REVIEWS OF MODERN PHYSICS VOLUME 26, NUMBER 1 JANUARY, 1954

Color Centers in Alkali Halide Crystals. II

FREDERICK SEITZ
University of Illinois, Urbana, Illinois

To Professor R. W. Pohl, on his seventieth birthday. Without his devotion this field would not have achieved maturity.

CONTENTS

I. INTRODUCTION

1.

IN 1946 the writer[1] presented in this Journal a survey of the observations and theory concerning crystals of the alkali halides which have been colored either by the addition of a stoichiometric excess of one of the constitutents or by ionizing radiations. This survey was stimulated by wartime research on the coloration of layers of the alkali halides with cathode-ray beams which extended in interesting ways the fundamental research that had been carried out on pure single crystals prior to 1940. As a contribution to the scientific literature, the review article did not close the subject, but rather had the intent of integrating the available information and focusing attention on aspects that might be studied with profit.

Our knowledge has increased appreciably during the intervening period of time as a result of contributions from a wide variety of investigations, and it appears profitable once again to attempt to summarize the present status of the topic with the hope that such a review will serve to consolidate the attention which the topic has earned and deserves. As in 1946, the survey will not imply any measure of closure; in fact the topic will probably remain active for many years to come. This continuing vitality stems from the circumstance that the typical alkali halide crystal represents a remarkable medium for the study of crystalline imperfections. The ideally perfect alkali halide crystal is exceedingly simple in structure, from the standpoint of both lattice and electronic systems. There is hope of understanding the nature of imperfections to a degree possible in few other solid systems. Moreover, the crystals can be obtained with comparative ease in a state of purity and perfection, and can be subject to a variety of physical measurements which also is almost unique among available materials, silicon and germanium being possibly the only exceptions. Still

---

[1] F. Seitz, Revs. Modern Phys. **18**, 384 (1946). Mention should be made here of the error in Eq. (1) of the 1946 paper. This equation, due to Smakula, relates the intensity of the *F* band, or a band arising from any other center, to the oscillator strength, the density of centers and properties of the medium. The factor represented as $(n'+2)^2$ in the denominator of the equation as given should be replaced by $(n'^2+2)^2$. This error occurred as a misprint in Smakula's original article and has been reproduced frequently. The writer gave the correct form in his book *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Eq. (8), p. 664, but carried over the original misprint in the 1946 article. The writer is indebted to R. L. Sproul for pointing out this error. See, also, footnote 22 of the paper by Sproul, Bever, and Libowitz, Phys. Rev. **92**, 77 (1953), as well as R. Hilsch and R. W. Pohl, Phys. Rev. **68**, 721 (1931).

further, they appear to exhibit in striking form a large number of physical and chemical properties of the type that are strongly influenced by the principal crystalline imperfections, namely, excitons, electrons and holes, vacant lattice sites, impurity atoms, and dislocations. To date no other type of crystal has permitted so clear a vista to the imperfection-determined properties.

Unquestionably the area of research in solid-state physics most nearly resembling that centering about the alkali halides, as far as subject matter, range, and thoroughness of investigation are concerned, is that dealing with the properties of silicon and germanium.[2] Actually the two fields are remarkably complementary rather than competitive: for example, optical techniques have played a prominent role in unraveling the properties of the alkali halides, whereas measurements of electron transport form the basis for most of the studies of silicon and germanium. Electrolytic conductivity is apparently of very minor interest in the monatomic semiconductors, whereas it has furnished the key for understanding the basic disorder in the alkali halides. Again, the mobilities of free electrons and holes are relatively small in the alkali halides, being capable of measurement only at low temperatures, whereas the mobilities are comparatively enormous in silicon and germanium. The salts are transparent throughout most of the air-transmitting ultraviolet and visible parts of the spectrum but eventually become opaque in portions of the infrared as a result of the stimulation of restrahlen. In contrast, the monatomic semiconductors transmit best in the infrared and are opaque in the visible and ultraviolet. Dislocations appear to play a small role in determining the properties of major interest in silicon and germanium, whereas they apparently are of primary importance in one of the most vital properties of the alkali halides, namely, their ability to darken under the action of ionizing radiations. In both cases, however, the intentional addition of impurities has provided much key information. Studies have been made with germanium for ranges of additonal agents extending from about 10^{14} to 10^{20} per cc; *F* centers have been observed for a slightly larger range. On the whole, investigators in each of the fields have much to gain by studying the techniques used in the other. In particular, the study of *F* centers will probably benefit by adopting as far as possible the purification techniques, such as zone melting, which are being developed for improvement of silicon and germanium.

It is particularly interesting to note the growth of research on the alkali halides on an international scale. After 1945 and until the Spring of 1953, the First Physical Institute at Göttingen continued, under the leadership of R. W. Pohl, to produce outstanding work in the field at the same high level of quality and quantity as prior to the war. However the work of this school, which, along with that of Przibram, played such a crucial role in establishing the field as something almost like a branch of physics, is now suitably matched by outstanding work from laboratories in many parts of the world. It appears that the study of colored alkali halides will persist as long as there is interest in the imperfection-determined properties of crystals.

II. SUMMARY OF 1946 VIEWPOINT

2.

It may be of value to summarize briefly the principal factors which constituted the expression of viewpoint presented in the previous review:

(a). Schottky defects predominate in the alkali halides at elevated temperatures. That is, near and just below the melting point, positive- and negative-ion vacancies are generated thermally in equal numbers as a result of thermal fluctuations and outweigh all other types of thermally induced defects (Fig. 1). These vacancies are responsible for the intrinsic electrolytic conductivity and diffusive transport observed in a highly reproducible manner at elevated temperatures. The positive-ion vacancies are substantially more mobile than those of opposite sign, the relative mobilities being governed by a Boltzmann factor with an activation energy of the order of 0.9 ev in crystals such as NaCl and KCl.

Divalent positive ions, present either accidentally or as a consequence of intentional addition, are accompanied by positive-ion vacancies (Fig. 1) which enhance the transport of positive ions. Such vacancies dominate at sufficiently low temperatures, for example below 560°C in typically pure KCl.

The frequency with which free positive-ion vacancies jump at room temperature was estimated to be of the order of 1 $\sec^{-1}$ in NaCl and KCl, whereas the corresponding jump frequency for negative-ion vacancies was judged to be of the order of 10^{-5} $\sec^{-1}$ by extrapolation of Tubandt's transport measurements. Since

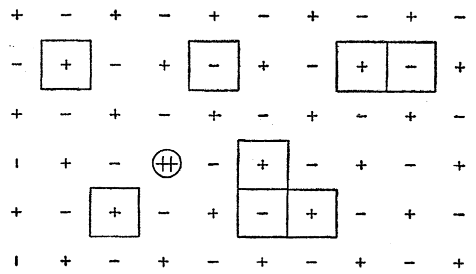


FIG. 1. Vacancies and vacancy clusters which play a prominent role in the theory of the alkali halides. As displayed from upper left to lower right and reading across, the units are: positive-ion vacancy; negative-ion vacancy; coupled pair of vacancies of opposite sign; divalent ion present substitutionally with associated positive-ion vacancy; cluster of two positive-ion vacancies and one negative-ion vacancy. It is believed that the coupled pair may diffuse faster than the isolated vacancies. It is also possible that the triple cluster diffuses rapidly.

---

[2] See, for example, W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1952).

many experiments, particularly those concerning the coagulation of color centers, indicate that negative-ion vacancies are transported near room temperature at rates far higher than this frequency will permit, it was assumed that a unit involving a negative-ion vacancy can jump much faster than the isolated negative-ion vacancy. Attention was focused on the pair, consisting of a positive- and negative-ion vacancy at nearest-neighboring sites. This unit was assumed to have an energy of association of the order of 0.9 ev in NaCl and KCl and to have an activation energy for jumping of the negative-ion vacancy of the order of 0.5 ev or less, corresponding to a jump frequency of at least 10^4 sec^{-1} at room temperature.

(b). The alkali halides may be colored, with introduction of the *F* band, either by the addition of a stoichiometric excess of alkali metal or by the use of ionizing radiations. Average densities of *F* centers as high as 10^{19} per cc can be produced both additively and by intense irradiation. Crystals colored additively have many advantages, for example, the coloration is relatively more stable, the pattern of absorption bands is simpler, and internal electronic currents, such as photocurrents, appear to be more nearly homogeneous. An appreciable amount of experimental evidence supports the view that *F* centers are properly represented by de Boer's model, that is, consist of an electron bound at a halogen-ion vacancy (Fig. 2). In particular the density measurements carried out by Estermann, Leivo, and Stern on crystals darkened by x-rays provided a direct support of the model.

Kleinschrod[3] observed that the *F* band is not a simple bell-shaped band, if examined under sufficient resolution, but possesses a shoulder and a tail on the short-wavelength side (Fig. 3). We shall designate the intensity associated with the shoulder as the "*K* band." Mott and Gurney[4] suggested that his shoulder is associated with transitions to discrete levels above the first excited state, whereas the tail is associated with transitions to the ionization continuum.

