

PREPARATION AND PROPERTIES OF CRYSTALLINE  
POTASSIUM CHLORIDE CONTAINING  
TRIVALENT CATION IMPURITIES

by

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PREPARATION AND PROPERTIES OF CRYSTALLINE  
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I. INTRODUCTION

Color Centers in KCl  
Crystals (41, p. 384-385, 400)

If a potassium chloride crystal is heated in alkali metal vapor it becomes colored. The resulting absorption band is called the F band and the absorption is said to be due to F centers. At room temperature the F band occurs at 560 mμ (millimicrons). According to the commonly accepted model the F center is composed of an electron trapped at a negative ion vacancy. Illumination of the colored crystal with light lying in the F band results in the formation of other absorbing centers and their accompanying absorption bands. Among these are the  $R_1$ ,  $R_2$ , and M bands.

Color Centers in KCl Crystals Containing  
Small Amounts of Alkaline  
Earth Chlorides (31, p. 73-83; 43)

If the potassium chloride crystal is not pure, but contains divalent ions of calcium, strontium, or barium, irradiation in the F band results in a new band lying on the long wavelength side of the F band. This



band is called the  $Z_1$  band. At room temperature the F and  $Z_1$  bands are not resolved; at  $-215^\circ\text{C}$  they are resolved and the  $Z_1$  band lies at 590 to 600 m $\mu$  depending upon the particular alkaline earth. If the crystal is then heated to about  $110^\circ\text{C}$ , the  $Z_1$  band is destroyed, the F band enhanced, and a new band, termed the  $Z_2$  band, appears. This band also lies on the long wavelength side of the F band. At  $-215^\circ\text{C}$  it occurs at 610 to 650 m $\mu$  depending upon the nature of the impurity. The heating of a crystal possessing a  $Z_2$  band results in the destruction of the band. If a crystal containing F and  $Z_2$  bands is irradiated at  $-90^\circ\text{C}$  with light lying in either band, two new bands appear -- the F' band and the  $Z_3$  band. The F' band occurs in suitably treated pure KCl; the  $Z_3$  band does not. The  $Z_3$  band lies on the short wavelength side of the F band.

Both Pick (31, p. 81 ) and Seitz (43) have proposed models for the Z centers. These are shown in Figure 1. A plus sign stands for a potassium ion, a minus sign for a chloride ion, and a double plus sign for a divalent cation. A plus or minus sign enclosed in a square indicates that the ion represented is missing -- that is, a vacancy exists. Electrons are denoted by e's.



Chiarotti, Fumi, and Giulotto (7, p. 317-320) have studied KCl:Sr crystals (KCl crystals containing small amounts of strontium chloride). They developed the  $Z_2$  band, bleached it with polarized light lying in the  $Z_2$  band, and measured the absorption using polarized light. Within the limits of experimental error they found no dichroism. This indicates that the center has cubic symmetry; however, they did not conclude that Seitz's model of the  $Z_2$  center is incorrect because the magnitude of the effect for which they were looking was not known and because of the possibility that the plane of the  $Z_2$  center may lie in the (110) rather than the (100) plane of the crystal.

West and Compton (47) investigated the luminescence of Z centers in KCl:Sr crystals. They excited the  $Z_2$  center with polarized light and studied the polarization of the emission from the center. They found the emission to be unpolarized, which again indicates that the  $Z_2$  center is a center of high symmetry. Hence, Pick's model of the  $Z_2$  center is in better agreement with the experimental data of West and Compton than is the model proposed by Seitz.

Both the Italian investigators (7, p. 317-320) and West and Compton noted that, as predicted by Seitz,

$Z_2$  centers were formed directly by slowly cooling the crystal from the temperature of additive coloration. Remaut and Dekeyser (35) studied the bleaching of the  $Z_2$  band in NaCl:Sr with polarized light and found that the absorption measured with light polarized in the same direction as the bleaching light showed the greatest decrease. Since there is experimental evidence in agreement with both the models proposed by Pick and those proposed by Seitz, both sets of models will be considered later in connection with possible bands arising due to the incorporation of trivalent impurities in KCl crystals.

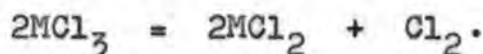
The models of both Pick and Seitz depict the divalent ions as occupying substitutional positions in the KCl crystal and not interstitial positions. Pick and Weber (32) determined the differences in density existing between pure KCl and KCl containing known amounts of calcium or strontium and plotted this density difference as a function of the impurity content. This is shown in Figure 2. The experimentally determined function (solid line) was then compared with the function that would result if the divalent ion occupied a site normally occupied by a potassium ion and if a positive ion vacancy was also created; this function is represented by a

dashed line. The hyphenated line shows the density change expected if the densities are simply additive. The good agreement shown by the solid and dashed lines is usually cited as indicating that the divalent ions enter the crystal in substitutional positions. However, the dashed line also represents the density change expected if the divalent ions occupy interstitial positions and two positive ion vacancies are created for every divalent ion introduced. In both cases two potassium ions are replaced by one divalent ion. All calculations were made on the assumption that the lattice parameter did not change. Pick and Weber pointed out that the difference between the experimental and predicted curves could be explained by assuming that some of the calcium chloride separated out of the KCl to form submicroscopic particles. Seitz (42, p. 12 ) has suggested that this difference may be explained by assuming that the incorporation of the divalent ions causes the lattice to shrink. A shrinkage of the lattice seems more compatible with the interpretation that the divalent ions occupy substitutional positions than with the interpretation that they occupy interstitial positions. To this extent the density data is in agreement with the assignment of divalent cations to substitutional positions.

We would like to propose that the data of Pick and Weber may be used to show that the calcium is incorporated into the KCl crystal as a divalent ion and not as a monovalent ion. The dotted line in Figure 2 shows the density change expected if the calcium in the crystal is in the +1 oxidation state. It is seen that the agreement between the experimentally determined line and that for divalent calcium is much better than that between the experimental line and that for monovalent calcium.

#### Objective of Present Work

It is of interest to consider what the result of incorporating trivalent cations into KCl crystals might be. It is possible that upon coloration such crystals would exhibit absorption bands analogous to the Z bands in that an electron might become trapped at the trivalent ion. On the other hand, it is possible that foreign ions added to the melt in the +3 oxidation state would be incorporated into the crystal in the +2 oxidation state as a result of the following reaction:



If this occurred, then coloration of such crystals might

result in a center consisting of a divalent ion and a trapped electron. Such centers would be essentially monovalent ions imbedded in potassium chloride and would be strictly analogous to some of the Z centers.

It is to be expected that, in general, the incorporation of impurity ions in KCl crystals grown from melts to which trivalent chlorides had been added would, regardless of the oxidation state of the impurity in the crystal, upon coloration give rise to new absorbing centers whose relationship to each other might be studied and for which it might be possible to deduce models. The object of the present work is the preparation of KCl crystals (single) containing ions of the Group III elements and the investigation of the optical absorption and ionic conductivity of such crystals.

#### Valency of Group III Elements in KCl Crystals

The specification of any model of a light absorbing center containing an impurity ion will include the charge on the impurity ion as an important characteristic. Although it might be possible to specify this charge, i.e., the valency of the ion, by considering the behavior of the absorption bands, it seems



highly desirable to determine the charge in a more direct manner.

Ionization Potentials (23, p. 295-298)

An indication of the oxidation state in which ions are likely to be incorporated into KCl crystals may be obtained from a consideration of the ionization potentials of the impurities. Knowledge of the valency is attained by calculating the net energy change involved in transforming a crystal containing impurity ions in one oxidation state to a crystal containing the ions in a different oxidation state. Lidiard has considered the processes and energy changes involved in transforming a KCl crystal containing  $\text{Ca}^{++}$  ions to one containing  $\text{Ca}^+$  ions.

Following Lidiard, one may calculate the energy change accompanying the transformation of a KCl crystal containing trivalent cations ( $\text{M}^{+++}$ ) to one containing divalent cations ( $\text{M}^{++}$ ). If two molecules of  $\text{MCl}_3$  are added to a perfect KCl crystal, six new cation and six new anion sites are created. If two molecules of  $\text{MCl}_2$  are added to a perfect KCl crystal, four new cation and four new anion sites are created. The second crystal may be obtained from the first one by performing the

processes listed below. Plus and minus signs are used in the conventional thermodynamic manner.  $N$  is the potential energy difference between the  $M^{++}$  ion in the crystal and the  $M^{+++}$  ion in the crystal;  $N$  includes energy terms associated with the repulsive, van der Waals, and coulombic forces.  $I$  is the ionization potential (third in this case) expressed in ev (electron volts).  $W_L$  is the average lattice energy per ion pair.

Process	Energy Change
1. Removal of two chloride ions from the crystal.	$2W^-$
2. Removal of one electron from each chloride ion.	$2A$
3. Combination of the two chlorine atoms to yield a chlorine molecule.	$-F$
4. Placement of the two electrons obtained from the chloride ions on the metal impurity ions. $2M^{+++} + 2e \rightarrow 2M^{++}$	$-2I + 2N$
5. Removal of the two pairs of vacant sites from the crystal.	$-2(W^+ - W^- - W_L)$

The Summation of the energy changes gives the net energy change,  $\Delta E$ .

$$\begin{aligned}\Delta E &= 2W^- + 2A - F - 2I + 2N - 2(W^+ - W^- - W_L) \\ &= 2A - F - 2I + 2N - 2W^+ + 2W_L\end{aligned}$$



If  $\Delta E$  is positive the impurity ions will enter the crystal as trivalent ions. If  $\Delta E$  is negative they will enter as divalent ions. The  $\Delta E$  is exactly the same as that for the transformation of a KCl crystal containing  $\text{Ca}^{++}$  ions to one containing  $\text{Ca}^+$  ions.

Lidiard has calculated the energy changes accompanying the reduction of several divalent ions to monovalent ions in NaCl and KCl. He further calculated the values which the second ionization potential must not exceed in order that the reduction of the divalent ion to a monovalent ion will not occur. For  $\text{Cd}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Sr}^{++}$  in KCl these values are 22.8, 22.7, and 21.5 ev, respectively. Since, except for host lattice displacements, the ionization potential is the only quantity in the expression for the net energy change which depends specifically upon the impurity ion, an indication of whether a normally trivalent ion enters a KCl crystal as a divalent ion may be obtained from a comparison of the third ionization potentials of the impurity elements with the limiting value which Lidiard had calculated, namely, about 22 ev. In Table I are shown the third ionization potentials of elements that usually exhibit a +3 oxidation state.

Table I (18, p. 200-201)

Element	Third ionization potential, ev
Al	28.4
Sc	24.8
Ga	30.7
Y	20.5
In	28.0
La	19.2
Ce	19.7
Fe	30.6
Sb	24.8
Bi	25.6

The ionization potentials of the rare earths are not known very completely. However, because of the great similarity among the rare earths the third ionization potential of these elements is assumed to be approximately 20 ev. It is apparent from Table I that of elements known to possess stable +3 oxidation states probably only yttrium and the rare earths may exist in KCl as trivalent ions. Since Lidiard's treatment contains some approximations and since the value 22 ev is an average of the values for cadmium, calcium, and strontium, there is some doubt as to whether even yttrium and the rare earth elements can exist in KCl in the +3 oxidation state.

### Ionic Conductivity

Ionic conductivity measurements provide, for consideration, another approach to valency determination. However, in this case it is not possible to predict from published data whether the ions will be in the +3 or the +2 oxidation state in KCl, but only to calculate whether ionic conductivity measurements will allow a choice to be made between the two oxidation states.

Before the application of ionic conductivity

measurements to the determination of oxidation state is considered the chief features of ionic conduction in KCl will be outlined. As can be seen from Figure 11 (curve for KCl-18-A) a graph of the logarithm of the specific ionic conductivity against the reciprocal of the absolute temperature consists of two straight lines having different slopes. Thus the relationship between the specific ionic conductivity ( $\sigma$ ) and absolute temperature (T) may be represented by the equation

$$\sigma = A \exp (-E/kT),$$

with appropriate values of A and E for the different regions of the curve. The point at which the lines intersect is called the knee. The conduction above the knee is called the intrinsic conduction and is characteristic of pure KCl. The conduction below the knee is termed the impurity conduction and varies from specimen to specimen. In the intrinsic region both potassium and chloride ions take part in the transport of charge. With decreasing temperature the transference number of the potassium ion increases. The ions move through the crystal by moving from one vacancy to another. Since the number of vacancies is less than the number of ions, the number of vacancies and their mobility govern the

ionic conduction. Thus it is convenient to consider the electrical charge as being transported by the vacancies rather than by the ions. Aside from gross defects in a KCl crystal, such as large dislocations, there are two sources of vacancies. Some of the vacancies are generated thermally and some ("permanent") vacancies exist to counterbalance electrically the effect of impurities having oxidation states other than  $\pm 1$ . Even KCl crystals grown with great care contain some impurities as shown by the work of Duerig and Markham (10). At the melting point of KCl the number of thermally generated vacancies is about  $10^{18}/\text{cm}^3$  (42, p. 14). Since this number is considerably greater than the number of impurity ions, it is to be expected that at high temperatures the conduction will be limited by the thermally created vacancies while at low temperatures the contribution to conduction by the permanent vacancies will be more important than that by the thermally created vacancies. In the high temperature region the  $E$  in the expression for the specific ionic conductivity is the sum of the energy for the creation of vacancies and the energy of activation for jumping (vacancy motion). In the low temperature region the majority of the vacancies taking part in the transport of charge are permanent ones and

the  $E$  in the expression for the specific ionic conductivity is the energy of activation for jumping only. This is reflected in the smaller magnitude of the slope of the curve in the impurity conduction region. The position of the knee and the magnitude of the conductivity in the impurity region is related to the impurity concentration and valency.

