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Direct current conductivity measurements on $\text{KCl}:\text{O}^-$ crystals were used to determine an enthalpy of 0.42 eV for the dissociation for anion-vacancy-oxide ion complex. The entropy of dissociation was found to be approximately $-4 \times 10^{-4} \text{ eV deg}^{-1}$. The intrinsic "activation" energy was found to be 1.91 eV as compared to 1.95 eV, the average literature value.

The Effect of Oxide Impurity on the Conductivity
of Potassium Chloride

by

Daberath Kouts

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THE EFFECT OF OXIDE IMPURITY ON THE CONDUCTIVITY OF POTASSIUM CHLORIDE

I. INTRODUCTION

The first published work on the conductivity of electricity through crystalline solids was that of the Curies in 1888 according to Jacobs and Tompkins (16). Their method consisted of placing a thin slice cut from a single crystal between two metal electrodes which were 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 given by

$$i = \frac{C\Delta V}{\Delta t} \quad (1)$$

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

$$\sigma = \frac{id}{V_0 A} \quad (2)$$

where d and A are the thickness and cross-sectional area of the crystal, respectively, and V_0 is the applied voltage.

Ionic crystals behaved quite different from metallic conductors. It was found that the current measured was time dependent. This

created difficulty in defining the conductance of an ionic crystal. Joffe' and Roentgen (17) showed that this decreasing current was due to a building up of a polarization voltage. Today a problem still exists as to a good definition of conductance when polarization is occurring. One school feels that the initial current, measured before polarization has occurred, should be used in computing the conductivity so consequently they use high frequency alternating current methods. Allnatt and Jacobs (1) studying ac polarization assume in their theoretical treatment that a space charge build up at the electrodes, which partially blocks the flow of current, is responsible for the polarization. Sutter and Nowick (25) belong to the second school. They feel that the final steady current should be used since polarization occurs due to dipole orientation. Neither method is completely correct. Alternating current gives conductivities that are too high while dc gives conductivities which are too low. This is due to dipoles, such as impurity-vacancy complexes, which would oscillate with the ac field and contribute to the current even though ions may not be migrating. When dc is used these dipoles align themselves and cause a decrease in the resultant field and consequently a current reading which is too low. Fortunately, though, up to several hundred degrees centigrade both methods agree quite well and much valuable information can be obtained from each.

It has been found by Tubandt, Reinhold, and Liebold (26), using

transport numbers of several alkali halide crystals, that Faraday's law was obeyed and both positive and negative ions are the charge carriers.

It has been found that when $\ln \sigma T$ is plotted vs. $1/T$ two nearly straight line segments are observed. The conductivity at low temperatures depends on the purity and previous history of the crystal and is referred to as the extrinsic or "impurity- and structure-sensitive" region. The high temperature segment is reproducible and appears to be an intrinsic property of the crystal. It is therefore referred to as the intrinsic conductivity of the crystal. The point where the two straight line segments intersect is called the "knee". This is shown in Figure 1.

Crystals Containing Divalent Impurities

Much work has been done in studying the effect of the addition of divalent cation impurities. The results showed that the extrinsic conductivity was greatly influenced by the presence of the divalent cation impurities. It was found that at temperatures near the knee the conductivity increased linearly with the impurity concentration.

Allnatt and Jacobs (2), while studying the effect of divalent cation impurities observed curvature in a plot of $\ln \sigma T$ vs. $1/T$ for pure KCl. They suggested that this curvature was due to anion conductivity along with the cation conductivity. Fuller (13)

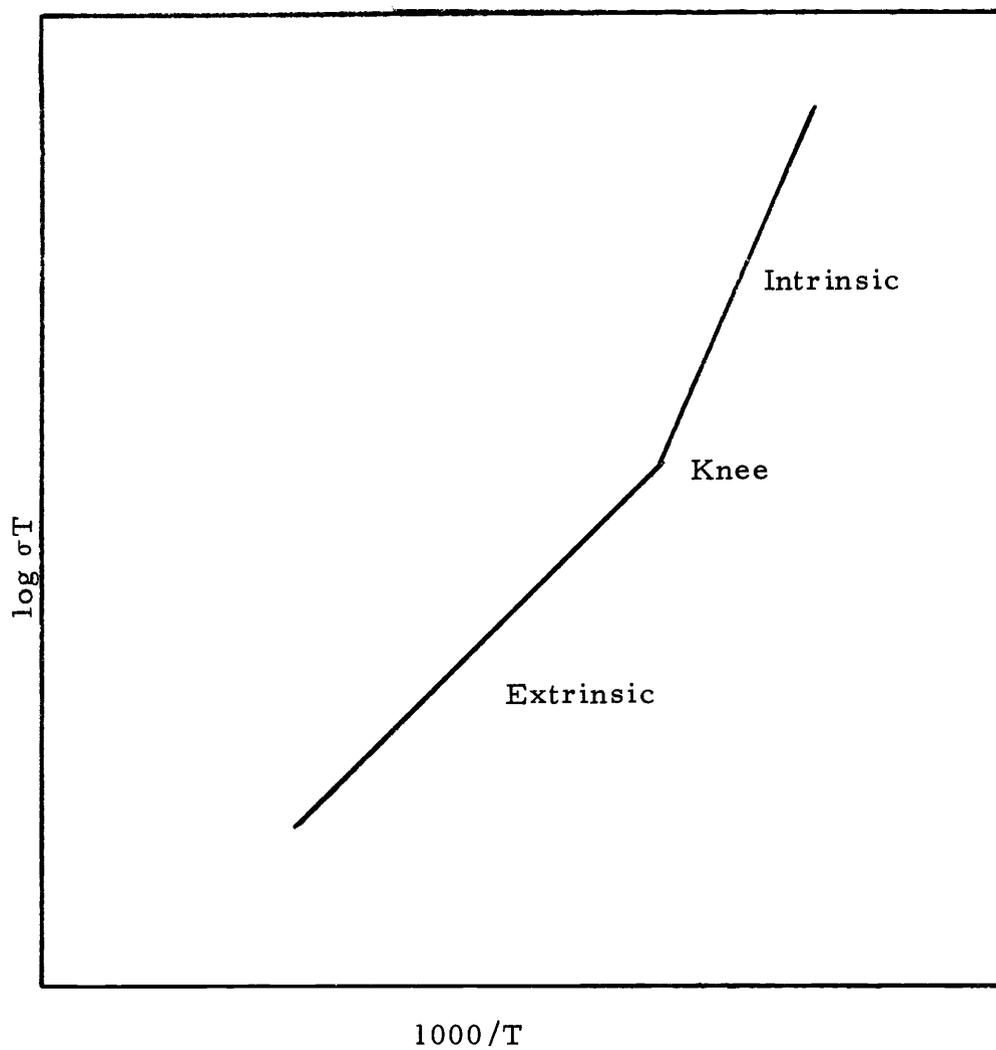


Figure 1. Theoretical conductivity curve.

substantiated this conclusion with chlorine-ion diffusion measurements on KCl. Rolfe (23) and Chandra (5, 6) have worked with KCl, KBr, and KI and various divalent cation and anion impurities to determine the effect of the impurity.

