REVIEWS OF MODERN PHYSICS VOLUME 18, NUMBER 3 JULY, 1946

Color Centers in Alkali Halide Crystals*

FREDERICK SEITZ
Carnegie Institute of Technology, Pittsburgh, Pennsylvania

I. INTRODUCTION

ALMOST every field of physics possesses a few problems which merit particular attention, both because they occupy a central position and because one has reasonable hope that, as a result of their inherent simplicity, they may eventually be understood in a complete fashion. The problems centering about the properties of atoms and molecules having one or two electrons occupied this position in the development of quantum mechanics; the problems centering about the properties of the very simplest nuclei occupy a similar position in nuclear physics. In the field of solids, the properties of the alkali halides have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a better and better understanding of some of the most interesting properties of all solids. In the present review article, the writer desires to survey certain aspects of the properties of the alkali halide crystals which have been discolored by various means in such a way as to contain the *Farbzentren* or *F-Centers* which Pohl[1] and his co-workers have subjected to so many careful experiments. This topic is particularly timely, since research carried out during the war in this country and in England, on the bombardment of screens consisting of thin deposits of alkali halides by cathode rays, has extended our knowledge of the properties of discolored alkali halides. The portions of this work that are of fundamental interest will be discussed in Section II.

Historically, the first observation of the discoloration of the alkali halides that can be induced by various means appears to be the work of Goldstein[2] late in the last century. He found that, when crystals of these materials are bombarded with cathode rays, they darken, each compound exhibiting its own characteristic color. For example, sodium chloride becomes yellow, and potassium chloride magenta. The same discoloration can be produced by x-rays. The entire subject remained of passing interest until Pohl and his co-workers subjected the discoloration to an extensive series of experiments over a ten-year period. It is a rather remarkable characteristic of this work that, although the investigators have never had a very deep interest in the fundamental interpretation of the properties of the discolored alkali halides in terms of modern atomic theory, the experiments they have carried out have been exactly those that are needed to furnish the basis for such an interpretation. This fact indicates that they possess a very deep intuitive sense concerning the physically important quantities which enter into the problem.

II. DARKENING WITH X-RAYS

Any of the alkali halides may be darkened readily by exposing the material to x-rays. The absorption bands which are produced in the most important part of the visible spectrum are shown in Fig. 1 for several crystals. These bell-shaped peaks are termed the *F*-bands.

The darkening produced by x-rays has been examined carefully by Molnar[3] under conditions

---

* A portion of the work presented in this review article was developed in the course of a project sponsored at the Carnegie Institute of Technology under contract OEMsr-900 by Division 14 of NDRC. The investigation carried on under this contract centered about the darkening produced by cathode rays, which is surveyed briefly in Section XI; however, much thought concerning the more fundamental aspects of the work, described in the earlier sections, was stimulated by the investigation of darkening by x-rays. Work closely parallel to that carried on at the Carnegie Institute of Technology was in progress at the Radiation Laboratory of the Massachusetts Institute of Technology, the Research Laboratories of the General Electric Company, the RCA Research Laboratories, and at the University of Bristol in England. The writer is deeply indebted to the members of these laboratories as well as to his colleagues, Professors Stern, Estermann, Maurer, and Lasof, for many stimulating discussions. Adequate credit can be given to the work of these investigators only when they publish their own contributions in detail.

[1] R. W. Pohl, Physik. Zeits. **39**, 36 (1938). More recent surveys are given in the book by N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), F. Seitz *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[2] E. Goldstein, Zeits. f. Instrumentkunde **16**, 211 (1896).

[3] J. P. Molnar (Unpublished work). The writer is indebted to Professor A. von Hippel for a copy of Molnar's thesis.

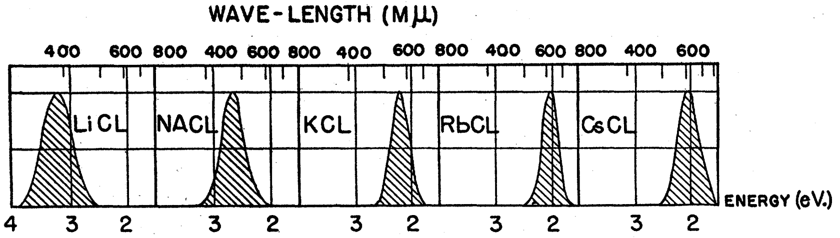

FIG. 1. The *F*-bands for several alkali halides.

in which the crystals were exposed to the radiation from a standard glass-windowed x-ray tube. His qualitative conclusions are as follows:

(a) In general, the darkening produced attains a saturation value which depends upon the temperature and the nature of the crystal as well as upon the intensity of the x-ray beam. Softer crystals, such as cesium and rubidium halides, are relatively difficult to darken near room temperature and lose their darkening rapidly, whereas potassium chloride and other light-metal chlorides and fluorides darken well and retain their darkening.

(b) The crystals darkened by x-rays exhibit new absorption bands other than the *F*-band. One of these bands, which will be called the *V*-band, appears on the ultraviolet side of the *F*-band and is shown in Fig. 2 for KCl. This band resembles closely bands which Mollwo[4] has produced in bromides by exposing the crystals to bromine vapor and which are associated with the presence of a stoichiometric excess of bromine. Another band appears on the long wave-length side of the *F*-band. This band, which we shall call the *M*-band in honor of its discoverer appears at about 8200A in KCl and at about 7200A in NaCl.

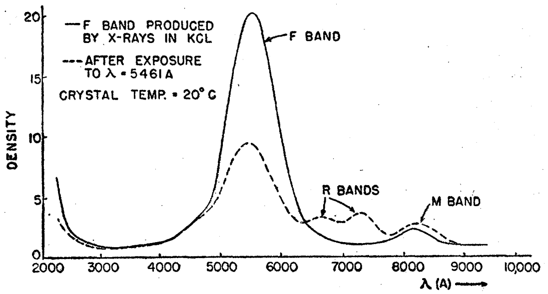

FIG. 2. The absorption bands produced in KCl by exposure to x-rays (after Molnar). The *F*-band, the *V*-band, and the *M*-band are shown.

More recently, Stern and Foner have found that the darkening produced with the use of an x-ray tube containing a beryllium window is much greater than that produced with ordinary x-ray tubes because the radiation of the former contains longer wave-lengths which are more strongly absorbed by the crystals.

It is reasonable to suppose that, when the crystals are irradiated with x-rays or are bombarded with electrons, some of the electrons that are normally bound to the halogen or alkali metal ions of the base material become loosened, wander through the lattice, and eventually become trapped at positions which they would not normally occupy. Thus the absorption bands illustrated in Fig. 1 may be the absorption spectra associated either with these displaced electrons or with the unfilled electron shells they leave behind when they are displaced. The discussion of subsequent sections will show that the *F*-band and the *M*-band are probably associated with the trapped electrons, whereas the *V*-band is related to the holes in the closed-shell structure.

When the crystals which have been discolored by irradiation are heated to a sufficiently high temperature, they bleach to the original colorless state. This process presumably is the result of the recombination of the trapped electrons and holes which is stimulated by the heating process. The relations between temperature and the speed of bleaching are fairly complex and will be discussed in a later section to avoid digression.

III. ADDITIVE COLORING

The *F*-bands may be induced in the alkali halides by heating them in the presence of alkali metal vapor and cooling the crystals rapidly to room temperature (i.e., *quenching*). There are several striking qualitative facts associated with this process:

(a) The discoloration is accompanied by the absorption of some of the alkali vapor by the

---

[4] E. Mollwo, Göttinger Nachrichten 1, 199 (1935); Ann. d. Physik 29, 394 (1937).

crystal; that is, the colored crystal contains a stoichiometric excess of alkali metal after the heating.

(b) The discoloration is characteristic of the crystal and not of the alkali metal used in the vapor. In other words, the *F*-band characteristic of KCl is induced in this crystal whether it is heated in the presence of potassium vapor or sodium vapor.

(c) The *V*-band is not found in these additively colored crystals; nor is the *M*-band observed if they are quenched sufficiently rapidly.

(d) If the crystal is cooled slowly after heating, instead of being quenched, the *F*-band is accompanied by additional absorption bands which are probably related to the presence of colloidal aggregates of the excess alkali metal.

(e) The additive coloring cannot be bleached by heat in the way that the discoloration produced by irradiation may be removed. A heating process of this type will merely induce aggregation similar to that produced by slow cooling.

Figure 1 shows the absorption bands associated with the additively colored crystals when suitably quenched. It is important to note that these bands may be made arbitrarily narrow by lowering the temperature sufficiently (see Fig. 3). This fact shows that the discoloration arises from a number of identical absorption centers which have the same bell-shaped absorption peaks. If the shape of the *F*-band were the result of the superposition of a large number of narrow absorption bands which arose from different types of absorbing centers, and hence were slightly displaced from one another, the resultant band would not contract in breath indefinitely as the temperature is lowered. Following Pohl, we shall call the absorbing centers responsible for the *F*-band the *F-centers*.

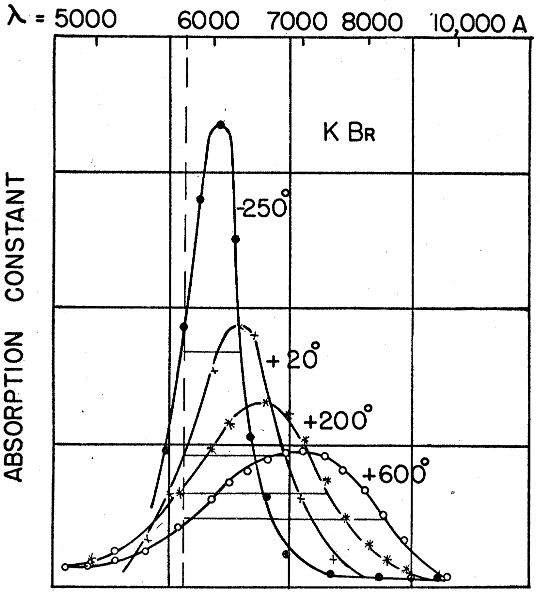

FIG. 3. The variation with temperature of the width of the *F*-band.

Kleinschrod[5] has shown that in the case of KCl the absorption coefficient of the additively colored crystals is proportional to the stoichiometric excess of alkali metal. In this case the excess of alkali metal was measured by dissolving the crystals in water and determining the amount of hydroxide present in the final solution. Now it has been shown by Smakula[6] that if a medium of refractive index n' contains a number n_0 of absorbing centers per unit volume which possess a bell-shaped absorption peak of the type exhibited by the *F*-centers, the relationship between the absorption coefficient α_m at the center of the band, the concentration of centers, and the width at half maximum of the band W, in energy units, is as follows:

$$n_0 f = \frac{18m}{\pi e^2 h}\,\frac{n'}{(n'+2)^2}\,\alpha_m W. \qquad (1)$$

Here e, h, m, and c are the usual atomic constants. The quantity f is the oscillator strength of the absorbing centers. For KCl this equation may be placed in the form

$$n_0 f = 1.06\cdot 10^{16}\alpha_m W, \qquad (2)$$

if n_0 is expressed in units of cm^{-3}, α_m is expressed in units of cm^{-1} and W is expressed in units of electron volts. This equation is very useful since it permits a very simple determination of the density of *F*-centers when α_m has been measured, provided f and W are known. The second of these quantities has been measured at room temperature for most of the alkali halides; however, f is accurately known only for KCl. In this case[5]

$$f = 0.81 \text{ (KCl)} \qquad (3)$$

---

[5] F. G. Kleinschrod, Ann. d. Physik **27**, 97 (1936).