The general mode of attack upon the problem of determining the oxidation state from conductivity data is as follows. If the impurity exists in the crystal in the +3 oxidation state and occupies a lattice position normally occupied by a potassium ion then two positive ion vacancies will be introduced for every impurity ion added. If it exists in the +2 oxidation state then only one positive ion vacancy will be introduced for every impurity ion added. Thus if the number of vacancies and the number of impurity ions can be determined or if the conductivity of crystals containing the ions in question can be compared with the conductivity of a crystal containing the same concentration of ions known to be divalent, it should be possible to calculate the valency of the impurity ion in the crystal. Let  $K_1$  represent the specific ionic conductivity of KCl crystals containing cations that



may be either trivalent or divalent. Let  $K_2$  represent the specific ionic conductivity of KCl crystals containing cations known to be divalent and at the same concentration as the ions whose valency is in question. Then, in the impurity conduction region,  $K_1/K_2 = 2$  if the ions whose valency is being determined are trivalent and  $K_1/K_2 = 1$  if they are divalent.

Before it is possible to conclude that ionic conductivity data can be employed to determine the valency of impurity ions in KCl crystals factors, other than the valency, which may affect the conductivity must be considered. The variation that may occur due to the specific nature of the impurity may be estimated from the data of Kelting and Witt (21, p. 706). At 372°C the conductivity of KCl:Ba is 0.70 that of KCl:Ca and the conductivity of KCl:Ba is 0.86 that of KCl:Sr. At 636°C the conductivity of KCl:Ba is 1.2 times that of KCl:Sr. Thus the variation due to the specific nature of the impurity rather than the valency, might easily account for 30% of the predicted difference between specific ionic conductivities of crystals containing divalent or trivalent cations. This is in the nature of a minimum value for the variability since the binding energy of trivalent ions and positive ion



vacancies may be rather different from that for divalent ions and positive ion vacancies. Hence it is not reasonable to attempt to conclude from ionic conductivity measurements whether the ions exist in the +3 or the +2 oxidation state in KCl.

### Density

It has been shown that neither the consideration of ionization potentials nor ionic conductivity is likely to permit the determination of the oxidation state of the incorporated impurity. The variation of density with impurity content will now be examined to determine whether it might provide a means of determining the valency of the impurity. Figure 3 shows the density change to be expected if an element having an atomic weight of 150 (a usable mean value for the atomic weight of the rare earth elements) is incorporated into the KCl crystal as the divalent ion or as the trivalent ion. The predicted density changes are calculated upon the assumption that the incorporation of the foreign ions does not lead to any change in the lattice parameter. It is seen that density measurements should permit the determination of the valency of the foreign ion. This type of determination has the advantage that the results

are not affected by the extent of binding between the foreign ions and positive ion vacancies, as are the results of ionic conductivity measurements. Such density measurements were not made during the present work.

#### Attempt to Predict Location of New Bands

As was mentioned previously the incorporation into KCl crystals of cations having a valency of two or three may lead to the formation of new absorption bands in colored crystals. Some consideration will now be given to the prediction of where such new bands might be located.

If it is assumed that the impurity ions are incorporated into the KCl crystal in the +3 oxidation state and that new bands arise from the formation of divalent ions upon coloration (and perhaps bleaching) then one may view the center as being hydrogen-like. However it should be noted that this likeness would be expected to be less for centers due to divalent ions of some Group III elements than for centers due to monovalent ions of Group II elements. The underlying (core) electrons of some Group III elements do not form a rare gas configuration; the underlying electrons of Group II elements form a rare gas configuration.

To date, attempts to calculate by such a point charge method the position of the Z bands of KCl containing small amounts of alkaline earth chlorides have not been successful. In view of this no attempt was made to calculate the expected position of bands due to trivalent impurities.

#### Prior Knowledge Concerning Trivalent Cations in Alkali Halides

There has been little reported work on trivalent cations in alkali halide single crystals. Hayes and colleagues (3, 16, 17) have studied the paramagnetic resonance, both before and after irradiation, of NaF single crystals grown from melts containing  $\text{Cr}^{+++}$ . They suggest that their results can be explained by assuming the chromium enters the lattice as  $\text{Cr}^{++}$  and becomes  $\text{Cr}^+$  upon irradiation. Schnerb and Bloch (39), working with KCl crystals grown from aqueous solution, found that  $\text{FeCl}_3$  causes deformation of the cubic form, resulting in opaque crystals. Schulze (40) considered the dependence of the ratio  $\text{Sm}^{++}/\text{Sm}^{+++}$  in KCl upon the concentration of the chlorinating atmosphere above the melt.

## II. EXPERIMENTAL

### Choice and Preparation of Trivalent Salts

Since it is an objective of this work to attempt to incorporate trivalent ions into KCl crystals grown from the melt, the requirements for the Group III elements to be used are that they have very stable +3 oxidation states, that the third ionization potentials be below 22 ev, and that the boiling points of the chlorides lie above the melting point of potassium chloride. The necessity for the second requirement was discussed in the introduction. The third requirement is necessary so that the trivalent salt will not sublime or evaporate out of the melt. Some compounds that do not meet all these criteria were tried briefly and then abandoned -- chromium, indium, and praseodymium chlorides.<sup>1</sup>

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<sup>1</sup>The crystal grown from the chromium doped melt was visibly colored. The  $\text{InCl}_3$  probably sublimed from the melt. A modification of a spot test described by Feigl (12, p. 200) was used to analyze a crystal grown from the indium doped melt; the results were negative, there being less than  $10^{17}$   $\text{In}^{+++}$  ions per cc crystal. Also in view of the value of the third ionization potential of indium (28 ev), it is not likely that  $\text{In}^{+++}$  can exist in KCl crystals. The melt containing praseodymium turned very dark, indicating that the praseodymium had been oxidized to an oxidation state higher than three.

Of the stable Group III elements, only yttrium and some of the rare earths possess all three of the desired properties. The trichlorides of lanthanum, gadolinium, dysprosium, samarium, neodymium, and yttrium have the desired boiling points and stable +3 oxidation states. The third ionization potentials of the rare earths probably lie in the neighborhood of 20 ev.

The preparation and storage of the anhydrous trichlorides of the rare earths (yttrium will be grouped with the rare earths) present some difficulties. If the chloride hydrate is heated in air some hydrolysis occurs with the resulting formation of the oxychloride. Heating the hydrate under an infrared lamp resulted in a product that was only partly soluble in water -- indicating the formation of the oxychloride. Hence it was necessary to employ more elaborate methods in order to obtain the anhydrous chlorides.

$\text{Sm}_2\text{O}_3$  was mixed with  $\text{NH}_4\text{Cl}$  and heated (34). Part of the product was placed in a porcelain boat which was then slipped into a test tube and the tube evacuated. The tube was heated by means of a tube furnace. The resulting  $\text{SmCl}_3$  was gray and only partly water soluble.

$\text{Nd}_2\text{O}_3$  was converted to the chloride by treatment with concentrated  $\text{HCl}$  rather than  $\text{NH}_4\text{Cl}$ . The crystals

(hydrate) were dried in a desiccator and then transferred to a porcelain boat. The boat was placed in a borosilicate glass tube, the center section being surrounded by a tube furnace. The tube was provided with fittings so that dry HCl gas could be passed over the chloride hydrate as it was warmed (20, p. 53-55). Water vapor condensed in both ends of the tube. The product hissed upon the addition of water and was almost completely soluble in water. The apparatus was modified so that in addition to HCl an inert gas could be streamed over the material being dried. This permitted the water given off by the hydrate to be carried away rapidly without the use of large quantities of HCl gas. Gadolinium, samarium, and yttrium chlorides were prepared from the hydrates by passing dry HCl and  $N_2$  over them at elevated temperatures. Two further modifications were made. The borosilicate glass tube was replaced by one having a high silica content (allowing the use of much higher temperature), and a platinum boat was used in place of the porcelain one. The hydrate of dysprosium chloride was heated while a stream of HCl and  $N_2$  was passed over it until all the water of hydration was driven off. Then the temperature was raised and the  $DyCl_3$  fused in an HCl atmosphere (2, p. 144). The product was pale green



and almost completely soluble in water. The fused  $\text{DyCl}_3$  was very hard and was ground in a mortar in order that portions of the preparation could be used.

All the methods described above yield products that must be removed from the drying apparatus and placed in some suitable storage container until such time as they are used. Even though the transfer from the drying apparatus to the desiccator was carried out rapidly, there was some exposure to the air, and, since small quantities were involved, nearly all the material was in contact with the atmosphere in the desiccator. These difficulties might have been circumvented by transferring, grinding (if necessary), and storing the material in a dry, inert atmosphere; however, it was simpler and gave greater assurance of non-deterioration of the product to use a drying method that did not involve transfer and storage problems. Figure 4 shows apparatus in which the hydrate could be dried and then stored in a sealed vial without the necessity for transfer between the vessel in which the dehydration took place and the vessel in which the anhydrous chloride was stored. A modification of this apparatus was constructed; this is shown in Figure 5. Several vials of anhydrous chloride could be prepared at one time.



It should be noted that the chlorides were not always the color listed in the handbook (19, p. 514, 516, 530, 582, 622). In particular, the  $\text{GdCl}_3$  always appeared somewhat gray or off-white. This was true of that prepared from commercially obtained chloride hydrate and from gadolinium recovered from melt residues.

### Growth of Crystals

The crystals were grown from the melt by a method usually credited to Kyropoulos (13, p. 15-16). In this method a cooled seed crystal is withdrawn from the melt. Porcelain, graphite, and platinum crucibles were used. Reagent grade and re-crystallized reagent grade KCl was used. Many pure crystals were grown for practice, for providing seed crystals, and for control purposes. One was grown in an HCl atmosphere to determine the effect, if any, of the HCl upon the ionic conductivity of KCl crystals.

Heating the anhydrous rare earth chloride and KCl until molten often resulted in a turbid melt; frequently, with the settling of the solid material to the bottom of the crucible, the melt became clear. If the anhydrous rare earth chloride was not placed in the crucible until the KCl had melted, the melt was usually

clear for a short while, then became turbid, and finally cleared, small solid pieces being visible on the bottom and sidewalls of the crucible. A jet of dry gas containing HCl directed at the melt surface prevented the development of turbidity and caused the melt to become clear if it had already become turbid. Argon was tried in place of the HCl; this resulted in a turbid melt. Nitrogen and argon were used to dilute the HCl and hence reduce the corrosiveness of the gas stream while at the same time preventing the access of oxygen and moisture to the melt.

Several attempts were made to prepare the anhydrous rare earth chlorides in the melt. A mixture of KCl, rare earth chloride hydrate, and  $\text{NH}_4\text{Cl}$  was heated until it fused; the resulting melt was turbid.

Some of the doped crystals were colorless; some contained white sections. The white sections were located approximately along the center line of the boule. They appeared to be approximately symmetrically located around the center line when viewed from along a line perpendicular to the center line. When viewed along the center line the white section often appeared as an X.

The formation of these white sections may be

explained as follows. It is expected that the solubility in KCl of the rare earth chlorides is greater at the melting point of KCl than at lower temperatures. Thus as the crystal formed the amount of rare earth chloride incorporated exceeded the amount that is soluble in the crystal at the lower temperature. Upon cooling of the crystal, some of the rare earth chloride formed a separate phase, resulting in a colloidal dispersion of the rare earth chloride in the crystal. The colloidal particles scatter light, giving the crystal the appearance of whiteness. This also occurs in crystals containing alkaline earth chlorides; however, in this case the necessary foreign ion concentration is much higher.

#### Analysis of the Crystals for Rare Earth Content

The rare earth content of the crystals was determined spectrophotometrically using Alizarin Red S (36) to form an absorbing complex with the rare earth ion. Usually one gram of crystal was dissolved in enough water to give 25 milliliters of solution. Five milliliters of this solution were used for the analysis. In some cases 200 milligrams of the crystal were dissolved in five milliliters of water and this solution used for

the analysis. The blank contained one gram of KCl in 25 milliliters of blank solution. Since the molar absorbancies of the Alizarin Red S complexes are the same for all the rare earth ions investigated, separate working curves (curves of absorbance per centimeter measured at 550 mμ vs gram-ion per liter of rare earth ion) for the various ions are not necessary. A working curve constructed using dysprosium and yttrium standards was used for most of the determinations.

#### Measurement of Ionic Conductivity

A vacuum system using a mercury diffusion pump was built for the vacuum deposition of electrodes on crystals. A crystal of KCl was supported on a ring above a tungsten filament around which silver wire was wrapped. The system was evacuated and the silver heated until there was a deposit of silver on the crystal. Then the system was opened, the crystal turned over, and an electrode deposited on the other side of the crystal. During the deposition of the second electrode the first electrode darkened and in one instance became nonconducting. The apparatus was modified so that it was not necessary to expose the first electrode to the atmosphere in order to orient the crystal in such a



manner that the second electrode could be deposited; this apparatus is shown in Figure 6.

A crystal with silver electrodes was placed in a cell for measuring ionic conductivity. The silver electrodes were destroyed during the conductivity measurements, both when used in air and in a partial vacuum. Gold electrodes were used and they also proved unsatisfactory. A cell employing platinum electrodes was designed and built. The platinum electrodes were cut from 0.005 inch platinum foil with a hollow ground paper punch. Lead weights were placed on the brass collar in order to press the electrodes firmly against the crystal; the pressure was three or four  $\text{kgm/cm}^2$ . This cell was later modified so that heavy platinum electrodes could be used. The modified cell is shown in Figure 7. A Model 68 Precision vacuum tube volt-ohmmeter (manufactured by Precision Apparatus Company, Inc.) was used to measure the resistance. An insulated double-pole-double-throw reversing switch was used to connect the vacuum tube volt-ohmmeter to the electrodes. This was necessary since touching the probes leads to erratic behavior of the vacuum tube volt-ohmmeter. A potential was applied to the crystal only during the taking of a measurement. The measurements were made in air.

## Coloration and Optical Measurements

Crystals to be colored were wrapped in copper foil and placed together with a piece of sodium in a copper tube which was then sealed, placed in a muffle furnace, and heated for approximately 24 hours in the vicinity of 500°C. These coloring bombs were quenched rapidly to room temperature by immersing them in water immediately upon removal from the furnace.