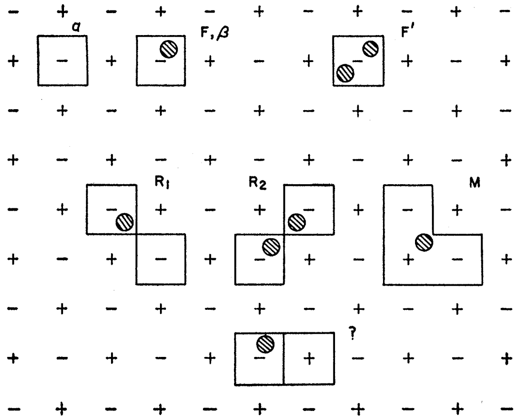


FIG. 2. Units believed to give prominent absorption bands in the pure alkali halides. Reading across and from the upper left-hand corner to the lower right, the units are: the negative-ion vacancy presumed to be responsible for the α band; the *F* center consisting of the negative-ion vacancy and an associated electron, responsible for the *F* band and β band; the *F*′ center obtained by adding a second electron to the *F* center; the R_1 and R_2 centers; the *M* center; a hypothetical center consisting of a pair of vacancies and an associated electron. There is no experimental evidence for the last-named center; it probably decomposes spontaneously by ejecting a positive-ion vacancy.

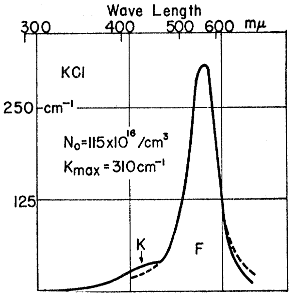


FIG. 3. The *F* band of KCl and the shoulder on the short-wavelength side, corresponding to the *K* band (after Kleinschrod).

Duerig and Markham (private communication) have investigated the ratio of the peak intensity of the *F* and *K* bands in KCl for crystals darkened with x-rays at liquid nitrogen temperature. About 50 different levels of darkening were attained in the various specimens employed in conjunction with the studies outlined in Parts VII and VIII of the present manuscript. The ratio had an average value of about 0.047, and no significant deviation was found in the various cases. At least twice as much variation was found in the ratio of the intensity of the V_1 band (Sec. 28) to that of the *F* band under similar conditions. While this study is not absolutely conclusive, it supports the view that the *K* band is an intimate part of the *F* band, an attitude which will be maintained in this article.

In an appropriate temperature range (between −130°C and −80°C for KCl), light absorbed in the *F* band bleaches the band at least partially and a new band, termed the *F*′ band, appears. The *F*′ band has been associated with an *F* center which has captured a second electron and been transformed into something that is the analog of a free negative ion, such as H^- (Fig. 2). *F*′ centers are thermally unstable above the temperature range in which they can be formed, whereas *F* centers are not ionized efficiently by light lying in the *F* band at temperatures lying below the range in which *F*′ centers are formed. In contrast, *F*′ centers are ionized by light absorbed in the *F*′ band at arbitrarily low temperatures.

(c). Crystals irradiated with ionizing radiations (charged particles, x-rays, or gamma rays) exhibit absorption bands in the ultraviolet not found in additively colored crystals. These bands, which were termed *V* bands, were associated with holes in the halogen-ion shells attached to positive-ion vacancies or aggregates containing such vacancies (see Fig. 28 for possibilities). It was also suggested that the *V* bands obtained in

---

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

[4] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 114.

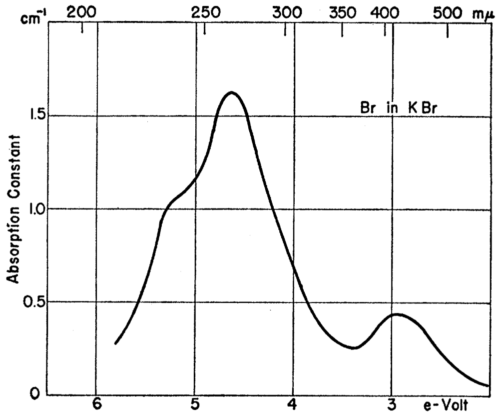


Fig. 4. The V bands observed by Mollwo in KBr containing excess Br. The two unresolved peaks on the left are commonly designated V_3 and V_2 in the order given from left to right. The peak near 3 ev is not generally observed at room temperature in x-rayed crystals, although it lies near the V_1 band.

this way are closely related to the absorption bands observed in the ultraviolet by Mollwo in crystals containing a stoichiometric excess of bromine or iodine (Fig. 4).

(d). F centers may be coagulated in times of the order of minutes by irradiating with light lying in the F band at suitable temperatures. Room temperature is adequate for KCl and NaCl, although the process is more rapid at higher temperatures. It was concluded that the negative-ion vacancies produced by ionization of F centers join with positive-ion vacancies, to form pairs, and are transported from one portion of the lattice to another in this form (see paragraph 1 of this section). The first products of coagulation are R_1, R_2, and M bands, which were associated, respectively, with the union of an F center and a vacant negative-ion site, another F center, and a pair of vacancies of opposite sign (Fig. 2). The M center can be bleached at least partially with light lying in the M band, at temperatures where it is formed, whereas the R centers are much more stable. Aggregates of F centers of colloidal dimensions, indistinguishable from colloidal particles of the alkali metal, are produced as the end result of such aggregation in additively colored crystals. In crystals colored by ionizing radiations, much of the coloration is lost during the process of coagulation, presumably as a result of the recombination of electrons and holes; however, complete bleaching is difficult in heavily irradiated crystals.

Essentially nothing was known about the behavior of the V bands during coagulation and bleaching. This topic was proposed as one for major research.

(e). Photoconductive measurements had been made in crystals containing F centers by the Göttingen group with particular success in the case of additively colored specimens. Such measurements provided values of the product of the efficiency η with which the centers are ionized by light and the distance ω which the free electrons travel before being trapped (*Schubweg* or displacement distance). In the range of temperature in which F' centers form and are stable, $\eta\omega/E$, where E is the strength of the applied electrostatic field, varies slowly with temperature and is inversely proportional to the concentration of F centers, in agreement with the view that the free electrons are produced with unit quantum efficiency and are captured by F centers. At lower temperatures the product $\eta\omega$ falls precipitously, in correspondence with the view that η drops to zero because the excited state attained by absorbing light in the F band is discrete and decays to the ground state unless the temperature is sufficiently high that thermal fluctuations cause further excitation to the ionization states.

The current is said to be *primary* in the range in which F' centers are stable during the time of measurement. It rises rapidly to a constant value at the start of illumination and remains constant thereafter as long as the field and light intensity are maintained constant and polarization does not occur. On the other hand, it continues to rise with time after the initial jump if the F' centers have a lifetime comparable to the time of measurement, for then the electrons are able to wander farther in the crystal after being freed from the F' centers. The more slowly varying component of current is called the *secondary* component.

The F' centers are also a source of photoelectrons. In this case the excitation appears to be directly to the ionization levels, so that η is unity over the entire range of temperature. The temperature dependence of $\eta\omega$ originates entirely in ω.

(f). Considerable thought was devoted to the manner in which color centers are generated by ionizing radiations. It was concluded that the density of free lattice vacancies or small clusters present in a virgin specimen is far too small to account for the densities of F centers that can be generated. It was concluded that the electrons, holes, and excitons produced by the ionizing radiations must have a "solvent" action upon the surface and upon cracks, permitting new vacant lattice sites to enter the lattice. Since typically intense darkening was found to occur even at liquid nitrogen temperature (unpublished wartime work of I. Estermann), it was concluded that normal thermal quanta play a secondary, and perhaps minor role, permitting pairs of vacancies or other highly mobile units to migrate away from the source and perhaps aiding other more potent sources of solvent action in their effect in a small but critical way. It was suggested that among the major factors involved in the solution process are the fluctuations in electrostatic charge which occur when neutral units containing one or more electrons, such as M centers, capture holes which annihilate the electrons and leave behind clusters of vacancies which contain strongly repelling constituents. It was proposed that electrostatic forces generated in this way may

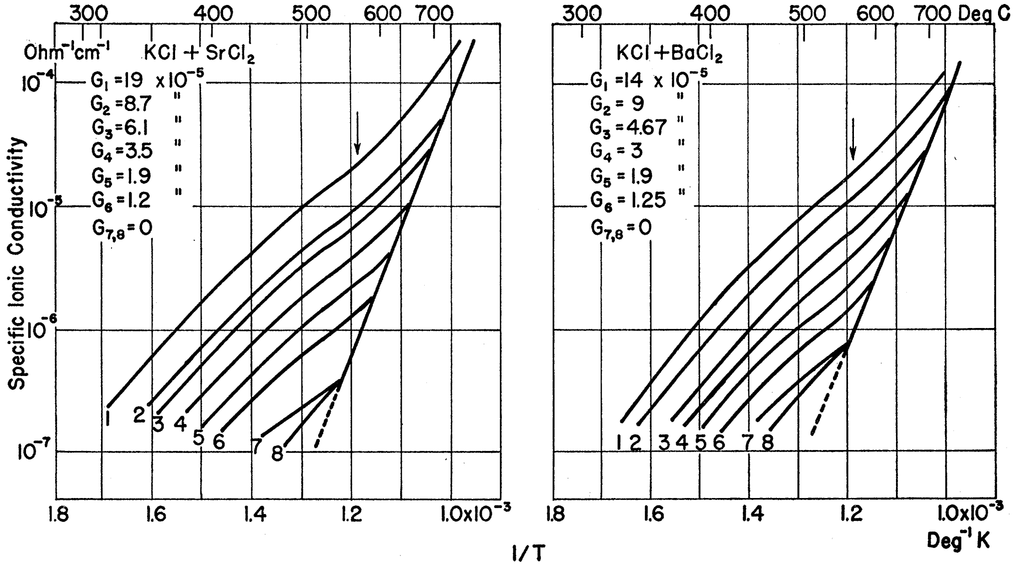


FIG. 5. The electrolytic conductivity of KCl crystals containing various amount of $SrCl_2$ and $BaCl_2$ (after Witt). The quantities G_i are the mole fractions of divalent addition. The steep straight lines on the right-hand side of the diagrams represent the intrinsic conductivity. Curves 7 and 8 are for the same specimens of maximum purity available.

produce the first loosening of vacancies from the surface or from cracks.