[6] A. Smakula, Zeits. f. Physik **59**, 603 (1930).

whereas for NaCl; as we shall see later

$$f \cong 0.7 \text{ (NaCl).} \tag{4}$$

There is a simple relation between the equilibrium concentration of F-centers in the crystal, n_f, and the concentration of alkali metal atoms in the vapor, n_v, at any given temperature. This relation is shown[7] in Fig. 4 for KCl. It will be seen that

$$n_f = Cn_v. \tag{5}$$

The quantity C is temperature dependent, as may be observed from the figure. One of the very important conclusions to be drawn from the existence of a relation of the type (5) is the fact that the process of forming F-centers is reversible, in the thermodynamical sense, and that it should be possible in some way to relate the existence of the centers to the bulk properties of the material. In the early period of the investigation of F-centers it was suggested, most notably by Smekal, that F-centers are related to cracks and imperfections in the crystal. The existence of an equation of the type (5) indicates that this can be the case only if the imperfections can be described with the use of the conventional principles of statistical mechanics.

It is interesting to note in passing that concentrations of F-centers corresponding to

$$n_f \cong 10^{19} \text{ per cc} \tag{6}$$

can be obtained, as is shown in Fig. 4. This means that deviations from ideal combining proportions of the order of about one part per thousand are readily achieved.

Additive coloration can be produced by electrolysis as well as by heating the crystal in the presence of alkali vapor. In order to do this, one end of the crystal is pierced with a pointed electrode which is made the cathode. The contact anode may be made by pressing a flat electrode against the opposite side of the specimen. If a current is now passed through the crystal when it is at an elevated temperature, F-centers will emerge from the pointed cathode and will migrate to the anode. Halogen gas is given off at the anode. The process behaves as if alkali metal atoms were produced at the cathode and played the same role as the metal atoms in the vapor when F-centers are produced by exposing the crystal to vapor.

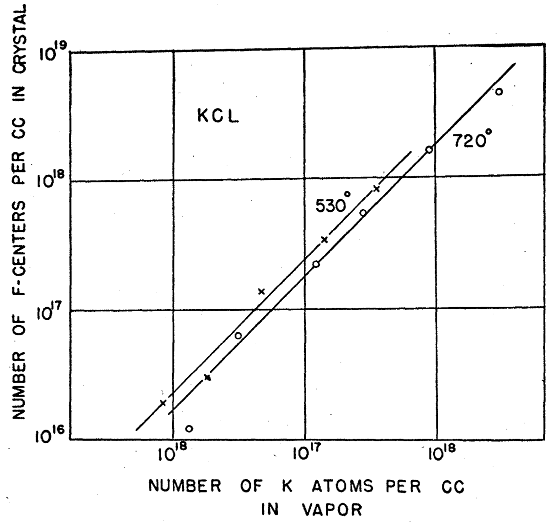

FIG. 4. Relation between concentration of F-centers in crystal of KCl and density of alkali metal atoms in vapor (after Rögener).

IV. PROPERTIES OF CRYSTALS CONTAINING F-CENTERS

Crystals containing F-centers possess a number of notable properties. Those which are of principal interest for the interpretation of the nature of the centers are as follows.

(a) Photo-Conductivity

Crystals irradiated with light lying in the F-band become photo-conducting. In the process of photo-conductivity it may be supposed that electrons are freed by the absorbed light quanta, wander for a certain distance in the direction of the applied field, and then become trapped. During the process of wandering while free, the electrons undergo Brownian motion so that the displacement in the direction of the applied field actually is a drift which is superimposed on the random motion. Under these conditions, which are characteristic of the migration of conduction electrons in metals, the velocity of drift v is given by an equation of the form

$$v = \beta E, \tag{7}$$

in which E is the electric field strength and β is the *mobility*. If the electrons behave as if perfectly free and possess a mass m, the mobility

---

[7] H. Rögener, Ann. d. Physik **29**, 386 (1937).

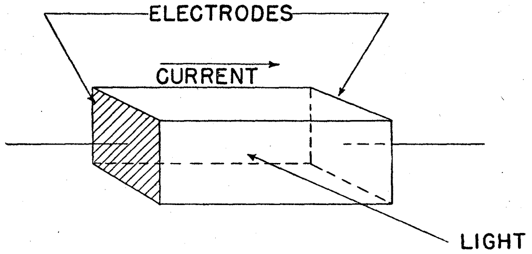

FIG. 5. Relation between specimen, electrodes, and light beam (see text).

may be expressed by means of the equation

$$\beta = (e/m)\tau \qquad (8)$$

in which τ is the time between successive collisions which deflect the electron. It follows that if the electron is free for a period of time T, the distance d which it will move in the direction of the applied field is

$$d = \beta E T. \qquad (9)$$

Now let us suppose that a specimen of crystal between two electrodes contains a uniform distribution of F-centers having density n_0 and that this portion of the crystal is uniformly irradiated with monochromatic light which is absorbed at the rate of Q quanta per cm² per sec. of the crystal in the plane exposed to the radiation (Fig. 5). Moreover let η be the probability that an electron is ejected whenever a light quantum is absorbed by an F-center. It may readily be seen that the current which crosses a plane through the crystal normal to the direction of the field is

$$I = Q\eta e d w, \qquad (10)$$

provided d is small compared with the spacing between electrodes. Here w is the width of the specimen in the direction normal to the field and normal to the direction of the incident radiation. This equation may also be placed in the form

$$I = Q\eta e\beta E T w \qquad (11)$$

with the use of Eq. (9). It follows that the quantity

$$I/QEwe = \eta\beta T = \eta d/E \qquad (12)$$

is independent of the field intensity and of Q.

Figures 6 and 7 show the dependence[8] upon temperature of $\eta\beta T$ for specimens of NaCl and KCl. It may be seen that the curves drop to very low values at temperatures near that of liquid air. As the temperature is increased they rise to a peak which occurs at −150°C for NaCl and −170°C for KCl. They then drop gradually before another comparatively rapid rise occurs near room temperature.

At temperatures below the second rise, which occurs at about 25°C for NaCl and at −75°C for KCl, the photo-current responds instantaneously to the light source, rising and falling abruptly as the light is turned on and off and remaining constant during periods of illumination. This type of photo-current is known as the *primary* photo-current. Above the temperatures corresponding to the second rise, the photo-current rises instantaneously as the light is switched on. However, it continues to grow for a period of time during the subsequent period of illumination until it again reaches a saturation or level value. Similarly, when the illumination is cut off the photo-current drops abruptly to a

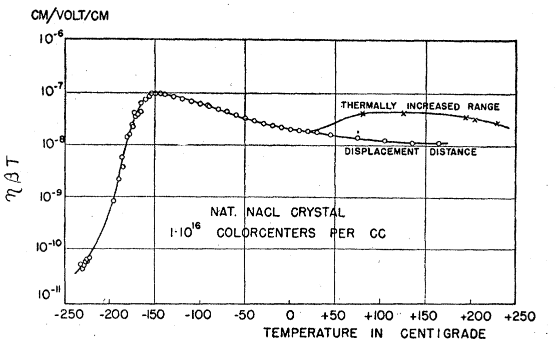

FIG. 6. The dependence of the photo-current, per unit field intensity and unit light intensity upon temperature, for the case of NaCl (after Rögener).

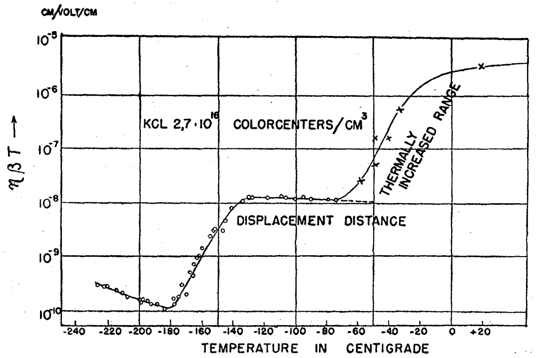

FIG. 7. Same as Fig. 6 for KCl (after Rögener).

---

[8] H. Rögener, Göttinger Nachrichten 3, 219 (1941).

fraction of the saturation value; however the remaining current takes a period of time to decay to the initial dark value. The portion of the photo-current which rises and falls comparatively slowly as the illumination is turned on and off is called the *secondary photo-current.* Both Figs. 6 and 7 show the values of $\eta\beta T$ for both the primary and secondary current.

The interpretation of the appearance of the primary and secondary currents is probably as follows. In the range of temperature in which only the primary current appears, the electrons freed by the radiation move a certain distance, become trapped, and remain trapped. The time during which they are free is small compared with the response time of the instruments used for measuring the current. In the range of temperature in which the secondary current is observed, the electrons are freed from the trapping centers as a result of thermal fluctuations, so that they can contribute to the photo-current for a long period of time after they have first been produced by the photons. Saturation occurs only when the freed electrons return to the centers from which they were originally released at the same rate as they are produced. Similarly, when the light is turned off only the component of photo-current corresponding to the initial displacement is removed. The electrons which are already free continue to migrate until they have been permanently trapped by the centers from which they were first released.

Pohl and his co-workers have called the distance d which the photoelectrons move in the direction of the field before being trapped for the first time the *displacement range.* The distance which they move before being permanently trapped in the range of temperature in which the secondary current is observed will be called the *thermally increased range.* When d becomes comparable to the electrode spacing the current does not continue to rise with E, as predicted by Eqs. (9) and (10), but attains a saturation value.

The fall in photo-current which is observed at very low temperatures, that is, below $-150°$C in NaCl will be discussed below.

It will be observed that the curve showing $\eta\beta T$ as a function of temperature in the case of KCl (Fig. 7) exhibits a rise with decreasing temperature at temperatures below $-180°$C. It may be seen that the break in slope of the curve is very sharp at the point where the slope changes sign. For reasons which will be discussed later, it is now believed that the centers responsible for this component of the photo-current are not the F-centers but are other centers, most probably colloidal aggregates of alkali metal. Since these centers should have an absorption band which differs from the F-band, it should be possible to test this hypothesis by examining the photoelectric response as a function of frequency in the low temperature region. Unfortunately this measurement has not yet been made.

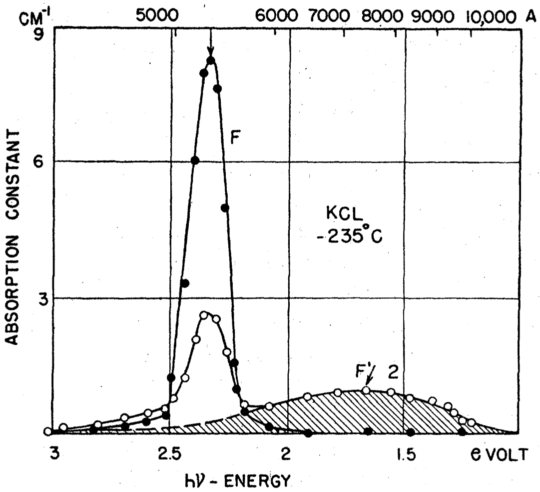

FIG. 8. The F- and the F'-bands in KCl. The F'-band was produced by irradiating the crystal with light lying in the center of the F-band (after Pick).

(b) The Production of F'-Centers

In the range of temperature in which only the primary photo-current is observed, that is below 25°C for NaCl and below $-75°$C for KCl, a new absorption band appears as the crystals are irradiated with light that is absorbed by the F-centers. This band is much broader than the F-band, and invariably has a peak on the red side of the F-band[9] (see Fig. 8). It differs strikingly from the F-band in a number of respects, one of the most notable of which is the fact that its width is relatively insensitive to temperature. Pohl has called it the F'-band. The F'-band evidently represents the absorption

---

[9] H. Pick, Ann. d. Physik **31**, 365 (1938).

caused by the electrons which have been trapped at the end of the primary range after being released photoelectrically from the F-centers. In accordance with this is the fact that the F'-band appears as a transient at higher temperatures where the secondary current is observed and the trapping centers are not stable.

Pick[9] has measured the quantum efficiency with which F-centers are destroyed during the production of F'-centers. The concentration of F-centers during the process was determined optically with the use of Eq. (2). Since the value of the oscillator strength f is accurately known only for KCl, the results obtained for this crystal are of particular interest. Figure 9 shows the quantum yield for destruction of F-centers for this crystal. It may be seen that the yield attains a value 2 at the highest temperatures in which the primary current appears and falls to lower values at lower temperatures. It is interesting to note that the knee of the efficiency curve occurs at the same temperature as the corresponding knee in the curves for $\eta\beta T$ in Fig. 7. Adequate correction must be made for the fact that the curve of Fig. 7 has a negative slope above the knee.

