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MASTER

NaCl

POLARIZED ABSORPTION MEASUREMENTS OF SODIUM CHLORIDE

WITH CALCIUM IMPURITY

Ca

Dennis E. Lauer

August, 1964

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Department of Physics and Astronomy

THE UNIVERSITY OF KANSAS

Lawrence, Kansas

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Point Defects in Ionic Crystals

Robert J. Friauf
Principal Investigator

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I. INTRODUCTION AND OBJECTIVES

(A) Nature of color centers

Many of the physical properties of crystalline solids seem to depend upon the presence of irregularities in the crystal structure, called "imperfections" or "defects". The study of color centers is concerned with the attempt to understand the structure and physical properties of these defects. Much work has been devoted to a determination and analysis of the optical properties of these defects, particularly on the most structurally simple solids, the alkali halide salts. A defect of particular interest in color center phenomena is the "lattice vacancy", in which an ion is missing from its normal lattice site, producing an effective charge of the opposite sign. In alkali halide crystals, the formation of these vacancies is believed to proceed by means of the "Schottky mechanism," whereby an ion leaves its lattice position to be deposited on the surface of the crystal, forming a new crystal layer and leaving a vacancy in the crystal interior. By using the Boltzmann equation and minimizing the free energy in the crystal it can be shown that the number of vacancies formed by the Schottky mechanism in the crystal at thermal equilibrium is⁽¹⁾:

$$n = N \exp (-E_s/2kT) \quad \text{if } n \ll N$$

where N = number of ions in the crystal

E_s = energy of formation for Schottky defects (approximately
2.0 electron volts in NaCl)

T = crystal temperature

k = Boltzmann's constant

This relationship predicts the presence of one vacancy in every 10^5 ions at room temperature for NaCl. The symbolic representation of a Schottky defect is shown in Figure 1a.

Vacancies may result from the absence of ions of either sign, taking on an effective charge equal but opposite in sign to the missing ion. Negative ion vacancies (Cl^-) are of particular interest in this work in their ability to attract electrons and negatively charged defect aggregates. A negative ion vacancy functions as a positively charged attractive center for any free electrons in the crystal lattice and, under the proper conditions, may trap an electron into a hydrogen-like configuration. The electron exists in discrete energy states, and transitions between these states result in the absorption or emission of radiation. Since this radiation is often in the visible wavelength range in many alkali halides, this anion vacancy-electron configuration is referred to as a type of "color center" called the "F Center".

The electron associated with a negative ion vacancy is depicted as shown in Figure 1b. The radiation absorbed in a particular optical transition of this F Center corresponds to a well defined absorption band in the optical spectrum, called the "F band". Under normal conditions this band accounts for the characteristic color which the given alkali halide assumes under coloration. In NaCl this F band is centered at approximately 460 millimicrons at room temperature, giving the crystal a yellowish-orange color. The location of the F band in the optical spectrum depends upon the type of crystal and its temperature.

FIGURE 1.a SCHOTTKY DEFECT

FIGURE 1.b F CENTER

(B) Energy Level Representation

A band picture of the energy level scheme for a NaCl crystal is shown in Figure 2, where the valence band represents the energies of the electrons bound to the lattice ions and the conduction band represents the energies of the photoconducting "free" electrons. Between these two bands exists a "forbidden band" of approximately 10 electron volts extent. When color centers are formed in the crystal, transitions can occur between localized energy levels located in the forbidden band. The F band is believed to arise from such a transition occurring between two energy levels of separation 2.72 electron volts in the forbidden band. The excited state of the F Center is believed to lie very close to the conduction band since it is observed from photoconductivity measurements that the electron in the excited state may be thermally excited into the conduction band relatively easily. The color center may also be optically "bleached" by exciting the trapped electron directly into the conduction band with appropriate irradiation. Also, any center will be thermally bleached to a certain extent at room temperature.

(C) Formation of Color Centers

Color centers may be formed by heating the crystal in a stoichiometric excess of alkali metal vapor (additive coloration) or by irradiation with X-Rays or Gamma Rays (irradiative coloration). During additive coloration, the alkali metal is absorbed onto the crystal surface, and its valence electron penetrates the crystal. Halogen ions diffuse to the surface, leaving negative ion vacancies in the crystal interior which attract the released free electrons to form color centers.

FIGURE 2. ENERGY BAND SCHEME FOR NaCl

In irradiative coloration, X-Rays incident upon the crystal produce large numbers of photoelectrons and may also create vacancies by a process still incompletely understood. Vacancy trapping of these photoelectrons produces color centers.

(D) Types of Color Centers

Under a variety of experimental conditions, more complicated color centers may be formed, consisting of aggregates of adjoining vacancies with one or more trapped electrons. Each type of center in a crystal of a given type has its own localized energy levels, transitions between which can give rise to optical absorption bands at wavelengths characteristic of the crystal. Figure 3a shows a composite graph of the locations of the various absorption bands in a pure alkali halide, and Figure 3b shows additional bands observed in an alkali halide crystal doped with a divalent impurity.

The presence of these bands in the optical spectrum implies the existence of either more energy levels for a given center or physically different center types. Models have been suggested by many investigators for the centers depicted in Figure 3. Models for the M, R and Z centers suggested by several investigators are shown in Figure 4.

(E) Polarized Bleaching

Clues to the structures of various color centers are obtained from a wide variety of experiments, one of which, devised by M. Ueta⁽⁵⁾, is based upon the idea that some centers may have a preferred axis for the absorption of light. Since centers can be effectively destroyed by optical bleaching with light in their optical absorption bands, a test of this hypothesis would be to bleach the crystal preferentially with

FIGURE 3.a

FIGURE 3.b

FIGURE 3. COMPOSITE OPTICAL ABSORPTION CURVES

light linearly polarized in a given direction with respect to the crystal axes, and then compare the absorption of the crystal for light polarized in the same direction and the absorption for light polarized in a perpendicular direction. If the two measured absorptions are dissimilar in the bleached band, this "dichroism" will indicate that a preferential absorbing axis exists in the center. Figure 5 illustrates Ueta's results from a polarized bleaching of the M band in potassium chloride at room temperature with light polarized in the (011) direction and subsequent measurement with light polarized in the (011) and (0 $\bar{1}$ 1) directions. When reference is made to light polarized in the (011) direction, the electric vector is oriented parallel to the (011) direction and in the (100) plane, perpendicular to the direction of propagation of the incident light (Figure 6).