It was evident in 1946 that the weakest elements of our understanding of the properties of crystals containing color centers were focused in the areas dealing with the nature and role of *V* centers and with the mechanism by which *F* centers are formed in well made virgin crystals under the action of ionizing radiation. The second topic in particular posed a number of fundamental questions. Fortunately the work of the intervening years has cast considerable light in the regions important for obtaining a clearer understanding of these two topics. Although we do not yet seem to have a completely clear picture of affairs, it does appear possible to advance a step or two nearer the final solution. In particular it is now realized[5] that dislocations probably are important sources of vacant lattice sites so that it is not necessary to postulate diffusion of vacancies from the surface or from a limited number of cracks and voids in specimens in order to explain uniform darkening over dimensions of the order of 0.1 mm.

The ensuing sections will be devoted to an analysis of information which has accumulated since 1946.

In this presentation, most of the research carried out on LiF will be by-passed. Crystals of this material exhibit some of the properties of the other alkali halides; however, in many ways they appear to demonstrate characteristics which are uniquely their own. It is difficult to say whether these differences are characteristic of the pure salt, or whether they are associated with possible contamination of the commercially available materials. The reader interested in the topic may explore the reference material[6] on his own.

III. PROPERTIES OF UNCOLORED SALTS

3. Influence of Divalent Ions on Electrolytic Conductivity

Several valuable extensions of the properties of uncolored salts have been made, particularly dealing with transport of ions.

Etzel and Maurer[7] and Bean[8] have analyzed experimentally the influence of known additions of cadmium and calcium halides on the electrolytic conductivity of NaCl; Wagner and Hantelmann[9] and Kelting and Witt[10] have made similar measurements on specimens of KCl containing additions of calcium, strontium, and barium chlorides, and Haven[11] has studied the influence of Mg^{++} on the lithium halides. Figure 5 shows the family of conductivity *versus* temperature curves obtained by Kelting and Witt for KCl possessing known additions of $SrCl_2$ and $BaCl_2$. In each of the figures, curves 7 and 8 are obtained from two specimens of KCl of the highest purity available, without specific addition of the divalent salts. The intrinsic component of electrolytic conductivity is most evident in these specimens, dominating the temperature range above about 560°C. The intrinsic

---

[5] F. Seitz, Phys. Rev. **80**, 239 (1950); Advances in Phys. **1**, 43 (1952).

[6] P. Pringsheim and P. Yuster, Phys. Rev. **78**, 293 (1950); A. Ghormley and H. A. Levy, J. Chem. Phys. **56**, 548 (1952); C. J. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953).

[7] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[8] C. Bean, thesis, University of Illinois, 1952 (unpublished).

[9] C. Wagner and P. Hantelmann, J. Chem. Phys. **18**, 72 (1950).

[10] H. Kelting and H. Witt, Z. Physik **126**, 697 (1949).

[11] I. Haven, Rec. trav. chim. **69**, 1259, 1471, 1505 (1950).

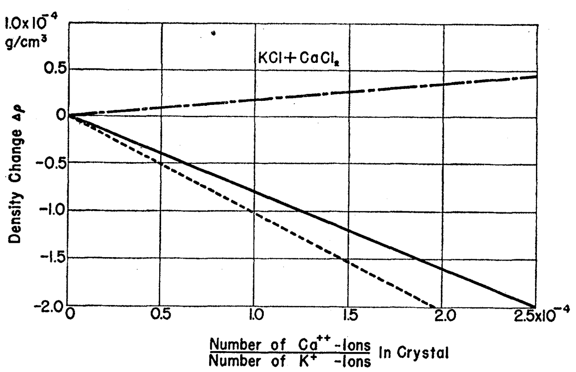


FIG. 6. The change in density as a function of divalent addition for KCl containing controlled amounts of $CaCl_2$. The full line is the best fit of the experimental results, whereas the lower dashed line represents the shift to be expected if the calcium ion plus vacancy occupied exactly the same volume as two potassium ions. The upper hyphenated curve represents the density to be expected if the densities of the two salts were purely additive.

component is all but hidden in specimens 1 in the two figures, corresponding to the addition of 19×10^{-5} mole fraction of $SrCl_2$ and 14×10^{-5} mole fraction of $BaCl_2$. The other investigators have obtained similar curves for NaCl. Bean has extended the lower limit of temperature of measurement in NaCl containing $CaCl_2$ to about 150°C.

It is interesting to note that Kelting and Witt have found that the ratio of the concentration of divalent addition in the melt to that in the crystal is very close to 10 if the crystals are grown at a rate slower than 0.01 mm per minute.

Pick and Weber[12] have measured the density of crystals of KCl containing known amounts of $CaCl_2$ and $SrCl_2$ and have demonstrated that the density varies in a manner very close to that to be expected if each divalent ion replaces two ions of potassium, substituting for one and leaving the other vacant. Figure 6 shows the measured change in density of the specimens containing calcium. The full line is the best fit of the experimental results; the dotted line represents the density to be expected if each Ca^{++} ion replaces two alkali metal ions and there is no change in lattice parameter; the broken line (upper curve) shows the relation to be expected if the densities of KCl and $CaCl_2$ are simply additive. It can be seen that the experimental curve lies very close to the dotted curve, although there is substantial deviation, indicative of a shrinkage in lattice parameter as a result of the addition of the divalent chloride.

In all of the experimental work, it is found that the component of ionic conductivity contributed by the divalent addition is almost strictly proportional to the amount of addition. This result is in accordance with the viewpoint that each divalent ion substitutes for an alkali metal ion and is accompanied by a positive-ion vacancy which is almost completely dissociated from it over the range of temperature for which the measurements are made. The dissociation apparently would not be quite complete in the case of NaCl containing $CdCl_2$, for Etzel and Maurer were able to detect a small nonlinear dependence not found in NaCl containing $CaCl_2$. The curves obtained by Kelting and Witt for KCl are linear within the experimental error, however, the observed coefficient connecting the increase in conductivity with the amount of divalent ion added seems to depend somewhat upon the divalent ion. Moreover, this coefficient is slightly dependent upon temperature.

Many of the investigators in this field have found it convenient to analyze their work with the use of a simple model by assuming that a positive-ion vacancy behaves as if completely free of the divalent impurity unless it is at one of the twelve next-nearest neighbor positions, in which case it is regarded as bound in a "complex" possessing a well-defined association energy. Forces which act at distances greater than the next-nearest position, such as those of electrostatic origin, are neglected. This model has the virtue that it is easy to treat theoretically for there is a sharply defined relation between the free and bound vacancy. The portions of partition functions dealing with mixing may be calculated with ease. On the other hand, it evidently must be used with caution since electrolytic effects associated with the Debye-Hückel cloud are not treated in more than a rudimentary fashion. We shall return to this topic later in the present part of the review (Sec. 6).

4. Mobilities and Jump Frequencies of the Positive-Ion Vacancies

Several very valuable quantities may be obtained from conductivity measurements of the type described in the last section, namely, the mobilities of the vacancies, the density of Schottky defects in the intrinsic range, and the association energies of the vacancies and their divalent ions. In the case of NaCl containing $CdCl_2$, Etzel and Maurer found that the mobility of the positive-ion vacancies could be expressed conveniently in the form

$$\mu = 19\,600/T\exp(-\epsilon_+/kT)\mathrm{cm}^2/\mathrm{volt\text{-}sec}(\mathrm{NaCl}), \quad (1)$$

where T is the absolute temperature and ϵ_+ has the value of 0.857 ev. This expression is valid for the range of temperature between 250°C and 400°C. Similarly, Bean, using additions of $CaCl_2$, found that ϵ_+ varies from 0.98 ± 0.02 ev in the temperature range from 160°C to 250°C to 0.78 ± 0.02 ev in the range from 550°C to 680°C. The corresponding values of the coefficient before the exponential are $4.6\times 10^3/T$ and $6.3\times 10^5/T$, respectively, in units of $\mathrm{cm}^2/\mathrm{volt\text{-}sec}$.

Kelting and Witt, working with KCl, obtained values of ϵ_+ that differed for each of the additions, namely, 0.79 ev, 0.86 ev, and 0.94 ev for $CaCl_2$, $SrCl_2$, and $BaCl_2$, respectively. The coefficient of the ex-

---

[12] H. Pick and H. Weber, Z. Physik 128, 409 (1950).

ponent is assigned a value of the order of 10 cm²/volt-sec. In a similar way, Wagner and Hantelmann derived a value of 0.78 ev for ϵ_+.

