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CHLORIDE SINGLE CRYSTALS

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A comparison was made of the d. c. conductivity of KCl:Pb^{2+} and KCl:PbO single crystals at temperatures greater than 325°C . The energy of activation was 0.72 ev for all crystals. Lead concentration was determined by chemical, optical and electrical methods. The half band width of the UV absorption band at 273 nm was 0.082 ev for both crystal sets although the oscillator strength in KCl:PbO crystals was suppressed.

It is concluded that the lead ion was not appreciably compensated by oxygen in the KCl:PbO crystals. Some oxygen appeared to be present to suppress the oscillator strength of lead.

The Conductivity of Lead Oxide Doped
Potassium Chloride Single Crystals

by

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THE CONDUCTIVITY OF LEAD OXIDE DOPED POTASSIUM CHLORIDE SINGLE CRYSTALS

I. INTRODUCTION

Within recent years remarkable progress has been made in the study of crystals. The alkali halides, in turn, have attracted many investigators. Large single crystals are available in nature or can easily be grown in the laboratory. The physical properties are isotropic because of the cubic symmetry of the lattice. For these reasons the alkali halides became very popular crystals on which to study the properties of insulators.

As the work on alkali halides progressed interest in the impurity effects increased. In 1937 Pohl (24), in a review of the literature, observed that the optical and electrical properties were very sensitive to the impurity content. In fact, many of the electrical properties were due to the interaction of the crystal with the impurity. Soon, one popular procedure was to take very pure salt and add a selected impurity.

Over the years most of the work on impurity conductivity has involved divalent cations such as Ca^{2+} , Sr^{2+} , Ba^{2+} (17), or Pb^{2+} (14). Some work has been done with divalent anions such as SO_4^{2-} (13) or CO_3^{2-} (5). Lidiard (25, p. 230) notes that attempts to add K_2O to KCl or Li_2O to LiCl fail because of the low solubility of these additives.

Research on transport properties has been reviewed recently by Süptitz and Teltow (28) and very recently by Barr and Lidiard (3).

Very little work has been done with alkali halides to which both anionic and cationic impurities had been added. Merlin and Reshina (21) added CaSO_4 to KCl and found that the impurities compensated each other and very little impurity conduction was observed. Fritz, Lüty and Anger (9) have shown that OH^- reacts with Ca^{2+} in such a way that the increased conductivity due to the Ca^{2+} is compensated. Similar effects were found by Allen (1) for both OH^- and oxygen reacting with Hg^{2+} in KCl.

Since OH^- and oxygen are among the most common unintentional impurities in commercial alkali halides it is important to know how extensively such compensation reactions occur. This study was undertaken to investigate the extent of such reactions with Pb^{+2} . The work reported in this thesis concerns the effect of PbO on the ionic conduction and optical absorption of KCl.

II. GENERAL RELATIONS

The band gap between the valence band and the conduction band of potassium chloride is 8.6 eV. For this reason KCl does not conduct electronically except in high fields or at high temperatures. However, KCl does conduct under milder conditions. Tubandt (29) showed that this conductivity is due to ionic migration, mostly cationic migration. Frenkel (8) in 1926 and Wagner and Schottky (30) in 1930 proposed point defect models which explained much of the behavior of ionic crystals.

These authors proposed that no crystal is perfect. Rather, all crystals contain defects and these defects follow the laws of thermodynamics. Frenkel proposed that ions, under the influence of thermal vibrations, move from a lattice site into an interstitial position. The vacancy left behind and the interstitial ion is known as a Frenkel defect. Wagner and Schottky proposed that both a cation and an anion leave their lattice sites and migrate to the surface of the crystal. The pair of vacancies left behind is known as a Schottky defect. In alkali halides the relative sizes of the ions make Schottky defects energetically favored and it is assumed that Schottky defects account for the defect properties of the alkali halides.

Another source of lattice defects is divalent impurities. A divalent cation is positive relative to the lattice while a cation vacancy

is negative. Thus, in order to maintain charge compensation, cation vacancies must be incorporated into the crystal in numbers equal to the number of divalent cations. Divalent anions are negative relative to the lattice and so anion vacancies must be incorporated into the lattice in numbers equal to the number of divalent anions.

The conductivity equations used in this paper will be developed in the same manner used by Fuller et al. (11) and similar in parts to the method used by Jacobs and Tomkins (15) and followed by Seevers (26) and Allen (1).

Conductivity is given by the equation

$$\sigma = \frac{id}{AV} \quad 2.1$$

where σ is the conductivity, i is the current, V is the voltage, d is the thickness of the conductor, and A is the area of the electrode. This equation was used to calculate conductivity from the experimental data.

Ionic conductivity in alkali halides is also given by the equation

$$\sigma = n_{\pi} e \mu_{\pi} + n_{\alpha} e \mu_{\alpha} \quad 2.2$$

where n and μ are the concentration and the mobility of an ion vacancy which contributes to the conductivity and e is the electronic charge. In the discussion that follows the π and α subscripts refer to the cation vacancy or anion vacancy respectively.

Furthermore, the mobilities are given by the equations

$$\mu_{\pi} = (4a_o^2 e v_{\pi} / kT) \exp(-\Delta g_{\pi} / kT) \quad 2.3$$

and

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

where a_o is the jump distance between two lattice sites, v is the vibrational frequency in the direction of a vacancy for the ions around that vacancy, k is the Boltzmann's constant, T is the temperature in degrees Kelvin, and Δg is the Gibb's free energy of activation for the jump of an ion into a vacancy.

Substituting equations 1. 3 and 1. 4 into equation 1. 2 we get the general expression for ionic conductivity in alkali halides:

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

III. THE CATION CONTRIBUTION TO CONDUCTIVITY

Lidiard (19, p. 252) showed that the fraction of current carried by the anion vacancies was 12 percent or less at 600°C for a pure crystal. This fraction decreased as the temperature decreased or as the cation impurity increased. Fuller et al. (11) obtained similar results. For this reason we may say that the anion vacancies do not contribute significantly to the conductivity of cation doped crystals in the temperature range used in this study.

Simplifying equation 2.5 we get

$$\sigma = (n_{\pi} 4a_o^2 e^2 v_{\pi} / kT) \exp(-\Delta g_{\pi} / kT) \quad 3.1$$

At this point we must point out the n_{π} is the concentration of cation vacancies that do in fact contribute to the conductivity. Many of the cation vacancies may not. For example, those bound in neutral complexes make no contribution to conductivity.

The next section will consider the way that n_{π} is related to the total divalent ion concentration and to the anion vacancy concentration.

It is easily shown (24, p. 258-261) that the product of the concentrations of the cation and anion vacancies is given by

$$(x_{+})(x_{-}) = \exp(-\Delta g_s / kT) \quad 3.2$$

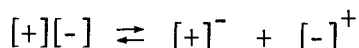
where x_+ and x_- are the mole fractions of the cation and anion vacancies respectively and Δg_s is the free energy of formation for a Schottky pair. Equation 3.2 assumes no interaction between defects. Since these defects have a net ionic charge, there are always long range Coulombic interactions. As a result the cation and anion vacancies are not distributed randomly with respect to one another. This will cause a decrease of the effective energy of formation. Lidiard shows that this can be taken into account roughly using the Debye-Hückel theory of electrolytes (20). Barr and Lidiard (3) evaluated this effect and found that it is less than 0.1 eV at high temperatures. In the temperature range of this study, then, the long range Coulombic interactions will not be significant.

Rewriting equation 3.2 in terms of sites per cm^3 we get

$$(n_+/N)(n_-/N) = \exp(-\Delta g_s/kT) \quad 3.3$$

where n_+ and n_- are the number of cation and anion vacancies per cm^3 , respectively, and N is the total number of cation or anion sites per cm^3 . It must be emphasized that n_+ and n_- refer to the total number of vacancies while n_π and n_α refer to those vacancies which contribute to the conductivity.

