$

This last equation shows that the field approaches e/Kr^2 for very small radii and $e/K_0 r^2$ for very large radii.

Simpson considered the effect of the six nearest positive ions on the potential field at the negative ion vacancy and concluded that the potential energy curve was practically flat from the center of the vacancy almost to the nearest positive ion. More distant shells of positive ions gave curves which were even flatter. The effect of the dipoles induced on the ions surrounding the vacancy by the effective charge was also considered. Mott and Littleton have calculated the magnitude of this effect for several shells of ions (19, pp.490-493). The potential energy curve due to the first

shell of positive ions and the first shell of negative ions is flat (except for the singularity at $r = a_0$) within 20 per cent for distances from 0 up to $0.9a_0$. Succeeding shells of dipoles give potential curves that are still flatter.

There remains the question of the effect of the medium on the electronic charge distribution. Simpson used Jost's model in which the material is treated as a uniform medium containing a spherical hole (of radius R) at the position of the missing ion. This model was also used by Tibbs in obtaining an expression for the potential energy at the center of the hole, that is, in atomic units,

$$V = \alpha/a + (1/R)(1 - 1/K),$$

where $\alpha = 1.7476$, the Madelung constant for a cubic lattice. Since the radius of the flat portion of the potential curve (discussed in the preceding paragraph) is of the order of R , it is reasonable to assume that they are equal.

The Variation Method

We have previously seen that the potential energy function to be used in the Schrödinger equation is

dependent upon the wave function, Ψ , of the electron trapped in the potential well described in Figure 25. Since the Schrödinger equation itself gives another relation between V and Ψ , the two can only be evaluated by a self-consistent method. A variation type method was used and before discussing the method in detail, it may be well to give the mathematical basis upon which the variation method is founded, (22,p.180).

In general, the integral $E = \int \phi^* H \phi d\tau$ gives an upper limit to the energy W_0 of the lowest state of a system. In this equation, H is the complete Hamiltonian operator, $H(\frac{1}{2}\pi i \frac{\partial}{\partial q}, q)$, for the system, and $\phi(q)$ is any normalized function of the coordinates of the system satisfying the conditions for a satisfactory wave function.

If the true wave function Ψ_0 of the lowest state were used in place of ϕ , E would equal W_0 , that is

$$E = \int \Psi_0^* H \Psi_0 d\tau = W_0.$$

If ϕ is not equal to Ψ_0 , we may expand ϕ to get

$$\phi = \sum_n a_n \Psi_n \quad \text{with} \quad \sum_n a_n^* a_n = 1$$

where $\Psi_0, \Psi_1, \Psi_2, \dots, \Psi_n$ constitute a complete

set of normalized orthogonal functions. Substitution of this expansion gives

$$E = \sum_n \sum_n a_n^* a_n \int \Psi_n^* H \Psi_n d\tau = \sum_n a_n^* a_n W_n.$$

Upon subtracting the lowest state energy W_0 from both sides, one obtains

$$E - W_0 = \sum_n a_n^* a_n (W_n - W_0).$$

Since $W_n \geq W_0$ for all values of n and the coefficients $a_n^* a_n$ are all positive or zero, we have

$$(1) \quad E - W_0 = \text{positive value, thus } E > W_0$$

$$\text{or} \quad (2) \quad E - W_0 = 0 \text{ and } E = W_0.$$

Hence $E \geq W_0$. This proves that E is always an upper limit to the lowest energy level W_0 . This theorem is the basis for the variation method of calculating the value of the lowest energy level of a system.

Simpson applied the variation method to electrons trapped in sodium chloride and in some silver halides. We shall use his method without modification. However, many of the mathematical details are filled in and generalized equations are obtained which may be used to calculate energy levels for F-center electrons in any alkali halide with the sodium chloride structure. These generalized

equations made it possible to calculate low temperature (-194°C.) energy levels for the F-center electrons. The effect of small errors in some of the crystal parameters was investigated and found to be considerable. In our calculations the variable parameters were evaluated to the third decimal place. This order of accuracy was thought desirable since the energy equations were sensitive to small changes in the variable parameters.

The details of the method used in the calculations which follow are given below:

- (a) Modified hydrogen-like wave functions were used for the 1s and 2p states since the model chosen for the F-center is a close approximation to a hydrogen atom. The initial wave functions were of the form,

$$\psi_{1s}^{\circ} = A_1 (1 + \mu r) e^{-\mu r}$$

$$\psi_{2p_z}^{\circ} = A_2 r e^{-\alpha r} \cos \theta .$$

Each of these functions contains only one variable parameter since calculations using equations having two parameters would be impractical. More will be said about the reasons for choosing the above 1s wave function.

- (b) The field in which the electron moves and hence its potential $V(r) = \int_{\infty}^r F(r) dr$ was calculated.

- (c) The final wave function was assumed to be similar in form to the appropriate initial wave function and of the form

$$\Psi_1 = B_1 (1 + \lambda r) e^{-\lambda r}$$

$$\Psi_2 = B_2 + e^{-\beta r} \cos \theta .$$

These functions were used in the variation integral to give

$$W_{1s} = \int_0^{\infty} \Psi_1^* \left[-\frac{1}{2} \nabla^2 \right] \Psi_1 dr \\ + \int_0^R \Psi_1^* V_0 \Psi_1 dr + \int_R^{\infty} \Psi_1^* V_{(\mu)} \Psi_1 dr$$

$$W_{2p} = \iiint_{0,0,0}^{\infty,2\pi,\pi} \Psi_2^* \left[-\frac{1}{2} \nabla^2 \right] \Psi_2 dr \\ + \iiint_{0,0,0}^{\infty,2\pi,\pi} \Psi_2^* V_0 \Psi_2 dr \\ + \iiint_{0,0,0}^{\infty,2\pi,\pi} \Psi_2^* V_{(\alpha)} \Psi_2 dr .$$

For the 1s wave function $\left[-\frac{1}{2} \nabla^2 \right]$ becomes

$$\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right]$$

since the wave function has no angular components. However, for the 2p wave function $\left[-\frac{1}{2} \nabla^2 \right]$ becomes

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} - \frac{1}{2r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) - \frac{1}{2r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

where the last term becomes zero when Ψ_{2p_x} is used. The three $2p$ wave functions are equivalent since the state is a degenerate one.

- (d) The best function of the forms in (c) were obtained by minimizing the energy W with respect to the variable parameter, that is, by setting $\partial W_{1s}/\partial \lambda$ and $\partial W_{2p}/\partial \beta$ equal to zero and solving the resulting equations for the respective parameters. This gave λ as a function of μ and β as a function of α .
- (e) In order for the final wave equations to be consistent with the initial wave functions, it was necessary to set $\mu = 1$ and $\alpha = \beta$. The resulting equations were solved for λ and β .
- (f) Substitution of these in the equations in (c) and in the expressions for W gave the required wave functions and energies.

Generalized expressions for λ and β and for W_{1s} and W_{2p} were desired, since values of these quantities were to be calculated for four alkali halides. These general expressions are given in outline form only since some of the algebraic steps involved were exceedingly long and cumbersome.

Generalized Equations for Variable Parameters and Energies

The 1s state will be considered first. In choosing a suitable wave function for the 1s state the function

$\Psi = A e^{-\mu r}$ was considered but discarded. The form of the potential function used to represent the "hole" dictated the choice of a suitable wave function. Let us consider the wave equation for an electron moving in a potential field such as that shown in Figure 25 (d).

That is,

$$\frac{d^2 \Psi}{dr^2} + (2m/\hbar^2)(E - V)\Psi = 0$$

where Ψ satisfies the usual conditions for a well-behaved wave function. Of immediate interest is the requirement that $\partial \Psi / \partial r$ be finite and continuous for all values of r .

The potential function of Figure 25 (d) may be treated as a "square well potential" for the purpose of establishing the qualitative behavior of the wave function for electrons in the bound states of the potential well. When $r < -R$, we have an exponential solution which increases with increasing r and curves upward. At $r = -R$, the kinetic energy becomes positive, and since Ψ is positive, the curvature becomes negative. The wave function begins to curve back toward $\Psi = 0$; the rate of curvature depending on $V_0 - |E|$. If $V_0 - |E|$ is

large enough, the slope of Ψ will be negative by the time we reach $r = R$. For $r > R$, Ψ begins to curve upward again, because $V_0 - |E|$ is negative. Only if $|E|$ is such that the slope at $r = R$ exactly matches the required slope of a decreasing exponential will Ψ remain bounded as $r \rightarrow \infty$. Between $r = -R$ and $r = R$ the slope, $\partial\Psi/\partial r$, passes from a positive to a negative value. If the requirement that $\partial\Psi/\partial r$ be everywhere continuous is to hold, then the slope must pass through a value of zero. This must occur at $r = 0$, since Ψ has spherical symmetry. In view of this criterion $\Psi = Ae^{-\mu r}$ was not satisfactory, whereas the function $\Psi_{1s}^0 = A_1(1+\mu r)e^{-\mu r}$ is satisfactory since

$$\frac{\partial \Psi_{1s}^0}{\partial r} = -\mu^2 A_1 r e^{-\mu r}.$$

By using the normalizing condition

$$1 = \int_0^\infty \Psi_{1s}^{0*} \Psi_{1s}^0 4\pi r^2 dr = 4\pi A_1^2 \int_0^\infty r^2 (1+\mu r)^2 e^{-2\mu r} dr$$

we find that $A_1^2 = \mu^3/7\pi$. Throughout these calculations atomic units will be used unless otherwise indicated, that is, the unit of length will be $a_H = 0.5285 \text{ \AA}$ and the unit of energy will be $2 R_{hc} = 27.060 \text{ e.v.}$

Since $p(r) = \int_0^\infty |\Psi|^2 4\pi r^2 dr$, we find by

straightforward substitution and integration that

$$f(r) = 1 - e^{-2\mu r} \left(\frac{2}{7} \mu^4 r^4 + \frac{8}{7} \mu^3 r^3 + 2\mu^2 r^2 + 2\mu r + 1 \right).$$

The field is given by $F(r) = (1/Kr^2)[1 - f(r)] + (1/K_0 r^3)f(r)$

$$\text{and } F(r) = 1/K_0 r^2 + C e^{-2\mu r} \left(\frac{2}{7} \mu^4 r^2 + \frac{8}{7} \mu^3 r + 2\mu^2 + 2\mu r^{-1} + r^{-2} \right),$$

$$\text{where } C = (1/K_0 - 1/K). \quad \text{Now } V(r) = \int_{\infty}^r F(r) dr$$

which gives

$$V(r) = -1/K_0 r + C r^{-1} e^{-2\mu r} + C e^{-2\mu r} \left(\frac{1}{7} \mu^3 r^2 + \frac{5}{7} \mu^2 r + \frac{9}{14} \mu \right).$$

The potential energy at the center of the hole is given by

$$V_0 = -1.7476/q_0 + (1/R)(1 - 1/K_0).$$

Using the final form of the 1s wave function

$$\Psi_1 = B_1 (1 + \lambda r) e^{-\lambda r}$$

where $B_1^2 = \lambda^3/2\pi$ from the normalizing condition, the variation integral becomes

$$\begin{aligned} W_{1s} = & 2\lambda^3/7 \int_0^{\infty} e^{-2\lambda r} (-\lambda^4 r^4 + 2\lambda^3 r^3 + 3\lambda^2 r^2) dr \\ & + 4\lambda^3 V_0/7 \int_0^R e^{-2\lambda r} (\lambda^2 r^4 + 2\lambda r^3 + r^2) dr \\ & - 4\lambda^3 C/7K_0 \int_R^{\infty} e^{-2\lambda r} (\lambda^2 r^3 + 2\lambda r^2 + r) dr \end{aligned}$$

$$+ 4A^3C/7 \int_R^\infty \left\{ e^{-2(\lambda+\mu)+} \left[\lambda + \left(2\lambda + \frac{19}{14}\mu \right) \lambda^2 \right. \right. \\ \left. \left. + \left(\lambda^2 + \frac{19}{17}\mu\lambda + \frac{5}{7}\mu^2 \right) \lambda^3 + \left(\frac{19}{14}\mu\lambda^2 + \frac{10}{7}\mu^2\lambda + \frac{1}{7}\mu^3 \right) \lambda^4 \right. \right. \\ \left. \left. + \left(\frac{5}{7}\mu^2\lambda^2 + \frac{2}{7}\mu^3\lambda \right) \lambda^5 + \frac{1}{7}\mu^3\lambda^2 + \mu^6 \right] \right\} d\lambda.$$