A Beckman Model DU, DK 1, or DK 2 spectrophotometer was used for the optical absorption measurements. A special crystal holder was designed for use at the temperature of liquid air; it is shown in Figure 8. Some difficulty was experienced with frosting of the windows. It was found that directing a stream of dry air or nitrogen at each window usually prevented frosting.

For some of the optical bleaching experiments a strong light source built by Mr. Donald Chittick was used. This apparatus employed a 750 watt projection lamp as a source. A filter made of two colored glass plates was used to isolate the F light; the transmission band of the filter extended from 520 to 600 mμ. An attachment which holds the DK 1 cuvette holder was made, thus obviating any need to remove the crystal holder

from the cuvette holder during bleaching periods.

Several crystals were colored by irradiation with x-rays using the General Electric X-Ray Corporation XRD instrument. A tube with a copper target was used. The voltage was approximately 35 kilovolts and the current in the range of 4 to 15 milliamperes.



### III. RESULTS AND DISCUSSION

#### Rare Earth Content of Crystals

Table II shows the results of the colorimetric analyses. The notation in the first column gives the host lattice, the added impurity element, the number designation of the crystal, and the number of the colored piece. A "P" in the second column means that a porcelain crucible was used to hold the melt, "C" a graphite one, and "Pt" a platinum one. The entry of more than one concentration for a given crystal means that more than one piece was analyzed.

From the small scatter of points on the working curve, the results of repeated measurement of standard solutions, and the analyses of pure KCl crystals, it is estimated that for the colorimetric method used the minimum detectable amount of rare earth in the crystals is about  $5 \times 10^{16}$  rare earth ions per cc crystal. The variability of the rare earth ion concentration from place to place within the crystal itself was large and for some crystals extended over two or more orders of magnitude. This is illustrated by the data concerning KCl-Gd-16. The occurrence of opaque sections in the crystals is further evidence that the crystals were

Table II

## Rare Earth Content of KCl Single Crystals

Crystal	Crucible	Atmos- phere	Rare earth ions $\times 10^{-17}$ per cc crystal	Appearance of piece used for analysis
KCl-Gd- 1	P	air	1.8	
2	C	air	2.5	colorless to slightly white
3	C	air	<0.5	
4	P	air	<0.5	colorless to very slightly white
5	P	air	0.71	colorless
6	P	air	1.6	
7	C	air	<0.5	cut next to white piece
8	C	air	<0.5	slightly white
9	P	air	44.	white
10	P	air	29.	white
12	P	HCl	<0.5	colorless
13	P	HCl	<0.5	colorless
14	P	HCl	<0.5	colorless
14-1			<0.5	
14			<0.5	colorless
15	P	HCl	133.	white
			<0.5	colorless
16	P	HCl	28.5	white
			7.3	white
			<0.5	colorless
			<0.5	colorless
16-1			<0.5	
KCl-Dy- 2	P	air	1.4	white
3	P	HCl	<0.5	colorless
			31.	white
4	P	HCl	<0.5	colorless
5	P	HCl	<0.5	colorless
KCl-Sm- 1	P	air	9.2	

Table II - Cont.

Crystal	Crucible	Atmos- phere	Rare earth ions $\times 10^{-17}$ per cc crystal	Appearance of piece used for analysis
KCl-Sm- 2	P	air	1.5	slightly white
3	P	air	1.4	white
4	P	air	<0.5	colorless
KCl-Nd- 1	P	air	<0.5	
KCl-Pr- 1	P	air	<0.5	colorless
		air	<0.5	
KCl-Y-1	P	air	0.90	very slightly white
2	P	air	0.68	colorless
		air	<0.5	
3	P	air	1.3	white
		air	<0.5	white
KCl- 2	P	air	<0.5	all the pure KCl crystals were free of white portions
4	P	air	<0.5	
6	C	air	<0.5	
8	C	air	<0.5	
9	P	air	<0.5	
10	P	air	<0.5	
		air	<0.5	
11	P	air	<0.5	
		air	<0.5	
12	P	air	<0.5	
12-2		air	<0.5	
13-3	P	air	<0.5	
18	Pt	HCl	<0.5	

very inhomogeneous with respect to rare earth ion concentration.

An estimate of the upper limit of the solubility of the trivalent ions (meaning  $\text{Dy}^{+++}$ ,  $\text{Gd}^{+++}$ ,  $\text{Sm}^{+++}$ , or  $\text{Y}^{+++}$  unless stated otherwise) in KCl grown from the melt and quenched to room temperature over a period of several hours may be made from Table II. This limit is about  $10^{17}$  trivalent ions per cc KCl for colorless crystals -- that is, approximately  $10^{-5}$  mole fraction. Hence, it is evident from Figure 3 that the density variation method cannot be used to determine the valency of the rare earth ions incorporated in KCl crystals since this concentration would result in an insignificant change in density from that of the pure crystal.

### Uncolored Crystals

#### Ultraviolet Absorption Spectra

A preliminary survey of the ultraviolet absorption spectra of uncolored crystals was made by means of the Beckman Model DK 2 spectrophotometer. The following crystals were investigated: KCl-1, KCl-4, KCl-7, KCl-8, KCl-10, KCl-11, KCl supplied by the Harshaw Chemical Company, KCl-Dy-1, KCl-Gd-1, KCl-Gd-3, KCl-Gd-7, KCl-Nd-1, KCl-Sm-1, and KCl-Sm-4. In general, a gradual

increase in absorption with decreasing wavelength occurred between 350 and 225 m $\mu$ . No peaks due to rare earth ions were found in the ultraviolet absorption spectra of the uncolored crystals; this is to be expected because of the low molar absorptivity of the ions (46, p. 261). Most of the rare earth chlorides, in aqueous solution, have absorption bands in the ultraviolet (33). KCl-4, KCl-9, and KCl-10 showed a flat peak centered around 203 to 204 m $\mu$ .

The Beckman Model DK 1 spectrophotometer was used to measure more accurately the ultraviolet absorption spectra of the following crystals: KCl supplied by the Harshaw Chemical Company, KCl-7, KCl-8, KCl-11, KCl-12, KCl-14, KCl-16 (platinum crucible used), KCl-Gd-7, KCl-Gd-12, KCl-Gd-17 (platinum crucible used), KCl-Sm-2, and KCl-Sm-4. The plots of absorbance per centimeter against wavelength are shown in Figures 9 and 10.

The ultraviolet absorption spectra of three pure KCl crystals grown from a platinum crucible were measured in the wavelength range of 350 to 195 m $\mu$ . The two crystals grown in air showed a large peak at approximately 204 to 206 m $\mu$ . The crystal grown in an HCl atmosphere did not have such a peak. Except for this peak the crystals showed only a general rise in absorption toward

the shorter wavelengths. Rolfe (37) and Etzel and Patterson (11) attributed the 204  $\mu$  band of KCl to "OH" in some form. Etzel and Patterson found that pre-melting the Kyropoulos charge in HCl gas removed the "OH" band. The absence of the 204  $\mu$  peak in the crystal grown in an HCl atmosphere is in agreement with their findings.

### Ionic Conductivity

Since the temperature at which the knee of the conductivity curve occurs and the magnitude of the impurity conductivity are both related to the purity of a crystal, it was thought that it might be possible to correlate rare earth ion concentration with ionic conductivity measurements, or, at least, to use such measurements to arrange crystals in the order of increasing rare earth ion concentration.

It was not possible to correlate the ionic conductivity data with the results of colorimetric analyses since crystal pieces whose trivalent ion concentrations were above the detection limit of the colorimetric method usually contained white sections. Such pieces are not suitable for correlation purposes as the trivalent ions present in the white portions probably do not make the



same contribution to the impurity conductivity as do the trivalent ions dispersed atomically. Also the concentration of atomically dispersed rare earth ions is probably a function of temperature for it would be expected that as the temperature of the crystal was raised some of the rare earth chloride present in colloidal form dissolved in the KCl crystal. If the colloidal particles completely dissolved at some temperature within the range over which the conductivity was measured, then it would be expected that the conductivity curve would show three regions, separated by two knees. First (meaning at the high temperature end of the curve) would come the intrinsic conduction region, then the normal impurity conduction region, and finally a region in which the impurity would be precipitating out as a separate phase. It should be noted that the occurrence of three sections in the curve depends on the amount of trivalent salt in excess of solubility being small. The ionic conductivity of three crystal pieces containing white sections was measured; the three distinct regions described were not found, as is evident from an examination of Figure 11\* (the capital letters are used to

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\*For purposes of clarity in presentation, the experimental points are not shown; the best lines through the experimental points are shown.

distinguish one piece of a crystal from another). For purposes of comparison the ionic conductivity of pure KCl is shown in Figure 11. The absence of three distinct regions in the conductivity curves is in agreement with the observation that a crystal piece containing a white section did not become transparent upon heating. At 750°C the white section had not disappeared; however, it did appear to have decreased in size.

The three distinct regions of the conductivity curve described above have been observed by Zückler for KCl crystals containing certain critical amounts of divalent chlorides [reported by Seitz (42, p. 21)]. Haven (15, p. 1507-1509) has made similar observations on lithium fluoride containing magnesium fluoride and from such observations determined the solubility of the magnesium fluoride in lithium fluoride as a function of temperature.

Although ionic conductivity data concerning crystal pieces containing white sections may not be correlated with the results of colorimetric analyses, such data may be used to calculate within an order of magnitude the solubility of rare earth ions in KCl. The necessary data were available for gadolinium doped KCl (Figure 11). The solubility of gadolinium chloride was estimated as described below. From Kelting and

Witt's plot of ionic conductivity at 372°C vs alkaline earth concentration (21, p. 706) the alkaline earth concentrations which would give rise to the observed ionic conductivity of KCl-Gd-16-A, KCl-Gd-16-C, and KCl-Gd-15-A were estimated. The gadolinium concentration is one-half of this since the introduction of one  $\text{Gd}^{+++}$  ion into KCl results in the formation of two cation vacancies while the introduction of an alkaline earth ion results in the formation of one vacancy. For all three crystal pieces the solubility thus estimated was  $2 \times 10^{17}$   $\text{Gd}^{+++}$  ions per cc crystal. In making the calculations the effect of the colloidal particles of gadolinium chloride imbedded in the KCl, the difference in cation vacancy binding of the alkaline earth ions and of the gadolinium ion, and the specific nature of the alkaline earth ions were neglected. Since the calculation is an "order of magnitude only" calculation, the two (in  $2 \times 10^{17}$ ) is not significant. Thus the solubility of gadolinium ions in KCl is about  $10^{17}$  ions per cc crystal. This value agrees with that estimated previously from colorimetric data.

The ionic conductivity of pure and gadolinium doped KCl grown in a platinum crucible is shown in Figure 12. Both crystals were grown in an HCl atmosphere.

It is seen that there were only small differences between the impurity conductivity of the pure and of the colorless, doped crystal pieces and that in one instance the impurity conductivity of a piece of pure KCl almost duplicated exactly that of a piece of doped KCl. This leads to the conclusion that, for the present, ionic conductivity measurements are not likely to be useful for ordering crystals according to rare earth ion content.

#### Additively Colored Crystals

##### Ultraviolet Absorption Spectra

Since it did not seem feasible to try to predict the location of possible new bands by a point charge calculation, an attempt was made to obtain some indication of where new bands might occur in the spectrum by considering the spectra of monovalent alkaline earth ions, divalent rare earth ions, and Z centers.

The ground state to first excited state transitions are known for the free monovalent ions  $\text{Ca}^+$ ,  $\text{Sr}^+$ , and  $\text{Ba}^+$  and are compared in Table III with the same transitions for the ions imbedded in KCl. The comparison was made for both the  $Z_1$  and  $Z_2$  bands since both have been depicted as arising from the monovalent ions. The

Table III

Comparison of Optical Transitions Occurring  
in Free Ions and Ions Imbedded in KCl

Element	Monovalent free ion		Z <sub>1</sub> center			Z <sub>2</sub> center		
	Band position mμ	ev	Band position mμ	ev	ΔE ev	Band position mμ	ev	ΔE ev
Ca	397	3.12	590	2.10	1.02	610	2.03	1.09
Sr	422	2.94	595	2.08	0.86	635	1.95	0.99
Ba	493	2.52	600	2.05	0.47	650	1.91	0.61



values given for the free monovalent ions were taken from the term level diagrams of Grotrian (14, p. 30, 36, 43). The Z band wavelengths listed are those occurring at  $-215^{\circ}\text{C}$  (31, p. 76). The difference in energy between the free monovalent ion transition and the Z center transition is given in the column headed  $\Delta E$ .

It is seen that a shift towards longer wavelengths of one-half to one ev occurred as a result of imbedding the ions in KCl. The ground state to first excited state transition in  $\text{Y}^{++}$  yields a line at 242 m $\mu$ , corresponding to 4.2 ev (14, p. 37). The same transition in  $\text{La}^{++}$  occurs at about 238 m $\mu$  (38, p. 627-628); for our purposes, this is not significantly different from the  $\text{Y}^{++}$  transition. A shift of this transition to lower energy by one-half to one ev would give a line in the crystal in the range 335 to 390 m $\mu$ . The corresponding transitions for the other rare earth elements are not known. It should be pointed out that the analogy between the alkaline earth ions and the rare earth ions is not at all rigorous since the ground state of the monovalent alkaline earth ions is an S state while that of  $\text{Y}^{++}$  and  $\text{La}^{++}$  is a D state.