Similar experiments have subsequently been performed to determine the dichroism of Z centers, which are produced in colored crystals containing minute amounts of certain divalent impurities. Chiarotti, Fumi and Giulotto⁽⁶⁾ performed the first polarized measurements on Z Centers and concluded that no dichroism existed in the Z₂ band in KCl with strontium impurity. Remaut and Dekeyser⁽⁷⁾ found a slight, temporary dichroic effect in the Z₂ band of additively colored NaCl with strontium impurity, located at 512 millimicrons with the bleaching light polarized in the (010) direction. The results of Remaut and Dekeyser are supported by observation of dichroism in the Z₂ band in NaCl with strontium impurity by Ishiguro, Sugioka and Takeuchi⁽⁸⁾ for (010) bleaching light, but

FIGURE 5. M BAND POLARIZED BLEACHING (UETA)⁵

FIGURE 6. POLARIZED BLEACHING ORIENTATIONS

these authors' measurements showing similar dichroism in KCl with strontium impurity contradicts Chiarotti's results. Several sources indicate that no dichroism exists in the Z_1 band. No polarized work has previously been performed on Z bands in NaCl with calcium impurity, so any clues as to the dichroic properties of these Z bands must be obtained from previous work on NaCl with strontium impurity, such as by Remaut and Dekeyser.

Because of the conflicting evidence concerning the dichroic properties of alkali halides doped with divalent alkaline earth impurities, it seemed desirable to study the dichroism of a doped crystal upon which little work had been done. No previous polarized absorption studies had been made upon calcium doped NaCl, and the presence of Z bands in its optical spectrum was still somewhat in doubt. J. E. Caffyn and B. K. Ridley⁽⁹⁾ reported an unresolved Z_1 band for calcium doped NaCl, located somewhere around 476 millimicrons. They also indicated the probable presence of a Z_2 band as well. No polarized measurements were performed by these authors however.

Strong evidence of dichroism in the Z_1 or Z_2 bands in calcium doped NaCl would add much information with which to interpret the structure of these centers.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

(A) Crystal Growth and Preparation for pure crystals

For precise and meaningful optical studies of color centers, single crystal specimens are necessary with a minimum of uncertainty in the impurity concentration. For this reason, most measurements were taken on crystals grown in air from a quartz crucible in the laboratory, in the withdrawal apparatus shown in Figure 7. A certain amount of evidence seemed to indicate the presence of a substantial amount of impurity in the commercially obtained sodium chloride crystals. A 725 watt, type 86 "Hevi-Duty" furnace was used in conjunction with a hollow inconel withdrawal rod approximately 20" in length. Air could be continuously circulated through this rod, maintaining it at a fairly uniform temperature during withdrawal. The crystal seed was formed around a 1" platinum needle on the end of the withdrawal rod. The inconel rod was withdrawn from the melt by means of a system of gears and motor, allowing withdrawal rates of 1.04, 0.52, 0.26, 0.13 or 0.06 inches per hour. It was determined that withdrawal rates of 0.26 or 0.13 inches per hour produced the best results.

The cylindrical furnace cavity of 8" depth and 5" diameter allowed ample space to insert a 150 ml. quartz beaker. A platinum furnace shield was placed between the beaker and the furnace coils. The cavity temperature was measured with a chromel-alumel thermocouple wired into a control and recorder circuit as shown schematically in Figure 8. The temperature of the melt surface could be regulated and controlled, under optimum conditions, to a tolerance of $\pm 1^{\circ}$ C. at 800° C.

FIGURE 7. FURNACE AND WITHDRAWAL APPARATUS

FIGURE 7

- A : Air hose connector
- B : Connecting rod to motor and gear drive
- C : Air outlet
- D : Outer support rod
- E : Needle mount attachment
- F : Platinum Needle
- G : "Hevi- Duty" furnace
- H : Platinum furnace shield
- I : Chromel- Alumel Thermocouple
- J : 150 ml. quartz beaker
- K : Soapstone support
- L : Sodium chloride melt

FIGURE 8. CONTROL AND RECORDER CIRCUIT

The melt material used was powdered analytical reagent grade NaCl. Typical impurity concentrations in the commercially pure NaCl are:

Ba⁺⁺: .001%

Ca⁺⁺, Mg⁺⁺, R₂O₃ ppt.: .000%

Heavy Metals: .0000%

Fe⁺⁺: .0000%

K⁺: .005%

Approximately 60 grams of NaCl was introduced into the quartz beaker, which had previously been decontaminated by refluxing with aqua regia, dilute hydrochloric acid, and deionized distilled water. With the beaker centrally placed in the furnace cavity, the NaCl was heated beyond its melting point (801° C) to 850° C, then slowly returned to approximately 810° C. It was determined that the proper surface temperature for withdrawal was reached when irregular "blotches" of a solid skim began to appear on the melt surface. As the rod was slowly withdrawn, the crystal generally grew initially in a conical form, then in the form of a cylinder after a chosen diameter was achieved. As the crystal grew and the melt became exhausted, the operating temperature of the furnace had to be lowered continuously. The withdrawal was continued until most of the melt was exhausted. The author's first crystals were grown in a flat-bottomed beaker, but it was later determined that larger crystals could be grown more easily if the beaker bottom were spherical in shape. To prevent the crystal from shattering after withdrawal was completed, the furnace was cooled slowly from 800° C to room temperature during a period of approximately twelve hours.