This work was concerned with the effect of the oxide ion on the conductivity of potassium chloride.

With this introduction we are ready to consider the theoretical foundations of ionic conductivity in detail.

II. THEORETICAL

In 1926 Frenkel (11) proposed that ions would move from a lattice site into an interstitial position under the influence of thermal vibrations. Four years later Wagner and Schottky (27) proposed that ions can leave their lattice sites and migrate to the surface of the crystal thereby leaving a vacant lattice position. Frenkel defects are vacancies and interstitial atoms formed in equal numbers while Schottky defects are just vacancies. In the alkali halides the relative size of the atoms make the formation of Schottky defects energetically more favorable than Frenkel defects. Therefore, in this work it was assumed that the only defects affecting the conductivity were Schottky defects and that conduction was due entirely to the movement of vacancies.

In the absence of an electrical field the vacancies will move by jumping from one lattice site to another of the same type due to the thermal motion of the ions. A negative ion vacancy has associated with it a net unit positive charge since it is surrounded by positive ions and a positive ion vacancy will have a net unit negative charge. Unless a field is applied the movement of the vacancies is random, therefore, no current flows. However, if a field is applied, the positive ion vacancies will migrate towards the positive electrode and the negative ion vacancies towards the negative electrode thus causing

current to flow. In order to increase the conductivity at a given temperature the concentration of vacancies must be increased. This may be accomplished by the addition of divalent impurities. As a divalent anion impurity is added an equal number of anion vacancies must form in order to maintain charge neutrality.

Ionic conductivity in an alkali halide crystal is given by the equation

$$\sigma = n_{\pi} e \mu_{\pi} + n_{\alpha} e \mu_{\alpha} , \quad (3)$$

where n_{π} and n_{α} are the number of positive and negative ion vacancy per cm^3 , respectively, μ_{π} and μ_{α} are the positive and negative ion vacancy mobilities, and e is the electronic charge.

The mobilities are given by the relationships

$$\mu_{\pi} = (4a_0^2 e v_{\pi} / kT) \exp (-\Delta g_{\pi} / kT) \quad (4)$$

and

$$\mu_{\alpha} = (4a_0^2 e v_{\alpha} / kT) \exp (-\Delta g_{\alpha} / kT) , \quad (5)$$

where a_0 is the jump distance (anion-cation separation distance), 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 is the absolute temperature. Substituting Equation (4) and (5) into Equation (3) we get the general expression for the ionic conductivity in alkali halides

$$\sigma = (n_{\pi} 4a_o^2 e^2 v_{\pi} / kT) \exp(-\Delta g_{\pi} / kT) + (n_a 4a_o^2 e^2 v_a / kT) \exp(-\Delta g_a / kT) . \quad (6)$$

If divalent anionic impurities are added to a crystal, the concentration of the negative ion vacancies will greatly increase thus decreasing the effective concentration of the positive ion vacancies. The decrease in concentration is not necessarily great enough for the effect of the positive ion vacancies to be neglected. This is due to the high mobility of the positive ion vacancies relative to that of the negative ion vacancies. In the case of the addition of divalent cation impurities it is possible to neglect the contribution of the negative ion vacancies to the conductivity (24).

For our purposes, it is useful to include the temperature variation of n_{π} and n_a in Equation (6). It can be shown (19) that the Schottky product is only temperature dependent and is given by

$$n_{\pi} n_a = N^2 \exp(-\Delta g_s / kT) = K_s , \quad (7)$$

where N is the total number of positive or negative ion sites per

cm^3 , either occupied or vacant, Δg_s is the standard Gibbs free energy of formation of a separated positive and negative ion vacancy pair, and K_s is the Schottky product constant. The standard state for vacancies is taken here as unit mole fraction.

Equation (7) is written assuming no interaction between defects. Since defects have a net ionic charge, a long-range coulombic interaction energy should be considered. Lidiard (20) used the Debye-Huckel theory of electrolytes to take this into account. Barr and Lidiard (3) evaluated this effect for alkali halides and found it to contribute less than 0.1 eV to Δh_s at higher temperatures, where Δh_s is the Schottky enthalpy of formation of a vacancy pair. The long range coulombic interactions will not be significant in this work due to the temperature range studied and the low defect concentration.

In any host crystal both anion and cation impurities will be present. Any intentionally added impurity is referred to as a dopant while the word "impurity" refers to any other foreign species. The law of electroneutrality must hold for all the charged species. Applied to alkali halides containing only singly charged species (divalent ions and vacancies), this relationship is

$$n_a + n_\pi = n_a + n_c, \quad (8)$$

where n_a and n_c are the concentrations, respectively, of free

divalent anions and cations, and n_{π} and n_a are the concentrations of free positive- and negative-ion vacancies, respectively. Divalent ions and vacancies in the form of neutral pairs or neutral complexes are not included in the concentrations of Equation (8). Since the crystal is doped with the oxide ion it is possible to assume that the concentration of cation impurities is negligible with respect to that of the anion impurities. That is

$$n_a - n_c \approx n_a \quad (9)$$

We can also assume that $n_a = n_x$, where n_x is the concentration of free oxide ions. Thus Equation (8) becomes

$$n_x + n_{\pi} = n_a \quad (8a)$$

It has been established by Gummer (14) that the following equilibrium holds:



where a is the negative ion vacancy and $O^{\bar{\cdot}} a$ is the dipole formed by the combination of the oxide ion and the vacancy. An equilibrium constant can be written for this equilibrium

$$K_d = \frac{n_d}{n_x n_a} \quad (11)$$

where n_d is the concentration of dipoles and K_d is the equilibrium constant.

The total oxide concentration originally added to the crystal is represented by n_o , where

$$n_o = n_x + n_d. \quad (12)$$

A diagram of a KCl crystal lattice is given in Figure 1a, showing the oxide ion, an anion vacancy and a dipole.

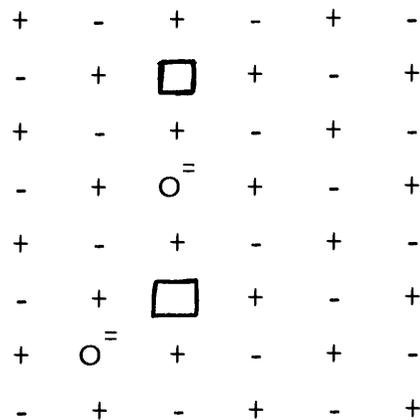


Figure 1a. KCl crystal lattice.