The short range interactions between vacancy pairs is described by the reaction



where $[+]^-$ and $[-]^+$ are the cation and anion vacancies respectively. The charges are relative to the lattice. In terms of the law of mass action we may write

$$\frac{(x_+ - x_\rho)(x_- - x_\rho)}{(x_\rho)} = \frac{1}{6} \exp(-\Delta g_b/kT) \quad 3.4$$

where x_ρ is the mole fraction of associated pairs and Δg_b is the Gibbs free energy of binding from which the configuration entropy has been removed.

Rewriting this in terms of numbers per cm^3 , and noting, for example, that $n_\pi = (x_+ - x_\rho)N$, we get

$$\frac{(n_\pi)(n_a)}{(N)(n_\rho)} = \frac{1}{6} \exp(-\Delta g_b/kT) \quad 3.5$$

where n_ρ is the number per cm^3 of associated vacancy pairs.

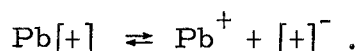
It is not possible to remove all the divalent cations from the salt and often these impurities are added. These impurity ions are incorporated into the crystal in accordance with the law of charge compensation. We may write:

$$n_c + n_- = n_+ \quad 3.6$$

where n_c is the number of divalent cations per cm^3 . Again, n_+ and n_- are the total number per cm^3 of the vacancies.

The cation impurity and a cation vacancy will associate to form

a complex. This complex will dissociate by the reaction:



The charges are relative to the lattice. In terms of the law of mass action we may write

$$\frac{(x_c - x_a)(x_+ - x_a)}{(x_a)} = \frac{1}{Z} \exp(-\Delta g_a/kT) \quad 3.7$$

where x_c and x_a are the mole fractions of the divalent cations and the associated complexes, respectively, and Δg_a is the standard free energy of association from which the configurational entropy has been removed, and Z , which is equal to 12 in KCl, is the number of nearest neighbor sites.

Rewriting this in terms of sites per cm^3 we get

$$\frac{(n_f)(n_\pi)}{(N)(n_a)} = \frac{1}{Z} \exp(-\Delta g_a/kT) \quad 3.8$$

where n_f is the concentration of unassociated divalent cations and n_a is the concentration of associated complexes.

The extent of Schottky pair association is of interest. Association of vacancy pairs is described by equation 3.5 and is independent of impurity concentration. Solving this equation for n_ρ we get

$$n_\rho = \frac{6(n_\pi)(n_\alpha)}{N} \exp(\Delta g_b/kT).$$

Economou and Sastry (10) report a value of 1.34 eV for Δh_b . No value for Δs_b was given. We can use Δh_b for a first approximation but the calculations can be order of magnitude only. Noting that N is $1.6 \times 10^{22} \text{ cm}^{-3}$ we get

$$n_p = (2 \times 10^{-11}) (n_\pi)(n_\alpha). \quad 3.9$$

The product $(n_\pi)(n_\alpha)$ can be calculated from equation 3.3. Beaumont and Jacobs (4) give a value of $\Delta g_s = 2.10 \text{ eV}$ at 323°C . Equation 3.3 becomes

$$(n_\pi)(n_\alpha) = 3.8 \times 10^{26} \text{ cm}^{-6} \quad 3.10$$

and equation 3.9 becomes

$$n_p = 10^{16} \text{ cm}^{-3}. \quad 3.11$$

We see that although the number of associated pairs is quite large and is a function of temperature only, they are neutral and make no contribution to conductivity.

A common assumption made is that all the divalent ions and vacancies are unassociated. It will be convenient to examine this assumption at this time.

The formation of ion-vacancy complexes is described by equation 3.8. If we let p be the degree of association then

$$pn_c = n_a$$

and

$$(1 - p)n_c = n_f.$$

Since the number of thermally generated vacancies is insignificant at low temperatures we can say

$$n_f = n_{\pi}.$$

Equation 3.8 becomes

$$\frac{(1 - p)^2}{p} = \frac{N}{12n_c} \exp(-\Delta g_a/kT). \quad 3.12$$

Krause (18) showed that Δg_a at 323°C is 0.47 ev. Using this value and noting that N is $1.6 \times 10^{22} \text{ cm}^{-3}$ we can solve equation 3.12 for p .

The lower limit of lead concentration in this study was

$$n_c = 1.0 \times 10^{16} \text{ cm}^{-3}.$$

Solving equation 3.12 by successive approximation we find

$$p = 1.9 \times 10^{-5}.$$

The upper limit of lead concentration is

$$n_c = 1.6 \times 10^{17} \text{ cm}^{-3}$$

and

$$p = 3.0 \times 10^{-4} .$$

The assumption that the divalent ion and its impurity are unassociated is reasonable over most of the temperature range of this study. It is not correct at the lowest temperatures. Equations which include association will be developed later. However, we will accept this assumption for the moment in developing equations for conductivity.

Since we assumed no association between divalent cation and a cation vacancy we may write

$$n_{\pi} = n_{+}$$

and

$$n_{\alpha} = n_{-} .$$

Substituting these into equations 3.5 and 3.6 and then eliminating n_{α} we get

$$n_{\pi} = \left[\left(\frac{1}{4} \right) n_c^2 + N^2 \exp(-\Delta g_s / kT) \right]^{1/2} + \left(\frac{1}{2} \right) n_c . \quad 3.13$$

At low temperatures the exponential term becomes very small compared to n_c and equation 3.13 becomes

$$n_{\pi} = n_c \quad 3.14$$

Substituting equation 3.14 into equation 3.1 we obtain the low temperature form of the conductivity equation, in the absence of

association,

$$\sigma = (n_c 4a_o^2 e^2 v_{\pi} / kT) \exp(-\Delta g_{\pi} / kT) . \quad 3.15$$

At high temperatures the exponential term of equation 3.13 becomes dominant and

$$n_{\pi} = N \exp(-\Delta g_s / 2kT) . \quad 3.16$$

Substituting this into equation 3.1 we get the high temperature form of the conductivity equation, in the absence of association,

$$\sigma = (4Na_o^2 e^2 v_{\pi} / kT) \exp[-(\Delta g_{\pi} + 1/2\Delta g_s) / kT] . \quad 3.17$$

At sufficiently low temperatures the formation of a complex between a divalent ion and its vacancy will have an effect upon the conductivity and we will now develop appropriate equations for this instance. At low temperatures the Schottky pair formation is suppressed and we get

$$n_{\pi} = n_f . \quad 3.18$$

We also let

$$n_{\alpha} = pn_c . \quad 3.19$$

Substituting equations 3.18 and 3.19 into 3.8 and solving for n_{π} we get

$$n_{\pi} = (Np n_c / Z)^{1/2} \exp(-\Delta g_a / 2kT) . \quad 3.20$$

This equation gives a better estimate of n_{π} at low temperatures where complex formation is important. Note that p is a function of both T and n_c , as exemplified by equation 3.12.