Evaluation of these integrals gave W_{1s} as a function of λ , R , and μ . After obtaining $\partial W_{1s}/\partial \lambda$ and setting $\mu=\lambda$, we obtained the equation below which eventually yielded a value for λ by successive approximations:

$$\frac{\partial W_{1s}}{\partial \lambda} = 0 = 0.42857\lambda + 0.57142RV_0 e^{-2\lambda R} (R^4\lambda^4 + 2R\lambda^3 + R^2\lambda^2) \\ + (e^{-2\lambda R}/14K_0) (8R^4\lambda^4 + 12R^3\lambda^3 - 16R^2\lambda^2 - 18R\lambda - 9) \\ - 0.57142C e^{-4\lambda R} (0.07142R^7\lambda^7 + 0.44643R^6\lambda^6 \\ + 0.95537R^5\lambda^5 + 0.17632R^4\lambda^4 - 2.6451R^3\lambda^3 \\ - 4.50168R^2\lambda^2 - 3.03436R\lambda + 0.7502).$$

The energy is given by

$$W_{1s} = 0.21428\lambda^2 + V_0 - V_0 e^{-2\lambda R} (0.28571R^4\lambda^4 \\ + 1.14285R^3\lambda^3 + 2R^2\lambda^2 + 1) \\ - (e^{-2\lambda R}/14RK_0) (4R^4\lambda^4 + 14R^3\lambda^3 + 18R^2\lambda^2 + 9R\lambda)$$

$$+ (0.57142 C e^{-4A/R/R}) (0.03571 R^7 A^7 + 0.30357 R^6 A^6 + 1.11161 R^5 A^5 + 2.21874 R^4 A^4 + 2.50334 R^3 A^3 + 1.50167 R^2 A^2 + 0.3754 R A).$$

In calculating the quantities necessary to determine the energy of the 2p state it is convenient to use as an initial wave function

$$\psi^0 = A_2 + e^{-\alpha r} \cos \theta.$$

Either of the two other 2p wave functions would serve equally well but would be more cumbersome.

Normalizing gives

$$1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} A_2^2 + e^{-2\alpha r} \sin^2 \theta \cos^2 \theta d\theta d\phi dr$$

since $d\tau = r^2 \sin \theta dr d\theta d\phi$, and $A_2^2 = \alpha^5/\pi$. The fraction of the electronic charge normally found within radius r is given by

$$f(r) = 1 - e^{-2\alpha r} \left(\frac{2}{3} \alpha^4 r^4 + \frac{4}{3} \alpha^3 r^3 + 2\alpha^2 r^2 + 2\alpha r + 1 \right)$$

which leads to

$$F(r) = 1/K_0 r^2 + C' e^{-2\alpha r} \left(\frac{2}{3} \alpha^4 r^2 + \frac{4}{3} \alpha^3 r + 2\alpha^2 + 2\alpha r^{-1} + r^{-2} \right)$$

where $C' = (1/K - 1/K_0)$. The potential of this field is

given by
$$V(\alpha) = \int_0^r F(r) dr$$

or $V_{(\alpha)} = -\frac{1}{K_0 r} - C'e^{-2\alpha r} \left(\frac{1}{3} \alpha^3 r^2 + \alpha^2 r + \frac{3}{2} \alpha + r^{-1} \right).$

The final 2p wave function must be of the form

$$\Psi_2 = B_2 + e^{-\beta r} \cos \theta \text{ where } B_2^2 = \beta^5/\pi \text{ from}$$

normalization. Substitution of this wave function in the variation integral gives

$$\begin{aligned} W_{2p} = & 4\beta^5/3 \int_0^\infty \left(2\beta r^3 - \frac{1}{2} \beta^2 r^4 \right) e^{-2\beta r} dr \\ & + 4\beta^5/3 \int_0^R r^4 e^{-2\beta r} dr + 4\beta^5/3 \int_R^\infty r^4 e^{-2\beta r} \left[-\frac{1}{K_0 r} \right. \\ & \left. - C'e^{-2\alpha r} \left(\frac{1}{3} \alpha^3 r^2 + \alpha^2 r + \frac{3}{2} \alpha + r^{-1} \right) \right] dr. \end{aligned}$$

Evaluation of this equation gave W_{2p} as a function of β , R , and α . An expression for $\partial W_{2p} / \partial \beta$ was obtained and set equal to zero after substituting $\alpha = \beta$. The following equation, which eventually yielded values of β , was the result:

$$\begin{aligned}
\frac{\partial W_{2f}}{\partial \beta} = 0 = & \beta + 4(RV_0/3 - 1/3K_0) e^{-2\beta R} R^4 \beta^4 \\
& - (e^{-2\beta R}/3K_0)(2R^3\beta^3 + 3R^2\beta^2 + 3R\beta + 1.5) \\
& + (c' e^{-4\beta R}/18)(4R^7\beta^7 + 9R^6\beta^6 + 1.5R^5\beta^5 \\
& - 31.125 R^4\beta^4 - 61.125 R^3\beta^3 - 45.8436 R^2\beta^2 \\
& - 22.9219 R\beta - 5.7304).
\end{aligned}$$

Finally the energy equation is:

$$\begin{aligned}
W_{2f} = & \beta^2/2 + V_0 - \frac{V_0}{3} e^{-2\beta R} (2R^4\beta^4 + 4R^3\beta^3 + 6R^2\beta^2 \\
& + 6R\beta + 3) - (\beta e^{-2\beta R}/6K_0)(4R^3\beta^3 + 6R^2\beta^2 \\
& + 6R\beta + 3) - (c' e^{-4\beta R}/18)(2R^7\beta^7 + 9R^6\beta^6 \\
& + 20.25 R^5\beta^5 + 26.25 R^4\beta^4 + 19.6875 R^3\beta^3 \\
& + 9.8437 R^2\beta^2 + 2.4609 R\beta).
\end{aligned}$$

Constants Needed for Evaluating Energies of 1s and 2p Levels

Table 17 shows a compilation of all the constants needed in the general equations derived above. The quantities tabulated are all given in atomic units; a_0 is the interionic distance, R is the radius of the hole left upon removing a negative ion from the lattice, V_0 is the potential energy at the center of this hole, and K , K_0 are the dielectric constants. The information needed in compiling this table was gathered from many sources. These sources are listed below with the methods of calculation used.

Table 17. Constants used in the generalized equations for W_{1s} and W_{2p} and the equations for the variable parameters λ and β .

| Crystal | a_0 | R/a_0 | R | V_0 | K | K_0 |
|--------------|-------|---------|------|--------|------|-------|
| NaCl | 5.325 | 0.940 | 5.03 | -0.218 | 5.62 | 2.25 |
| KCl | 5.938 | 0.838 | 4.98 | -0.188 | 4.68 | 2.13 |
| KBr | 6.216 | 0.865 | 5.38 | -0.175 | 4.78 | 2.33 |
| KI | 6.670 | 0.896 | 5.98 | -0.157 | 4.94 | 2.69 |
| KCl | 5.897 | 0.834 | 4.92 | -0.189 | 4.33 | 2.12 |
| -194°C. | | | | | | |
| *KCl 20°C | 5.938 | 0.855 | 5.08 | -0.190 | 4.68 | 2.17 |

Column 1. The alkali halides are listed here and the temperature is 20°C. unless indicated otherwise. For *KCl_{20°C.}, the R/a_0 value is that obtained by Mott and

Littleton.

Column 2. Values for the interionic distance were obtained from ASTM x-ray cards with the exception of the -194°C . value for KCl. This low temperature value was calculated from the coefficient of expansion and the value of a_0 at 20°C . (1,p.153). Mean values of the coefficient of expansion, $\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)$, were used as tabulated by Dayal. They were as follows:

| Temperature $^{\circ}\text{K}$ | $\alpha \times 10^6$ | ΔT | $\alpha \Delta T$ |
|-----------------------------------|----------------------|---------------|-------------------|
| 89-194 | 89.7 | 115° | 0.0103 |
| 194-273 | 101 | 79° | 0.0080 |
| 273-323 | 110 | 20° | <u>0.0022</u> |
| | | | $\Sigma 0.0205$ |

Using the total $\alpha \Delta T$, we have

$$\begin{aligned}
 V_{-194^{\circ}\text{C}} &= V_0 (1 - \alpha \Delta T) \\
 \text{and } a_{0_{-194^{\circ}\text{C}}} &= [V_0 (1 - \alpha \Delta T)]^{\frac{1}{3}} \\
 &= a_{0_{+20^{\circ}\text{C}}} (0.9795)^{\frac{1}{3}} \\
 a_{0_{-194^{\circ}\text{C}}} &= 5.897 \text{ atomic units.}
 \end{aligned}$$

Column 3. The ratios in this column were calculated by means of a first order approximation method developed in a paper by Mott and Littleton (19, pp.490-493). A first order approximation was used because of the excessive labor involved in solving the equations for the higher order approximations. Mott and Littleton used a value of 2.33 for K_0 of NaCl whereas the better value 2.25 was used in our calculations. The value of K_0 for KCl was taken as 2.13 in place of 2.17. By using the first order approximation, all of the results were kept on a consistent basis. Details of the method are given in the Appendix.

Column 4. This column gives values of the radius of the hole in the crystal left upon removing a negative ion from the lattice.

Column 5. Values of the potential energy at the center of the hole are listed here. That is,

$$V_0 = -\alpha/q_0 + (1/R)(1 - 1/K_0)$$

where α is Madelung's constant (1.7476) for a cubic lattice of the NaCl type.

Column 6. Here are listed values of the dielectric constant K for static fields (18, p.12). The value for KCl (-194° C.) was obtained from a paper by

Eucken and Büchner in which they plotted the temperature dependence of the dielectric constant K (3,p.343). That is, $K(-194^{\circ} \text{ C.}) = 0.925 K(20^{\circ} \text{ C.})$.

Column 7. In this column we find values of the high frequency dielectric constant K_0 . (18, p.12). The value of K_0 for $\text{KCl}(-194^{\circ} \text{ C.})$ was obtained by using the temperature coefficient of refractive index ($dn/dt = -2.87 \times 10^{-5}$) at 8.84μ (12,pp.461-462).

In order to determine the effect of small changes in R/a_0 and therefore, changes in R on the 1s and 2p energies, calculations were made using the first order approximation of Mott and Littleton for R/a_0 of KCl at 20° C (19, p.493).

Energies of the 1s and 2p Levels in Alkali Halide F-Centers

In solving the equations for λ and β , the difference between the sum of the positive terms and the sum of the negative terms was reduced to 0.25 per cent or less by successive approximations. This difference corresponded to two units in the third decimal place for λ and to about one unit in the third decimal place for β . The values of the parameters λ and β and the energies of the 1s and 2p levels are shown in Table 18.

