

AN ABSTRACT OF THE THESIS OF

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Title: ELECTRICAL CONDUCTIVITY OF ADDITIVELY COLORED
POTASSIUM CHLORIDE CRYSTALS

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When the dc conductivities of various pure KCl crystals were compared it was found that crystals grown under an HCl atmosphere, from salt purified by ion exchange, exhibited lower knee temperatures than any of the crystals studied. These knee temperatures were found to be approximately 350°C . From this the total divalent cation concentration was estimated to be $1.8 \times 10^{14} \text{ cm}^{-3}$. It was also found that no absorption bands were present, in ion exchange purified crystals, in the region between $185 \text{ m}\mu$ and $300 \text{ m}\mu$.

The conductivities of colored KCl crystals were found to be much greater than for uncolored crystals. Above approximately 400°C the current decreased with time according to the expression $i/i_0 = 1 - c(t-t_0)$, where t_0 was the time when the current was i_0 . c was found to depend on temperature according to the expression $c = 17,000 \exp(-1.12 \text{ eV}/kT) \text{ sec}^{-1}$.

The decrease in current was associated with a loss of F-centers from the crystals. Optical scanning of partially bleached crystals showed that, during bleaching, a definite boundary was formed between a colorless region at the surfaces and a colored region in the interior.

The electronic transport number was determined to be 0.96 at 400°C. Thus the increased conductivity was attributed to ionized F-centers.

Plots of $\log_{10}\sigma$ vs. $1000/T$ were linear with two different slopes, depending on the history of the sample. If gold contacts were evaporated onto freshly cleaved crystals rectification was observed. The rectification could be eliminated by either heating the colored crystals for five minutes, at temperatures greater than approximately 500°C, after applying the contacts, or by sanding the crystals prior to applying the contacts. Accompanying the loss of rectification was a decrease in the conductivity and an increase in the activation energy for conduction, from 1.13 eV to 1.22 eV.

Plots of σ , at a given temperature, vs. $n_F^{\frac{1}{2}}$ were found linear. From this, and the theory of rectifying contacts, a calculation of the thermal ionization energy for F-centers was made. The value obtained was 2.04 eV.

Conductivity and electronic transport number measurements were made on CaCl_2 -doped KCl crystals. From observations that the

conductivity was not changed significantly after coloring and that the electronic transport number was less than 0.15, it was determined that the calcium remained divalent after coloring.

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ELECTRICAL CONDUCTIVITY OF ADDITIVELY COLORED POTASSIUM CHLORIDE CRYSTALS

I. GENERAL INTRODUCTION

Types of Color Centers

Research on color centers began late in the nineteenth century when Goldstein (12) found that alkali halide crystals bombarded with cathode rays acquired characteristic colors. However it was not until the 1930's, when Pohl (44) became interested in this phenomenon, that any large-scale research was conducted to determine the cause of this coloration. Since that time investigators throughout the world have become actively engaged in this field and a great deal of knowledge has been accumulated. It has been found that many different species of crystals can be colored in a variety of different ways, the most important of which are additive coloration by heating the crystals in the presence of their metallic or nonmetallic constituents, electrolytic coloration and coloration by ionizing radiation. Alkali halide crystals have been by far the most thoroughly investigated and are the most completely understood.

Upon coloring these crystals several new absorption bands are introduced which cannot be found in uncolored crystals. The locations of these bands varies depending on the crystal species and the intensities vary depending on the method by which the bands are generated.

A brief discussion of some of the centers which give rise to these bands is given in the following paragraphs. For a more thorough description the reader is referred to the works of Shulman and Compton (48) and of Markham (37).

Trapped Electron Centers

If alkali halide crystals are additively colored by heating with alkali metal and then quenched to room temperature the only absorption band observed is the F-band. The absorbing centers responsible for this band are known as F-centers. A great deal of evidence has now been accumulated in support of the de Boer model of the F-center (48, p. 60-69). This model consists of an electron trapped at a halide ion vacancy (9).

Additional color centers can be formed in crystals which contain F-centers by either heating or exposing the crystals to light. If the crystals are exposed to light at room temperature or heated to slightly above room temperature in the dark new absorption bands are formed which occur on the long wavelength side of the F-band and result from aggregates of F-centers. The simplest of these aggregate centers is the M-center. A more descriptive name for this center is the F_2 -center since it has been quite well established to consist of two F-centers occupying adjacent anion positions. Similarly there are R- and N-centers which are thought to be F_3 - and F_4 -centers

respectively and undoubtedly higher aggregates.

In addition to the aggregate centers consisting of small numbers of F-centers there are centers composed of large numbers of F-centers which form colloidal metal particles. These centers are formed by warming alkali halide crystals containing F-centers to a few hundred degrees centigrade in darkness.

Trapped Hole Centers

There also exist another group of color centers referred to as V-centers and labeled as V_1 , V_2 , V_3 , etc. These centers are known as trapped hole centers and are formed by the same techniques as the trapped electron centers except that methods must be used which leave the crystal with an excess of halogen rather than an excess of metal. During coloration by ionizing radiation, however, trapped electron and trapped hole centers are formed simultaneously leaving the crystal containing an excess of neither constituent. Investigations of the V-centers have not been carried out to nearly as great an extent as for the F- and aggregate centers and consequently models have not been established for any V-center which is stable at room temperature. However models for the V_k -center and the H-center, which is similar to the V_k -center, have been established by spin resonance. The V_k -center consists of a hole trapped by a pair of adjacent halide ions, each occupying its normal lattice position. The

H-center consists of a hole trapped by four halide ions. The atoms form a linear array with the center pair occupying a single lattice position.

Impurity Centers

There also exist certain color centers which can be found only in crystals containing particular impurities. Among this group are the Z-centers which are labeled Z_1 , Z_2 , Z_3 and Z_4 . These centers are formed in colored alkali halide crystals which contain alkaline earth impurity ions. Although none have been verified, various models have been proposed for these centers, the most frequently referred to being those of Pick (40, 41) and of Seitz (50). These models all consist of electrons trapped at various combinations of alkaline earth cations and positive and negative ion vacancies.

Determination of F-Center Concentration

The concentration of F-centers, n_F , can be calculated by use of Smakula's equation (55) or from the revised form given by Dexter (11). The latter result is

$$n_F f = 0.82 \times 10^{17} \frac{n}{(n^2 + 2)^2} A, \text{ cm}^{-3}, \quad (1.1)$$

where f is the oscillator strength and n the refractive index. A

is the area under the absorption curve and must be expressed in units of ev cm^{-1} in Equation (1.1). In computing A the absorbance must be given in common-logarithmic units rather than natural-logarithmic units. The F-band is not truly Gaussian or Lorentzian but usually it is assumed Gaussian for purposes of calculation. If this is done A is given by the expression

$$A = (\pi/4 \ln 2)^{\frac{1}{2}} \alpha_m W, \quad (1.2)$$

where α_m is the absorption coefficient at the band maximum and W is the band width at one-half the maximum height. From Equations (1.1) and (1.2) we obtain

$$n_F f = 0.87 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_m W, \text{ cm}^{-3}. \quad (1.3)$$

The oscillator strength, f , has been determined from Equation (1.3) using known values for n_F . The value given by Sonder (58) is 0.59 for potassium chloride. Konitzer and Markham (33) have measured W at room temperature and give the value 0.34 ev. The refractive index, n , for potassium chloride is 1.492 at the F-band location.

α_m is given by the relation

$$\alpha_m = (2.303/d) \log_{10}(I_0/I),$$

where d is the thickness in centimeters, I the intensity of transmitted light and I_0 the intensity of incident light.

The absorbance per cm is related to the absorption coefficient by the expression

$$A_m = a_m / 2.303. \quad (1.4)$$

Combining Equations (1.3) and (1.4) and using the values for f and W given above gives

$$n_F = 0.97 \times 10^{17} A_m. \quad (1.5)$$

With Equation (1.5) it is possible to calculate F-center concentrations in potassium chloride crystals from absorption spectra taken at room temperature.

Electrolytic Coloration and Conductivity

In the early stages of color center research Pohl (43) became particularly interested in electrolytic coloration and the subsequent migration of the F-center cloud in an electric field. The experiments were performed by placing a crystal between a pointed cathode and a flat anode, each usually being made of platinum. If the crystal was then heated to several hundred degrees centigrade and a field of several hundred volts per centimeter applied a colored cloud would flow out of the pointed electrode in a funnel shape. It was also observed that during this time halogen was produced at the positive electrode

leaving the crystal containing an excess of alkali metal just as in the case of additive coloration. Also during the injection of F-centers the current was observed to increase until the front of the color cloud reached the positive electrode. At this time the current would attain a steady value. Reversing the polarity would cause the color to move back across the crystal and vanish into the pointed electrode. The current would decrease as the cloud was withdrawn until it attained a minimum value characteristic of the uncolored crystal. From the observed migration velocity, v_b , of the F-center cloud Stasiw (59) calculated the F-center mobility, μ_F , in potassium chloride crystals at several temperatures using the relation

$$v_b = \mu_F E, \quad (1.6)$$

where E is the electric field strength. Stasiw considered other means of finding the mobility, one of which was the steady-state method. This method was subsequently developed by Smakula (56) who studied a large number of different alkali halide crystals. The method employed was to allow the injected color cloud to fill the entire region between the two electrodes. When this had occurred the current would attain its steady-state value. By subtracting the current before any F-centers were injected from the steady-state current Smakula was able to calculate the current due to F-centers and hence the mobility of the color cloud from the relation

$$\mu_F = J/n_F eE, \quad (1.7)$$

where J is the current density measured at the flat electrode, n_F the concentration of F-centers or excess metal, e the electronic charge and E the electric field strength. When this was done he found that μ_F was given by the empirical equation

$$\mu = \mu_0 \exp(-U/kT), \quad (1.8)$$

where μ_0 is a constant of the order of $100 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ and U an activation energy for the process. U was found to be approximately 1.0 ev in potassium chloride.

At the time these experiments were conducted a satisfactory model for the F-center had not been established. Therefore a theoretical interpretation of the results could not be made. It was not until after the de Boer model had been proposed that Mott and Gurney (39) were able to examine the results in detail and give a theoretical interpretation. Pohl (43) did give a qualitative discussion however which is easily understood. His explanation is essentially as follows.

As the crystal is warmed a fraction of the F-centers become thermally dissociated producing free electrons. In the presence of an electric field these electrons are accelerated toward the positive electrode. They only travel a short distance however before they are recaptured by ionized F-centers and rendered immobile. It is only

during the time when the electron is trapped that it is visible as an F-center and only during the time it is free that it can migrate. It is due to repeated dissociation, migration and recombination that the F-centers appear to move while in reality it is the free electrons which actually are migrating.

The interpretation of these results by Mott and Gurney is based on the de Boer model of the F-center which was described earlier as an electron trapped at a halide ion vacancy. As did Pohl, Mott and Gurney assumed that the migration of the color cloud was due to the dissociation and recombination of F-centers. Starting with this assumption and the assumptions that the concentration of negative ion vacancies already present was much greater than for ionized F-centers and that classical statistics applied, they were able to arrive at two conclusions. The first was that U in Equation (1.8) was actually given by the relation

$$U = E_F - \frac{1}{2}E_S, \quad (1.9)$$

where E_F is the thermal ionization energy of the F-center and E_S the energy necessary to form a separated positive and negative ion vacancy pair from the perfect crystal. The second was that the conductivity at any given temperature should be proportional to the F-center concentration. Unfortunately the experiments of Stasiw and of Smakula were not of such a nature that the second point could be

checked.

Gravitt, Gross, Benson and Scott (21) conducted an experiment similar to that of Stasiw in which corrections were made for the inhomogeneity of the electric field. They obtained $U = 1.3 \text{ ev}$ for potassium chloride. These experimenters assumed the calculations of Mott and Gurney to apply.

Shamovskii, Dunina and Gosteva (52) conducted a somewhat different experiment in which the conductivity, σ , of additively colored potassium chloride crystals was measured. They found that the conductivity of the colored crystals was much greater than that of the uncolored crystals and that below approximately 470°C plots of $\log_{10}\sigma$ vs. $1/T$ were linear, with slopes corresponding to $U = 1.03 \text{ ev}$. These authors gave a theoretical treatment of the problem, based on Fermi-Dirac statistics, assuming nearly all anion vacancies came from ionized F-centers, and arrived at the conclusions that $U = \frac{1}{2}E_F$ and that the conductivity at a given temperature should be proportional to the square root of the F-center concentration. They made no effort to check this latter point however.

Jain and Sootha (28) measured the conductivity of additively colored potassium chloride crystals and found that in the temperature range of 300°C to 500°C the conductivities of the colored crystals were much greater than for uncolored crystals. These authors attributed the increase in conductivity to thermionic emission from

colloidal metal formed by coagulation of F-centers during heating.

Maycock (36) measured the conductivity of additively colored potassium chloride crystals and found the conductivity of the colored crystals to be much less than for the uncolored crystals.

Tomka (61) compared the conductivities of additively colored alkali halide crystals which had been thermally bleached with the conductivities of uncolored crystals. He found that the bleached crystals exhibited a lower conductivity than the uncolored crystals.

Markham (46, p. 113-124) discusses the experiments of Stasiw and Smakula and cites the work of Pekar. Pekar calculated the thermal ionization energy, E_F , for the F-center from a purely theoretical approach. The value obtained agreed very well with twice the activation energy obtained by Smakula. This good agreement has been used to argue that Fermi-Dirac statistics applied, that U is equal to $\frac{1}{2}E_F$ and that the conductivity should be proportional to the square root of the F-center concentration. Markham disagrees with Pekar's conclusions and argues that the results of Mott and Gurney are truly correct.

At this point the reasons for conducting the present experiments should be mentioned. It was felt that conductivity measurements would be useful in determining the oxidation states of alkaline-earth impurities in colored potassium-chloride crystals. It will be pointed out in Section II that divalent impurities increase the ionic conductivity

while monovalent impurities do not. Thus if, in the process of coloration, the divalent impurities are reduced to the monovalent state the ionic conductivity should subsequently be reduced from that characteristic of uncolored crystals. Knowledge of the oxidation state of an impurity, such as calcium, would then be helpful in choosing models for the various Z-centers.

Before beginning the experiments on colored crystals containing calcium it was necessary to study colored pure crystals in order to separate the properties of the impurities from the properties of the host crystal in their absence. As a result it is felt that a better understanding of the conduction process in these crystals has been obtained and that answers to many of the questions arising from the experiments discussed above have been found.

II. CONDUCTIVITY OF UNCOLORED ALKALI HALIDE CRYSTALS

Introduction

Before continuing further with a discussion of the experiments performed it is necessary to point out that impurities present in alkali halides have notable effects on the behavior of colored crystals. For this reason a brief series of experiments was performed in an effort to determine the most pure crystals available in reasonable quantities. It is a difficult and time consuming problem to make a thorough investigation of the purity of alkali halide crystals but fortunately there are two simple methods which indicate the degree of purity. These two methods are optical absorption spectroscopy and ionic conductivity. In the following paragraphs we will give a detailed discussion of ionic conductivity after which the spectra of various crystals will be discussed.

Empirical Observations

Pure Crystals. According to Jacobs and Tompkins (27) the first published work of note on the conduction of electricity through crystalline solids was that of the Curies in 1888. Their method of measurement was to place a thin slice cut from a single crystal between two metal electrodes connected to a high voltage supply in series with a fiber electrometer. After a time Δt the electrometer

would measure a potential ΔV . The current, i , flowing in the crystal was then given by

$$i = C\Delta V/\Delta t, \quad (2.1)$$

where C is the total capacitance of the crystal, electrometer and leads. The conductivity, σ , could then be calculated from the expression

$$\sigma = id/V_o A, \quad (2.2)$$

where d and A are the thickness and cross-sectional area of the crystal respectively and V_o is the applied potential.

A phenomenon quite different from that in metallic conductors was discovered for ionic crystals. The current measured was found to be time dependent, decreasing to a final value over a period sometimes as great as several days. This introduced considerable difficulty in defining the conductivity. Joffé and Roentgen (29) showed that the decrease in current was due to the building up of a polarization voltage, since on disconnecting the electrode from the power supply and grounding it, a current flowed through the electrometer in the direction opposite to that of the original current. Today there still exists considerable controversy concerning an unambiguous definition of conductivity when polarization is occurring, and there are two different schools of thought. One school believes the initial

current, measured before polarization has occurred, should be used in computing the conductivity and consequently they use high frequency alternating current methods. Allnatt and Jacobs (1) belong to this school and have studied alternating current polarization and give a theoretical treatment assuming that a space charge build up at the electrodes, which partially blocks the flow of current, is responsible. The second school argues that the final steady current should be used. Belonging to this group are Sutter and Nowick (60) who have investigated polarization by direct current methods. Their feelings are that the polarization occurs due to dipole orientation. The author believes that neither method gives truly correct results. ac gives conductivities that are too high while dc gives conductivities that are too low. This is because dipoles, such as impurity-vacancy complexes, would oscillate with the ac field and contribute to the current even if ions were not migrating. If dc is used these dipoles would align themselves and cause a decrease in the resultant field and consequently a current reading which is too low. Fortunately both ac and dc methods usually agree quite well at temperatures of a few hundred degrees centigrade and much valuable information can be obtained from each.

Tubant, Reinhold and Liebold (62) determined the transport numbers in several alkali halide crystals. They found that Faraday's law was obeyed, with both positive and negative ions being the charge carriers. The positive ion transport number was near unity but

decreased slightly with increasing temperature.

In general it is found that when $\log_{10}\sigma$ is plotted vs. $1/T$ two straight-line segments are observed (see footnote 1 on page 21). The high temperature segment is reproducible and appears to be an intrinsic property of the crystal. For this reason it is referred to as the intrinsic conductivity. The conductivity at lower temperatures depends on the previous history of the crystal. This region is referred to as the extrinsic or "structure sensitive" region. The point where the two straight-line segments intersect is called the "knee."

Crystals Containing Divalent Cations. Kelting and Witt (31) conducted an extensive investigation of the effect of adding divalent alkaline earth ions to alkali halide crystals. Their results showed quite emphatically that the extrinsic conductivity in these crystals was strongly influenced by the presence of the divalent cationic impurities. In fact at temperatures near the knee the conductivity was found to increase linearly with the impurity concentration.

With this brief introduction we should now be ready to consider the theoretical foundations of ionic conductivity in detail.

Theoretical Interpretation of Ionic Conductivity

Qualitative Discussion. A simple explanation of the observations mentioned above is based on the modern theory of lattice defects

proposed by Frenkel (19) and by Wagner and Schottky (63). According to these authors no crystal is absolutely perfect but contains certain types of defects. The most important are known as Frenkel and Schottky defects. Frenkel defects are formed by atoms being removed from their normal positions taking up new position at interstitial sites. Schottky defects are formed when atoms migrate to the surface of the crystal leaving vacant lattice positions within the crystal. Thus Frenkel defects are described as vacancies and interstitial atoms formed in equal numbers while Schottky defects are described merely as vacancies. Since in alkali halides the relative sizes of the atoms would make the formation of Schottky defects energetically more favorable than Frenkel defects, it is assumed that Schottky defects are present in much greater numbers. It is because of these defects that the alkali halides are able to conduct an electric current.

In the absence of an electric field the vacancies will move about by jumping from one lattice position to another of the same type due to the thermal motion of the ions. Each vacancy has associated with it a net unit charge caused by the surrounding ions. A negative ion vacancy will have a net unit positive charge and a positive ion vacancy a net unit negative charge. Since the motion of the vacancies is random no net current flows. However if an electric field is applied the positive ion vacancies will preferentially move toward the positive electrode and the negative ion vacancies toward the negative

electrode thus causing an electric current to flow. Since the magnitude of the current depends on the concentration of vacancies any method by which the vacancy concentration is increased will correspondingly increase the conductivity. It is because of this that divalent cationic impurities cause an increase in the conductivity since when divalent cations are incorporated into alkali halide crystals they bring in an excess positive charge. In order to compensate for this excess charge positive ion vacancies must be formed in concentrations equal to that of the impurities. The increase in positive ion vacancies causes a corresponding increase in the conductivity. It is due to this dependence on divalent cation concentration that ionic conductivity is useful in determining the purity of alkali halide crystals. This will be discussed more thoroughly in the following paragraphs.

Quantitative Discussion. Since derivations of the conductivity equations can be found in several review articles and texts (27; 34, p. 258-279; 32, p. 477-488) only the final results will be given here.

The ionic conductivity, σ , in alkali halides is defined by the relation

$$\sigma = n_{\pi} e \mu_{\pi} + n_{\alpha} e \mu_{\alpha}, \quad (2.3)$$

where n_{π} and n_{α} and μ_{π} and μ_{α} are the numbers per cm^3 and mobilities of the positive and negative ion vacancies respectively and e is the electronic charge. The mobilities are given by the

expressions

$$\mu_{\pi} = (4a_o^2 e v_{\pi} / kT) \exp (-\Delta g_{\pi} / kT) \quad (2.4)$$

and

$$\mu_{\alpha} = (4a_o^2 e v_{\alpha} / kT) \exp (-\Delta g_{\alpha} / kT) \quad (2.5)$$

where a_o is the jump distance and v_{π} and v_{α} are the vibrational frequencies, in the direction of the vacancies, for the positive ions surrounding a positive ion vacancy and for the negative ions surrounding a negative ion vacancy respectively. Δg_{π} and Δg_{α} are activation free energies for the jump of a positive ion into a positive ion vacancy and for a negative ion into a negative ion vacancy respectively. k is the Boltzmann constant and T the absolute temperature. Since the transport number for the negative ions is much less than for the positive ions, except at high temperatures, the second term on the right in Equation (2.3) is usually neglected and the conductivity written as

$$\sigma = (4n_{\pi} e^2 a_o^2 v_{\pi} / kT) \exp (-\Delta g_{\pi} / kT) \quad (2.6)$$

with the aid of Equation (2.4). This expression is not complete however until the manner in which n_{π} varies with temperature and impurity concentration is known.

It is easily shown (34, p. 258-259) that the product of the positive and negative ion vacancy concentrations is a function of the

temperature only and is given by

$$n_{\pi} n_{\alpha} = N^2 \exp(-\Delta g/kT), \quad (2.7)$$

where N is the total number of positive or negative ion sites per cm^3 , either occupied or vacant and Δg is the Gibbs free energy of formation of a separated positive and negative ion vacancy pair.

Regardless of the precautions taken it is impossible to remove completely all of the divalent cations from alkali halide crystals. Since the incorporation of these ions must be done without violating the law of charge compensation we can write

$$n_{\text{x}} + n_{\alpha} = n_{\pi}, \quad (2.8)$$

where n_{x} is the number of divalent cations per cm^3 . Eliminating n_{α} from Equations (2.7) and (2.8) and solving for n_{π} gives

$$n_{\pi} = \left[\frac{1}{4} n_{\text{x}} + N^2 \exp(-\Delta g/kT) \right]^{\frac{1}{2}} + \frac{1}{2} n_{\text{x}}. \quad (2.9)$$

At low temperatures, where the exponential term is negligible, Equation (2.9) reduced to

$$n_{\pi} = n_{\text{x}}. \quad (2.10)$$

At high temperatures the exponential term dominates and Equation (2.9) becomes

$$n_{\pi} = N \exp(-\Delta g/2kT). \quad (2.11)$$

Substituting Equation (2.10) into Equation (2.6) and writing

$$\Delta g_{\pi} = \Delta h_{\pi} - T\Delta s_{\pi} \text{ gives}$$

$$\sigma = (4n_x e^2 a_o^2 v_{\pi} / kT) \exp(\Delta s_{\pi} / k) \exp(-\Delta h_{\pi} / kT) \quad (2.12)$$

as the low temperature expression for the conductivity, where Δh_{π} and Δs_{π} are the changes in the activation enthalpy and entropy respectively, associated with the jump of a positive ion into a positive ion vacancy. If Equation (2.11) is used with Equation (2.6) we obtain, after writing $\Delta g = \Delta h - T\Delta s$, the expression

$$\sigma = (4Ne^2 a_o^2 v_{\pi} / kT) \exp[(\Delta s_{\pi} - \frac{1}{2}\Delta s) / k] \exp[-(\Delta h_{\pi} + \frac{1}{2}\Delta h) / kT] \quad (2.13)$$

for the high temperature conductivity where Δh and Δs are the enthalpy and entropy of formation of a separated positive and negative ion vacancy pair respectively. From Equations (2.12) and (2.13) we see that if $\log_{10}\sigma$ is plotted vs. $1/T$ two nearly straight line segments should be observed.¹ At low temperatures the slope will be given by $-\Delta h_{\pi} / 2.303k$ and at high temperatures by $-(\Delta h_{\pi} + \frac{1}{2}\Delta h) / 2.303k$. This leaves only v_{π} , Δs_{π} and Δs as

¹Very slight departures from linearity would result from the T in the denominators of Equations (2.12) and (2.13). Thus actually $\log_{10}\sigma T$ rather than $\log_{10}\sigma$ should be plotted vs. $1/T$. This procedure results in only a small change in the curves and is often not practiced.

unknowns. Unfortunately there are only two equations from which these three unknowns can be obtained. For this reason ν_{π} is usually taken to be equal to the transverse lattice vibrational frequency, which for potassium chloride is $4.25 \times 10^{12} \text{ sec}^{-1}$ (5). If this assumption is made extrapolation of the low and high temperature portions of the conductivity plot to $1/T = 0$ enables us to calculate Δs_{π} and Δs . Once Δh and Δs are known Equation (2.11) can be used to estimate the concentration of positive ion vacancies at any temperature greater than the knee temperature in the conductivity curve. Below the knee $n_{\pi} = n_x$. At the conductivity knee both Equations (2.12) and (2.13) apply and can therefore be set equal. This gives

$$n_x = N \exp(\Delta s/2k) \exp(-\Delta h/2kT_k), \quad (2.14)$$

where T_k is the temperature at which the knee occurs. It is by the use of Equation (2.14) that conductivity data can be used to estimate the total divalent cation concentration in alkali halide crystals. This equation can be put in a more useful form by using $\Delta s = 4.63 \times 10^{-4} \text{ ev } ^\circ\text{K}^{-1}$ and $\Delta h = 2.259 \text{ ev}$ as given by Beaumont and Jacobs (6). When this is done we obtain

$$n_x = 2.4 \times 10^{(23-5700/T_k)}, \text{ cm}^{-3}. \quad (2.15)$$

Equation (2.15) will prove very useful and will be considered again in

evaluating the experimental results, but first we will discuss the procedure for preparing crystals and making conductivity measurements used in the present work.

