

## Colloids in Additively Colored Sodium Chloride

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A study has been made of the formation of colloids in additively colored sodium chloride. Both natural and synthetic single crystals were additively colored by heating in a vapor of sodium and by injecting electrons from a point cathode. Subsequent irradiation with ultraviolet light and heating of the synthetic crystals produced an absorbing type colloid throughout the crystal. The same treatment applied to the natural crystals produced  $F$  centers throughout the bulk of the crystal and absorbing type colloid specks at localized points in the crystal. In the synthetic crystals the formation of these colloids is shown to be related to the presence of hydroxyl ions in the crystals prior to coloration. In the natural crystal the formation of such colloids is dependent upon the presence of small occlusions of water distributed randomly in the crystal prior to coloration.

### INTRODUCTION

FOR the purpose of this paper color centers produced either by additive coloration or by ionizing radiation will be divided into two general classes. In the first class are atomically dispersed centers such as  $F$ ,  $M$ , and  $R$  centers. In the second class are the colloid centers which are generally ascribed to aggregates of the alkali metal. It is the second class of centers upon which the present work is focussed. The early work on colloids in the alkali halides is well summarized by Seitz<sup>1</sup> and Prizbram.<sup>2</sup> Most of the work on the formation of colloids involves the use of crystals in which  $F$  centers are present. A band attributed to colloids is subsequently produced by heating an additively colored crystal containing  $F$  centers to a few hundred degrees centigrade. It is well known<sup>3</sup> that some alkali halides, e.g., KCl, when additively colored, are relatively free of colloids. Even if a KCl crystal is slowly cooled from the additive coloring temperature of 500 to 700°C a prominent  $F$  band appears. In contrast, an additively colored NaCl crystal must be rapidly quenched in order to obtain a prominent  $F$  band. In the present work the absence of  $F$  centers after additive coloration was desirable and hence NaCl slowly cooled from the additive coloration temperature was used.

Compton<sup>4</sup> has shown that a colloid-type band appears in synthetic NaCl crystals which have been irradiated with 1.3-Mev electrons or Co<sup>60</sup> gamma rays. This band was readily detectable at doses above 10<sup>8</sup> roentgens. Its formation was attributed to the presence of OH<sup>-</sup> ions in melt-grown crystals.

The present work indicates that the absorbing-type colloid band (henceforth referred to as the  $\Delta$  band) formed by heating an additively colored crystal containing  $F$  centers is due to the presence of OH<sup>-</sup> ions in the melt-grown crystal prior to the additive coloration. It will also be shown that the appearance of a

blue color in certain portions of slowly cooled additively colored natural NaCl is due to the presence of occluded water in the crystal prior to the additive coloration. It is necessary to point out at this time that a distinction should be made between the large aggregates of colloidal metal which decorate dislocation lines and grain boundaries<sup>5</sup> regardless of whether synthetic or natural crystals are used, and the colloid formed upon heating an additively colored crystal which contains  $F$  centers. It is the latter colloid whose presence depends upon the reaction of the metallic sodium at the additive coloring temperature with the hydroxyl or water content of the crystal.

### EXPERIMENTAL PROCEDURE

The sodium chloride used in these experiments was obtained from various sources. The synthetic crystals were obtained from Harshaw Company, Optovac Company, or grown in our laboratory by the Kyropoulos technique. The natural crystals from Baden-Baden, Germany were obtained from the Smithsonian Institution, Washington, D. C. The additive coloration experiments were initially carried out using doubly and triply distilled sodium. It was soon apparent that such precautions were not necessary, and subsequent colorations were carried out without distilling the alkali metal. Although different additive coloring temperatures were tried (i.e., 550°C, 650°C, 750°C) there was little effect of the coloring temperature on the subsequent optical measurements. The data were taken on crystals colored at 650°C for 18 hours unless otherwise noted. After additive coloration the crystals were cooled to room temperature in about 6–8 hours. All crystals were additively colored in a stainless steel bomb whose mass determined the rate at which the crystal cooled. Crystals containing various amounts of hydroxyl were additively colored together with the natural NaCl which contains no measurable amount of hydroxyl. The presence of hydroxyl in the crystals was determined by measuring the absorption spectra

<sup>1</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

<sup>2</sup> K. Prizbram, *Irradiation Colours and Luminescence* (Pergamon Press, New York, 1956).