Table 18. Compilation of calculated values for electronic 1s - 2p transitions in alkali halides. (The calculated values for the variable parameters λ and β are also given.)

| Salt | F-band Max. e.v. | λ | W_{1s} (e.v.) | β | W_{2p} (e.v.) | W_{2p-1s} (e.v.) | Obs.-calc. ΔW e.v. |
|----------------|------------------------|-----------|--------------------|---------|--------------------|-----------------------|-------------------------------|
| NaCl | 2.67 | 0.524 | -3.32 | 0.361 | -0.75 | 2.57 | +0.10 |
| KCl | 2.19 | 0.489 | -2.81 | 0.297 | -0.46 | 2.35 | -0.16 |
| KBr | 1.96 | 0.471 | -2.64 | 0.306 | -0.52 | 2.12 | -0.16 |
| KI | 1.75 | 0.444 | -2.40 | 0.310 | -0.58 | 1.82 | -0.07 |
| KCl -194°C. | 2.27 | 0.491 | -2.81 | 0.295 | -0.46 | 2.35 | -0.08 |
| *KCl 20°C. | 2.19 | 0.490 | -2.87 | 0.310 | -0.53 | 2.34 | -0.15 |

* Calculations based on Mott and Littleton value of 0.855 for R/a_0 .

Final Wave Functions and Electron Density Distribution Curves for 1s and 2p Levels in F-Centers

The final forms of the 1s and 2p wave functions are listed below showing the numerical values of the constants determined in the calculations described above. For the 1s state we have: (20° C. unless otherwise indicated)

| | |
|-------------------|---|
| NaCl | $\bar{\Psi}_1 = 0.0809 (1 + 0.524r)e^{-0.524r}$ |
| KCl | $\bar{\Psi}_1 = 0.0729 (1 + 0.489r)e^{-0.489r}$ |
| KBr | $\bar{\Psi}_1 = 0.0690 (1 + 0.471r)e^{-0.471r}$ |
| KI | $\bar{\Psi}_1 = 0.0623 (1 + 0.444r)e^{-0.444r}$ |
| KCl (-194° C.) | $\bar{\Psi}_1 = 0.0733 (1 + 0.491r)e^{-0.491r}$ |

and for the 2p state:

| | |
|-------------------|---|
| NaCl | $\bar{\Psi}_2 = 0.0441 r e^{-0.361r} \cos \theta$ |
| KCl | $\bar{\Psi}_2 = 0.0271 r e^{-0.297r} \cos \theta$ |
| KBr | $\bar{\Psi}_2 = 0.0292 r e^{-0.306r} \cos \theta$ |
| KI | $\bar{\Psi}_2 = 0.0302 r e^{-0.310r} \cos \theta$ |
| KCl (-194° C.) | $\bar{\Psi}_2 = 0.0267 r e^{-0.295r} \cos \theta$ |

All of the coefficients were derived using atomic units, hence r must be in these units also.

The 1s and 2p wave functions for NaCl are plotted in Figure 26. Atomic units are used and the relative spacing of the ions in the lattice is shown as well as the Bohr radii. It is of interest to determine the

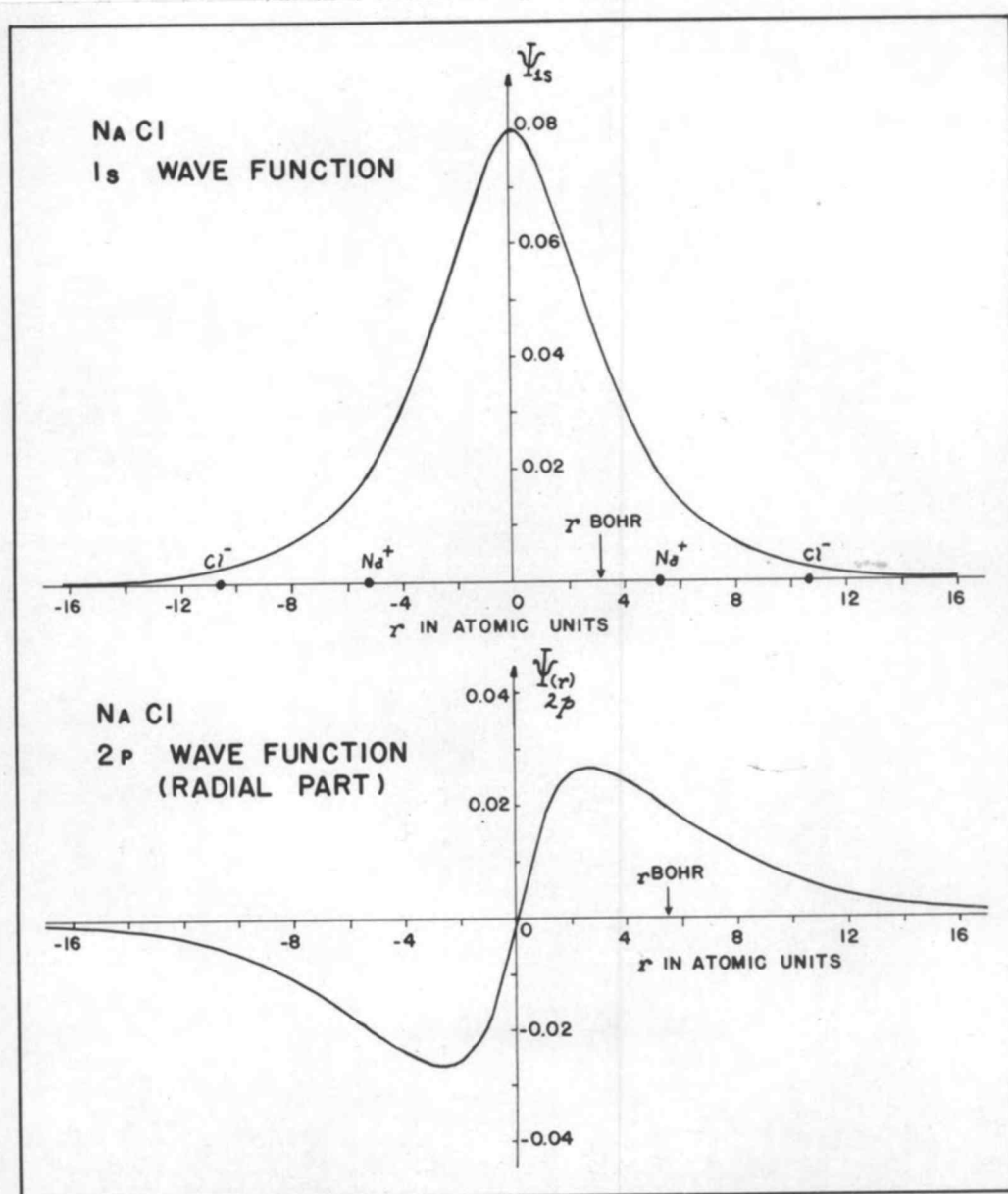


FIGURE 26. WAVE FUNCTIONS FOR F-CENTER ELECTRONS IN SODIUM CHLORIDE AT 20°C.

electron density distribution curves for both 1s and 2p states, since such curves give the Bohr radii and information as to how the electron behaves in the crystal.

Such curves are shown in Figure 27 for the crystals at 20° C. while Figure 28 gives the results for KCl at 20° C. and -194° C. The Bohr radius for the 1s state was obtained by maximizing the distribution

function $4\pi r^2 \Psi_{1s}^2$ with respect to r. Thus

$$4\pi r^2 \Psi_{1s}^2 = (4\lambda^3/\pi) r^2 (1 + \lambda r)^2 e^{-2\lambda r}$$

$$\frac{d}{dr} (4\pi r^2 \Psi_{1s}^2) = (4\lambda^3/\pi) [e^{-2\lambda r} (2 + 4\lambda r^2 - 2\lambda^3 r^3)]$$

which gave $0 = 1 + 2\lambda r - \lambda^3 r^3$

as the equation to be solved for r.

For the 2p state the equation is much simpler, that is

$$4\pi r^2 \Psi_{2p(r)}^2 = 4\beta^5 r^4 e^{-2\beta r}$$

$$\frac{d}{dr} (4\pi r^2 \Psi_{2p(r)}^2) = (4\beta^5/3) (4r^3 - 2\beta r^4) e^{-2\beta r}$$

and the equation to be solved for r is $0 = 4r^3 - 2\beta r^4$,

and $r = 2/\beta$. In Table 19 the Bohr radii are listed for several alkali halides.

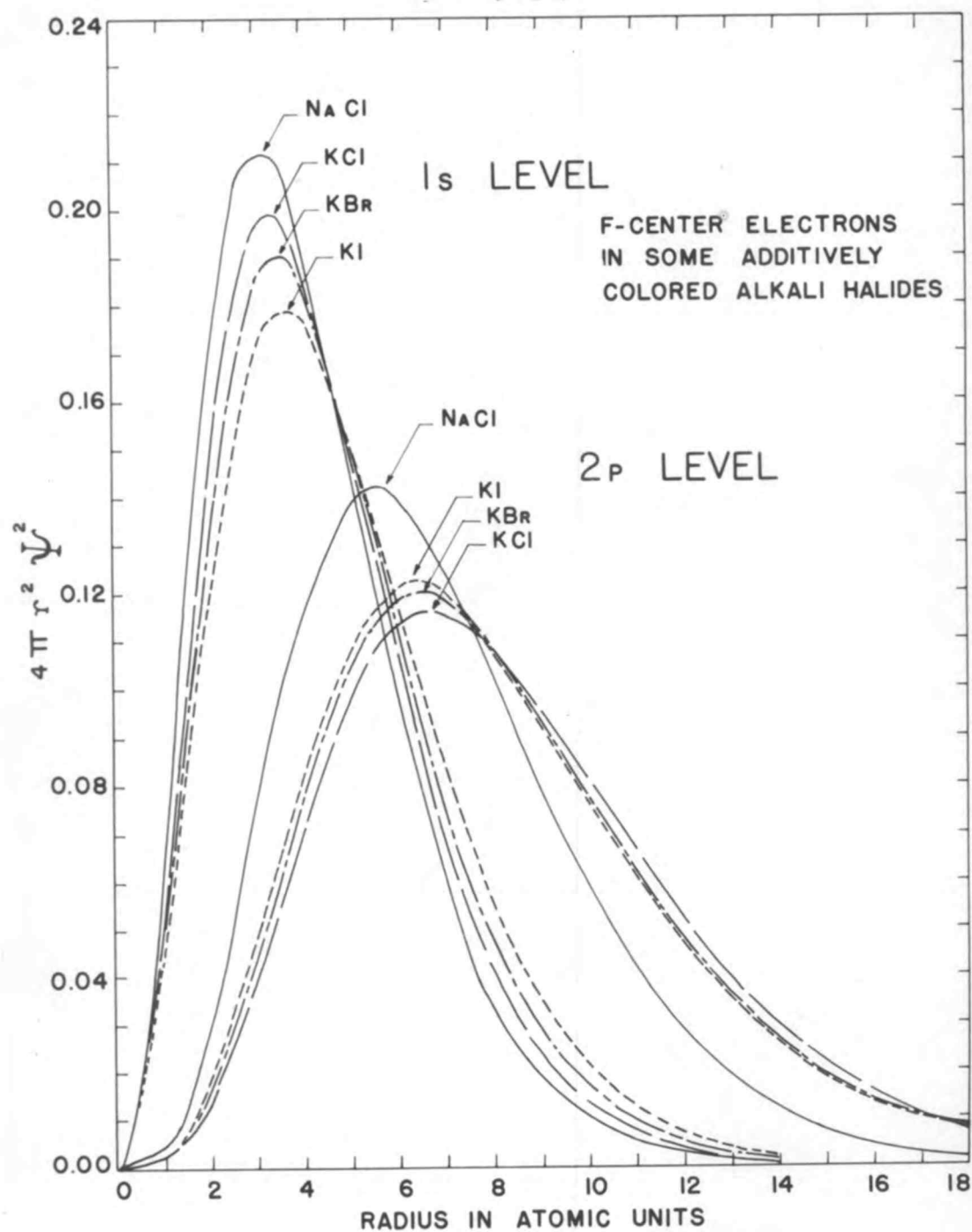


FIGURE 27. ELECTRON DENSITY DISTRIBUTION CURVES FOR SOME ALKALI HALIDES AT 20° C.