The diffusion coefficient D_{v+} of the vacancies may be evaluated from the measured mobilities with use of the Einstein relation

$$\mu = (e/kT)D_{v+}, \tag{2}$$

where e is the electronic charge and T is the absolute temperature. The frequency ν_+ with which the vacancies jump may be determined, in turn, with use of the relation

$$D_{v+} \cong \nu_+ r_0^2/6 \tag{3}$$

in which r_0 is the spacing between neighboring positive-ion vacancies. If one expresses ν_+ in the form

$$\nu_+ = \nu_{0+}\exp(-\epsilon_+/kT), \tag{4}$$

where ν_{0+} is a constant, it is found that this constant has a value close to 10^{14}sec^{-1} for both NaCl and KCl. The values of ν_+ computed at 300°K are close to 1 sec^{-1}. On the other hand, the values found near 100°K are close to 10^{-25}sec^{-1}.

Haven[11] has examined the electrolytic conductivity of the lithium halides containing additions of the corresponding magnesium halide. He placed particular emphasis upon the behavior in the vicinity of the knee of the conductivity curve and showed that the interpretation of the enhanced conductivity, based on the introduction of extra positive-ion vacancies, gives a far better interpretation of the observations than other hypotheses which have been made in the course of the development of the topic. The magnesium halide appears to be highly soluble in the corresponding lithium halide since quantities of the former in the vicinity of 1 percent can be introduced into solution in the range of temperature where measurements are made. It was found that the conductivity varies linearly with the amount of divalent ion present at any given temperature in the impurity range. This result suggests that the association energy of the complexes is small; however, as we shall see in Sec. 6, this conclusion can be drawn with complete safety only as a result of more careful analysis than is possible with the data available in Haven's publications.

The activation energies for migration of the positive-ion vacancies in the salts found as a result of this work are as follows:

	LiF	LiCl	LiBr	LiI
ϵ_+	0.65 ev	0.41	0.31	0.38
ϵ_f	2.68	2.12	1.80	1.34

The quantities ϵ_f are the energies of formation of pairs of separated positive- and negative-ion vacancies, determined from ϵ_+ and the values ϵ_i of the activation energy associated with the ionic conductivity in the intrinsic range by the relation

$$\epsilon_i = \epsilon_+ + \epsilon_f/2. \tag{5}$$

Cunnell and Schneider[13] have studied the slopes of the log *versus* $1/T$ curves in the impurity range in specimens of KCl, LiF, KBr, NaCl, and KI and have found that the magnitude of the slope increases with decreasing temperatures in all of these cases, as in the NaCl+CaCl$_2$ system described in connection with Bean's work. Thus it appears that this effect is fairly general. One would be tempted to ascribe the changing slope to association were it not for the fact that Bean has concluded that the association energy is small in the system he studied (see Sec. 6).

These investigators have also studied the influence of quenching upon the ionic conductivity in the impurity range and have found that the conductivity is suppressed. This was found to be the case, for example, in specimens of KCl quenched from 750°C. Interestingly enough the conductivity was lower in specimens which were cooled from 750°C to room temperature over a 36-hour period than in "normally" treated specimens, although the conductivity was lowest of all in quenched crystals. Qualitatively, these results do not seem difficult to explain. The quenching process is not rapid enough to retain the vacancies generated in the intrinsic range but only those associated with multivalent ions. The quenched specimens contain quenching strains and hence possess dislocations which may entrap some of the positive-ion vacancies and reduce the conductivity. It is possible that some of the impurities and the vacancies associated with them precipitate in the specimens which are annealed so that they do not contribute to the conductivity.

5. Densities of Schottky Defects

It is possible to estimate the density of Schottky defects in the intrinsic range from the measured mobility of the positive-ion vacancies and the measured electrolytic conductivity in the intrinsic range, provided it is assumed that positive-ion vacancies account for the overwhelming share of electrolytic current in the intrinsic range, as seems to be the case. Following this procedure, Etzel and Maurer obtain for the density of Schottky defects in NaCl,

$$n = 1.2\times10^{23}\exp(-\epsilon_f/2kT)\text{cm}^{-3}(\text{NaCl}), \tag{1}$$

where $\epsilon_f = 2.02$ ev is the energy of formation of a separated pair of positive- and negative-ion vacancies. The quantity n has a value of about 10^6 cm^{-3} at room temperature. The fractional density $f = n/n_0$, where n_0 is the density of ion pairs, is

$$f = 5.4\exp(-\epsilon_f/2kT)(\text{NaCl}). \tag{2}$$

Kelting and Witt have found that the corresponding value of ϵ_f for KCl is 2.4 ev, whereas Wagner and Hantelmann obtained a value of 2.1 ev. The first of these two values is probably the more reliable.

The density of Schottky defects at the melting point

---

[13] F. A. Cunnell and E. E. Schneider (unpublished).

may be determined either from equations of the form (1) or from the magnitude of the addition of divalent ion that is needed to double the intrinsic conductivity at the melting point. From Eq. (1) we obtain a density of 2×10^{18} per cc for NaCl at the melting point, whereas the corresponding number for KCl is 1.2×10^{18} per cc. The value for KCl corresponds to a value of 6.7×10^{23} cm^{-3} for the coefficient in (1). This, in turn, corresponds to a value of f, equivalent to (2), given by

$$f=42\exp(-\epsilon_f/2kT)(\text{KCl}). \tag{3}$$

In other words, both crystals possess a fractional density of Schottky defects very close to 0.01 percent at their melting points.

Values of ϵ_f and ϵ_+ for the lithium halides, obtained by Haven, were listed at the end of Sec. 4. It may be noted that the value of ϵ_+ for LiCl is somewhat smaller than the values for NaCl and KCl.

Straumanis[14] has carried out a careful study of the density and the x-ray-determined lattice parameter of sodium chloride crystals prepared by sublimation at 800°C. He has found that the molecular weight of NaCl obtained in this way is 58.430 ± 0.016, to be compared with the chemical molecular weight 58.454. Straumanis believes that the difference of 0.024 lies outside the experimental error and that, as a result, it is necessary to conclude that the specimens of NaCl on which the measurements have been made contain pores to the extent of about 4.1×10^{-4} mole. He proposes that the porosity may be derived from retained vacancies corresponding to the equilibrium value of Schottky defects at 800°C. Actually the required mole fraction of vacancies is very nearly equal to the value of f in Eq. (2) at the melting point (800.4°C), namely, 1×10^{-4} mole. Thus if we are willing to assume that Eq. (2) may be in error by a factor of about 4, Straumanis' conclusion is not contradicted by the results of electrolytic measurement. It is not reasonable to assume that the porosity is associated with free vacancies, for f drops by at least a factor of ten during cooling in the intrinsic range. Instead, to retain Straumanis' viewpoint, it is necessary to assume that the Schottky defects condense to form voids of some kind instead of vanishing at dislocations or at the surface, where their disappearance would return the density to its ideal value for the more nearly perfect lattice containing no defects more serious than dislocations. The specimens were annealed for ten minutes in air at 500°C before the density measurements were made. It is also necessary to assume that this short annealing treatment did not decrease the porosity of the crystals.

The results of the experiments on density measurement are very provocative in the sense that they raise a fundamental question concerning the origin of the vacancies associated with F centers when crystals are darkened with ionizing radiations. There is abundant evidence (see Secs. 15 and 32), such as that provided by Estermann, Leivo, and Stern,[15] that the density decreases when F centers are produced in the range corresponding to 10^{-4} mole, as if dislocations, rather than pores of the type implied by Straumanis' observations, act as major sources for the vacant sites. In any case, a major fraction of the investigations dealing with F centers has been carried out for a range of concentration sufficiently small that pores of the type postulated by Straumanis could provide all of the vacancies needed, that is, the range of F center concentration below 8×10^{18} F centers per cc, on the average. We shall assume in the following sections of this review that pores do not constitute the preferred source of vacant lattice sites and that dislocations play an essential role. This procedure is based on the evidence that the density of normal crystals decreases when F centers are formed by ionizing radiations.

In this connection, it is interesting to note that Fürth and Humphreys-Owen[16] have studied the scattering of light from a number of natural crystals of NaCl and have presented evidence which suggests that such crystals contain inhomogeneities which the investigators believe may be cubes possessing an edge length of 2300A. They suggest that the blocks may be mosaic units, however, it is difficult to believe that such units would have the requisite regularity. It is possible that the scattering is associated with voids of the type suggested by Straumanis.

6. Association Energies

As was remarked in Sec. 3, Etzel and Maurer have found that the increase in conductivity of NaCl containing CdCl_2 is not quite proportional to the amount of CdCl_2 added. This result presumably is indicative of a small degree of association between the divalent ion and its vacancy. These investigators have come to the conclusion that the energy of association of the pair is about 0.3 ev. In contrast, Bean, who studied the influence of CaCl_2 upon NaCl, found no evidence for association in this system and concluded that the energy of association is less than 0.08 ev. Bean's work permits somewhat higher precision in the determination of the energy of association because the measurements were extended to lower temperatures.