The fact that two F-centers are destroyed for each light quantum absorbed can be explained only if we assume that the photoelectron is trapped by an F-center. Then both the F-center from which the electron was released and the F-center by which it is captured will be lost. It follows that the F'-center must be the result of adding an electron to an F-center.

Figure 10 shows the quantum yield curve analogous to Fig. 9 for NaCl. This curve was obtained by setting f equal to unity. The fact that the saturation value of the yield is 1.4 instead of 2 in this case suggests that f actually is 0.7 instead of 1.0 for NaCl.

If the F-centers are the trapping centers which determine the displacement range of the photoelectrons, we should expect this range to vary inversely as the first power of the concentration of F-centers at any given temperature and field strength. Figure 11 shows[10] that $\beta d/E$ varies in this way.

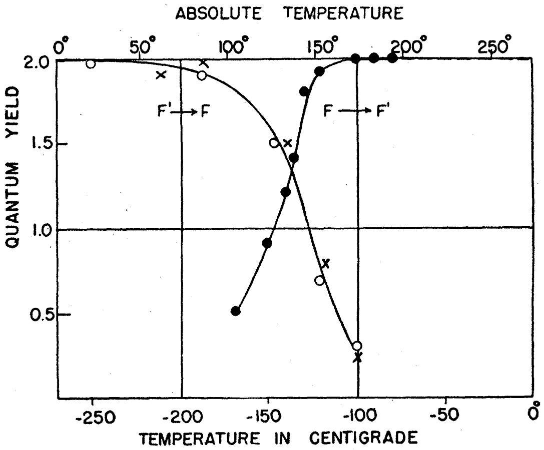

FIG. 9. Curves showing the quantum yield for the reactions $F\rightarrow F'$ and $F'\rightarrow F$ induced by light quanta in KCl (after Pick); the value $f=0.83$ is used.

The rapid drop in yield of the reaction $2F\rightarrow F'$ at low temperatures indicates that η, the quantum yield for release of photoelectrons, actually drops in the corresponding fashion at low temperatures. In other words, the absorbed light quanta stimulate the F-centers but do not always produce photoelectrons. This conclusion is in complete agreement with the drop in photoelectric current at low temperatures shown in the curves of Figs. 6 and 7.

F'-centers may be destroyed by irradiating the crystal with light absorbed by the F'-band, the original F-centers being formed in the process. This light may be chosen so that it does not overlap the F-band since a part of the F'-band extends well on the red side of the F-band (see Fig. 8 for example). Pick has investigated the quantum yield of formation of F-centers in the reaction $F'\rightarrow 2F$ as a function of temperature. The result for KCl is shown in Fig. 9, along with the curve for the reverse reaction. It will be observed that the reaction $F'\rightarrow 2F$ proceeds with optimum efficiency at very low temperatures and falls as the temperature is raised. As we shall see below, this fall is probably the result of a decrease in the capture cross section for formation of F-centers as the temperature is increased.

The variation of the photoelectric current induced by the excitation of F'-centers is shown in Fig. 12 for KCl. These measurements were made during the war by Domanic.[11] It will be seen that a photo-current accompanies the absorption of light by F'-centers. This current drops

---

[10] G. Glaser, Göttinger Nachrichten 3, 31 (1937).

[11] F. Domanic, Ann. d. Physik 43, 187 (1943).

with decreasing temperature below −140°C. Careful analysis shows that the knee for the curve of Fig. 12 occurs at the same position as that of Fig. 7. This in turn is at the same position of the knee of Fig. 9. It is to be noted that the photo-current arising from the F'-centers rises with decreasing temperature below −200°C. This rise is not to be confused with the rise at the corresponding temperature that is shown in Fig. 7 and which, as mentioned above, is believed to be related to colloidal particles of alkali metal. The change in slope from positive to negative values as the temperature decreases is much more nearly continuous in the case of Fig. 12 than in the case of Fig. 7. Moreover, the photo-current observed in the low temperature range when F'-centers are present is about 10 times larger than that which would be observed if the F'-centers were absent. We may conclude that the F'-centers yield photoelectrons with a quantum efficiency approaching unity at *arbitrarily low temperatures*.

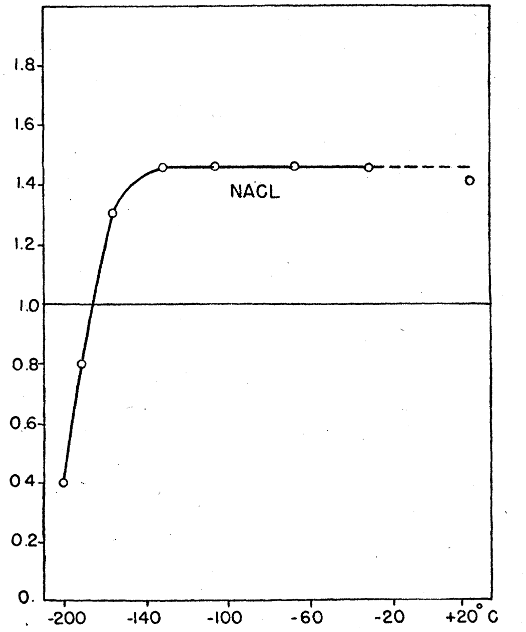

Fig. 10. Quantum yield for the reaction $F \rightarrow F'$ in NaCl (after Pick). The value $f = 1$ is used.

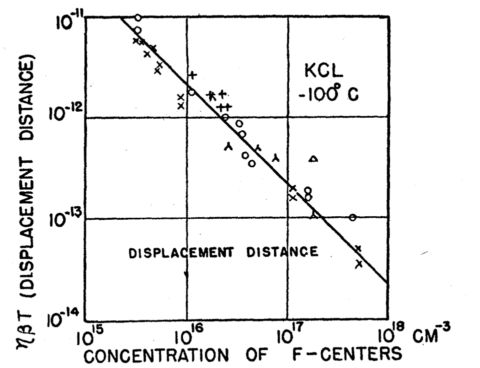

Fig. 11. Dependence of the displacement distance upon concentration of F-centers (after Glaser).

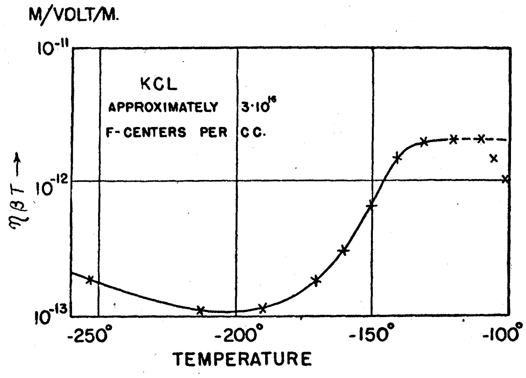

Fig. 12. Photoelectric yield of F'-centers (after Domanic). It is to be noted that the photoelectric current can be observed at 20°K.

If a photoelectron that has been ejected from an F'-center is to produce an F-center, the electron must be captured by an ionized F-center, that is, by an F-center which has previously lost an electron. The photoelectron has the alternate choice of being captured by a normal F-center and reforming an F'-center. From the shape of the quantum yield curve for the reaction $F' \rightarrow 2F$, and the shape of the curve showing the photoelectric current as a function of temperature for stimulation of F'-centers, we may conclude that the photoelectrons from F'-centers have a longer range at comparatively high temperatures where the quantum efficiency for production of F-centers from F'-centers is lowest, and conversely. This conclusion, in turn, indicates that the probability that an ionized F-center will capture an electron passing near it increases with decreasing temperature. The increase in capture cross section with falling temperature has the effect both of decreasing the displacement distance for the photoelectrons and of increasing the efficiency of forming F-centers.

We may now attempt to draw some general conclusions concerning the F-centers and the

F'-centers from properties described above. The fact that the F'-centers can be ionized with all wave-lengths lying in the F'-band and at all temperatures strongly suggests that this band represents a transition from a single discrete level to an ionization continuum (see Fig. 13). Thus the F'-center possesses exactly those properties which we associate with free singly charged negative ions of the type of H^-, F^-, Cl^-, and so forth. These ions presumably possess one discrete level lying beneath a continuous spectrum of levels corresponding to states in which the extra electron is free.

Since an F'-center is formed by adding an electron to an F-center, it follows that the latter possesses one unit less of electronic charge. Moreover, it is clear that the F-band arises from a transition between two discrete levels because the F-band becomes very narrow at low temperatures. If we were dealing with free atoms, this fact would strongly suggest that the F-center is either neutral or positively charged. The same conclusion cannot be safely drawn from this observation alone in the crystalline case, however, for it is possible that a negative ion could possess two or more discrete levels in a crystal. On the other hand, the fact that the absorption associated with the continuum of levels, which must lie somewhere above the discrete level (or levels) associated with the F-center, is very weak strongly suggests that the electron responsible for the absorption is moving in a Coulomb field. For this concentration of oscillator strength in the first transition is characteristic of systems in which the valence electron moves in a Coulomb field, such as the neutral hydrogen atom and the alkali metal atoms.

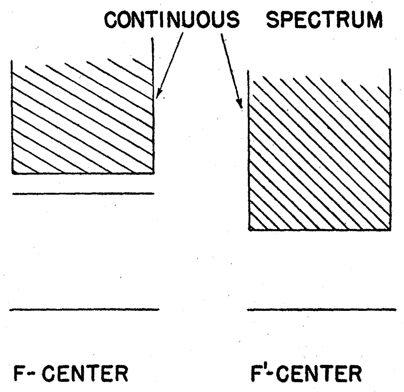

FIG. 13. The nature of the energy levels in F-centers and F'-centers.

Now there are three ways in which a Coulomb field could be generated at regions within an otherwise neutral crystal (see Fig. 14):

(a) By introducing an extra positive ion, such as an ion of alkali metal atom.

(b) By removing a negative ion, that is, an ion of halogen, from the lattice.

(c) By polarizing the medium relative to a point center. This could be done, in principle, by holding a negative charge at a point within the crystal, allowing the polarization charge to accumulate and then rapidly removing the charge. This Coulomb field would be transitory if the negative charge were removed; however, if the charge were an electron, the system of negative charge plus induced charge could be stable in the sense that each would maintain the other in position. This process of *self-trapping*, which was first postulated by Landau,[12] evidently could occur in any ionic crystal.

In the first two of these cases it is clear that an electron moving in the Coulomb field could have all the essential properties of an F-center since the system would resemble qualitatively an hydrogen atom or an alkali metal atom. Moreover, the properties of the F'-center, obtained by adding an extra electron to the system, would also be in good qualitative accordance with the observed properties since this system would be the counterpart of a singly charged negative ion such as H^- or Cl^-.

The properties of self-trapped electrons have not yet been investigated with sufficient thoroughness on purely theoretical grounds to make it possible to say whether or not they would have the properties of F-centers. In any case, as we shall see below, there are good reasons for believing that the actual F-centers are not electrons trapped in this way.

V. LATTICE IMPERFECTIONS

The fact that ionic crystals conduct an electrolytic current which obeys Ohm's law at sufficiently high temperatures shows that these crystals possess imperfections at elevated temperatures. This observation is attributed to

---

[12] L. Landau, Physik. Zeits. Sowjetunion **3**, 664 (1933).

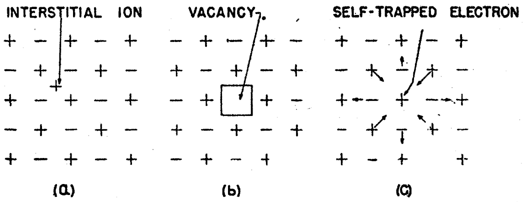

FIG. 14. Three ways of obtaining a Coulomb field within a crystal. (a) Interstitial positive ion. (b) Negative-ion vacancy. (c) Self-trapped electron.