The four Equations (7), (8a), (11), and (12) can be used to describe the system. If K_d , K_s , and n_o are known, it can be seen, since there are four unknowns, that these equations can be solved simultaneously. The solution, in the form of a cubic equation in n_π , can be used to determine n_π as a function of temperature which, in turn, allows the calculation of n_o , n_x , and n_d . The

solution is

$$n_{\pi}^3 + (n_o + K_d K_s - n_c) n_{\pi}^2 - (K_d K_s n_c - K_s) n_{\pi} - K_d K_s^2 = 0 . \quad (13)$$

The coefficients of n_{π}^2 and n_{π} contain n_c . In the first case n_c will be negligible, when compared to n_o , but in the second case the term involving n_c may not be negligible, since its negligibility is dependent upon the magnitudes of K_s and K_d . In most cases it is possible to show that it can be neglected. Equation (13) is similar to the relationship derived by Beaumont and Jacobs (4), with the exception that their derivation was based on an excess of cation impurities.

At the temperature extremes for the conductivity curve it should be possible to determine n_{π} and n_a as less complicated functions of temperature. At low temperatures $n_{\pi} \ll n_a$ so from Equation (8a)

$$n_a = n_x , \quad (14)$$

Substituting Equation (14) into Equation (3) the conductivity at low temperatures is given by

$$\sigma = n_x \frac{4a_0^2 e^2 \nu_a}{kT} \exp(-\Delta g_a / kT) . \quad (15)$$

In order to use this equation n_x must be determined as a function of temperature. Since Equation (14), holds Equation (11) and (12) can

be used to express

$$n_x n_a = \frac{n_o - n_x}{K_d} \quad , \quad (16)$$

According to Gummer (14) it is possible to assume $n_x \ll n_o$. This assumption, along with the low temperature relationship expressed in Equation (14), gives

$$n_a = \left(\frac{n_o}{K_d} \right)^{1/2} \quad , \quad (17)$$

The equilibrium constant, K_d , expressed in Equation (11) can be expressed as

$$K_d = \frac{12}{N} \exp(\Delta g_d / kT) \quad , \quad (18)$$

where $-\Delta g_d$ is the dissociation free energy for the breaking apart of a dipole. Substituting Equation (18) into (17) and solving for n_a gives

$$n_a = \left(\frac{n_o N}{12} \right)^{1/2} \exp(-\Delta g_d / 2kT) \quad . \quad (19)$$

Substituting this result into Equation (15) for n_x gives

$$\sigma = \left(\frac{n_o N}{12} \right)^{1/2} \frac{4a_0^2 e^2 v_a}{kT} \exp(-\Delta g_d / 2kT) \exp(-\Delta g_a / kT) \quad (20)$$

for the conductivity at low temperatures. Using the relationship

$$\Delta g = \Delta h - T\Delta s, \quad (21)$$

where Δh and Δs are the enthalpy and entropy, respectively, the conductivity can be expressed as

$$\sigma = \left(\frac{n_o N}{12}\right)^{1/2} \frac{4a_0^2 e^2 v_a}{kT} \exp(\Delta s_d/2k) \exp(\Delta s_a/k) \exp(-\Delta h_d/2kT) \exp(-\Delta h_a/kT), \quad (22)$$

where subscript d refers to the dissociation of dipoles [reverse of Equation (10)], and the subscript a refers to the jump activation.

From Equation (22) it can be seen that, in a plot of $\ln \sigma T$ vs. $1/T$, the slope at low temperatures will give $-(\Delta h_a + 1/2 \Delta h_d)/k$.

At high temperatures the mobility of the cation vacancy will dominate while that of the anion vacancy will become zero. Referring to Equation (8a) n_x will become negligible since, in the intrinsic region, the concentration of vacancies becomes dominant. Thus

$$n_\pi = n_a. \quad (23)$$

The temperature dependence of n_π can be determined from Equation (7) as

$$n_\pi = N \exp(-\Delta g_s/2kT). \quad (24)$$

Using Equations (24) and (3) the conductivity in the high temperature

region becomes

$$\sigma = \frac{4a_0^2 e^{2\nu_\pi} N}{kT} \exp(-\Delta g_s / 2kT) \exp(-\Delta g_\pi / kT) . \quad (25)$$

Substituting Equation (21) into Equation (25) gives

$$\sigma = \frac{4a_0^2 e^{2\nu_\pi} N}{kT} \exp(\Delta s_s / 2k) \exp(\Delta s_\pi / k) \exp(-\Delta h_s / 2kT) \exp(-\Delta h_\pi / kT), \quad (26)$$

where the s subscript refers to the Schottky pair formation energy and π refers to the jump energy for a positive ion vacancy. From Equation (26) it can be seen that a plot of $\ln \sigma T$ vs. $1/T$ will have a slope of $-(\Delta h_\pi + 1/2 \Delta h_s) / k$ for the intrinsic conductivity.

Equations (22) and (26) still have ν_α , ν_π , N , Δs_s , Δs_d , Δs_α and Δs_π to be determined. ν_α and ν_π , following Beaumont and Jacobs (4), may be given the value of $4.25 \times 10^{12} \text{ sec}^{-1}$, which is the transverse lattice frequency for potassium chloride and N equals $1.603 \times 10^{22} \text{ cm}^{-3}$. This leaves only the entropy values as unknowns. If the curve in the low temperature region is extrapolated to $1/T = 0$, we can determine $\Delta s_\alpha + 1/2 \Delta s_d$ while extrapolation of the high temperature curve gives $\Delta s_\pi + 1/2 \Delta s_s$.

Between the low and high temperature regions the behavior of $\ln \sigma T$ with $1/T$ is very complicated. Its value is given by Equation (6) with n_π found from Equation (13) using K_d and K_s , as determined from the high and low temperature data. Then n_α is

found from Equation (7).

At the knee, σT_j given by Equation (22), is equal to that given by Equation (26). After setting these quantities equal and solving for n_o , we find

$$n_o = 12N \frac{\exp(\Delta s_d/k) \exp(2\Delta s_a/k) \exp(-\Delta h_d/kT_K) \exp(-2\Delta h_a/kT_K)}{\exp(\Delta s_s/k) \exp(2\Delta s_\pi/k) \exp(-\Delta h_s/kT_K) \exp(-2\Delta h_\pi/kT_K)}, \quad (27)$$

where T_K is the knee temperature.