An attempt was made to grow single crystals in a sealed, evacuated quartz tube. The advantages of this technique, if feasible, would be to eliminate the introduction of foreign impurities, particularly OH^- ions during the growing process, and also the process would be easier to control. The crystalline NaCl, sealed in the pre-cleaned and evacuated quartz tube, was inserted into a double furnace arrangement, and withdrawn at a rate of 0.26 inches per hour at a temperature of $850^\circ \text{C} \pm 1^\circ \text{C}$. Approximately one hour after the withdrawal had begun, it became evident that the tube had cracked. Examination of the tube revealed that the NaCl had reacted with the quartz, almost eating through the tube in many places. It was decided that, in spite of the obvious advantages of this crystal-growing technique, all further crystals would be grown by withdrawal from the melt. This technique of the growing of crystals in an evacuated container may still be feasible with more experimentation.

The crystals were cleaved for optical measurements using a hammer and razor blade, previously decontaminated with acetone, benzene, trichloroethylene and deionized distilled water. The best optical surfaces were obtained when the cleavage was made with a single stroke along a cleavage plane. In cases in which the optical surface was not perfectly smooth, the crystal was waterpolished by rubbing the faces on a flattened piece of wet silk, and drying with a piece of lens paper. It was never found to be possible, by waterpolishing, to obtain any surface as optically perfect as that obtained by proper cleavage, but the absorption of even the most crudely waterpolished crystals differed from that of a visually perfect crystal by only, at most, 0.02 absorption units over

most of the visible wavelength region. Because of the geometry of the optical measuring apparatus, it was necessary to cleave the crystals to a minimum dimension of 8 mm. along the face. All crystals used were less than 2 mm. in thickness.

(B) Crystal Growth and Preparation for doped crystals

The technique involved in growing doped crystals was identical to that in growing pure crystals, except that a specific amount of anhydrous calcium chloride was added to the melt to allow positive divalent calcium ions to enter the crystal lattice substitutionally. The water of hydration present in the commercial $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was removed prior to weighing by heating in a Cenco drying oven for three days at over 200°C . Since the calcium chloride hydrated rapidly after removal from the oven, it was necessary to weigh the compound immediately after removal. The proportion of CaCl_2 in the melt was expressed in "mole fraction", F , and determined from the relative masses and molecular weights of the doping and base compounds.

By the withdrawal technique, four doped crystals were grown, of which three were suitable for optical measurements:

D - 1 : Ca^{++} -doped NaCl ($F = 5.7 \times 10^{-3}$)

D - 2 : Ca^{++} -doped NaCl ($F = 9.0 \times 10^{-3}$)

D - 3 : Ca^{++} -doped NaCl ($F = 4.0 \times 10^{-2}$)

D - 4 : Ca^{++} -doped NaCl ($F = 6.0 \times 10^{-2}$)

P - 1 : Pure NaCl, homegrown ($F = 0$)

With the exception of D-3, which was unacceptable for optical measure-

ments because of the brittleness of this highly-doped crystal, dozens of good optical specimens were obtained from all crystals. Portions of crystal D-4 were also unusable due to the presence of a "milky" texture, ascribed to colloidal aggregates of impurities in this heavily doped crystal. It became apparent that an upper limit in doping concentrations at approximately 5×10^{-2} mole fraction had been attained, above which the crystals became translucent and brittle.

The afore-mentioned impurity concentrations referred to the calcium chloride proportion in the melt. The impurity concentration in the growing crystal, however, is invariably less than the melt concentration, and is related to it through a "segregation coefficient", which is the ratio of the two concentrations and is less than one. This coefficient depends upon the portion of the growing crystal considered, the withdrawal rate, and the nature of the base crystal and the doping compound. A study of this segregation coefficient was performed by Kelting and Witt⁽¹⁰⁾ upon potassium chloride crystals with strontium, calcium, and barium doping, withdrawn at various rates. An attempt was made by the author to correlate the data and conclusions of Kelting and Witt on KCl to the author's situation with NaCl. Obviously, however, many assumptions and approximations had to be made, and the results obtained were of questionable accuracy. It was evident, however, that this segregation coefficient was in the neighborhood of 0.1, i.e. the crystal concentration was approximately one-tenth that of the melt.

The $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ used was of analytical reagent grade and contained the following proportions of impurities:

Ba^{++} : .005%

Heavy Metals: .0005%

Fe^{++} : .001%

Mg^{++} : .005%

Alkali Metals: .03%

Sr^{++} : .1%

(C) Crystal coloration

All crystals used for optical measurements were colored by X-irradiation at room temperature for specific time intervals. Three different X-Ray Units were used for various experimental purposes: a Norelco unit provided by Dr. Gilles of the University of Kansas Chemistry Department, a Westinghouse 150 kv and a General Electric "Maxitron" 250 kv unit, both provided by Dr. Hoecker of the University of Kansas Radiation Biophysics Department. Initial attempts at crystal coloration were performed on the Norelco unit at voltages of approximately 45 kv and filament currents of 10 ma. The use of this unit was discontinued when it was found optically that the crystal cross-section was not being irradiated uniformly in the X-ray beam. All subsequent measurements were performed on the Westinghouse or G.E. units.

The intensity of coloration is dependent upon the intensity of the X-Ray beam and the temperature, type, and purity of the crystal. The coloration of a particular crystal was controlled by varying the

distance from the X-ray target, the exposure time, the tube current or by adding filters, which filtered out the softer components of the X-rays. For most irradiations, an aluminum filter of 1.2 mm. thickness was used, but a copper filter was also used occasionally. Crystals D - 2 and D - 4 were irradiated so as to produce an approximate unit absorption, which involved using X-ray tube voltages of 120-140 kv, currents of 5-15 ma, and distances from the target of approximately five inches. Exposure times ran from 5 minutes to 20 minutes. The dosage rates used, determined with a radiation dosimeter, were approximately 150,000 roentgens per hour.

It was observed that the rate and extent of coloration depend to an extraordinary degree upon the impurity content of the crystal. A series of measurements were made, (Graph No. 1), of the peak F-band absorptions for continuous irradiation times on a Harshaw pure NaCl crystal and a D - 1 calcium doped NaCl crystal of doping concentration 5.7×10^{-3} mole fraction. All coloration-affecting parameters of the systems were kept the same for both crystals.

