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# Color Centers in Alkali Halides

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An area of solid state physics that has become important with the increasing use of transistors centers upon crystal imperfections. The type of imperfections dealt with in this project concern the defects within a crystal's lattice. This type of defect may be of various kinds with Frenkel or Schottky defects being the simplest. The former is a defect caused by ion pairs in an ionic substance that vacate their normal lattice position and become bound at interstitial locations. The second type of defect occurs when ion pairs near the crystal surface migrate to a position at the surface, thus leaving both a positive and a negative vacancy in their place. Other ions deeper in the crystal may then migrate to vacancies



Holtz

and in this manner the vacancies become evenly distributed throughout a given crystal. Which type of disorder that will predominate in a given crystal is dependent upon ionic sizes, the van der Waals forces, and the dielectric constant. If the difference in ionic size is relatively small and if the dielectric constant and van der Waals forces are likewise small, as in the case of the alkali-halides, the Schottky defects will predominate.

The purpose of this investigation is to examine Schottky defects in alkali-halides. Although they occur in pairs, only the anion vacancies lend themselves to the trapping of electrons. Thus, this project concerns only the anion portion of the Schottky defects.

In the alkali-halides, Schottky defects can be investigated visually by heating the crystal in an atmosphere of one of its constituents, by X-ray or electron bombardment, electrolytic injection, or by subjecting the crystal to certain ultraviolet wavelengths of light. When this is done, areas of color can be made to form in the otherwise colorless crystals. These color centers are believed to be electrons that become trapped at the anion vacancies. Electrons may be removed from certain alkali-halides, and in this manner "holes" are generated in the crystal.

In my investigation I injected electrons into high purity crystals of NaCl, KCl, KBr, KI, RbCl, and CsBr and calculated my data from voltage readings, temperature measurements, time recordings, and resistance measurements.

My experimental apparatus consisted of a furnace of insulating bricks with ports for observation, a pyrometer (I worked in the range of 800°-900°K), a millimeter, a voltmeter, a variable voltage source ranging from 0-450 volts direct current, a reversing switch (to change the field direction through the crystal), a projection lamp, a voltage regulator to control the furnace temp-

erature, an ohmmeter, and two electrodes. Special care must be taken in designing the electrodes. The cathode must be pointed to achieve maximum field intensity at the point of injection because of the IR drop due to the constriction of the lines of current flow in the crystal near the contact. The electrodes must also be of a high work function metal and must be relatively inert. I used two strips of stainless steel for my electrodes with a stainless steel screw filed to a point for the cathode. I also used platinum foil between the crystal and electrodes to prevent reactions between the crystal and the stainless steel. My pyrometer consisted of a chromel alumel thermocouple connected to a galvanometer. I used a scale to relate the galvanometer readings to the temperature of the furnace.

Migration of color centers is an interesting process. First the crystal must be at a high temperature. This is to form the necessary vacancies, as their number is exponentially dependent on temperature. Also, for electrons to travel through the crystal they must possess enough energy to enter the conduction band of the crystal where they are relatively free to travel throughout the lattice. The crystal must also possess the necessary energy for electrolytic conduction to take place under the applied field. Then, when the point is negative, three processes occur: 1. electrons become trapped at anion vacancies, 2. anions migrate toward the anode, and 3. cations migrate toward the cathode. The end result is a heavy concentration of anion vacancies near the cathode. Thus, if the electric field intensity is high enough for electron injection, then the concentration of color will be at the cathode, which is verified by experiment.