III. EXPERIMENTAL

Purification of Potassium Chloride

Reagent grade potassium chloride salt was purified by an ion exchange technique developed by Fredericks, Rosztoczy and Hatchett (9, p. 3-4). The salt was dissolved in deionized water up to a concentration of 25 weight percent. In order to remove undissolved particles the solution was first filtered through Whatman No. 1 filter paper, then poured through a column of potassium form Bio-Rad analytical grade Chelex 100, and then through the chloride form of Dowex AG-2. These resins are very efficient in the removal of aliovalent impurities such as alkaline earth, lead, ferric, and sulfate ions. They are not effective however in removing monovalent ions such as bromide ions. The purified solution was evaporated to dryness at 60°C in a vacuum oven using a water aspirator. After drying the salt was stored in closed polyethylene containers. A detailed description of the purification process can be found in a report by Fredericks, Schuerman and Lewis (10, p. 3-14).

Potassium Superoxide

Any intentionally added impurity will be referred to as a dopant while the word impurity will refer to ions present in the sample that

were not intentionally introduced.

Potassium superoxide, KO_2 , was obtained at a purity of 97-99% from Alfa Inorganics Co.

The dopant purity was not as critical as that of the potassium chloride because its concentration in the bulk was between 10^{-4} and 10^{-6} mole fraction so that the impurities in the dopant only contributed 10^{-6} to 10^{-8} mole fraction to the impurity in the crystal.

Growth

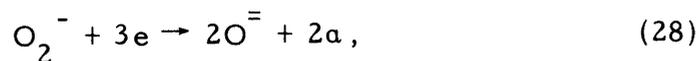
All $\text{KCl}:\text{O}^=$ crystals were grown using the Kyropoulos method. A detailed description of the crystal growing apparatus was presented by Holmes (15, p. 21-39).

Potassium chloride salt was placed in a quartz crucible and dried under vacuum at 300°C overnight. HCl was bubbled through the system for about 1/2 hour; then the system was sealed under the HCl atmosphere for another 1/2 hour. After this time the HCl was again bubbled through the system for several minutes; then the system was purged with dry oxygen gas. Oxygen was allowed to flow at a high rate until the melt was saturated; the flow rate was then decreased and held at a slow flow rate while the crystal was grown. The seed crystal of KCl was lowered into the melt and allowed to melt back some in order to ensure a clean growing surface free from secondary seeds. The cold finger assembly was then raised up slightly to reduce

the seed-crystal contact area. This process seemed to reduce the strains and dislocations in the crystal (21). The melt temperature was decreased and the water flow through the cold finger was increased so that the melt would solidify on the seed. After the crystal started to grow the KO_2 was added and the crystal slowly pulled from the melt. The rate of crystal growth was controlled by the furnace temperature and the water flow. A single crystal of about 100 grams was obtained after six hours of growing time. This growing procedure was developed by Paul (22).

Coloration

The technique of coloration in Pyrex ampoules used by Seevers (24, p. 58-81) was not applicable for crystals with substituted oxidizing anions. These crystals required longer times and/or higher temperatures for coloration than did pure potassium chloride crystals. In this work the coloration was used to reduce the superoxide ion to the oxide ion by reaction with F centers which supplied free electrons. The reaction was



where a represents the negative ion vacancy. For higher temperature coloration a Vycor tube or a stainless steel bomb, designed by

Paul (22), was used. For coloration in Vycor a sample was placed near the sealed end of a tube followed by a Pyrex ampoule containing potassium. Constrictions were made in the tube, to keep the crystal and ampoule separated, then evacuated and sealed. By heating the Vycor tube near the Pyrex ampoule it was possible to break the ampoule allowing the potassium metal to escape. The tube was placed in a horizontal furnace set at 650°C for about 12 hours. The time is not crucial as long as the crystal was completely colored, since the crystal was bleached after the coloration was finished. The tube was broken and the extent of coloration, or rather the reduction of the superoxide, was checked with ultra violet light. When the reaction was complete the crystal had a yellow-green color when observed with UV light. If the reaction was not complete the crystal was placed in another Vycor tube and the process repeated. If the reaction was complete the crystal was placed in another Vycor tube, evacuated and heated in the furnace until all evidence of color was gone. This bleaching process took about 24 hours.

A stainless steel bomb was also used for coloration. The bomb was placed in a double furnace. Each furnace was a Hoskins Tube Furnace controlled by an EP Controls ProportioNull Model 1300 temperature controller. The temperature of the upper furnace controlled the rate of coloration and the lower furnace temperature determined the F-center concentration. Increasing the lower

furnace temperature increased the potassium metal vapor pressure in the bomb. This also sped up the reduction of the superoxide ion. The lower furnace was set at 750 and the upper furnace at 1100, corresponding to about 400°C and 590°C, respectively.

Determination of Oxide-Ion Concentration

The crystals were then cleaved to the desired sample size of 2 cm x 2 cm x 1 cm for the conductivity measurements and placed in a furnace set at 600°C for 2 minutes, then quenched to room temperature. The crystal was then placed in a Perkin Elmer Model 450 UV-Visible-NIR Spectrophotometer set for UV absorbance measurements. A spectrum was taken and from it the concentration of oxide ion was determined using the equation

$$n_{\text{O}} = (2.76 \times 10^{16})(2.303)A \quad (29)$$

where A is the absorbance per cm at $\lambda = 285 \text{ nm}$ (8).

Computations

All computations were done using a Hewlett-Packard Model 9100 desk computer.

Electrode Evaporation

Gold contacts were evaporated onto the surfaces of the crystal. The sample was mounted in a crystal holder and positioned directly over a molybdenum wire filament 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 it with a variable transformer until the gold had evaporated, some of which condensed on the crystal. The sample was turned over and the process was repeated. The edges of the crystal were cleaved with a razor blade to ensure no metallic conduction around the crystal. A more detailed description of this procedure was given by Seevers (24, p. 29-31).

The crystal holder was designed with a masking ring for 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 on the crystal. The opposite face of the crystal was completely covered with gold.