Experimental

Salt Purification

A variety of potassium chloride crystals was grown from different starting materials and compared with crystals commercially available from Vinor Laboratories and from Harshaw Chemical Company. One batch of granular potassium chloride was obtained from Johnson, Matthey & Co., Ltd. and another from Anderson Chemical Co. A third source of salt was recrystallized reagent grade material and a fourth source was potassium chloride purified by ion exchange. The process of purification by ion exchange was similar to that developed by Fredericks, Rosztoczy and Hatchett as cited in the work of Holmes (25, p. 9-10).

The principle, utilized for recrystallization, involved precipitation of potassium chloride from a saturated solution by absorption of hydrogen chloride gas (8, p. 469). The chief advantage of this method is that it allows precipitation from hot solution. Thus the impurities more soluble in hot solution do not precipitate readily. The first portion of the precipitate was discarded since it would be

expected to contain some of the less soluble impurities. A diagram of the apparatus is shown in Figure 1. In this method concentrated sulfuric acid is allowed to drip from (E) into concentrated hydrochloric acid, contained in (D), liberating hydrogen chloride gas. The gas is then bubbled through concentrated hydrochloric acid in (B) to remove any sulfuric acid being carried over. The hydrogen chloride then passes over the saturated solution of potassium chloride and is absorbed. The increased concentration of chloride ions in solution precipitates potassium chloride through the common ion effect (42, p. 179).

Crystal Growth

The details of crystal growth will be discussed only briefly here since the procedure was identical to that used by Holmes (25, p. 21-39) and is discussed by him in considerable detail.

The Kyropoulos method was used and the procedure employed was to melt the potassium chloride, contained in a quartz crucible, under a controlled atmosphere of hydrogen chloride to remove any traces of hydroxide and carbonate impurities. After the salt had melted, a seed, which was secured to a water-cooled cold finger, was lowered until it was in contact with the melt. A crystal would then begin to grow on the seed. By regulating the rate at which the seed was withdrawn and accurately controlling the furnace temperature

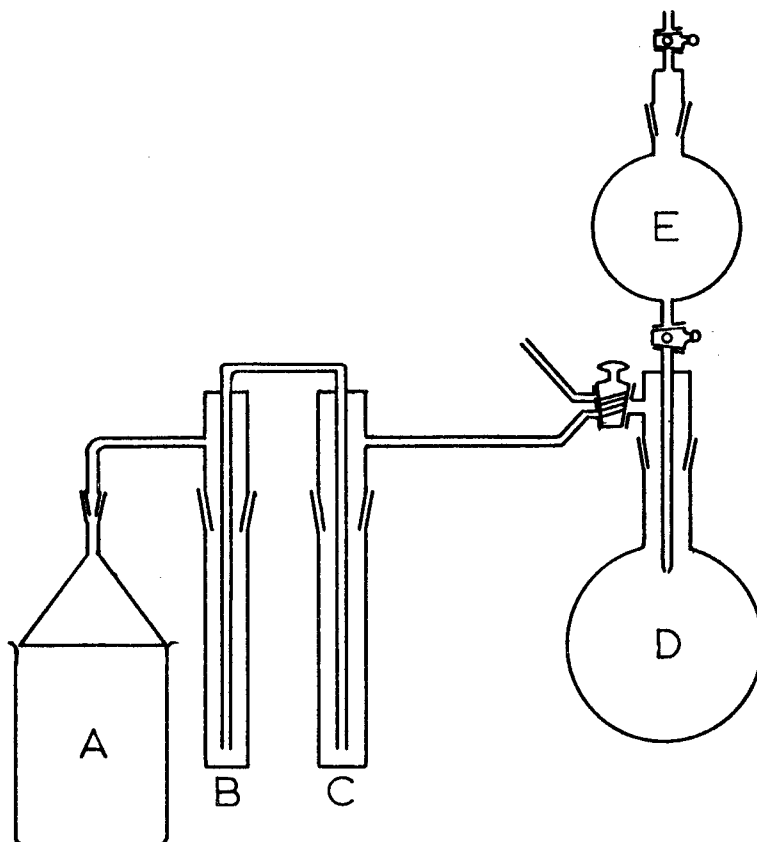


FIGURE 1. Schematic diagram of recrystallization apparatus. (A) Saturated KCl solution. (B) Bubbler containing concentrated HCl solution. (C) Trap. (D) Concentrated HCl solution. (E) Concentrated H₂SO₄ solution.

single crystals as large as $3 \times 3 \times 5 \text{ cm}^3$ could be obtained. Usually once crystal growth had begun the hydrogen chloride atmosphere was replaced by argon. No detectable differences in the crystals were observed when this was done.

Conductivity Measurements

A conductivity cell was constructed and is shown schematically in Figure 2. The assembly (K) was made of stainless steel because of its low heat-conducting properties and also to furnish electric shielding. The separate parts were fitted together with O-ring seals to insure that a vacuum could be maintained. The electrical leads (E) were of 1/16 inch nickel wire to insure rigidity and a low noise level. Metal to glass seals (D) were used for connecting the power supply and electrometer. The cell was equipped with two vacuum valves (A), one of which could be connected to a vacuum pump and the other to an argon tank. A guard ring (G) was used (14, p. 38-40) into which a chromel-alumel thermocouple was inserted. The thermocouple well and guard ring assembly were held by a Swagelock seal (C) equipped with a teflon insert and could be adjusted by loosening the seal. One phosphor-bronze spring (J) served to ground the guard ring and a second was used in connecting the low potential lead to one of the BNC connectors. The purpose of the guard ring was to eliminate surface conduction and to also help maintain a more uniform

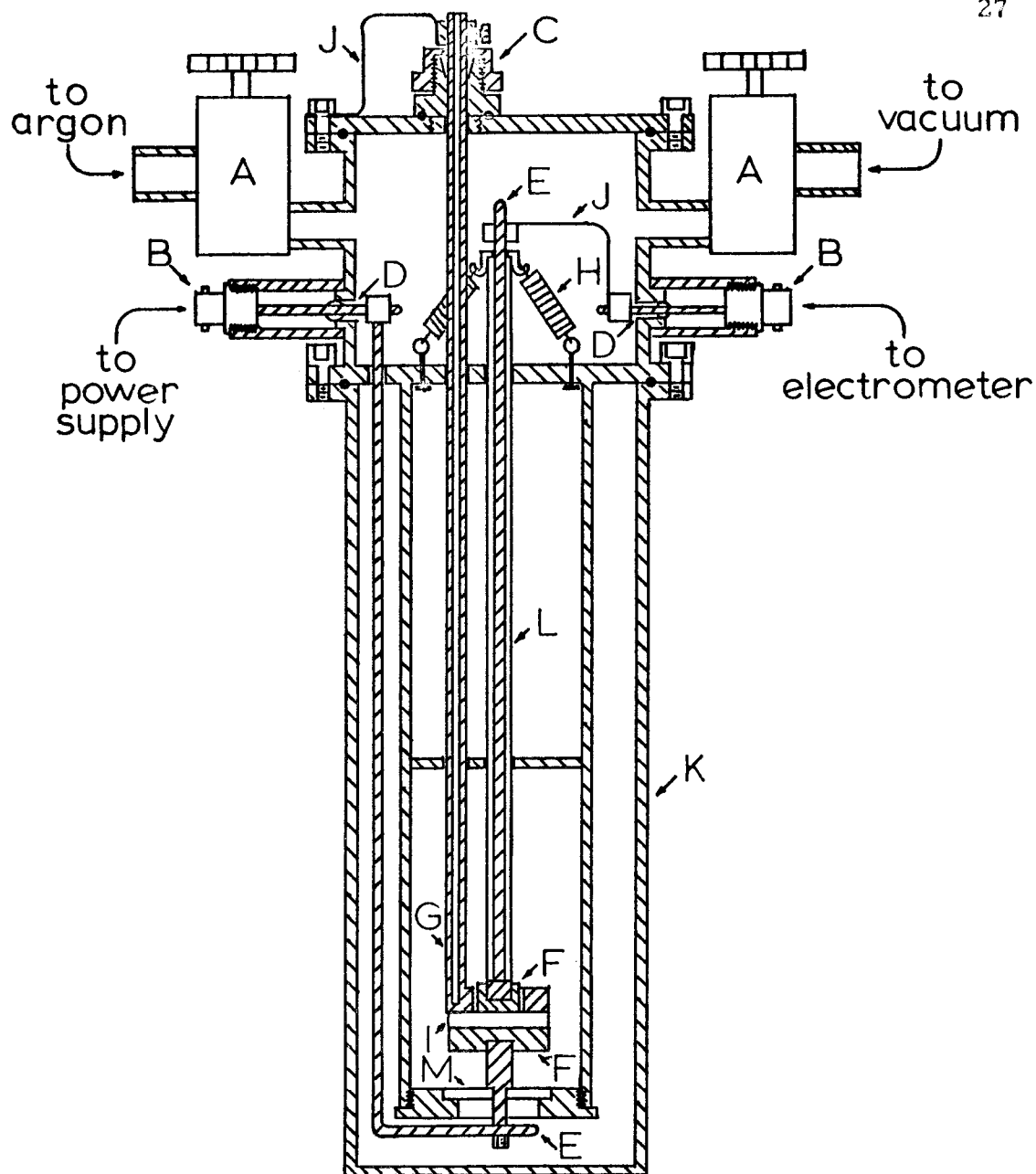


FIGURE 2. Cross sectional diagram of the conductivity cell. (A) Vacuum valves. (B) BNC connectors. (C) Swagelock seal with teflon insert. (D) Metal to glass seals. (E) Nickel wires. (F) Graphite electrodes. (G) Thermocouple well and guard ring. (H) Stainless steel springs. (I) Sample. (J) Phosphor bronze springs. (K) Stainless steel container. (L) Quartz tube. (M) Quartz disc.

electric field between the graphite electrodes (F). The crystal (I) was mounted between the electrodes and held under spring tension by two stainless steel springs (H). A quartz rod (L) was used to hold the upper, movable electrode while the lower, rigid electrode was seated on a quartz disc (M).

The lower portion of the cell, containing the sample, was inserted into a Marshall furnace, which was accurately controlled to $\pm 0.5^{\circ}\text{C}$ by a Barber-Coleman series 620 power controller and a Wheelco model 407 temperature regulator.

The circuit used consisted of the conductivity cell, a Keithley model 241 regulated dc voltage supply and a Keithley model 610A electrometer connected in series. A diagram of this arrangement is shown in Figure 3. Also shown in the figure is the guard ring assembly. All electrical leads were of shielded coaxial cable to maintain a low noise level.

The samples were prepared by cleaving them to dimensions of approximately 15mm x 15mm x 1.5mm and evaporating gold contacts onto the surfaces. The assembly for gold evaporation is shown in Figure 4. The sample (B) was mounted in the crystal holder (A) and positioned directly over a molybdenum wire filament (C) on which small pieces of gold were placed. The chamber was evacuated to about 2×10^{-4} mm mercury pressure. The filament was heated by controlling with a variac until the gold had evaporated, some of which

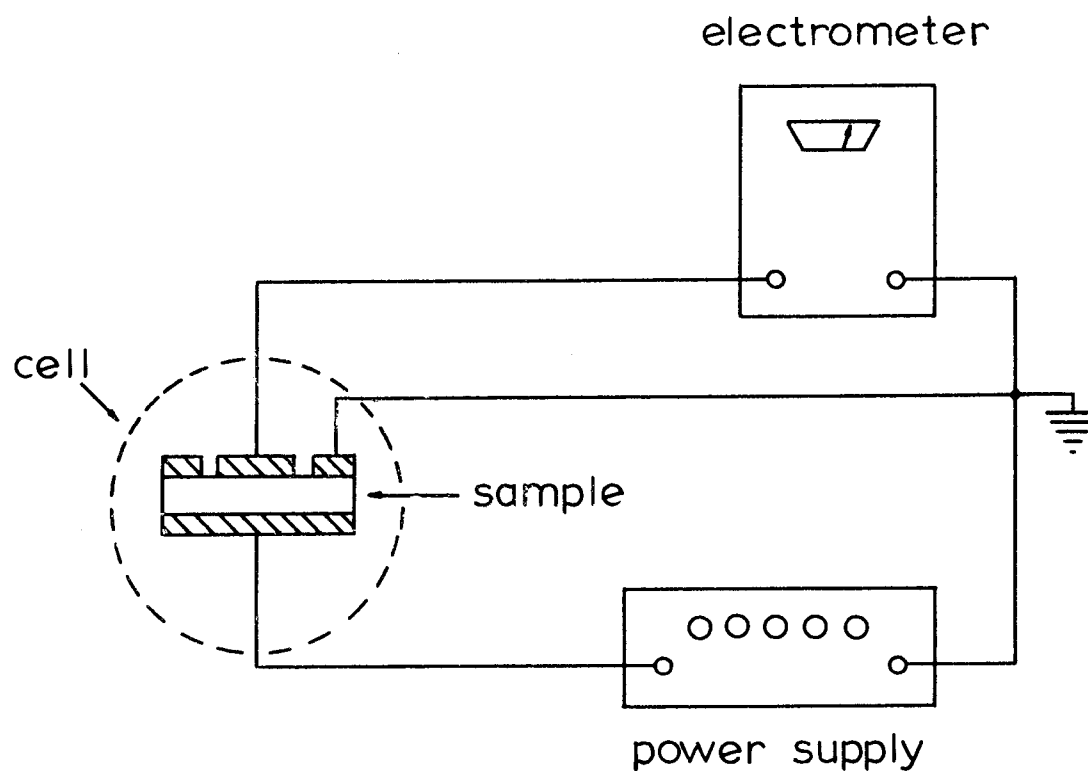


FIGURE 3. Circuit diagram for conductivity measurement. The circuit consists of a Keithley model 610A electrometer, a Keithley model 241 d.c. power supply and the conductivity cell. Note the use of a guard ring on the sample.

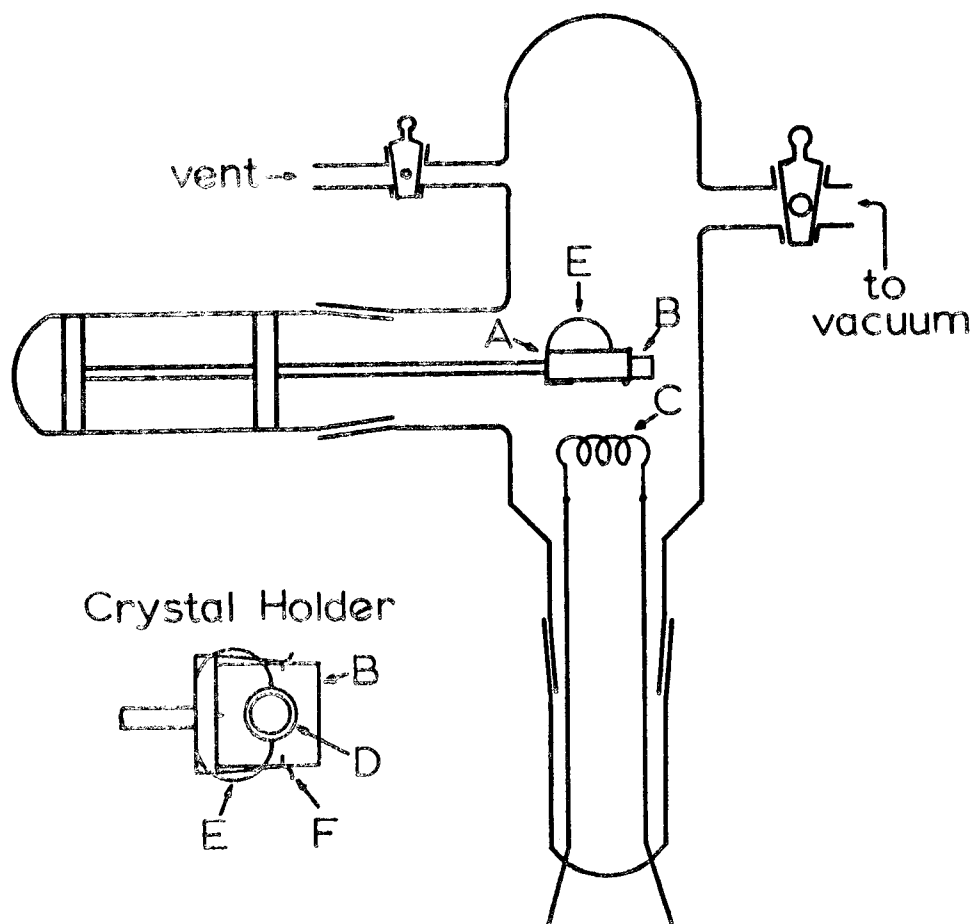


FIGURE 4. Schematic diagram of apparatus for evaporating gold contacts onto crystals. (A) Crystal holder (also shown separately). (B) Crystal. (C) Molybdenum wire filament. (D) Masking ring. (E) Phosphor-bronze wire spring for holding masking ring. (F) Phosphor-bronze leaf spring for holding crystal. The diagram is not drawn to scale.

would have condensed on the crystal. The sample was turned over and the process repeated for the other side. After plating both sides the sample was removed and the edges cleaved off with a razor blade.

The crystal holder was designed with a masking ring (D) on one face of the crystal. The ring was held in position by two fine phosphor-bronze wire springs. This masking ring served to separate the guard ring contact from the electrometer contact. The reverse face of the crystal was completely plated with evaporated gold.

Once the sample had been prepared it was placed in the conductivity cell under an atmosphere of purified argon. The cell was mounted in the furnace and connected to the electrometer and power supply. The furnace was set to the desired temperature and the conductivity measured. The furnace was always allowed to reach this temperature and remain there for several minutes, before measurements were made, to insure thermal equilibrium in the sample. The current, i , flowing in the electrometer was then measured after a voltage, V , had been applied to the crystal and the conductivity, σ , calculated from the relation

$$\sigma = id/VA, \quad (2.16)$$

where d and A are the crystal thickness and area of the upper electrode respectively.

Polarization effects were only slight and occurred only at low

temperatures. In all cases it was the final current, after polarization had reached a maximum, which was used in Equation (2.16) for computing the conductivity. It was found that when evaporated gold contacts were used Ohm's law was obeyed over a wide temperature range. This is shown in Figure 5 where the current has been plotted vs. voltage at several different temperatures. The obedience to Ohm's law was observed even if polarization had occurred.

Results and Discussion

Conductivity of Pure Potassium Chloride Crystals

Nonlinear Intrinsic Conductivity. When conductivity measurements were made on crystals grown from potassium chloride purified by ion exchange, it was found that the intrinsic conductivity was not perfectly linear when $\log_{10}\sigma$ was plotted vs. $1000/T$, but actually showed two linear regions. The temperature where these two regions met corresponded to approximately 450°C . This can be seen in Figure 6 where $\log_{10}\sigma$ has been plotted vs. $1000/T$ for a crystal grown from salt purified by ion exchange. This effect has also been observed by Gründig (22) and by Beaumont and Jacobs (6). The explanation given by Gründig, and used by Beaumont and Jacobs in evaluating their results, is that both cation and anion conduction is important with the former dominating at lower temperatures and the

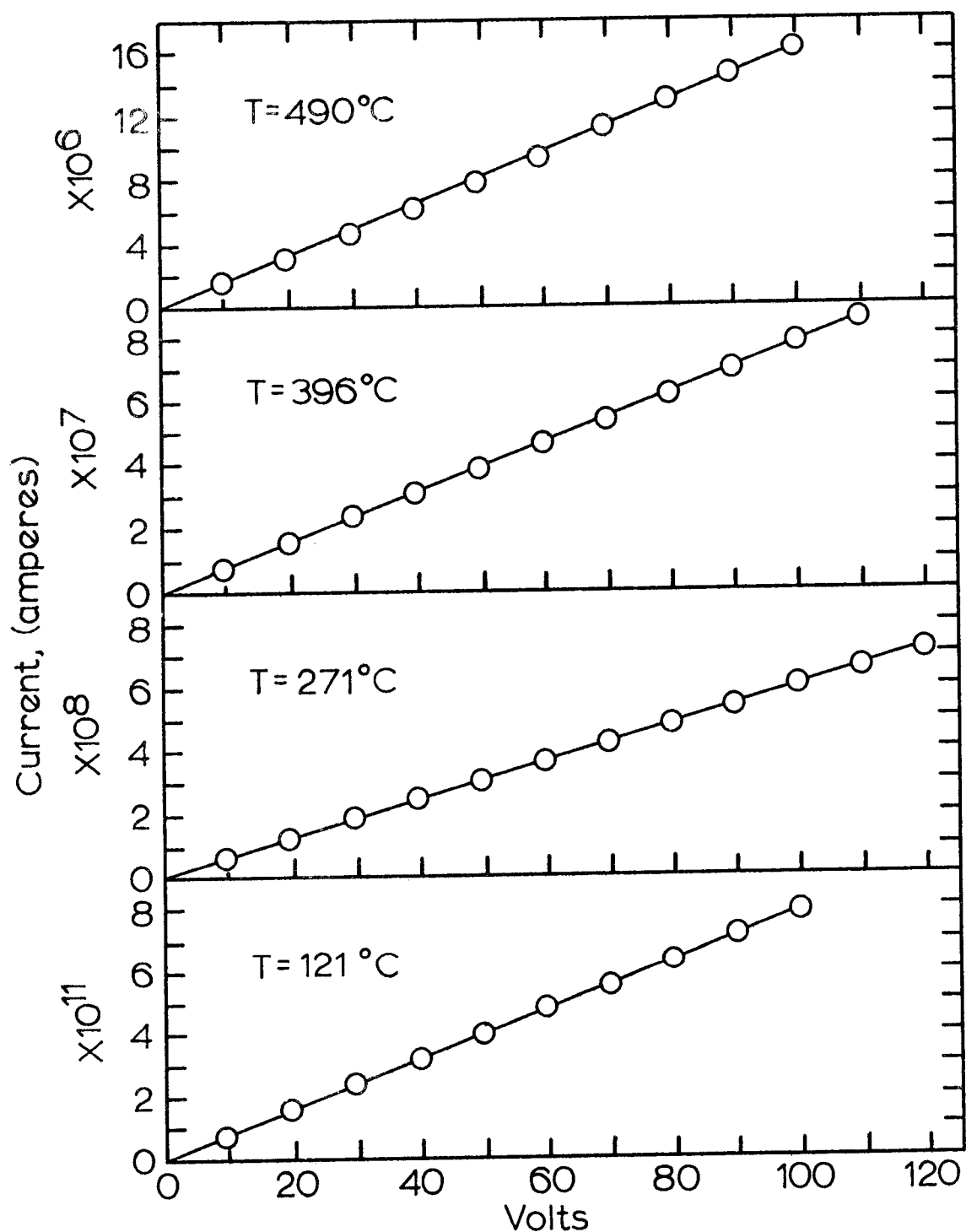


FIGURE 5. Current vs. voltage plots. The curves show the obedience to Ohm's law, at several different temperatures, when evaporated gold contacts are used.