The ultraviolet absorption spectra (200 to 360 m $\mu$ ) of the following additively colored crystals were



measured both before and after bleaching with light lying in the F band: KCl-Dy-2-2, KCl-Dy-3-1, KCl-Dy-4-1, KCl-Gd-16-1, KCl-Sm-1-2, KCl-Sm-3-2, KCl-Y-2-2, KCl-13-3, and KCl-20-1 (the uncolored crystal supplied by Harshaw Chemical Company). Several of these crystals, KCl-Dy-2-2, KCl-Dy-3-1, KCl-Y-2-2, KCl-13-3, and KCl-20-1, showed shoulder or slight absorption band in the 330 to 360  $\mu$  region before bleaching. Upon bleaching of the F band the absorption in the range 330 to 360  $\mu$  increased in most cases. It may be that this band arises from impurities usually present in pure KCl.  $Al^{+}$  (14, p. 60), by arguments of the preceding paragraph, should display absorption at about 300 to 350  $\mu$ ;  $Mg^{+}$  (14, p. 22) at about 330 to 360  $\mu$ . Both aluminum and magnesium have been found in pure KCl crystals (10). In the case of some of the doped crystals there may be a contribution to absorption in the 330 to 360  $\mu$  region by divalent rare earth ions.

The ultraviolet absorption spectra of several crystals (KCl-12-1, KCl-Y-2-1, KCl-Y-2-2, KCl-Y-2-3, KCl-Y-2-4, KCl-Y-3-1 and KCl-Y-3-2) that had been subjected to varying amounts and kinds of bleaching were measured. Two of these, KCl-Y-2-3 and KCl-Y-2-4, showed a slight shoulder or absorption band in the

range 330 to 360  $\mu$ . The absorption of additively colored crystals in the range 330 to 360  $\mu$  was not investigated further, as it did not provide a distinction between pure and doped crystals.

Five crystals, KCl-13-3, KCl-Y-2-1, KCl-Y-2-2, KCl-Y-2-3, and KCl-Y-2-4, exhibited a strong absorption at about 215  $\mu$ . This is probably the U band. The U band is commonly ascribed to the presence of hydride ion in the crystal. The half-width (more precisely half-height width) of the band in KCl-Y-2-3 was measured (taking the absorption at 240  $\mu$  to be that due to the KCl) and found to be 0.54 to 0.55 ev. This is to be compared with the value of 0.55 ev or 0.57 ev given by Lüpke (24, p. 5) and Martienssen (25, p. 494), respectively. The occurrence of the U band in only colored KCl-Y-2 and KCl-13-3, but in no other crystals, is as yet unexplained.

#### Absorption Spectra in the Visible Region

If the rare earth ions were reduced to monovalent ions on coloring, then the spectra of the free monovalent ions, rather than the divalent ions, should be considered in any attempt to obtain an indication of the spectral range in which

absorption due to rare earth ions might occur. The transition from the ground state to the first excited state for  $Y^+$  and  $La^+$  occurs at about 400 and 700 m $\mu$ , respectively (26, p. 743; 38, p. 635). Reference to Table III shows that such centers might give rise to bands lying near the Z bands or on the long wavelength side of them.

The absorption spectra, measured at room temperature, in the range 400 to 1100 m $\mu$  of the additively colored, doped crystals did not show any new resolved bands. In Table IV are tabulated the results of absorption measurements made at room temperature. The crystals were cut and mounted on the sample holder under a red safety lamp except for sections whose absorption spectra were measured with the Beckman Model DK 2 spectrophotometer, these being mounted on the sample holder in subdued white light.

The F center concentration was calculated from the Smakula equation (44, p. 607) using a value of unity for the oscillator strength. "Before" and "After" have reference to optical bleaching; the crystals were bleached with either white light or F light (560 m $\mu$ ). For some crystals more detailed information about the bleaching light is given in the footnotes to Table IV.

Table IV

F Band Half-widths of Colored, Pure and Doped KCl

Crystal	F centers x 10 <sup>-17</sup> cm <sup>-3</sup>	Half-width		Instrument, Beckman Model
		Before, ev	After, ev	
KCl- 7-1	0.40	0.34	0.34	DK 2
12-1	1.5	0.36	0.39	DU
12-2	1.2	0.37	0.40	DU
12-3	0.66	0.36	0.40	DU
12-3	0.74	0.36	0.38 <sup>a</sup>	DK 1
			0.41 <sup>b</sup>	
		Ave. 0.36		
KCl-Dy- 4-1	1.0	0.36 <sup>c</sup>	0.40 <sup>a</sup>	DK 1
Gd- 1-1		0.35		DK 2
Gd-16-1	1.0	0.38	0.40 <sup>d</sup>	DK 1
			0.58 <sup>e</sup>	
KCl-Sm- 1-2		0.40	0.40	DK 2
Sm- 3-1		0.44	0.46	DK 2
Sm- 3-1	0.48	0.38	0.47	DU
Sm-3-3	1.5	0.37		DU
KCl- Y- 2-1	1.5	0.37	0.42 <sup>a</sup>	DU
Y- 2-2	1.9	0.36		DK 1

Table IV - Cont.

Crystal	F centers x $10^{-17}$ cm $^{-3}$	Half-width		Instrument, Beckman Model
		Before, ev	After, ev	
KCl-La-1-1	1.3	0.36	0.37	DU
La-2-1		0.37	0.40	DU
La-3-1		0.39		DU
		Ave. 0.38		

a- After 5 min. bleaching with Chittick's source.

b- After 20 min. bleaching with Chittick's source.

c- One side of F band extrapolated.

d- After 10 min. bleaching with F light from DK 1, slit = 0.5 mm.

e- Treatment d plus more than 20 min. bleaching with light from Chittick's source.

The use of Chittick's source resulted in a rise in temperature of the crystal and holder. The bulb of a thermometer was placed in the position normally occupied by the crystal being bleached. The temperature rose ten degrees in five minutes and about 20 degrees in 30 minutes. The variation with temperature of F band half-width was calculated on the assumption that it is proportional to the square root of the absolute temperature (29, p. 116). The calculation showed that in the neighborhood of room temperature the half-width increases 0.003 ev for every five degrees increase in temperature.

A correlation of the half-width of the F band with the trivalent ion concentration was not possible due to the inhomogeneity of the crystals with respect to rare earth ion concentration and the detection limit of the colorimetric method employed.

The half-width of the F band in pure KCl at room temperature has been given variously as 0.35 (27, p. 63), 0.359 (45, p. 18), 0.38 (5, p. 5) ev. A few of the doped pieces exhibited large half-widths before bleaching. A few also underwent a rather large increase in half-width upon optical bleaching.

To determine whether the F band in doped crystals



could be resolved into two bands absorption spectra were measured at liquid air temperatures. No resolution was obtained. Figures 13, 14, and 15 show the low temperature absorption spectra of KCl-12-1, KCl-Sm-3-3, and KCl-Y-2-1. After intense bleaching the KCl-Sm-3-3 showed high absorption in the 600 to 750 m $\mu$  region; it did not show any resolved  $R_1$  and  $R_2$  bands.

The occurrence of the large half-widths before optical bleaching and the increase in half-width upon bleaching can be accounted for if, upon bleaching, a band underlying the F band is formed in addition to those occurring in pure KCl (22; 30, p. 446-447). The large half-width before bleaching could be attributed to unintentional bleaching, caused by F light output of the safety lamp, exposure of crystal during cell holder positioning, etc. With respect to the possible formation of bands underlying the F band, it should be noted that among the absorption bands of  $\text{SmCl}_2$  in aqueous solution are two well defined bands occurring at 559 and 473 m $\mu$  (4). The formation of  $\text{Sm}^{++}$  ions upon bleaching of a colored crystal would thus be expected to give rise to bands underlying the F band as there is usually a close correlation between the position of bands in aqueous solution and in KCl crystals.

Alternatively the large half-width present in some crystals before bleaching may be accounted for in the following way. In a crystal containing  $10^{17}$  trivalent ions per cc about one F center in 100 will have a trivalent ion within ten atomic diameters. Such centers will suffer a depression of the energy level of the excited state, whose wave function extends at least this distance; this will shift the absorption to longer wavelengths and cause a broadening of the F band. However, until it is possible to correlate half-widths with at least relative rare earth ion concentrations it is not possible to conclude with finality that rare earth ions lead to the formation of a new band which underlies the F band.

The failure to observe definitely a new band may be due, aside from the possibility that none exists, to the low concentration of rare earth ions and hence of such traps as may be attributed to them or their influence on other color centers. There is the possibility that upon coloring the number of rare earth ions (whatever their oxidation state) in the crystals is decreased due to the reduction of some to the free metal by the electrons used to form the F centers. In this regard it may be noted

that the white sections of the crystals do not color.

Sometimes the white sections contained black specks after additive coloration. A crystal containing a white section was colored under such conditions that the F center concentration would be about  $10^{18}$  F centers per cc crystal. Upon dissolution of the colored crystal in water a small amount of black material was found. This reacted vigorously with dilute HCl and the resulting solution tested high in rare earth content.

#### X-ray Colored Crystals

The irradiation of KCl crystals with x-rays results in the formation of absorption bands, some of which occur in additively colored crystals and some of which are peculiar to irradiated crystals (1, 6, 8, 9, 28, p. 81). Those bands peculiar to irradiated crystals are termed V bands.

Although the white sections of doped crystals could not be colored additively they were colored by irradiation with x-rays. If it is assumed that the coloration shown by the white sections is due to the KCl in which the colloidal particles of the rare earth chlorides are imbedded and that such KCl contains the maximum amount of rare earth ions soluble in KCl at a

temperature several hundred degrees below the melting point of KCl, then it is to be expected that irradiation of the white sections of crystals would yield colored crystals showing the maximum effect of the trivalent ions (subject to the limitation of their solubility in KCl).

### Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of fourteen crystals were measured, the crystals irradiated, and the spectra again measured. The measurement of the spectra before irradiation permitted corrections to be made for any absorption due to the uncolored crystal. The crystals investigated were KCl-10-X-1, KCl-18-X-1, KCl-18-X-2, KCl-Dy-2-X-1, KCl-Dy-2-X-2, KCl-Dy-3-X-1, KCl-Gd-17-X-1, KCl-Gd-17-X-2, KCl-Sm-1-X-1, KCl-Sm-1-X-2, KCl-Sm-2-X-1, KCl-Sm-3-X-1, KCl-Sm-3-X-2, and KCl-Y-2-X-1 (the X has been inserted in the usual crystal designation to emphasize the fact that the crystals were colored by irradiation). All crystals exhibited a broad absorption band having its maximum absorption in the range 215 to 230 m $\mu$ . Some crystals possessed a band in the vicinity of 325 m $\mu$ . In such crystals there was also a shoulder on the long wavelength side of the band

occurring in the neighborhood of 225 m $\mu$ . Figures 16 and 17 show the spectra of KCl-Dy-2-X-2 and KCl-Sm-2-X-1. The 225 m $\mu$  band is probably a composite of the  $V_2$  and  $V_3$  bands. According to Casler, Fringsheim, and Yuster (6) the  $V_2$  and  $V_3$  bands of KCl occur at 232 and 216 m $\mu$ , respectively, at room temperature. The relative sizes of the  $V_2$  and  $V_3$  bands depend upon the temperature at which the crystal was irradiated and the type of irradiation. The reported shape of the composite band varies somewhat from investigator to investigator (6).

Both the band centered around 320 to 325 m $\mu$  and the band located around 225 m $\mu$  underwent a slight decrease upon bleaching of the crystal in the F band. Data concerning the absorption of the x-ray colored crystals in the 275 to 350 m $\mu$  range are given in Table V. Dorendorf (9) found two small bands in the 275 to 350 m $\mu$  range. He called these the  $V_6$  and  $V_7$  bands; at  $-180^\circ\text{C}$  they occur at 334 and 300 m $\mu$ , respectively. A comparison of the wavelengths given for the  $V_2$  and  $V_3$  bands at room temperature (6) and at  $-180^\circ\text{C}$  (9) showed that the shift caused by temperature change is 4 m $\mu$ . This is no larger than the disagreement between investigators concerning the wavelengths of the V bands. Hence it is expected that if the  $V_6$  and  $V_7$  bands occur at room temperature



Table V  
Absorption in the 275-350 mμ Region  
of Irradiated Crystals

Crystal	Irradiation period min. <sup>a</sup>	Existence of and position of bands mμ	Appearance of uncolored crystal
KCl-10-X-1	210	none	colorless
KCl-18-X-1	180	none	colorless
KCl-18-X-2	180	none	colorless
KCl-Dy-2-X-1	150	320	colorless
KCl-Dy-2-X-2	60	325	
KCl-Dy-3-X-1	150	none	white
KCl-Gd-17-X-1	180	none	white
KCl-Gd-17-X-2	180	none	colorless
KCl-Sm-1-X-1	15	none	slightly milky
KCl-Sm-1-X-2	30	see footnote b	milky
KCl-Sm-1-X-2	180	see footnote b	
KCl-Sm-2-X-1	210	none	colorless
KCl-Sm-3-X-1	120	325	slightly milky



Table V - Cont.

Crystal	Irradiation period min. <sup>a</sup>	Existence of and position of bands mu	Appearance of uncolored crystal
KCl-Sm-3-X-2	15	325	milky
KCl-Y-2-X-1	60	none	

a- The current was 10 to 15 milliamperes.

b- KCl-Sm-1-X-2 was irradiated for thirty minutes, the spectrum measured, irradiated for 180 additional minutes, and the spectrum measured. After the first irradiation the crystal showed a symmetrical band at 225 mu with faint bands at 300 and 345 mu. After the second irradiation the 225 mu band was still symmetrical, the 300 mu band had disappeared as such, and the 345 mu band had increased. The band at 345 mu was very low, broad, and unsymmetrical.

they will occur at approximately 334 and 300  $\mu$ , respectively. Thus the band observed at about 325  $\mu$  in some of the irradiated crystals may be a composite of the  $V_6$  and  $V_7$  bands observed by Dorendorf in pure KCl. However, the spectrum of KCl irradiated at 20°C and measured at -180°C did not show any discernible  $V_6$  and  $V_7$  bands (Figure 3e of Dorendorf). From Dorendorf's spectrum of KCl irradiated and measured at 20°C it is estimated that the ratio of the absorption at the  $V_3$  peak to that at 325  $\mu$  is 20. Thus, although the band observed in the present work at about 325  $\mu$  may be a composite of the  $V_6$  and  $V_7$  bands, it is much stronger than those observed by Dorendorf.