Conductivity Measurements

The conductivity cell, designed by Seevers (24), is shown in Figure 2. This was used for all measurements. The crystal was placed in the conductivity cell which was evacuated to 2×10^{-4} mm mercury pressure and filled to a slightly positive pressure with

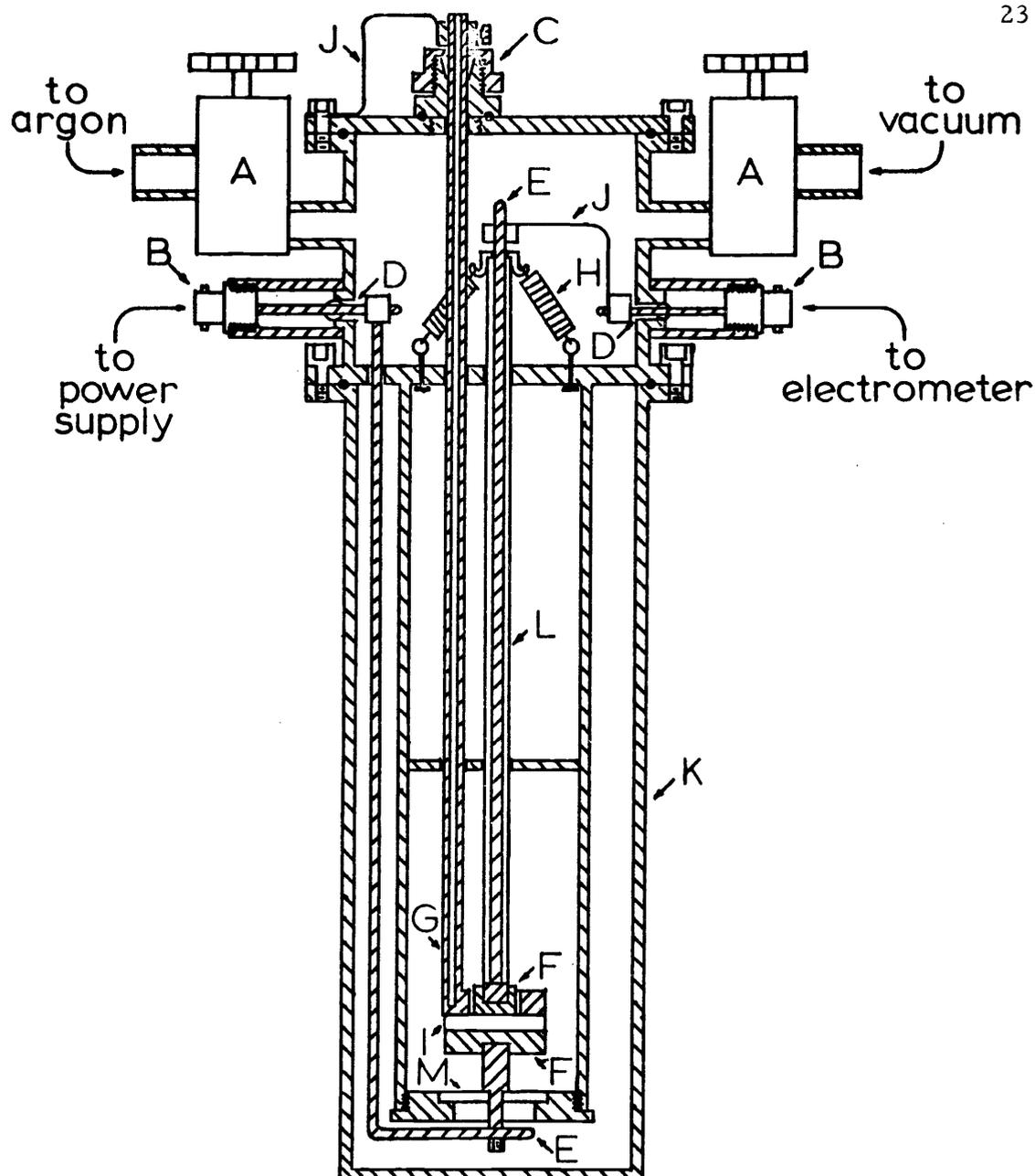


FIGURE 2. Cross sectional diagram of the conductivity cell. (A) Vacuum valves. (B) BNC connectors. (C) Swagelock seal with teflon insert. (D) Metal to glass seals. (E) Nickel wires. (F) Graphite electrodes. (G) Thermocouple well and guard ring. (H) Stainless steel springs. (I) Sample. (J) Phosphor bronze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

argon. This slight positive pressure was used to ensure good electrical contact between the crystal and electrodes. This caused a slow distortion of the crystal at high temperatures; the thickness decreased and the area increased. This change in the sample shape is unfortunate but preferable to poor electrode contact, which would lead to large errors in conductivity if undetected. Ideally the length and area of the crystal should have been measured after each run. Due to the use of the guard ring the area was assumed to have a limit and the thickness was determined both before and after each run in this work.

The lower portion of the cell, containing the sample, was inserted into a Marshall Company 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.

The cell was allowed to come to each temperature and allowed to equilibrate for several minutes before any voltage was applied. This delay ensured thermal equilibrium at each temperature.

Polarization effects were slight and occurred only at low temperatures. In all cases it was the final current, after polarization had reached a maximum, that was used in Equation (2) to determine

the conductivity. This choice was based on the assumption that the polarization resulted from the rotation of dipoles within the crystal. It was found that when evaporated gold contacts were used Ohm's law was obeyed over a wide temperature range. The results for one of the crystals can be seen in Figure 3 where the voltage has been plotted vs. current at several temperatures. The voltage was applied in both positive and negative direction with the same results. The obedience of Ohm's law was found even when polarization occurred.

It was also found that the current was constant for any given temperature over several hours for all crystals checked. This was a good indication that thermal stability was reached by the $\text{KCl}:\text{O}^{\ominus}$ crystal.