To eliminate optical bleaching, the crystals were wrapped in aluminum foil during irradiation and unwrapped and mounted only in total darkness. The problem of thermal bleaching could not be completely avoided since all irradiations were performed at room temperature, and an unavoidable time interval elapsed between irradiation and the time in which the crystal could be reduced to liquid nitrogen temperature. Graph No. 2 shows some measurements which were taken to investigate the rate at which thermal bleaching occurred at room temperature in total

GRAPH NO. 1 : F BAND PEAK ABSORBANCE DURING IRRADIATION

GRAPH NO. 2 : THERMAL BLEACHING AT ROOM TEMPERATURE

darkness. These results indicate that the thermal bleaching is most pronounced immediately after irradiation, and that the crystal should be measured immediately thereafter, or kept at liquid nitrogen temperature. Crystals kept at liquid nitrogen temperature for several days showed no appreciable bleaching.

No significant optical measurements were made with additively colored crystals because of the extreme coloration difficulties for NaCl. However, several techniques were developed which, if pursued, should produce usable additively colored NaCl crystals. Initial attempts were made using an evacuated quartz tube containing the crystal and metallic sodium. Little success was achieved by heating the crystal and sodium to a wide variety of common and independent temperatures. Initial attempts failed due to incomplete coloration, so subsequent attempts involved increasing the coloration temperature and quantity of sodium until an attempt at a two-hour coloration resulted in an implosion of the tube. It was evident that the sodium metal was reacting with the quartz tube walls at a faster rate than with the crystal. This additive coloration method was subsequently discontinued. The next additive coloring attempts were made with a stainless steel, then an inconel, coloration "bomb". Partial coloration in some cases was attained, but not sufficient for optical measurements. Temperatures approaching the melting point of NaCl were used, along with excessive amounts of sodium metal. The difficulties encountered seemed to be characteristic of NaCl crystals, since similar techniques employed on KCl crystals produced excellent results.

(D) Optical Measurements

A combination crystal holder and dewar were constructed and adapted to the sample compartment of the Perkin-Elmer Model 350 Spectrophotometer. The crystal holder, shown in Figure No. 9, consisted of a brass support, through which a $\frac{1}{4}$ inch aperture was drilled and countersunk, and two rectangular copper plates, one of foil thickness, between which the crystal could be wedged by a screw adjustment. The crystal holder was joined thermally to the cold finger of a brass dewar of approximately one liter capacity. Through the direct metallic connection from dewar to crystal, the crystal could be reduced from room temperature to liquid nitrogen temperature fifteen minutes after the introduction of liquid nitrogen into the dewar. No thermocouple was used, but it was found by optical measurements that the crystal had reached liquid nitrogen temperature ten minutes after the liquid nitrogen in the dewar ceased to boil. Through the use of a vacuum shield about the liquid nitrogen container, which could attain approximately 10 microns of pressure by means of a fore pump, a supply of liquid nitrogen could be maintained in the dewar for several hours.

Most optical measurements were taken using the Perkin-Elmer Model 350 Spectrophotometer. The function of a spectrophotometer is to compare the optical absorbance or transmittance of two specimens. Light originating from a tungsten lamp (for visible and near infrared measurements) or a hydrogen lamp (for ultraviolet measurements) passes through a quartz prism monochrometer unit which produces nearly monochromatic light. It then passes through a "chopper" and, after undergoing numerous reflections, is incident upon a "beam splitter", which divides and directs the

FIGURE 9. CRYSTAL HOLDER AND DEWAR

FIGURE 9

- A : Connector Tubing to fore pump
- B : Outer dewar wall
- C : Vacuum shield
- D : Cold finger of dewar
- E : Sample compartment wall of P-E Spectrophotometer
- F : Copper conductors
- G : Quartz windows
- H : Thin rectangular copper sheet, against crystal

beam into the sample and reference compartments. The two intensities are optically compared with a photosensitive detector (a photocell for visible and ultraviolet light and a lead sulfide cell for near infrared light). The detector information is relayed to a recording system where the absorbance or transmittance of the crystalline sample, relative to a reference standard, is plotted in absorbance or transmittance units as a function of the wavelength of the incident light.

The reference optical standard was arbitrary, usually consisting of one of a set of reference screens provided with the instruments. Prior to the measurement of a colored crystal, a baseline would normally be established on the recording chart, in which the absorption of the uncolored crystal, relative to the absorption of a pre-selected reference screen in the reference compartment, was recorded as zero absorbance (or 100% transmittance) for all wavelengths desired. To assure zero absorbance for all wavelengths, a series of resistors, comprising a compensator bank were repeatedly adjusted until the absorbance plot converged to a straight baseline. This, then, was the reference standard with which all subsequent optical measurements on the colored crystal were compared,

By Lambert's Law of Optical Absorption, the fractional decrease in the optical intensity of light passing through a material is the same for successive equal segments of path through the material.

$$dI/I = -\alpha dx$$

$$\ln I/I_0 = -\alpha x$$

where I = the intensity of the incident light after a distance x
has been traversed in the material

I_0 = the intensity of the incident light

α = the "absorption coefficient"

Optical measurements were recorded on the Perkin-Elmer in units of
"absorbance" defined as

$$A = \log_{10} I/I_0$$

or in units of "transmittance" defined as

$$T = I/I_0$$

Therefore, $A = -\log_{10} T$.

Or, in terms of the absorption coefficient

$$A = \frac{\alpha x}{\ln 10} = (0.434) \alpha x$$

The crystal itself is not the only factor tending to limit
the beam intensity reaching the detectors. In addition, absorbance is
reduced by:

- (1) restricting apertures in the sample compartment
- (2) quartz windows on the dewar
- (3) reflection and absorption losses in polarizing elements
- (4) extraneous reflections

These all are compensated for, however, by maintaining the same physical
conditions with the sample run as when the baseline was established prior
to the run. All absorptions were then measured relative to the uncolored
crystal.