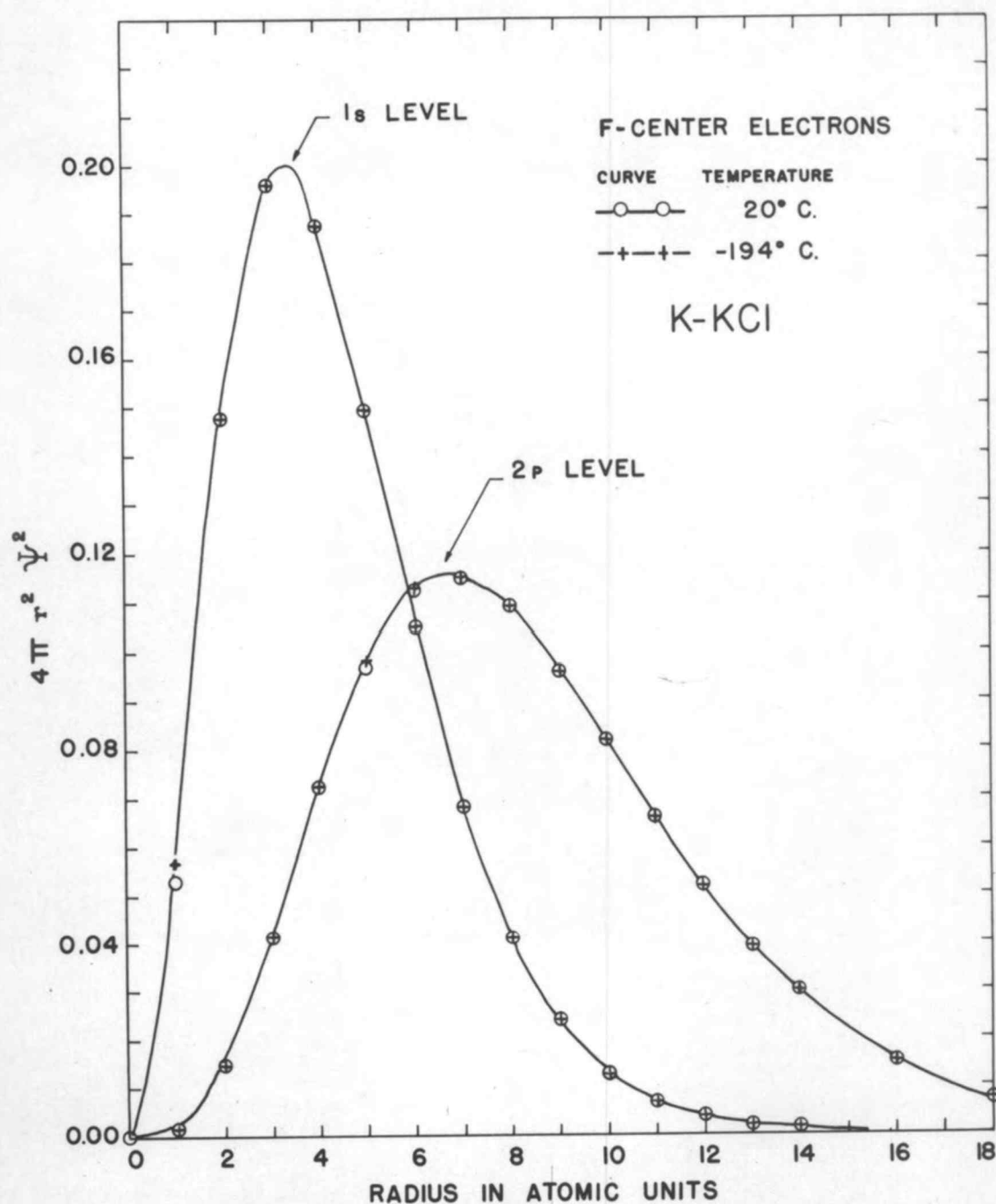


FIGURE 28. ELECTRON DENSITY DISTRIBUTION CURVES FOR K-KCl AT 20° AND -194° C.

Table 19. Mean Bohr orbit radii for F-center electrons in 1s and 2p states.

| Salt | r_{1s} (atomic units) | r_{2p} (atomic units) | r_{1s} (Angstroms) | r_{2p} (Angstroms) | Interionic distance a_0 (Angstroms) |
|-----------------|----------------------------|----------------------------|-------------------------|-------------------------|---|
| NaCl | 3.10 | 5.54 | 1.64 | 2.93 | 2.814 |
| KCl | 3.30 | 6.73 | 1.74 | 3.56 | 3.138 |
| KBr | 3.43 | 6.54 | 1.81 | 3.46 | 3.285 |
| KI | 3.63 | 6.45 | 1.92 | 3.41 | 3.525 |
| KCl -194° C. | 3.29 | 6.78 | 1.74 | 3.58 | 3.114 |

Thermal Activation Energy for F-Center Electrons (2p State to Conduction Band)

In the section on energy level calculations we have seen that the trapped electron may occupy either of at least two bound states and still be considered as an F-center. It is possible for the electron in the excited 2p state to receive energy from the vibrating lattice and thereby pass into the conduction band.

The various symbols to be used in the following discussion are shown graphically in Figure 29. The symbols are those used by Mott and Gurney and their method of estimating the thermal activation energy will be extended to F-centers (18, pp.160-162). Simpson has calculated this energy for F-center electrons in

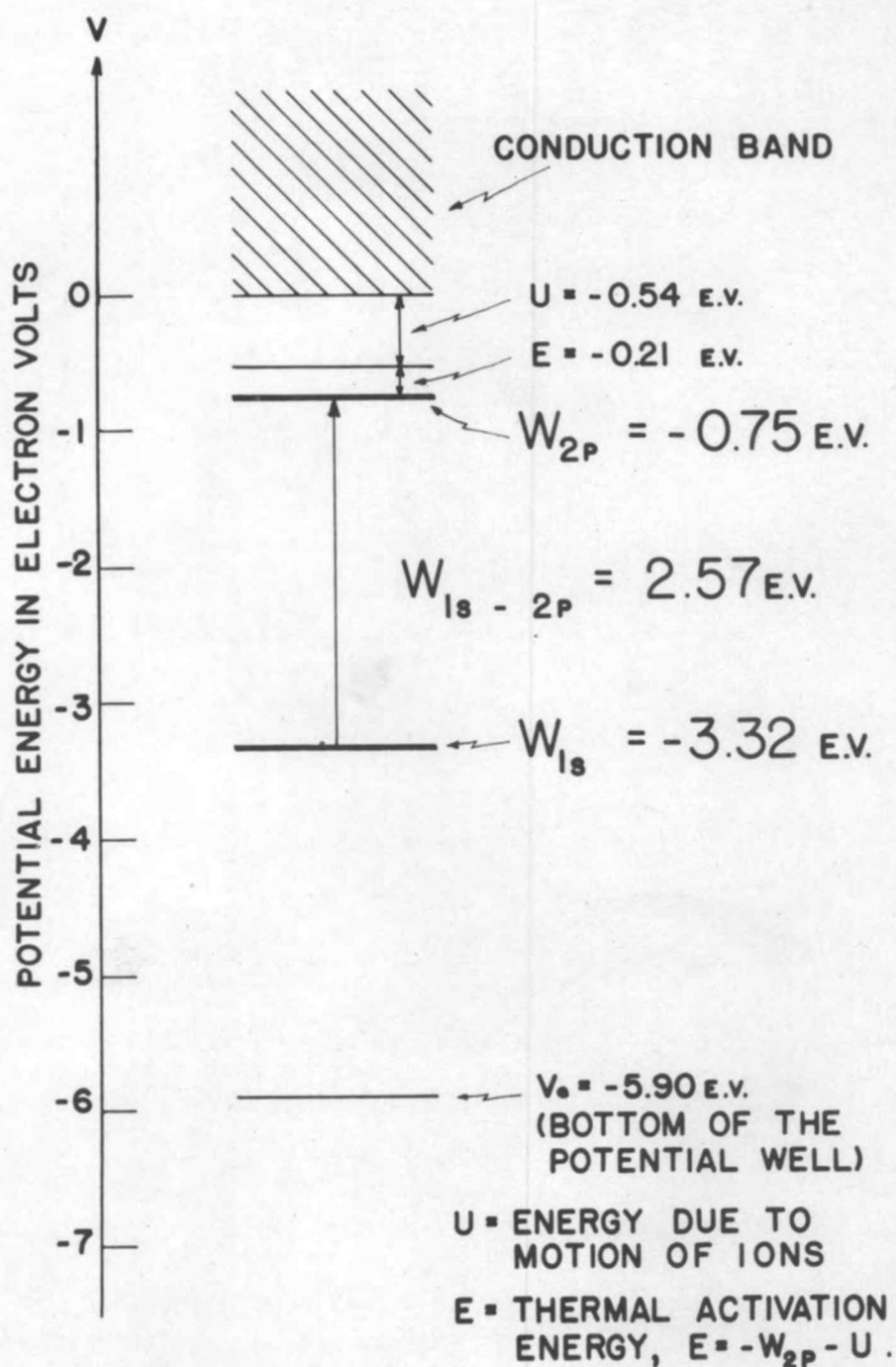


FIGURE 29. SCHEMATIC DIAGRAM SHOWING THE RELATIONSHIP OF THE F-CENTER ENERGY LEVELS CALCULATED FOR SODIUM CHLORIDE, 20°C.

NaCl (34, pp.278-280).

When an electron in an excited level, such as the 2p level in Figure 29, absorbs a quantum of energy corresponding to W_{2p} it moves into the conduction band. Before this absorption process occurs the ions surrounding the F-center are in equilibrium, and after the electron has been removed to a distant point in the lattice the ions will no longer be in equilibrium, and will move into new positions of equilibrium. During this movement the ions give up the energy called U in the diagram. The thermal activation energy is then given by

$$E = -W_{2p} - U.$$

According to Mott and Gurney the energy of the medium per unit volume is $(ED)/8\pi$, where E is the field and $D = e/r^2$ is the electric displacement. We have seen in the discussion under theoretical considerations that the field is

$$E = e/Kr^2 + (e\cancel{p}_{(r)}/r^2)(1/K_0 - 1/K),$$

where e is the electronic charge.

Therefore

$$(1/8\pi)(ED) = (1/8\pi)\left[e/Kr^2 + (e\cancel{p}_{(r)}/r^2)(1/K_0 - 1/K)\right]\frac{e}{r^2}$$

and since the volume element is $4\pi r^2 dr$

$$(1/8\pi)(ED) 4\pi r^2 dr = \frac{r^2 dr}{2} \left[e/Kr^2 + (e f_{(r)}/r^2)(1/K_0 - 1/K) \right] \frac{e}{r^2}.$$

This is the energy of an element of the medium of radius r after the electron has been moved but before the ions have taken up new positions of equilibrium. After the ions take up their new positions the energy of this element becomes

$$\frac{r^2 dr}{2} (e/Kr^2)(e/r^2) = \frac{1}{2} dr \frac{e^2}{Kr^2}.$$

The energy given up by the medium is the difference of these two quantities integrated over the region R to ∞ .

Thus in atomic units

$$U = \int_R^\infty \frac{1}{2} \left[\frac{1 - f_{(r)}}{K} + \frac{f_{(r)}}{K_0} - \frac{1}{K} \right] \frac{dr}{r^2}$$

$$U = \int_R^\infty \frac{1}{2} \left(\frac{1}{K_0} - \frac{1}{K} \right) \frac{f_{(r)} dr}{r^2}.$$

Since we are considering transitions from a 2p state we must use

$$f_{(r)} = 1 - e^{-2\beta r} \left(\frac{2}{3}\beta^4 r^4 + \frac{4}{3}\beta^3 r^3 + 2\beta^2 r^2 + 2\beta r + 1 \right).$$

$$\text{Hence } U = \frac{1}{2} \left(\frac{1}{K_0} - \frac{1}{K} \right) \int_R^{\infty} \left[\frac{1}{x^2} - e^{-2\beta x} \left(\frac{2}{3} \beta^4 x^2 + \frac{4}{3} \beta^3 x + 2\beta^2 + 2\beta x^{-1} + x^{-2} \right) \right] dx$$

$$\text{and } U = \frac{1}{2} \left(\frac{1}{K_0} - \frac{1}{K} \right) \left\{ \frac{1}{R} - e^{-2\beta R} \left[\frac{\beta}{3} (R^2 \beta^2 + 3R\beta + 5) + \frac{1}{R} \right] \right\}.$$

This equation was applied to the crystals listed in Table 20 with the results shown.