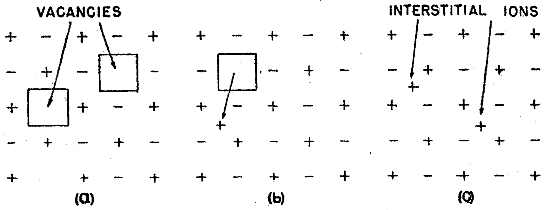

FIG. 15. Three mechanisms of formation of lattice defects (a) Vacancies, (b) Interstitial atoms and vacancies, (c) Interstitial atoms alone.

Frenkel[13] who pointed out that the crystals could not be ionic conductors unless a fraction of the ions were wandering about the crystal lattice in a more or less random fashion. The applied field superimposes a directional component to the otherwise random motion.

Schottky,[14] Wagner,[15] and Jost[16] carried out careful investigations of the nature of the imperfections that occur in various types of crystals and are responsible for the ionic conductivity. There are two principal types that are of general interest, namely interstitial atoms and vacancies. Vacancies may be formed by the migration of atoms or ions to the surface, where they form additional layers to the lattice, or by the migration of atoms or ions from normal lattice sites to interstitial positions. In the second case both vacancies and interstitial atoms are formed together. Interstitial atoms or ions may also be formed by migration from surface layers to the interior. These three types of processes are illustrated schematically in Fig. 15 for a crystal of the alkali-halide type. It is an essential part of the theory based on Frenkel's observation that these imperfections are produced in a thermodynamically reversible manner at sufficiently high temperatures because of the entropy gained by the lattice as a result of the increase in disorder, that is, for exactly the same reason that a solid or liquid sublimes at sufficiently high temperatures.

Figure 16 shows[17] the ionic conductivity of a number of alkali halide crystals as a function of temperature. It is convenient to present the data by plotting the logarithm of the conductivity as a function of the reciprocal of the absolute temperature. Two general features are exhibited by all of these curves. First, the ionic conductivity is independent of the history of the specimen for a range of temperature just below

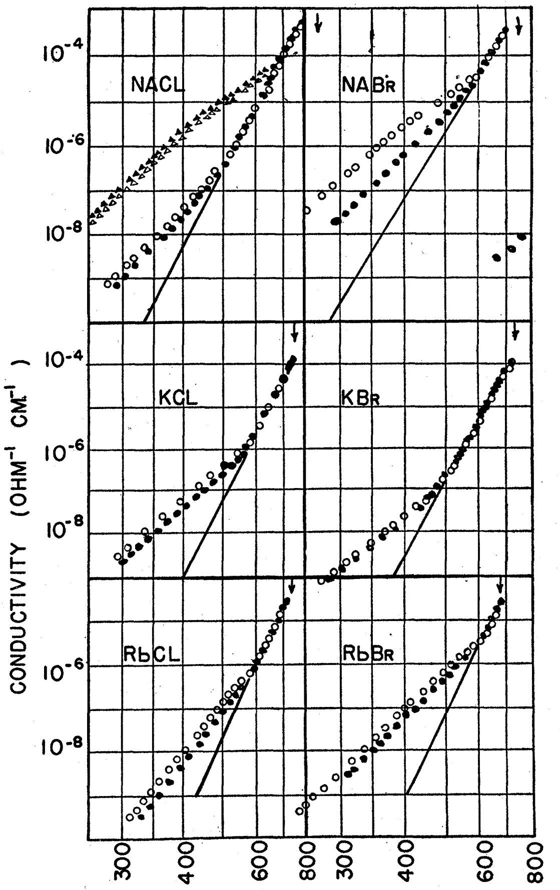

FIG. 16. The ionic conductivity of several alkali halide crystals (after Lehfeldt). The logarithm of the conductivity is plotted as a function of $1/T$.

---

[13] J. Frenkel, Zeits. f. Physik **35**, 652 (1926).

[14] W. Schottky, Zeits. f. physik. Chemie **B29**, 335 (1935).

[15] C. Wagner and W. Schottky, Zeits. f. physik. Chemie **B11**, 163 (1930), *et seq.*

[16] W. Jost, J. Chem. Phys. **1**, 466 (1933); Zeits. f. physik. Chemie **A169**, 129 (1934), **B32**, 1 (1936); *Diffusion und Chemische Reaktion in festen Stoffen* (Steinkopf, Leipzig, 1937).

[17] W. Lehfeldt, Zeits. f. Physik **85**, 717 (1933).

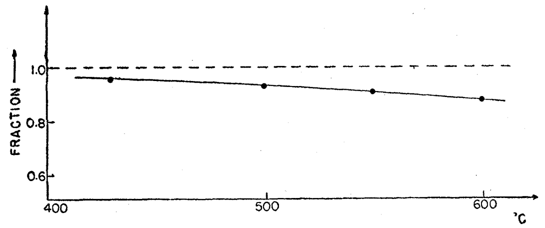

FIG. 17. The fraction of ionic transport by positive ions in KCl (after Tubandt).

the melting point. In this range the conductivity is a unique function of the temperature, that is, it is independent of the path by which that temperature was achieved, and obeys the equation

$$\sigma = A \exp(\epsilon/kT) \qquad (13)$$

in which A and ϵ are constants. Second, the conductivity curves exhibit a bend at sufficiently low temperatures. In the range below this bend the conductivity depends upon the previous history of the specimen and upon its impurity content. We may place certain broad restrictions upon the way in which imperfections form in ionic crystals because of the charges the ions possess. For example, if one type of atom leaves the surface and migrates *as an ion* into the interior of the crystal through interstitial channels it is necessary that an equivalent number of ions of opposite charge migrate at the same time. For otherwise the interior of the crystal would become charged relative to the surface. The same type of condition applies when one of the ions forms vacancies by migrating to the surface of the lattice.

Now Schottky and Jost have shown that it is exceedingly unlikely that interstitial ions occur in any appreciable quantity in the alkali halides. The reason for this is that the energy required to force an alkali metal ion or a halogen ion into an interstitial position is prohibitively high. Mott and Littleton[18] have carefully refined the type of calculations carried out by Schottky and Jost. They have shown in the case of NaCl, for example, that the energy required to take a Na^+ ion from a normal lattice position to an interstitial position is 2.9 ev, whereas the energy required to form a pair of vacancies is 1.86 ev. Thus the number of interstitial ions is less than one percent of the number of vacancies, even at the melting point. These calculations, which are based upon Born's treatment of the interaction of ions in ionic crystals, are as firmly grounded as any calculations in the field of solids. They play a very important role in the theory of *F*-centers, for they rule out the possibility that an *F*-center is an electron attached to an interstitial alkali metal ion. Similar calculations show that the energy required to form vacant lattice sites by moving ions to the surface of the crystal are in the range of practical interest.

As a result of the theoretical work, we conclude that mechanisms (b) and (c) shown in Fig. 15 for the formation of imperfections are to be ruled out and that only mechanism (a) is permissible. Since the interior of the crystal must remain electrostatically neutral, it follows from the argument presented previously that vacancies of both types must occur in equal numbers in normal uncolored alkali halide crystals. This vacancy mechanism of conduction is in agreement with Tubandt's observation[19] that both ions conduct electrolytically in the alkali halides at sufficiently high temperatures. Figure 17 shows, for example, his measurement on the relative transport of Cl and K ions in KCl at various temperatures. This observation does not include alternative mechanisms, of course, for both ions could conduct even if interstitial ions were responsible for the electrolytic current.

Now if ϵ' is the energy required to form a positive- and a negative-ion vacancy by moving the pair of ions to the surface of the crystal, a simple theory shows that the density n of vacancies at a given temperature T is, under conditions of thermodynamical equilibrium,

$$n = NC \exp(-\epsilon'/2kT). \qquad (14)$$

Here N is the density of molecules and C is a constant. If the only source of change in entropy associated with the presence of vacancies were that related to the permutation of the vacancies among the possible lattice sites, C would be unity. Actually, C should differ from unity because the ions near the vacancies will be somewhat more loosely bound than the ions in the bulk of the crystal and hence will have a lower vibrational

---

[18] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485, 500 (1938).

[19] C. Tubandt, *Handbuch der Experimental Physik*, Vol. XII.

frequency than the average ion. This factor will have the effect of raising C. Now the calculation leading to (14) is based on the assumption that ϵ' is independent of temperature. Actually this quantity will be temperature dependent. If the temperature dependence is assumed to be of the form

$$\epsilon' = \epsilon'_0 + aT, \tag{15}$$

in which ϵ'_0 and a are independent of temperature, Eq. (14) may be replaced by an equation of the form

$$n = NC' \exp(-\epsilon'_0/2kT), \tag{16}$$

in which C' is a constant which involves a. Mott and Gurney[20] have found on the basis of calculations of a that C' may be as large as 10^3 or 10^4.

Einstein[21] has shown that the contribution to the electrical conductivity from any migrating ion or vacancy is related to the concentration of the migrating unit and its diffusion coefficient D by the equation

$$\sigma = e^2 nD/kT, \tag{17}$$

in which e is the charge carried by the ion or vacancy. If ϵ''_0 is the temperature independent part of the activation energy for diffusion, D may be expressed in the form

$$D = D_0 \exp(-\epsilon''_0/kT), \tag{18}$$

in which D_0 is a constant. According to simple theories of diffusion, D_0 is of the order of 10^{-2} cm^2 sec.$^{-1}$; however observed values of this quantity frequently deviate from this by a factor of 100 or more.

Equation (17) may also be expressed in the form

$$\sigma = nev, \tag{19}$$

in which v, the mobility, is

$$v = eD/kT. \tag{20}$$

Now if we compare Eq. (13) with (17) in the light of Eqs. (14) and (18), we may conclude that

$$\epsilon = \tfrac{1}{2}\epsilon'_0 + \epsilon''_0. \tag{21}$$

Thus ϵ is a complex constant involving both the activation energy for formation of vacancies and that for diffusion.

Several investigators have proposed a simple method of determining ϵ''_0 from conductivity *versus* temperature diagrams of the type shown in Fig. 16. It is to be noted that these curves can be regarded in good approximation as if composed of two linear portions: A relatively steep portion just below the melting point and a second portion at lower temperatures. The upper portion is, as remarked previously, essentially independent of the previous history of the crystal and of its impurity content. It seems safe to conclude that in this region of temperature n is varying in accordance with Eq. (14). The temperature at which the break between the two linear portions occurs is dependent upon the specimen; however, the slope of the low temperature portion is nearly the same for all specimens of a given material. This result suggests that at the temperature at which the break in the $\log \sigma$ *versus* $1/T$ curve occurs, Eq. (14) ceases to operate and the density of carriers remains constant. Thus the slope of the low temperature linear portion, according to this view, should be the activation energy ϵ''_0 for diffusion of these carriers.

There are several reasons why the concentration of carriers should become "frozen" at sufficiently low temperatures. In the first place, it is possible that during the time in which measurements are made the diffusion necessary to establish the equilibrium corresponding to Eq. (14) may not have time to take place. In the second place, it is possible that impurity ions having higher valence than the normal ions of the crystal may have vacancies associated with them. For example, a divalent lead ion in a lattice of the alkali halides will have a vacant positive ion site associated with it for reasons of electrical balance

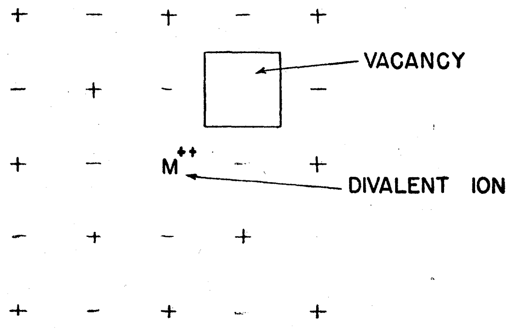

FIG. 18. Vacancy in lattice of typical alkali halide accompanying divalent ion.

---

[20] N. F. Mott and R. W. Gurney (see reference 1), Chap. 2.

[21] A. Einstein, Ann. d. Physik **17**, 549 (1905).