In order to study the polarized properties of doped, colored crystals, a linearly polarizing crystal element was mounted in the spectrophotometer beam path as shown in Figure 10. A prism possessing a large acceptance angle, flat faces to eliminate displacement of the beam, and a very high degree of linear polarization is the "Ahrens" prism, which was used throughout. The Ahrens prism consists of three wedge-shaped prisms, cemented together with balsam, transmitting the extraordinary ray, but causing the ordinary ray to be totally reflected from the balsam layer, as shown in Figure 11.

One would expect, on the basis of the multiple reflections undergone in the Perkin-Elmer beam path, that the light incident upon the crystal would be elliptically polarized, and this was verified. Therefore, to assure that the intensity of the linearly polarized light incident upon the detectors was unchanged during rotation of the Ahrens prism, the incident light had to be depolarized prior to its incidence on the Ahrens. Several depolarizing devices were considered, including various compensators, such as the Soleil, but these were unacceptable for use over a range of wavelengths. The depolarizer actually used was a "pseudo-depolarizer" suggested by R.H. Hughes⁽¹¹⁾. As shown in Figure 12, the pseudo-depolarizer consists of a Wollaston prism with a special thin wedge angle of 15 minutes. The optic axis of the wedge is oriented at an angle of 45° relative to the optic axes of the Wollaston. It was found that the transmittance of the light leaving the entire polarized attachment was 40% of the initial transmittance and varied by only approximately 1% by rotation of the Ahrens prism for all wavelengths. It was observed that this 1% optimum variation in transmittance could only be achieved

A : Wollaston Pseudo-depolarizer

C : Quartz Window

B : Ahrens Prism

D : Crystal Holder and Dewar

FIGURE 10. POLARIZER MOUNT

FIGURE 11. AHRENS PRISM 12

FIGURE 12. WOLLASTON PSEUDO-DEPOLARIZER 11

with a proper orientation of the pseudo-depolarizer; otherwise this variation would reach 4% to 5%. The presence of the 1% variation might be ascribed to a polarized sensitivity of the detector.

The polarizer attachment to the dewar consisted of a mount for a stationary pseudo-depolarizer adjacent to a housing for the Ahrens prism, which could be rotated either manually or by a low-speed synchronous motor (Figure 10). For manual operation, the housing was supplied with a 90° stop, allowing the prism to be rotated through 90° by adjustment from outside the sample compartment. Preliminary studies were made using the continuous drive, but all crystal measurements were taken by manual rotation of the Ahrens. Any dichroism in the colored crystals would then be observed as a difference between two absorption curves run with the Ahrens placed at orientations 90° apart.

The direction of polarization of the light incident upon the crystal could be accurately determined by observing the orientation of the wedge line on the face of the Ahrens prism when the prism was placed in the polarizer mount. The mount had a permanent circular scale, marked to the nearest 3 degrees of arc, thus allowing an estimate of the polarizer orientation to approximately 1 degree of arc.

Considerable care was exercised to insure that the crystal sample was oriented properly with respect to this accurately known polarization direction. A thin metal "lip" was joined to one of the rectangular copper plates with sealing wax and its upper edge was carefully oriented parallel to the dewar supports. The variation of the crystal axes from the $[010]$ and $[001]$ directions was probably less than 1 degree.

It was also known that the (100) face of the crystal was accurately perpendicular to the incident polarized light, because this crystal plane cleaved far more readily than any other. A little practice insured that this was indeed the plane cleaved.

III. EXPERIMENTAL RESULTS

(A) Preliminary Measurements

Prior to any attempts to study the polarized characteristics of impurity induced color centers in NaCl, certain preliminary measurements were taken to become acquainted with the characteristics of this crystal and the experimental techniques involved.

In order to avoid thermal bleaching as indicated in Graph No. 2, all crystals were mounted in the dewar in total darkness within 30 minutes of irradiation. Individual experiments were performed in sequence, and if it became necessary to interrupt any sequence of experiments, the crystal was immediately reduced to liquid nitrogen temperature until the experiment could be resumed. Rabin⁽¹³⁾, however, notes that the effect of thermal bleaching is less in calcium doped alkali halides than with any other doping compound.

Numerous experiments were performed on D - 1 crystals to determine suitable conditions for the irradiative process in order to obtain an approximate 2.0 absorbance for pure and calcium doped NaCl crystals. During these experiments, the remarkable differences in coloration over specific time intervals between pure and doped NaCl became evident. Careful measurement of F band peak absorbance for various irradiation times are summarized in Graph No. 1. In all of these measurements, performed on a Beckman Model DK-1 Spectrophotometer, care was taken to ensure that the doped and pure NaCl crystals, irradiated for any given time interval, were treated identically, that is, given the same irradiation intensity, identical measuring procedures, the same

time interval between irradiation and measurement, the same orientation of the crystal in the beam path (relative to its orientation in the X-Ray unit), crystals of approximately the same thickness, etc. These measurements indicate that the calcium doped NaCl crystal colors much more rapidly and completely than a comparably treated pure NaCl crystal. Etzel⁽¹⁴⁾ also demonstrated a direct correlation between the amount of calcium in the NaCl crystal and the extent of coloration for a given irradiation interval, using crystals of various calcium contents; the heavier dopings invariably producing more coloration. These results were also confirmed by Caffyn and Ridley⁽⁹⁾.

In all bleaching processes, the bleaching was performed in the Perkin-Elmer sample compartment with the spectrophotometer beam, set to allow a spectral bandpass of approximately 20 millimicrons. It was decided advisable to bleach in this manner rather than to remove the crystal and holder from the sample compartment for each bleaching cycle, even though a narrower bandpass might have been achieved with appropriate filter combinations. Removing the crystal from the sample compartment for bleaching purposes would have increased the experimental uncertainty through the likelihood of general optical bleaching or thermal bleaching, or even accidental reorientation of the crystal in the holder.