Table 20. Thermal activation energy E , (2p state to conduction band) for alkali halides.

| Salt | R | β | W_{2p} (e.v.) | U (e.v.) | E (e.v.) |
|---------------|------|---------|--------------------|-------------|-------------|
| NaCl | 5.03 | 0.361 | 0.75 | 0.54 | 0.21 |
| KCl | 4.98 | 0.297 | 0.46 | 0.45 | 0.01 |
| KBr | 5.38 | 0.306 | 0.52 | 0.39 | 0.13 |
| KI | 5.98 | 0.310 | 0.58 | 0.29 | 0.29 |
| KCl -194°C | 4.92 | 0.295 | 0.46 | 0.43 | 0.03 |
| *KCl 20°C | 5.08 | 0.310 | 0.53 | 0.45 | 0.08 |

*Calculations based on Mott and Littleton value of 0.855 for R/a_0 .

CHAPTER VI

DISCUSSION AND SUMMARY OF RESULTS

Sources of Error in the Experimental Work

An estimation of the magnitude of the errors in the measurements involved in determining F-center concentration from absorption curve data has been made by Scott and Smith (31, p.984). No attempt will be made to determine the errors inherent in the approximations made in deriving the Smakula equation. However, it must be noted that the oscillator strength f was taken to be unity. This assumption affects all of the concentrations the same way and the concentrations herein can be converted to absolute values as soon as accurate oscillator strengths are determined for the various alkali halide F-center electrons.

Small random errors were introduced in the optical density measurements from inaccuracies due to dark current drift, 100 per cent transmission settings, optical density scale settings, and positioning of the sample. However, these errors were largely eliminated by taking the mean of several concentration determinations at each temperature. In this way the probable

error in the mean was reduced to less than 3.5 per cent. This mean probable error also reflects systematic errors arising from the following sources: (a) thickness measurements, (b) the mean value used for the band width, W , at half maximum, and (c) the choice of a base line for calculating the maximum value of α .

The thickness measurements were made microscopically with a micrometer eyepiece and 10X objective. Errors in these measurements were only 0.1 to 0.2 per cent and could be ignored. A sufficiently large number of observations was made on the F-band width at half maximum in order to reduce the probable error in the mean to less than one per cent for the 20° C. data and to less than two per cent for the -194° C. data listed in Table 2. Reasons for using a mean value for W have been stated previously.

By far the largest single source of error occurs in the choice of a base line, representing no absorption, from which α maximum is measured. For the curves where there is little if any overlapping of the colloidal band the choice of a base line was conditioned by the results shown in Figure 7. In these cases the error introduced was probably not greater than 5 per cent for the most unreliable curves. A much larger error in α maximum resulted when it was found necessary to

construct a base line by the method described in Chapter II for overlapping bands. This error was probably of the order of 10 per cent for the curves showing largest overlap. However, it is believed that this error does not exceed 5 per cent for the concentration values used in obtaining the heats of formation of F-centers in potassium bromide and potassium iodide. From these considerations, the overall probable error in the reported concentrations is about 7 per cent.

Results of Thermal Stability Measurements on F-centers in Potassium Bromide and Potassium Iodide

In the measurements on the thermal stability of F-centers, it was assumed that at a specific temperature an equilibrium existed between the F-centers and a higher aggregate, referred to as "colloidal" centers. The nature of this equilibrium was inferred from the following observations:

- (1) The concentration of F-centers at a given temperature was independent of the total concentration of color centers. See Figures 9 and 13.
- (2) The "colloidal" band did not appear in crystals having less than the saturation concentration of F-centers.

These facts suggested that the equilibrium is a heterogeneous one, that is, the higher aggregate constitutes

one phase (solid) and the F-centers constitute the dispersed (or dissolved) phase. The equilibrium established in these additively colored crystals is similar to that established between a partially soluble solute and its saturated solution.

The rate of coagulation of F-centers is indicated roughly by the time required to reach equilibrium at each temperature. However, more accurate measurements will have to be made before the activation energy for the coagulation process can be calculated. The heating times reported for the potassium iodide crystals do not show such a well defined trend as those for potassium chloride and potassium bromide. Two factors contribute to this condition, (a) the temperature interval is considerably smaller, and (b) longer heating times led to excessive bleaching.

In order to calculate ΔH for the process

"colloidal" centers \longrightarrow F-centers

the data of Tables 7 and 9 were plotted to give Figure 12. In this figure, the logarithm of the equilibrium F-center concentration ($\ln K$) is plotted against $1/T$. Values of ΔH for a given temperature are obtained by measuring the slope of the curve, at the particular temperature, and using it in the integrated form of the

equation

$$d \ln K/dT = \Delta H/RT^2.$$

One justification in using this method for determining ΔH for the process above is the fact that the plots in Figure 12 resulted in nearly straight lines. The curvature noticed at both ends of the temperature range is probably due to several factors. One contributing factor, especially at low temperatures, is the greatly magnified effect of the systematic errors introduced in choosing the proper base line. At the lower temperatures the colloidal band predominates and overlapping plays an increasingly important role in making the F-band appear larger than it actually is. At the higher temperatures the mechanism of coagulation may be quite different, that is, some of the higher aggregates may not exist at all. The quenching rate also becomes important at the higher temperatures.

Over a rather limited temperature range the curves may be considered straight and their respective slopes used for evaluating ΔH . The values obtained are listed in Table 21. It is of interest to note that the values of ΔH for KCl and KBr are approximately twice as large as the values of W_F , the energy of formation of F-centers from the vapor, for these crystals (18, p.145, and 27, p.390). Until more exact information concerning the structure of the higher aggregates is obtained no

Table 21. Heats of formation of F-centers from higher aggregates (colloidal centers) in additively colored alkali halides.

| <u>Crystal</u> | <u>Temperature °C</u> | <u>ΔH Kcal/mole</u> | <u>ΔH e.v./mole</u> |
|----------------|---------------------------|--|--|
| KCl | 350 | $8.0 \pm 0.3^*$ | 0.346 ± 0.013 |
| KBr | 325 | 11.4 ± 0.4 | 0.495 ± 0.017 |
| KI | 340 | 9.0 ± 0.3 | 0.390 ± 0.013 |

* Value for KCl taken from data of Scott and Smith.

theoretical calculation of ΔH will be feasible.

New Band in the Absorption Spectrum of Additively Colored Potassium Iodide

A hitherto unreported band was discovered in the absorption spectrum of additively colored potassium iodide. The properties and characteristics of this band are summarized as follows:

- (1) The band appears only in the absorption spectrum of crystals which have been heated for long periods of time (from 90 to 250 hours) at about 600° C. in the coloration process.
- (2) The band has a maximum which occurs at a wave length between 650 and 670 millimicrons.
- (3) Temperature has no apparent effect on either the location of the band maximum or the width of the band at half maximum height, in the range 20° to -194° C.

- (4) This band was very stable toward light of 650 to 670 millimicrons wave length and gave no observable optical products.
- (5) Crystals in which the band appeared gave reproducible results when heated and quenched. That is, the centers responsible for the absorption band could be formed by heating at a specific temperature and then quenching in carbon tetrachloride.

Experiments on the thermal stability of the 650 millimicron band established the following facts:

- (1) The band maximum appeared at 665 millimicrons when the four crystals were quenched from 300° C.
- (2) Lower temperature (275° C.) favors the 650 millimicron band formation.
- (3) Temperatures above 300° C. lead to conversion to F-centers and even to centers absorbing at longer wave lengths.
- (4) In one of the crystals heated at 328° C., the presence of F-centers was demonstrated by illuminating with light of 695 millimicrons wave length. The height of the band decreased and the maximum shifted toward shorter wave length. This behavior was observed in several samples.

No definite conclusions can be drawn from the above data as to the necessary conditions for preparing crystals having the new absorption band. However, it appears that both concentration and heating time are variables which should be investigated further. The effect of impurities is unknown since the uncolored samples were taken from different stocks of potassium iodide.

The behavior of this new band is very much the same as the "colloidal" band which appears on the long wave length side of the F-band. Points of similarity are:

- (1) No apparent shift in band maximum on lowering temperature of observation.
- (2) Illumination with light of wave length corresponding to the band maximum has no apparent effect.
- (3) The thermal behavior is very much the same with respect to F-center formation. That is, both bands are formed from F-centers at the lower temperatures while at the higher temperatures the F-centers predominate.

However, this comparison can be taken only so far and then we must face the fact that the absorption maxima of the two bands are separated by nearly 250 millimicrons. In addition the conditions under which the bands are produced are not similar.

Much work remains to be done on this new band before even its qualitative behavior is understood. Nevertheless, it is of interest to speculate as to the nature of the centers responsible for the 650 millimicron absorption band. Turning our attention momentarily to additively colored sodium chloride, we find that a strong absorption occurs near 550 millimicrons which is attributed to the presence of colloiddally dispersed sodium (26, p.191).

Evidence that the absorption is characteristic of colloidal sodium was obtained when the following formula,

derived from theoretical considerations, gave an absorption band almost identical to the experimental band:

$$K = 36 \pi N_v V \frac{1}{\lambda} \frac{\frac{n^2 x}{n_u}}{\left[\left(\frac{n}{n_u} \right)^2 + \left(\frac{n x}{n_u} \right)^2 \right]^2 + 4 \left[\left(\frac{n}{n_u} \right)^2 - \left(\frac{n x}{n_u} \right)^2 + 1 \right]}.$$

In this equation K is the absorption coefficient, N_v is the number of colloidal particles per unit volume, V is the volume of a single particle, λ is the wave length, n is the refractive index of the metal, n_u is the refractive index of the host lattice, and nx is the extinction coefficient. Little information is available concerning N_v and V . However, since these quantities are constant it is possible to calculate the contour of the absorption band by using the remaining terms on the right hand side of the equation. Values of n and nx have been measured for sodium and potassium as a function of wave length (9, p.244, and 10, pp.183-184). The calculations for sodium in sodium chloride place the band maximum at about 540 millimicrons.

An estimation of the wave length of the colloidal band maximum can be made when $n \ll (nx)$. This restriction is certainly true for sodium chloride. The equation

$$(nx)_{\text{Metal}} = \sqrt{2} \cdot n_u$$

holds for the band maximum. Therefore, it is merely a matter of examining the $(nx) = f(\lambda)$ curves and determining the wave length for which the equation above is satisfied. Results of these calculations are shown in Table 22.

Table 22. Calculated band maxima for colloidal absorption bands in alkali halides

| <u>Crystal</u> | <u>n_u</u> | <u>$(nx)_M$</u> | <u>$\lambda_{\text{Max.}\mu}$</u> | <u>Observed Band Max. μ</u> |
|----------------|-------------------------|----------------------------|--|--|
| NaCl | 1.55 | 2.19 | 540 | 550 |
| KCl | 1.49 | 2.11 | 730 | 725-775 |
| KBr | 1.56 | 2.21 | 760 | 800-850 |
| KI | 1.66 | 2.35 | 800 | 800-875 |

It must be emphasized that the calculated values of $\lambda_{\text{Max.}}$ are only approximate for the potassium salts since the $(nx) = f(\lambda)$ curve for potassium was extrapolated considerably (200 millimicrons) beyond the experimental data. However, since the slope of the curve changes slowly near the region of interest, the extrapolated values of (nx) may be acceptable. The remarkable agreement between observed and calculated values of $\lambda_{\text{Max.}}$ for potassium chloride and potassium iodide may be fortuitous.