Substituting equation 3.20 into equation 3.1 we get

$$\sigma = [(Np n_c / Z)^{1/2} 4a_o^2 e^2 v_{\pi} / kT] \exp[-(\Delta g_{\pi} + 1/2 \Delta g_a) / kT] . \quad 3.21$$

Equations 3.15, 3.17 and 3.21 can be cast into a more useful form by substituting for each Δg the corresponding function,

$\Delta h - T \Delta s$. Equation 3.17 becomes

$$\sigma = (4Na_o^2 e^2 v_{\pi} / kT) \exp[(\Delta s_{\pi} + 1/2 \Delta s_s) / k] \exp[-(\Delta h_{\pi} + 1/2 \Delta h_s) / kT] , \quad 3.22$$

equation 3.15 becomes

$$\sigma = (n_c 4a_o^2 e^2 v_{\pi} / kT) \exp(\Delta s_{\pi} / k) \exp(-\Delta h_{\pi} / kT) , \quad 3.23$$

and equation 3.21 becomes

$$\sigma = [(Np n_c / Z)^{1/2} 4a_o^2 e^2 v_{\pi} / kT] \exp[(\Delta s_{\pi} + 1/2 \Delta s_a) / k] \exp[-(\Delta h_{\pi} + 1/2 \Delta h_a) / kT] . \quad 3.24$$

Experimentally, a plot of $\log \sigma T$ vs. T^{-1} should give a graph of three intersecting curves as shown in Figure 1. The high temperature curve, called the intrinsic curve, will be a straight line and

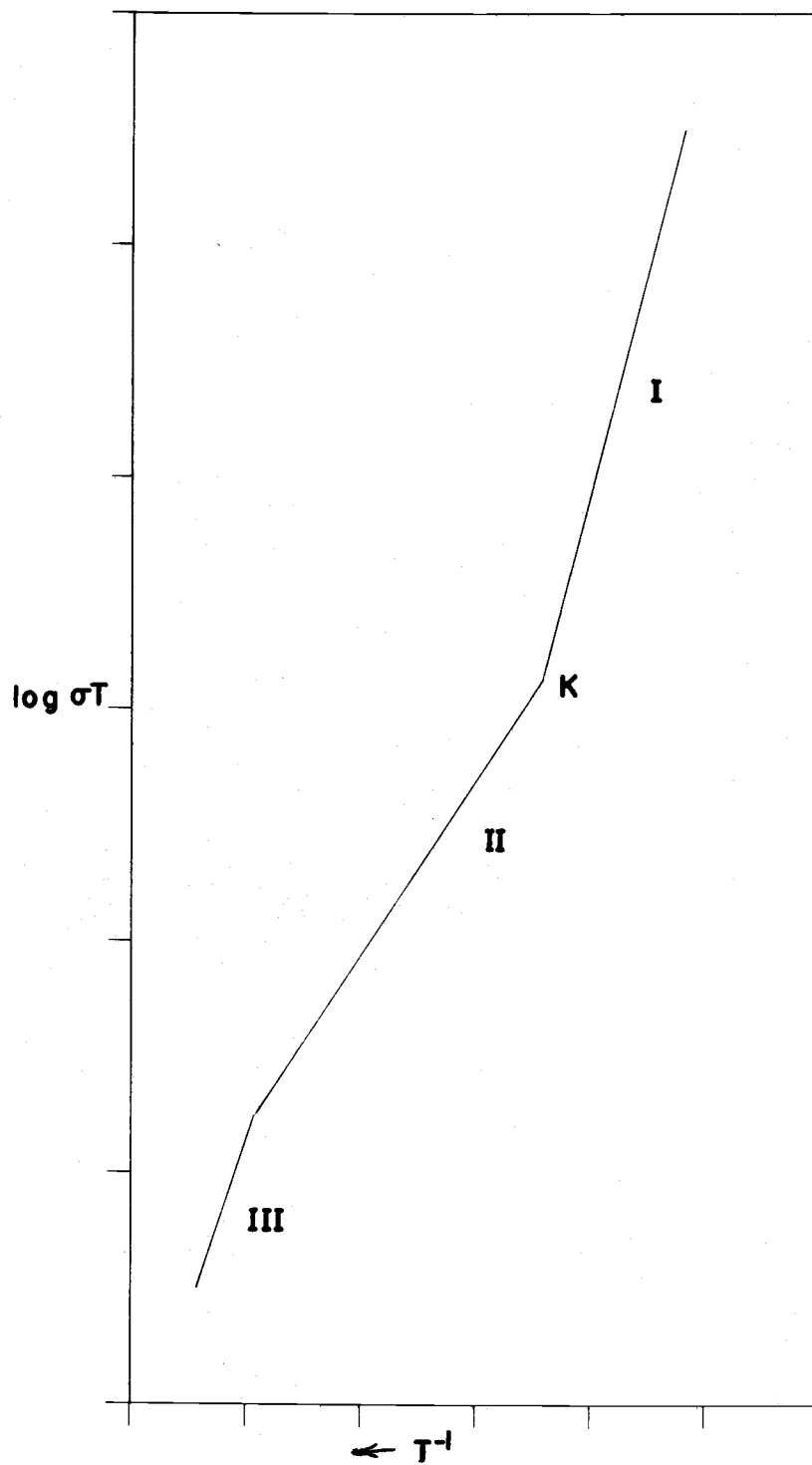


Figure 1. Conductivity curve showing extrinsic associated (I), extrinsic unassociated (II), intrinsic (III), and knee (K).

described by equation 3.22. The middle temperature curve, called the extrinsic unassociated curve, will be a straight line and described by equation 3.22. The lowest temperature curve, called the extrinsic associated curve, is described by equation 3.24. The extrinsic associated curve will be curved somewhat because of the temperature and concentration dependence of p .

At the intersection of the intrinsic and the extrinsic unassociated curves we can solve equation 3.15 and 3.17 simultaneously for n_c and get

$$n_c = N \exp(-\Delta g_s / 2kT_k) \quad 3.25$$

where T_k is the knee temperature or the temperature of the intersection. If we use $\Delta g_s = \Delta h_s - T\Delta s_s$ and the values of $\Delta s_s = 4.65 \times 10^{-4}$ ev/k and $\Delta h_s = 2.259$ ev found by Beaumont and Jacobs (4) the total divalent ion concentration can be estimated by

$$n_c = 2.4 \times 10^{(23 - 5700/T_k)} \quad 3.26$$

This formula is very useful and was used frequently during this study.

IV. THE ANION CONTRIBUTION TO CONDUCTIVITY

Previously we have ignored the effects of the anion impurities and the anion vacancies. Having made this simplification we developed equation 3.1 through 3.26. It is now important to reconsider this simplification as applied to KCl:PbO.

Fuller and Reilly (10) have analysed the anion contribution to the intrinsic conductivity. They report that a plot of $\log \sigma T$ vs. T^{-1} shows a slight curvature in the intrinsic region. Beaumont and Jacobs (4) also report the curvature to be slight. Chandra and Rolfe (5) report a curvature that is slight in the case of KCl:CO₃²⁻. These workers attribute this curvature to the contribution of the anion vacancies. In the present experiments, the intrinsic region has not been investigated in detail because it will not contribute to the understanding of the problem.

Of greater interest in the crystal KCl:PbO is the effect of the divalent anion upon the extrinsic conductivity. Rewriting equation 2.5

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

we see that we have three types of variables to consider: Δg , v , and n .

At present we have no reliable values for v_{+} or v_{-} . So it

is assumed that they are equal to each other (10) and equal to the transverse lattice frequency which is $\nu = 4.25 \times 10^{12} \text{ sec}^{-1}$ (2).

The relationship of n_{π} to n_{α} is more complex and several possibilities must be considered. Should the lead oxide be dissolved as Pb^{+2} and as O^{-2} in equal concentrations, then electrical neutrality can be maintained without the formation of vacancies. Merlin and Reshina (21) have studied the system $\text{KCl}:\text{SO}_4^{-2}:\text{Ca}^{+2}$ and found mutual compensation between the SO_4^{-2} and the Ca^{+2} . In the $\text{KCl}:\text{PbO}$ system the UV absorbance spectrum will show a normal peak at 273 nm for the Pb^{+2} while the O^{-2} peak would be obscured by the lead peaks which occur at shorter wave lengths. However, since no vacancies need form, the intrinsic conductivity will extend to a much lower temperature and we would find

$$n_o \approx n_e \gg n_c \quad 4.1$$

where n_e is the concentration of lead as determined chemically and n_o is the concentration of lead as determined optically.

More likely, the solubility of Pb^{2+} in the solid exceeds that of O^{2-} so that Pb^{2+} and O^{2-} are not incorporated in the crystal in equal concentrations. In this event some of the conductivity due to the Pb^{2+} would be compensated by the O^{2-} . A normal absorption peak at 273 nm would be observed but the O^{2-} would again be obscured. We would find

$$n_o \approx n_e \neq n_c . \quad 4.2$$

In the extreme case the O^{2-} would be insoluble and we would find

$$n_o \approx n_e = n_c . \quad 4.3$$

The PbO may dissolve as a neutral molecule. In this event the relative sizes of the atoms involved make it likely that the PbO will occupy two adjacent sites and no vacancies will form. The UV spectrum could show a distortion or shift of the peak at 273 nm due to the effect of the oxygen upon the lead. The conductivity would be that of a pure crystal. The concentration relationships would be

$$n_e \gg n_c . \quad 4.4$$

The relationship of n_e to n_o is not easily predicted.