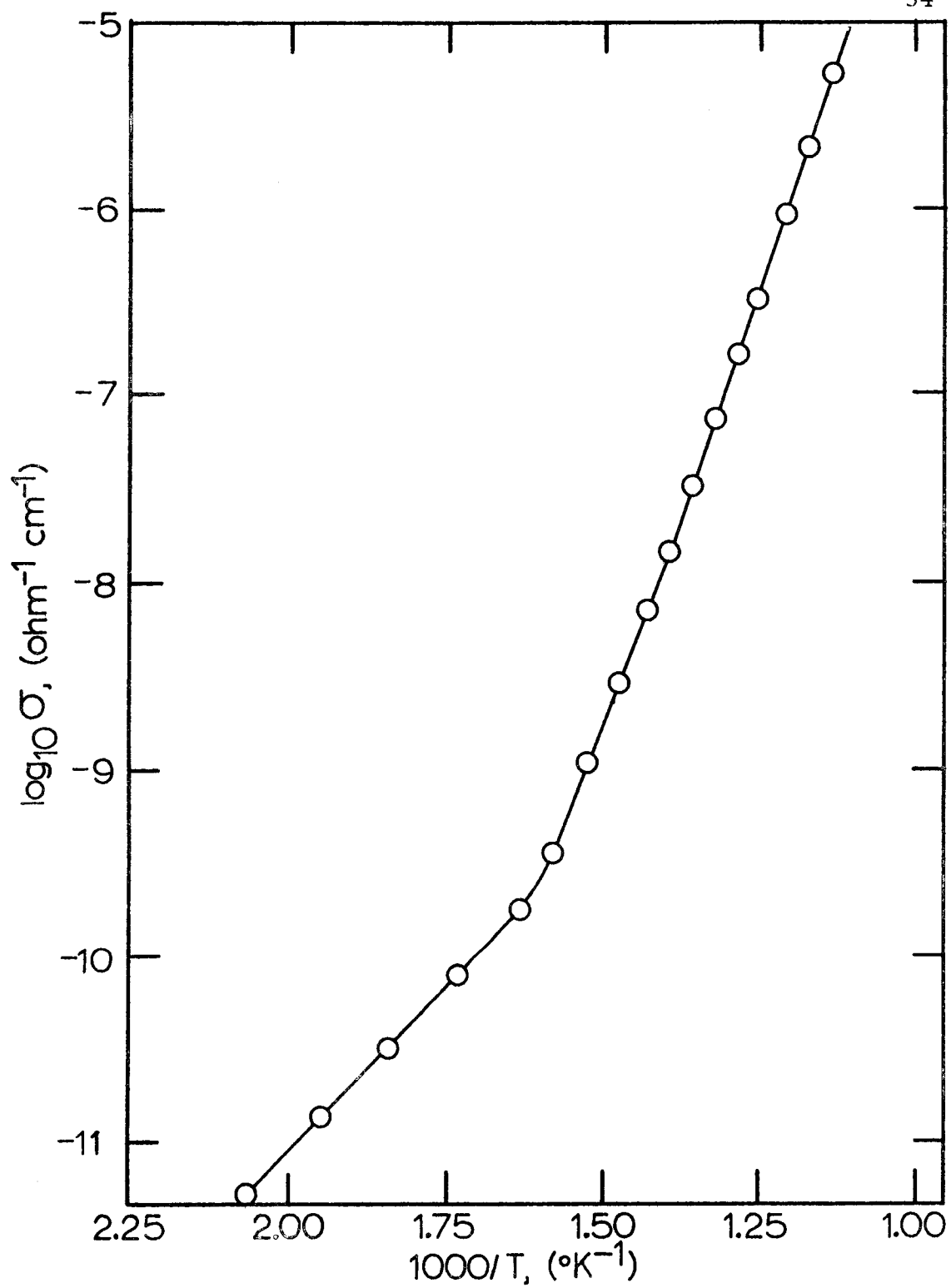


FIGURE 6. Plot of $\log_{10} \sigma$ vs. $1000/T$. Note the discontinuity in the intrinsic slope at $1000/T \approx 1.4$.

latter at higher temperatures. Obviously the reason this effect has not been observed more frequently is that it is only recently that crystals of low enough knee temperatures have become available. Most of the knee values quoted in the literature are greater than 450°C . Thus the extrinsic conductivity had obscured this interesting effect.

Activation Enthalpies. From the slope of the extrinsic portion of the conductivity curve shown in Figure 6, an activation enthalpy, Δh_{π} , equal to 0.70 ev was obtained. This is in excellent agreement with the value of 0.709 ev obtained by Beaumont and Jacobs (6). This also helps demonstrate that, as far as activation enthalpies are concerned, it does not matter whether ac or dc is used since these authors used ac methods while dc methods were used in the present work.

The departure from a single linear curve for the intrinsic conductivity introduces some ambiguity into defining the activation enthalpy in that region. For that reason the values for Δh_{π} and Δh obtained by Beaumont and Jacobs will be used when it is necessary to know these values. These authors give $\Delta h_{\pi} = 0.709 \text{ ev}$ and $\Delta h = 2.259 \text{ ev}$.

The Effect of Strong Fields. It was found that if fields of approximately 1000 volts per cm were applied to potassium chloride

crystals at temperatures of about 600°C or greater two interesting effects were observed. The effect noticed first was that the crystals became nearly intrinsic with regard to their conducting properties. This effect is exhibited in Figure 7 where the conductivity, measured with increasing temperature, is shown before applying a strong field and with decreasing temperature after applying a strong field. It is seen that the latter points fall almost perfectly on a line corresponding to the intrinsic conductivity.

The second effect is exhibited in Figure 8 where we have shown a spectrum taken of the crystal used in Figure 7 after completion of the conductivity measurements. Two absorption bands have been introduced, one at $305\text{ m}\mu$ and one at $230\text{ m}\mu$. The band at $230\text{ m}\mu$ can be identified as arising from V_2 -centers. The band at $305\text{ m}\mu$ has not been identified. The correct model for the V_2 -center is not known but it is believed to involve positive ion vacancies which have trapped holes. Seitz (51) has proposed a model consisting of two adjacent positive ion vacancies which have trapped a pair of holes. Thus the reduction in conductivity could arise from holes being trapped at positive ion vacancies. Since a hole bears a net unit positive charge and a vacancy bears a net unit negative charge, a combination of the two is electrically neutral and is unaffected by an electric field. The conductivity is thus decreased due to the removal of free positive ion vacancies. The holes presumably were injected from the positive electrode when the strong field was applied.

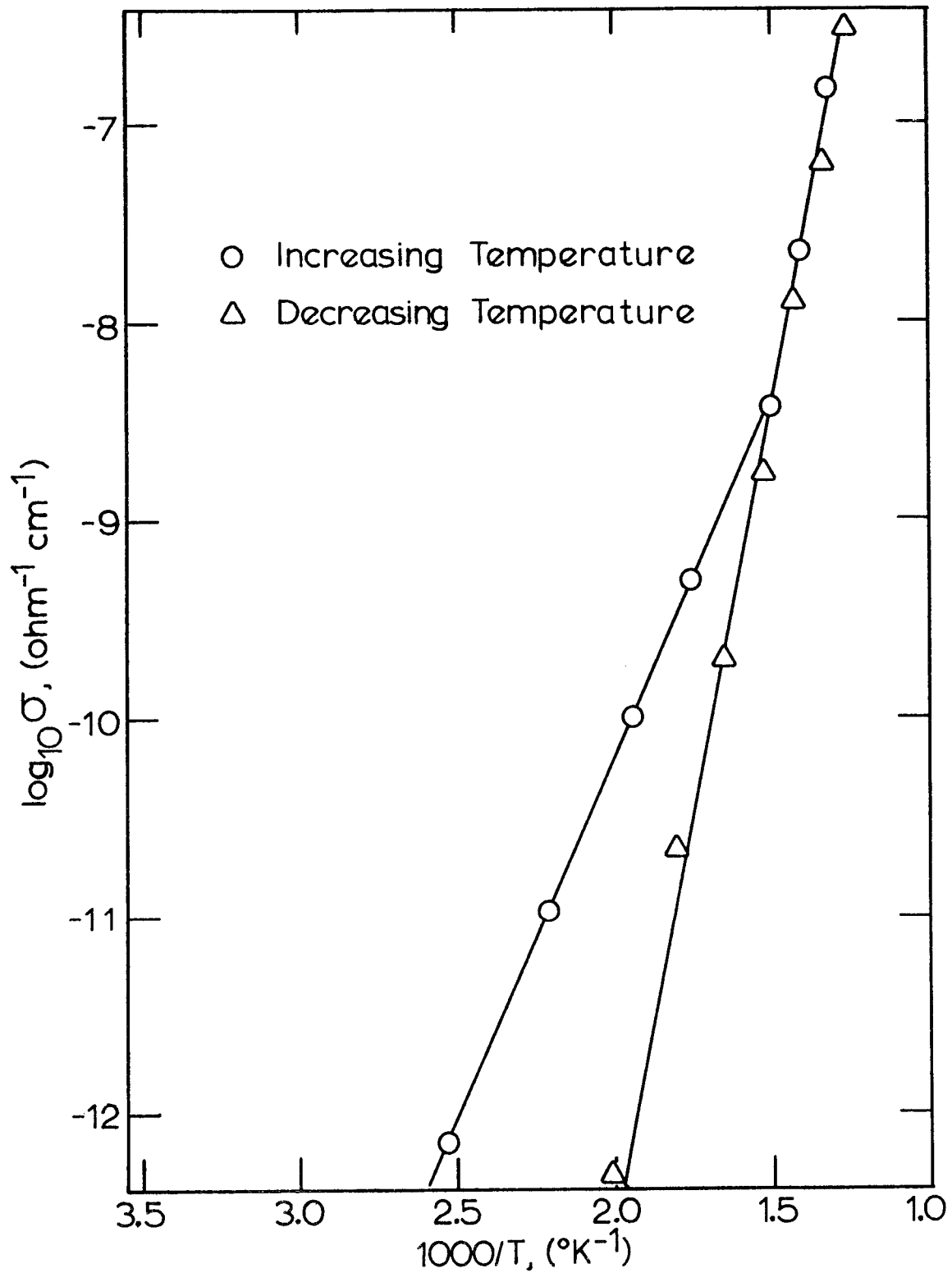


FIGURE 7. Plot showing the effect on the conductivity of applying moderate electric field at high T.

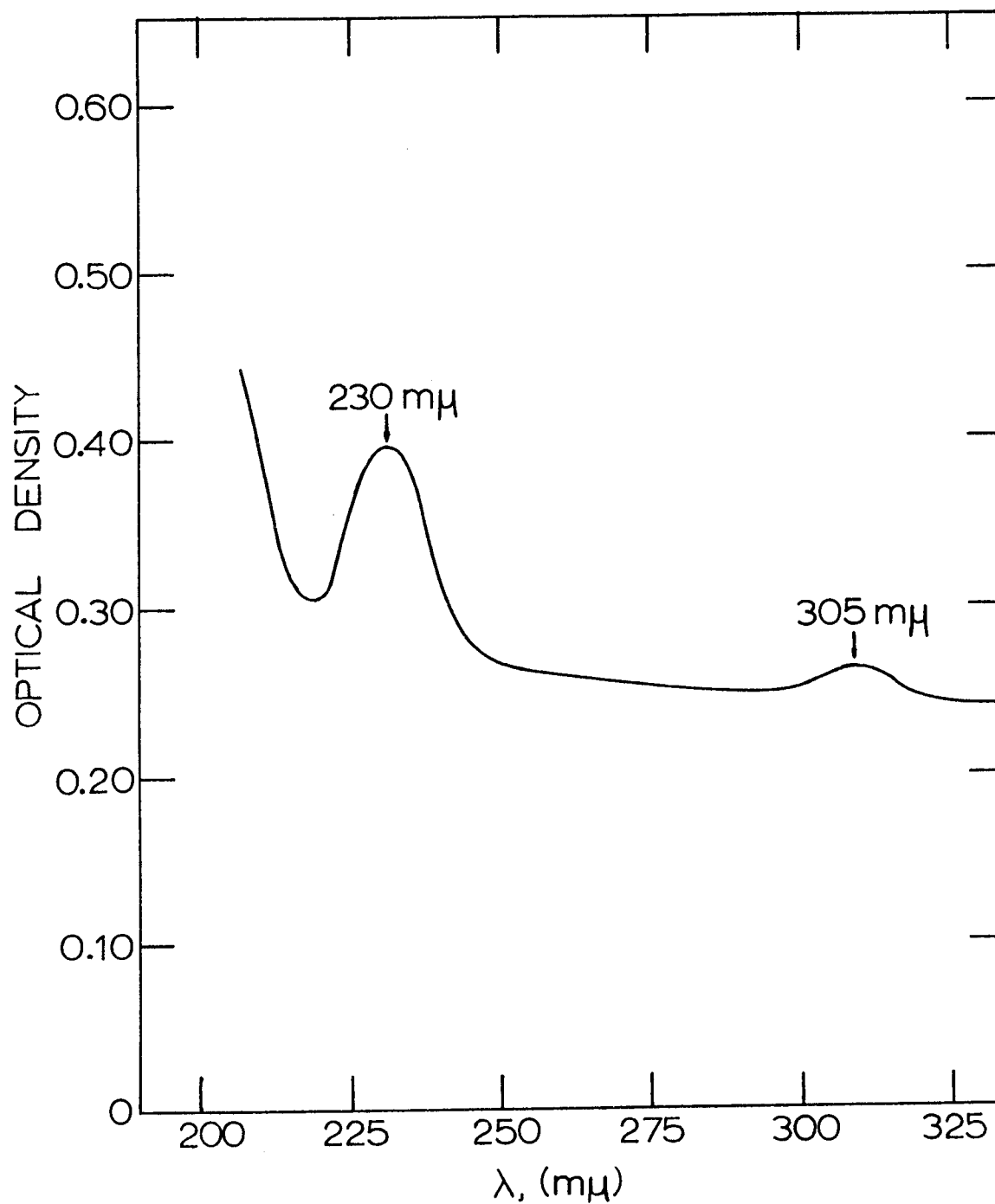


FIGURE 8. Plot showing the presence of absorption bands after conductivity measurements were made at high temperatures under a field strength of several hundred volts per centimeter.

Conductivity of Potassium Chloride Crystals Containing Calcium Ions

Since calcium-doped potassium chloride crystals were needed for work to be discussed later five crystals were grown from melts containing 7.7×10^{-6} , 3.3×10^{-5} , 6.9×10^{-5} , 9.3×10^{-5} and 1.4×10^{-5} mole fractions of calcium chloride respectively. No absorption bands in the region between 185 μ and 400 μ could be found in these crystals. Conductivity measurements were made between 50°C and 700°C the results of which are shown in Figure 9.

In an effort to determine the concentration of calcium actually incorporated in the crystals the knee temperatures were taken from Figure 9 and substituted into Equation (2.15). The results are shown in Table 1 where the concentrations calculated are compared with the concentrations added to the melt. The knee temperatures are also shown. Comparing the first and last columns in the table shows that about 10% of the calcium is actually incorporated in the crystal lattice.

Table 1. Estimated Ca^{2+} concentration for CaCl_2 -doped crystals.

Ca^{2+} Concentration in melt, (mole fraction)	Knee temperature, (°K)	Ca^{2+} Concentration by Equation (2.15), (mole fraction)
7.7×10^{-6}	833	2.1×10^{-6}
3.3×10^{-5}	862	3.6×10^{-6}
6.9×10^{-5}	909	8.1×10^{-6}
9.3×10^{-5}	930	1.1×10^{-5}
1.4×10^{-4}	943	1.4×10^{-5}

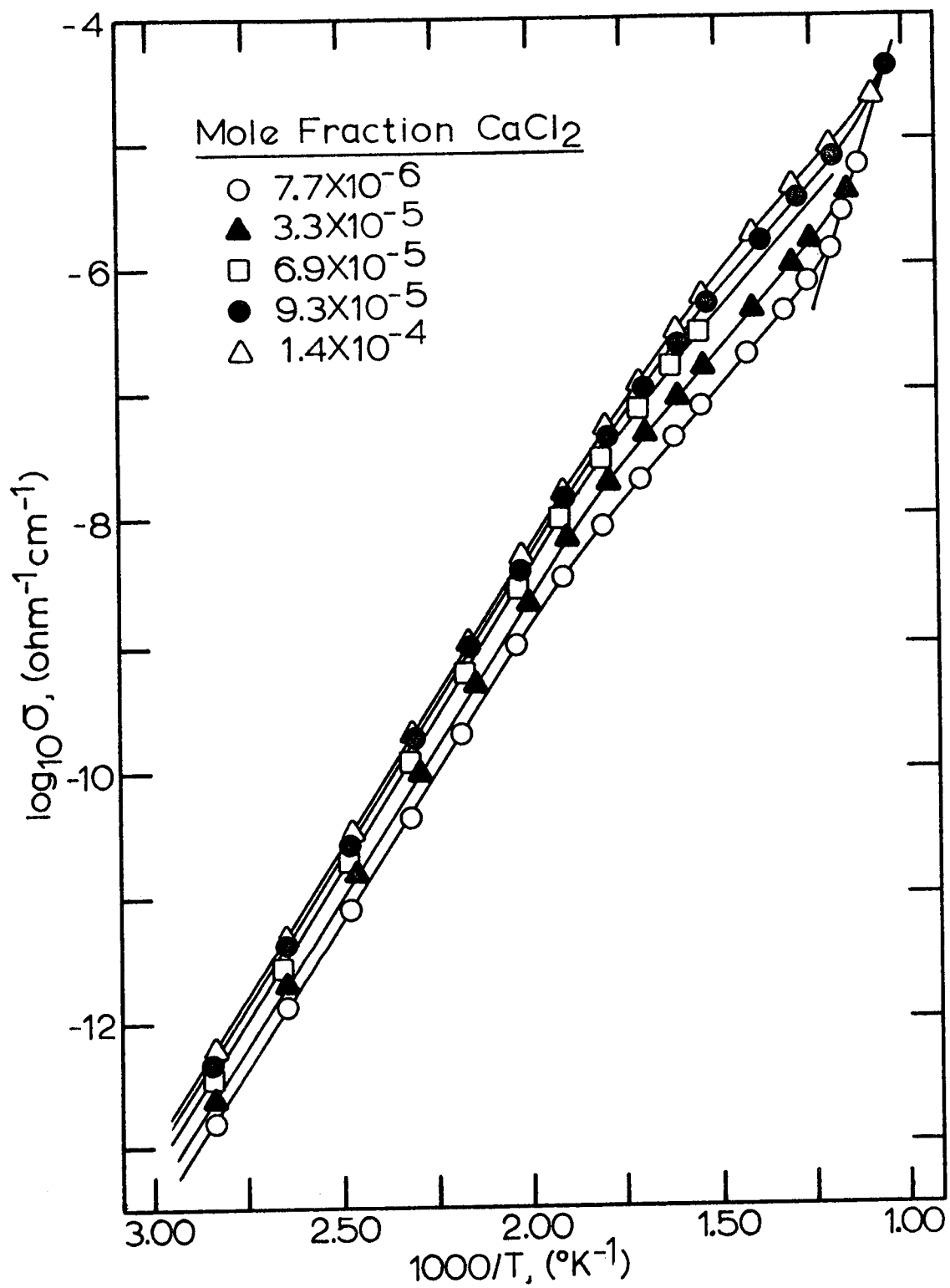
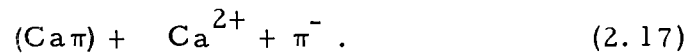


FIGURE 9. Conductivity plot of several CaCl_2 -doped crystals.

Examining Figure 9 we see that the extrinsic region exhibits two distinct slopes. The greater slope at lower temperatures can be attributed to association between Ca^{2+} ions and positive ion vacancies. The corresponding reaction can be written as



The corresponding equilibrium constant will be given by

$$\frac{(n_{+})(n_{\pi})}{(N)(n_{c})} = \exp(-\Delta G_{d}/kT), \quad (2.18)$$

where n_{π} , n_{+} and n_{c} are the concentrations of positive ion vacancies, unassociated calcium ions and calcium-vacancy complexes respectively. N is the total number of positive ion sites per cm^3 .

ΔG_{d} is the standard free energy of dissociation for reaction (2.17) and can be written

$$\Delta G_{d} = \Delta H_{d} - T\Delta S_{d}, \quad (2.19)$$

where ΔH_{d} and ΔS_{d} are the enthalpy and entropy respectively.

At low temperatures we will also have

$$n_{\pi} = n_{+}. \quad (2.20)$$

Using Equations (2.18), (2.19) and (2.20) and assuming only a small fraction of the complexes dissociated gives

$$n_{\pi} = (Nn_c)^{\frac{1}{2}} \exp(\Delta S_d/2k) \exp(-\Delta H_d/2kT). \quad (2.21)$$

Since we have assumed only a small fraction of the complexes dissociated n_c will be essentially the same as the total concentration of CaCl_2 , n_x , in the crystal. Using Equations (2.21) and (2.6) gives

$$\sigma = (Nn_x)^{\frac{1}{2}} (4e^2 a_o^2 v_{\pi}/kT) \exp[(\Delta s_{\pi} + \frac{1}{2}\Delta S_d)/k] \exp[(\Delta h_{\pi} + \frac{1}{2}\Delta H_d)/kT]. \quad (2.22)$$

We see from Equation (2.22) that at lower temperatures the slope of the plots in Figure 9 should be equal to $-(\Delta h_{\pi} + \frac{1}{2}\Delta H_d)/(2.303k)$.

This gives $\Delta h_{\pi} + \frac{1}{2}\Delta H_d = 0.95 \text{ ev}$.

At higher temperatures we assume all of the Ca^{2+} ions to be dissociated and n_{π} in Equation (2.6) will be equal to n_x , the concentration of CaCl_2 in the crystal. This gives

$$\sigma = (4n_x e^2 a_o^2 v_{\pi}/kT) \exp(\Delta s_{\pi}/k) \exp(-\Delta h_{\pi}/kT). \quad (2.23)$$

From Equation (2.23) we see that the slope just below the intrinsic region should be equal to $-\Delta h_{\pi}/(2.303k)$. This gives $\Delta h_{\pi} = 0.70 \text{ ev}$, identical to the value obtained from pure crystals grown from ion exchange purified potassium chloride. ΔH_d is then calculated to be 0.50 ev in good agreement with the value of 0.52 ev obtained by Gründig (23).

Examining Equations (2.22) and (2.23) we see that at low

temperatures the conductivity should be proportional to $n_x^{\frac{1}{2}}$ while at higher temperatures it should be proportional to n_x . That this is indeed true can be seen from Figure 10 and Figure 11. In these figures the concentrations of CaCl_2 plotted was taken from the last column of Table 1. The linearities are good considering the accuracy with which one can determine the concentration of CaCl_2 in the melt.

Comparison of Various Pure Potassium Chloride Crystals

Conductivity. As a comparison for divalent cation concentration conductivity measurements were made on the following crystals: (1) crystals grown from potassium chloride purified by ion exchange; (2) potassium chloride crystals obtained from Harshaw Chemical Co.; (3) crystals grown from potassium chloride obtained from Anderson Chemical Co.; (4) crystals grown from potassium chloride obtained from Johnson, Matthey & Co., Ltd.; (5) potassium chloride crystals obtained from Vinor Laboratories; (6) crystals grown from recrystallized potassium chloride as discussed above. A plot of $\log_{10} \sigma$ vs. $1000/T$ for these crystals is shown in Figure 12. The ion exchange salt is seen to exhibit a much lower extrinsic conductivity than any of the others and thus appears to be much lower in total divalent cation concentration. In Table 2 the concentrations of divalent cation impurities, estimated from Equation (2.15), are given for the crystals shown in Figure 12. Also shown are the various knee

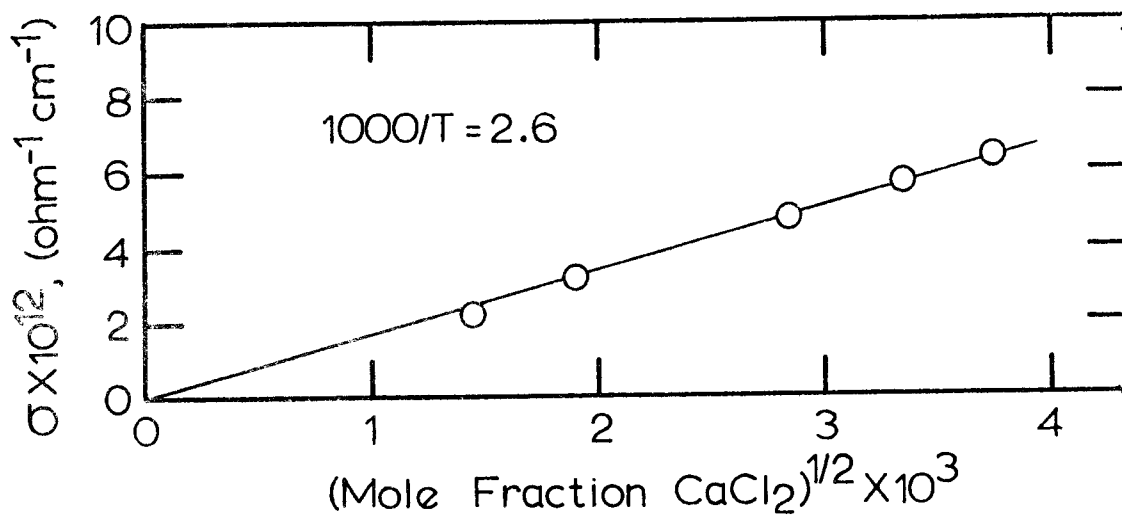


FIGURE 10. Plot showing the dependence of the conductivity, at low temperature, on the mole fraction of CaCl_2 in the crystal, estimated from equation (2.15).

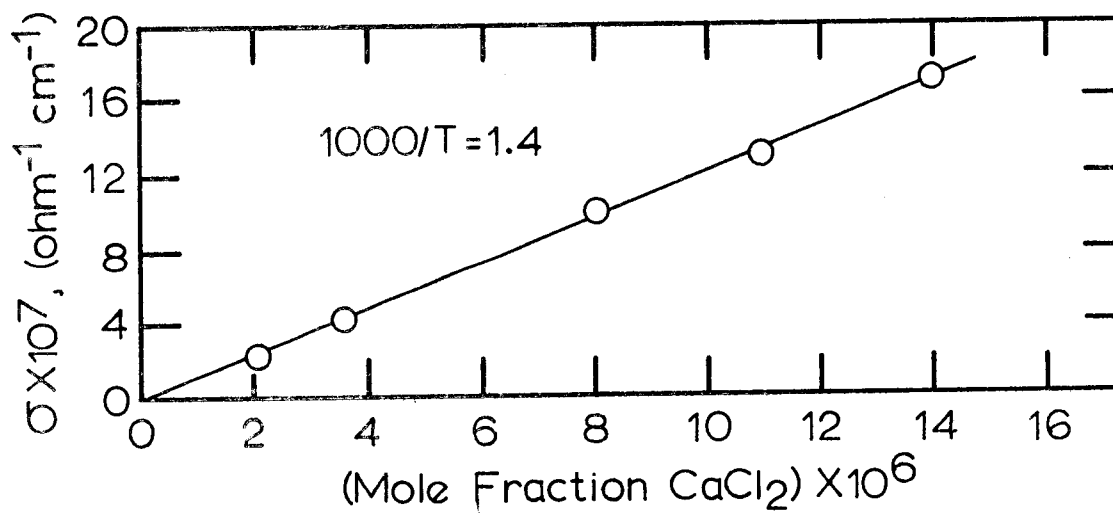


FIGURE 11. Plot showing the dependence of the conductivity, at high temperature, on the mole fraction of CaCl_2 in the crystal, estimated from equation (2.15).