(B) Absorption bands in lightly calcium doped NaCl

On the basis of several articles concerning Z Centers in divalent impurity-doped alkali halides, the Z_1 band was expected to lie to the long wavelength side of the F band. The work of Caffyn and Ridley⁽⁹⁾ on calcium doped NaCl suggested that this Z_1 band might lie

in the immediate proximity of the F band, possibly not even resolvable. With the possibility of detecting the presence of the Z band only as a shift in the F band peak position, a series of measurements were therefore performed to establish the precise location of the F band peak in a pure Harshaw NaCl crystal and to compare this to the carefully measured F band peak in a calcium doped (D - 1) NaCl crystal at room temperature and liquid nitrogen temperature immediately after irradiation. The best results were:

Room Temperature:	Pure NaCl:	468 $m\mu$
	Ca-doped (D - 1) NaCl:	470 $m\mu$
Liquid N ₂ Temperature:	Pure NaCl:	459 $m\mu$
	Ca-doped (D - 1) NaCl:	458 $m\mu$

The one or two millimicron differences are well within the experimental spread of about 3 millimicrons. Therefore, no conclusions could be drawn concerning the presence or absence of the Z₁ band in doped crystal D - 1 (5.7×10^{-3} m.f. CaCl₂).

In the absence of definitive results on freshly-irradiated D - 1 crystals, attempts were made to develop the Z₁ band in these crystals by unpolarized bleaching in the F band at 470 millimicrons for approximately six hours, taking observations at appropriate intervals. The results obtained from crystal D - 1 - 1 were then compared to the results of a similar absorption measurement on pure Harshaw crystals (still bleaching at 470 $m\mu$ as before). A small irregularity which was not present in the pure crystal was indeed observed in the doped crystal on the long wavelength side of the F band, but the variation between the curves was almost within the limits of machine error.

In an attempt to enlarge this irregularity on the infrared side of the F band, a more heavily doped crystal D - 2 ($F = 9.0 \times 10^{-3}$) was grown. Based on the idea that the absence of an appreciable Z band in the doped crystals was in part due to a coagulation of the calcium ions producing a subsequent reduction in the Z center density, the D - 2 (and D - 4) crystals were generally heat-treated prior to X-irradiation. This should have the effect of dispersing these aggregates. The heat treatments varied, but they generally consisted of holding the crystal at a temperature near its melting point (of about 770°C) for over twelve hours, then lowering it to an intermediate temperature (approximately 500°C) for a few more hours, then removing it from the furnace to cool in air. In many cases, particularly with thick crystals, these temperature changes were too extreme, resulting in shattered or fogged crystals. All crystals so treated were processed in platinum crucibles to minimize contamination.

Irradiation and subsequent unpolarized F band bleaching of crystal D-2-7 ($F = 9.0 \times 10^{-3}$) seemed to stimulate a band development in the 500 millimicron region and a slight, almost imperceptible, shift of the F band peak toward longer wavelengths. The absorption spectrum of this crystal before and after one hour of 450 millimicron unpolarized bleaching is shown in Graph No. 3, where it is compared to that of a pure, homegrown NaCl crystal subjected to similar treatment. Still no Z band resolution was observed, however, indicating the need for crystals containing still higher doping concentrations.

(C) Studies of the M Band in NaCl

A two-fold study was made of the M band in X-irradiated pure and calcium doped NaCl; first to investigate the possible presence of a Z_4 band in the doped crystal, second to study the dichroism of the M band in a pure NaCl crystal.

Z_4 bands have been detected in additively colored KCl crystals doped with strontium impurity⁽¹⁵⁾, located close to, and on the long wavelength side of, the M band. In an attempt to detect the presence of this band in freshly irradiated NaCl with calcium doping, careful measurements of the position of the M band peak absorbance were taken, and compared to the corresponding peak position in a pure Harshaw NaCl crystal. The presence of an unresolved Z_4 band would be observed as a peak shift toward longer wavelengths in the doped crystal. The best results were:

Room temperature	Pure NaCl :	742 m μ
	Ca-doped (D - 1) NaCl :	741 m μ
Liquid N ₂ temperature	Pure NaCl :	728 m μ
	Ca-doped (D - 1) NaCl :	727 m μ

Again, as in the case of the unresolved Z_1 band, the difference in peak position are within the limits of experimental error.

Attempts were made to observe dichroism in the M band of P-1-3, a homegrown, pure NaCl crystal. It had been observed that maximum M band development occurred after approximately one hour of irradiation with light in the F band. Consequently, after 45 minutes of unpolarized bleaching at room temperature at a wavelength of 450 millimicrons, the

M band was bleached with [100] light at 740 millimicrons for 5 minute and 15 minute intervals, after which time the M band was effectively bleached out. No conclusive dichroic effects were observed. Undoubtedly, one of the reasons for this was the fact that the M bands in X-irradiated NaCl could not be developed to any great extent in either pure or doped samples.

M band development in the calcium doped crystals was observed to be invariably smaller, immediately after irradiation, than in a similarly treated pure crystal, either Harshaw or homegrown. The largest M band ever developed in a calcium doped NaCl crystal had a peak absorption of only approximately 0.05 absorption units. The largest M band ever developed in a pure NaCl crystal had a peak absorption of 0.10 absorption units, for X-irradiated crystals. However, a single measurement of a relatively weakly additively colored doped NaCl crystal fragment indicated that a much larger M band could be achieved in an additively colored crystal.

(D) Hydroxide Impurity Bands

On the basis of a suggestion by H.W. Etzel and D.A. Patterson⁽¹⁶⁾ that hydroxide ions present in the crystal might account for the near absence of a substantial Z band in calcium doped NaCl, absorption measurements were taken on uncolored calcium doped NaCl (D - 1) and (D - 2), homegrown pure NaCl (P - 1), and Harshaw pure NaCl crystals far into the ultraviolet (Graph No. 4). Measurements taken in the ultraviolet region of the optical spectrum necessitated the introduction of different measurement techniques. The hydrogen lamp was used as a source, and the sample and reference compartments were purged with gaseous nitrogen to eliminate the atmospheric absorption bands which predominate at these

wavelengths. The limit of the spectrophotometer was also reached in these measurements, which were carried down to 175 millimicrons, presenting a moderate amount of uncertainty in the absorbance due to instrument noise. This uncertainty was always less than ± 0.03 absorption units, however.