Holmes (14) found that the thermal history of the lead doped crystal effected the UV absorbtion quite strongly. He found that quenching of the crystal from high temperatures was needed to get maximum peak height at 273 nm. Holes also found that the presence of oxygen in the crystal caused suppression of the absorption band. For these reasons we cannot expect the concentration as determined optically to be the same as determined chemically, unless oxygen is strictly excluded and proper quenching methods are used.

None of the above allow for any contribution of the divalent anions to the extrinsic conductivity. The second term of equation 1.5

is still not needed to describe the system. Therefore, in this study no conclusions can be drawn about Δg_{α} . Some conclusions can be drawn about n_{α} from the optical and the conductivity data.

V. EXPERIMENTAL

Preparation of Materials

In research on the electrical properties of solids, the preparation of materials is of major importance.

The crystals used in this project were grown in quartz tubes. The PbCl_2 and PbO were prepared in Vycor tubes. It was found that improperly cleaned glassware had a very deleterious effect upon the results and so an adequate cleaning procedure was important. Two methods were satisfactory. In the first method the glass was soaked for several hours in aqua regia and then repeatedly rinsed with distilled deionized water. In the second method the glass was soaked for several hours in alcoholic KOH and rinsed repeatedly with distilled water. It was then soaked in hydrochloric acid for several hours and then repeatedly rinsed with distilled deionized water. In both procedures should any water bead on the surface the whole procedure was repeated. The glass was then dried in a drying oven and stored. In all cases if the glass was not used within five days it was cleaned again.

The method of purifying KCl was developed by W. J. Fredericks and his colleagues and is described elsewhere (7). Only an outline of the process will be given here.

A 20 percent solution of reagent grade, thallium free KCl in distilled deionized water was passed over Chelex 100 cation chelating resin which was in the potassium form. This resin removed most of the undesirable cations. The resulting solution was then passed over AG2-X10 anion exchange resin which was in the chloride form. This resin removed most of the undesired anions. The resulting high purity KCl solution was evaporated to dryness and stored.

Reagent grade $\text{Pb}(\text{NO}_3)_2$ was dissolved in distilled deionized water and the PbCl_2 was precipitated with reagent grade hydrochloric acid. The precipitate was filtered and repeatedly washed with distilled deionized water. The washed PbCl_2 was transferred to an evaporating dish and dried in the drying oven. The dry PbCl_2 was then transferred to a Vycor tube which had two constrictions spaced equally along it. The PbCl_2 was vacuum dried. The PbCl_2 was next distilled through the constrictions with a stream of HCl gas. The distilled PbCl_2 was sealed in the third section of the Vycor tube under about a third of an atmosphere of HCl.

Reagent grade $\text{Pb}(\text{NO}_3)_2$ was again dissolved in distilled deionized water and $\text{PbO} \cdot \text{H}_2\text{O}$ was precipitated by the addition of reagent grade KOH. The $\text{PbO} \cdot \text{H}_2\text{O}$ was filtered and washed repeatedly with distilled deionized water. The slurry of $\text{PbO} \cdot \text{H}_2\text{O}$ was next placed in a Vycor tube and dried under a vacuum. The vacuum was first drawn by a water aspirator and then by a mechanical pump which was

protected by a liquid nitrogen trap. The dry $\text{PbO} \cdot \text{H}_2\text{O}$ was converted to PbO by quickly heating it to 600°C under vacuum. The vacuum was maintained by the mechanical pump. Lead hydroxides and all other lead oxides are unstable with respect to PbO at temperatures above 550°C (23, p. 688).

All crystals were grown by the Stockbarger method using existing apparatus; only the method of drying and doping¹ will be given here. Pure KCl was placed in a quartz tube and heated to 200°C . It was left at this temperature for a few hours under an atmosphere of HCl . The HCl was evacuated with the water aspirator which was now protected with a liquid nitrogen trap. The process was repeated at 400°C and again at 600°C . The KCl was then melted and an atmosphere of Cl_2 was introduced. After a few minutes this was drawn off by a water aspirator and HCl was introduced. The HCl was then drawn off and the Cl_2 added. This procedure was repeated several times. The final application of gas was a mixture of the two and was applied for several hours. The Cl_2 oxidizes certain impurities while the HCl removes traces of water. The oxidized impurities and the water were evaporated out of the molten KCl . The mixture was drawn off first with the water aspirator and then by the mechanical pump. In all pumping operations a liquid nitrogen trap was maintained

¹A doped crystal is a crystal to which some impurity has been intentionally added. The impurity added is referred to as the dopant.

between the pump and the vacuum system. This protected the pumps and prevented back diffusion of oil or water. Since, even with trapping, these gases may corrode the mechanical pump, the mechanical pump was used during the final pumpdown only and then just for two minutes. Care was exercised to remove the Cl_2 and the HCl as either of these gases react with PbO .

If at this time an undoped crystal was wanted the quartz tube was sealed under vacuum and transferred to the crystal growing furnace. If a doped crystal was wanted the PbCl_2 or PbO was now added. The dopant was added by the doping unit shown in Figure 2. One end of the bore of stopcock A was plugged with epoxy glue. The dopant was pored down tube C into the empty half of the plugged stopcock and the stopcock turned 180° . The dopant would then fall onto the molten KCl . The amount of dopant added was uncertain because an indeterminate amount of it remained in the stopcock, clung to the curve of the glass tube or landed on the shoulder of the quartz tube. After the dopant was added the quartz tube was sealed under vacuum. It was then inverted two times to insure a good mix of KCl and dopant and the tube transferred to the growth furnace.

About 36 hours were required to grow a crystal. The tube was then removed from the furnace, broken and the crystal removed. The crystal was next annealed in a vacuum by heating it at 600°C for a few hours and then slowly cooling it to room temperature. The annealed