The measurements of Kelting and Witt and of Haven do not allow one to make a significant evaluation of the energy of association for the specimens of KCl comparable to the foregoing.

Reitz and Gammel[17] have employed the Born-Mayer version of the ionic theory, with the adaptations introduced by Mott and Littleton,[18] to compute the

---

[14] M. E. Straumanis, Am. Mineralogist 38, 662 (1953).

[15] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).

[16] R. Fürth and S. P. F. Humphreys-Owen, Nature **167**, 715 (1951).

[17] J. R. Reitz and J. L. Gammel, J. Chem. Phys. **19**, 894 (1951).

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

energy of association of positive-ion vacancies and Cd^{++} ions in sodium chloride. They have arrived at a value of 0.44±0.1 ev, the uncertainty arising from the cumulative calculation error. This value is remarkably close to the estimate of 0.3 ev made by Etzel and Maurer. Unfortunately the ionic theory has limited accuracy in calculations of this type. For example, Mott and Littleton have obtained an energy of 0.51 for the activation energy of migration of a positive-ion vacancy, whereas the observed value is nearer to 0.80 ev, as we have seen in Sec. 4.

In this connection, Bean has pointed out that the ionic radii of Cd^{++} and Ca^{++} are so nearly alike (1.03A and 1.06A, respectively) that one would expect calculations such as those of Reitz and Gammel for the two ions to differ only with respect to the change in polarization energy of the divalent ion with and without the vacancy. The polarizability of the Cd^{++} ion is about twice that of the Ca^{++} ion (1.08×10^{-24} and 0.47×10^{-24} cm^3, respectively), however the polarization energy of the foreign ion changes by only about 0.06 ev during removal of the vacancy from the Cd^{++}, so that this does not appear to be sufficient to account for the difference.

Bassani and Fumi[19] have extended the calculations of Reitz and Gammel in a detailed treatment of the association energies of positive-ion vacancies and the divalent ions Cd^{++}, Ca^{++}, and Sr^{++} in NaCl and KCl. They included a treatment of the influence of the Born-Mayer repulsive or overlap energy for more than nearest neighbors and, as a result, found it desirable to determine anew the energy required to form positive-ion vacancies. The values obtained for this quantity are 4.65 ev and 4.35 ev for NaCl and KCl, respectively. The corresponding values obtained by Mott and Littleton are 4.62 ev and 4.47 ev, respectively. These are in substantial but not exact agreement, the differences between the results of the different investigators arising from the difference in accuracy of treatment of the overlap terms. The association energies of the divalent ions and positive-ion vacancies calculated by Bassani and Fumi are as follows:

	Cd	Ca	Sr
NaCl	0.38 ev	0.38	0.45
KCl	0.32	0.32	0.39

The value for Cd^{++} in NaCl is very nearly the same as that found by Reitz and Gammel, namely, 0.44±0.1 ev.

According to the calculated results there should be little difference in the association energies for Cd^{++} and Ca^{++} in NaCl, in contrast with the measurements made by Bean in crystals containing $CaCl_2$. Evidently one must conclude either that the calculations are highly unreliable in the case of Ca^{++} or that Bean's measurements do not give the proper value of the dissociation energy for reasons which are obscure at present. The calculations suggest that the association energies should be appreciably smaller in KCl than in NaCl. This result is not contradicted by the measurements made by Kelting and Witt on specimens of KCl containing Ca^{++}, Sr^{++}, and Ba^{++}; however, their experimental work does not provide a rigorous means for ascertaining the magnitude of the association energies in the specimens.

The Goldschmidt radii for Cd^{++}, Ca^{++}, and Sr^{++} are 1.03A, 1.06A, and 1.27A, which are in the same sequence as the relative values of the association energies found in both NaCl and KCl. The Goldschmidt radius for Na^+ is 0.98A so that in this case the divalent ions are increasingly misfit in the sequence of ascending association energy. The opposite is true for the potassium salt since the radius of K^+ is 1.33A. Actually the divalent ions are highly misfit in both cases because of their extra positive charge. This charge attracts the surrounding halogen ions, drawing them nearer the divalent ion. The association energy increases with the radius of the impurity ion because the displacement of the negative ions is inhibited and the extra positive charge is screened less.

Lidiard[20] has investigated the magnitude of the corrections to the simple theory of association of vacancies and divalent ions arising from the long-range nature of the Coulomb forces between the carriers and their oppositely charged counterparts. The Coulomb interaction induces clustering of the two charged units about one another, that is, the formation of a Debye-Hückel cloud about each. Since the existence of the long-range forces implies that the energy of association of the vacancy and divalent ion does not drop abruptly to zero as the two are separated beyond the nearest like-neighbor difference in lattice spacing but falls relatively gradually, it follows that the vacancies may gain some of the entropy of mixing associated with detachment without sacrificing all of the energy of association. On the other hand, unless the vacancies are well separated from the positive charges, they will not have the same degree of freedom of motion allotted to them in the simple theory once they have moved away from the nearest-neighbor position but will be impeded to some extent by the relatively fixed divalent ions.

We shall continue to use the term "complex" in the ensuing discussion to designate the state of association of the positive-ion vacancy and divalent ion in which the two are in one of the twelve nearest like-neighboring positions in the NaCl lattice. Other distances of separation will be regarded as corresponding to various states of dissociation of the pair. It is clear that any of the principles derived from the alkali halides will be applicable to other systems with appropriate modification of the physical constants and geometry. In fact most of the basic ideas were first developed for dis-

---

[19] F. Bassani and F. G. Fumi, Phil. Mag. (to be published).

[20] A. B. Lidiard, Phys. Rev. 94, 29 (1954).

cussion of aqueous solutions of ions; some were applied to crystals of the silver halides by Teltow.[21]

To gain simplicity, Lidiard assumed that the only source of interaction of the vacancies and divalent ions is the Coulomb potential $e^2/k_s r$, in which e is the unit of electronic charge, k_s is the static dielectric constant, and r is the separation, which is restricted to the discrete values permitted by lattice geometry, at least for small distances. This procedure, though expedient for semiquantitative purposes, has disadvantages in a strictly quantitative way. For example, if k_s is given its proper value for NaCl, namely 5.62, the interaction energy for the nearest-neighbor distance is about 0.6 ev, which is probably much larger than the actual energy of association for any of the divalent ions studied to date. On the other hand, if the parameters appearing in the electrostatic interaction, such as k_s, are adjusted to give a better value of the association energy for the nearest-neighbor distance, the potential will be erroneous at larger distance. Lidiard's procedure has enough virtues, in spite of this defect, that it is a valuable contribution to the topic.

The entropy of mixing is very easy to evaluate when the simple association model is employed, being determined by the number of ways in which the vacancies can be arranged. As a result, the free energy of the system of vacancies plus divalent ions is easy to evaluate, if the vibrational entropy be regarded as independent of the degree of association, and leads to the well-known equilibrium relation

$$n_c n_0/(n_d-n_c)^2 = z\exp(e^2/k_s r_0 kT) \tag{1}$$

in which n_c is the density of positive-ion vacancies that are tied in complexes, n_0 is the number of ions of the base material of a given kind per unit volume, n_d is the density of divalent ions, and r_0 is the distance between nearest like neighbors. The quantity n_d-n_c evidently is the number of vacancies or divalent ions not tied in complexes. z is the symmetry number of the complex, namely, 12 for the NaCl lattice if the complex is defined in the manner described earlier.

When the Coulomb nature of the interaction potential is taken into account, the free energy of the system is more complex, but may be evaluated with the use of methods due to Bjerrum. The relation replacing (1) is

$$\frac{n_c n_0}{(n_d-n_c)^2} = z\exp\left(\frac{1}{kT}\left[\frac{e}{k_s r_0} - \frac{e^2}{k_s}\,\frac{\kappa}{1+\kappa r_1}\right]\right). \tag{2}$$

Here the new quantities are r_1, which is the next-nearest like spacing, and

$$\kappa^2 = 8\pi(n_d-n_c)e^2/k_s kT. \tag{3}$$

The reciprocal of κ measures the attenuation distance of the Debye-Hückel atmosphere about an ion. This distance is about 8×10^{-8} cm at $T=1000$°K when (n_d-n_c) is 2×10^{19} per cc, corresponding to a fractional concentration of 10^{-3} dissociated complexes. The first term in brackets in the exponent is the same as that appearing in (1), whereas the second represents a correction factor arising from the circumstance that not all the association energy is lost when the pair and divalent ion become separated by a distance of r_1 or greater. This term is small compared with the first for concentrations $(n_d-n_c)/n_0$ near to or less than 10^{-5} in the range of temperature in which most measurements are made, but becomes appreciable for larger concentrations.

An analysis of Eq. (2) shows that the degree of dissociation is very small until the temperature is about $0.1T_0$, where T_0 is defined by the relation

$$kT_0 = e^2/k_s r_0, \tag{4}$$

and then increases rapidly. The fraction dissociated is over 0.9 for $T=0.2T_0$ if n_d/n_0 is equal to or less than 10^{-4}, whereas it is barely 0.7 for $T=0.8T_0$ when n_d/n_0 is 10^{-2}. In other words, dissociation occurs relatively rapidly with increase in temperature when the concentration of divalent ions is not greater than 0.01 percent but occurs slowly for concentrations as high as 1 percent.