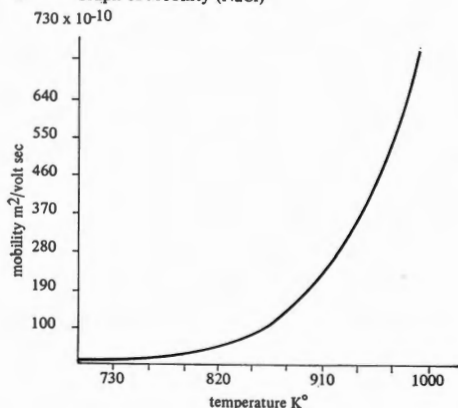
If the polarity is reversed, making the flat electrode negative, the cloud passes out of the crystal through the point. This is because the positive pointed electrode has a high attraction for electrons and the electric field across the crystal is great enough to remove the electrons from the vacancies to the conduction band again where they are pushed out of the crystal by the electric field.

If KBr or KI is used as the crystal, it is possible to inject holes or electrons into the crystal. Holes are believed to be electrons removed from the valence band of negative ions. Hole injection is done when the point is positive. A yellow cloud then spreads from the point to the cathode. Because of the polarity, negative ions and positive vacancies concentrate near the pointed anode. Because of the ionic size of Br<sup>-</sup> and I<sup>-</sup>, with their electrons in the d orbital, at this temperature only a small electric field is needed to raise an electron from its valence band to the conduction band, where it may be removed from the crystal. Both electrons and holes may be injected into KI at the same time if both electrodes are pointed. This may be true with KBr likewise, although I didn't try it.

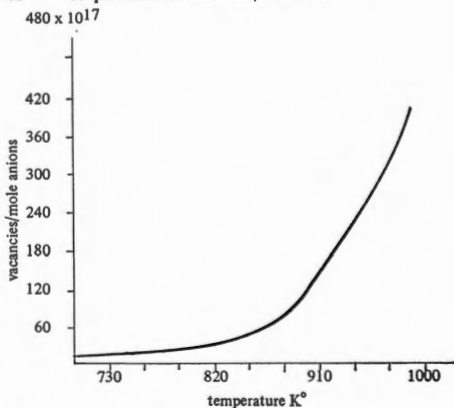
With sodium chloride when the voltage was about 300 volts and the temperature 980°F a light red cloud began to spread across the crystal when the point was negative. After the cloud reached the anode, the current was

reversed and the cloud receded out of the crystal. As the temperature increased (the voltage was kept constant), the speed of the cloud increased as did the intensity of the cloud, while the color remained red. The shape of the cloud corresponded with the lines of current flow. When the cathode was pointed and the anode was flat, the cloud was fan shaped, spreading out from the contact point. When both electrodes are pointed, the cloud follows an elliptical path with a heavy concentration in a line from cathode to anode. With two points the electron flow does not spread much and in a short time a path is melted across the crystal due to electrical heating. The temperature of the crystal is about 1110°F, while the melting point for NaCl is 1470°F. A path can be melted through faster in other alkali-halides, such as with KI a path was melted across after only 40 seconds at 1000°F (melting point 1270°F).

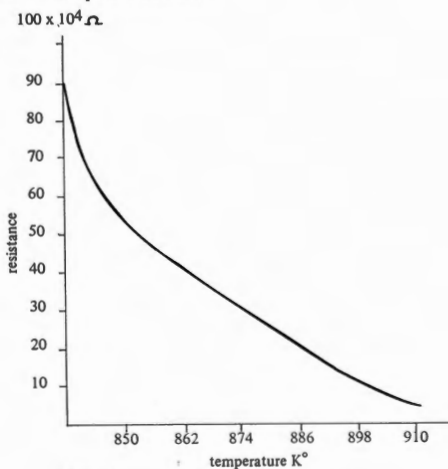
I Graph of Mobility (NaCl)



II Graph of anion vacancies/mole anions



III Graph of Resistance



(The resistance is Ω per 1.27 x 10<sup>-2</sup> meters.)

After an NaCl crystal has cooled to room temperature, the color center changes from red to a combination of blue, red, and yellow. The final color may be different within the same crystal due to foreign ions, different energy levels for various trapped electrons, and concentration of vacancies at one end of the crystal.