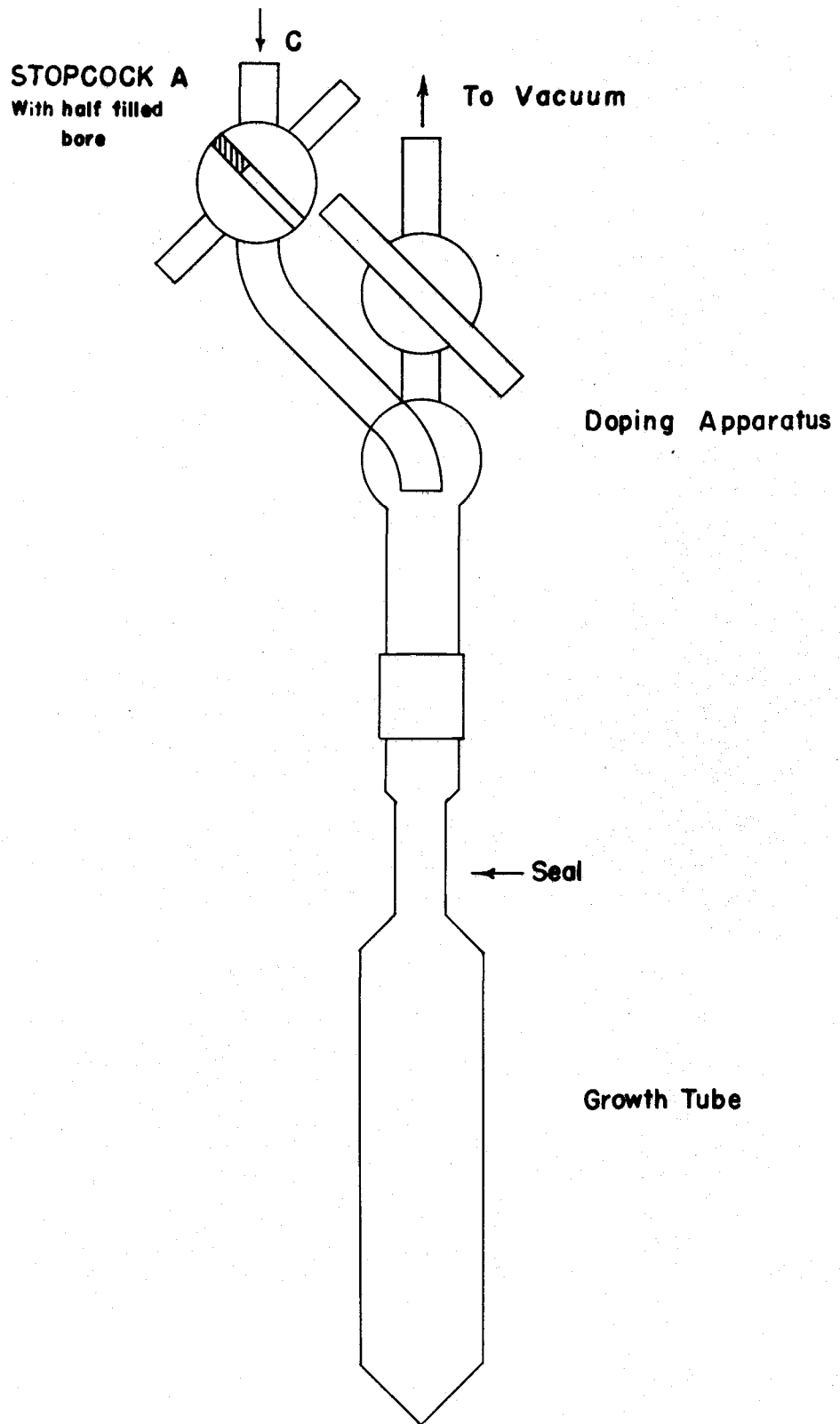


Figure 2. Arrangement of doping apparatus and crystal growth tube.

crystal was cleaved and stored in a desiccator.

After an absorption spectrum was taken, carbon electrodes were applied to the crystal. Carbon was selected for the electrodes because of the work of Mikata, Sano and Tomiki (22) and of Sano and Tomiki (25). These workers found that carbon, of all the electrode materials commonly used, gave reversible results for the conductivity measurements. In this laboratory carbon offers an additional advantage because the contacts in the conductivity cell were graphic and junctions of different materials were avoided.

Carbon was plated onto the crystal using existing apparatus. Most of the surface moisture was removed by drawing a high vacuum with the oil diffusion pump and maintaining it for 24 hours as it was found that small traces of moisture on the crystal surface would prevent the carbon from adhering. The carbon was then evaporated onto the surface from an 1/8 inch carbon rod (United Carbon Co., Spectrographic grade "A").

One side of the crystal was covered with carbon as a continuous electrode. The other electrode was divided into two areas by placing a stainless steel ring on the crystal prior to plating as shown in Figure 3. The inner circle, used as the pickup electrode, had an area of 0.552 cm^2 , which is A of equation 2.1. The outer area was grounded. This arrangement eliminated most of the noise of the system. After plating the crystal edges were cleaved so that the

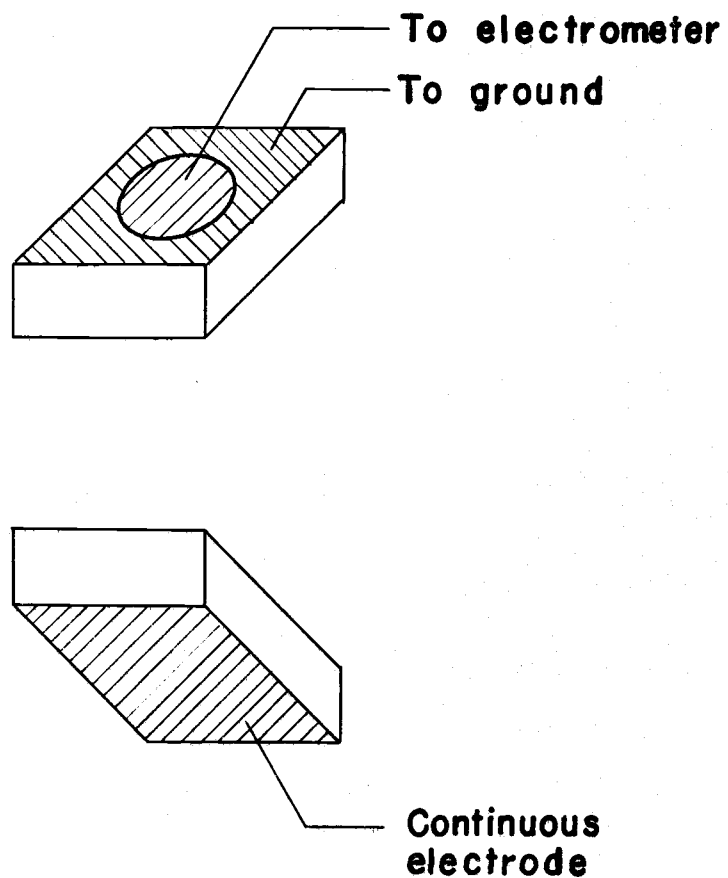


Figure 3. Arrangement of the electrodes on the crystal. Two views of the same crystal.

electrodes were insulated from each other.

Measurements

Prior to carbon plating the UV absorption spectrum was taken using a Perkin-Elmer model 450 UV-Visible-NIR Spectrophotometer. The lead concentration was estimated by means of the equation

$$n_o = (1.076 \times 10^{16}) A_m \text{ cm}^{-3} \quad 5.1$$

where A_m is the absorbance per cm at the peak of the absorption band at 273 nm. This equation is an adaptation of the work of Sibley, Sonder and Butler (27).

After the UV spectrum had been taken and the carbon electrodes applied the conductivity was measured.

The conductivity cell used in this study was designed by R. E. Seevers (26, p. 26-29).

A high vacuum was drawn in the cell and maintained for several hours to remove most of the water which might be in the cell. Next, dry argon was admitted until a slight positive pressure was in the cell. The cell with the crystal was heated. The lower portion was about 300°C and the upper portion was about 75°C. The hot argon was then drawn off and a high vacuum again drawn and maintained until the cell cooled to room temperature. Dry argon was again admitted to a positive pressure and the cell put into the furnace for

conductivity measurements. This procedure for drying the cell was developed by Allen (1).

The furnace used for the conductivity measurements was a Marshall Metallurgical testing furnace controlled by a model 407 Wheelco temperature controller and a Barber-Coleman mode 620A power controller.

Ghita and Hauret (12) showed by optical measurements that heating a lead doped crystal to about 350° C and leaving it at this temperature for about eight hours would cause most of the lead ion vacancy complexes to dissociate. Accordingly, the cell and crystal were left for eight hours at this temperature prior to making the conductivity measurements. Except for a single crystal of undoped KCl all conductivity measurements were made with 350° C as the initial temperature. The one undoped crystal had an initial temperature of about 175° C.