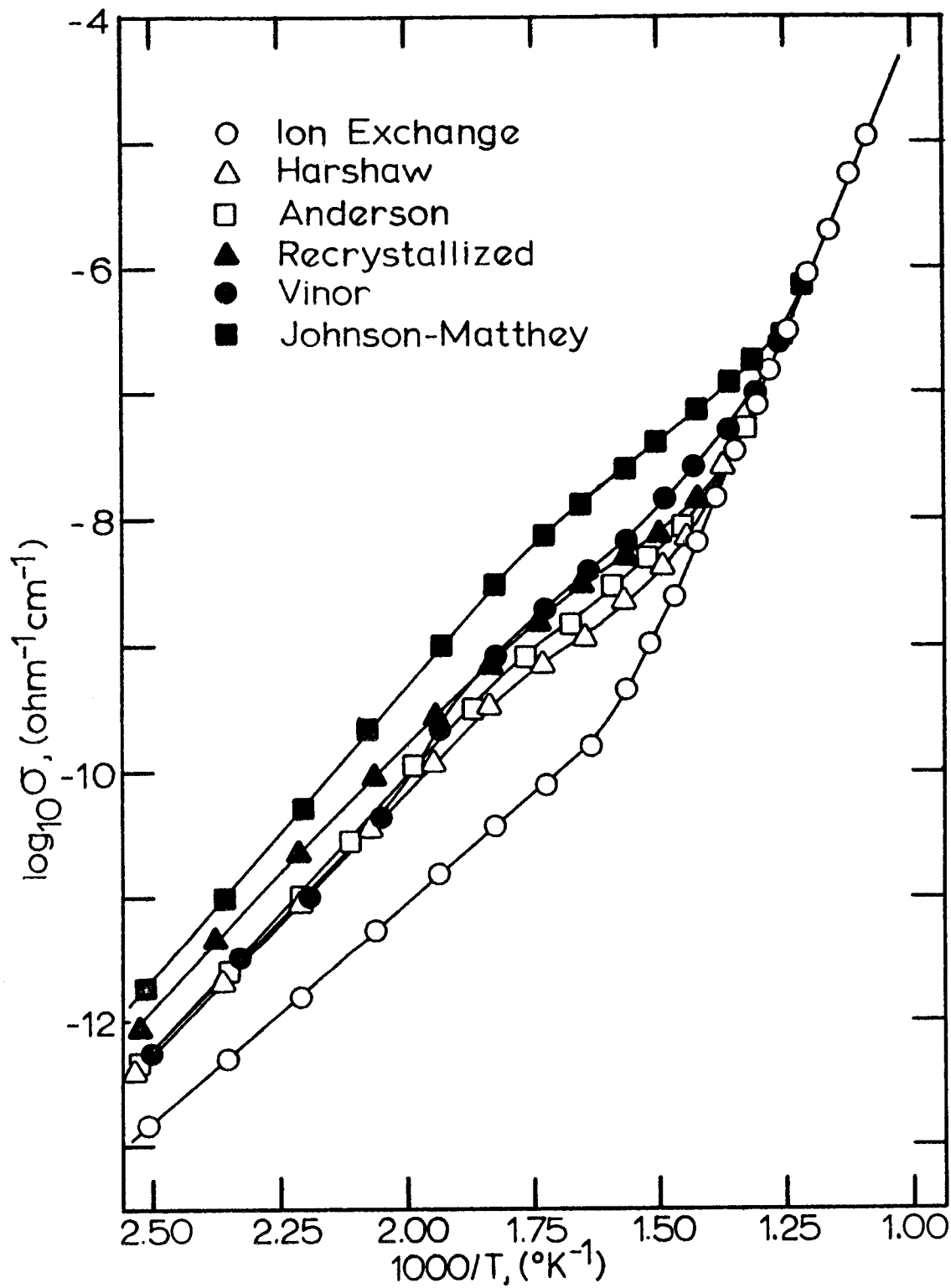


FIGURE 12. Conductivity plot of various pure crystals.

temperatures for the different crystals. By examining the column on the right we see that the divalent cation concentration ranges over nearly two orders of magnitude with the ion exchange crystal giving the lowest value. It should also be noted that the crystal grown from recrystallized potassium chloride appears remarkably low in divalent cations considering the simplicity of the purification process.

Table 2. Estimated divalent cation concentration for various crystals.

Material	Knee temperature, (°K)	Divalent cation conc., (cm ⁻³)
Ion exchange	625	1.8 x 10 ¹⁴
Harshaw	702	1.8 x 10 ¹⁵
Anderson	714	2.4 x 10 ¹⁵
Recrystallized	722	3.1 x 10 ¹⁵
Vinor	763	7.9 x 10 ¹⁵
Johnson-Matthey	797	1.7 x 10 ¹⁶

Next we will examine the spectra of these various crystals in an effort to observe any further impurities which might be present.

Spectra. Since many impurity ions are known to give rise to characteristic absorption bands in the ultra-violet region of the spectrum, measurements were made in an effort to detect their presence. The instrument used was a Perkin-Elmer model 450 recording spectrophotometer. The various room temperature spectra, for the region between 185 m μ and 300 m μ , are shown in Figure 13 for the crystals discussed above. By examining the figure it can be seen

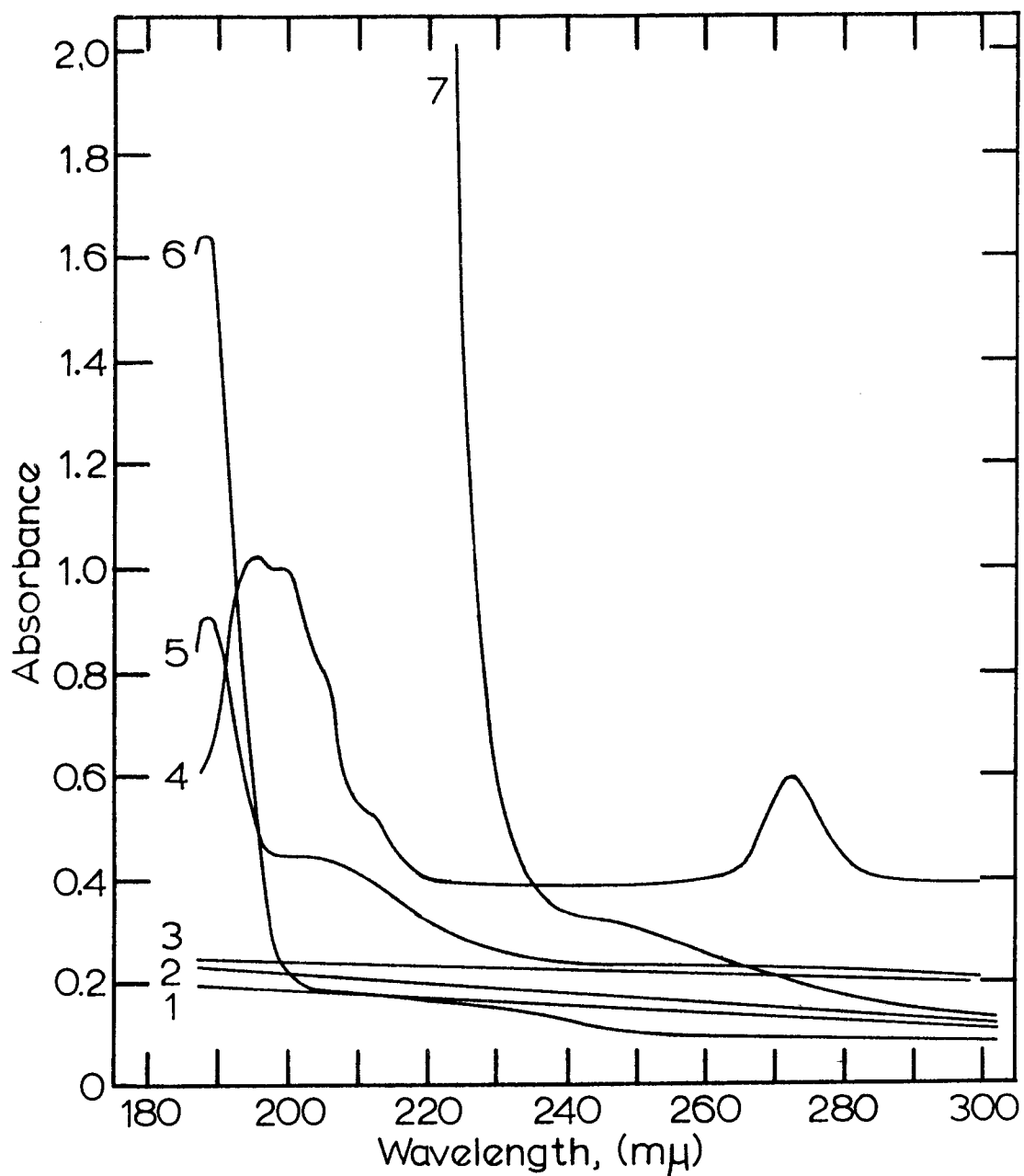


FIGURE 13. Spectra of various pure crystals. (1) Anderson. (2) Ion exchange. (3) Recrystallized. (4) Johnson-Matthey. (5) Vinor. (6) Harshaw. (7) Same as (5) with increased path length.

that the crystal grown from potassium chloride obtained from Anderson Chemical Co., the crystal grown from potassium chloride purified by ion exchange and the crystal grown from potassium chloride purified by recrystallization show no absorption bands in this region. The crystal grown from potassium chloride obtained from Johnson, Matthey & Co. shows a group of absorption bands in the region between 190 μ and 220 μ and a single band at 273 μ . The potassium chloride crystals obtained from Vinor Laboratories and from Harshaw Chemical Co. show absorption bands peaking at 188 μ and some broad absorption to the long wavelength side of the 188 μ bands. In Table 3 a listing of the absorption bands characteristic of some of the more common impurities is given for potassium chloride crystals. Comparing Figure 13 with Table 3 enables us to identify the peaks at 273 μ and 196 μ , in the Johnson-Matthey crystal, as due to Pb^{2+} impurities. There is also an indication of OH^- in this crystal and perhaps the Vinor crystal. The intense 188 μ peak has not been identified.

It was found that the Vinor crystal exhibited a strong luminescence, the maximum intensity of which occurred when excited with light of approximately 260 μ wavelength. The room temperature spectrum of this luminescence, measured with the Perkin-Elmer model 450 spectrophotometer using a spectro-photo-fluorometer attachment, is shown in Figure 14. It can be seen that the spectrum is

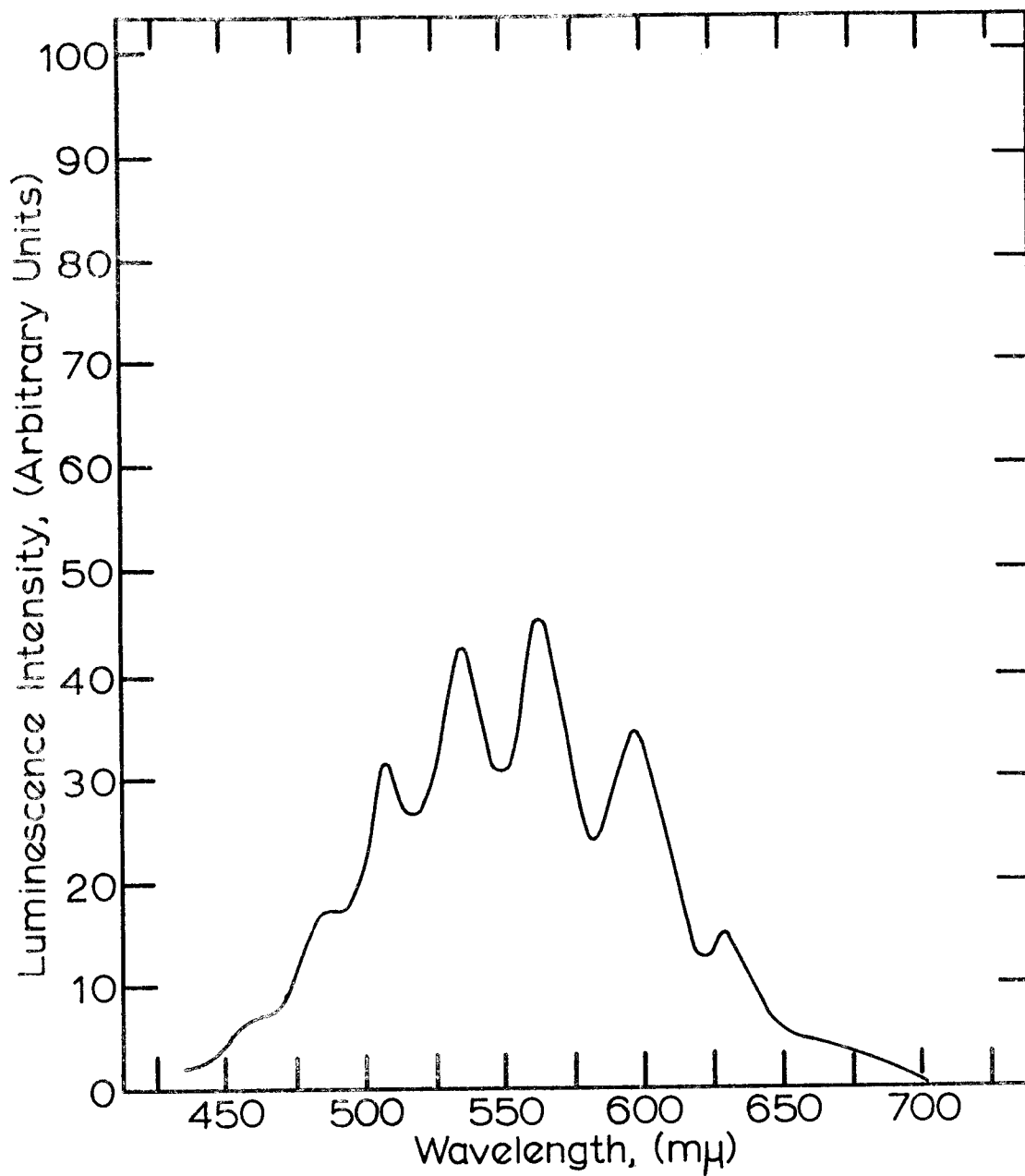


FIGURE 14. Luminescence spectra of Vinor crystal. The irradiation was at 260 mμ.

quite complicated, exhibiting seven peaks in the region between 450 $m\mu$ and 650 $m\mu$. It is somewhat surprising that such an intense emission is observed with 260 $m\mu$ excitation since the absorption, at this wavelength, is very weak. The emitting centers responsible for this luminescence undoubtedly involve oxygen since Ewles and Barmby (18) and Rolfe, Lipsitt and King (47) found similar spectra in potassium chloride crystals which contained this impurity. Ewles and Barmby suggested that the center was O_2^+ but later Rolfe, Lipsitt and King showed, by use of spin resonance, that it was actually O_2^- .

Table 3. U-V absorption spectra of impurities in potassium chloride.

Impurity	λ_1 , ($m\mu$)	Reference	λ_2 , ($m\mu$)	Reference
Ag ⁺	217.5	17	229	17
As ⁵⁺	280	3		
Bi ³⁺	340	35		
Cu ²⁺	265	54		
Ga ⁺	213	35	218	15
Ge ²⁺	215	18	275	15
In ⁺	230	65	385	65
Pb ²⁺	196	24	273	24
Sb ³⁺	250	2		
Sn ²⁺	226	26	232	25
Sn ⁴⁺	230	3	265	3
Tl ⁺	196	24	247.5	64
Tl ³⁺	250	3	280	3
Yb ³⁺	244	13	272	13
OH ⁻	204	16		

Interpretation. From the spectra alone one can only conclude that crystals grown from Anderson salt, crystals grown from ion exchange purified salt and crystals grown from salt purified by recrystallization are equally pure since none of these exhibits any absorption bands between 185 $m\mu$ and 300 $m\mu$. However a comparison of the ionic conductivities of these three crystals indicates that crystals grown from salt purified by ion exchange are considerably lower in total divalent cation concentration than are either of the other two. From these considerations one must conclude that the crystals grown from salt purified by ion exchange are indeed more pure than any of the other five studied. For this reason all of the experiments discussed in the following sections were conducted on crystals grown from potassium chloride purified by ion exchange.

III. DIFFUSION OF F-CENTERS IN POTASSIUM CHLORIDE CRYSTALS

Introduction

General

In this section we will discuss the problem of F-center diffusion. This subject is important to the present work for a knowledge of the diffusion mechanism would be helpful in explaining how conductivity occurs in colored crystals. Also knowing how F-centers migrate from point to point within the crystal would be useful in understanding how aggregate centers such as M, N and R as well as colloids are formed from F-centers.

Very little work has previously been done, aside from that of Mizuno, concerning the diffusion of F-centers. Mizuno and Miyamoto (38) measured the rate of diffusion of F-centers into potassium chloride during coloration and found that diffusion occurred along disordered interfaces much more rapidly than through the bulk of the crystal. No actual mechanism for diffusion was given by these authors however.

The problem of measuring the diffusion of F-centers is particularly difficult because their movement cannot be followed by radio-tracer methods as is usually done in work of this type. In the present work an entirely different technique was employed but before

discussing the experimental details we will take up the topic of diffusion in general.

Theory of Diffusion

Fick's Laws of Diffusion. We will not go into the details of deriving the diffusion equations since this has been done elsewhere (53, p. 1-6; 7, p. 1-8) but we will give the details directly.

When atoms of a particular species diffuse into a solid the flux, J , and the gradient of the concentration, n , of the diffusing atoms are usually found to be related through Fick's first law:

$$J = - D \text{ grad } n, \quad (3.1)$$

where D is called the diffusion coefficient and has the units of $\text{cm}^2 \text{ sec}^{-1}$ in cgs units. Frequently experiments are conducted so that the flux is measured in one direction only in which case Equation (3.1) becomes

$$J = - D \frac{\partial n}{\partial x}. \quad (3.2)$$

Equation (3.2) is most useful if a steady state exists but is valid even if this is not the case. If a steady state does not exist a second differential equation known as Fick's second law is more easily used. This equation is

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial n}{\partial x} \right). \quad (3.3)$$

Equation (3.3) was written for the general case. If D is constant it reduced to

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}. \quad (3.4)$$

Steady-State Solutions, with D Constant. For the steady-state case the concentration, n , does not change with time and Equation (3.4) becomes

$$D \frac{\partial^2 n}{\partial x^2} = 0 \quad (3.5)$$

or simply

$$\frac{\partial^2 n}{\partial x^2} = 0 \quad (3.6)$$

It is easily seen that

$$n = Ax + B \quad (3.7)$$

is a solution to Equation (3.6). A and B are constants and can be determined from the boundary conditions of the problem.

Nonsteady-State Solutions, with D Constant. The most general solution to Equation (3.4) is obtained by considering the diffusion of a substance i from a semi-infinite solid A into a semi-infinite solid B when A and B are in contact. The boundary conditions are

$$n_i = 0 \quad \text{for } x < 0, \quad \text{at } t = 0$$

$$n_i = n_i^0 \quad \text{for } x > 0, \quad \text{at } t = 0.$$

We have taken $x = 0$ to be the plane where A and B meet.

These boundary conditions lead to the solution

$$n_i(x, t) = \frac{1}{2} n_i' [1 + \operatorname{erf}(x / 2D^{\frac{1}{2}} t^{\frac{1}{2}})], \quad (3.8)$$

where erf means error function and is defined by the equation

$$\operatorname{erf}(z) = (2/\pi^{\frac{1}{2}}) \int_0^z \exp(-u^2) du. \quad (3.9)$$

The integral on the right has been solved numerically and tables of solutions exist in numerous references (53, p. 13).

The above solution dealt with a semi-infinite system. The simplest solution for a finite system, in which D is constant inside the boundaries and infinite outside, is obtained by assuming that there are solutions which are the product of a function, $T(t)$, of time and a function, $X(x)$, of distance. These solutions are discussed by Shewmon (53, p. 15-16), who shows that the most general types are an infinite series of the form

$$n(x, t) = \sum_{n=1}^{\infty} (A_n \sin C_n x + B_n \cos C_n x) \exp(-C_n^2 Dt), \quad (3.10)$$

where A_n , B_n and C_n are constants.

Diffusion with a Moving Boundary. The solutions given above do not apply to the case where two substances interdiffuse in such a manner that a distinct boundary exists between them. Crank (7, p. 99-120) has discussed this problem in detail and shows that in order for diffusion to occur in this manner the diffusion coefficient cannot be constant. The simplest case results when the diffusion coefficient changes discontinuously, at a particular concentration, from one constant value to a different constant value. Crank's treatment shows that the position, X , of the boundary at any time, t , is given by an expression of the form

$$X = C(t-t_0)^{\frac{1}{2}}, \quad (3.11)$$

where C is a constant and t_0 is the time when $X = 0$. The velocity of the boundary is obtained by differentiating Equation (3.11) with respect to time. The result is

$$v_b = \frac{1}{2}C(t-t_0)^{-\frac{1}{2}}. \quad (3.12)$$

Equation (3.12) shows that the migration velocity of the boundary is not constant but decreases as t increases.

The moving boundary problem has been introduced here because it is found that when F-centers diffuse out of a crystal a sharp boundary can be observed between a colorless region near the surfaces and a colored region in the interior of the crystal.

With this brief introduction we are now ready to discuss the experiments performed in the present work.

Experimental

Measurements of Diffusion Rate

It was found that when conductivity measurements were made on colored potassium chloride crystals, at constant temperatures greater than approximately 400°C , the current decreased slowly with time. This decrease was observed even if no field was applied between measurements. The rate of diffusion of F-centers was determined indirectly by observing the rate at which this decrease occurred. The decrease was obviously due to loss of F-centers from the crystals and thus was expected to be a measure of the rate at which they diffused out. The procedure used was as follows.

Crystals, which had been colored by a method to be described later, were prepared for conductivity in the same manner as the uncolored crystals discussed in Section II. Each crystal was individually placed in the conductivity cell, under an argon atmosphere, and heated to the desired constant temperature. The current was then periodically measured with the time of each measurement being recorded. An electric field was placed across the crystals only during the time when the measurements were being made. Weak fields of

approximately 0.5 volts per centimeter and short measurement times of approximately five seconds were used so as not to appreciably effect the migration of F-centers. After several measurements had been made the temperature was increased and the procedure repeated.

Optical Scanning

In order to study the manner in which the F-center concentration varied with distance from the crystal surfaces optical scanning procedures were utilized. The apparatus used was constructed by Holmes and its description is given in the discussion of his work (25, p. 57-62). The procedure followed was to hold the colored crystal at approximately 500°C for at least 30 minutes. This time was sufficient to form a colorless layer approximately 0.5 mm thick at the surfaces. A thin piece was then sliced from the center of the crystal so as to give a cross-sectional representation showing the colored and uncolored regions. This piece was mounted in the scanning apparatus and placed in the Beckman model DK-1 spectrophotometer, the wavelength being fixed at 556 m μ . The crystal was then slowly moved past the slit as the optical density was recorded.

Coloration Procedure

The crystals were all prepared by additive coloration using potassium metal. The samples were wrapped in aluminum foil to

prevent exposure to light and placed in a piece of pyrex tubing. The tubing had previously been necked down at about four inch intervals into four segments. The samples were placed in one end of the tubing and the potassium in the other. The open end, into which the potassium has been inserted, was closed and the other end connected to a vacuum pump. This assembly is sketched in Figure 15. The sample, G, is shown in chamber D and the potassium, F, in chamber A. After a vacuum of about 10^{-3} mm mercury pressure had been obtained, chamber A was heated with a torch until the potassium had distilled into chamber B. The tubing was then closed between chamber A and chamber B, the potassium distilled into C, the tubing closed between chambers B and C and chambers A and B removed. After sealing the tubing between chambers D and E, chambers C and D were removed. This would then leave chambers C and D, which contained the potassium and crystal respectively, sealed but connected by the small opening between them. This piece of tubing was then mounted vertically so that the lower chamber, containing the potassium, was inside one tube furnace and the upper chamber, containing the crystal, was inside a second tube furnace. This arrangement is shown in Figure 16. The furnaces, A and B, were Hoskins type FA120 electric furnaces and were controlled separately by EP ProportioNull 1300 series controllers. This arrangement allowed the temperature of the crystal, C, which determined the rate of

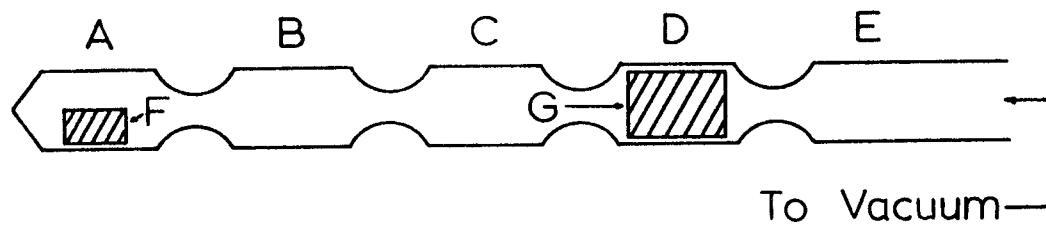


FIGURE 15. Diagram of assembly used in preparing crystals for coloration. (F) Potassium metal. (G) Crystal.