(see Fig. 18). Koch and Wagner[22] have shown, in fact, that the low temperature portion of the conductivity curve of crystals of monovalent ions is very sensitive to the presence of divalent ions in just the manner to be expected from these considerations. It is evident that experiments could readily be devised to indicate in a given case whether or not the freezing is caused by the lengthening of the time needed for diffusion of the vacancies. For if this were the cause, it should be possible to lower the conductivity at a temperature below the bend of the curve by annealing the specimen for a sufficient length of time. Experiments of this type do not appear to have been carried out.

Lehfeldt[17] has made accurate measurements of ϵ in Eq. (13) for a number of alkali halide crystals. In the case of KCl, for example, which we shall use as a typical alkali halide crystal, ϵ is 2.1 ev. Using his conductivity curve for KCl we find that the low temperature portion of the log σ *versus* $1/T$ plot has a slope corresponding to 0.82 ev. Since this is ϵ''_0, according to the foregoing interpretation of the bend in the curve, it follows that

$$\begin{aligned}\epsilon'_0&=2.56\text{ ev},\\ \epsilon''_0&=0.82\text{ ev}.\end{aligned}\tag{22}$$

In the specimen used for this calculation, the bend in the conductivity curve occurs at about 560°C.

We may next ask for the value of n corresponding to the knee of the conductivity curve for the speciment of KCl used in this estimate. Setting ϵ'_0 in Eq. (14) equal to 2.56 ev and taking C' as 5.10^3, the approximate value obtained by Mott and Gurney, we find

$$n/N\sim 10^{-4}\tag{23}$$

or

$$n\sim 1.5\cdot 10^{18}\text{ per cc.}\tag{23a}$$

At first sight this result suggests that the density of vacant lattice sites in any crystal that has been taken near the melting point and is then cooled moderately slowly to room temperature is of the order of 2×10^{18} per cc. This conclusion must be subject to further analysis, however. The foregoing calculation leads us to the density of carriers at the temperature at which this density becomes frozen. It is possible that additional clusters which do not act as carriers of vacancies are also present at this temperature. In order to become oriented, we may attempt to determine the density of pairs of vacancies of opposite sign which have combined under their mutual forces of attraction, in much the same way that the atoms or molecules in a vapor may combine to form clusters.

At a distance r that is large compared with atomic dimensions a positive and a negative ion vacancy will have an electrostatic energy of interaction that is given by the equation

$$\epsilon_p=e^2/\mu r,\tag{24}$$

in which e is the charge on the vacancy and μ is the static dielectric constant of the crystal. If we set μ equal to 4.9, the value for KCl, and set r equal to the distance between nearest unlike neighbors in the KCl lattice, namely 3.14A, we find

$$\epsilon_p=0.93\text{ ev}\tag{25}$$

which provides us with an estimate of the energy of combination of a pair of vacancies.

According to statistical mechanics the relation between the number of combined pairs of vacancies m, and the number of isolated vacancies n is

$$Nm/n^2=6\exp(\epsilon_p/kT).\tag{26}$$

Here N is the density of available sites and the factor 6 enters because the pair of combined vacancies can be oriented in 6 different ways in the KCl lattice. Using the relation (23) we readily find that at 560°C

$$m/n\cong 4.$$

This shows that the density of pairs is comparable with the density of isolated carriers. It follows that a substantial number of the vacancies produced during an excursion in temperature near the melting point may be in the form of clusters so that the total number that is frozen in could be much larger than the value of about 2×10^{18} per cc derived above (see Eq. (23a)).

It should be emphasized again at this point that the value (23a) is based upon the estimate of C' in Eq. (14) made by Mott and Gurney. Since this calculation could easily be in error by a factor 10, it follows that the foregoing line of

---

[22] E. Koch and C. Wagner, Zeits. f. physik. Chemie **B38**, 295 (1937).

reasoning leaves us with considerable uncertainty regarding the number of frozen vacancies. This uncertainty would be greatly reduced in magnitude if the mobility of the vacancies in the alkali halides were determined by the methods which Koch and Wagner[22] applied to the silver halides. For this would allow us to determine D in the relation (17) and hence evaluate n. Unfortunately the necessary experiments have not yet been carried out.

VI. INFLUENCE OF VACANCIES UPON CRYSTAL DENSITY

We shall now consider the changes in crystal density[23] which may be expected to accompany the introduction of vacancies into a lattice. We may confine our attention to the case in which the vacancies in the lattice do not carry a resultant electric charge so that the surrounding medium is not subject to the polarizing action of a Coulomb field. This case evidently does not correspond to that of an isolated positive or negative ion vacancy. However, it actually is of more practical interest, for as we shall see below, the charged vacancies undoubtedly are clustered into uncharged groups at temperatures at which the densities of crystals are usually measured.

When an ion pair is removed from the interior of the lattice and placed on the surface two factors influence the density:

(a) In the first place, an additional unit cell is added to the crystal so that its volume is increased by an amount v_c equal to the volume of this cell. This term will not in itself alter the lattice parameters of the crystal. Per ion pair the density will be lowered by a factor $(1-v_c/V_0)$ in which V_0 is the initial volume of the specimen.

(b) In the second place, the ions in the vicinity of the vacancies produced will shift their positions and thereby strain the surrounding lattice. This strain will be accompanied by a change in lattice parameter and, as a result, by a change in density. The factor by which the density is changed as a result of this effect is much more difficult to compute than the factor discussed in (a).

In order to obtain an understanding of the density change to be associated with effect (b), we may consider the problem from a somewhat idealized viewpoint. Let us assume that the cavity left by the removal of the ion-pair is a sphere. The removal of the ion-pair from this cavity will cause a strain in the surrounding lattice which will be similar to that which would be obtained by placing the sphere under a hydrostatic pressure P (positive or negative). If the surrounding medium were perfectly isotropic and obeyed Hooke's law, the original volume of the crystal V_0 would, according to elasticity theory,[24] be changed to the value V' given by the equation

$$V'=V_0-v_c+v'_c+(P/k)v_c. \tag{27}$$

Here v_c is the initial volume of the spherical cavity, which is equal to the volume of the unit cell, v'_c is the altered value of the volume of the cavity. P is the pressure that would be required in the cavity to produce the elastic strain at large distances from the cavity, and k is the compressibility of the medium. The relation between P and the shift δr in the radius of the cavity is given by the equation[24]

$$P=4\mu(\delta r/r), \tag{28}$$

when the medium is elastic even in the vicinity of the cavity. Here r is the radius of the cavity, which is related to v_c by the equation

$$4\pi r^3/3=v_c, \tag{29}$$

and μ is related to Young's modulus E and Poisson's ratio σ in the manner

$$\mu=E/2(1+\sigma). \tag{30}$$

Since the elastic constants of all materials rise as they are compressed and fall as they are expanded, it follows that the deviations from Hooke's law which occur in practice for the atoms in the immediate vicinity of the cavity will be different in compression and expansion. In brief, the effective value of P will be smaller than that given by (28) when δr is positive and will be larger in absolute magnitude when δr is negative.

Proceeding under the assumption of perfect

---

[23] A number of investigators have appreciated the influence that lattice vacancies would have upon the densities of crystals; however, O. Stern was the first investigator to recognize that available experimental techniques for determining density were sufficiently precise to provide a crucial test of the vacancy theory of *F*-centers. The density measurement carried out under Stern's guidance are described briefly in Section IX.

[24] A. E. H. Love, *Elasticity* (Dover Publications, New York, 1945), p. 98, pp. 175–176.

elasticity, we find from (27)–(29) that when $\delta r/r$ is small compared with unity, the change in volume of the crystal is

$$[3+(4\mu/k)](\delta r/r)v_c. \tag{31}$$

The ratio $4\mu/k$ may be expressed entirely in terms of Poisson's ratio

$$4\mu/k=6(1-2\sigma)/(1+\sigma),$$

so that this quantity is of the order of magnitude 2. Thus the numerical coefficient in (31) is about 5.

We see from (31) that both contributions (a) and (b) to the volume of the crystal are positive when δr is positive. Thus in this case the density of the crystal definitely decreases as vacancies are introduced. On the other hand, if δr is negative, the second term, arising from a change in lattice spacing, tends to compensate for the first. It would be a highly accidental occurence if these two terms were to cancel one another exactly, and in fact, we can safely assume that this will not be a general occurrence. On the other hand, the possibility cannot be left out of consideration. We see from (31) that the possibility of nearly exact compensation of the two terms appears when $\delta r/r$ is of the order of 0.2.

Mott and Littleton[18] have determined the displacement of the ions in the immediate vicinity of the positive and negative-ion vacancies in NaCl and have come to the conclusion that these ions move away from the vacancy by a distance corresponding to $\delta r/r\sim 0.1$. In carrying out this calculation, the investigators assumed that the vacancies are separated from one another so that the medium surrounding each is subject to the polarizing action of a Coulomb field arising from the dearth of positive or negative charge. For this reason the results are not precisely applicable to the case of interest to us. In fact the sign of $\delta r/r$ could easily be opposite to that found by Mott and Littleton. The magnitude of their result indicates, however, that it is rather improbable that a contraction in lattice constant will almost completely compensate for the addition of unit cells to the lattice, even though this possibility cannot be completely excluded. As a result, we shall assume in the following that the density of the alkali halides varies with the number of pairs of vacancies in accordance with the relation.

$$\delta\rho/\rho_0=-a(n/N). \tag{32}$$

Here ρ_0 is the ideal density of a crystal in which there are no vacancies, n/N is the ratio of the number of pairs of vacancies to the number of sites in the lattice, a is a constant near unity and $\delta\rho$ is the decrease in density accompanying the presence of the n vacancies.

TABLE I. Probable error, in parts per million for the factors appearing in N_A (after Birge).

Crystal	M	ρ	d^3	φ	Error in N_A	Value of $N_A\cdot 10^{-23}$
Calcite	50	37	16.5	13	65	6.02314 ±0.00039
Sodium chloride	51	37	60		87	6.02401 ±0.00052
Diamond	20	34	89		97	6.02343 ±0.00059
Lithium fluoride	32	45	120		132	6.02319 ±0.00080
Potassium chloride	40	37	68		86	6.02324 ±0.00052
Adopted average value						6.02338 ±0.00023

In connection with Eq. (32), it is interesting to note the following theorem. When n pairs of vacancies are formed by removing the pairs to the surface, the volume V of the crystal is changed by the following amount

$$\delta V=nv_c+\delta V_0.$$

Here v_c is the volume of the cell occupied by a molecule and δV_0 is the change in the initial volume V_0 of the crystal caused by the change in lattice parameters alone. Thus the first term on the right-hand side gives the increase because of the addition of new unit cells to the lattice whereas the second term describes the change caused by the shift in dimensions of the unit cells of the crystal. Dividing this equation by V_0, we obtain

$$\delta V/V_0=(n/N)+(\delta V_0/V_0), \tag{33}$$

where $N=V_0/v_c$ is the number of cells in the specimen initially. Now

$$\delta V/V_0=-\delta\rho/\rho,$$

where ρ is the initial density and $\delta\rho$ is the change in density. Similarly

$$\delta V_0/V_0=\delta v_c/v_c,$$

in which δv_c is the change in v_c caused by the change in lattice spacing. Thus Eq. (33) is equivalent to

$$(\delta\rho/\rho)+(\delta v_c/v_c)\equiv\delta(\rho v_c)/\rho v_c=n/N. \tag{34}$$

Hence we see that the fractional change in the product ρv_c is equal to the fraction of vacant lattice sites, regardless of the value of the constant a in Eq. (32). In effect the dependence of ρ upon the parameter a is compensated by the dependence of v_c upon the same quantity. It follows that the variation in the density of vacancies from one specimen of a given material to another can be determined by studying the variation of the product ρv_c. Variations of this type have been carried out in connection with the determination of Avogadro's number N_A by precision measurements of the lattice constants of crystals,[25] a topic which we may review with profit at this point.