<sup>3</sup> Z. Gyulai, *Z. Physik* **35**, 411 (1925); **37**, 889 (1926).

<sup>4</sup> W. Dale Compton, *Phys. Rev.* **107**, 1271 (1957).

<sup>5</sup> S. Amelinckx, *Phil. Mag.* **1**, 269 (1956).

from 184  $m\mu$  through 240  $m\mu$  before additive coloration and noting the magnitude of the 185  $m\mu$  band.<sup>6</sup>

Crystals were also additively colored by injecting electrons at 600° using a point cathode. These crystals were slowly cooled by merely cutting off the power to the furnace, and removing the crystal a few hours later when the furnace had reached room temperature.

Hydrided crystals were produced by heating additively colored crystals to 700°C in an atmosphere of hydrogen for about 6 hours. The specimens used were less than 0.25 mm in thickness.

The optical absorption spectra were measured using a Cary Model 14 M spectrophotometer. Data were taken from 800  $m\mu$  to 184  $m\mu$  at room temperature and at liquid nitrogen temperature.

### EXPERIMENTAL RESULTS

Synthetic and natural crystals of sodium chloride that have been simultaneously additively colored and slowly cooled are strikingly different in color when removed from the bomb. By transmitted light the synthetic crystals are uniformly blue and the natural crystals are yellow. There are some patchy blue areas in the natural crystals which will be discussed in detail later. Microscopic examination of all of the crystals by reflected light indicates the presence of colloidal particles of about 0.1 $\mu$  to 1.0 $\mu$  decorating grain boundaries. Extinction measurements on these crystals indicate that the natural crystal contains *F* centers and the synthetic crystals contain a small amount of a scattering type colloid in the 580  $m\mu$  to 620  $m\mu$  region (the position varies somewhat depending upon the source of the crystal). In addition, the synthetic crystals have a *U* band at 192  $m\mu$  and two longer wavelength ultraviolet bands at 228  $m\mu$  and 288  $m\mu$ . The presence of the *U* band is due to the

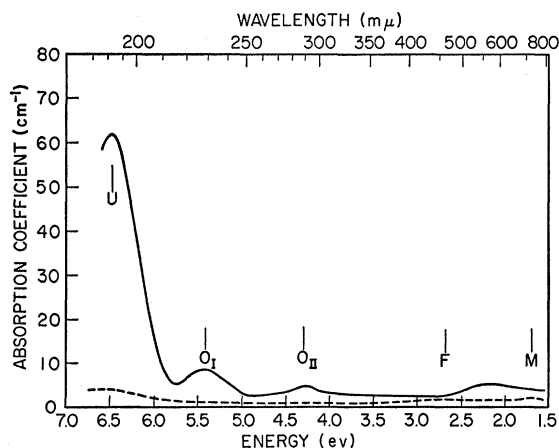


FIG. 1. Absorption spectra of additively colored sodium chloride. Both crystals were slowly cooled from the additive coloring temperature of 650°C. Solid curve—synthetic single crystal; dashed curve—natural single crystal.

<sup>6</sup> H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

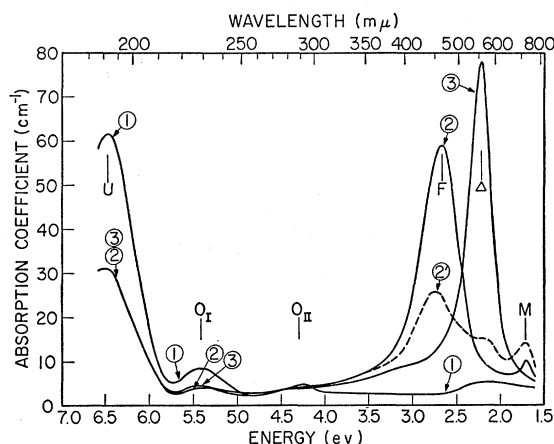


FIG. 2. Production of an absorbing type colloid band ( $\Delta$  band). Curve 1—synthetic crystal as received from bomb. Curve 2—after exposure to ultraviolet radiation from a hydrogen arc lamp. Curve 2'—after exposure to light from a tungsten lamp. Curve 3—after being heated to 420°C for two minutes.