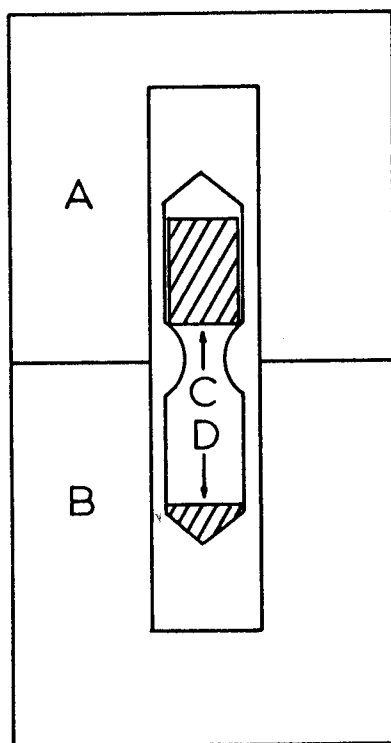


FIGURE 16. Diagram of furnace assembly used in coloration. (A) and (B) Furnaces. (C) Crystal. (D) Potassium metal.

coloration, and the temperature of the potassium, D, which determined the metal vapor pressure and hence the concentration of F-centers, to be chosen independently. This procedure was adopted to maintain the crystal at a much higher temperature than the potassium and thus color the crystals fairly rapidly. Even by this method it was found that at least four days were needed to color the crystals uniformly.

Determination of F-Center Concentrations

After a crystal was colored the concentration of F-centers was determined. To do this a thin piece, approximately 0.5 mm thick, was cleaved from the central portion of the crystal and its thickness measured with a micrometer. This piece was then wrapped in aluminum foil and placed in a furnace which had been preheated to about 300°C. The crystal was heated at this temperature for about five minutes after which it was rapidly removed from the furnace and placed between two brass bars which had been precooled in liquid nitrogen. This quenching procedure was found sufficient to remove all absorption bands other than the F-band. If the crystal was heated to temperatures greater than approximately 500°C a sufficient number of F-centers were lost at the surfaces to cause erroneous results in the calculations.

After the crystal had been quenched it was placed in a Beckman

model DK-1 spectrophotometer being careful to expose the crystal only to light passed through a red filter. The absorption spectrum was measured and the absorbance determined at 556 m μ . The F-center concentration was then calculated from Equation (1.5) using the measured absorbance and the crystal thickness.

Results and Discussion

Results of Diffusion Rate Measurements

It was found that the rate at which the current decreased, at various constant temperatures, was greatly affected by how high the temperature actually was. Below approximately 400°C the rate was too slow to be accurately measured. Above 400°C the rate increased rapidly with temperature until approximately 500°C. Above this temperature the current was nearly constant. This last effect was undoubtedly due to the intrinsic ionic conductivity becoming larger than the conductivity due to the F-centers. This effect will be discussed in Section IV.

It was found that when the ratio of the current i , measured at time t , to the current i_0 , measured at time t_0 , was plotted vs. $t - t_0$ the resulting curves were linear. Thus current and time are related by the equation

$$i/i_0 = 1 - c(t-t_0) \quad (3.13)$$

where c is a constant. A plot showing this behavior is given in Figure 17. The plot is given for a crystal containing 3.4×10^{16} F-centers per cm^3 . The different curves are for different temperatures as are indicated in the figure. The slopes of the various curves are equal to c in Equation (3.13) which is seen to increase with increasing temperature.

In Figure 18 we show the result of plotting $\log_{10} c$ vs. $1000/T$ for several different crystals of various thickness and F-center concentrations. It is interesting to note that the points all fall on the same linear curve for $1000/T < 1.4$. For $1000/T > 1.4$ the points from two of the crystals fall on this same curve, however the points for the remaining three crystals fall above this curve. The reason for the differences in behavior can be traced to the treatment prior to making measurements. The two crystals that exhibit linear behavior over the entire range were heated at approximately 500°C for five minutes before measurements were made. This heating had the effect of diffusing some of the F-centers near the surfaces out of the crystals. The remaining three crystals were placed directly in the conductivity cell without any preheating. These three crystals then initially lost F-centers at a faster rate than the two preheated crystals and therefore have larger values of c . After the F-centers very near the surfaces had been lost the rate of decrease in current became equal for all of the crystals. This point corresponds to

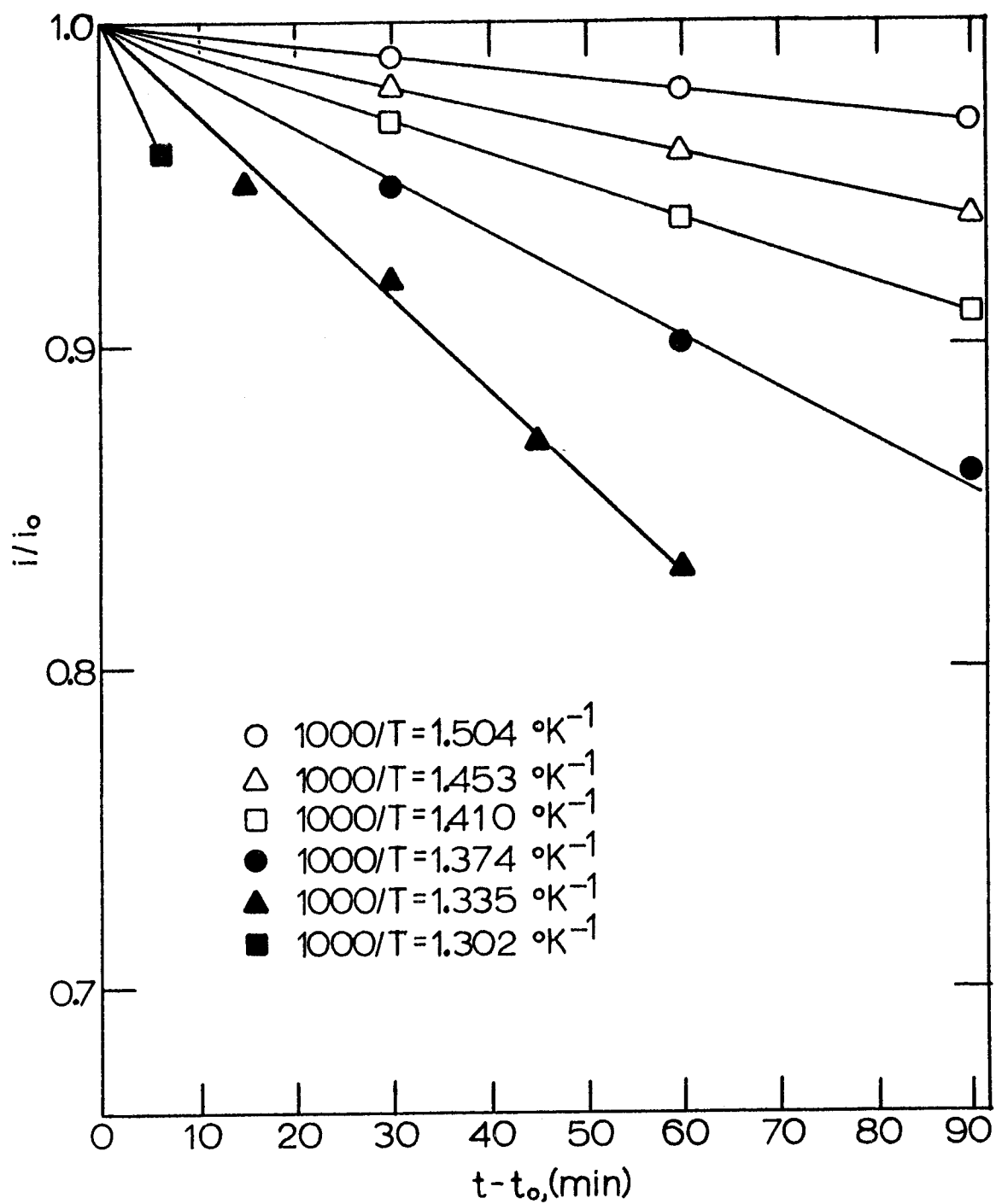


FIGURE 17. Plot showing the decrease in current with time. The electric field was not applied between measurements.

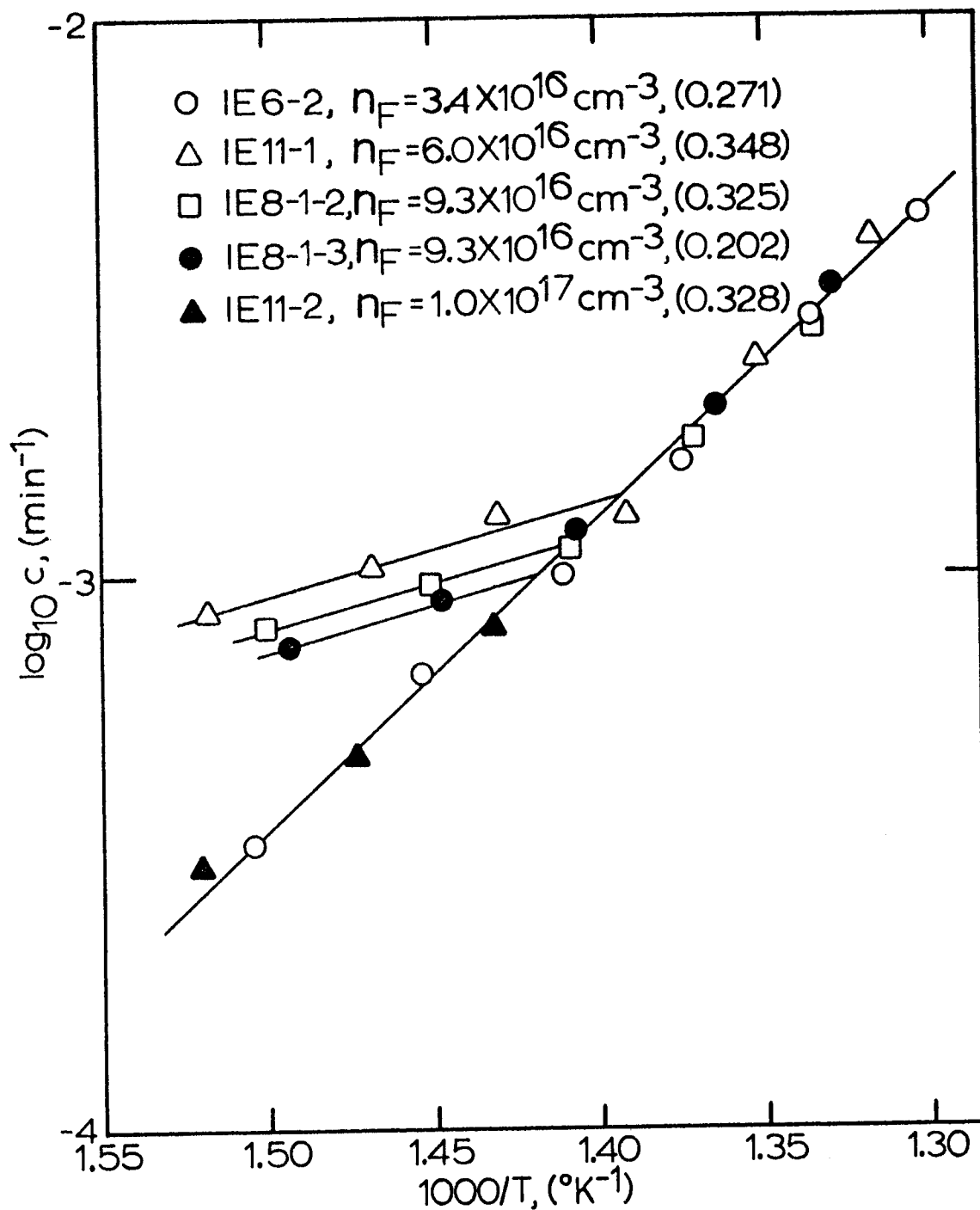


FIGURE 18. Plot showing the dependence of the rate constant, c , on temperature. The crystal thickness, in centimeters, is shown in parentheses.

$1000/T = 1.4$ in Figure 18. A quantitative discussion of this behavior will be taken up later in this section.

The linear behavior for the two preheated crystals, at all temperatures considered, and for all of the crystals at high temperatures indicates that the constant, c , in Equation (3.13), is related to temperature by the equation

$$c = c_0 \exp (-E/kT), \quad (3.14)$$

where c_0 is a constant and E is an activation energy. E is found from the slope of the curve to be equal to 1.12 eV and c_0 is found from the intercept to be equal to $1.7 \times 10^3 \text{ sec}^{-1}$.

Results of Optical Scanning

The results of scanning the boundary between the colored and uncolored regions of a crystal are shown in Figure 19. In this figure the origin is taken at the center of the crystal. The spikes appearing on each side are caused from scattering at the edges of the crystal. As it appears here, Figure 19 does not give a true description of the F-center concentration as a function of distance in the crystal. The error results from using a slit of finite width to study the concentration gradient. A discussion of the corrections for broadening observed when using narrow slits is given by Jones (30). When these corrections and corrections for scattering are applied to the curve in

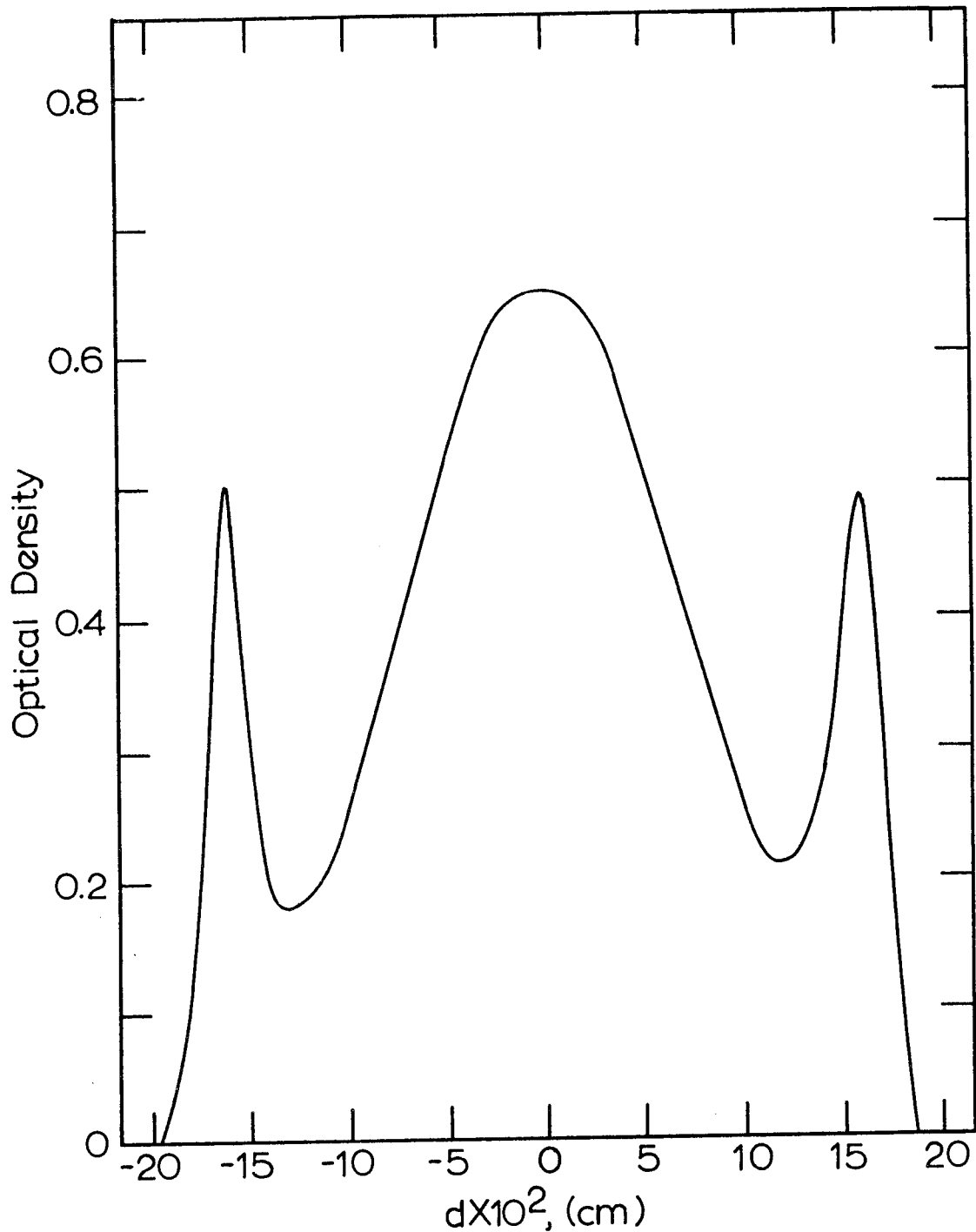


FIGURE 19. Plot of optical density at $556 \text{ m}\mu$ vs. distance from crystal center: The crystal had been heated to allow loss of F-centers at the surfaces. The spikes on each side are due to the crystal edges.

Figure 19 the curve shown in Figure 20 results. The vertical dashed lines show the edges of the crystal. From the curve we see that on each side of the crystal there is a region approximately 0.05 cm thick in which the optical density, and consequently the F-center concentration, is very low. Between this region and the center of the crystal there is a region approximately 0.07 cm thick over which the F-center concentration increases rapidly. In the central region the F-center concentration is constant. The region where the concentration increases rapidly then constitutes the boundary between a nearly colorless region and a highly colored region. It is found that this boundary moves into the crystal as the F-centers are lost from the surfaces. This then corresponds to a moving boundary problem and must be considered as such in any complete treatment.

Interpretation

To give an exact solution to the problem is exceedingly difficult and demands more information than is presently available. We pointed out above that any complete treatment would require the considerations of a moving boundary between the colored and colorless regions. A simple moving boundary treatment does not lead to satisfactory results however since Equation (3.13) cannot result unless the boundary moves with a constant velocity while Equation (3.12) shows that the velocity is not constant but decreases with time. It

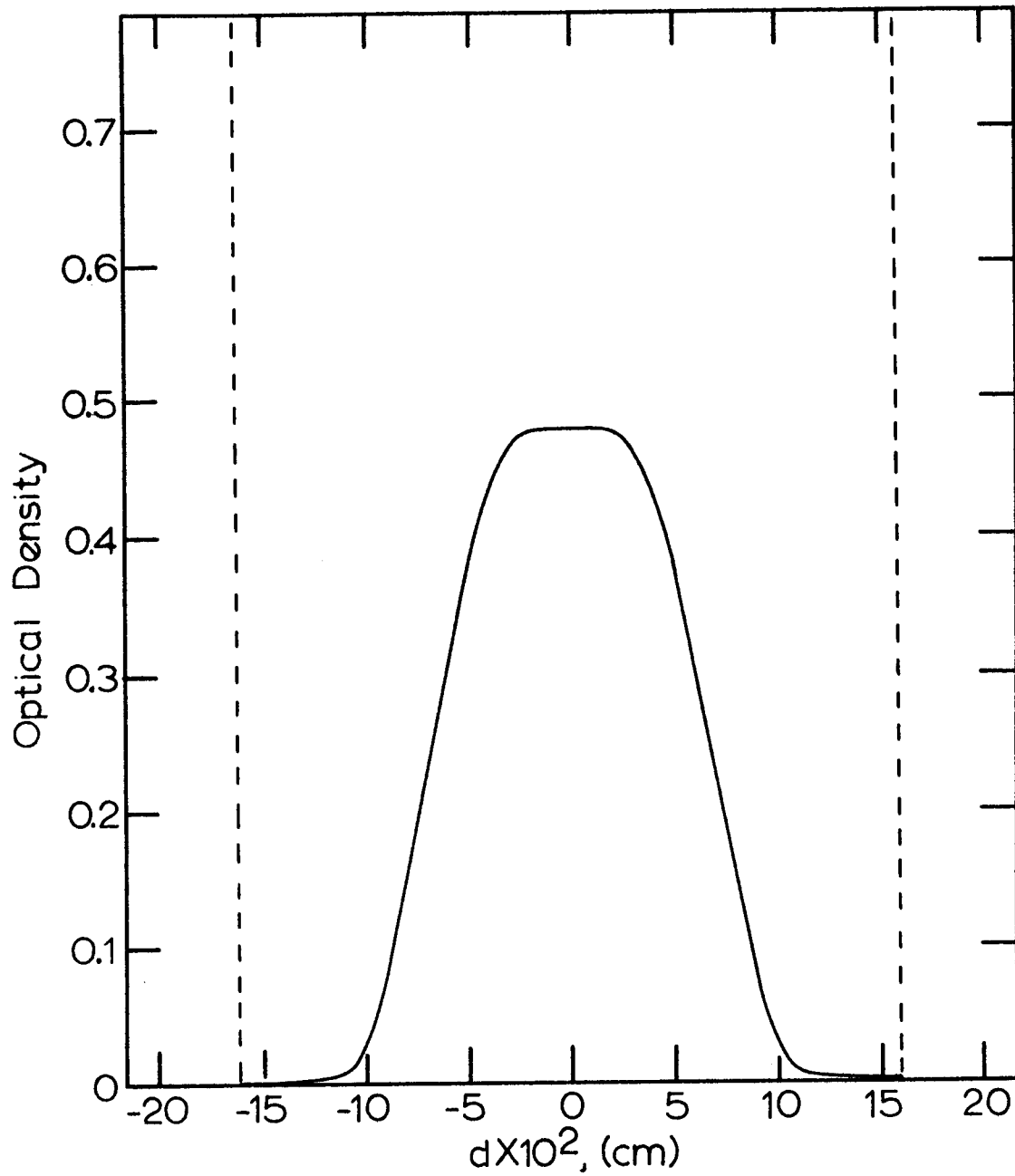


FIGURE 20. Plot of the curve in Fig. 19 after correcting for scattering and broadening due to finite slit width. The dashed lines indicate the edges of the crystal.

also should be mentioned that diffusion profiles such as those shown in Figures 19 and 20 cannot be obtained for a system in which a substance is diffusing with a single constant diffusion coefficient. This indicates that Equations (3.8) and (3.10) are not satisfactory solutions for the present case.

It seems reasonable to suppose that c in Equation (3.13) is proportional to the diffusion coefficient for F-center migration since the decrease in current is obviously due to loss of F-centers from the crystal. We can obtain an approximate, but certainly not exact, solution, which shows this proportionality, by assuming that D is constant. The solution we desire is then obtained from Equation (3.10) by applying the boundary conditions

$$\begin{aligned} n_F &= n'_F & \text{for } 0 < x < d & \text{ at } t = 0 \\ n_F &= 0 & \text{for } x = d \text{ and } x = 0 & \text{ at } t > 0. \end{aligned}$$

Here d is the thickness of the crystal, which is considered to be in the form of a thin slab. The average concentration, \bar{n}_F , is given by Shewmon (53, p. 16-19) to be

$$\bar{n}_F = (8n'_F / \pi^2) \sum_{j=0}^{\infty} (2j+1)^{-2} \exp \{ -[(2j+1)\pi/d]^2 Dt \}. \quad (3.15)$$

For $\bar{n}_F \leq 0.8n'_F$ the first term in the series is an excellent

approximation to the solution. In this case we have

$$\bar{n}_F = (n'_F 8/\pi^2) \exp - (\pi^2 D t / d^2). \quad (3.16)$$

In Section IV it will be shown that the conductivity, and consequently the current, is proportional to the square root of the F-center concentration. Thus we can write, at constant applied voltage,

$$i/i_0 = \bar{n}_F^{1/2} / \bar{n}_0^{1/2}, \quad (3.17)$$

where \bar{n}_0 is the average F-center concentration when the current is i_0 . Using the averages given by Equation (3.16) in Equation (3.17) gives

$$i/i_0 = \exp[-(\pi^2 D / 2d^2)(t-t_0)], \quad (3.18)$$

where we have taken t_0 to be the time when the concentration was \bar{n}_0 . For times short enough so that $\pi^2 D(t-t_0)/2d^2 \ll 1$ we can expand Equation (3.18), keeping only the first two terms, and obtain

$$i/i_0 = 1 - (\pi^2 D / 2d^2)(t-t_0). \quad (3.19)$$

Comparing Equations (3.13) and (3.19) we see, by this approach, that c and D are proportional and are related by the expression

$$c = \pi^2 D / 2d^2. \quad (3.20)$$

In using Equation (3.16) instead of Equation (3.15) we assumed $n_F \leq 0.8 n'_F$. This is true if sufficient time has elapsed; however, for the three crystals exhibiting the anomalously high values for c this was not the case. For the two crystals which had been preheated the approximation was valid.

If we write

$$D = D_o \exp (-E/kT) \quad (3.21)$$

we have, according to Equation (3.20),

$$D_o = (2d^2/\pi^2)c_o. \quad (3.22)$$

Using $d = 0.2 \text{ cm}$ and the experimental value of $1.7 \times 10^3 \text{ sec}^{-1}$ for c_o gives $D_o = 14 \text{ cm}^2 \text{ sec}^{-1}$. From this value and Equation (3.21), with $E = 1.12 \text{ ev}$, we obtain

$$D = 14 \times 10^{-(5650/T)}, \text{ cm}^2 \text{ sec}^{-1}. \quad (3.23)$$

From this equation we estimate D , at 500°C , to be $7 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$.

We mentioned earlier that diffusion with a moving boundary, as is observed in colored crystals, cannot occur if the diffusion coefficient is constant. To obtain diffusion profiles, such as those shown in Figures 19 and 20, the diffusion coefficient must be much larger in the region near the surfaces, where the concentration gradient is low,

than in the interior, where the concentration gradient is large. Thus it is obvious that the above calculation of D is at best a crude approximation.