It may be added that the process of dissociation contributes to the specific heat of the salt. The contribution per mole of solvent reaches a peak of $0.03R$ when $T=0.1T_0$ if $n_d/n_0=0.01$. Although this is small, there is evidence that Kanzaki[22] has observed it in silver chloride containing $CdCl_2$.

When the vacant lattice sites are perfectly free of the divalent ions their contributions to the ionic conductivity is given by the relation

$$\sigma = (n_d-n_c)e\mu, \tag{5}$$

where (n_d-n_c) is the density of completely free vacancies and μ is their mobility, which may be expressed in terms of the jump frequency by relations of the type discussed in Sec. 4. Lidiard has discussed the correction factor to be introduced as a coefficient in this relation when the long-range electrostatic attraction is taken into account and has obtained the following quantity, based on work of Onsager and Pitts:

$$1-\frac{e^2\kappa}{3k_s kT(\sqrt{2}+1)(1+\kappa r_1)(\sqrt{2}+\kappa r_1)}. \tag{6}$$

In the simple theory of association, for which the coefficient (6) does not occur and for which (5) is valid, n_d/σ is a linear function of σ for fixed temperature, whereas the relationship deviates strongly from linear behavior for small values of σ if the coefficient

---

[21] J. Teltow, Ann. Physik 5, 71 (1949); see also earlier work of Stasiw and Teltow.

[22] H. Kanzaki (private communication to Lidiard).

(6) is introduced. Lidiard has shown that when the experimental measurements for the system NaCl $+CdCl_2$ obtained by Etzel and Maurer at four temperatures are plotted in the way suggested by this fact, appreciable deviations from linear behavior are found, although the experimental scatter at low values of σ is fairly large. The fractional additions of $CdCl_2$ in the experiments covered the range from zero to 6.5×10^{-4}. Lidiard found that a very good fit could be obtained for $T_0=3900°K$, corresponding to an association energy of 0.35 ev for the complex. In deriving this value, the mobility was eliminated by plotting, at each temperature, the values of σ relative to the value at the highest concentration. The values of T_0 derived from the four temperatures agreed to within 7 percent. It may be pointed out again that Etzel and Maurer had inferred a value of about 0.3 ev from the cruder analysis based on the simple association theory, whereas the value calculated by Reitz and Gammel[17] and Bassani and Fumi is about 0.4 ev, as described earlier in this section.

The mobility calculated by employing the dissociation energy obtained in this way has the form of Eq. (1) of Sec. 4 with almost exactly the same value of ϵ_+. The numerical coefficient is 21 200 cm^2-deg/volt-sec instead of 19 600.

As mentioned earlier, the use of $T_0=3900°K$ in deriving the mobility, instead of a value nearer 7000°K corresponding to the true value of $e^2/k_s r_0$ for NaCl, implies that the influence of the Coulomb terms at large distances is underestimated.

The data needed for this type of analysis were not available to Lidiard for other systems.

Lidiard has also employed his treatment of association to attempt an interpretation of the dielectric resonances observed by Breckenridge.[23] He has drawn the following conclusions:

(1) There should be a peak in dielectric resonance related to the jumping of the vacancy in the complex among the twelve positions neighboring the divalent ion and in interchange with this ion. The two jump processes combine to yield a single relaxation time

$$\tau=\tfrac{1}{2}(\nu_1+\nu_2), \tag{7}$$

where ν_1 and ν_2 are the jump frequencies for the two processes.

(2) There should be a background dielectric loss arising from the oscillations of the vacancies in the ion cloud. This increases with increasing temperature, as a result of the increase in mobility of the vacancies, and decreases with increasing frequency.

(3) Breckenridge has observed more than one peak in dielectric resonance. Some of these additional peaks may be the result of the motion of quenched-in clusters of vacancies of opposite sign, possibly in conjunction with divalent ions.

Haven[24] has searched for peaks in dielectric loss in specimens of NaCl containing $CaCl_2$ in the range extending to 0.14-mole percent. He has found only one peak which protrudes unambiguously above the background loss arising from the normal electrolytic conductivity and varies with the amount of divalent addition. The temperature extended from 69°C to 125°C in the measurements. The resonant frequency is the same for both divalent additions and depends upon temperature in the manner $\nu_0\exp(-\epsilon/kT)$ where $\epsilon\sim 0.7$ ev and $\nu_0\sim 10^{13}$ sec^{-1}. It appears, at the present time, either that this is the only peak associated with orientation of the complex, as described in (1), and that the other peaks observed by Breckenridge may originate in factors other than the divalent impurities and the positive-ion vacancies associated with them, or that the equipment used by Breckenridge had superlative resolution.

7. Diffusion Measurements

Increasing emphasis has been given to the measurement of diffusion coefficients in the alkali halides with use of radioactive tracers during recent years. For example, Mapother, Crooks, and Maurer[25] have measured the self-diffusion coefficient of radioactive Na in relatively pure NaCl and NaBr, whereas Aschner[26] has extended this work to include specimens of NaCl and KCl containing divalent impurities. Similar work has been carried out by Witt[27] on specimens of KCl containing $SrCl_2$. On the complementary side, Schamp[28] has investigated the diffusion of radioactive Br in NaBr.

The measurements of Mapother, Crooks, and Maurer extend from 350°C to 700°C and hence cover a substantial portion of the transport range on either side of the temperature at which the electrolytic conductivity possesses a knee. Since it is believed that the overwhelming part of the electrolytic current is carried by sodium-ion vacancies in this temperature range (see Secs. 3 and 8), these observations provide a test of the Einstein relation (2) of Sec. 4 connecting diffusion and electrolytic conductivity. It was found that this relation is very closely obeyed in the intrinsic range in both NaCl and NaBr. Small deviations occur at the highest temperatures in such a direction that the diffusion coefficient calculated from the conductivity is somewhat higher than the value determined directly. This deviation can be explained readily in terms of the

---

[23] R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948); **18**, 913 (1950); R. G. Breckenridge in *Imperfections in Nearly Perfect Crystals*, Edited, W. Shockley, Chairman (John Wiley and Sons, Inc., New York, 1952), p. 219. See, also, the work of Henvis, Davisson, and Burstein, Phys. Rev. **82**, 774 (1951), which failed to duplicate the details of this work.

[24] Y. Haven, J. Chem. Phys. **21**, 171 (1953).

[25] Mapother, Crooks, and Maurer, J. Chem. Phys. **18**, 1231 (1950).

[26] J. F. Aschner, thesis, University of Illinois.

[27] H. Witt, Z. Physik **134**, 117 (1953).

[28] H. W. Schamp, thesis, University of Michigan, 1951 (unpublished). Paper by Schamp and Katz (to be published).

small contribution to the conductivity from negative-ion vacancies. For example, Tubandt found that the chloride ions carry about 7.1 percent of the current at 625°C.

On the other hand, there are much larger deviations from the Einstein relation, of the order of 2 or so, at temperatures below the knee of the conductivity curve, in both chloride and bromide. The sign of this deviation is opposite to that found in the intrinsic range, that is, the measured diffusion coefficient is larger than that determined from the conductivity, as if an uncharged agent were responsible for a part of the diffusive transport.

Aschner[26] investigated specimens of NaCl containing intentional additions of $CdCl_2$ in the range from zero to 3×10^{-4} parts per mole. Although the specimens having the smallest nonvanishing amounts of cadmium, namely, 4.3×10^{-5} mole fraction, possessed a higher electrolytic conductivity in the impurity range than the relatively pure specimens employed by Mapother, Crooks, and Maurer, the Einstein relation was obeyed more closely in the former. An increasingly larger relative deviation from this relation was found, however, as the amount of cadmium increased, as if the ratio of the measured diffusion coefficient to that computed from the ionic conductivity varies more or less linearly with the concentration of Cd. We shall return to this point after discussing Witt's observations.

The fact that the purest specimens investigated by Mapother, Crooks, and Maurer did not obey the Einstein relation, whereas the specimens having a relatively small amount of cadmium did, suggests that the first specimen posesses an impurity which exhibits strong association and diffuses exceedingly rapidly so that it contributes to self-diffusion of the Na ions without contributing appreciably to the ionic conductivity. Its influence is masked in the specimens containing cadmium because of the enhancement of electrolytic conductivity in the latter. The unknown element may, for example, be an agent which has a valence higher than two, such as Al^{+++} or Fe^{+++}.

Witt[27] has carried out a similar series of measurements of conductivity and self-diffusion on specimens of KCl containing known amounts of $SrCl_2$ as additional agents. The investigation extended from about 400°C to somewhat over 600°C. This range covers the knee of the conductivity curve in the purest specimen, but not in those containing 3.2, 8.9, and 33×10^{-5} mole parts of Sr. The precision attained was probably not as high because the amounts of radioactive isotope available to Witt were not so profuse; however, the results appear unambiguous. It was found that the measured diffusion coefficient was about 2.4 times larger than that calculated from the measured ionic conductivity with use of the Einstein relation over the entire range of measurement including the intrinsic range in the purest specimens. Within the accuracy of measurement, this ratio is independent of the concentration of added agent.