It is observed from Graph No. 4 that, whereas the absorbance of the pure Harshaw, D - 1, and D - 2 crystals varies little down to 175 millimicrons, the homegrown pure crystal (P - 1) (grown in air) developed a remarkable absorption, beginning at approximately 200 millimicrons. This absorption is believed due to the presence of hydroxide ion impurities in the homegrown crystal. It is difficult, however, to resolve any absorption peaks in Graph No. 4. Etzel and Patterson⁽¹⁶⁾ observed such a hydroxide band in pure NaCl at 185 millimicrons. They also failed to observe the band in a calcium doped NaCl crystal. They interpreted this to mean that the unassociated calcium ions in the crystal were combining with the hydroxide ions to form either CaOH^+ or Ca(OH)_2 , with the consequent annihilation of the hydroxide band. This would also, then, have the effect of reducing the number of calcium ions available for Z center formation, thus explaining the minuteness (or absence) of any observed Z band in crystals grown in air in the laboratory. The absence of the hydroxide band in the commercial Harshaw pure crystal may be attributed either to the presence of accidental impurities or to the growth of their crystals in the absence of air. J. Rolfe⁽¹⁷⁾, on the other hand, observed the hydroxide band at 190 millimicrons in his Harshaw pure NaCl crystals.

These results forboded a limitation upon the extent of Z band development in calcium doped NaCl. Two channels of approach were indicated. The crystals could be doped more heavily, relying on a fair proportion of calcium ions being trapped in Z center configurations before reacting with the hydroxide ions. However, it was later observed that an upper limit on the doping concentration in NaCl existed, so there was a possibility that it might be impossible to add enough CaCl_2 to the crystal to obtain appreciable Z center concentration and still not cause colloidal aggregates characteristic of overdosing. The second approach, which is currently being pursued by R. J. Friauf and R. Mellott at the University of Kansas, is to build a crystal-growing apparatus in which the crystal may be grown in an inert atmosphere.

(E) Z-band development with higher doping concentrations

Highly doped crystals D - 3 and D - 4 of mole fractions 4.0×10^{-2} and 6.0×10^{-2} , respectively, were grown in air, but crystal D - 3 proved to be too hard and brittle for proper cleavage. This indicates an approach to the upper limit for the calcium doping of NaCl. Although portions of crystal D - 4 had a milky texture, many usable crystals were obtained. These were the only crystals upon which Z band polarized absorption measurements were attempted.

Prior to any polarized measurements on crystals, a series of tests were run to determine the optimum orientation of the pseudo-depolarizer in the beam path so as to minimize the apparent dichroism in non-dichroic measurements. Under these optimum conditions, and absorbance change of approximately 0.02 absorption units is observed as the Ahrens prism is rotated through 360° . Therefore, any true dichroism in a

crystal sample would be observed as an absorbance change beyond this value when the Ahrens polarizer is rotated through 90° .

In no polarized absorption measurements taken on D - 4 crystals, with the exception of crystal D - 4 - 3, were any significant dichroic effects observed at any wavelength outside of the limits of experimental error. Therefore all graphs (except that of D - 4 - 3) representing absorption runs are depicted as single curves, corresponding to either orientation of the Ahrens prism.

Since the D - 4 crystals represented the only hope of observing dichroism in the Z band, several attempts were made to develop such a band, and to bleach it selectively in various directions of polarization. Even in cases in which no resolved Z band was observed, polarized bleaching was performed in the hope of observing a dichroism in a particular wavelength regions.

Graph No. 5 shows the absorption spectrum of crystal D - 4 - 2 immediately after irradiation at 140 Kv, 5 ma for 3 minutes (curve 1) and after 102 minutes of $[100]$ bleaching at room temperature in the F band at a wavelength of 450 ± 10 millimicrons (curve 2). As always, no dichroism was observed at any wavelength for measurements taken in the $[100]$ and $[010]$ directions at liquid nitrogen temperature. These curves are representative of measurements taken frequently during the bleaching process. No band formation was observed during this relatively short bleaching cycle.

A similar series of measurements was performed on another sample, using a different polarized bleaching direction. Graph No. 6 represents crystal D - 4 - 3 immediately after irradiation for 8 minutes

at 120 kv, 5 ma (curve 1) and after 45 minutes of $[011]$ bleaching at room temperature and at a wavelength of 470 millimicrons (curve 2).

Two features of these curves are interesting; an apparent dichroism in the F band after measurement with light polarized in the $[011]$ and $[0\bar{1}1]$ directions, even prior to polarized bleaching, and also an apparent band resolution on the long wavelength side of the F band. K. G. Bansigir and E. E. Schneider⁽¹⁸⁾ observed a similar phenomenon in X-irradiated pure NaCl under similar polarized bleaching conditions. They identified their two resolved peaks, located at 457 and 452 millimicrons with the M_F and R_F bands respectively, and they observed considerable dichroism in these bands. These authors interpreted this dichroic behavior in terms of the application of stress to the crystals. It is of interest to note that D - 4 - 3 was the only crystal of the D - 4 series of crystals not heat-treated prior to irradiation. Consequently, studies were made of the D - 4 crystals through crossed Ahrens prisms. The birefringent properties of the Ahrens' allowed the regions of stress to be viewed visually with the apparatus shown in Figure No. 13. Considerable stress was indeed observed in the D - 4 crystals. Subsequent experiments were performed with crystals selected to be relatively stress-free.