reaction of hydroxyl ions present in the synthetic crystals with sodium during the additive coloration.<sup>6</sup> Figure 1 shows the spectra of a typical synthetic crystal and a natural crystal. Such crystals are relatively inert to further heat treatment provided that the additive coloring temperature is not exceeded.

*F* centers are produced in the synthetic crystals by irradiating into the *U*-band region with an Allen hydrogen-arc lamp equipped with a lithium fluoride window. The irradiation decreases the *U* band, the 228  $m\mu$  band, and the 288  $m\mu$  band. Subsequent heating of the crystal containing *F* centers to about 400°C removes the *F*-band absorption and produces a strong  $\Delta$  band. If the *F* centers in a crystal are optically bleached *R*, *M*, and *N* bands will be produced, but subsequent heat treatment at 400°C will nevertheless produce the same  $\Delta$  band. The *U* band is unchanged by the heat treatment, but the 228  $m\mu$  and the 288  $m\mu$  bands are partially restored. These sequences are shown in Fig. 2. If a synthetic crystal which has been additively colored at 750°C is baked in a stream of hydrogen at 700°C the 228  $m\mu$  and the 288  $m\mu$  are removed and only the hydride band at 192  $m\mu$  remains. The 228  $m\mu$  and the 288  $m\mu$  bands will henceforth be referred to as the *O*<sub>I</sub> and *O*<sub>II</sub> bands, respectively. Irradiation of this crystal at room temperature with ultraviolet light produces an *F* band. Subsequent heating of this crystal to about 400°C restores the *U* band and no  $\Delta$  band appears. This is shown in Fig. 3.

If crystals containing different amounts of "OH" band at 185  $m\mu$  are additively colored at the same temperature, exposed to the same number of ultraviolet quanta, and then heated for the same length of time at the same temperature, then the resulting  $\Delta$  band is found to be proportional to the magnitude of the "OH" absorption band in the crystal prior to treatment. This is shown in Fig. 4.

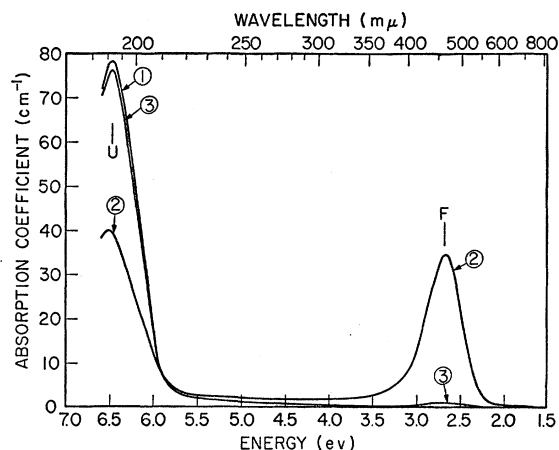
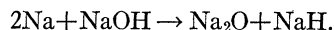


FIG. 3. Absence of the  $\Delta$  band in hydrided sodium chloride. Curve 1—synthetic crystal after hydriding. Curve 2—after exposure to ultraviolet radiation from a hydrogen arc lamp. Curve 3—after being heated to 420°C for two minutes.

After additively coloring and slowly cooling natural crystals, spectral absorption measurements indicate that the bulk of the crystals contain  $F$  centers. Random patches of blue color are present and are apparent to the naked eye. Closer examination of these areas with a 100X microscope indicates the presence of a bubble in the center of each blue patch. If such a crystal is irradiated with ultraviolet light, the volume immediately surrounding the blue area becomes deeply colored with  $F$  centers. Subsequent heating of the crystal produces a  $\Delta$  band encompassing only the volume around the bubbles. Spectral measurements indicate that the band in these localized areas of the natural crystal is the same band that appears in the synthetic crystals after ultraviolet irradiation and heat.