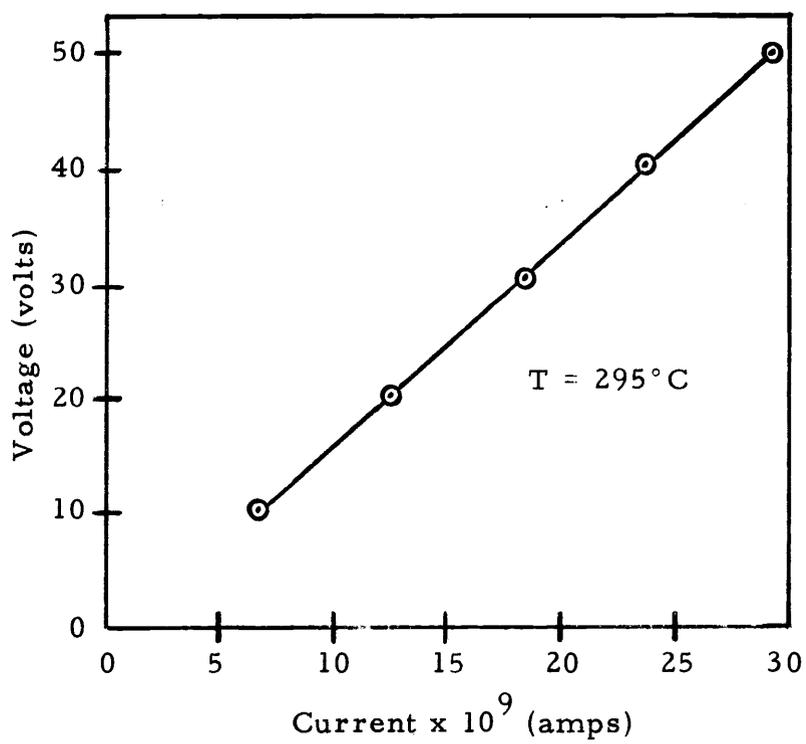
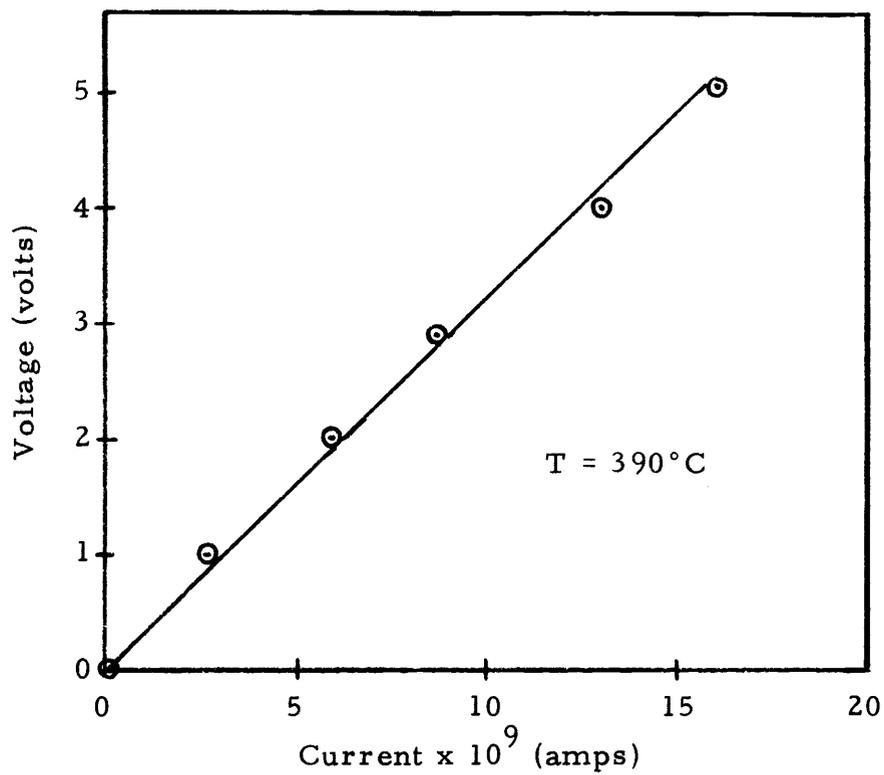


Figure 3. Voltage vs. current plot.

IV. RESULTS AND DISCUSSION

The conductivity of five $\text{KCl}:\text{O}^{\equiv}$ crystals, of varying oxide concentrations, was determined. Even though the form of Equations (22) and (26) show that the slope of the curve of $\log \sigma T$ vs. $1/T$ should be used to find the appropriate enthalpy terms, the exclusion of T from $\log \sigma T$ effects the value of the enthalpy by less than the amount of estimated experimental error. For this reason the data is presented as $\log \sigma$ vs. $10^3/T$.

For simplicity we defined an empirical "activation" energy, E_A , related to the slope of the above curves by

$$E_A = -2.303k(\text{slope}). \quad (30)$$

Figures 4, 5, and 6 are examples of the plots obtained.

From the data in the approximately linear regions the best fit to the equation

$$\sigma = A \exp(-E_A/kT) \quad (31)$$

was found by least-squares analysis, for both low and high temperature regions. Table 1 gives the results for the five crystals. Along with E_A values for the two temperature regions, A values, the knee temperature and the oxide concentration, determined by optical absorption, is given. The knee temperature was found graphically

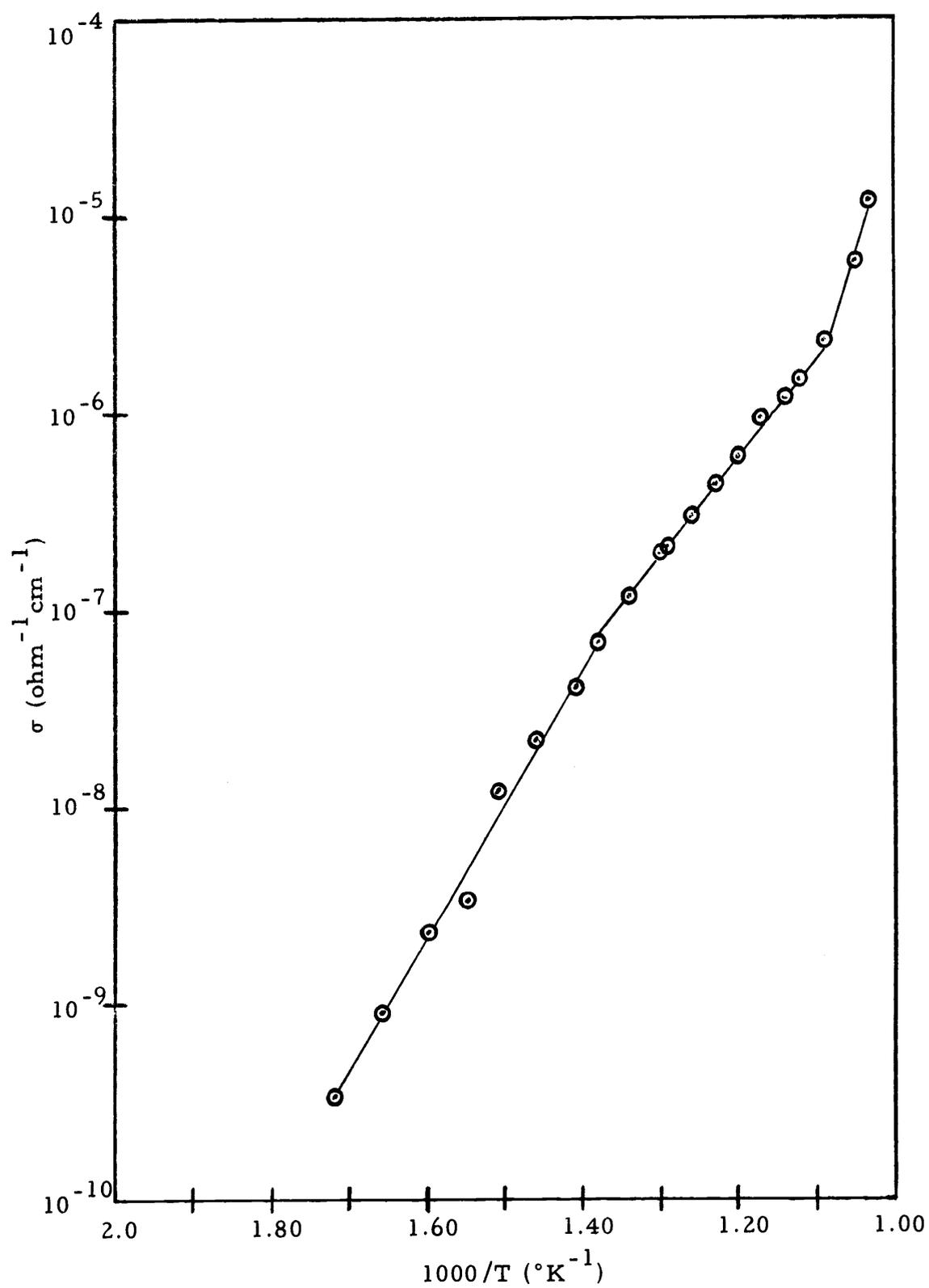


Figure 4. Conductivity curve for crystal 1.