The above calculations indicate that the 650 millimicron band in potassium iodide is not due to colloidal potassium. While on this subject of colloidal dispersion we should discuss the possibility that the 650 millimicron absorption band is due to colloidal iodine. Coloration of the potassium iodide crystals was accomplished under rigorous reducing conditions, that is, in an atmosphere of potassium vapor. This factor alone would seem to preclude the possibility of oxidation of iodide ions to free iodine which could then form a colloid. Mollwo has prepared potassium iodide crystals containing excess iodine (16, p.216). Absorption curves of these crystals are shown in Figure 30. The new band at 650 millimicrons is shown on the plot for comparison.

Further investigations in the ultraviolet region would be helpful in determining the role, if any, played by colloidal iodine in the 650 millimicron band formation. An obvious experiment would be to heat a potassium iodide crystal at 600° C. for about 250 hours in the absence of potassium vapor and then in the presence of the vapor. Comparison of the ultraviolet spectra would show the relative amounts of iodine (if any at all). The band with maximum at 430 millimicrons was observed in several crystals in which the 650 millimicron band occurred.

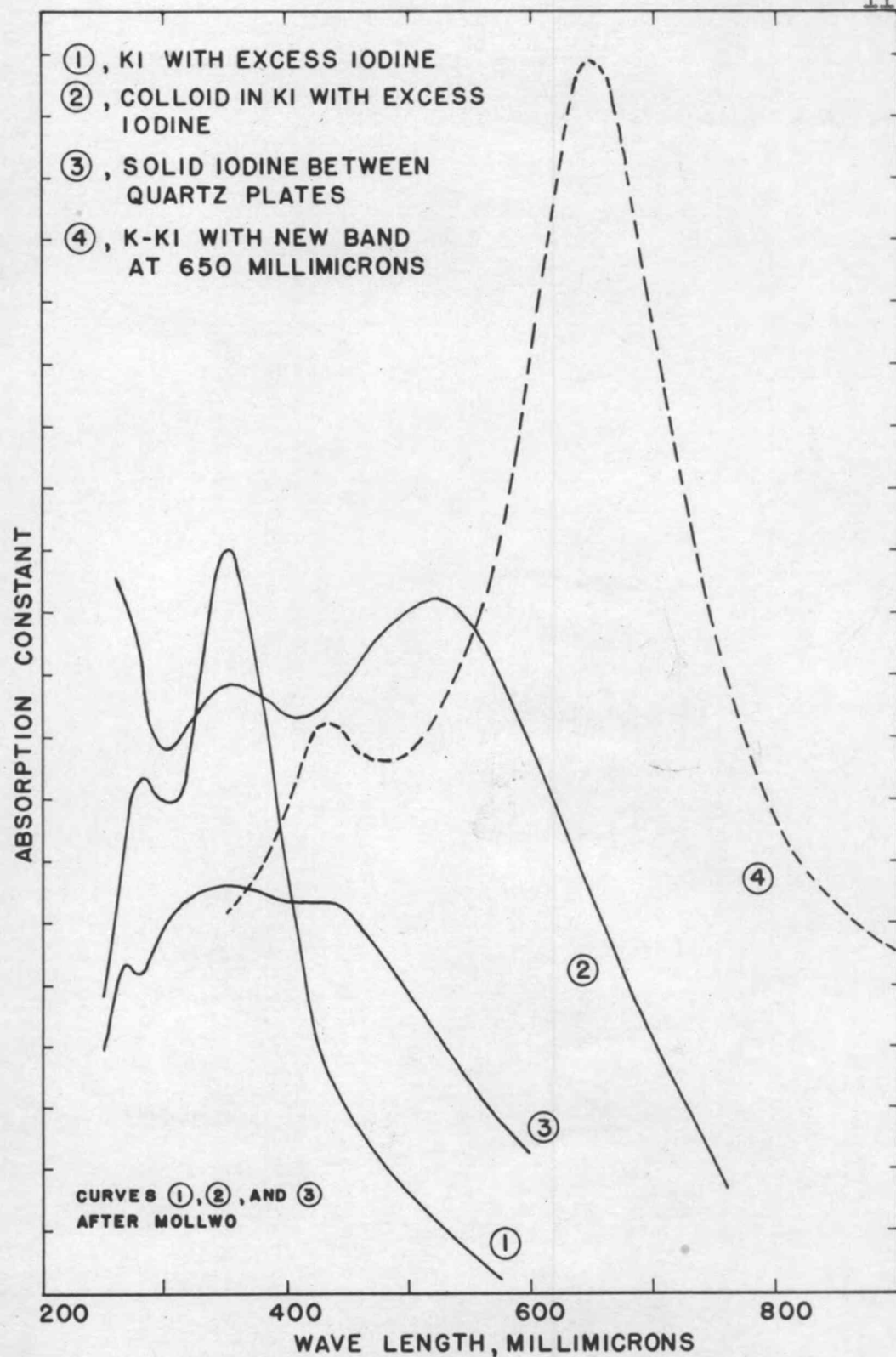


FIGURE 30. ABSORPTION CURVES FOR KI CRYSTALS WITH EXCESS IODINE AND A K-KI CRYSTAL WITH THE NEW BAND AT 650 MILLIMICRONS.

This band can be seen in curve 4 of Figure 30. Perhaps this band is related in some manner to the presence of free iodine in the crystal. A rather poorly defined peak may be discerned in curve 3 of Figure 30 at approximately 430 millimicrons. An interesting experiment could be conducted upon a potassium iodide crystal having an absorption spectrum similar to curve 4 of Figure 30 by heating in an atmosphere of iodine vapor at 600° C. Any growth of the band at 430 millimicrons might then be attributed to the presence of iodine in the crystal.

Results of some photoconductivity experiments on colored alkali halides led Oberly to suggest the existence of two kinds of F-centers (20, p.1257). Petroff has also postulated the existence of two types of F-centers to explain the bleaching of F-centers in potassium bromide (23, p.453). Smakula has proposed the presence of two kinds of F-centers in additively colored alkali halides to account for the variation of the absorption curve half-height width (35, p.605). However, Markham has been able to explain some of the above phenomena without assuming the existence of two types of F-centers (14, p.433). Without further information, it is impossible to establish any relationship between these different types of F-centers and the centers responsible for the 650 millimicron band in potassium iodide.

Information Obtained from Low Temperature Absorption
Spectra of Some Alkali Halides

Table 13 shows the temperature dependence of the F-band maximum. The wave lengths are probably correct to ± 5 millimicrons. This estimate holds for the data of Table 14, which shows the location of the bands produced in the additively colored alkali halides by F-band light. Examination of the curves in Figure 11 reveals appreciable differences in the degree of definition of the bands at room temperature and at -194°C . Qualitatively it appears that the R_1 -, R_2 - and M-bands are more sharply defined at both temperatures in KCl than in KBr than in KI. This behavior may be explained in part by considering the relative separations of the band maxima. In Table 23 are shown the energies in electron volts separating the various band maxima. The fact that the energy differences are largest for the bands in KCl would be conducive to the existence of more sharply defined bands since there would be less tendency for the bands to overlap. However, thermal vibrations of the lattice cause broadening of the absorption bands and consequently overlapping.

Table 23. Separation of the various band maxima in additively colored alkali halides at -194°C .

| Salt | (F-band) -(R ₁ -band) e.v. | (R ₁ -band) -(R ₂ -band) e.v. | (R ₂ -band) -(M -band) e.v. |
|------|---|---|--|
| KCl | 0.414 | 0.190 | 0.152 |
| KBr | 0.342 | 0.160 | 0.152 |
| KI | 0.359 | 0.138 | 0.144 |

Mott and Gurney have shown that the effect of thermal vibrations on the breadth of the absorption band of an electron trapped at a vacant lattice point may be estimated theoretically by the equation

$$h \Delta\nu = (h \nu_0 kT)^{\frac{1}{2}}$$

In this equation h is Planck's constant, k is the Boltzmann constant, T is the absolute temperature, and ν_0 is of the same order as the absorption frequency (18, p.116). Applying this equation to the F-, R₁-, R₂- and M-bands leads to the interesting results shown in Table 24.

If the R₁ -, R₂ - and M-bands of KCl and KI at 20°C . are broadened to the extent indicated by the calculated $h \Delta\nu$, sufficient overlapping would occur to reduce the sharpness of the bands to that observed in Figure 20. The agreement between calculated and observed

Table 24. Calculated and observed band widths for trapped electrons in some additively colored alkali halides.

Potassium Chloride

| Band | (78° K) | | | | (293° K) | | | |
|---------------------------------|---------|----------------|----------------|-------|----------|----------------|----------------|-------|
| | F | R ₁ | R ₂ | M | F | R ₁ | R ₂ | M |
| λ_0 (m μ) | 540 | 660 | 735 | 805 | 560 | 670 | 735 | 830 |
| $h \Delta \nu$ e.v. | 0.124 | 0.112 | 0.106 | 0.101 | 0.236 | 0.216 | 0.206 | 0.194 |
| Observed width (W/2) e.v. | 0.135 | 0.12 | 0.07 | 0.06 | 0.180 | - | - | - |

Potassium Iodide

| Band | (78° K) | | | | (293° K) | | | |
|---------------------------------|---------|----------------|----------------|-------|----------|----------------|----------------|-------|
| | F | R ₁ | R ₂ | M | F | R ₁ | R ₂ | M |
| λ_0 (m μ) | 670 | 835 | 915 | 1030 | 700 | ~835 | ~915 | 1060 |
| $h \Delta \nu$ e.v. | 0.111 | 0.100 | 0.091 | 0.090 | 0.214 | 0.193 | 0.184 | 0.172 |
| Observed width (W/2) e.v. | 0.117 | 0.09 | 0.06 | 0.06 | 0.219 | - | - | - |

widths is good for the F- and R₁-bands at the lower temperature.

Samples of additively colored KBr #30 and KI #18 were sent to the Applied Physics Laboratory of Johns Hopkins University where their absorption curves were measured at 300°, 78° and 5° K. by Mr. Reuel T. Platt, Jr., under the direction of Dr. J. J. Markham. These curves

are reproduced in Figures 31 and 32. The band maxima observed for KBr are, in millimicrons, as follows:

| <u>Temperature</u> | <u>F</u> | <u>R₁</u> | <u>R₂</u> | <u>M</u> | <u>N</u> |
|--------------------|----------|----------------------|----------------------|----------|----------|
| 300° K | 625 | --- | --- | 925 | --- |
| 78° K | 605 | 730 | 805 | 890 | --- |
| 5° K | 597 | 725 | 802 | 885 | 1090 |

For KI the F-band maxima are 700, 669, and 662 millimicrons at 300°, 78°, and 5°K, respectively. It is interesting to note that the broad band in KI with maximum near 850 millimicrons closely resembles the R'-band in KCl reported by Scott and Bupp (29, p.342).