In order to describe the diffusion process we must consider three possible mechanisms. One is the migration of the electron while the center is thermally ionized. The second is the exchange of positions of a halide ion and an F-center electron. The third is that shown in Figure 21. In order for an F-center to migrate, by this mechanism, it must first be in contact with a negative ion vacancy.

The first of these mechanisms offers a possible explanation of why calcium-doped crystals color more rapidly than pure crystals. As electrons flow into the crystal, becoming trapped at negative ion vacancies, the interior of the crystal becomes negatively charged and the surface becomes positively charged. This soon establishes a potential barrier over which further migration of electrons cannot occur. In order for coloration to continue positive charge must flow into the crystal or negative charge must flow out. Thus, by this mechanism, the rate of coloration would depend on the ionic conductivity of the material. The calcium-doped crystals, being more conductive, would color more rapidly than pure crystals.

The second mechanism should not be affected by changes in either the positive or negative ion vacancy concentrations. For that reason it will not be considered important at the temperatures of the

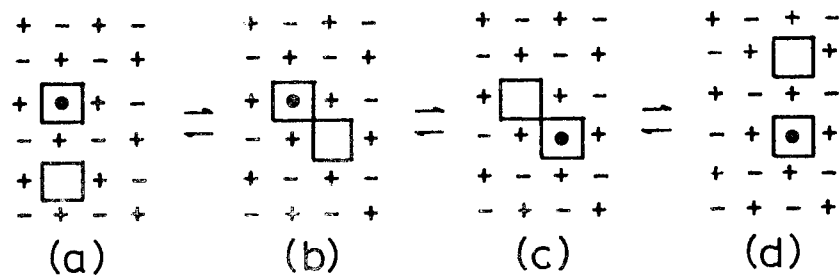


FIGURE 21. Proposed mechanism for diffusion of F-centers. (a) A portion of the crystal containing separated F-center and negative ion vacancy. (b) The vacancy has moved into a position adjacent to the F-center. (c) The F-center electron is momentarily localized in the adjacent vacancy. (d) The remaining vacancy has moved away leaving the F-center advanced one lattice plane from its original position.

experiments.

Examining Figure 21 we see that, by the mechanism shown there, the diffusion of F-centers depends on the concentration of negative ion vacancies. Thus we would not expect aggregate centers to be formed readily at low temperatures unless the crystals contained divalent anionic impurities which would require compensating negative ion vacancies. Crystals grown in air are known to contain oxide and hydroxide (which is converted to oxide on coloration). This could explain why colloid centers are formed readily in Harshaw crystals while it has been found impossible to form them in ion exchange purified potassium chloride crystals grown under an HCl atmosphere. The presence of high concentrations of negative ion vacancies, due to oxide impurities, could also be responsible for the anomalous behavior, at low temperatures, in the diffusion coefficient for chloride ions into Harshaw potassium chloride, determined by Fuller (20).

Similarly this explains why crystals that contain divalent cation impurities do not form colloids while pure crystals do. The divalent cations require compensating positive ion vacancies which in turn suppress the anion vacancy concentration through the Schottky product rule, Equation (2.7). This suppression of the anion vacancies causes a corresponding suppression of the diffusion coefficient for F-centers and hence they are unable to migrate together to form higher aggregates. If this mechanism is correct, however, we should observe a

decreased coloration rate in calcium-doped crystals rather than an increased rate. It can also be shown that the magnitude of the diffusion coefficient, estimated for the mechanism shown in Figure 21, is not nearly as large as the experimental value estimated from Equation (3.23). The discrepancy is much too great to be attributed to experimental error.

In view of these last considerations the mechanism just considered obviously cannot be responsible for the observed rate of diffusion.

Elimination of the second and third mechanisms requires that we consider the first mechanism further. A problem also exists here in that the activation energy, E , in Equation (3.21), does not agree with the expected value. We mentioned above that the rate of coloration should depend on the ionic conductivity of the crystal. Thus E should be the same as the activation energy for ionic conduction. In the region where the diffusion was measured this activation energy was approximately 1.9 eV which is considerably larger than the value of 1.12 eV found for E .

From the foregoing discussion it is apparent that certain problems still exist concerning each of the possible mechanisms and that, on the basis of the present experiments, a choice between them cannot be made.

IV. CONDUCTIVITY OF PURE POTASSIUM CHLORIDE CRYSTALS CONTAINING F-CENTERS

Introduction

In Section I the reader was introduced to some of the problems which have arisen concerning the conductivity of crystals containing F-centers. In this section an attempt has been made, through special types of experiments, to answer certain questions related to those problems. The questions considered here can be summarized as:

- (1) Do the charge carriers originate from F-centers or colloids?
- (2) Are the carriers electrons or ions?
- (3) What is the mechanism for conduction?
- (4) Can the thermal ionization energy of the F-center be determined from conductivity measurements and if so what is its value?
- (5) Why is it that some authors report a decrease in the conductivity after coloring while others report an increase?

The experimental techniques used to find the answers to these questions involve conductivity and transport number measurements on colored crystals and are discussed in the following paragraphs.

Experimental

Conductivity Measurements

Crystals containing from 1.3×10^{16} F-centers cm^{-3} to

2.5×10^{17} F-centers cm^{-3} were used. The crystals were grown from potassium chloride purified by ion exchange. The coloration procedure and method of determining the F-center concentration was discussed in Section III. The procedure followed in making conductivity measurements was the same as discussed in Section II with the exception that three different methods were employed for treating the crystals prior to measurements. The first method was the same as with the uncolored crystals, i. e., gold contacts were evaporated onto freshly cleaved samples, after which their conductivities were measured. The second method was also to evaporate gold contacts onto freshly cleaved samples, but before measuring their conductivities the samples were held for five minutes at approximately 500°C . After the crystals had been cooled to room temperature conductivity measurements were then made. In the third method the surfaces of the crystals were sanded with size 0 polishing paper before the gold contacts were applied.

Transport Measurements

An experiment was designed and conducted in such a manner that the F-center transport number could be determined. The procedure was to sandwich a colored crystal between two uncolored crystals and place all three in a conductivity cell in the usual manner. The cell was then heated to the desired temperature and a potential

applied across the crystals. After a measured length of time the cell was cooled to room temperature and the distance that the boundary had moved determined by cleaving the clear region from the colored crystal, at several different places. The thickness of each piece was measured with a micrometer and the average calculated.

The assembly is shown in Figure 22 where B is the colored crystal and A and C are the uncolored crystals. d is the distance that the boundary moved and F and D are the electrodes. The guard ring, E, served to keep all points on the upper surface at nearly the same potential and thus helped maintain a uniform electric field within the crystals.

Results and Discussion

Results When Contacts are Applied to Freshly Cleaved Samples

In Figure 23 $\log_{10}\sigma$ has been plotted vs. $1000/T$ for four crystals containing different concentrations of F-centers and compared with an uncolored crystal. The results of this plot are in qualitative agreement with the findings of Jain and Sootha (28) and of Shamovskii, Dunina and Gosteva (52) but do not agree with those of Maycock (36) who found the conductivity of colored crystals to be less than for uncolored crystals.

At lower temperatures the conductivity plot is linear with a

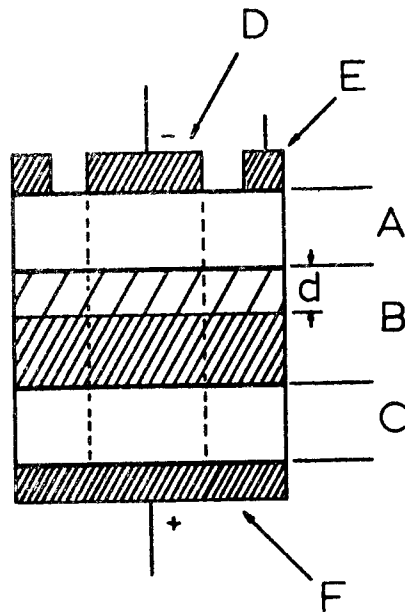


FIGURE 22. (A) and (C) Uncolored crystals. (B) Colored crystal. (d is the distance the colored region moved during the experiment). (D) Electrode. (Area=0.495 cm²). (E) Guard ring. (F) Electrode. The colored region did not cross the boundary into crystal C.

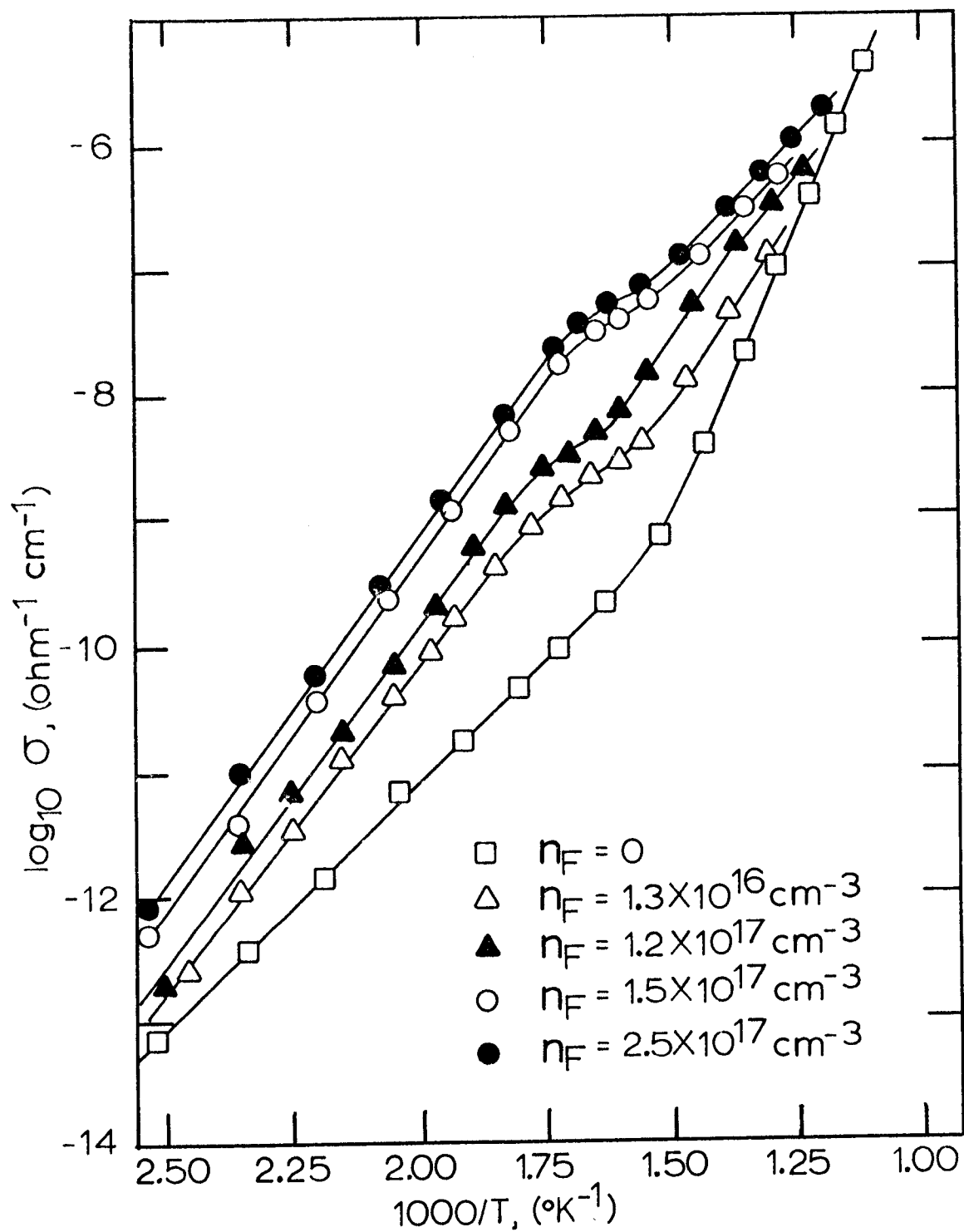


FIGURE 23. Effect of additive coloration on conductivity.

slope corresponding to an activation energy of 1.13 ev. At temperatures corresponding to $1000/T \approx 1.75$ the conductivity begins to increase more slowly until $1000/T \approx 1.6$. At this point the conductivity begins to increase rapidly. In the present work it was found that the low temperature conductivity, below this nonlinear region, was not very reproducible but varied considerably between two samples of the same crystal. The high temperature conductivity, above the nonlinear region, was found to be quite reproducible however.

The region between $1000/T \approx 1.75$ and $1000/T \approx 1.6$ appears as a shoulder on the conductivity plot. Shamovskii, Dunina and Gosteva observed this same type of shoulder on their conductivity plots but terminated their experiments before it was possible to ascertain whether the conductivity would again increase rapidly at higher temperatures. These authors interpreted the shoulder as being due to loss of F-centers from the crystal. This would cause the conductivity to decrease to that characteristic of an uncolored crystal as the F-centers were lost. However if this were the case in the present experiments the rapid increase in the conductivity at higher temperatures should not be observed.

Results When Crystals are Heated and Quenched Before Measurements

When gold contacts were evaporated onto freshly cleaved samples and then the sample heated at approximately 500°C for five

minutes, after which they were quenched to room temperature, their behavior was changed remarkably. After this treatment plots of $\log_{10}\sigma$ vs. $1000/T$ were almost linear over the entire range of measurements with the conductivity at high temperatures the same as the high temperature conductivity characteristic of crystals which had not been heated and quenched. This behavior is shown in Figure 24 where $\log_{10}\sigma$ is plotted vs. $1000/T$ for two crystals containing different concentrations of F-centers. Also shown for comparison is an uncolored crystal. Some departure from linearity at high temperatures was observed if thin crystals were used. This was avoided by using crystals of approximately two mm thickness. Presumably the reason for the nonlinearity was that F-centers were diffusing out of the crystals, i. e., the reason proposed by Shamovskii, Dunina and Gosteva for the shoulder in their conductivity plots. If thick crystals were used the relative loss was much less than if thin crystals were used and hence the relative decrease in the conductivity was much less for thick crystals than for thin crystals.

Results When Surfaces are Sanded Before Applying Contacts

It was found that sanding the crystal surfaces with size 0 polishing paper, before evaporating on the gold contacts, had, in nearly every case, the identical effect as the heating and quenching treatment. Again the low temperature conductivity was decreased to an

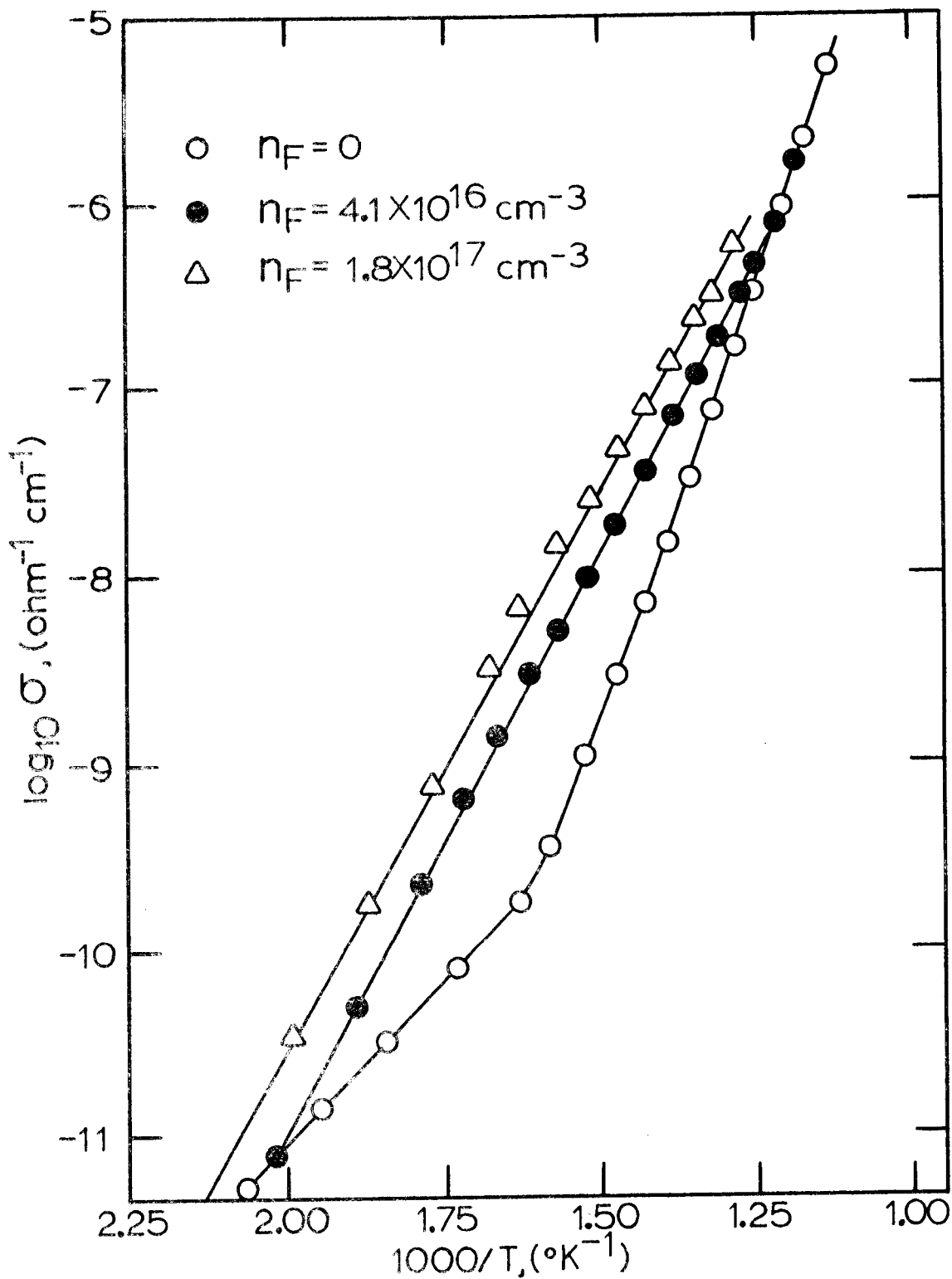


FIGURE 24. Conductivity plot of colored crystals after having been heat-treated.

extension of the high temperature conductivity exhibited by freshly cleaved crystals. It was also found the Ohm's law was accurately obeyed for the sanded or heated crystals whereas a slight departure was observed for the freshly cleaved samples. This behavior is shown in Fig. 25 where we have plotted the current vs. voltage for a freshly cleaved crystal and for a sanded crystal.

Dependence of Conductivity on F-Center Concentration

In addition to the above it was found that the conductivity of the sanded or heated crystals or the high temperature conductivity of the freshly cleaved crystals was highly reproducible. This allowed the dependence of the conductivity of F-center concentration to be determined. The dependence is shown in Fig. 26 where we have plotted the conductivities at $1000/T = 1.5$, for several different crystals containing different concentrations of F-centers, vs. the square root of the F-center concentration. It is easily seen that the points fall on a straight line through the origin indicating that the conductivity is proportional to the square root of the F-center concentration.

Results of Transport Measurements

The data taken during the measurement, for a crystal containing 9.5×10^{16} F-centers cm^{-3} , are listed in Table 4. The current was permitted to flow for one hour, after which the average was

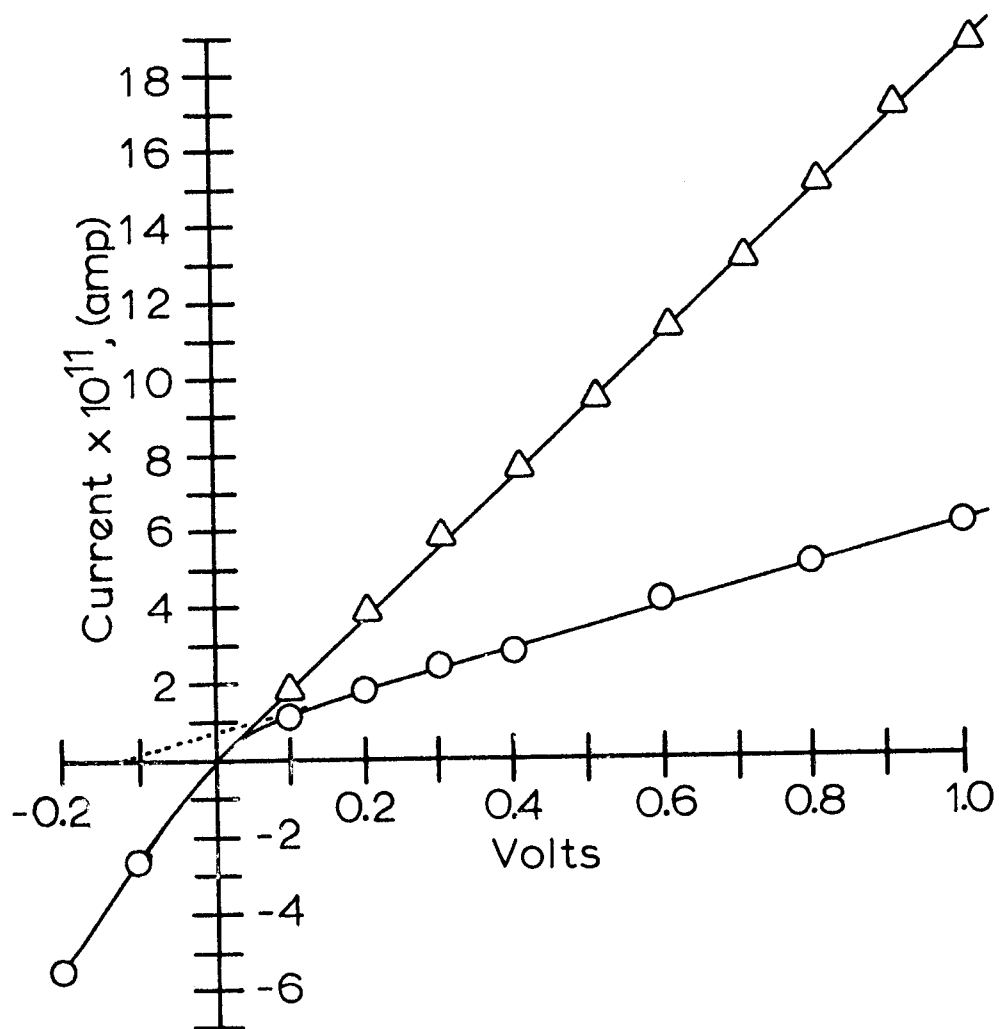


FIGURE 25. Plot showing the effect of sanding the crystal surfaces before applying contacts. (Δ , sanded; \circ , freshly cleaved).

calculated to be 1.95×10^{-7} amp. This amounted to a total charge of 7.0×10^{-4} coulombs. The F-center transport number was calculated from the relation

$$t_F = Q_F / Q_t, \quad (4.1)$$

where Q_F is the charge transported by the F-centers and Q_t is the total charge transported. Q_F was calculated from the expression

$$Q_F = eAdn_F, \quad (4.2)$$

where e is the electronic charge, A is the area of the measuring electrode, n_F is the concentration of F-centers and d is the average distance which the F-center cloud had moved during the experiment.²

To calculate t_F we take $e = 1.6 \times 10^{-4}$ coulomb, $A = 0.495 \text{ cm}^2$, $n_F = 9.5 \times 10^{16} \text{ cm}^{-3}$, $d = 0.089 \text{ cm}$ and $Q_t = 7.0 \times 10^{-4}$ coulomb. Using these values in Equations (4.1) and (4.2) gives $t_F = 0.96$. This value is sufficiently near unity to rule out any mechanism for conduction which does not involve F-centers directly.

²Loss of F-centers from the crystal due to diffusion to the surfaces would cause d to be larger than if no diffusion occurred. For the time and temperature involved this effect was less than the experimental error in determining d and caused no additional problem.

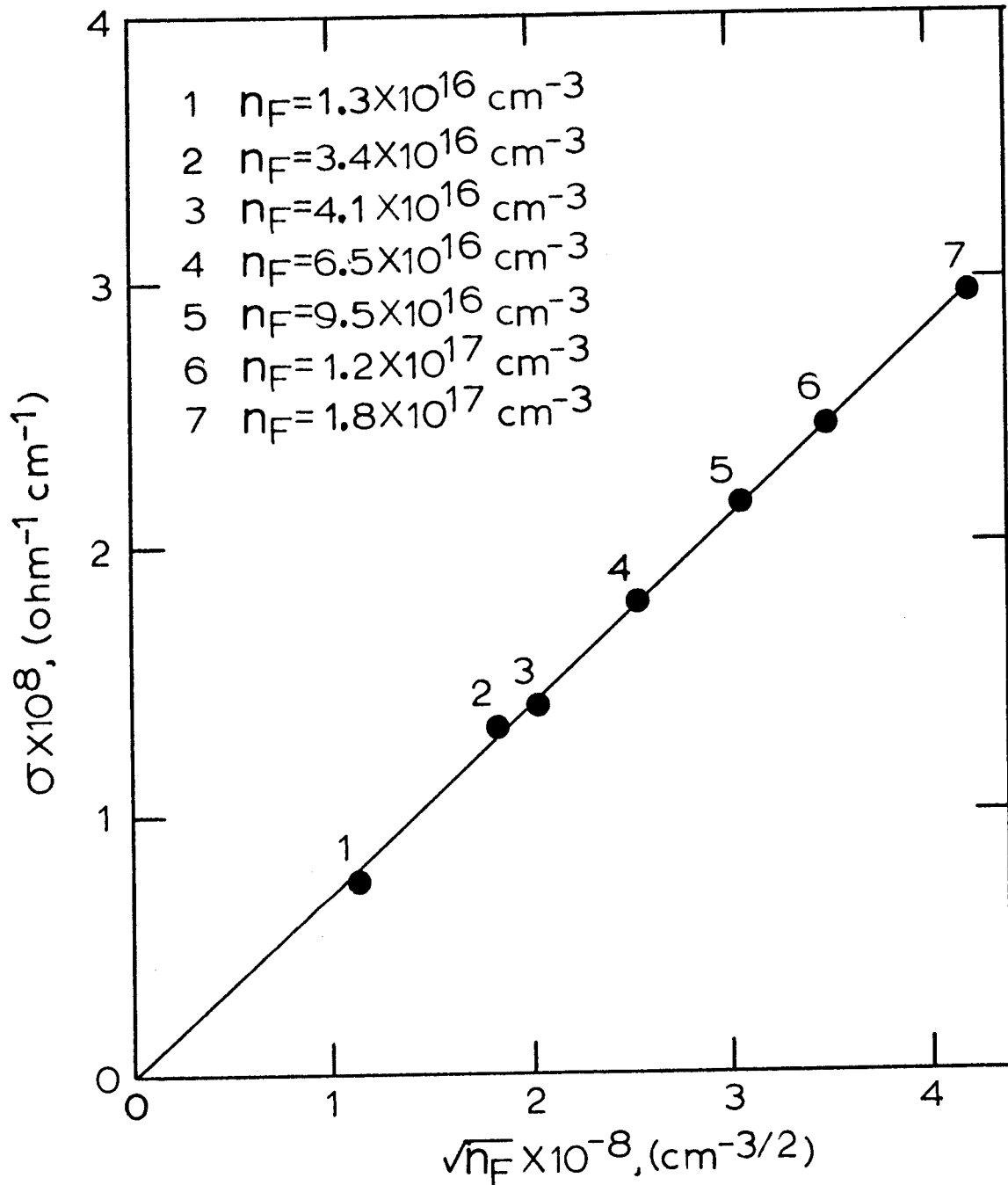


FIGURE 26. Dependence of conductivity on F-center concentration. ($1000/T = 1.5 \text{ }^\circ\text{K}^{-1}$).