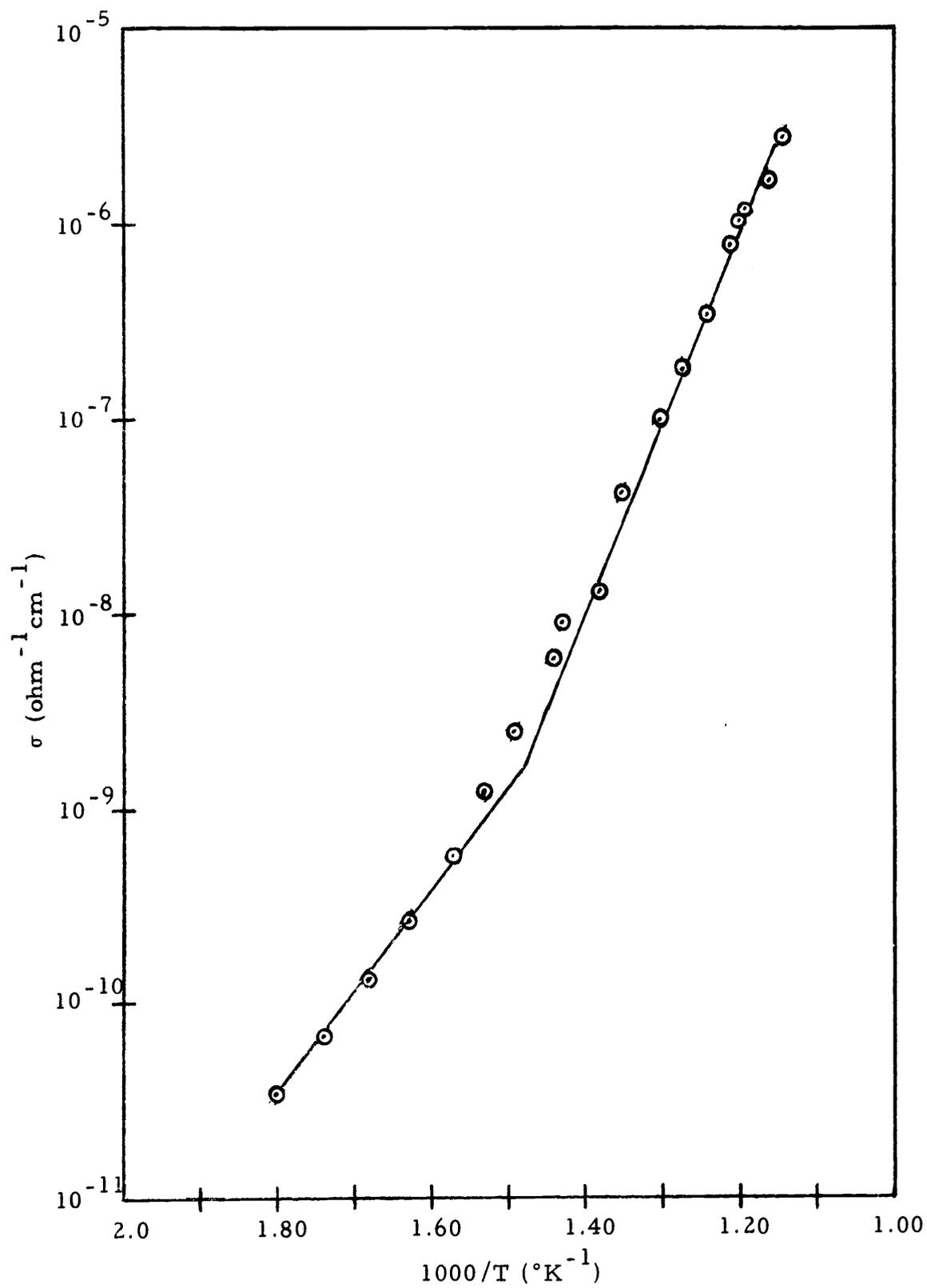


Figure 5. Conductivity plot for crystal 2.