Attributing the absence of a strongly developed Z band to too brief bleaching times, more lengthy bleaching cycles were initiated on crystal D - 4 - 4. Curve 1 of Graph No. 7 shows the crystal immediately after irradiation for 5 minutes at 140 kv, 15 ma. Curve 2 depicts the absorption after 6 hours of $[011]$ bleaching at 480 millimicrons. Curve 3 shows the result of further bleaching to a total time of 15 hours, 25 minutes, indicating that curve 2 represented the approximate maximum

A : Ahrens Prism
B : Crystal Sample

C : Quartz Plate
D : Ahrens Prism

FIGURE 13. CROSSED POLARIZERS FOR STRESS ANALYSIS

growth of the band adjoining the F band. After a total of 20 hours, 25 minutes of 480 millimicron bleaching, similar polarized bleaching was begun at 510 millimicrons (the estimated new band peak). Curve 4 shows the result of 3 hours, 40 minutes of 510 millimicron polarized bleaching. Interpretable results were few because of the fact that any formed bands were fairly completely bleached before any 510 millimicron bleaching was performed. No dichroic effects were observed.

Crystal D - 4 - 5 was bleached with unpolarized light at 450 millimicrons for 4 hours, 30 minutes to build up the new band completely. Curve 1 of Graph No. 8 represents the crystal immediately after irradiation for 6 minutes at 140 kv., 15 ma; and curve 2 represents the absorption after 4 hours, 30 minutes of unpolarized bleaching. Polarized bleaching at 510 millimicrons was commenced immediately in the $[011]$ direction, with curve 3 representing the result of 10 minutes bleaching, and curve 4 representing 130 minutes of bleaching. These curves can be compared to the corresponding curves of Graph No. 9, which are the absorption curves run on pure, homegrown NaCl crystal P - 1 - 5 under optical treatment identical to that given to crystal D - 4 - 5. Any difference in the corresponding curves of Graphs Nos. 8 and 9 should be due to the presence of calcium impurity in the crystal. The new band was developed to its greatest extent in this measurement but, as always, no dichroism with $[011]$ and $[0\bar{1}1]$ measurement light was observed.

IV. DISCUSSION OF RESULTS

The most obvious and consistent result of this investigation is a complete lack of any dichroic effect in any of the bleaching orientations or crystal doping concentrations used. The only dichroism observed was in crystal D - 4 - 3, and this appears to be a consequence of the presence of an unusual amount of stress in the crystal structure during bleaching.

Several possible reasons may be given for the absence of dichroism in these crystals.

(1) There exists no preferred optic axis for the centers under investigation. If, indeed, a Z_1 band was observed, this interpretation would be supported by some investigators, rejected by others.

(2) A preferred axis exists, but the band was never developed sufficiently to allow the absorptive differences to be observed outside the limits of experimental error. This could presumably be checked by devising methods to increase the free calcium content of the crystals, or by performing still longer bleaching cycles.

(3) All X-irradiations were performed at room temperature, with a time lag of not less than 20 minutes until the crystal could be reduced to liquid nitrogen temperature. Also, all bleachings were performed at room temperature. It is possible that the centers formed during these irradiations were indeed selectively oriented, but reoriented themselves randomly through ionic motion before liquid nitrogen temperature could be achieved for measurement. This eventuality could be investigated by designing a crystal holder and dewar which would allow X-irradiation as well as bleaching at liquid nitrogen temperature.

(4) Kleffstra⁽²⁾ found that in KCl:Sr at room temperature, a significant amount of thermal decomposition of Z_1 centers occurred, forming Z_2 centers or more F centers, thus further reducing any observed dichroic effect in the Z_1 band. It is also interesting to observe that Kleefstra reported that no dichroism could be observed in KCl:Sr in the Z_1 or Z_2 bands in the absence of the Z_4 band. During the investigation of the relative peak positions of the M band in doped and pure NaCl, it was concluded that no detectible shift could be observed, throwing doubt on the existence of a Z_4 band in NaCl:Ca. Indeed, no Z_1 dichroism was observed.

(5) Another explanation for the apparent lack of dichroism in the 510 millimicron band may be that while the crystal is being bleached with polarized light, those selectively bleached 510 millimicron centers may regain an electron from the F centers which are being bleached simultaneously (the wavelength of the bleaching light always overlapped the F band to some extent).

As observed in Graph Nos. 3, 7, 8, and 10, a band development occurred at approximately 510 millimicrons in the calcium doped NaCl crystals. Comparison with the pure, homegrown NaCl crystals, treated in an analogous manner, such as in Graph No. 9, indicate that this band is associated in some way with the presence of calcium in the crystal. Its position on the low energy side of the F band corresponds to Caffyn and Ridley's⁽⁹⁾ observed low energy shift of the F band peak in their calcium doped NaCl crystals. As observed in Graph Nos. 3, 7, and 8, this 510 millimicron band can be developed by room temperature bleaching of the F band to some maximal value, after which, further irradiation causes

the band to recede. A comparison of similarly treated crystals of different doping concentrations (Graph No. 10) indicates that the band development at any bleaching stage is larger in the more heavily doped crystals.

Whether or not this 510 millimicron band can be identified with the F band peak shift observed by Caffyn and Ridley⁽⁹⁾ would be difficult to determine, since to this authors knowledge, no band at 510 millimicrons wavelength has previously been resolved in calcium doped NaCl.

The sparsity of conclusive results previously indicated does not, however, necessarily imply that the study of this type of doped crystal would be fruitless. First, all experiments were performed on X-irradiated crystals, with no attempts at gamma coloration. Also, additive coloration measurements could give information on the Z_2 band, and possibly a Z_4 band, if they exist. M band dichroism could also be examined in more detail, since the M band appears much more prominently in additively colored NaCl crystals. Even with X-irradiated crystals, the studies of the hydroxide band in these crystals indicate that the Z bands would be more effectively developed by a proper crystal growing procedure. Thus even the lower doping concentrations may yield surprising results. In addition, with equipment designed to allow X-irradiation and bleaching at liquid nitrogen temperature, perhaps a latent dichroic effect might be observed in the more lightly doped crystals. An attempt could also be made to observe the 345 millimicron band reported by Caffyn and Ridley⁽⁹⁾ in calcium doped NaCl. More careful heat treatment of the crystals would eliminate the anomaly depicted in Graph 6 and could also serve to disperse the calcium ions for more extensive Z center formation.

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