Figure 4 shows a diagram of the circuit used to measure the conductivity. A Keithly model 240A high voltage power supply provided the potential and the current was measured with a Keithly model 610A electrometer. The conductivity was calculated in accordance with equation 2.1. The temperature was measured with a chromel-alumel thermocouple calibrated by R. E. Seevers (26) at the ice point, the steam point and the freezing points of cadmium and aluminum. The temperature of the cell was increased 20° to 25° C

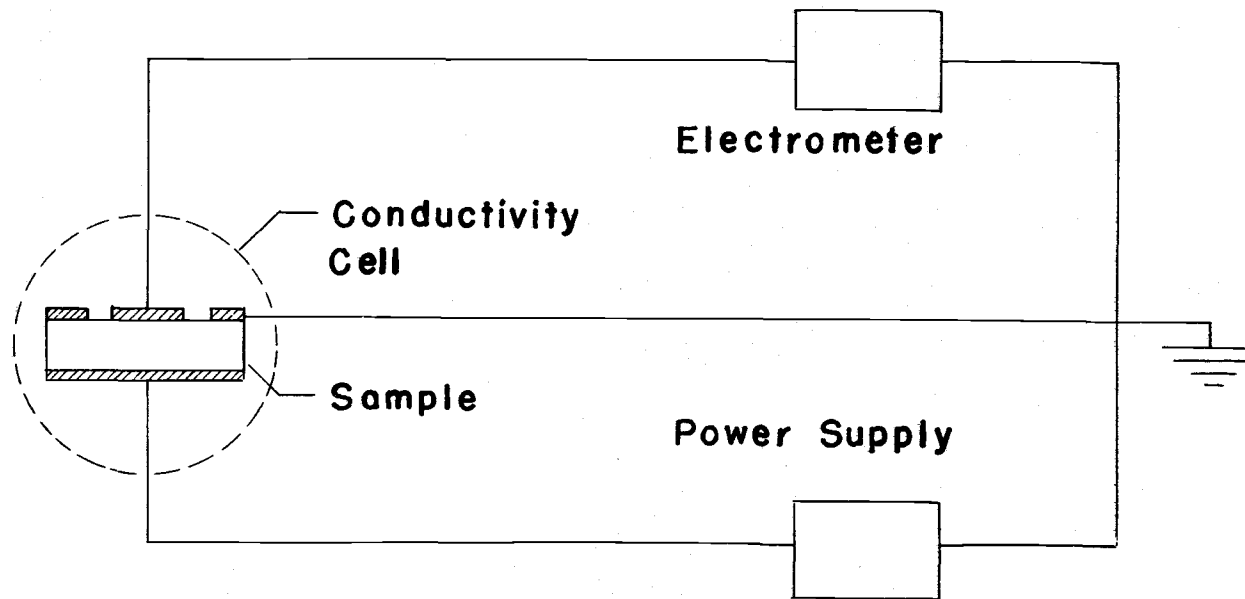


Figure 4. Circuit diagram of conductivity apparatus. Adapted from SeEVERS (26 p. 45).

after each measurement until a few points of the intrinsic curve were determined. The temperature was then lowered 20° to 25° C and the conductivity again determined. The process was continued until the initial temperature was reached. Except for the crystals of undoped KCl only a few data points were taken of the intrinsic conductivity because the temperatures were high enough that plastic deformation of the crystal could occur.

At frequent intervals during the run the electrodes were tested to see that they were ohmic and nonrectifying. The former was tested by increasing the voltage and seeing that the conductivity was constant. The latter was tested by reversing the potential and seeing that the conductivity was constant.

After the conductivity measurements the crystals were dissolved in distilled deionized water. KCl from the stock KCl used to grow the crystals was added until the solutions were one molar in KCl. The resulting solutions were analyzed for total lead content by the hanging drop rapid scan polarographic technique. The solutions were stripped for ten minutes by applying a potential of +1.5 volts. A conventional rapid scan was done next. The scan was started at -0.3 volts, decreased to -1.3 volts and back to -0.3 volts. Total scan time was two seconds. The current voltage relationship was displayed on a storage oscilloscope and photographed.

The oscilloscope was a Tektronic type 564 storage oscilloscope

with a Tektronic type 205 polarographic time base and a type 300 polarographic amplifier. The time base supplied the potential for both stripping and scanning. The camera was an Annalab type 3000 series single frame oscilloscope camera with a Polaroid-Land back. The film was Polaroid type 47 film.

A Hewlett-Packard Calculator model 9100A was used for the calculations.

VI. DISCUSSION OF ERROR

The applied voltage is known to be within one percent. The electrometer is accurate to three percent of a full scale deflection. This could lead to an error of 12 percent on some measurements. Temperature is within one degree.

The intersection of the extrinsic unassociated and the intrinsic curves is difficult to locate because of the curvature at this portion of the graph. This could lead to an error of about five percent in estimation of total divalent ion concentration.

It was found late in the research that the spectrophotometer was not linear in absorbance. The amount of nonlinearity was variable and intermittent. However, the error was less than five percent.

The polarographic analysis was subject to several sources of error. The hanging drop was changed after each determination and so the drop area was changed. Forming of the drop and attaching it to the gold electrode wire was standardized and the error due to area change was held to a minimum. The oscilloscope had a constant charging error which became relatively large as the concentration decreased. Reading the peak height introduced error due to the width of the trace. At low concentrations the base line was poorly defined. The error at low concentration was about ten percent and at high concentration the error was about two percent.

A source of error, which cannot be reliably assessed, arises from differences in history of the crystals. For example, the Stockbarger crystal growth method puts strains into the crystal which are not fully relieved by annealing. These strains are then relieved somewhat during the conductivity measurements and the measurements effected in an unpredictable manner.

Considering the above sources and estimates of error, it is concluded that the error in determining concentration by means of electrical conductivity probably does not exceed 20 percent, while that in determining concentration by chemical means probably does not exceed 15 percent.

VII. RESULTS AND DISCUSSION

The conductivity of four crystals of KCl:Pb^{2+} , four crystals of KCl:PbO and two crystals of pure KCl was studied. The results for KCl:Pb^{2+} are shown in Figure 5 and the results for KCl:PbO are shown in Figure 6. On each figure the results for the pure KCl crystals are shown.

Pure KCl Results

Pure KCl crystals, having a thickness of 6.2 mm or 3.4 mm, showed no observable absorbance due to impurities in the range of 200 nm to 400 nm. Noise in the background absorbance was such that any absorbance peak greater than 0.005 above background would have been distinguished.

The knee temperature for both crystals is 440°C . Only a few data points could be taken for crystal 2 and so the value for Δh_π is not reliable even though it compares quite well with the value for crystal 1.

Beaumont and Jacobs (4) and Fuller and Reilly (10) both point out that the intrinsic curve deviates from a straight line. They attribute this effect to the contribution of the anion vacancies to the conductivity. For this reason, values for Δh_s extracted from such curves are inaccurate. The results of these two crystals, which