In the present work no 325  $\mu$  band was observed in pure KCl. It may be that this band is due to divalent rare earth ions. That such ions would absorb in this region has been discussed previously. The absence of such a band in additively colored crystals may be explained by assuming that under the strong reducing conditions that exist during additive coloration the rare earth ions are reduced to monovalent ions. Alternatively, since bands in the vicinity of 325  $\mu$  have been observed in pure KCl crystals colored by irradiation at low temperatures, it may be that the rare

earth ions serve to stabilize at room temperature centers which otherwise exist only at low temperatures.

#### Absorption Spectra in the Visible Region

Fourteen pieces cut from doped crystals and six pieces cut from pure crystals were irradiated and the spectra measured (current was 4 to 15 milliamperes). No new absorption bands were observed. Several of the doped crystals exhibited high absorption on the short wavelength side of the F band. The F band half-width of nine pieces was measured (three pure and six doped) and found to vary from 0.34 to 0.39 ev before bleaching and from 0.36 to 0.43 ev after bleaching. There was no correlation between added impurity and half-width.

#### Summary

In summary one may make the following statements about trivalently doped KCl.

1. The chlorides of dysprosium, gadolinium, samarium, and yttrium were only very slightly soluble in KCl single crystals at room temperature. The solubility was probably less than  $10^{17}$  ions per cc crystal.

2. The ionic conductivity of doped crystals containing opaque sections differed markedly from that of pure KCl while that of colorless ones did not.
3. Additively colored crystals, both pure and doped, occasionally showed a slight absorption band or shoulder at about 340 mμ. Reasons have been advanced to show that this absorption may be due to monovalent or divalent impurity ions (either ones intentionally added to the KCl or ones accidentally present in the KCl).
4. The added impurities did not give rise, at room temperature, to any new resolved bands in the visible region in colored crystals; however, in some instances the F band was broadened.
5. The ultraviolet absorption spectra of x-ray colored, doped crystals often exhibited a broad band at approximately 325 mμ. It may be that this band is due to divalent rare earth ions imbedded in KCl or to absorption by a center usually found only at lower temperatures but stabilized at room

temperature by the rare earth ion.

#### Comments on Further Work

Before any further work is done on the properties of KCl containing trivalent cations it is highly desirable that a method be devised for growing very pure KCl crystals and an analytical method be developed for the measurement of small trivalent ion concentrations. Then the production and characteristics of the 325 mμ band might profitably be investigated. Studies of darkenability and bleaching rates of trivalently doped KCl might also prove highly useful in the interpretation of the mechanism of F center formation and photochemical destruction.

## Pick's Models

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 $Z_1$  Center

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 $Z_2$  Center

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 $Z_3$  Center

## Seitz' Models

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 $Z_1$  Center

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$\begin{array}{ccccccc} & & & e & & & \\ & & & \boxed{+} & \boxed{-} & & \end{array}$

 $Z_2$  Center

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$\begin{array}{ccccccc} & & & ee & & & \\ & & & \boxed{-} & \boxed{+} & & \end{array}$