In the crystal method of determining N_A, the lattice constants of crystals such as calcite, rock salt, potassium chloride, diamond, and lithium fluoride are compared with the accurately measured spacing of a ruled grating. The molar volume of any given crystal is determined with the use of the molecular weight and accurately measured values of the density. N_A is then computed by taking the ratio of the molar volume and the molecular volume. The basic equation for N_A when this method is employed is

$$N_A = M/(2\rho\varphi d^3). \qquad (35)$$

Here M is the molecular weight of the crystal, ρ is the density, φ is a geometrical constant which may be taken as unity for cubic crystal, and d is the lattice parameter.

It should be noted that the quantity in the denominator of Eq. (35) is essentially ρv_c, which satisfies the relation (34).

Table I, taken from Birge's most recent survey,[25] of the atomic constants contains his estimate of the probable error of the measurement of each of the quantities in (35) for five crystals which have been studied extensively. It is to be emphasized that the probable errors in d^3 exclude a component of about 60 parts per million arising from uncertainty in the true relation between in the Siegbahn values of x-ray wave-lengths and the true values, as determined from the ruled grating. This uncertainty which is the same for all crystals, can be neglected when a comparison of the relative values of the quantities listed is made.

The first fact of interest that we may glean from this table is that the probable error in the product $\rho d^3\varphi$ is less than 1 part in 10^4 for all the crystals except LiF, for which the best x-ray measurements were on powdered specimens. We may infer from this that the variation in the density of vacancies within the well-chosen specimens of a given substance that were used in the various measurements is less than 1 part in 10^4.

Next, we note that except in the case of LiF, the errors in the relative values of N_A are less than 1 part in 10^4. Moreover, Birge comes to the conclusion that it is most probable that the crystals give the same value of N_A to better than 1 part in 10^4, or to use his own words, "Probably the most important conclusion to be drawn from the remarkable consistency of the results from the five different crystals is that such crystals must be geometrically perfect, to better than one part in 10,000." In making this statement, Birge assumes that the materials studied have such a wide range of chemical and physical properties that it is exceedingly unlikely that all would have a density of vacancies that is greater than 1 in 10^4 and yet would be the same within all of the specimens to less than 1 part in 10^4.

One method of testing this general conclusion concerning the perfection of crystals is to compare the value of e, the electronic charge, derived from the best value of N_A with the use of the equation

$$e = F/N_A,$$

in which F is the Faraday constant, with the best value determined from the oil drop experiment. Unfortunately, the latter method appears to be too inaccurate to provide us with a reliable check on the crystal method. The evidence that does exist suggests that the value of e determined from the oil drop experiment is larger than that determined from crystal data by as much as 1 part in 10^3. This could mean that the observed density is lower than the ideal density by about 0.1 percent. However, it does not seem safe to take this indication seriously at the present time.

Another procedure is to compare the value of e determined from crystal data with the other atomic constants in the manner that is customarily done with the Birge-Bond diagrams or similar nomograms in which the Rydberg constant is used to establish a link between e, h, and m. Birge has shown that the crystal value of e is

---

[25] See the review by R. T. Birge, *Reports on Progress in Physics* (1941), Vol. 8, p. 90; Am. J. Phys. **13**, 63 (1945).

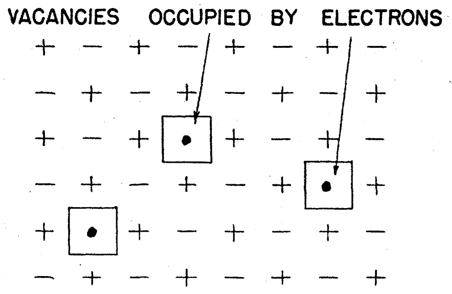

FIG. 19. De Boer's model of the *F*-center.

consistent with all the constants except some older values of h/e which are probably not trustworthy. Newer values of h/e are consistent with the crystal e. If the older values of h/e are assumed to be correct, the true value of e would be lower than the crystal value so one would infer that the observed values of ρv_c are ***higher*** than the values for an ideal crystal by as much as 0.3 percent.

Another method of drawing conclusions concerning the density of crystal imperfections is that developed by Hutchison and Johnston[26] who have used precision measurements of the density and relative lattice spacing of crystals to obtain relationships between the atomic and molecular weights of the constituents. These values have been used in the survey leading to Table I. For example, using data for lithium fluoride and calcite and the molecular weights of lithium and calcium carbonate, they are able to compute the atomic weight of fluorine from the relation

$$M(F)=\left[\frac{M(\mathrm{CaCO_3})\rho(\mathrm{LiF})}{\rho(\mathrm{CaCO_3})\varphi}R_g{}^3\right]-M(\mathrm{Li}). \quad (36)$$

Here $M(A)$ is the atomic or molecular weight of compound A, $\rho(A)$ is the corresponding density, φ is the geometrical constant of the calcite lattice, and R_g is the ratio of the lattice parameters of lithium fluoride and calcite.

The coefficient of M in the brackets in Eq. (36) is just the ratio of v_c for the two crystals. Thus one limit to the accuracy with which the atomic weights can be related by this method is set by the accuracy with which the difference in density of vacancies in the specimens is known.

In all of this work the specimens of alkali halides were artificial single crystals which were grown by the Kyropolous method. In order to obtain consistent results it was necessary to anneal 50° below the melting point for at least four hours. If this was not done, the measured densities were usually higher by as much as 3 parts in 10^4 and were sometimes lower by the same amount. The agreement between the value of density for the artificial crystals annealed in this way, and for the best natural crystals of the same materials determined by other investigators, is good to within a few parts in 10^5.

The atomic weights for fluorine obtained in this way by comparisons of the data for lithium fluoride with that for calcite, diamond, sodium chloride, and potassium chloride agree to within 2 parts in 10^4 with the most reliable values obtained by other methods. It follows either that the observed values of ρV_c agree with the ideal values to within this limit or that the percentage difference between the actual and ideal values is larger but is the same for all crystals measured to within this limit of accuracy. As in the determination of N_A, the second possibility might be considered seriously if we were dealing only with alkali halides having a similar origin and history. However, it is difficult to believe that the artificial alkali halides crystals would have the same degree of imperfection as the natural alkali halides, calcite, and diamond.

To summarize, the existing data on the fundamental constants and atomic weights suggest that the difference between the observed and real density is less than 1 part in 10^4.

VII. NATURE OF *F*-CENTERS

We are now in a position to consider once again the nature of the *F*-centers in the alkali halides. At the end of Section IV we saw that *F*-centers are probably either electrons that are trapped to lattice imperfections of the type that have thermodynamical origin, or are electrons that have become self-trapped in the lattice. Now the calculations of Schottky and Jost and Mott and Littleton make it seem exceedingly unlikely that the lattice imperfections of interest are interstitial ions when *F*-centers are formed by x-ray bombardment at room temperature since the density of these is negligible compared with the density of

---

[26] D. A. Hutchison and H. L. Johnston, J. Am. Chem. Soc. **62**, 3165 (1940); Phys. Rev. **62**, 32 (1942); D. A. Hutchison, Phys. Rev. **66**, 144 (1944); J. Chem. Phys. **10**, 383 (1945).

negative-ion vacancies. Thus if the first type of explanation is valid, the *F*-centers should be electrons attached to negative-ion vacancies. This interpretation was first proposed by de Boer[27] who suggested that when the alkali atoms are heated in the presence of alkali metal vapor, chlorine ions diffuse to the surface of the crystal and combine with the atoms of the vapor to form new layers of lattice. The valence electrons initially attached to the alkali metal atoms wander into the crystal and become attached to the negative ion vacancies. (See Fig. 19.) According to this picture, the *F'* centers consist of vacancies to which two electrons are attached. (See Fig. 20).

We are now at a position to attempt to decide between de Boer's picture and that based on the self-trapping of electrons. The second model has two very serious difficulties associated with it:

(1) In the first place, if the *F*-centers are electrons which have become self-trapped, the positive ions which accompany these electrons when the discoloration is produced by heating the crystal must reside in interstitial positions. The calculations of Mott and Littleton,[18] Mott and Gurney,[1] and Tibbs[28] show that this process probably requires appreciably more energy than de Boer's mechanism. For example, in the case of NaCl these calculations show that the energy required to form an *F*-center from an alkali atom by de Boer's process is 0.23 ev. This method of calculation yields results that are in close agreement with the values obtained from an analysis of the equilibrium between vapor and solid in cases in which they are known. On the other hand, even if the self-trapped electron gains as much energy in the self-trapping process as it would in combining with a vacant halogen-ion site, the energy required to form an interstitial ion plus a self-trapped electron is 1.1 ev. Actually it is safe to assume that an electron would gain more energy by residing in a vacancy if these are available than by being self-trapped. For the vacancy has a positive Coulomb field associated with it and hence would attract a self-trapped electron. Since the polarization field of the vacancy and that of the self-trapped electron would just cancel when the electron and vacancy join, it follows that the end result is the same as that obtained by placing the electron in the vacancy in the first place. In brief, de Boer's mechanism requires at least 1 ev less energy than the mechanism of self-trapping does.

(2) Mott and Gurney have pointed out that the relation between the equilibrium density of *F*-centers and the vapor pressure (see Fig. 4), which correspond to a monomolecular reaction, favors de Boer's mechanism. For according to it, the basic equation of equilibrium may be written

$$\text{Alkali atoms (vapor)} \rightleftarrows \text{(electron trapped to vacancy).} \quad (37)$$

In the self-trapping mechanism, on the other hand, we have

$$\text{Alkali atom (vapor)} \rightleftarrows \text{(interstitial ion)} + \text{(self-trapped electron)} \quad (38)$$

which is of bimolecular form. One might argue that this reasoning is invalid because the electrons and interstitial ions could combine; however in this case one runs into the objection that the *F*-centers cannot be electrons attached to interstitial positive ions because they may be formed by x-ray bombardment at room temperature under conditions in which the density of interstitial ion should be negligible.

We are led, then, by a logical sequence of arguments to the conclusion that de Boer's interpretation of *F*-centers in terms of electrons bound to vacant halogen-ion sites has overwhelming support. It is important to note that the theoretical calculations based on the theory of ionic crystals play a very important role in this sequence of arguments.

VIII. MOBILITIES OF CARRIERS

The analysis of Section V, based on Fig. 16, has led us to the conclusion that the activation

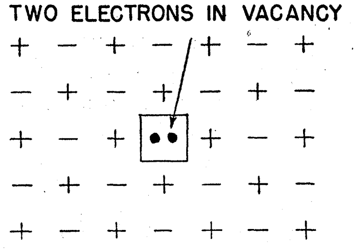

FIG. 20. *F'*-centers.

---

[27] J. H. de Boer, Recueil des Trav. Chim. d. Pays-Bas **56**, 301 (1937).

[28] S. R. Tibbs, Trans. Faraday Soc. **35**, 1471 (1939).

energy ϵ''_0 for the migration of the carriers in KCl is 0.82 ev. It follows from the discussion of that section that these carriers are principally positive-ion vacancies at temperatures below 560°C.

The theory of the migration of ions in crystals indicates that the frequency with which a carrier jumps is given by the equation

$$\nu=\nu_0 \exp(-\epsilon''_0/kT) \tag{39}$$

in which

$$\nu_0 \cong 10^{13} \text{ sec.}^{-1}. \tag{40}$$

Using this value of ν_0 and the foregoing value of ϵ''_0, we find that near room temperature (300°K), the frequency ν_+ with which the carriers in KCl jump is

$$\nu_{+(300°\text{K})}=10^{-0.6} \text{ sec.}^{-1} \cong 1 \text{ sec.}^{-1}. \tag{41}$$

An extrapolation of Tubandt's data[19] on the relative mobility of the positive and negative carriers in KCl indicates that at room temperature the ratio is

$$\nu_-/\nu_+=10^{-5}. \tag{42}$$

Hence

$$\nu_{-(300°\text{K})}=10^{-5} \text{ sec.}^{-1}. \tag{43}$$

These results show that if at room temperature a crystal contained about 10^{18} isolated positive- and negative-ion vacancies they would combine into pairs in the course of a day as a result of the migration of the positive-ion vacancies. The negative-ion vacancies would be essentially immobile during this time. Actually, the decay of the isolated vacancies would not be exponential with time because of the bimolecular nature of the reaction.