### DISCUSSION

The data of Fig. 4 indicate that the formation of the absorbing type colloid ( $\Delta$  band) is dependent upon the presence of hydroxyl ions in the synthetic crystals. The work of Williams<sup>7</sup> shows that the reaction of sodium with sodium hydroxide above 300°C proceeds as follows:



The crystal at the additive coloring temperature contains free electrons some of which cause the above reaction when they are trapped at sodium ions whose nearest neighbor is a hydroxyl ion. A discussion of the kinetics of the resulting dissociation will not be attempted here. The products of the dissociation are predicted by the above equation. The hydride ion is present in the form of a normal  $U$  center (see Fig. 1). The bands described in Fig. 1 as  $O_I$  and  $O_{II}$  are ascribed to the presence of the other product of the dissociation,

$O^=$ . These absorption bands are removed when a thin crystal is baked at 700°C in an atmosphere of hydrogen. If the spectra are measured at 78°K, the absorption band designated as  $O_I$  narrows, increases in magnitude, and the peak shifts to higher energy. This band is about as sensitive to lattice vibrations as the  $F$  or  $U$  bands, indicating that it is not a colloidal type center. From previous work it is known that the  $O_I$  band is associated with a donor type center.<sup>8</sup> Data on the  $O_{II}$  band are not as extensive. This band is removed by the hot hydrogen treatment. Low temperature spectral measurements on this band do not show a marked dependence on the  $O_{II}$  band on the lattice environment. The dependence shown in Fig. 4 does not imply that the hydroxyl ion itself is responsible for  $\Delta$ -band formation. The colloid does not form upon heating a virgin crystal, nor upon heating the slowly cooled additively colored crystal, but only after heating an irradiated additively colored crystal. It has been experimentally determined that the irradiation need not be from an ultraviolet source, but may be x rays, gamma rays, or electrons. Since the irradiation ionizes the  $U$  and  $O_I$  centers, it is possible that either of these centers may be the nucleation center for colloid formation. The ionized  $U$  center is ruled out as a nucleation center because it is present in the hydrided crystals, which form no colloids after irradiation and heating. The electron centers formed by the irradiation (i.e.,  $F$ ,  $M$ ,  $R$ , etc.) at room temperature are only an intermediate step in the formation of the colloid by heat. Figure 2 shows that it makes no difference if the electrons are distributed as shown in curve 2 or 2', the same  $\Delta$  band forms upon heating the crystal. The transition from curve 1 directly to curve 3 of Fig. 2 may be achieved by simply heating the crystal during irradiation. It is

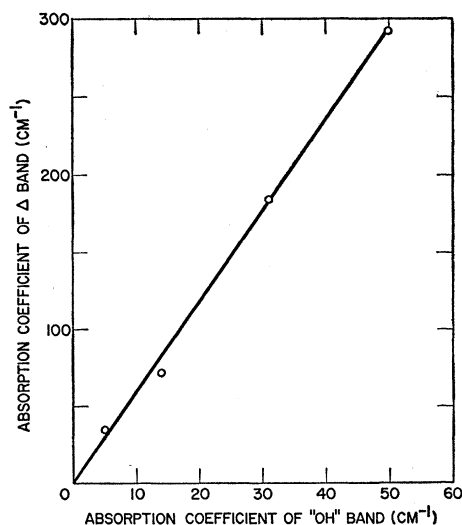


FIG. 4. Relationship in various synthetic crystals between the "OH" band and the  $\Delta$  band.

<sup>7</sup> D. D. Williams, Naval Research Laboratory NRL Memorandum Report No. 33, 1952 (unpublished).

<sup>8</sup> H. W. Etzel, Bull. Am. Phys. Soc. 2, 126 (1958).

suggested that the ionized  $O_I$  center or this center in combination with a lattice defect is responsible for the growth of the  $\Delta$  band.