 $Z_3$  Center

Figure 1. Models of the Z Centers



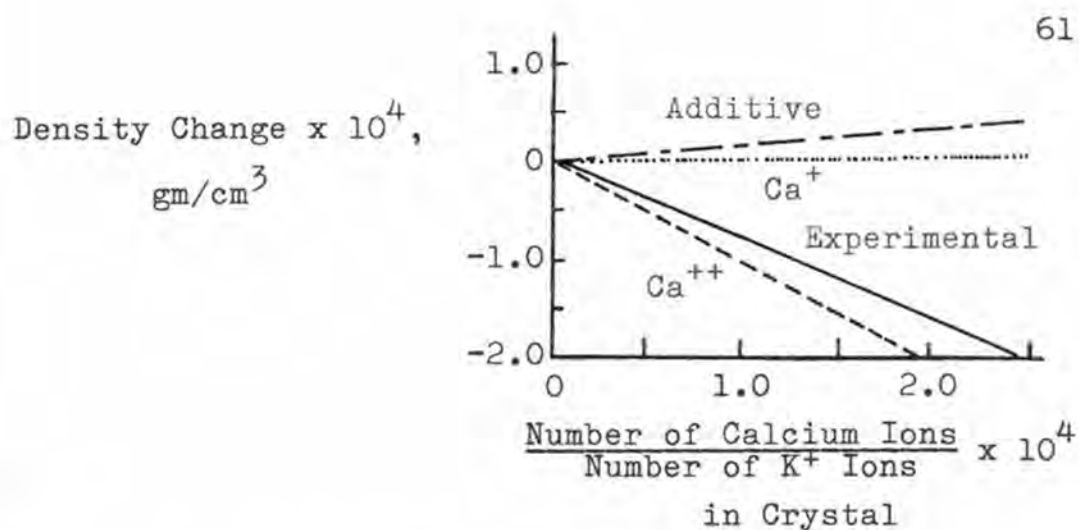


Figure 2. Variation of Density with Calcium Content

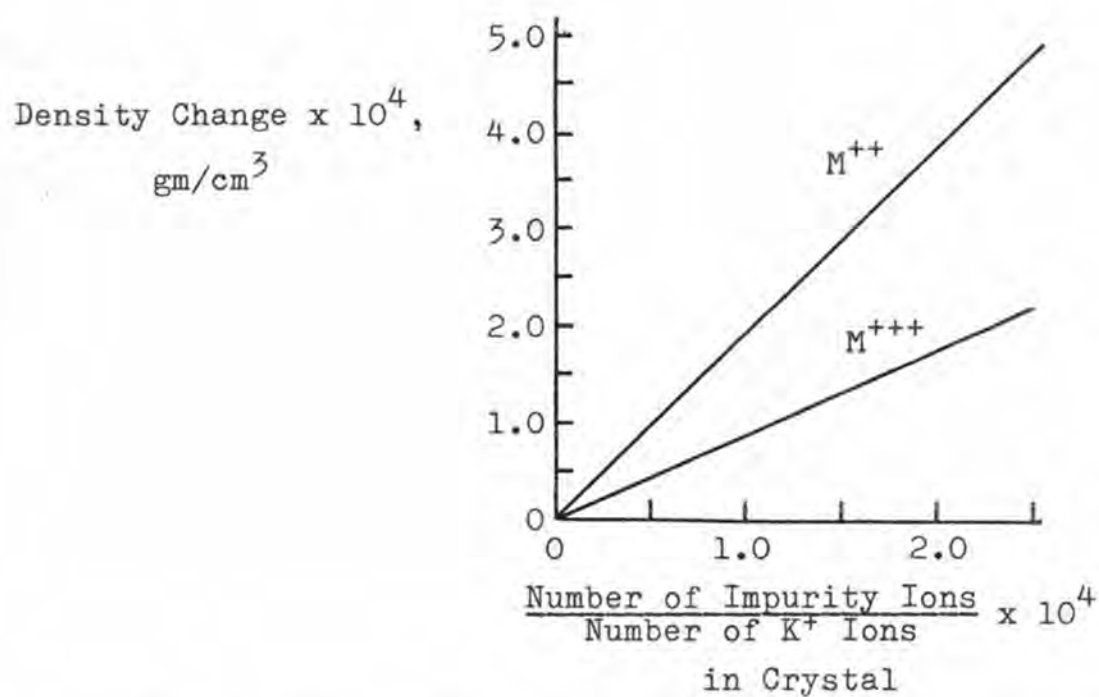


Figure 3. Variation of Density with Impurity Content

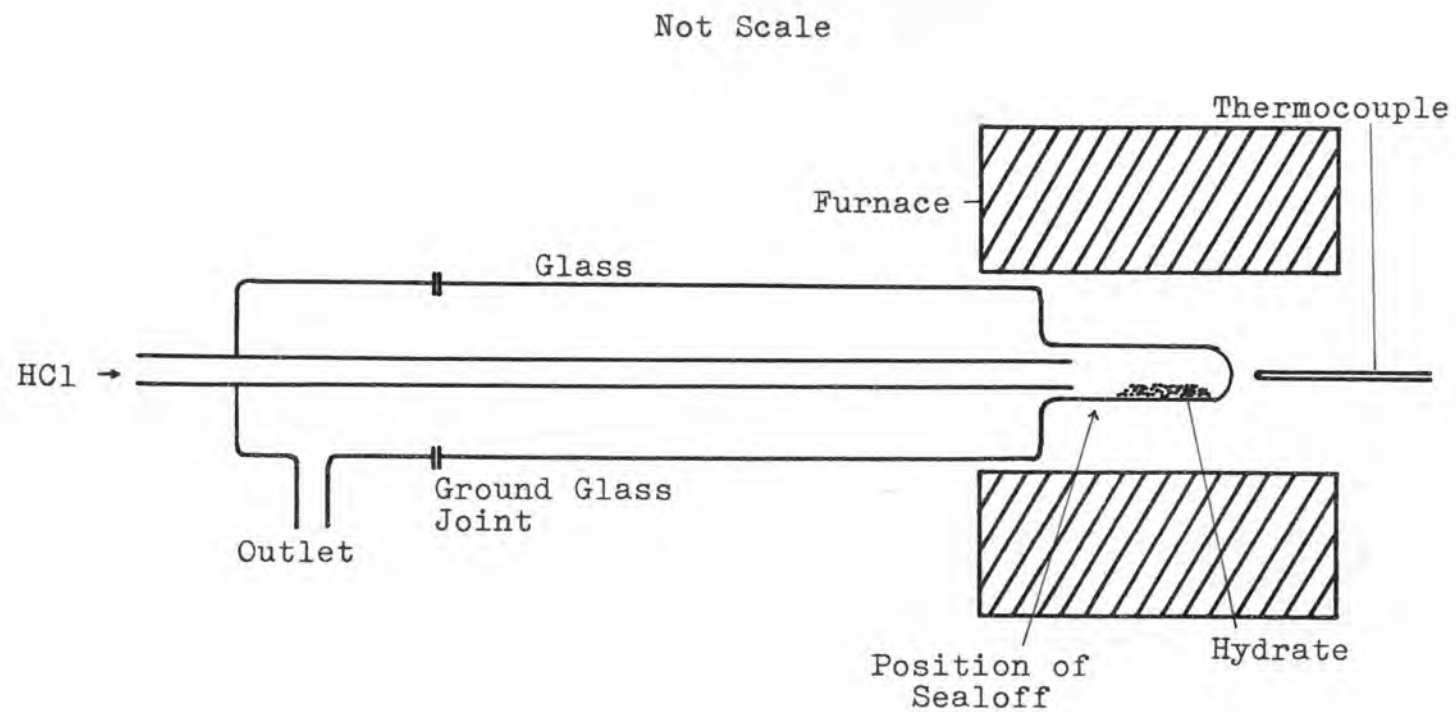


Figure 4. Dehydration Apparatus

Not to Scale

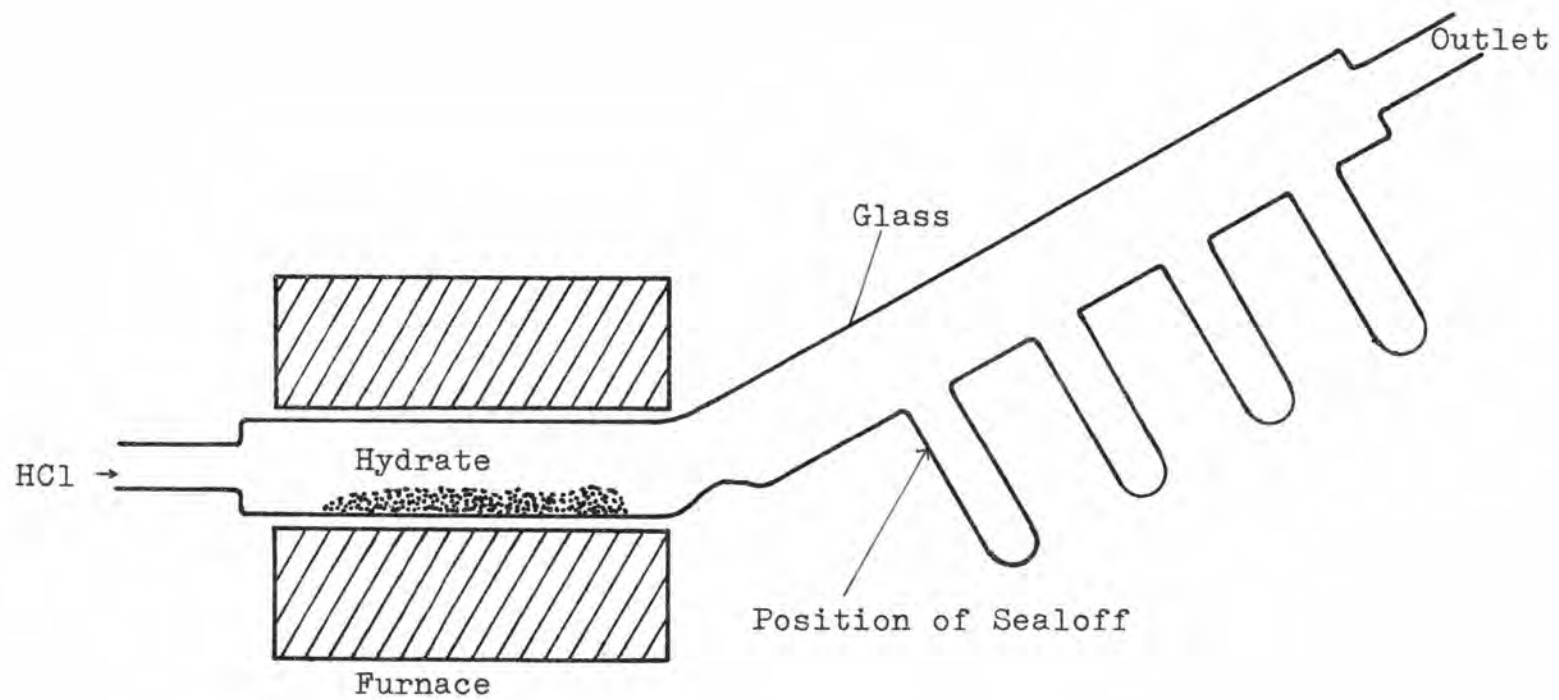


Figure 5. Dehydration Apparatus

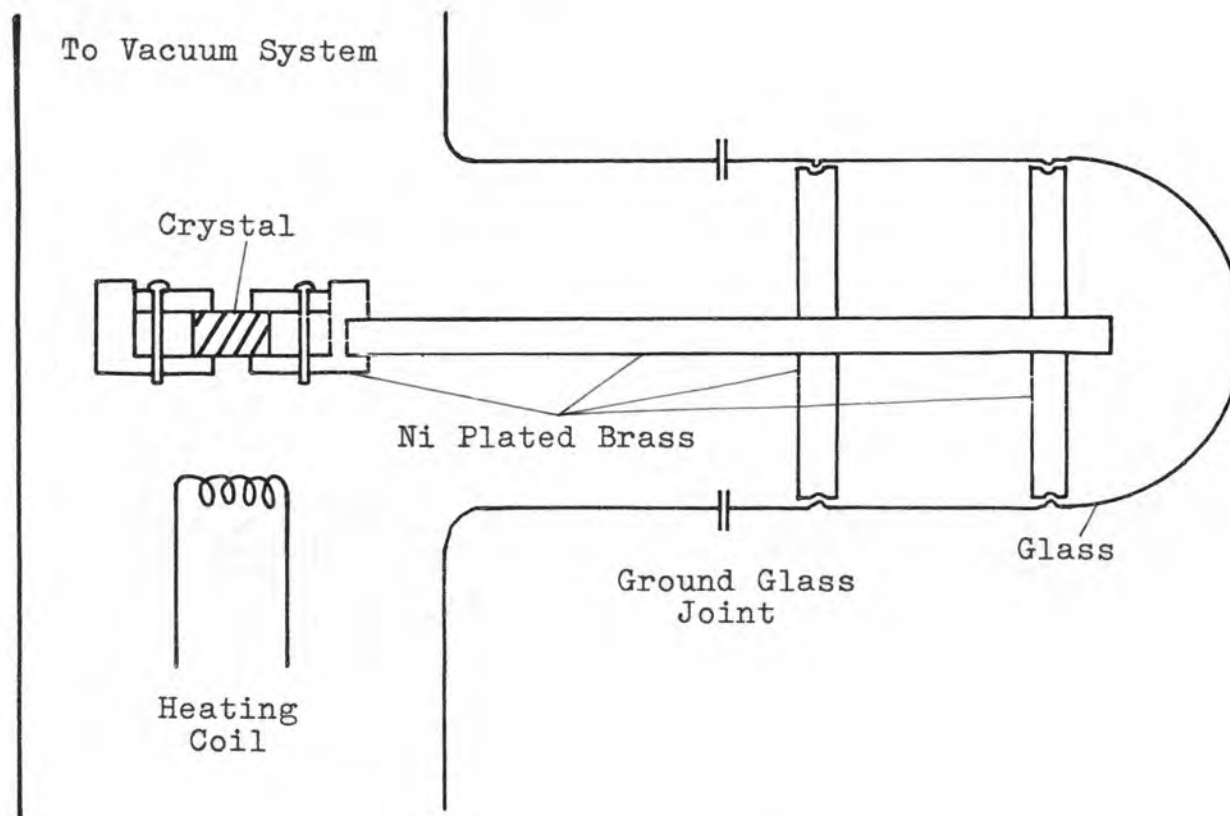


Figure 6. Schematic Diagram of Apparatus Used for Deposition of Metal Electrodes on Crystals