If we assume that the jump-time is constant and that there are initially n_0 negative-ion vacancies, the decay of single vacancies obeys the equation

$$n=n_0/(1+\nu n_0 t/N), \tag{44}$$

in which t is the time and N is the density of sites. This equation is not strictly valid, however, for the jump-time of a positive-ion vacancy will be influenced by its proximity to a negative-ion vacancy because of the electrostatic attraction of the two. The magnitude of this effect may be estimated as follows. The potential energy between two charges in a crystal is

$$\epsilon=-e^2/\mu r, \tag{45}$$

provided r, the distance of separation, is large compared with the lattice spacing. Here e is the charge and μ, as previously, is the dielectric constant. It follows that when the charges are moved toward each other by a distance δr, the change in energy is, in first approximation,

$$\delta\epsilon=(e^2/\mu r^2)\delta r. \tag{46}$$

If a is the spacing between neighboring unlike ions, this may be written in the form

$$\epsilon=(e^2/\mu a)(\delta r/r)(a/r). \tag{47}$$

The coefficient e_2/r is 0.93 ev for KCl. Since $r=2a$ for the most direct line of motion, the coefficient of this factor is

$$\sqrt{2}a^2/r^2, \tag{48}$$

which is 0.09 for $r/a=4$. Thus under these circumstances the activation energy for jumping would be lowered by about 0.04 ev when the positive-ion vacancy jumps toward the negative-ion vacancy and would be raised by the same amount when it jumps away from it. It follows that at room temperature a positive-ion vacancy which has approached a negative-ion vacancy by a distance corresponding to $r=4a$ has about 10 times greater probability of jumping toward the latter than away from it.

It is clear, in any event, that the corrections introduced by the attraction would be such as to decrease the time required for combination of the two type of vacancies to a value substantially less than a day.

If the positive-ion vacancies are accompanied by divalent positive ions, such as Pb^{++}, instead of by negative-ion vacancies, as would be the case in a crystal containing a trace of lead chloride, the same conclusion can be drawn. That is, the vacancies will combine with the oppositely charged imperfection in the course of several hours at the most.

It is interesting to note that at 560°C (833°K), the jump frequencies have the values

$$\begin{aligned}\nu_{+(833°\text{K})}&=10^8 \text{ sec.}^{-1},\\ \nu_{-(833°\text{K})}&=10^7 \text{ sec.}^{-1}.\end{aligned} \tag{49}$$

These values are such that a positive-ion vacancy would combine with the negative-ion vacancies in a time of the order of 10^{-4} sec. if the density of the latter were 10^{18} per cc. This time is so short that

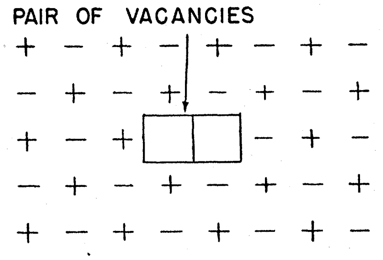

FIG. 21. The configuration of ions about a pair of vacancies.

we may be certain that most of the coagulation will actually occur during cooling.

One of the interesting questions which arises at this point is that of the mobility of pairs of vacancies. It would be interesting to know whether these possess sufficient mobility to aggregate into larger clusters as pairs or whether larger aggregates could form only by the migration of isolated positive- and negative-ion vacancies to clusters that have already formed. This question has not yet been given careful quantitative consideration; however it is clear, as has been pointed out by Huntington,[29] that pairs of vacancies will be much more mobile than negative-ion vacancies. This may be seen from Fig. 21 in which the configuration of positive- and negative-ions in the vicinity of a pair of vacancies is shown. It follows that the ions of a given kind are much less restricted in jumping into the vacancy in their own lattice as a result of the absence of the ion of opposite sign.

IX. PRODUCTION OF *F*-CENTERS BY X-RAYS

We are now in a position to discuss the mechanism by which color centers are produced as a result of exposure to x-rays. The primary effect of the x-rays will be the release of photoelectrons which will move through the lattice at a high rate of speed and thereby produce secondary electrons and holes. These secondary units will wander about until they are either trapped in the lattice or recombine. Since self-trapped electrons and holes do not appear to be stable at the temperatures at which observations are usually made, we may conclude that the self-trapped charges have sufficient mobility to move until they find more stable locations. Thus in cases in which recombination of the electrons and holes does not occur, the charges will ultimately come to rest at vacancies.

The discussion of the preceding sections demonstrates that the vacancies will be clustered into groups, the smallest of which are neutral pairs. Let us consider what will happen when an electron approaches a pair of vacancies. The calculation leading to (25) show that the energy of combination of a pair is about 1 ev. On the other hand, the calculations of Mott and Gurney[30] indicate that the energy of binding of an electron and a halogen-ion vacancy is nearer 2.0 ev. Thus the electron makes much better use of the field of the halogen vacancy than the positive-ion vacancy does. We may conclude that the electron will be trapped by the pair and that the bond between the positive-ion vacancy and the halogen-ion vacancy will be greatly weakened thereby. We shall assume that, following the capture of an electron, the pair falls apart under the action of thermal fluctuations, and the positive-ion vacancy wanders off, leaving an *F*-center.

By analogy, we may conclude that a hole will also be captured by a pair of vacancies. Since the negative-ion vacancies are much less mobile than the positive-ion vacancies, it is unlikely that the former wander away very rapidly after capture has taken place. It is to be emphasized that during extensive exposure to x-rays, in which a state of equilibrium is established, any given vacancy may act as the trapping center for successive secondary charges which are annihilated by recombination with charges of opposite sign. Thus at any given time, there will be present, in the equilibrium state, both pairs and isolated vacancies to which electrons and holes are attached and which are in all stages of recombination and dissociation. This equilibrium is clearly not one in which the law of detailed balance will hold. For example, the process of annihilation of a trapped electron by recombination with a free hole, will not be reversed by the generation of a trapped electron and a free hole at the vacancy at which the electron is trapped.

If the vacancies are clustered into groups larger than pairs, the process of darkening is somewhat

---

[29] Private communication.

[30] N. F. Mott and R. W. Gurney, see reference 1, page 143.

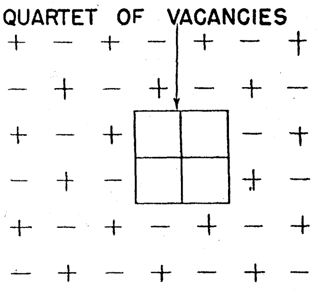

Fig. 22. A quartet of vacancies.

more complicated, although the same general principles employed in the preceding paragraphs can be used to understand the formation of *F*-centers. Suppose, for example, that the vacancies are aggregated into groups of quartets (see Fig. 22). In this event, *F*-centers could be formed by the following sequence of processes:

(a) A quartet captures a pair of electrons and ejects two positive-ion vacancies. The resulting unit, which consists of a pair of bound *F*-centers, will have a close schematic resemblance to a H_2 molecule. In particular the first excited state will probably be adiabatically connected with the ground state, as in a H_2 molecule, so that it will not be possible to produce photoelectrons by excitation to the first excited state, as is the case for *F*-centers (see Fig. 23). We shall designate this type of center, consisting of a pair of *F*-centers, an F_2-center.

(b) The pair of associated *F*-centers captures two holes which annihilate the electrons previously attached to the vacancies. The resulting pair of halogen vacancies will repel one another and tend to migrate apart by a distance of several interatomic spacings under the action of this repulsive force. The pair will probably not be able to separate very far without additional assistance because of the low mobility of halogen vacancies. If either one of the vacancies captures an electron, the two vacancies will probably migrate together again to form a center which is an F_2-center that has lost one electron. We shall call this center and $F_2{}^+$-center.

(c) If, before the partly separated pair of halogen vacancies has an opportunity to capture an electron, a positive-ion vacancy happens by, it will combine with either one or both of the halogen vacancies. If the pair consisting of a positive and a negative-ion vacancy is mobile, it will happen, during a certain fraction of these encounters between a positive-ion vacancy and a slightly separated pair of halogen vacancies, that the positive ion vacancy will migrate away with one of the halogen vacancies, leaving the other completely isolated. Thus an isolated *F*-center will be formed when either the isolated halogen vacancy or the pair captures an electron. It should be noted that the comparatively high mobility of pairs is probably guaranteed if quartets of vacancies are formed, for the most direct mechanism for their formation is as the result of combination of pairs.

Thus we see that if aggregates of vacancies larger than pairs occur in the crystal, *F*-centers will be formed as the result of exposure to x-rays provided sufficient mobility of pairs is assumed. It is evident that many other combinations of vacancies, electrons, and holes will be formed at the same time and that in the equilibrium state these units will be transforming into one another by processes which do not obey the law of detailed balance. The most interesting combinations, other than *F*-centers are as follows:

(a) Holes trapped by positive-ion vacancies. These centers are probably responsible for the *V*-absorption band (Fig. 2) observed in the ultraviolet after exposure to x-rays. The same units can be formed by heating the crystals in halogen atmosphere and obtaining a stoichiometric excess of halogen in a way similar to that used in obtaining *F*-centers by additive coloring. This process has been studied by Mollwo.[4]

(b) The unit formed by combining a pair of vacancies and an *F*-center (Fig. 24). This unit may be formed in many ways: By combination of an *F*-center with a passing pair; as the result of capture of an electron by a quartet with ejection of a positive-ion vacancy; as the result of electron capture after a positive-ion vacancy has been captured by a pair of halogen vacancies; as the result of the capture of a positive-ion vacancy by an $F_2{}^+$ center. One of the basic problems of interest in connection with these centers is that of deciding whether or not the electron can be released photoelectrically at normal temperatures, as the electrons attached to *F*-centers can be. This problem appears to be too complex to decide on the basis of calculations. We shall see below that there is evidence to indicate that these centers are responsible for the *M*-band observed by Molnar on the long wave-length side of the *F*-band.

(c) The F_2^+- and the F_2-centers. In accordance with the definitions introduced in earlier paragraphs of this section, these consist of pairs of halogen vacancies which have captured one or two electrons, respectively. By analogy with the facts for diatomic molecules, represented in Fig. 23, we may suppose that photoelectrons are not formed when these centers absorb light. Instead, the vacancies separate somewhat so that the first excited state and the ground state get much closer together. The system then makes an almost adiabatic transition to the ground state and returns to its initial condition. As we shall see in the next section, there is reason for believing that certain color centers that are produced when crystals containing *F*-bands or *M*-bands are irradiated with light lying in these bands correspond to the F_2- and F_2^+-centers.

At this point we reach one of the most interesting problems that arises in connection with the darkening of the alkali-halides: Is it practical to produce *F*-centers at room temperature by x-ray irradiation as the result of migration of vacancies from the surface of the crystal? If not, the limit to darkening that can be achieved is determined by the density of vacancies that is present within the crystal before irradiation. If so, the attainable limit may be much higher.

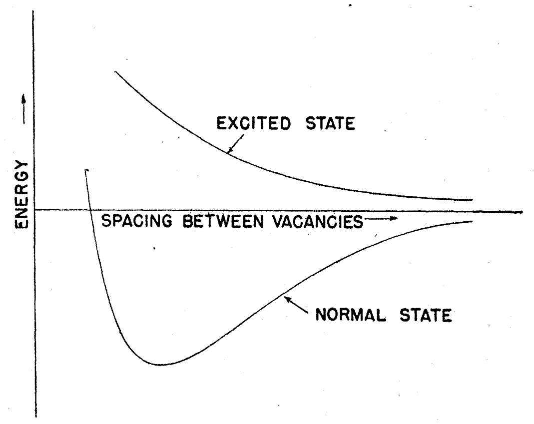

FIG. 23. The behavior of the normal and excited energy states of a pair of negative-ion vacancies, to which one or two electrons are attached, as the distance between the vacancies is varied. It will be seen that the levels approach one another at large spacings.