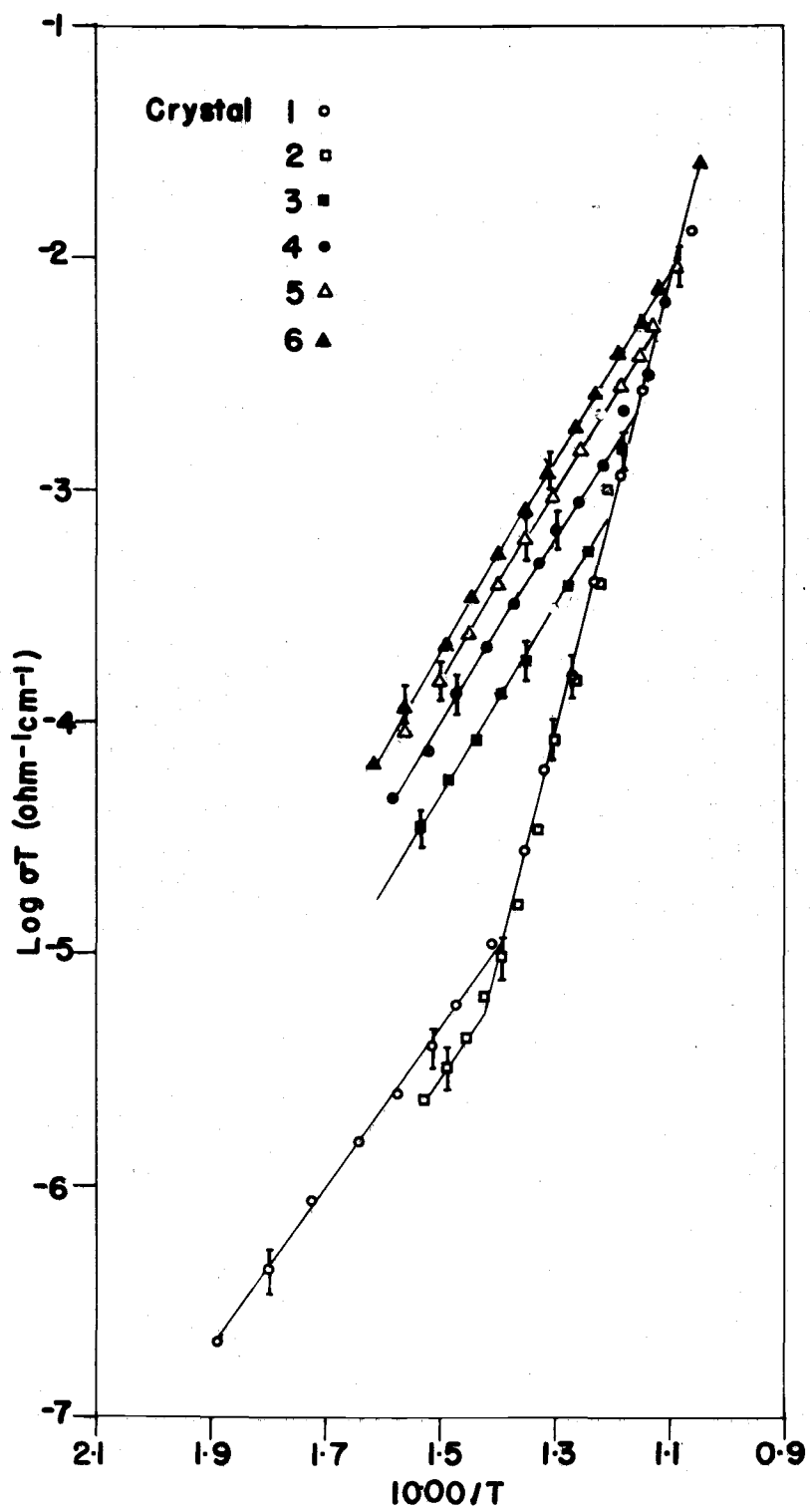


Figure 5. Conductivity curves for the KCtPb^{2+} crystals and the undoped crystals. Vertical lines show 20 percent error.

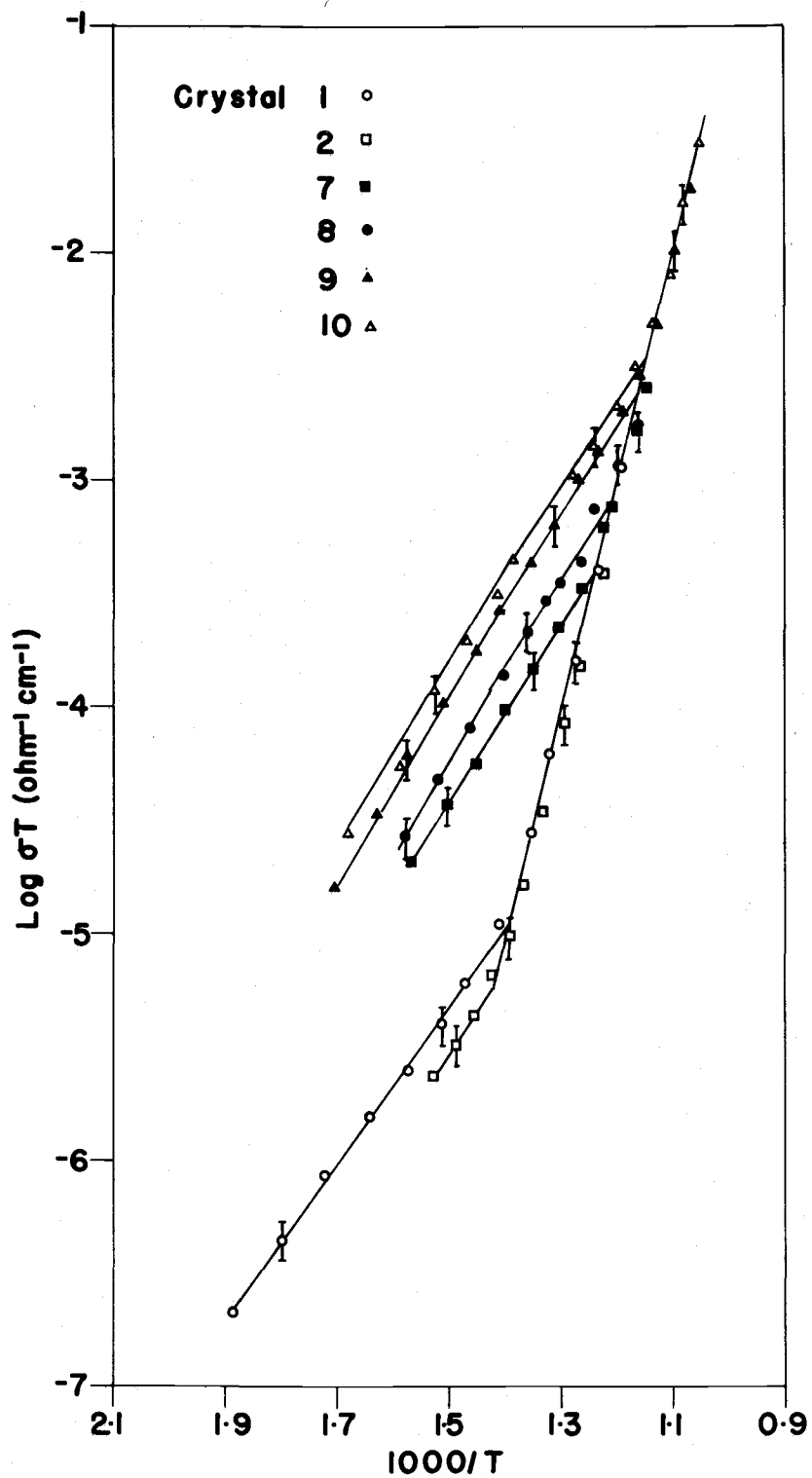


Figure 6. Conductivity curves for the KCl:PbO crystals and the undoped crystals. Vertical lines show 20 percent error.

agree quite well with each other, are tabulated in Table 1.

Table 1. The results of the conductivity measurements on pure KCl.

Crystal	Starting Temperature	Knee Temperature	h	h_s
1	175°C	440°C \pm 5°	-0.71 ev	-2.26 ev
2	350°C	440°C \pm 5°	-0.74 ev	-2.20 ev

The computer fit a Least-Squares equation of the form

$$\sigma T = B \exp(\Delta h/kT) \quad 6.1$$

to the experimental data. The best fit to the experimental intrinsic points for crystal 1 was

$$\sigma T = (1.10 \times 10^8) \exp(-1.84 \text{ev}/kT) \quad 6.2$$

and the best fit to the experimental intrinsic data for crystal 2 was

$$\sigma T = (2.26 \times 10^8) \exp(-1.88 \text{ev}/kT) \quad 6.3$$

The exponential term of equation 6.2 agrees quite well with the value found by Fuller and Reilly (14) and so equation 6.2 was used to calculate the intrinsic contribution to the experimentally observed conductivity in the extrinsic range. An example of the corrections made is given in Table 2.

Table 2. Experimental and corrected values of σT . Included is an example of the computer output. Example is taken from crystal 5.

σT Experimental	σT Corrected	Temperature °C	Output of the computer showing the parameters of the Least-Squares fit to the corrected σT
4.07×10^{-4}	3.97×10^{-4}	444	R: 0.999
6.40×10^{-4}	6.13×10^{-4}	468	Δh : -0.72 eV
9.61×10^{-4}	8.88×10^{-4}	494	B: 48.3
1.54×10^{-3}	1.34×10^{-3}	524	
2.16×10^{-3}	1.72×10^{-3}	547	

The KCl:Pb²⁺ Results

The results of the various measurements made on the KCl:Pb²⁺ crystals are tabulated in Table 3. The concentration of lead in each crystal as determined by various methods agree within the experimental error. The greatest variation is between the electrically and the chemically determined concentration. The total divalent ion concentration, as determined electrically, was calculated for each crystal by means of equation 3.26.