An interesting situation is also obtained if a crystal is cleaved in the center at right angles to the direction of current flow. After cleavage the two halves are pressed together again to simulate a grain boundary. This was done with NaCl and KCl with the result that color centers formed only in the half with the pointed cathode. The center spread in a heavy cloud from the point to the fracture but did not cross it. When a crystal of NaCl and one of KBr were pressed together color centers did not form at all, although the two crystals did fuse together as did the two halves of both NaCl and KCl.

The following is a table of the results of electron injection and hole injection in different alkali-halides.

Table 1  
Coloration at 600°C

Type	Coloration at 600°C		Coloration room temp.
	Electron Injection	Hole Injection	Electron Injection
NaCl	red	.....	red, blue, yellow
KCl	blue	.....	magenta
KBr	blue-green	yellow	blue
KI	blue-green	yellow	blue
RbCl	blue-green	.....	blue
CsBr	blue	.....	blue-green

Most of my calculations were for NaCl. One aspect that was investigated was the mobility of the carrier front.

Mobility is defined as

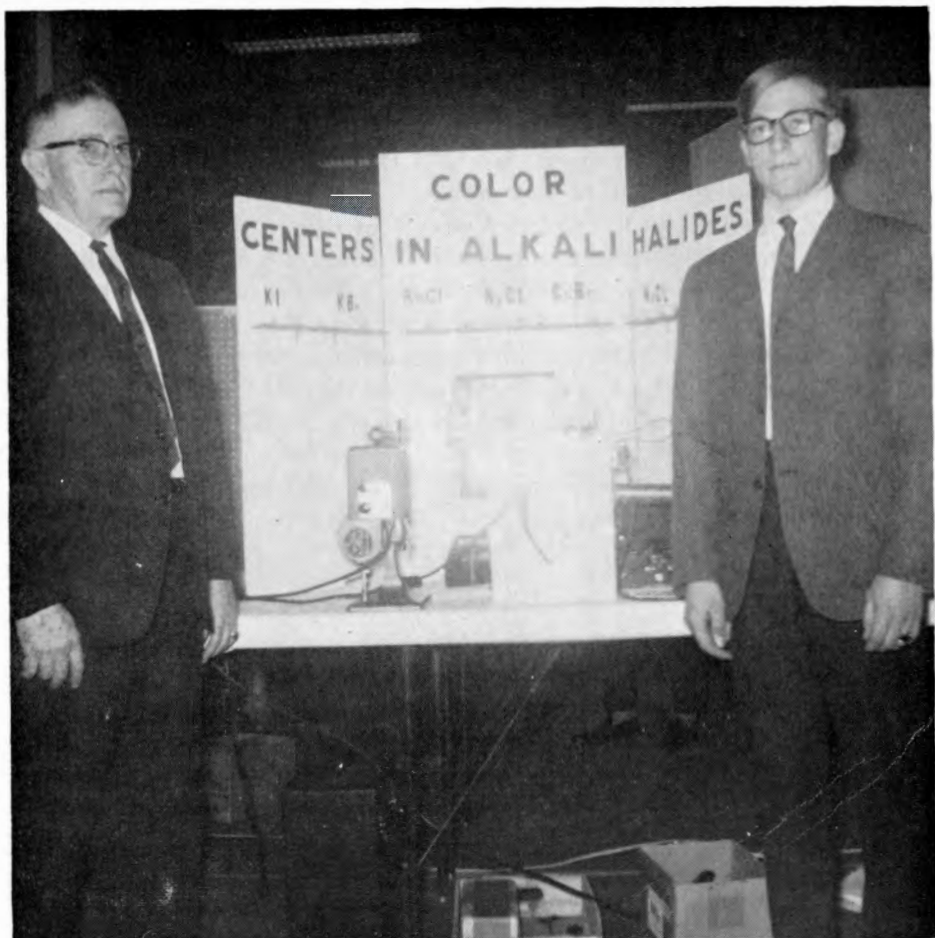
$$\frac{V}{E} \quad \text{equation 1}$$

in which V is the speed of migration and E is the electric field intensity. Graph I shows mobility vs. temperature and follows an exponential path quite similar to Graph II, which is a calculation of the anion vacancies per mole of sodium chloride, according to the equation

$$\frac{n_v}{N} = e^{-\frac{(\Delta G_f)}{2RT}} \quad \text{equation 2}$$

in which  $n_v$  is the vacancies (either positive or negative) per unit volume, N is the number of anions or cations per unit volume, e is the base of naperian logarithms,  $\Delta G_f$  and R are constants, and T is absolute temperature.