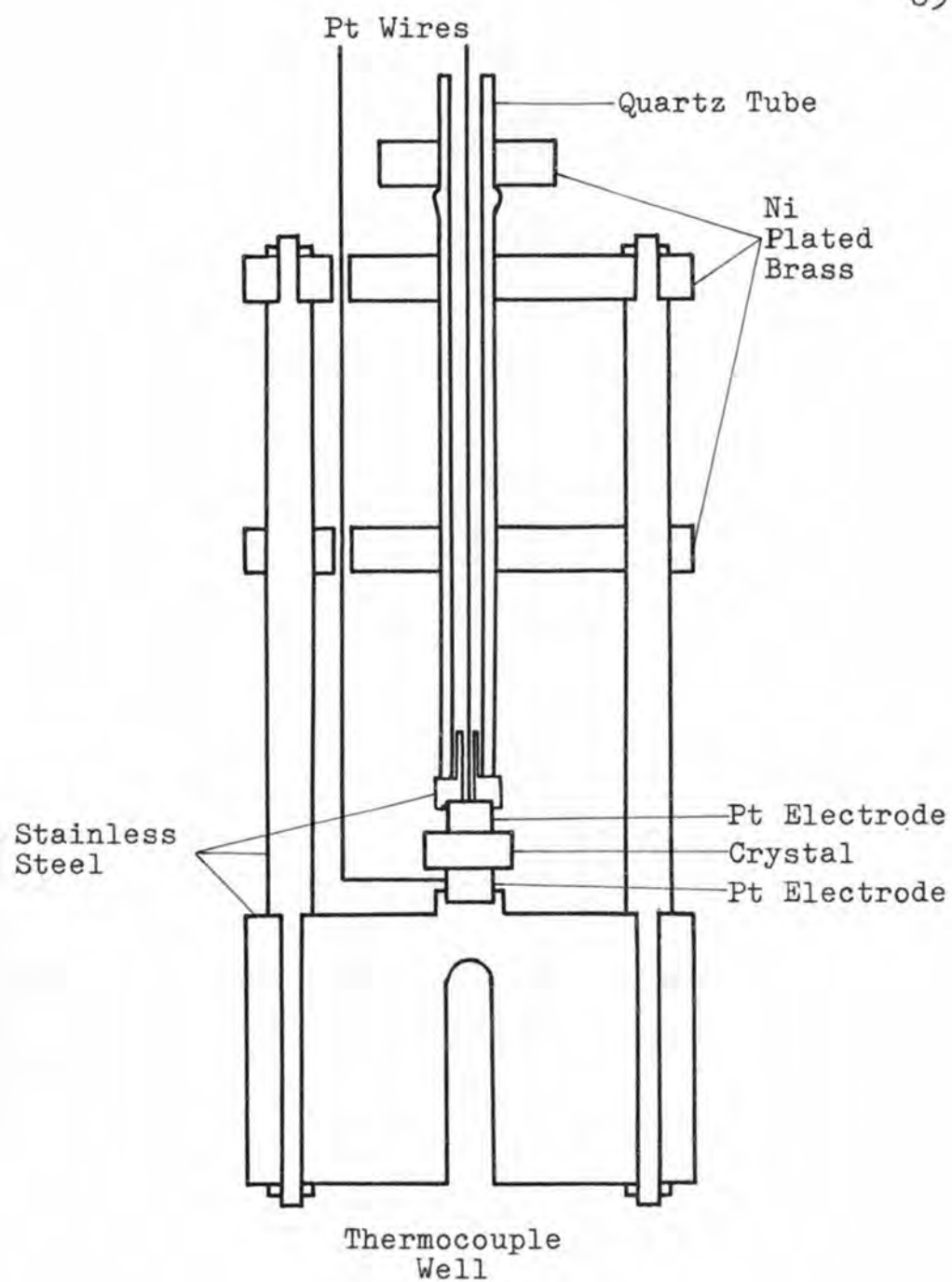


Figure 7. Schematic Diagram of Ionic Conductivity Cell

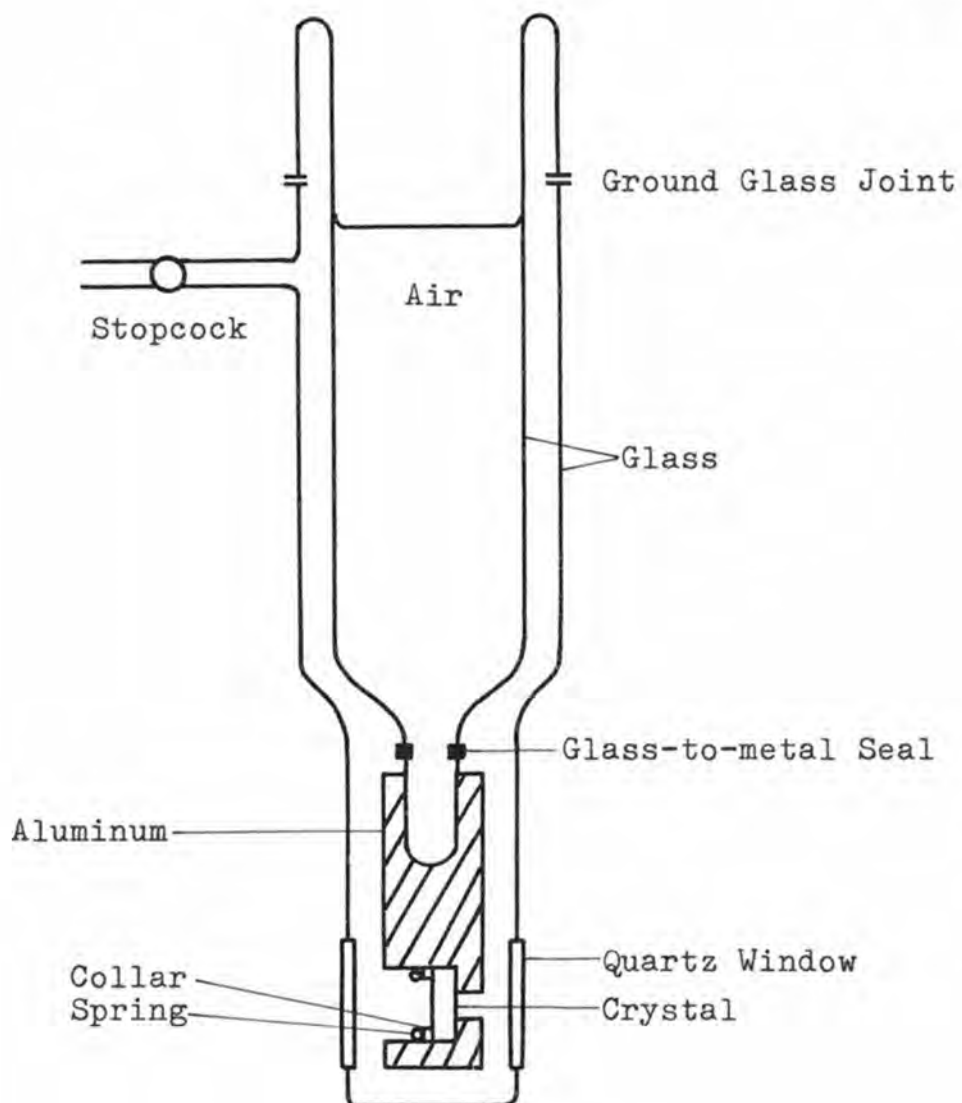


Figure 8. Schematic Diagram of Absorption Cell for Use at Low Temperatures



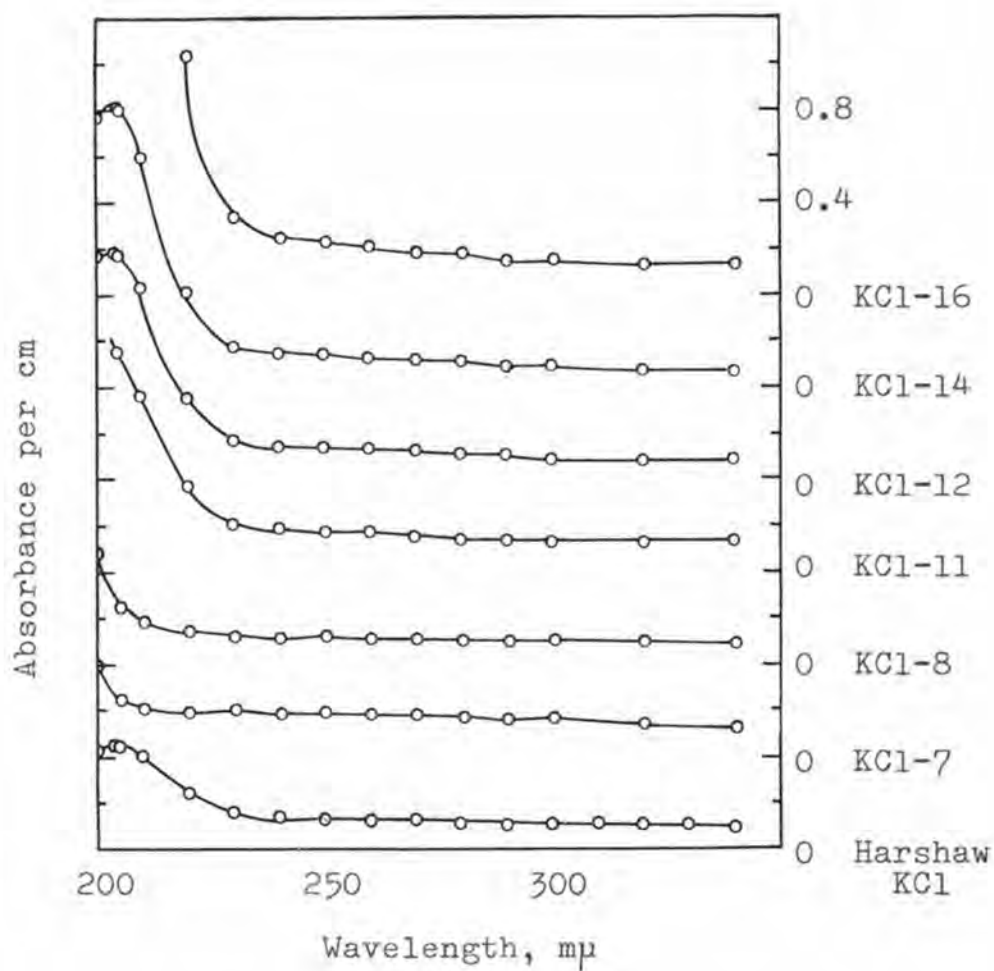


Figure 9. Ultraviolet Absorption Spectra of Pure KCl Crystals

1. KCl-Gd-7
2. KCl-Gd-12
3. KCl-Gd-17
4. KCl-Sm-2
5. KCl-Sm-4

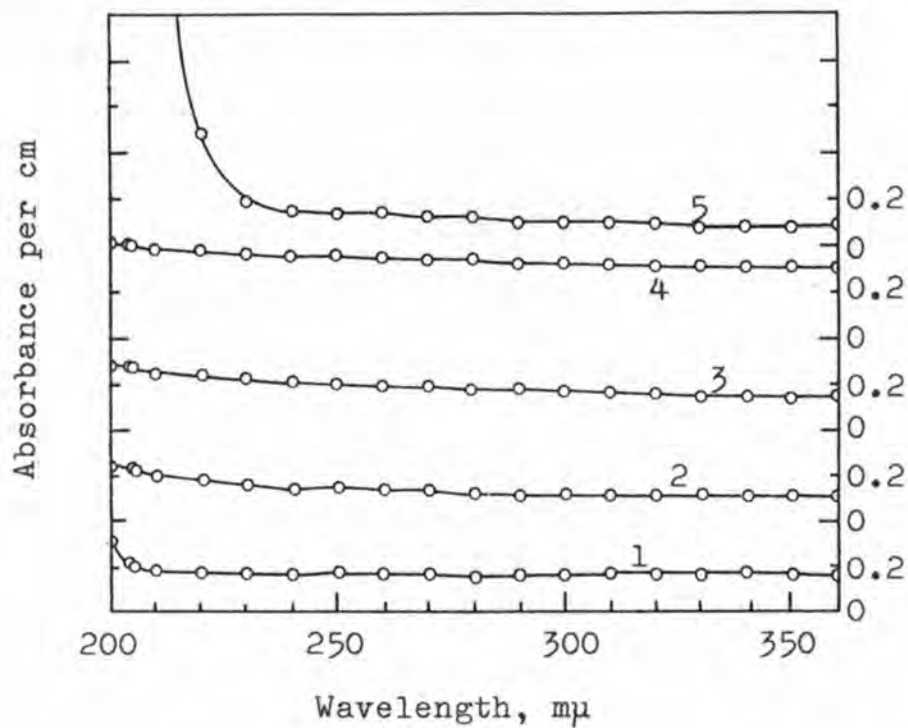


Figure 10. Ultraviolet Absorption Spectra of Doped KCl Crystals

1. KCl-Gd-15-A (contained white section)
2. KCl-Gd-16-A (contained white section)
3. KCl-Gd-16-C (contained white section)
4. KCl-18-A

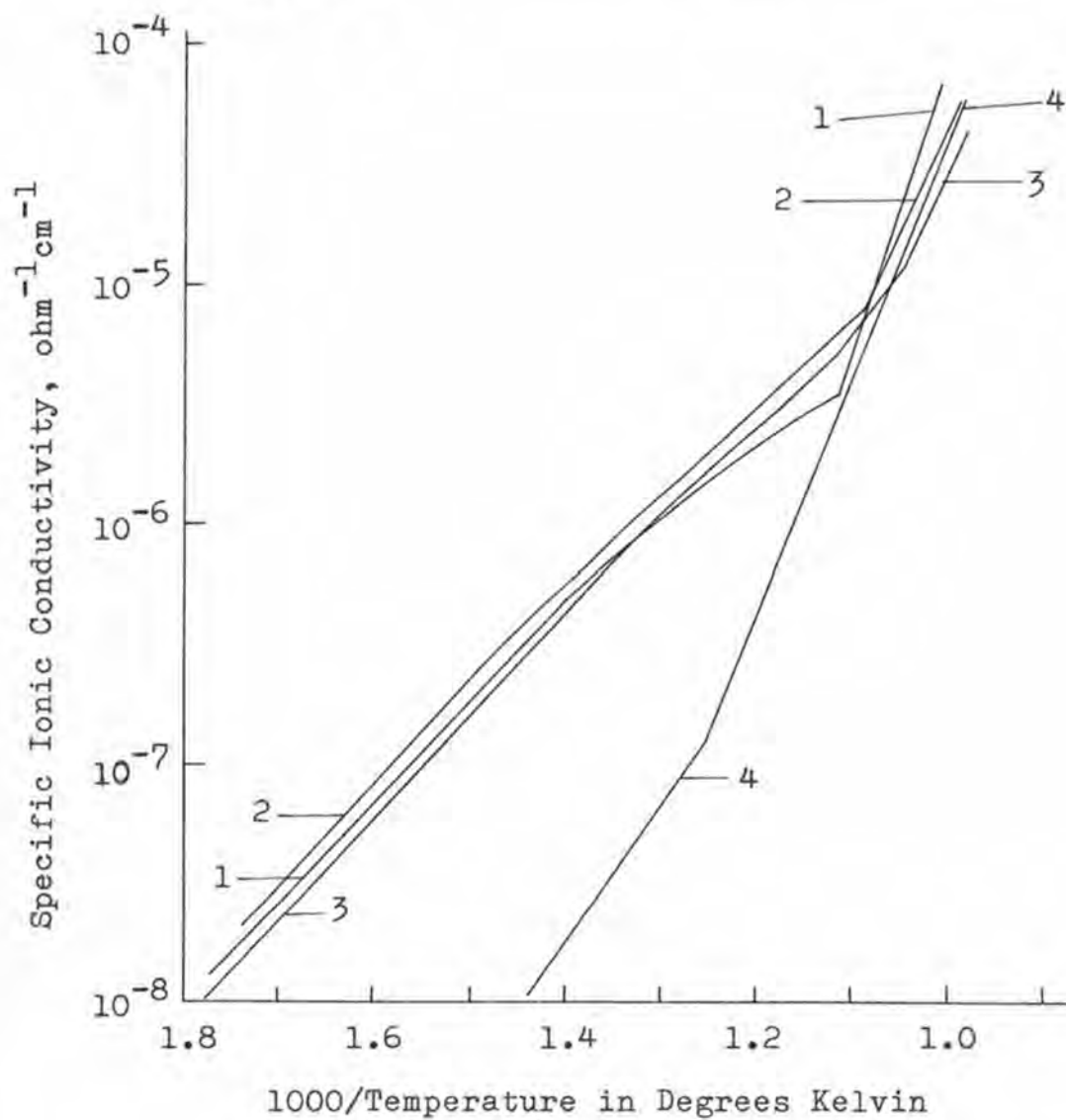


Figure 11. Ionic Conductivity of Crystals

1. KCl-18-A
2. KCl-18-B
3. KCl-Gd-17-A
4. KCl-Gd-17-B
5. KCl-Gd-17-C (contained white section)

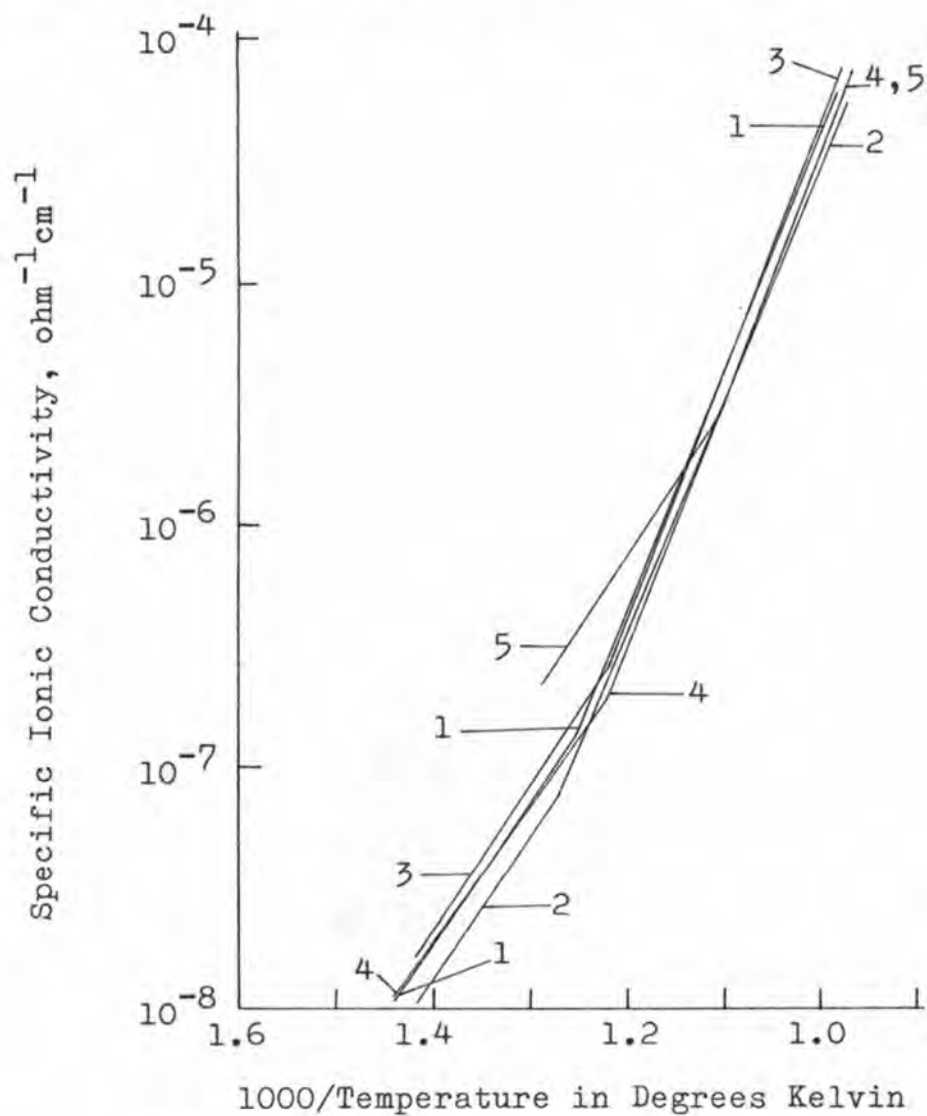


Figure 12. Ionic Conductivity of Crystals  
(All crystals grown in a Pt crucible)