The KCl:PbO Results

The electrically and chemically determined concentrations agree well with each other. The values for Δh_{π} agree well with the results for a pure crystal. Table 4 is a tabulation of the

Table 3. The results of the measurements made upon the four KCl:Pb^{2+} crystals.

Lead Concentration $\times 10^{-16}$, cm^{-3}			$\frac{n_e - n_o}{n_e}$	$\frac{n_e - n_a}{n_e}$	Δh_π , ev
(Electrically)	(Optically)	(Chemically)			
2.4	2.4	2.2	0.00	0.1	0.75
5.4	5.0	5.7	0.07	-0.1	0.73
11.0	10.4	11.6	0.06	-0.1	0.72
14.1	13.6	14.9	0.04	-0.1	0.73
Average:			0.04 ± 0.12	-0.05 ± 0.15	

Table 4. The results of the measurements made upon the four KCl:PbO crystals.

Lead Concentration $\times 10^{-16}$, cm^{-3}			$\frac{n_e - n_o}{n_e}$	$\frac{n_e - n_a}{n_e}$	Δh_π , eV
(Electrically)	(Optically)	(Chemically)			
1.6	1.1	1.3	0.3	0.3	0.72
3.3	2.6	3.3	0.2	0.0	0.72
5.9	3.8	6.1	0.4	0.0	0.72
6.3	4.2	6.2	0.3	0.0	0.72
Average:			0.3 ± 0.12	0.07 ± 0.15	

measurements made on the KCl:PbO crystals.

Association of Lead Ion and Its Vacancy

Although the initial starting temperature of 350°C was chosen to minimize the ion-vacancy association, some association did remain. An estimate of Δh_{ca} can be made from the data by means of equation 3.24. The data points are few and so, although the least squares program fit an equation to the data very well, any estimate of Δh_{ca} is inexact. The lowest concentration of both the KCl:Pb²⁺ series (crystal 3) and the KCl:PbO series (crystal 7) did not yield a value of Δh_{ca} as the concentration of complexes was negligible at the temperatures of interest. Table 4 is a tabulation of the estimates of the association enthalpy.

Ultraviolet Absorption Results

The half width of the 273 band in all crystals, except the highest and lowest lead concentration (crystals 6 and 7) were in agreement with each other (both KCl:Pb²⁺ and KCl:PbO). Table 5 is a tabulation of the half width results for all crystals. The band shape at 273 nm is probably not affected by the possible presence of oxygen in the crystals and estimation of lead concentration will be affected only by a change in oscillator strength.

In the KCl:PbO crystals the absorption on the short

Table 5. The estimates of the enthalpy of divalent cation-vacancy association.

Crystal	Lead Concentration (Electrically) $\times 10^{-16}, \text{cm}^{-3}$	$\Delta h_{ca}, \text{ev}$
3	2.4	-----
4	5.4	-0.26
5	11.6	-0.28
6	14.1	-0.30
7	1.6	-----
8	3.3	-0.22
9	5.9	-0.24
10	6.3	-0.26

wavelength side of the lead peak was greater than zero. In some crystals there was a slight peak at about 250 nm. This was suggestive of the presence of the superoxide ion, which has a very broad absorption peak at 250 nm.

One annealed KCl:PbO crystal was tested to observe the effects of thermal history upon UV absorption. An absorption spectrum was taken and the crystal heated to 600°C. After a few minutes at this temperature it was quenched to liquid nitrogen temperature and another absorption spectrum taken. The lead concentration was estimated by means of equation 5.1 for each spectrum. The annealed but not quenched concentration was $4.23 \times 10^{16} \text{cm}^{-3}$ while the annealed and quenched concentration was $6.42 \times 10^{16} \text{cm}^{-3}$. The

band width for the peak at 273 nm became narrower (Table 6) but not enough to account for the increase in the height of the absorption band.

Calculating the ratio

$$\frac{6.42 - 4.23}{6.42} = 0.34$$

we see that it is approximately the same as the ratio

$$\frac{n_e - n_o}{n_e}$$

for the KCl:PbO crystals as given in Table 4.

Table 6. The half width values of the crystals for the absorption at 273 nm.

Crystal	Lead Concentration (Electrically)	Half Width, ev
	$\times 10^{-16}, \text{ cm}^{-3}$	
3	2.4	0.082
4	5.4	0.083
5	11.0	0.082
6	14.1	0.089
7	1.6	0.077
8	3.3	0.080
9	5.9	0.082
10	6.3	0.082
	(Optically)	
11	4.23 (before quenching)	0.089
	6.42 (after quenching)	0.081

Holmes (14) and Sibley et al. (34) report an oscillator strength of 0.11. These investigators used very pure salt and carefully excluded oxygen. Holmes quenched his to liquid nitrogen temperature. Kaifu (16), on the other hand, did not take special precautions to exclude oxygen and reported an oscillator strength of 0.075. Calculating the relative effect of oxygen upon the oscillator strength as

$$\frac{0.11 - 0.075}{0.11} = 0.32$$

which is approximately the same as the ratios listed above.

Conclusions

Since, in KCl:PbO, the concentration of Pb^{2+} as determined electrically (upon the assumption that every Pb^{2+} ion is compensated by a cation vacancy) is equal to the concentration determined by chemical analysis, it is concluded that lead is not appreciably compensated by O^{2-} in these crystals. The estimated uncertainty in the relative difference $[(n_e - n_a)/n_e]$ was calculated from the estimated error in the electrical, optical, and chemical determination of concentration as follows. Since n_e and n_a are subject to errors estimated as 20 percent and 15 percent, respectively, the estimated extreme limits for the relative difference $(n_e - n_a)/n_e$ are given by $(1.20 - 0.85)/1.20$ and $(0.80 - 115)/0.80$, or +0.29 and -0.44. The mean of these residuals is ± 0.37 . The error in the mean of four

measurements is given by

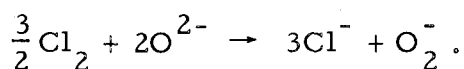
$$P = 0.68 \frac{4(0.37)^2}{(4)(3)}^{1/2} = 0.15 . \quad 6.4$$

We see, consequently, that compensation of up to around 15 percent of the lead ions by oxide could occur and still escape detection.

The mean value of the relative difference involving n_o , for which the estimated error is ten percent, is found in the same way and is subject to a probable error of 0.12. Clearly the result here, which is positive, is not indicative of compensation.

Two possible mechanisms which would account for the data are as follows. First, oxide has a low solubility in KCl (19, p. 230) and so more lead than oxide would dissolve in the crystal. Only a small amount of oxide would be present.

Second, the Cl_2 gas used to oxidize the impurities is somewhat soluble and so a small amount could be still dissolved in the KCl when the PbO was added. The Cl_2 could react with the O^{2-} to form the soluble superoxide, according to



The amount of superoxide incorporated can only be a trace because only slight evidence of O_2^- in the UV absorption was noted in the KCl:PbO crystals. Clearly, O_2^- would not serve to compensate Pb^{2+} because of its unit charge.

The presence of any oxygen in the crystal would have an effect upon the oscillator strength, since, as already noted, Holmes (14) found that quenching was necessary to get maximum oscillator strength. Since the KCl:PbO crystals used in these experiments were annealed, the optically determined concentration should be less than the electrically or chemically determined concentrations, provided they contain some oxygen. The evidence favors the conclusion that oxygen in some form is incorporated into the KCl:PbO crystals.

In summary we find that lead was not appreciably compensated by the oxygen. Some trace of oxygen, perhaps as a superoxide, appears to be present to suppress the oscillator strength. The mechanism of suppression is at present unknown.

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