Table 4. Current observed when 100 volts were applied during transport measurement.

Time, (min)	Temperature, (°C)	Current $\times 10^7$, (amp)
0	399	2.09
5		2.03
10		2.00
15		1.98
20		1.95
25	400	1.97
30		1.95
35		1.95
40		1.94
45		1.93
50		1.93
55	400	1.95
60		1.92
Average ¹		1.95

¹Corrected for electrometer drift of $+0.04 \times 10^{-7}$ amp hour⁻¹.

Interpretation

As a means of comparing the conductivities of colored crystals, σ_c , with the conductivities of uncolored crystals, σ_n , Jain and Sootha plotted the ratios, σ_c/σ_n , of these crystals vs. temperature. A similar plot from freshly cleaved crystals used in the present work is shown in Figure 27 for two crystals containing different concentrations of F-centers. Curve 1 in the figure is for a crystal containing 6.5×10^{16} F-centers per cm^3 and curve 2 is for a crystal containing 2.2×10^{16} F-centers per cm^3 . These curves are very similar to those obtained by Jain and Sootha except that the maximum values of the ratios is considerably greater in the present work. This

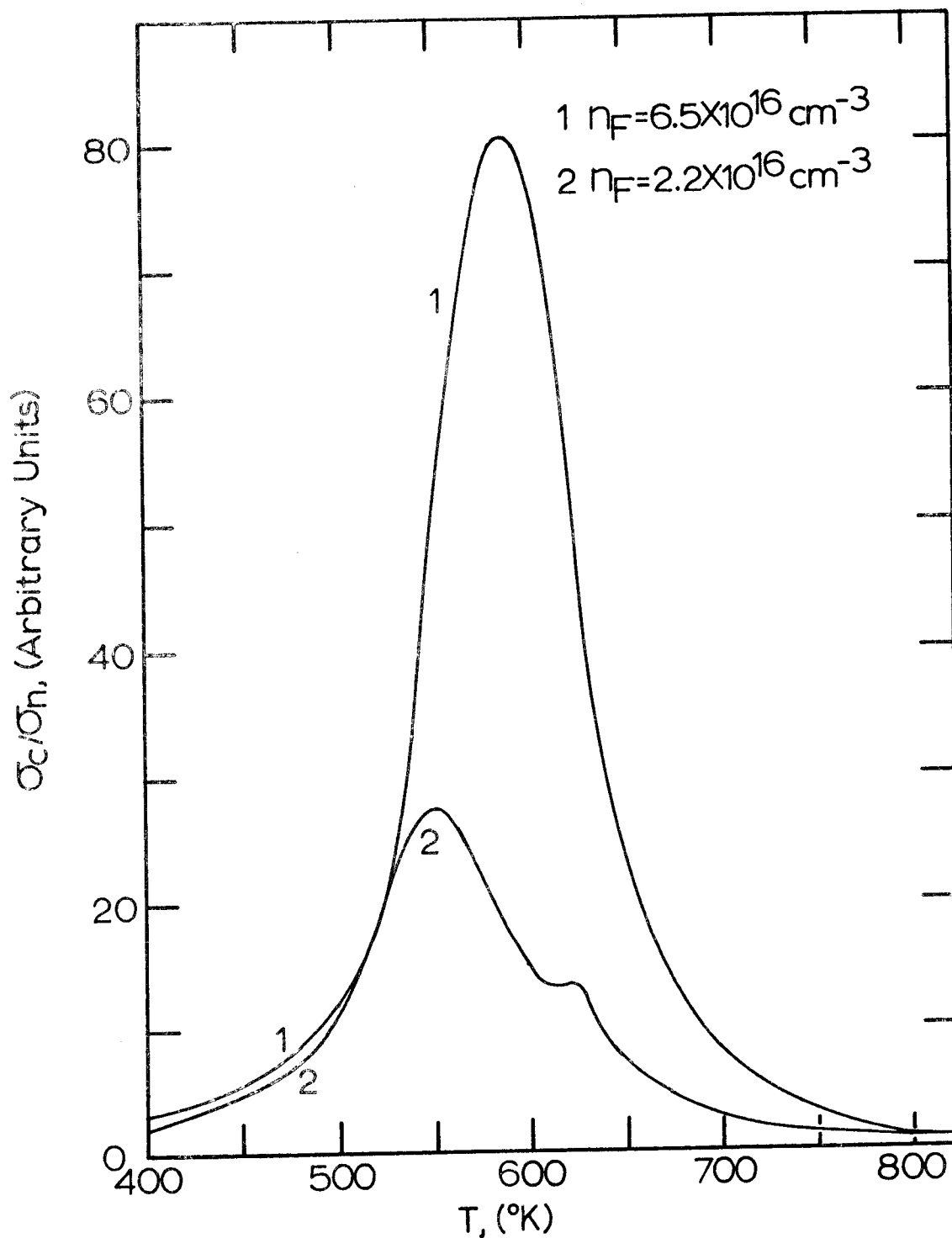


FIGURE 27. Plot of σ_c/σ_n vs. absolute temperature for two crystals containing different F-center concentrations.

is undoubtedly due to the greater purity, and hence lower extrinsic conductivity, σ_n , for the crystals used in the present experiments.

In Figure 27 a second peak in curve 2 is observed at $T \approx 620^\circ\text{K}$. This effect was not reported by Jain and Sootha.

Jain and Sootha also found that if $\log_{10} n_F$ was plotted vs. $1000/T'$, where T' is the temperature for which σ_c/σ_n is a maximum, a straight line was obtained. A plot showing these values taken from the curves in Figure 27 together with the values obtained by Jain and Sootha is shown in Figure 28. The fact that the points taken from Figure 27 fall on the same line with the points given by Jain and Sootha indicates that the increased conductivity of the colored crystals is from the same origin in both cases. Jain and Sootha believed the origin of this increased conductivity to be colloidal metal particles. They found that when the crystals they used were heated slowly, as was the case during conductivity measurements, colloids were readily formed. The increased conductivity was thought due to thermionic emission of electrons from these colloids rather than being directly from F-centers. Using this assumption these authors calculated the energy of formation of an F-center from colloidal metal to be 0.8 ev in potassium chloride. There are several discrepancies in this theory however which indicate their interpretation is not correct.

Scott, Smith and Thompson (49) studied the formation of

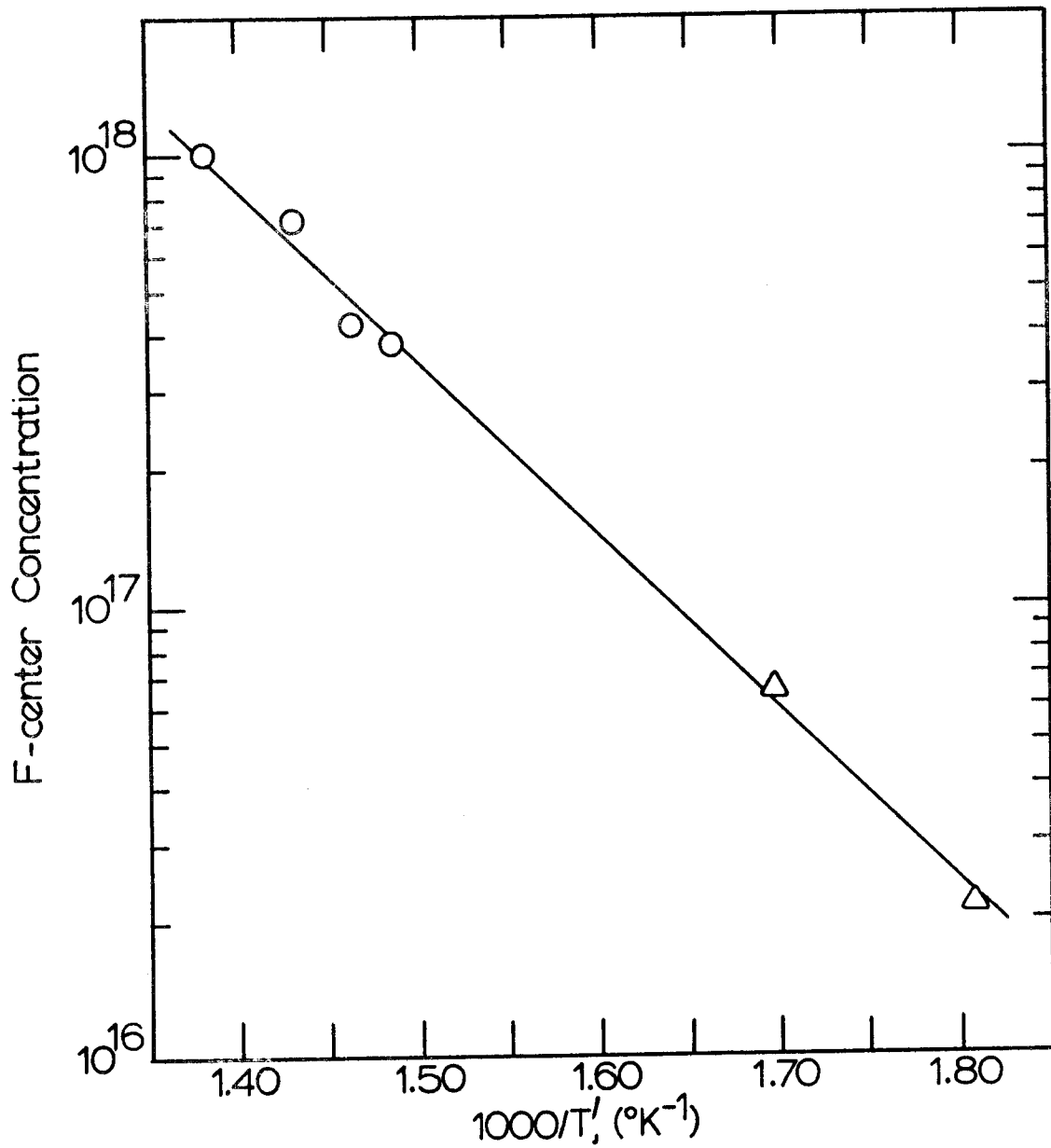


FIGURE 28. Plot showing the dependence of the peak position on F-center concentration. The circles are from Jain and Sootha while the triangles are from the present work. T' is the temperature for which σ_c/σ_n is a maximum.

colloids from F-centers. They found that the energy of formation of an F-center from colloidal particles to be 0.35 ev in potassium chloride. These authors also found that a heterogeneous equilibrium existed between the colloids and F-centers and that the equilibrium concentration of F-centers was independent of the initial concentration provided there were a sufficient number initially present to form the colloids. In Fig. 29 a plot of the equilibrium concentration of F-centers vs. $1000/T$ is shown, as taken from the data of Scott, Smith and Thompson. The equilibrium points are indicated by circles in the figure and are connected by the smooth curve. The triangles are for the crystals shown in Figure 27 and are not equilibrium points but correspond to the values of n_F and $1000/T$ for which the maximum in the σ_c/σ_n ratio occurs for the crystals. The fact that these points fall below the curve indicates an insufficient number of F-centers are present to form colloids. Thus the increased conductivity in the crystals, shown in Figure 27, cannot be due to colloidal particles. In fact it was found that colloids could not be formed, under any conditions, in the crystals grown from salt purified by ion exchange.

It is difficult to understand how the conductivity could be proportional to the square root of the F-center concentration if the conductivity were due to thermionic emission from colloids. Also the findings that the F-center transport number was near unity does not

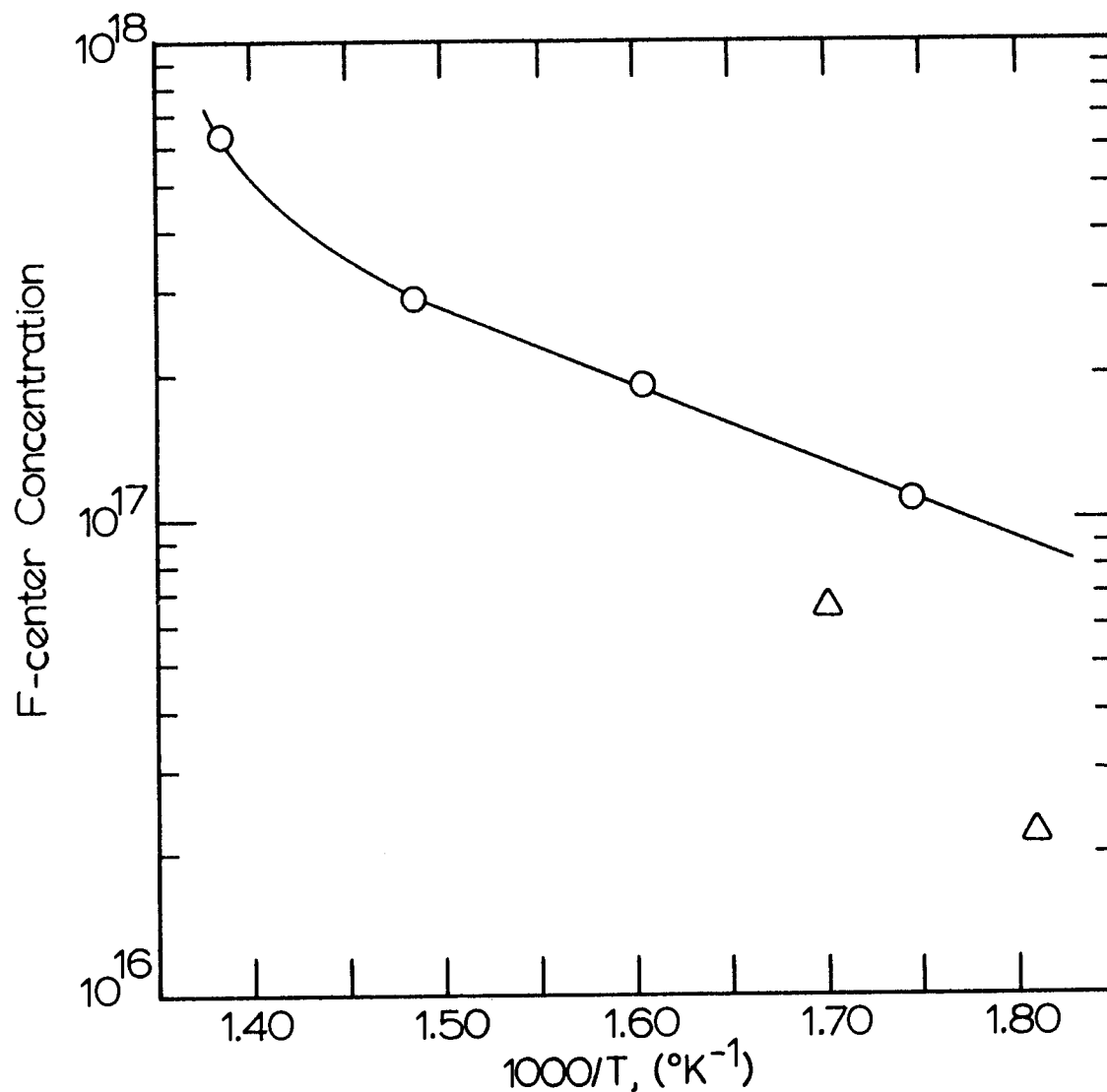


FIGURE 29. Plot showing the concentration of F-centers in equilibrium with colloids. The equilibrium points are shown as circles. The triangles are for the crystals shown in Fig. 27 with the temperature corresponding to the points where σ_c/σ_n is a maximum.

appear in agreement with the interpretation of Jain and Sootha.

Therefore it appears that the findings of these authors was incorrectly interpreted.

On the basis of the above discussion we can conclude, for the answer to the question concerning the source of the charge carriers that they originate from F-centers rather than colloids. In order to answer the remaining questions we turn to a discussion of the transport and conductivity measurements.

We are concerned with whether the carriers are electrons or ions and what the actual mechanism is. One possible mechanism, which can be eliminated immediately, is that conduction occurs due to F-center migration without ionization. This type of conduction would occur due to the fraction of F-centers always adjacent to negative ion vacancies. The F-centers would move through the crystal since when an F-center and a vacancy come into contact the electron could move into the vacancy without witnessing a potential barrier. This is because an F-center adjacent to a vacancy is just an F_2^+ -center and the wave function of the electron must be spread out over both vacancies. The expression for the conductivity due to F-center diffusion in this manner would be given by the Nernst-Einstein relation

$$\sigma_D = n_F e^2 D / kT, \quad (4.3)$$

where D is the diffusion coefficient for F-centers moving through a vacancy mechanism similar to that shown in Figure 21. However when D was estimated from theory, and used in Equation (4.3), σ_D was found to be much less than the experimental value. For that reason this solution is not satisfactory.

A second mechanism for conduction which leads to the square root dependence is shown schematically in Figure 30. Here the increased conduction in the colored crystals would be due to the formation of positive ion vacancies from F-centers. This is accomplished by the trapping of the F-center electron by one of the neighboring potassium ions forming a neutral potassium atom. This atom would be forced into the negative ion vacancy since this vacancy is much more nearly the same size as the potassium atom as can be seen in Figure 31 where we have drawn to scale a potassium atom in a chloride ion site. The vacant potassium ion site could then move away and contribute to the conductivity as is indicated in Figure 30c.

The square root dependence would arise from the thermodynamic equilibrium between F-centers and neutral potassium atoms occupying chloride ion sites. The equilibrium is written as



where F indicates an F-center, K° indicates a potassium atom in a chloride ion site and V_{+} indicates a positive ion vacancy. The

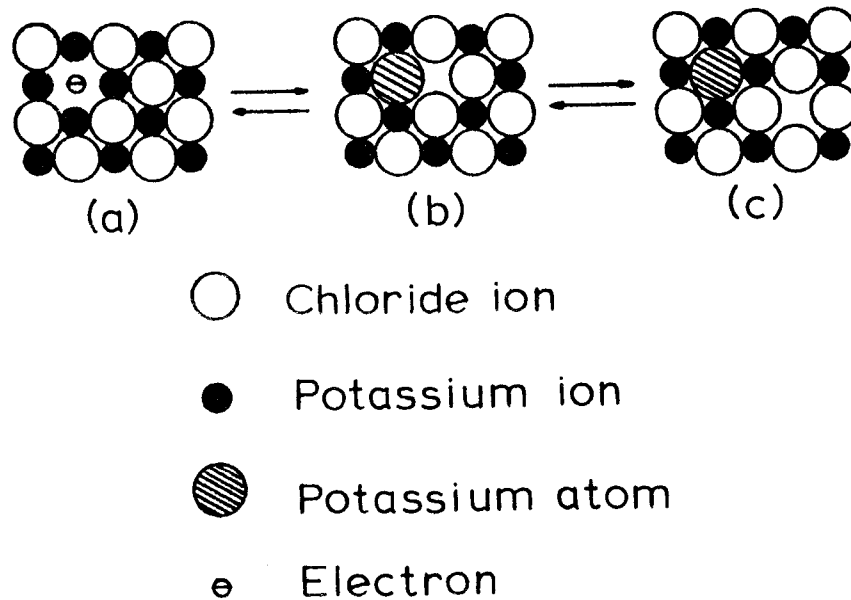
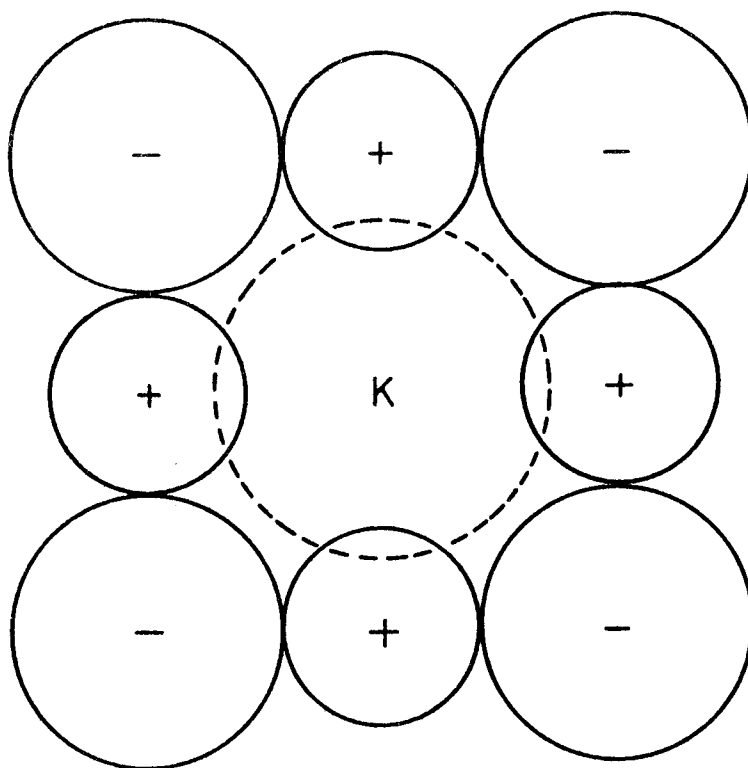


FIGURE 30. Schematic diagram showing the production of potassium ion vacancies from F-centers. (a) Normal F-center. (b) Potassium ion having trapped electron forming neutral atom. Steric effects force the atom into chloride ion vacancy leaving potassium ion site vacant. (c) Potassium atom in chloride ion site and potassium ion vacancy having become completely separated.



- Chloride ion (1.81\AA)
- + Potassium ion (1.33\AA)
- K Potassium atom (2.25\AA)

FIGURE 31. Scale model showing a potassium atom occupying a chloride ion site. The radii, expressed in angstrom units, are shown in parentheses.

equilibrium constant for reaction (4.4) would be

$$\frac{(n_{K^o})(n_{\pi})}{(N)(n_F)} = \exp(\Delta S/k) \exp(-\Delta H/kT), \quad (4.5)$$

where n_{K^o} is the number of potassium atoms per cm^3 , n_{π} the number of positive ion vacancies per cm^3 , N the total number of positive or negative ion sites per cm^3 and n_F the number of F-centers per cm^3 . ΔS and ΔH are the standard entropy and enthalpy of reaction (4.4) respectively. We assume n_{π} to be much greater than in the uncolored crystal so that we could write

$$n_{K^o} = n_{\pi}. \quad (4.6)$$

We also can assume that only a small fraction of the F-centers are converted into potassium atoms so that n_F is nearly constant and equal to the total concentration of excess metal. From this assumption and Equations (4.5) and (4.6) we obtain

$$n_{\pi} = n_F^{\frac{1}{2}} N^{\frac{1}{2}} \exp(\Delta S/2k) \exp(-\Delta H/2kT). \quad (4.7)$$

The conductivity for a positive ion vacancy mechanism was given by Equation (2.6) as

$$\sigma_{\pi} = (4n_{\pi} e^2 a_o^2 v_{\pi} / kT) \exp(\Delta s_{\pi} / k) \exp(-\Delta h_{\pi} / kT), \quad (2.6)$$

where e is the electronic charge, a_o the lattice parameter and ν_π the vibrational frequency of a potassium ion adjacent to a positive ion vacancy. Δs_π and Δh_π are the entropy and enthalpy for the jump of a positive ion vacancy from one site into a neighboring site. Combining Equations (4.7) and (2.6) gives

$$\sigma_\pi = n_F^{\frac{1}{2}} (4N e^2 a_o^2 \nu_\pi / kT) \exp[(\Delta s_\pi + \frac{1}{2} \Delta S)/k] \exp[-(\Delta h_\pi + \frac{1}{2} \Delta H)/kT]. \quad (4.8)$$

From Equation (4.8) we see that if the behavior of the crystals were described by reaction (4.4) the conductivity would be proportional to $n_F^{\frac{1}{2}}$ with $E_{obs} = \Delta h_\pi + \frac{1}{2} \Delta H$.

The transport measurements depended on the migration of F-centers. From Figure 30c it is apparent that potassium atoms could not move in an electric field. Thus in any particular volume of the crystal the concentration of F-centers must remain constant since they are in equilibrium with the potassium atoms. From this requirement we see that the mechanism just described cannot be correct since it would not give rise to a moving boundary.