It was found (in NaCl) that all of the electrons injected into the crystal actually became trapped at F centers (or anion vacancies). This was done by determining the amperage through the crystal and comparing this value



*Science Seminar Instructor Mr. Dickinson (left) and Hotz.*

with the possible anion vacancies for that particular temperature by Equation 2. At  $840^{\circ}\text{K}$  the time required for one mole of  $\text{NaCl}$  anion vacancies to be filled with one electron each was thirty-three minutes. Actually the time would be greater than this because much of the current through the crystal is electrolytic, or is a transfer of ions rather than a conduction of electrons. As I never injected electrons into  $\text{NaCl}$  crystals for longer than twenty minutes, this indicates I had not completely filled all the anion vacancies for any or my crystals. As  $\text{F}$  centers migrate through a given crystal, some will merge together forming a larger vacancy capable of trapping more electrons than the single vacancies could have. This will also tend to increase the total number of electrons that can be injected into  $\text{NaCl}$ . If the electrolytic current could be distinguished from the electronic, then I could calculate the fraction of vacancies filled after a given time. From this could also be found the average time that an electron spends at a given

vacancy at the injection temperature and the lattice constants that an electron travels between trapping sites.

Other areas of experimental research with color centers would include experimenting with other alkali-halides and measuring the absorption bands of the various color centers with a spectrometer. Thus an almost unlimited amount of research can still be done with color centers in alkali-halides, whether experimental or mathematical in nature.

1. Bronstein, L. and Hersh, H., "Demonstration of Electron and Hole Injection in Alkali-Halides," *American Journal of Physics*, 1957, p. 306.
2. Garner, W. E., *Chemistry of the Solid State*, Butterworths Scientific Publications, London, 1955.
3. Sproull, Robert Fletcher, "Color Centers in Salt Crystals," *Chemistry*, Volume 37, June, 1964, p. 30.

## Open Letter to the Members of ISTS

This year we celebrate the twenty-fifth anniversary of the National Science Teachers Association. Time has seen many changes in science education in the nation and in Iowa. It is for this reason that the regional meetings of ISTS have as their theme "Twenty-five Years of Science Education—The Story of a Revolution."

This revolution has included the Iowa Science Teachers Association. From a group of only a few teachers, we have now become the largest section of the Iowa Academy of Science.

Through the Science Short Course scheduled for Ames in March, as well as the other meetings sponsored by the Science Teachers Section, we are striving to help teachers keep up with this revolution in science education.

Despite the present accomplishments, the fact is that only one in five science teachers in the state belong to their professional organization. If each teacher who is a member would convince one other person of the merits of joining, ISTS could aid that

much more in the revolution in science education.

With the advent of Science Coordinators, I see the classroom teacher taking a lesser role in the activities of the group. This is a natural trend, but one which must not occur. The person ISTS is most concerned with is the one who has direct contact with the students. Many of you have talents which will aid other teachers. Offer your services to ISTS, we will provide the opportunity for you to contact other teachers and benefit in turn from them.

The future of science education looks as bright as the past. New programs are being tested every year. For the first time elementary science is becoming active. Elementary teachers even see benefits in joining State and National Science Teachers Associations. If this trend continues, at the fiftieth anniversary we will be able to look back and say that it was indeed a golden era for science education.

George F. Chapman  
Dubuque, Iowa  
President ISTS