Distribution of Color Centers in Nonhomogeneously Colored Crystals

The data in Table 16 show that the relative concentration of F-centers to M-centers is constant within experimental error, at points well removed from the surface of KCl and KBr crystals. If this were not true, it would mean that the formation of M-centers was related in some complicated way to the concentration of F-centers. In the last column of Table 16 are shown values of the equilibrium constant for the process



The constancy of these values for K' shows that there is

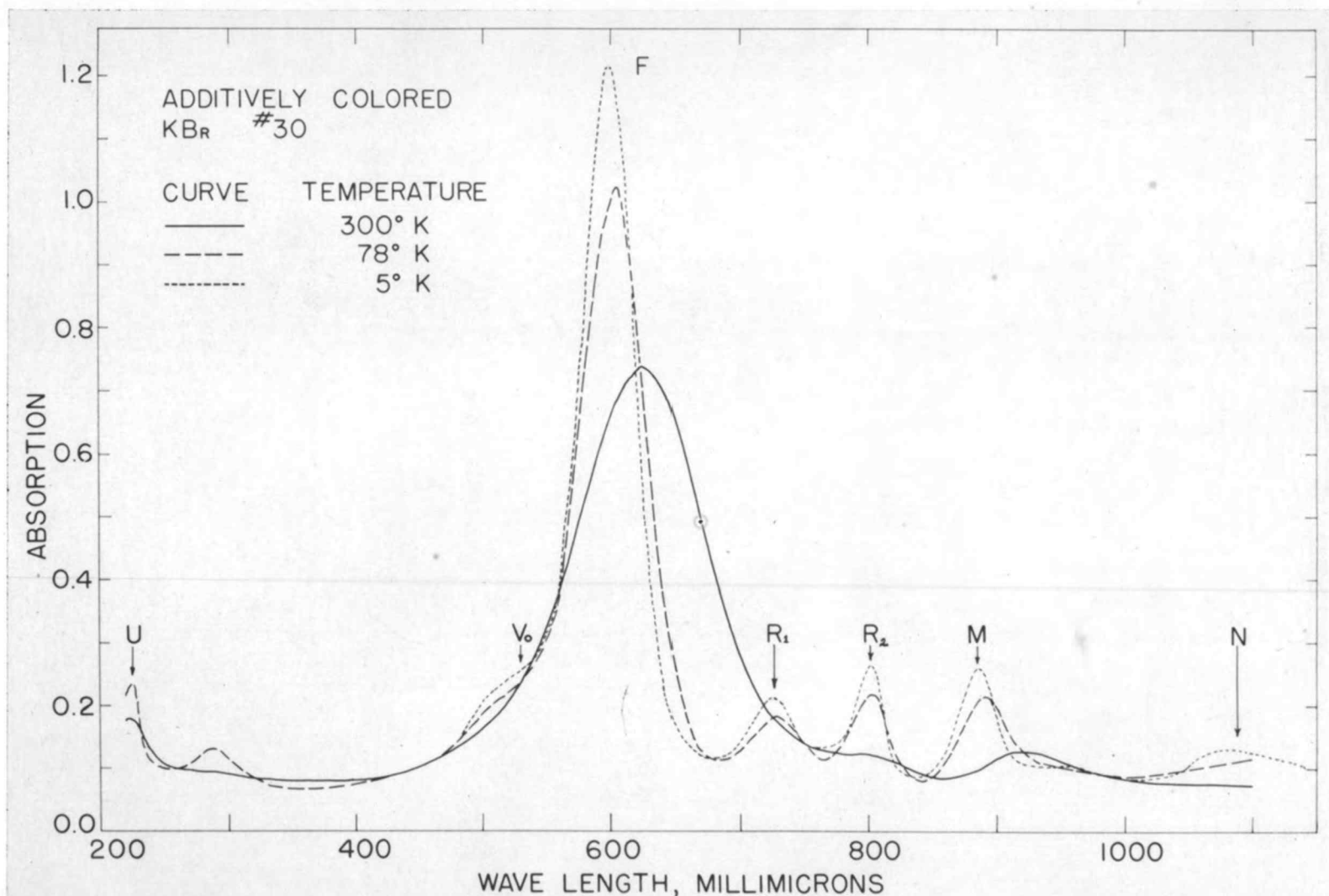


FIGURE 31. ABSORPTION CURVES FOR K-KBr AT 5°, 78°, AND 300° K.

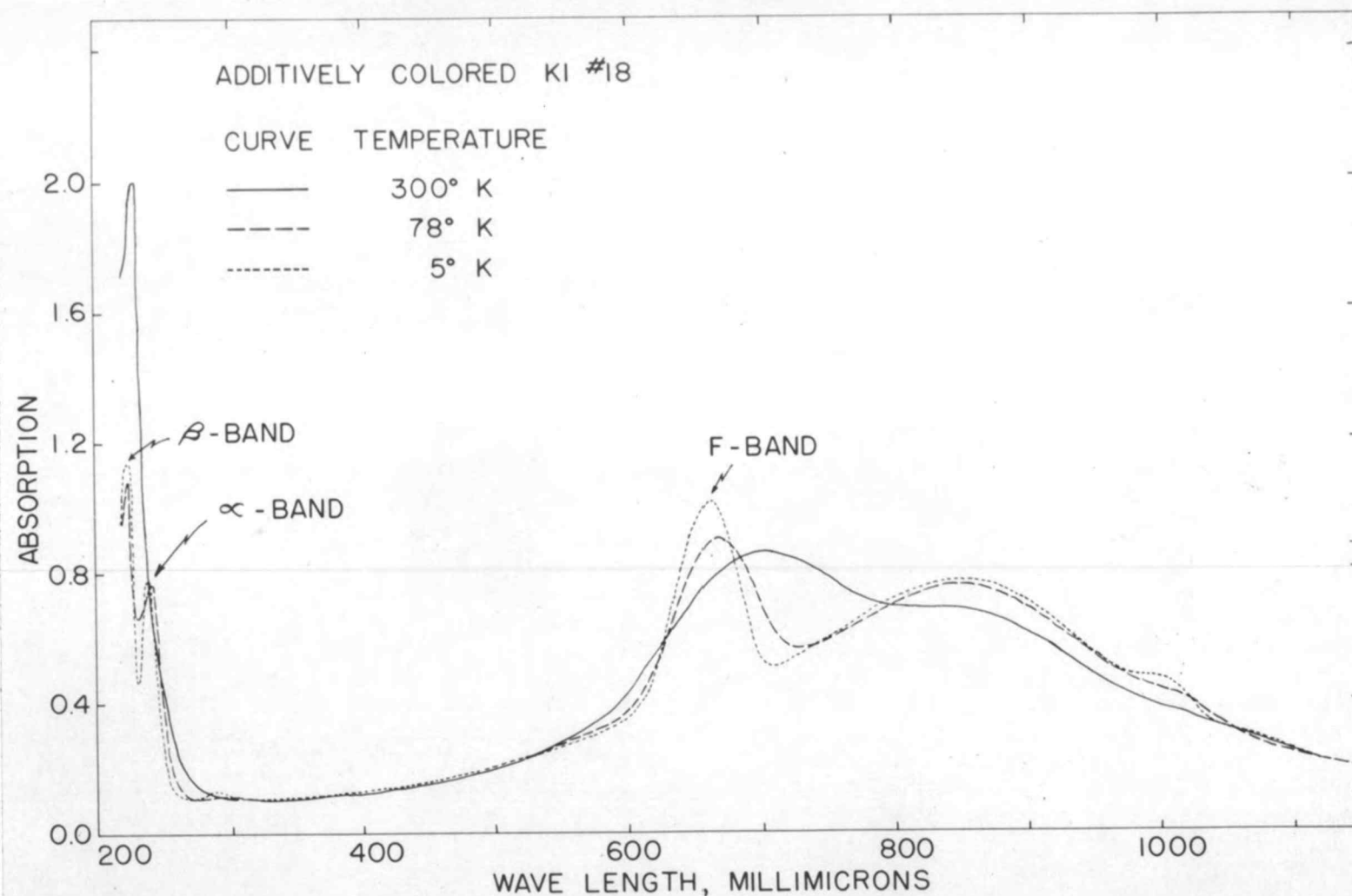


FIGURE 32. ABSORPTION CURVES FOR K-KI AT 5°, 78°, AND 300° K.

a rapidly attained thermal equilibrium between F- and M-centers. Furthermore, the equilibrium involves one F-center per M-center. A summary of the information concerning the nonhomogeneously colored crystals is given below:

| <u>Crystal</u> | <u>Coloring Temperature</u> | <u>Heating Time</u> | <u>K'</u> | <u>Average Deviation</u> |
|----------------|-----------------------------|---------------------|-----------|--------------------------|
| K-KCl 25 | 600° C. | 4.5 hrs. | 0.068 | \pm 0.003 |
| K-KCl 26 | 600° | 4.0 | 0.078 | \pm 0.004 |
| K-KBr 28 | 600° | 0.5 | 0.025 | \pm 0.002 |

The results obtained are in accord with the commonly accepted theory of F-center formation, that is, the electrons which are formed from the potassium atoms at the surface of the crystal by thermal ionization diffuse through the crystal until trapped at a negative ion vacancy. Thus the distribution of F-centers in a non-homogeneously colored crystal depends in part on the rate of diffusion of the electrons into the crystal and also the rate of diffusion of the negative ion vacancies (Schottky defects) into the crystal. These diffusion processes are logarithmic in form and one would expect the F-center concentration to follow a logarithmic distribution. Thus a plot of the logarithm of the F-center concentration against the distance from an

external face should result in a straight line. Figure 24 shows such plots and the results are in general agreement with the above arguments.

Energy Levels of Electrons in F-Centers in Alkali Halides

Equations have been derived which may be used to obtain the variable parameters needed to calculate the energies of the 1s and 2p states of an electron trapped at a negative ion vacancy in any alkali halide having a NaCl structure. These calculations can be carried out if values of the constants in Table 17 can be found. The generalized equations hold only for the model assumed to represent the F-centers.

The agreement between calculated and observed energies for the 1s-2p transition giving rise to the F-band is quite good in view of the many assumptions and approximations involved. For sodium chloride our calculations gave $W_{2p-1s} = 2.57$ e.v. while Tibbs obtained $W_{2p-1s} = 2.5$ e.v. using a different method. The observed energy for the F-band maximum is 2.67 e.v. It is not understood how Simpson obtained the value 2.2 e.v. for this transition unless he neglected small terms in the equation for determining the parameters λ and ρ . Undoubtedly part of the discrepancy lies in the fact that we used a slightly different value for the

dielectric constant K_0 .

It should be emphasized that the potential energy function used in these calculations is only a close approximation. However, the error introduced from this source is probably small. A much more serious error is introduced by assuming that the field of the negative ion vacancy is spherically symmetrical. Smoothing over of the potential functions of the first shell of positive ions gives rise to another source of error. These ions would have a very marked effect on the shape of the 2p wave function, thereby causing it to spread over a larger volume of the crystal than in the case of the model used. The net effect of these approximations is to make the energy calculated for the 2p level too large in magnitude. That is, an electron in the 2p level would be too far below the conduction band.

Evidence has been obtained experimentally by Pohl and theoretically by Gurney and Mott that in the case of NaCl the 2p level lies about 0.1 e.v. below the conduction band (7, p.511 and 25, p.13). This value was obtained from observations on the temperature dependence of the photocurrent in colored alkali halides.

It is of interest to note that the magnitude of the energies of the 1s and 2p levels is quite sensitive to the value used for R/a_0 . This is demonstrated by the

data of Table 18 for KCl and $^*\text{KCl}_{20^\circ \text{C.}}$. The results for the latter were obtained by using a value of R/a_0 larger than the former by only 2 per cent. However, the energy W_{2p-1s} changed by only 0.01 e.v. This indicates that the values of W_{2p-1s} are not very sensitive to small errors in R/a_0 , R being the radius of the hole formed upon removal of a negative ion and a_0 being the interionic distance.

The calculations on KCl at -194°C. led to some interesting results. Apparently the wave equations obtained for -194°C. represent the behavior of the electron better than those for 20°C. since the difference between observed and calculated W_{2p-1s} values is only -0.08 e.v., which is approximately one-half of the difference for the 20°C. values. We may infer from this that the model chosen to represent the F-center is capable of giving good results for calculations in this temperature interval. The magnitude of the observed shift in the position of the F-band maximum (going from 20°C. to -194°C.) is 0.08 e.v. Apparently the calculated shift is zero (or for $^*\text{KCl}_{20^\circ \text{C.}}$ it is 0.01 e.v.). However, it should be noted that if we assume the 20°C. value for W_{2p-1s} to have the same accuracy as the -194°C. value, that is, having a difference from the observed value of only -0.08 e.v., then the calculated shift in the F-band

maximum becomes 0.08 e.v. This agrees exactly with the observed value and could well be accidental. That this agreement is not entirely accidental is demonstrated by the fact that using W_{2p-1s} values for $^*KCl_{20^{\circ}C}$. and $KCl_{-194^{\circ}C}$. gives a shift of 0.01 e.v. which, furthermore, is in the correct direction, that is the F-band maximum shifts toward higher energies.