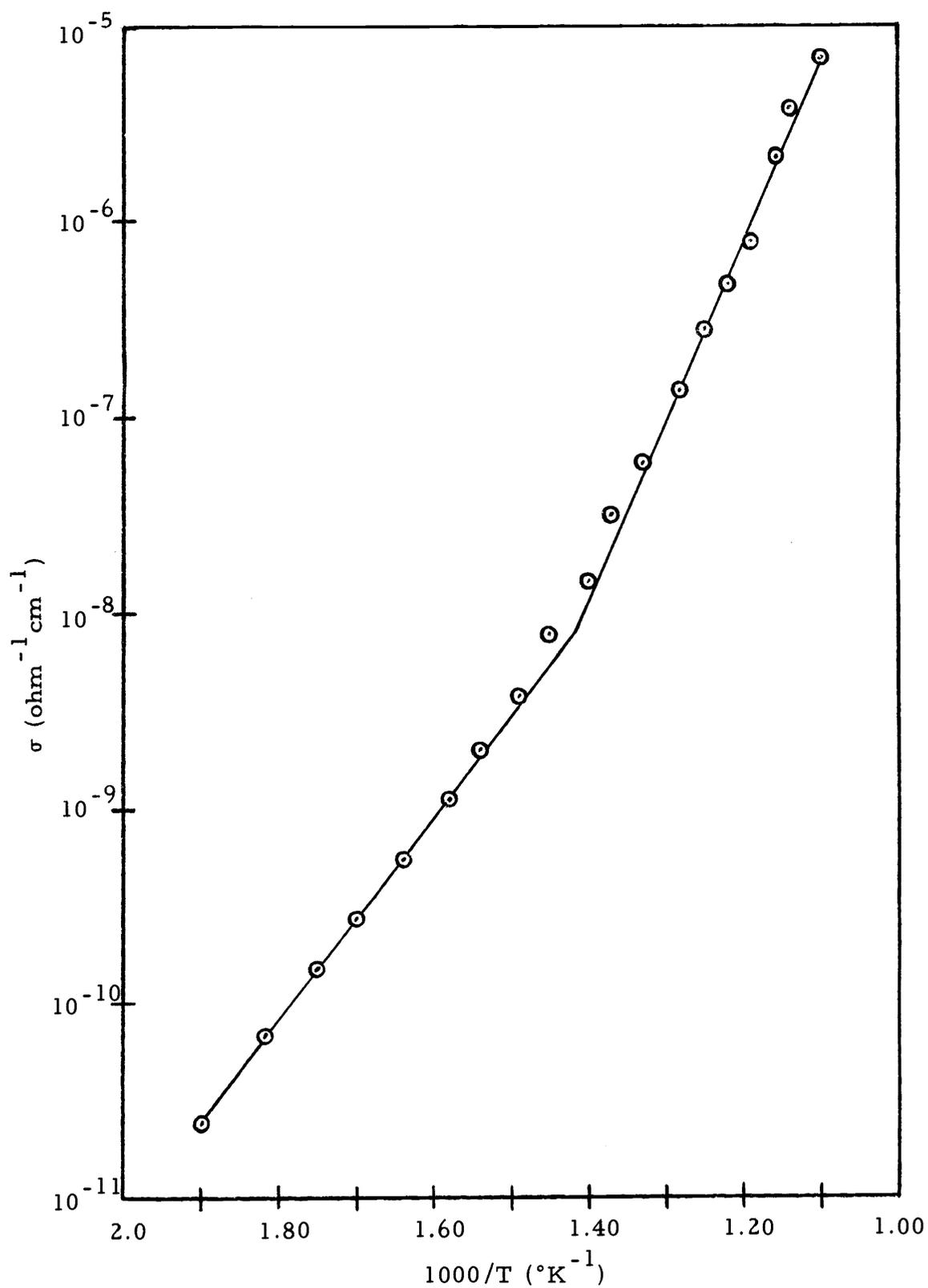


Figure 6. Conductivity plot for crystal 4.

Table 1. Results of conductivity measurements.

Crystal	n_o (centers/cm ³)	A		E_A		Knee Temperature (°C)
		High Temp. ohm ⁻¹ cm ⁻¹	Low Temp. ohm ⁻¹ cm ⁻¹	High Temp. (ev)	Low Temp. (ev)	
1	9.8×10^{16}	---	1.8	--	1.08	~ 560
2	3.7×10^{15}	3×10^3	9.0	1.85	1.24	412
3	3.7×10^{15}	3×10^5	9.2	1.86	1.29	400
4	1.6×10^{15}	3×10^5	0.3	1.84	1.03	436
5	1.8×10^{16}	1×10^7	0.3	2.04	1.15	441
6	2.7×10^{16}	3×10^5	1.5	1.95	1.12	441
Average		10^5 ^a	3	1.91	1.18	

^a average of log A

by extending the low temperature curve and the high temperature curve until they intersect.

Upon averaging the E_A values obtained at high temperatures a value of 1.91 ev was obtained. This value agrees well with literature values for the intrinsic conductivity of KCl. Beaumont and Jacobs (4, p. 1497) list various E_A values for the intrinsic conductivity. Their values range from 1.79 to 2.16 ev. They also express an average, as of 1962, of literature values as 1.95 ev. Another method of obtaining E_A is to add the appropriate values of $1/2 \Delta h_s$ and Δh_π . Using the values cited in Chandra and Rolfe (5, p. 413) a value of 1.96 ev was obtained.

For the low temperature region E_A was found to average 1.18 ev. Using an average value tabulated by Chandra and Rolfe (5) for Δh_a as 0.97 ev it is possible to calculate a value of 0.42 ev for Δh_d . This may be compared with the value calculated theoretically for the binding energy between Sr^{2+} and a cation vacancy in KCl, 0.39 ev, and that found experimentally for Mn^{2+} , 0.41 ev (3).

The low temperature value of E_A for crystal 4 was omitted in obtaining the average value. Since the crystal has the lowest oxide-ion concentration, it was likely that the assumption of nearly-complete association (i. e., $n_x \ll n_o$) was not valid. In this case E_A approaches Δh_a rather than $\Delta h_a + 1/2 \Delta h_d$. The value observed,

1.03 ev, does indeed approach the average Δh_a given above.

On the other hand, the behavior of crystal 1, containing the highest oxide concentration illustrates an additional feature. At temperatures below 1000/1.5°K the aggregation of the dipoles into double dipoles is evident. It has been shown by Gummer (14) that this occurs to a significant extent at high oxide concentrations and moderate temperatures. Thus the slope will contain a contribution from the binding energy between two dipoles. For this reason, only the linear portion between 1000/1.5°K and the knee was used in finding E_A . It would be interesting to study the effect of high concentrations of oxide on the conductivity of KCl further. After more results are obtained it would be possible to determine the binding energy for the double dipole.

Also given in Table 1 are the pre-exponential factors, A , for the extreme temperature regions. The average was found to be 10^5 for the high temperature region.

The pre-exponential term was calculated for the intrinsic region using Equation (26) and the entropy values of Beaumont and Jacobs (4). The value found was 5.6×10^4 at 800°K. Considering the uncertainty in determining pre-exponential factors the agreement is very reasonable. The low temperature factors are of use in finding the appropriate entropies, but at the present, Δs_a is not well enough established to make it worthwhile to calculate Δs_d .

Figures 5 and 6 show the curvature in the knee region and the variance of knee temperature with the oxide content. They also show the change in the extrinsic conductivity when the oxide concentration is changed. The curvature in the knee region may be ascribed most simply to the addition of the two exponential contributions to the conductivity; however, this is an oversimplification, as the correct value of σ is given by the full solution of Equations (13) and (7) as previously described.

From the data shown in Figure 5 we can draw the plausible conclusion that dissociation of the dipoles is incomplete throughout the entire temperature range below the knee temperature; otherwise the conductivity curve would show a downward curvature near the knee as the slope should then correspond only to an activation energy Δh_{α} rather than the quantity $(\Delta h_{\alpha} + 1/2 \Delta h_{\text{d}})$.

If dissociation is incomplete at an oxide concentration of approximately $3 \times 10^5 \text{ cm}^{-3}$ K_{d} must be larger than about 2×10^{-16} at 350°C . Taking this lower limit as the value of K_{d} and using $\Delta h_{\text{d}} = 0.42 \text{ ev}$ it may be calculated that $\Delta s_{\text{d}} = -4 \times 10^4 \text{ ev deg}^{-1}$. This is the lower limit on the value of the entropy.

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