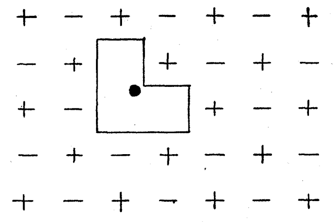

FIG. 24. The center formed by combining an *F*-center and a pair of vacancies. These centers may be responsible for the *M*-band. The electron will be distributed between the two negative-ion vacancies.

It follows from the discussion of Section VI that the best available evidence suggests that in well-annealed crystals of the alkali halides the fraction of vacant lattice sites is probably less than 1×10^{-4}. Since the number of molecules per cc in KCl is 1.6×10^{22}, it also follows that the highest darkening which should be possible in such crystals if vacancies do not migrate in appreciable quantities from the surface corresponds to 1.6×10^{18} *F*-centers per cc; that is, about 2×10^{18} per cc. Now densities as high as 2×10^{18} have been produced unambiguously in well-annealed crystals which have been exposed to the radiation from an x-ray tube with a beryllium window (see section II). Somewhat greater darkening has been produced by the same method; however the exact magnitude of the density of centers has not yet been determined to sufficient accuracy because of the experimental difficulties involved in such determination. These difficulties center about the problem of cleaving plates of the crystals that are sufficiently thin to transmit an appreciable fraction of the radiation lying near the peak of the *F*-band, so that α_m can be determined and used in connection with Eq. (2).

Now careful density measurements, carried out by Stern, Estermann, and Leivo with the use of the flotation method show that crystals which have been darkened by x-rays to the point of containing about 2×10^{18} *F*-centers per cc have a density that is lower than the value before irradiation by about 1 part in 10^4. Since the parameter a in Eq. (32) is probably very close to unity, the measurements suggest very strongly that in these cases the major portion of the vacancies *diffuse from the surface of the crystal.* This in turn indicates that the initial undarkened crystals are perfect to better than one part in ten thousand, in agreement with Birge's conclusion based on the consistency of the values of N_A determined from different crystals with the use of the x-ray method.

It should be emphasized that the estimates of the jump frequencies for halogen vacancies which were made in section VIII show that at room temperature individual halogen vacancies could not diffuse into the lattice from the surface in any time of practical interest without some assistance. The existing evidence on x-ray darkening indicates that equilibrium is established within a day at the levels of darkening studied to date. An isolated halogen-ion vacancy would have jumped only a few lattice distances in this time. In contrast, the observed darkening extends to a depth of the order of 0.1 mm. Thus if vacancies diffuse from the surface during the darkening process, they must migrate in the form of neutral pairs. We may readily estimate an upper limit for the activation energy for such diffusion. If the pairs migrate a distance of 10^{-2} cm in one day (10^5 sec.), the diffusion coefficient must be greater than 10^{-9} cm^2 per sec. Now the diffusion coefficient obeys an equation of the form

$$D=D^2 \exp\left(-\epsilon/kT\right)$$

in which D^2 is usually of the order of 10^{-2} cm^2 per sec., but may be as large as 1.0. Taking the latter value we find that at room temperature

$$\frac{\epsilon}{2.3kT}<9,$$

so that ϵ must be 0.5 ev or less. This value is not entirely out of reason, for as we have seen in Section V (Eq. (22)) the activation energy for migration of positive-ion vacancies is only 0.82 ev.

X. THE BLEACHING AND TRANSFORMATION OF CENTERS

We saw in Section IV that F-centers in additively colored crystals may be transformed into F'-centers and vice versa if the crystals containing them are irradiated with light lying in the proper region of the spectrum and if the temperature lies in a certain range. There are two additional observations of this kind that are of considerable interest because they throw additional light on the factors which influence the formation of color centers. The two observations are as follows:

(a) Coagulation of F-centers with light

Glaser and Lehfeldt[31] have found that the F-centers in crystals which have been additively colored may be made to coagulate by irradiating them with white light at temperatures above the range in which F'-centers are formed (room temperature and above for KCl). In order to appreciate this fact it should be realized that isolated F-centers can be produced at room temperature in crystals which have been additively colored at elevated temperatures only by quenching very quickly from the elevated temperatures to room temperature. If the crystals are allowed to cool slowly the F-centers aggregate into clumps and the F-band is subordinate to the absorption bands associated with the "colloidal" aggregates. This behavior is, of course, exactly what is to be expected from the thermodynamical origin of F-centers. The crystal which contains atomically dispersed F-centers at room temperature is in a thermodynamically unstable state. Glaser and Lehfeldt's results show that irradiation with light will bring about an approach to the equilibrium state.

The basic experimental facts are these: Twenty minutes of irradiation with a strong arc at room temperature is sufficient to coagulate atomically dispersed F-centers to a point at which the F-band is completely absent. In the early stages of this process a band similar to Molnar's M-band appears on the long wave-length side of the F-band.

We may conclude that the irradiation, which undoubtedly ionizes the F-centers, establishes a chain of processes whereby the halogen vacancies are able to diffuse together. It is clear that the halogen vacancies cannot diffuse without assistance if the conclusions concerning the jump frequency derived in section VIII are correct. It follows that the transport of vacancies must take place via the migration of neutral pairs. This fact suggests the following mechanism: The photoelectrons which are ejected from the F-centers are trapped by centers from which

---

[31] G. Glaser and W. Lehfeldt, Göttinger Nachrichten **2**, 91 (1936); G. Glaser, *ibid.* **3**, 31 (1937).

positive-ion vacancies may be released as a result of the capture of electrons. These centers may be either neutral pairs, quartets, or higher aggregates of pairs, or divalent positive ions which have positive-ion vacancies attached to them, as impurities such as Mg^{++} or Pb^{++} would. The positive-ion vacancies which are released diffuse about, combine with the ionized F-centers and transport them to other F-centers to form aggregates. The positive-ion vacancies will be released from these aggregates when the latter have captured a sufficient number of photo-electrons. Thus it is clear that the positive-ion vacancies do not become used in this process, but merely serve in the nature of a catalyst for the aggregation.

Since the aggregation takes place in a time of the order of 10^3 seconds, it follows that the migration of positive-ion vacancies and the carriers which transport the negative-ion vacancies must be sufficiently rapid that they can migrate between at least two centers in this time. Inasmuch as the radius of the sphere of action of the carriers is probably somewhat larger than 1 interatomic spacing, we may conclude that the carriers must go of the order of 10^3 lattice distances in a typical case in which the density of F-centers is of the order of 5×10^{17} per cc. Thus the jump-time of the carriers should be of the order of 1 sec. or less. This line of reasoning seems to rule out the possibility that the halogen vacancies diffuse alone, as we have concluded previously, and suggests that the jump time for pairs is not greater than 1 sec.

According to this mechanism of aggregation we should expect the centers consisting of a pair of vacancies attached to an F-center to appear very early among the products of aggregation and hence to be clearly visible. Actually, an investigation of Glaser and Lehfeldt's data shows that the M-band undoubtedly is one of the first products of the process. This is one very good reason for identifying this band with the center shown in Fig. 24.

(b) The Generation of *R*-Centers

As we have pointed out in Section IX, Molnar found that M-centers appear automatically along with F-centers when the latter are produced by irradiation with x-rays. In connection with this discovery he investigated the manner in which the two bands are altered when the crystal is irradiated with monochromatic radiation lying in either band and is at a temperature at which F'-centers are not produced. These investigations are obviously closely related to those carried out by Glaser and Lehfeldt. The difference lies in the fact that in the former, the light intensity used was less and the range of frequency smaller than in the latter, so that the results obtained correspond to a more refined study of the products formed in the initial part of Glaser and Lehfeldt's investigation.

Two significant results were observed. First, the F-band and M-bands can be transformed into one another in a manner similar to that in which the F- and F'-bands transform. This result strongly suggests that the M-centers yield photo-electrons when they absorb light lying in the M-band. The details of transformation of the F- and M-bands into one another differ from those for the F- and F'-centers, however, in the sense that a fraction of the intensity of both bands is lost in each transformation. The lost absorption strength emerges in a set of bands which appear between the F-band and M-band. These bands, which we shall call the R-bands since they absorb red light in the case of KCl which has been studied most extensively, have the interesting characteristic that they cannot be converted into any of the other bands by light which they absorb. In other words, they are very stable under irradiation with visible light. We may infer from the work of Glaser and Lehfeldt that the centers responsible for the R-bands are the first aggregates of F-centers. This suggests, in turn, that we should identify them with the F_2- and $F_2{}^+$-centers described in the previous sections. As we saw there, it is not unreasonable to suppose that these centers should be stable when stimulated to the first excited level. The R bands may be seen in Fig. 2.

XI. THE DARKENING PRODUCED WITH CATHODE RAYS

All of the effects that are produced in the alkali halides by irradiation with x-rays may be duplicated with the use of cathode rays. There are, however, differences in degree which probably result from that fact that the depth to which ordinary cathode rays penetrate is much less than the distance in which x-rays are absorbed. The general similarity of the processes is not surprising, of course, since x-rays have as their most important effect the generation of fast photoelectrons which have all of the attributes of cathode rays.

We shall not attempt a detailed presentation of the effects of cathode-ray bombardment here since the results will not add anything to the fundamental principles which have been presented in the preceding sections. The writer must hasten to say that the darkening produced by cathode rays actually is of more practical interest than that produced by x-rays; however, the first process is subject to sufficiently less control that it has not proved as useful in obtaining a deeper insight into the mechanism of darkening. It should be remarked in passing, that it has been possible to show that the density of *F*-centers approached values of the order of 10^{19} and greater in evaporated deposits of KCl that have been darkened by cathode rays. Although these values are larger than we would expect to obtain in well-annealed single crystals unless vacancies were able to diffuse from the surface of the crystals, we cannot take the attainment of such darkening as positive evidence for the existence of such diffusion since the crystals in the evaporated films may be far from perfect.

It is interesting to note that there seems to be an upper limit to the darkening attainable by cathode-ray bombardment of about 10^{19} centers per cc. It is possible that when this density is reached the electrons in the *F*-centers are able to tunnel to the positive holes.

SUMMARY

1. The alkali halides may be darkened by a variety of methods which fall into two important groups. In one group are those methods which produce a crystal with a stoichiometric excess of alkali metal; in the other group are those which do not alter the composition. Darkening by heating in the presence of alkali metal vapor is characteristic of the first type of method, whereas the darkening produced by x-rays or cathode rays is characteristic of the second. The coloration produced in the visible part of the spectrum is identical in the two cases for most crystals. However, Molnar has shown that there are important differences in the ultraviolet part of the spectrum.

2. A straightforward series of arguments, based upon the observed experimental facts concerning darkened crystals and the ionic theory of the alkali halides, lead to the conclusion that the visible coloration of the most common alkali halides is related to the presence of electrons which are trapped in vacant halogen-ion sites.

3. Investigations on crystals darkened very heavily by x-rays from a beryllium-windowed tube and of crystals darkened by cathode rays show that such darkening is associated with extensive ionic diffusion, even at room temperature. The same fact is supported by studies of the coagulation of color centers under the action of light.

4. Recent measurements of the changes in density which accompany heavy darkening by x-rays, by Stern, Estermann, and Leivo, provide substantial support for the vacancy theory of color centers in the alkali halides and show that halogen-ion vacancies must be transported from the surface to the interior of the crystal in such darkening.

5. A quantitative comparison of the transport rate of positive- and negative-ion vacancies with the rate at which heavy darkening is produced in the alkali halides indicates that the halogen-ion vacancies cannot diffuse to the interior without assistance. It is proposed that the diffusion takes place by means of coupled pairs of positive- and negative-ion vacancies.

6. One consequence of the investigation of the heavy darkening of the alkali halides by x-rays is the fact that well-annealed single crystals are probably perfect to better than one part in 10^4. This conclusion, which has been made independently by Birge, supports the view that one of the most precise methods of determining the electronic charge is that based on the determination of the lattice spacing of good crystals by x-rays.