Deviations, between the observed diffusion coefficient and that calculated from the conductivity of the type observed in NaCl and KCl, imply the presence of a diffusion mechanism which does not involve the transport of net charge. The neutral carriers would have to diffuse about as rapidly as positive-ion vacancies if present in the same concentration, or much faster if present in smaller concentration. Among the migrating units which possess the requisite qualities, the neutral pair of vacancies, formed by combination of a positive- and negative-ion vacancy, and the coupled unit consisting of the divalent impurity and its associated positive-ion vacancy, have been considered by Mapother, Crooks, and Maurer. Since they observed the effect only in the impurity range in NaCl and NaBr, they were naturally led to assume that the second imperfection, namely, the associated impurity and vacancy is the neutral agent responsible for the extra diffusion. This explanation could also be employed qualitatively in the impurity range in the case of KCl, studied by Witt. He has shown, however, that his results are not in agreement with the simple association theory when dependence upon impurity concentration is considered. Since the density of unassociated positive-ion vacancies is much larger than the density of negative-ion vacancies in the impurity range, it is easily demonstrated that the density of associated impurity-vacancy pairs should be proportional to the square of the density of positive-ion vacancies. Or, expressed in another way, the fraction of the divalent ions in complexes at a given temperature increases linearly with the total addition of divalent salt. On the other hand, the ionic conductivity, and hence the diffusion coefficient calculated from it with use of the Einstein relation, is proportional to the first power of the density of unassociated positive-ion vacancies. Measurements of the ionic conductivity show, as we have seen, that the conductivity is proportional to the impurity content in the impurity range. It follows readily from these relations that the ratio of the contribution to the diffusion coefficient from the impurity-pair complexes to the diffusion coefficient computed from the ionic conductivity should vary linearly with the impurity concentration. Actually the ratio appears to be independent of impurity concentration in Witt's measurements for KCl. We saw previously, however, that this linear relation actually appears to be obeyed in Aschner's measurements on NaCl containing $CdCl_2$, a result supporting the view that cadmium-vacancy complexes contribute appreciably to self-diffusion in the impurity range of this system. It is to be hoped that the diffusion coefficients of the divalent ions will be measured eventually.

At the moment there does not appear to be a simple way of explaining Witt's observations on KCl containing $SrCl_2$. One might explain the deviation from the Einstein relation in the intrinsic range on the assumption that the vacancy pairs present contribute as much to self-diffusion as the positive-ion vacancies in KCl, but not in NaCl or NaBr. The possibility is excluded in the second case by the work of Schamp (to be discussed later). The source of the deviation in the impurity range would still be unexplained, however. It may be pointed out that Lidiard's modifications of the theory of complex formation, described in Sec. 6, show that the fraction of divalent ions tied in complexes increases appreciably with increasing concentration of the divalent addition even though the variation is not exactly linear, as in the simple theory. Hence it does not appear that the influence of long-range Coulomb effects can be called upon to provide a constant fraction of complexes.

Aschner[26] has carried out careful and extensive measurements on KCl similar to Witt's both in the impurity and intrinsic ranges. He has found deviations from the Einstein relation in the impurity range, but not in the intrinsic range even though he has made diffusion measurements between 550° and 670°C. Thus in the second respect his results differ in an important qualitative way from those obtained at Göttingen. It would appear that Witt's measurements contain a systematic error of unknown origin, at least in the intrinsic range. Results similar to Witt's were found in specimens which were discolored because of an unknown contamination.

It is interesting to note that Mapother[29] has found that the self-diffusion coefficient of Na in NaCl is decreased by a factor in the neighborhood of three if the layer in which diffusion is occurring is subject to x-irradiation during the diffusion process. It must be emphasized that this decrease is found only in the impurity range, not in the intrinsic range. The implication of the work appears to be that the positive-ion vacancies which originate from the presence of the divalent ions (or ions of higher valence) are made relatively immobile during irradiation and are not able to contribute to the transport of the sodium ions of the lattice to the same extent they normally would. Since the effect is not observed in the intrinsic range, it seems necessary to conclude that the foreign ions assist in the process of immobilization. A reasonable conclusion is that the foreign ions, positive-ion vacancies, and either electrons or holes form relatively stable units which endure a sufficient fraction of time to suppress the normal density of unassociated vacancies. In support of this view, Cunnell and Schneider[13] have found that the ionic conductivity of KCl and NaCl is decreased when the materials are darkened with x-rays, as if at least a fraction of the positive-ion vacancies associated with impurities become bound in color centers during the darkening. The conductivity is not reduced to the intrinsic value as a result of darkening, so that an appreciable number of the vacancies remain free. The original conductivity of the specimens is not completely restored when they are heated to the vicinity 250°, where what is presumed to be complete bleaching occurs. This effect merits further study.

{*Note added in proof.*—E. A. Pearlstein [Phys. Rev. **92**, 881 (1953)] has observed a decrease in the electrical conductivity of NaCl as a result of proton bombardment, analogous to the decrease in diffusion coefficient observed by Mapother following x-irradiation. The bombardment temperature was near 50°C, but the conductivity measurements were made between 100°C and 500°C. The effect may be annealed almost completely by going to temperatures near 500°C. Again, it seems most reasonable to the writer to suppose that the carriers responsible for conductivity are tied down by the capture of electrons or holes, perhaps because the ions neighboring the vacancies are drawn more closely together when the vacancy captures a neutralizing charge and impede migration. See, also, the abstract by Nelson, Sproull, and Caswell [Phys. Rev. **90**, 364 (1953)] on a similar effect.}

There is a slight possibility that the self-diffusion coefficient is influenced appreciably by the migration of vacant lattice sites which are neither immediately adjacent to the divalent ions nor completely free but are constrained to move within the Debye-Hückel cloud until they obtain sufficient energy to leave. During this period they should not contribute to the normal conductivity, but should aid the alkali metal ions in the vicinity to diffuse. This effect clearly can be important on the scale needed to interpret Witt's results only if the second term in (6) of Sec. 6 is near unity in absolute value, for this term provides a measure of the restraining action of the long-range Coulomb forces. Actually this term does not become greater than 0.2 in the range of temperature and concentration of normal interest, so it does not seem adequate to interpret Witt's results.

Schamp and Katz[28] have carried out tracer measurements of the diffusion of Br in NaBr over the range from 350°C to 700°C. The observations above 450°C are particularly interesting since they lie primarily in the intrinsic range and make it possible to estimate the activation energy for the migration of negative-ion vacancies. The results in this range correspond to the relation

$$D_{\mathrm{Br}}^* = 50\exp(-\epsilon'/kT)\,\mathrm{cm}^2/\mathrm{sec}\,(\mathrm{NaBr}), \tag{1}$$

where ϵ' has a value of 2.02 ev. In this case the activation energy ϵ' presumably satisfies the relation

$$\epsilon' = \epsilon_- + \epsilon_f/2 \tag{2}$$

in which ϵ_- is the activation energy for migration of the negative-ion vacancy and ϵ_f is the energy of formation of a separated pair of opposite sign. Since an analysis of the conductivity data for NaBr shows that ϵ_f

---

[29] D. E. Mapother, Phys. Rev. 89, 1231 (1953).

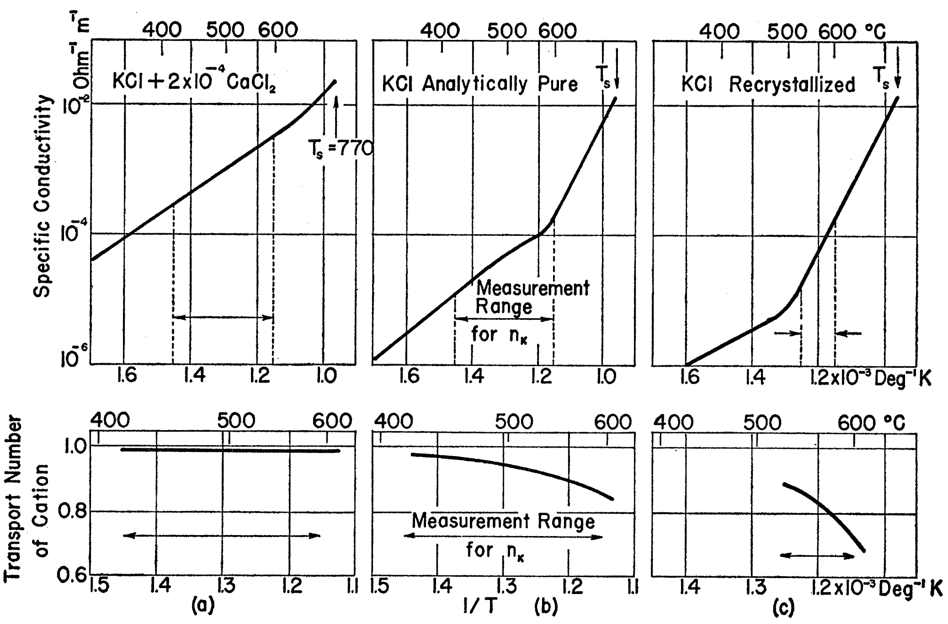


Fig. 7. The specific conductivities and transport numbers of the cations for three types of specimen of KCl, as functions of the reciprocal of the absolute temperature (after Kerkhoff). Specimen (a) was intentionally treated with $CaCl_2$, whereas specimens used for (b) were prepared by single crystallizations of standard materials. In contrast, specimen (c) was prepared from recrystallized material and was particularly pure.