The elimination of the two mechanisms mentioned above leads us back to the original interpretation given by Pohl that the increased conductivity is due to ionized F-centers. If we assume that an F-center ionizes to give an electron in the conduction band of the crystal and a negative ion vacancy the behavior exhibited in Figures 23

and 24 can be explained. Consider the region in Figure 23 for $1000/T \gtrsim 1.75$ remembering that this figure was for freshly cleaved samples. In this region conduction occurs between both electrodes by an entirely electronic mechanism. The contacts are non-ohmic because the crystal is behaving as an n-type semiconductor whose work function is less than the work function of the gold contacts (4, p. 340-344). At $1000/T \approx 1.75$ the rate of loss of F-centers due to diffusion becomes significant causing the slow formation of a very thin layer, at the surfaces, which is nearly void of F-centers. This layer serves as a potential barrier over which the electrons must pass in order to reach the electrodes. During the formation of this layer conduction through it is both electronic and ionic becoming increasingly ionic as the layer broadens. Eventually the layer reaches a thickness great enough so that conduction through it is entirely ionic. This would correspond to $1000/T \approx 1.6$. For values of $1000/T \lesssim 1.6$ conduction occurs in two parts. Between the electrodes and the colored portion of the crystal the current is ionic and is carried by migrating vacancies. In the colored portion of the crystal the current is carried by electrons. Electronic conduction through the colored region could only be possible if accompanied by a movement of the forward and trailing boundaries between the two regions. If this were not the case there would be a charge build up at these boundaries. In order for the forward boundary to advance

the conduction electrons must overcome the potential barrier and penetrate the uncolored region of the crystal. They only move a short distance before becoming trapped at negative ion vacancies forming new F-centers in the previously uncolored region.

Heating the crystal at approximately 500°C causes the loss of F-centers at the surface to occur before the measurements are begun and hence the conductivity is that exhibited in Figure 24. There is no region where a transition from electronic to electronic plus ionic occurs since the conductivity is electronic plus ionic at all temperatures. The contacts are ohmic since the evaporated gold is in contact with the uncolored portions of the crystal. We mentioned in Section II that when gold was evaporated onto uncolored potassium chloride crystals the contacts were ohmic.

Sanding caused the same effect as heating since roughening the surfaces before applying the contacts causes a potential barrier to the electrons to be formed. It is then energetically more favorable for conduction to occur at the surfaces by ionic transport than by electrons penetrating the barrier.

It was mentioned earlier that the activation energy for conduction in freshly cleaved crystals was 1.13 ev while in heated or sanded crystals the activation energy was 1.22 ev. The reason for the increase after heating or sanding is that movement of the boundary between the colored and uncolored regions requires that the electrons

penetrating into the uncolored region have sufficient energy to overcome the potential barrier. The decrease in the conductivity after heating or sanding is thus due to the increase in the activation energy from 1.13 ev to 1.22 ev.

We are now ready to give a quantitative discussion of the behavior exhibited in Figures 24 and 26. To do this we consider the F-centers to behave as donor levels in a semiconductor and have a thermal ionization energy, E_F . E_F is then the energy necessary to remove an electron from an F-center and place it in the conduction band of the crystal. Application of Fermi-Dirac statistics to these centers leads to the expression (45, p. 122-132).

$$\frac{n(n+n_a)}{n_F - n} = (2\pi m^* kT/h^2)^{3/2} \exp(-E_F/kT), \quad (4.9)$$

where n is the concentration of electrons in the conduction band, n_F the concentration of F-centers at 0°K , n_a is the concentration of negative ion vacancies in excess of the concentration necessary to accommodate all of the electrons in the conduction band and m^* is the effective mass of an electron in the conduction band. There are two limiting cases which are of interest.

Case I. $n_a \gg n$, $n_F \gg n$. This leads to the expression obtained by Mott and Gurney (39, p. 140-143) if one takes

$$n_a = N \exp(-E_S/2kT), \quad (4.10)$$

where N is the total concentration of negative ion sites in the crystal and E_S is the energy to form a separated positive-negative ion vacancy pair. Mott and Gurney obtained

$$n = (n_F/N)(2\pi m^*kT/h^2)^{3/2} \exp[-(E_F - \frac{1}{2}E_S)/kT]. \quad (4.11)$$

The equation defining conductivity is written as

$$\sigma = e\mu n, \quad (4.12)$$

where e is the electronic charge, μ is the mobility and n is the concentration of carriers. Using Equations (4.11) and (4.12) gives

$$\sigma = e\mu (n_F/N)(2\pi m^*kT/h^2)^{3/2} \exp[-(E_F - \frac{1}{2}E_S)/kT]. \quad (4.13)$$

Aside from the fact that Equation (4.13) fails to predict the square root dependence of the conductivity on the F-center concentration it can be shown incorrect by yet another argument. The magnitude of the conductivity, as predicted from Equation (4.13), can be estimated and compared with experiment. In order to do this it is necessary to decide on what value to assign μ . Little data are available but we will assume that the values obtained by Redfield (46) can be applied at high temperatures. Redfield found that μ was

approximately $10 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ at room temperature and was decreasing slowly with increasing temperature. For our calculation we will take $\mu = 1 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$, $n_{\text{F}} = 10^{17} \text{ cm}^{-3}$, $N = 1.6 \times 10^{22} \text{ cm}^{-3}$, $m^* \simeq m = 9.1 \times 10^{-28}$ grams, $T = 673^\circ \text{ K}$ and $E_{\text{F}} - \frac{1}{2}E_{\text{S}} = 1.1 \text{ ev}$. This gives $\sigma \simeq 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$. This is lower than the observed value of approximately $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ by a factor of 10^6 . Such a large difference makes it obvious that if Equation (4.13) were correct the conductivity due to ionized F-centers would not be observable but would be hidden by the much greater ionic conductivity.

An effect that is missing but should be observed if Case I is correct is that when $\log_{10} \sigma$ is plotted vs. $1000/T$ the curve should contain two linear segments rather than being composed of only one. This would arise from the change in the expression for n_{α} at the knee temperature characteristic of an uncolored crystal. In Section II we wrote the Schottky product as

$$n_{\alpha} n_{\pi} = N^2 \exp(-\Delta g/kT). \quad (2.7)$$

Below the conductivity knee Equation (2.10) was found to hold. Therefore we can write

$$n_{\pi} = n_{\text{X}}, \quad (2.10)$$

where n_{X} is a constant equal to the concentration of divalent cation

impurities. Substituting Equation (2.10) into Equation (2.7), using $\Delta g = \Delta h - T\Delta s$, and solving for n_a gives

$$n_a = (N^2/n_x) \exp(\Delta s/k) \exp(-\Delta h/kT). \quad (4.14)$$

If this expression for n_a is used in Equation (4.9), together with the assumptions from Case I, we obtain for n the expression

$$n = (n_F n_x / N^2) (2\pi m^* kT / h^2)^{3/2} \exp(-\Delta s/k) \exp[-(E_F - \Delta h)/kT] \quad (4.15)$$

and for σ the expression

$$\sigma = e\mu (n_F n_x / N^2) (2\pi m^* kT / h^2)^{3/2} \exp(-\Delta s/k) \exp[-(E_F - \Delta h)/kT]. \quad (4.16)$$

From Equation (4.16) we see that below the knee temperature characteristic of an uncolored crystal plots of $\log_{10} \sigma$ vs. $1000/T$ should be linear with slopes equal to $-(E_F - \Delta h)/2.303k$.

Above the knee temperature $n_a = n_\pi$. Using this equality in Equation (2.7) with $\Delta g = \Delta h - T\Delta s$ gives

$$n_a = N \exp(\Delta s/2k) \exp(-\Delta h/2kT). \quad (4.17)$$

Using Equation (4.17) in Equation (4.9), together with the Case I assumptions, gives for n , the expression

$$n = (n_F / N) (2\pi m^* kT / h^2)^{3/2} \exp(-\Delta s/2k) \exp[-(E_F - \frac{1}{2}\Delta h)/kT] \quad (4.18)$$

and for σ the expression

$$\sigma = e\mu (n_F/N) (2m^*kT/h^2)^{3/2} \exp(-\Delta s/2k) \exp[-(E_F - \frac{1}{2}\Delta h)/kT]. \quad (4.19)$$

Thus above the knee temperature plots of $\log_{10}\sigma$ vs. $1000/T$ should be linear with slopes given by $-(E_F - \frac{1}{2}\Delta h)/2.303k$.

Comparing this value for the slope above the knee with that below the knee shows that there should also be a knee in the conductivity plots for colored crystals which occurs at the same temperature as for uncolored crystals. Even if the square root dependence of the conductivity on the F-center concentration occurred accidentally, perhaps due to an $n_F^{-\frac{1}{2}}$ dependence of μ , the failure to observe this predicted knee indicates that Case I is definitely not correct.

Case II. $n_a \ll n, n_F \gg n$. Under these conditions Equation (4.9) reduces to

$$n = n_F^{\frac{1}{2}} (2m^*kT/h^2)^{3/4} \exp(-E_F/2kT). \quad (4.20)$$

Using Equation (4.12) and (4.20) gives

$$\sigma = e\mu n_F^{\frac{1}{2}} (2m^*kT/h^2)^{3/4} \exp(-E_F/2kT). \quad (4.21)$$

Equation (4.21) leads to the desired square root dependence but is not what one would expect. This can be seen from calculations of n_a . For an estimation of n we will again take

$\mu = 1 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ and $\sigma = 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. Substituting these values into Equation (4.12) gives $n \approx 10^{11} \text{ cm}^{-3}$.

From the data of Fuller (20) on the diffusion of chloride ions in uncolored potassium chloride we can estimate n_a . Fuller gives the expression

$$n_a = N \times 43.9 \times \exp(-2.31/2kT) \quad (4.22)$$

where $N = 1.6 \times 10^{22} \text{ cm}^{-3}$. Since $\sigma = 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ at $1000/T \approx 1.5$ we will use this value of T in Equation (4.22) to obtain $n_a = 10^{15} \text{ cm}^{-3}$. From this calculation we see that $n_a \gg n$ which indicates that Case I should be correct rather than Case II. This is the usual assumption and consequently Equation (4.13) is frequently used to calculate E_F .

If Case II is actually correct the obvious implications are that the concentration of negative ion vacancies in colored crystals is much less than in uncolored crystals. We will assume Case II to be correct and that the conductivity is given by Equation (4.21). This equation applies only if the contacts are ohmic and no colorless region exists in the crystal. This would correspond to the curves in Figure 23, for $1000/T > 1.75$, except that the contacts are slightly non-ohmic. The behavior of these crystals closely follows the theoretical predictions for rectifying contacts between a semiconductor and a metal. Dekker (10, p. 351-354) shows that the magnitude

of the current density vector should be given by

$$J = [\mu e(V_0 + V)/x_0]n \exp(-eV_0/kT)[1 - \exp(-eV/kT)], \quad (4.23)$$

where V_0 is a contact potential; V is the applied potential; x_0 is the thickness of a layer, at the surfaces, formed due to loss of electrons to the electrode from the crystal; and n is the concentration of electrons in the conduction band of the crystal at a point far removed from the contacts.

If $V \gg e/kT$ plots of J vs. V should be linear since, under this condition, Equation (4.23) reduces to

$$J = [\mu e(V_0 + V)/x_0]n \exp(-eV_0/kT). \quad (4.24)$$

By referring to the line drawn through the circles in Figure 21 we see that this is indeed the case. Thus extrapolation of the linear portion of the curve to $J = 0$ enables us to determine V_0 . By this method we obtain $V_0 = 0.11$ volts.

The concentration of electrons, at the electrodes, in the conduction band of the crystal is given by multiplying the right hand side of Equation (4.20) by $\exp(-eV_0/kT)$. The observed conductivity then becomes

$$\sigma = e\mu n_F \frac{1}{2} (2\pi m^* kT/h^2)^{3/4} \exp[-(eV_0 + \frac{1}{2}E_F)/kT]. \quad (4.25)$$

From the slope of the curves in Figure 19 we obtain $eV_o + \frac{1}{2}E_F = 1.13\text{ev}$. Thus we have $E_F = 2.04\text{ ev}$. This value for $\frac{1}{2}E_F$ should be compared with the values for the activation energy, E_A , given in Section I. The value obtained here is in good agreement with the values obtained by Smakula (1.00 ev) and by Shamovskii, Dunina and Gosteva (1.03 ev) but does not agree with the value obtained by Gravitt, Gross, Benson and Scott (1.3 ev). Since these latter investigators determined E_A from the rate of movement of the colored region, in a partially colored crystal, it would appear that they actually were measuring $\frac{1}{2}E_F + E_b$, as discussed below, rather than just $\frac{1}{2}E_F$. If this assumption is made there is fairly good agreement between their results and the results of the present work.

The equation corresponding to the curves in Figure 24 is obtained by multiplying the right hand side of Equation (4.21) by $\exp(-E_b/kT)$ to give the conductivity corresponding to the fraction of electrons, in the conduction band of the colored portion of the crystal, with sufficient energy to overcome the potential barrier, E_b , between the colored and uncolored regions. This then gives, for σ , the expression

$$\sigma = e\mu n_F^{\frac{1}{2}} (2\pi m^* kT/h^2)^{3/4} \exp[-(\frac{1}{2}E_F + E_b)/kT]. \quad (4.24)$$

From the slope of the curves in Figure 20 we obtained

$\frac{1}{2}E_F + E_b = 1.22 \text{ ev.}$ Using the value of 2.04 ev for E_F we obtain $E_b = 0.20 \text{ ev.}$

At the beginning of this section four questions were posed for which we hoped to provide answers. These questions were: (1) Do the charge carriers originate from F-centers or from colloids? (2) Are the carriers electrons or ions? (3) What is the mechanism for conduction? (4) Can the thermal ionization energy of the F-center be determined from conductivity measurements and if so what is its value? From the discussion just presented the answers to these questions appear to be: (1) The charge carriers originate from F-centers rather than from colloids. (2) The carriers are electrons and not ions. (3) The mechanism is conduction in the conduction band by electrons thermally ionized from F-centers. (4) The thermal ionization energy can be determined from conductivity measurements. If contacts are applied to freshly cleaved crystals the thermal ionization energy is twice the observed activation energy less a contact potential of 0.11 ev. Application of this correction gives 2.04 ev for the thermal ionization energy. If the crystals are heated at 500°C or greater for approximately five minutes and then quenched or if the crystals' surfaces are sanded before applying the contacts the observed activation energy will be larger than one-half the thermal ionization energy. This increase results since an electron must acquire additional energy before it can penetrate into the layer of

uncolored crystal formed, at the surfaces, during heating or sanding. The increase amounts to 0.20 ev.

It should be noted that the energy necessary for optical excitation of an F-center electron from the ground state to an excited state approximately 0.1 ev below the bottom of the conduction band is 2.3 ev. Thus the ground state is at least 2.4 ev below the bottom of the conduction band for optical excitation. The fact that the thermal ionization energy of 2.04 ev is less than this value is to be expected as has been pointed out by Mott and Gurney (39, p. 160). This is because optical excitations follow the Franck-Condon Principle whereas thermal excitations do not. Smith (57, p. 29-30) calculated the difference between the thermal and optical energies to be approximately 0.4 ev in potassium chloride. This is in excellent agreement with the value obtained from the present experiment.

V. CONDUCTIVITY OF COLORED POTASSIUM CHLORIDE CRYSTALS CONTAINING CALCIUM IONS

Introduction

It has been found that when calcium ions are added to alkali halide crystals the rate of additive coloration is greatly increased. It was mentioned in Section I that new color centers, known as Z-centers, can be formed in these crystals which are not observable in pure crystals and thus, in some way, must be associated with the calcium impurities.

Since divalent impurity ions increase the extrinsic conductivity while monovalent impurities do not it was believed that conductivity measurements would be helpful in determining the oxidation state of calcium after additive coloration. It would be expected that if the calcium ions actually trapped electrons and became reduced to the monovalent state that the extrinsic ionic conductivity would become reduced to that characteristic of pure crystals. Knowledge of the oxidation state would then be beneficial in determining models for the Z-centers as well as helping to determine the role calcium plays in increasing the rate of additive coloration.

It was also mentioned at the beginning of Section IV that we would discuss the question: Why is it that some authors report a decrease in the conductivity after coloring while other report an

increase? A likely answer would be that the decrease is due to reduction of the divalent cationic impurities responsible for the extrinsic ionic conductivity. To observe a substantial decrease after coloring the impurity content of these crystals would have to be high enough to cause the extrinsic conductivity to be considerably greater than that due to F-centers. Otherwise an increase would be observed.

A second possible reason would be that the crystals used by the investigators reporting the decreases contained substantial concentrations of hydroxide impurities. During coloring the hydroxide ions would be converted to oxide. The presence of the oxide impurities would then require compensating negative ion vacancies. These negative ion vacancies would suppress the positive ion vacancy concentration, and therefore the extrinsic conductivity, through Equation (2.7).

Since calcium and other alkaline earth ions are very common impurities in alkali halide crystals investigations to determine the effect of coloration on the ionic conductivity would serve to determine which, if any, of these reasons is correct.

Experimental

Conductivity Measurements

The calcium-doped crystals discussed in Section II were used in the conductivity and transport measurements in this section. The

crystals were additively colored by the method discussed in Section III. However the duration of coloration was never greater than two days. In all cases the F-center concentrations appeared uniform. The concentration of F-centers was determined from the optical density at 556 m μ as was also discussed in Section III.

The Z_1 -band was found to be readily formed by irradiating with white or F light at room temperature but always bleached to pure F-band above approximately 125°C. At no time was the Z_2 -band observed. The reason for this is unknown.

Conductivity measurements were made both on crystals which had been exposed to light after which they were heated to approximately 600°C and quenched and on crystals which were not quenched after exposure. No difference was observed in the conductivities after quenching.

Transport Measurements

Transport measurements were conducted on the additively colored calcium-doped crystals to determine whether the conductivity measured was primarily ionic or electronic. The same technique was employed as was used in Section IV to determine the electronic transport number in additively colored pure crystals. However the current was greater in the calcium doped crystal so that a somewhat lower temperature could be used.

Results and Discussion

Conductivity Measurements

Measurements were made on five calcium doped crystals. In general no appreciable change in the conductivity could be found after coloring. The conductivity did change somewhat but the change was usually slight and could be accounted for by precipitation of the calcium ions during the coloring period. The results for the crystal containing 9.3×10^{-5} mole fraction calcium is shown in Figure 32. The conductivity before coloring is indicated by the circles and the conductivity after coloring to an F-center concentration of $2.3 \times 10^{17} \text{ cm}^{-3}$ is indicated by the triangles. The conductivity at lower temperatures is seen to be slightly less for the colored crystal but at temperatures just below the knee the conductivities become equal. The identical knee temperatures is good evidence that the concentrations of divalent calcium ions are the same in both crystals. There still exists the possibility that the ionic conductivity in the colored crystal has been suppressed to a very low value and that the observed conductivity is electronic resulting from ionized F-centers. The identical knee temperatures would then be accidental. That the conductivity is truly ionic was determined by the electronic transport number measurements which are discussed in the following paragraphs.

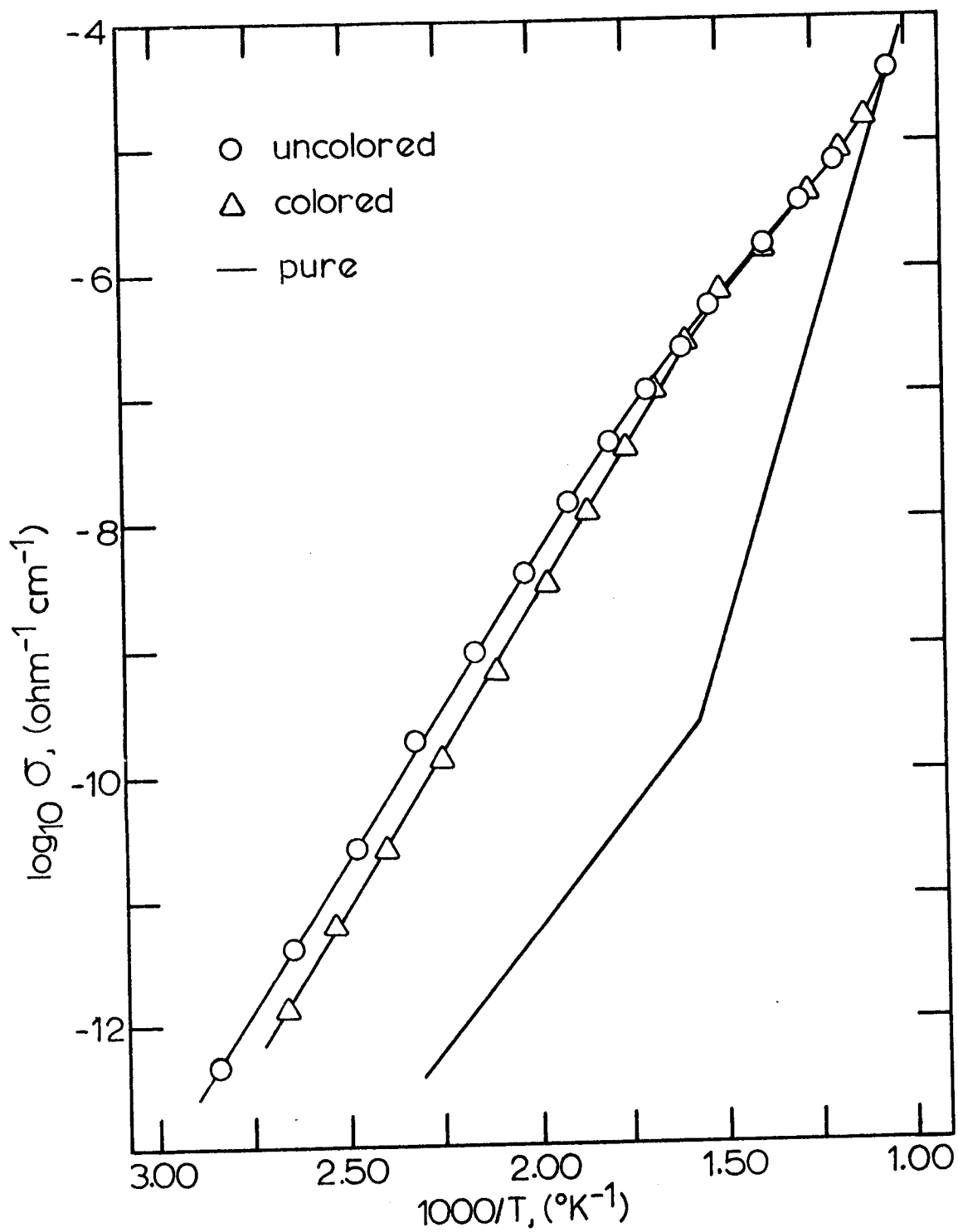


FIGURE 32. Plot showing the effect of additive coloration on the conductivity of a calcium-doped potassium chloride crystal.

Transport Measurements

For the measurements a crystal containing 1.2×10^{17} F-centers per cm^3 was placed between two uncolored crystals. The assembly was placed in the conductivity cell and heated to 319°C . A potential difference of 100 volts was applied for one hour over which time the temperature increased to 321°C . The data taken is presented in Table 5. The average current, after correcting for an electrometer drift of 0.04×10^{-7} amps per hour, was 1.71×10^{-7} amps. This amounted to a total charge of 6.16×10^{-4} coulombs. The furnace was turned off at the end of the measurements and the crystal quickly cooled to room temperature. It was found that the boundary between the colored and uncolored regions had moved only slightly. The distance was so small that an accurate measurement could not be made but an upper limit of 0.01 cm permitted a calculation of the upper limit on the F-center transport number to be made. This calculation was made using Equations (4.1) and (4.2) with $d < 0.01$ cm, $Q_t = 6.16 \times 10^{-4}$ coulombs and $n_F = 1.2 \times 10^{17} \text{ cm}^{-3}$. The remaining parameters were the same as previously. This gives $t_F < 0.15$. Thus we must have $t_i > 0.85$, where t_i is the ionic transport number. This indicates that the conductivity of the colored crystals is substantially ionic. From this deduction and the observation that the colored and uncolored crystals exhibit the same knee

temperature we can conclude that the oxidation state of calcium is unchanged on coloring and thus these ions remain divalent.

Table 5. Current observed when 100 volts were applied during transport measurements.

Time, (min)	Temperature, ($^{\circ}$ C)	Current $\times 10^7$, (amp)
0	319	----
5		1.74
10		1.71
15		1.68
20		1.65
25	319	1.65
30		1.68
35		1.72
40	320	1.73
45		1.78
50		1.80
55		1.83
60	321	<u>1.85</u>
	Average ¹	<u>1.71</u>

¹Corrected for electrometer drift of $+ 0.04 \times 10^{-7}$ amps per hour.

Since calcium remains divalent after coloration any mechanism proposed, whereby these ions increase the rate of additive coloration, must be one which does not require the reduction to the monovalent state. Obviously knowledge of such a mechanism would be beneficial in understanding the coloration process but the results of this investigation provide no further clues.

We now are in a better position to choose between the two possible reasons we have offered for the decrease in conductivity observed by certain investigators. It seems reasonable to expect that

calcium would be representative of the alkaline earth ions and thus its behavior should be typical of that group. Since the usual divalent impurities are alkaline earth ions it is unlikely that the decrease in the conductivity occurs because of a reduction of these ions to the monovalent state. It is more probable that the second reason listed is correct and that the decrease is due to the formation of oxide ions from hydroxide ions and the subsequent suppression of the positive ion vacancy concentration.

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