The formation of the  $\Delta$  band in the natural NaCl occurs only in localized areas. The portions of the crystal in which this colloid will appear can be predicted by close examination of the crystal after additive coloration. Faint dots of blue can be seen, and under a 100X microscope each blue dot has within it one or more bubbles. By reflected light the dot area shows Tyndall scattering. Since the natural crystals are grown from solution, it is reasonable to expect that the bubbles contain some water. During additive coloration the water reacts with the sodium, and now in these localized areas the initial conditions for promoting the growth of an absorbing type colloid are present. Optical absorption measurements in the immediate area of the bubble indicate the presence of a  $U$  band, and a trace of  $O_I$  band. The behavior, then, of the area immediately surrounding the bubbles in natural NaCl is identical with that of the bulk of the synthetic NaCl containing hydroxyl ion impurities.

Scattering type colloids which decorate grain boundaries form in all sodium chloride crystals which are slowly cooled from the additive coloring temper-

ature. It appears reasonable to conclude from the present work that the formation of an absorbing type colloid band in additively colored sodium chloride is due to the presence of impurities acting as nucleation centers. The formation of absorbing type colloid bands<sup>9</sup> observed in other alkali halides after additive coloration may be due to the presence of hydroxyl ions<sup>6,10</sup> in these melt grown crystals.

Since the natural crystal contains no hydroxyl ions, the areas in the crystal free of bubbles contain  $F$  centers after additive coloration. These  $F$  centers are present whether the crystal is slowly cooled or quenched from the additive coloring temperature; the only optical difference is that the slowly cooled crystal will also be decorated.

#### ACKNOWLEDGMENTS

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<sup>9</sup> A. B. Scott, W. A. Smith, and M. A. Thompson, *J. Phys. Chem.* **57**, 757 (1953).

<sup>10</sup> J. Rolfe, *Phys. Rev. Letters* **1**, 56 (1956).

### Crystal Potential and Energy Bands of Semiconductors. III. Self-Consistent Calculations for Silicon\*

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An approximately self-consistent crystal potential is constructed for Si from a superposition of free-atom core and a sampling of crystal valence band charge densities. Valence-core exchange is calculated directly from core wave functions while valence-valence exchange is included using momentum-independent and momentum-dependent approximations taken from the results for a free-electron gas. The resulting crystal potential is surprisingly similar to one previously obtained by Woodruff from a superposition of free-atom charge densities. The calculated valence wave functions in the core region differ substantially from those of Woodruff because of the variational method used by him to calculate wave functions in that region. As a result the calculated energy gap is changed from Woodruff's value of 4 eV to about 1.5 eV, in substantially better agreement with the experimental value (1.1 eV). The various uncertainties in the calculation are listed; it is concluded that the relative position of levels near the band gap should be correct to within about 1 eV. Effective masses are also calculated and compared with experiment; the agreement is quite good.

#### I. INTRODUCTION

THIS is the third paper of a series<sup>1,2</sup> whose object is to present a careful study of the crystal potential seen by electrons in the covalently bonded semiconductors and to calculate the energy bands resulting

therefrom. The problem—rewarding in that experimental verification of the results is possible—is difficult on two counts. First there is the mathematical difficulty of obtaining good wave functions; this was solved for diamond by Herman<sup>3</sup> using the method of orthogonalized plane waves<sup>4</sup> (OPW) and by us in I using the repulsive potential method.<sup>5</sup>

<sup>3</sup> F. Herman, Ph.D. thesis, Columbia University, 1953 (unpublished).

<sup>4</sup> C. Herring, *Phys. Rev.* **57**, 1169 (1940).

<sup>5</sup> J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959), hereafter called PK.

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<sup>1</sup> L. Kleinman and J. C. Phillips, *Phys. Rev.* **116**, 880 (1959), hereafter called I.

<sup>2</sup> L. Kleinman and J. C. Phillips, *Phys. Rev.* **117**, 460 (1960).