These observations are consistent with the assumption that an F-center is an electron trapped at a negative ion vacancy and that thermal effects are responsible for the observed temperature shift of the F-band maximum. Further calculations will have to be made before the quantitative nature of the thermal effects is understood.

There is no significant difference in the electron density distribution functions for KCl at $20^{\circ}C$. and at $-194^{\circ}C$. These curves are shown in Figure 28 for the 1s and 2p levels. The Bohr orbit radii at the two temperatures differ very little. From the curves of Figure 27 it is apparent that in the 1s levels the electrons have a negligible distribution beyond about 14 atomic units (7.4 Ångstroms or approximately 2.1 to 2.6 interionic distances). For the 2p levels the electrons have a sizeable distribution at 14 atomic units and are spread out over about 18 to 25 atomic units (9.5 to 13.2 Ångstroms or

approximately 3.3 to 4.0 interionic distances). It would be interesting to have electron density distribution curves for 2p levels of NaBr and NaI to see if the trend in the Bohr orbit radii is the same as that observed for KCl, KBr, and KI. The fact that the calculated Bohr orbit radius for the 2p level of KCl is larger than that for KI may be attributed to the effect of the ions immediately surrounding the F-center. In KCl these ions are much closer than in KI, hence they exert a greater tendency to spread the electron through the crystal.

Thermal Activation Energy from 2p State to the Conduction Band

The values of E , the thermal energy required to raise the electron from the 2p level to the conduction band, in Table 20, should be regarded as approximations only since there may be considerable error present in the W_{2p} values. However, a comparison of the values of E for KCl at 20°C . and at -194°C . shows that more thermal energy is required at the lower temperature regardless of the fact that the W_{2p} energies are identical. This may be attributed to the smaller contribution made by the motion of the ions, which is to be expected at the lower temperature.

Experiments on rates of optical bleaching of

F-centers at various temperatures should be performed in order to obtain the necessary data for calculating the thermal activation energies for the various alkali halides studied in this investigation. Such information could then be compared to that in Table 20 and conclusions drawn as to the probable accuracy of the W_{2p} values and thus indirectly the validity of the calculations involved in obtaining W_{2p} and U (the energy given up by the ions surrounding a former F-center when they move to new positions of equilibrium).

The low value of the activation energy (0.01 e.v.) for KCl at 20° C. would predict that at any instant $e^{-0.01/0.025}$ or about 0.7 of the electrons would have sufficient thermal energy to pass into the conduction band. This means that the rate of optical destruction of the F-band should be dependent only on the rate of absorption of light quanta.

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A P P E N D I X

APPENDIX I

Derivation of the Smakula Equation

Smakula has applied classical dispersion theory to the F-center bands of the alkali halides in order to ascertain the concentration of the centers (35, pp.603-608). The following assumptions were made by Smakula:

- (a) The polarizability of the bulk material (the pure alkali halide) is given by the expression

$$\alpha = \frac{3}{4\pi n_0} \frac{n'^2 - 1}{n'^2 + 2}, \text{ where } n' \text{ is}$$

the refractive index of the pure salt in the vicinity of the F-band and n_0 is the number of oscillators.

- (b) The complex polarizability of the electrons in the F-centers may be represented by the corresponding polarizability function for a single absorption line, that is,

$$\frac{n_0 e^2}{4\pi^2 m} \frac{f}{\nu_F^2 - \nu^2 + i\nu\nu'}$$

In this expression, n_0 = density of F-centers, ν_F is the frequency at the center of the absorption band, ν' is the damping frequency, and f is the oscillator strength of the transition (32, pp1662-664).

These assumptions were based on the following conditions:

- (a) The F-center is an electron trapped in a halogen ion vacancy, and excitation of this

electron gives rise to the F-center band.

- (b) The extinction coefficient of the pure alkali halide is zero in the vicinity of the F-center bands. This seems reasonable, since these bands are usually far removed from the fundamental absorbing region.
- (c) The refractive index of the pure salt is usually constant near the F bands.

With these preliminary considerations in mind we may now derive the desired equation. The complex refractive index is given by $N = n - ik$, where k is the extinction coefficient. The complex polarizability, α_c , is given by

$$\frac{N^2 - 1}{N^2 + 2} = \frac{4\pi}{3} n_0 \alpha_c .$$

Hence

$$(1) \frac{(n-ik)^2 - 1}{(n-ik)^2 + 2} = \frac{4\pi}{3} n_0 \left[\frac{3}{4\pi n_0} \left(\frac{n'^2 - 1}{n'^2 + 2} \right) + \frac{e^2}{4\pi^2 m} \frac{f}{(\nu_F^2 - \nu^2) + i\nu \nu_F' \nu} \right]$$

$$(2) \frac{(n-ik)^2 - 1}{(n-ik)^2 + 2} = \frac{n'^2 - 1}{n'^2 + 2} + \frac{n_0 f e^2}{4\pi^2 m} \left[\frac{1}{(\nu_F^2 - \nu^2) + i\nu \nu_F' \nu} \right] .$$

The refractive index of the colored crystal may be represented by $n = n' + \Delta n$ and the frequency of the absorption by $\nu = \nu_F + \Delta \nu$. Substitution of these expressions in Equation (2) gives

$$\frac{(n' + \Delta n - ik)^2 - 1}{(n' + \Delta n - ik)^2 + 2} = \frac{n'^2 - 1}{n'^2 + 2} + \frac{n_0 f e^2}{4\pi^2 m} \left[\frac{1}{\nu_F^2 - (\nu_F + \Delta \nu)^2 + i\nu_d'(\nu_F + \Delta \nu)} \right].$$

Separating the real and imaginary parts of this equation gives rise to two equations. They are, for the real parts

$$\Delta n = -\frac{n_0 f e^2}{18\pi m} \frac{(n'^2 + 2)^2}{n'} \left[\frac{\Delta \nu (2\nu_F + \Delta \nu)}{\Delta \nu^2 + (2\nu_F + \Delta \nu)^2 + \nu_d'^2 (\nu_F + \Delta \nu)^2} \right]$$

and for the imaginary parts

$$k = \frac{n_0 f e^2}{18\pi m} \frac{(n'^2 + 2)^2}{n'} \left[\frac{\nu_d' (\nu_F + \Delta \nu)}{\Delta \nu^2 + (2\nu_F + \Delta \nu)^2 + \nu_d'^2 (\nu_F + \Delta \nu)^2} \right].$$

The damping frequency ν_d' is eliminated from this equation by expressing it in terms of $\Delta \nu_{1/2}$ or $\Delta \nu$ for which k is half its maximum value k_m . This leads to

$$n_0 f = \frac{9m k_m \nu_F}{\pi e^2} \frac{n'}{(n'^2 + 2)^2} \frac{\Delta \nu_{1/2} (2\nu_F + \Delta \nu_{1/2})}{(\nu_F + \Delta \nu_{1/2})^2}.$$

In using this equation it is convenient to express the frequencies in electron volts and k in terms of α which is given by $I/I_0 = e^{-\alpha d}$

where d is the thickness of the absorbing crystal and I_0 is the original intensity. Thus, using the optical

density D gives $\alpha = \frac{2.303 D}{d}$. The relation between

k and α is $k = \alpha \lambda / 4\pi$.

At low temperatures ν_F is much greater than $\Delta\nu_{1/2}$ and the equation for $n_0 f$ simplifies to give

$$n_0 f = 1.31 \times 10^{17} \frac{n'}{(n'^2 + 2)^2} \alpha_m W$$

where W is the width of the absorption curve at half maximum in electron volts, that is $2 \Delta\nu_{1/2}$.

Accurate values of the oscillator strength f are not available for the alkali halides, therefore f was assumed to be unity.

APPENDIX II

Method of Calculating the Ratio R/a_0 for Negative Ion
Holes in Alkali Halides

The equations used in this section were developed by Mott and Littleton (19, pp.490-493). In the derivation of their equation giving the potential at the center of the hole left upon removing a negative ion from the lattice it was assumed that the ions were fixed in a rigid lattice. The polarizabilities of the ions are denoted by α_1 (for the negative ions) and α_2 (for the positive ions). Values of α_1 and α_2 are shown in Table 25. These quantities were calculated from the mole refraction data of Pauling for the free ions (21, p.198). That is, $\alpha = 3R/4 \pi N$, where R is the mole refraction and N is Avogadro's number.

Table 25. Mole refraction (R) and polarizabilities (α) of some free ions.

| Ion | Mole Refraction R | $\alpha_1 \times 10^{24}$ | $\alpha_2 \times 10^{24}$ |
|-----------------|-------------------------|---------------------------|---------------------------|
| Na ⁺ | 0.457 | --- | 0.1811 |
| K ⁺ | 2.12 | --- | 0.8401 |
| Cl ⁻ | 9.30 | 3.685 | --- |
| Br ⁻ | 12.14 | 4.811 | --- |
| I ⁻ | 18.07 | 7.161 | --- |

When a negative ion is removed from a cubic lattice six positive ions are left all equidistant from the point previously occupied by the negative ion. If a charge is placed at this point, dipoles will be induced on all the surrounding ions. The magnitude of the dipole induced on any one ion depends on the charge as well as the magnitude of the dipoles on all the other ions. Because of this complication, it is necessary to use an approximation method in evaluating the potential at the center of the hole.

Mott and Littleton obtained the following equation (to the first order) for the potential at the center of the hole:

$$V = -\frac{Q}{a} (6.3346 M_1 + 4.1977 M_2) - \frac{6\mu}{a^2} .$$

In this equation, Q is the charge at the center of the hole and a is the interionic distance in cm. The coefficients of the M terms arise through a summation over all the lattice points of type 1 and type 2, respectively. The dipoles on the six nearest neighbors are denoted by μ . Furthermore, let $\mu = Qam$, $\beta_1 = \alpha_1/a^3$, and $\beta_2 = \alpha_2/a^3$

$$m = \frac{\beta_2 (1 - 1.965 M_1 - 0.388 M_2)}{(1 + 2.371 \beta_2)}$$

$$M_1 = \frac{2\alpha_1}{\alpha_1 + \alpha_2} \frac{1}{4\pi} (1 - 1/\kappa_0)$$

$$M_2 = \frac{2\alpha_2}{\alpha_1 + \alpha_2} \frac{1}{4\pi} (1 - 1/\kappa_0) .$$

Thus

$$V = -\frac{Q}{a} (6.3346 M_1 + 4.1977 M_2 + 6m)$$

and the potential at the center of the hole is

$$V_0 = \frac{Q}{4\pi a} (1 - 1/\kappa_0) .$$

Schottky and Jost, in their treatment of the energies of holes in crystals, arrived at the following equation for the potential at the center of the hole,

$$V_{S,J} = -\frac{Q}{R} (1 - 1/\kappa_0)$$

where R is the radius of the hole. The ratio $-V/V_0$ is evaluated by using

$$-V/V_0 = 4\pi (6.3346 M_1 + 4.1977 M_2 + 6m) / (1 - 1/\kappa_0)$$

which is combined with $V_{S,J}$ to give $R/a_0 = 4\pi/(V/V_0)$. The values of R/a_0 listed in Table 26 for NaCl and KCl differ slightly from those of Mott and Littleton since slightly different values of K_0 were used.

Table 26. Potentials (to the first order) when a charge Q is placed at a negative lattice point. The radius of the hole at the vacant negative ion point is R and a_0 is the interionic distance.

| <u>Salt</u> | <u>NaCl</u> | <u>KCl</u> | <u>KBr</u> | <u>KI</u> | <u>KCl-194°</u> |
|-------------|-------------|------------|------------|-----------|-----------------|
| $-V/V_0$ | 13.369 | 14.992 | 14.532 | 14.026 | 15.066 |
| R/a_0 | 0.940 | 0.838 | 0.865 | 0.896 | 0.834 |

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