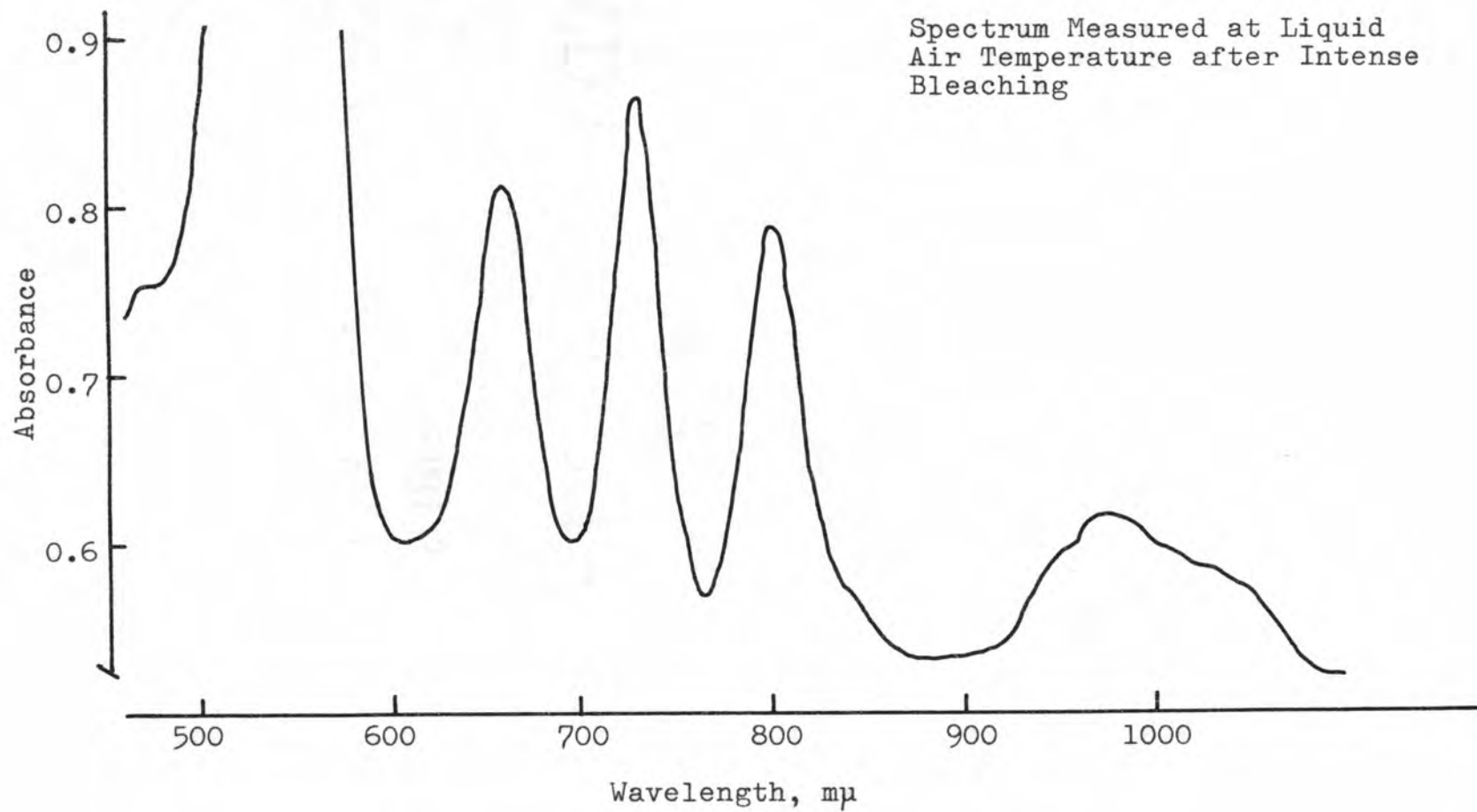


Figure 13. Spectrum of Bleached KCl-12-1

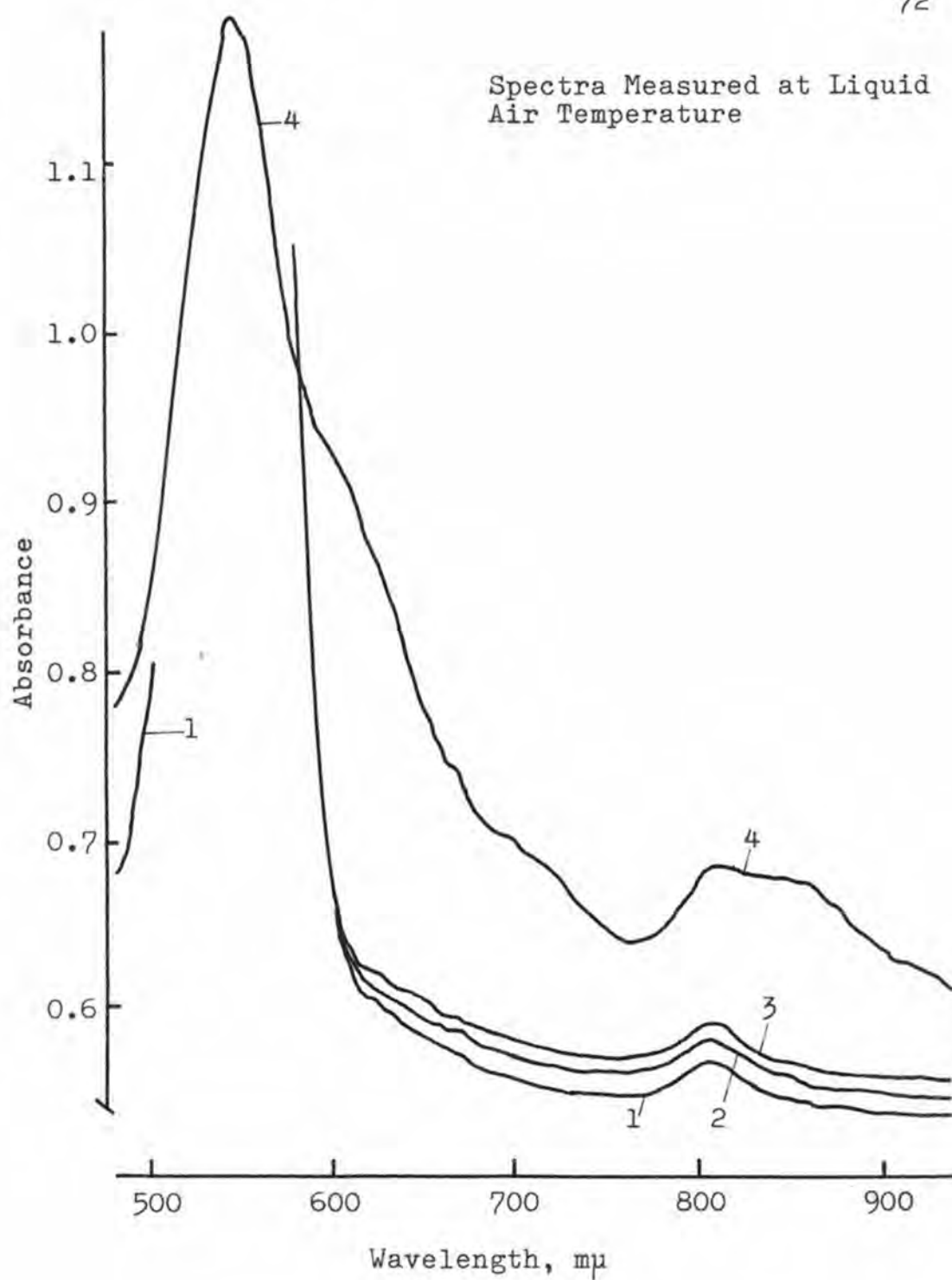


Figure 14. Spectra of KCl-Sm-3-3



## Legend

1. untreated
2. after bleaching with F light at liquid air temperature for 20 minutes
3. after bleaching with F light at liquid air temperature for 40 minutes
4. after bleaching with white light at room temperature for one hour in addition to treatments listed above

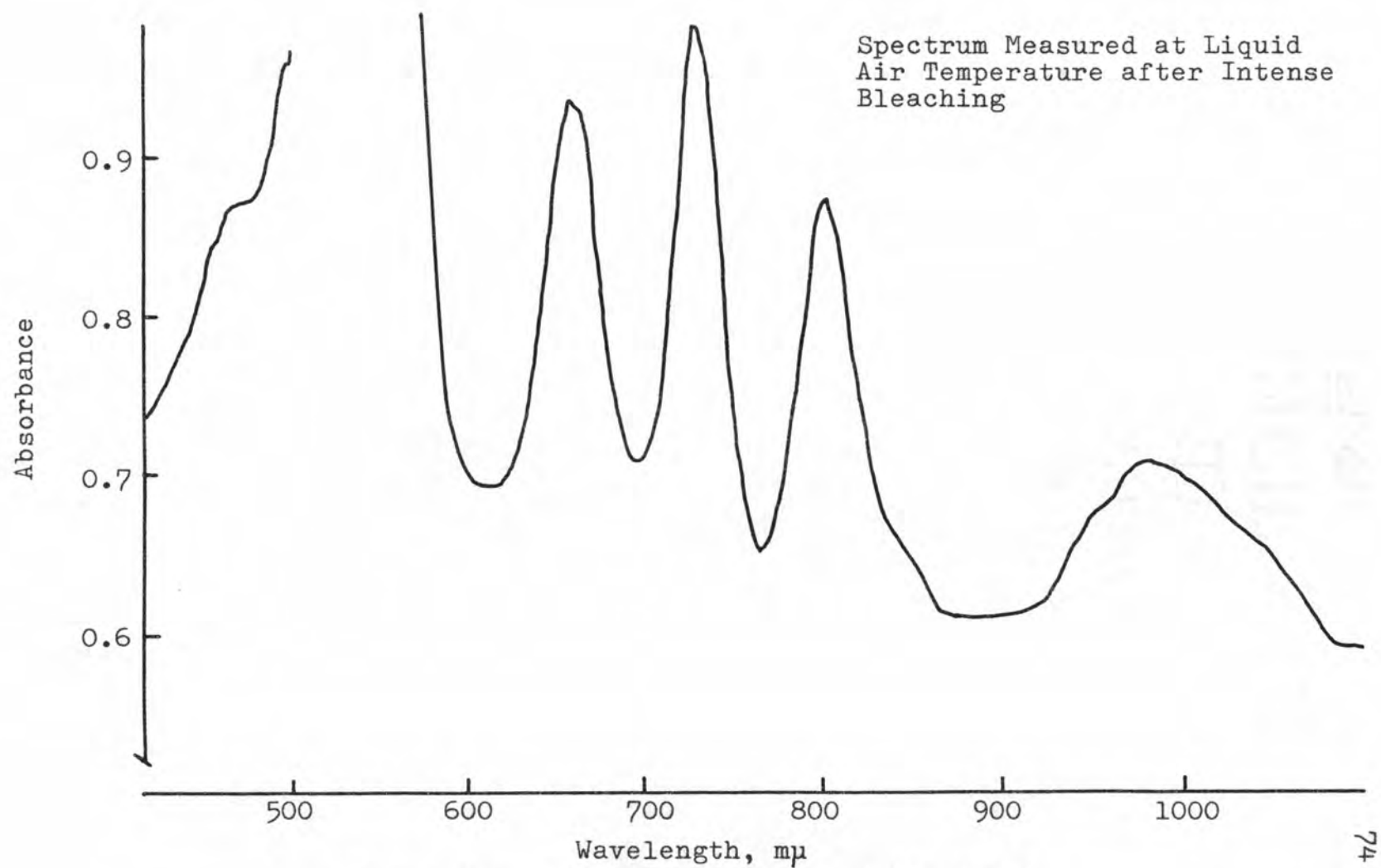


Figure 15. Spectrum of Bleached KCl-Y-2-1

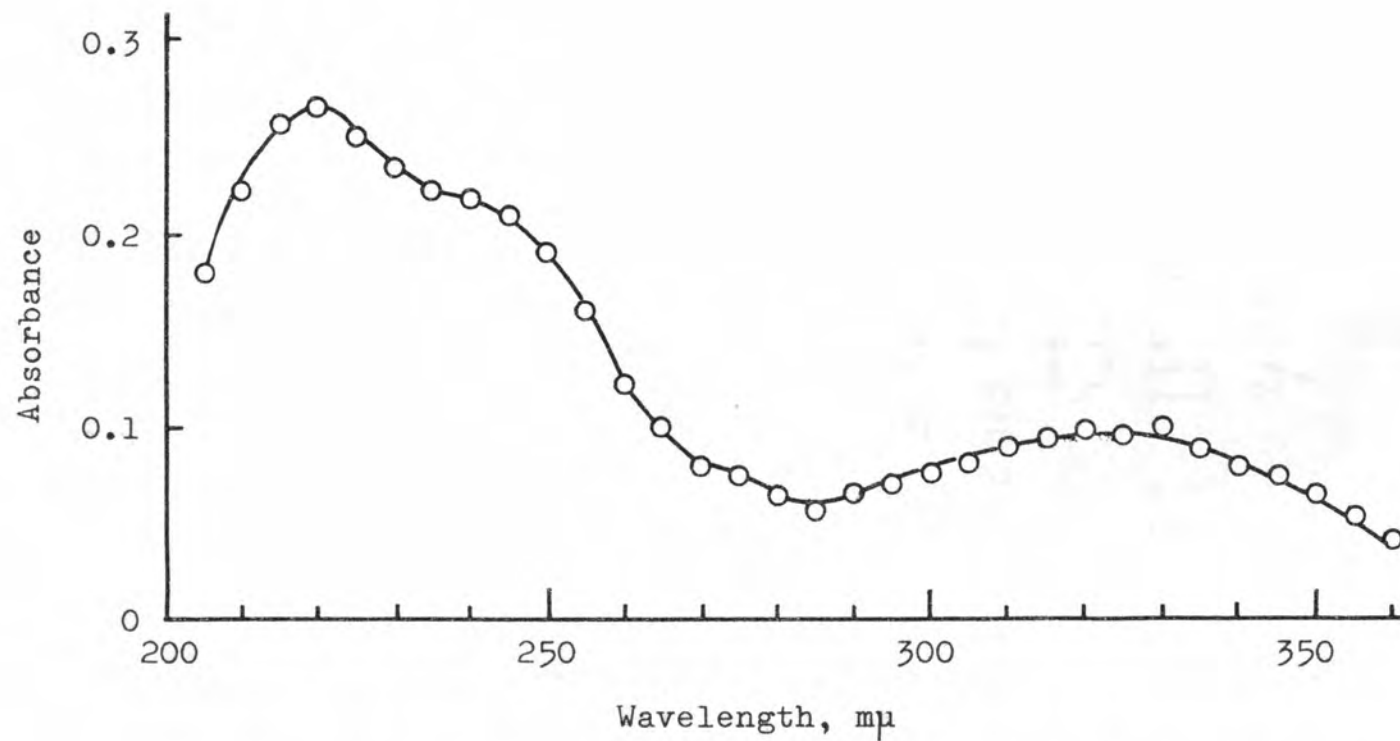


Figure 16. Ultraviolet Absorption Spectrum of KCl-Dy-2-X-2

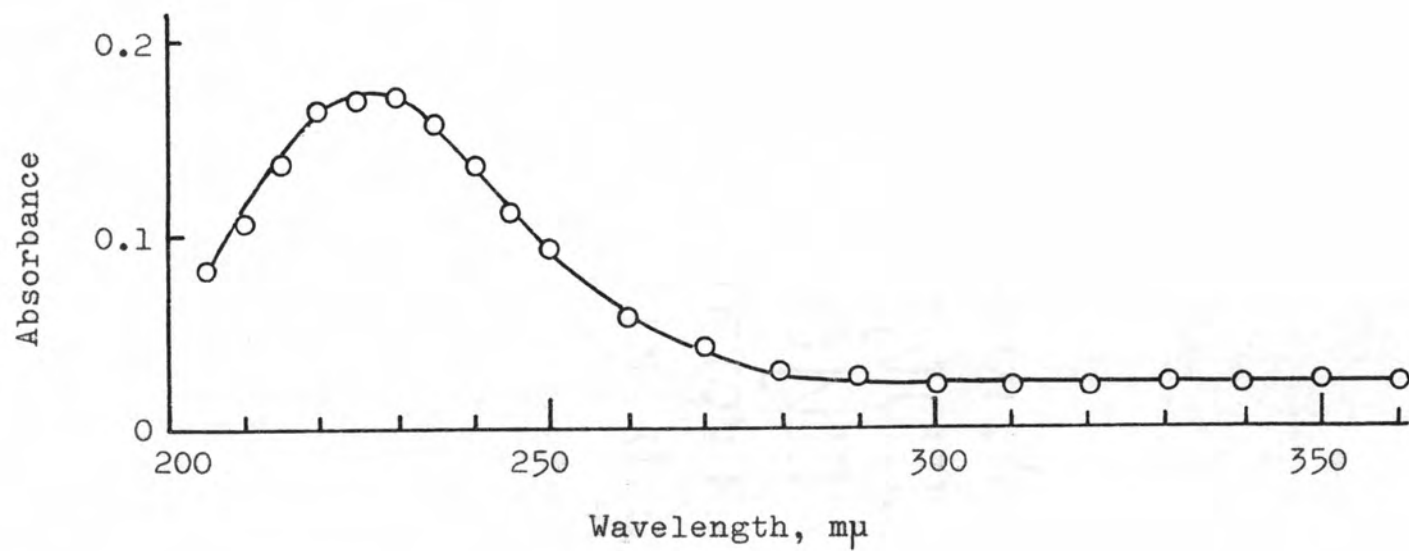


Figure 17. Ultraviolet Absorption Spectrum of KCl-Sm-2-X-1

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