$=1.71$ ev, and $\epsilon_+=0.80$ ev, it follows that

$$\epsilon_-=1.17 \text{ ev (NaBr)}. \qquad (3)$$

Among other things, this provides the interesting relation

$$\epsilon_- - \epsilon_+ = 0.37 \text{ ev (NaBr)}. \qquad (4)$$

In addition, the ratio $D_{\mathrm{Br}}^*/D_{\mathrm{con}}$, where D_{con} is the diffusion coefficient computed from the total conductivity with use of the Einstein relation (2) of Sec. 4, is the transport number n_- of the negative ion. This quantity has the form

$$n_- = 11.5\exp(\epsilon_+ - \epsilon_-)/kT\text{(NaBr)} \qquad (5)$$

which varies from 0.044 at 435°C to 0.166 at 600°C.

The diffusion coefficients measured at temperatures below 420°C are notable principally by the fact that they are much smaller than the values computed from the measured electrolytic conductivity, which combines the transport of both ions. This shows that the positive-ion vacancies dominate in the low-temperature range and that the negative-ion vacancies are not coupled with them in an important way in determining the transport effects, at least to temperatures as low as 360°C. In particular, pairs of the type shown in Fig. 1 do not play an important role in the normal diffusion of NaBr in this range of temperature.

Although the diffusion coefficient (1) is composite in the sense that it contains the product of the jump frequency for negative-ion vacancies and the probability that a given halogen ion have a vacancy as a neighbor, the value of the cofficient of the Boltzmann factor appears to be consistent with the measured quantities for NaCl and KCl described in the preceding parts of this section. Herring and Bardeen[30] have shown that in the face-centered cubic lattice

$$D_{\mathrm{Br}}^* = 0.90 f D_{V-}, \qquad (6)$$

where D_{V-} is the diffusion coefficient for negative-ion vacancies and f is the fraction of halogen sites vacant. In NaCl and KCl the coefficient of the Boltzmann factor in f is of the order of 10 [See Eqs. (6) and (7), Sec. 4]. If we assume that $D_{V-}\sim\nu_- r_0^2$, we conclude from (1) that the coefficient of the Boltzmann factor in ν_- lies between 10^{14} sec^{-1} and 10^{16} sec^{-1}, which we may regard as "normal."

8. Direct Measurement of Transport Number in KCl

Kerkhoff[31] has subjected the measurements of Tubandt and Ronge and Wagner[32] on the transport numbers in KCl to a careful re-examination. The work of the earlier investigators extended between 435°C and 600°C and was carried out on specimens of "typical" purity for which the knee of the conductivity curve is near 560°C. Thus impurity-induced positive-ion vacancies dominate over most of the range. Kerkhoff recrystallized material until the knee was near

---

[30] C. Herring and J. Bardeen in *Imperfections in Nearly Perfect Crystals*, Edited, W. Shockley, Chairman (John Wiley and Sons, Inc., New York, 1952), p. 261.

[31] F. Kerkhoff, Z. Physik **130**, 449 (1951).

[32] G. Ronge and C. Wagner, J. Chem. Phys. **18**, 74 (1950).

500°C, corresponding to a tenfold increase in purity, and measured the transport number n_+ for the positive ion between 525°C and 600°C. n_+ is found to range from 0.88 at 525°C to a value between 0.69 and 0.72 at 600°C. In contrast, Tubandt's and Ronge's and Wagner's values extended from 0.956 at 435°C and 0.941 at 500°C to 0.884 at 600°C. In other words, purification led to a significant change at the higher temperatures. The various transport measurements are shown in Fig. 7.

Since electronic conductivity is negligible in normal specimens of the alkali halides at the temperatures for which the transport measurements are made, the relation

$$n_+ + n_- = 1 \tag{1}$$

may be used to compute values of n_- from n_+. The densities of positive- and negative-ion vacancies are identical in the intrinsic range of electrolytic conductivity so that the ratio n_+/n_- is equal to the ratio ν_+/ν_- of the jump frequencies of the two types of vacancy. The writer has attempted to fit the values of this ratio derived from Kerkhoff's data to a Boltzmann factor and has obtained the result

$$\nu_+/\nu_- = 0.44 \times 10^{-6} \exp(-(\epsilon_+ - \epsilon_-)/kT)(\text{KCl}), \tag{2}$$

where $(\epsilon_+ - \epsilon_-) = -1.18$ ev. The quality of the fit leaves much to be desired as Fig. 8 shows. If anything, one would be tempted to draw the line slightly steeper in order to weight the high-temperature points somewhat more. The difference

$$\epsilon_- - \epsilon_+ = 1.18\text{ev}(\text{KCl}) \tag{3}$$

is surprisingly large compared with the value 0.37 ev for NaBr [Eq. (4), Sec. 7]. Similarly, the coefficient of the Boltzmann factor in (2) is surprisingly small, as if the change in entropy of the system in going from the normal to the activated state is much larger during the diffusion of the chlorine vacancy than during diffusion of the potassium vacancy. We saw previously [Eq. (4), Sec. 4] that the coefficient of the Boltzmann factor in the expression for ν_+ has a normal value, close to 10^{14} sec^{-1}. The relation (2) implies that the corresponding coefficient in the expression for ν_- is nearer 10^{19} sec^{-1} and hence is subject to serious question. It is unfortunate that a long-lived radioactive isotope of chlorine is not available.

In any event, it is evident that ϵ_- is about 1 ev larger than ϵ_+ in the case of KCl. It follows that the jump frequency of the negative-ion vacancy at room temperature must be very small compared with 1 sec^{-1}, of the order of 10^{-10} sec, or considerably less. The same general conclusion, namely, that ν_+ is near 1 sec^{-1} at room temperature, whereas ν_- is considerably smaller, namely 10^{-5} or much less, would seem to be true for NaBr and KBr.

Zückler[33] has studied the ionic conductivity of crystals of KCl possessing sufficient divalent addition that this addition precipitates at low temperatures to form colloids which scatter light. An interesting case is that of KCl containing about one part in 10^3 of $CdCl_2$. This material is clear and transparent at temperatures above about 550°C and displays the typical linear intrinsic and impurity ranges in the log conductivity *versus* $1/T$ plot above this temperature, with the connecting knee which occurs at about 700°C. Below 550°C, however, the conductivity curve has a second knee, followed by a linear region possessing a slope steeper than that in the impurity range, although not as steep as in the intrinsic range. The crystal becomes turbid in this range showing Tyndall scattering. Apparently colloids of $CdCl_2$ about 100A in size have formed, although a fraction of the cadmium ions, governed by a Boltzmann factor, remain in solution in the crystal. The activation energy associated with the increased slope of the conductivity curve in the low-temperature region is presumably the sum of the activation energy for migration of the positive-ion vacancies and the heat of solution of the "vapor" of divalent ions in equilibrium with the colloids. A rough determination of the slope of the lower linear portion

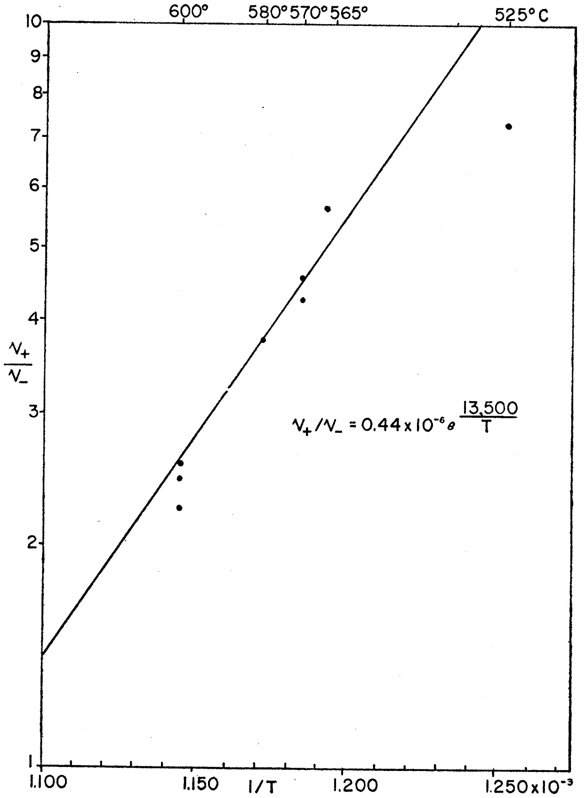


FIG. 8. The logarithm of the ratio of the jump frequencies of the positive- and negative-ion vacancies in KCl, as determined from Kerkhoff's measurements [specimen (c) in Fig. 7], as a function of the reciprocal of the absolute temperature. The straight line represents a moderately conservative fit of the scattered experimental points.

---

[33] K. Zückler, thesis, Göttingen University, 1949.

of the log conductivity curve leads to a value of about 0.7 ev for this heat of solution.

9. Other Theoretical Calculations

Several other calculations merit discussion at this point.

Dienes[34] has attempted to estimate the activation energy for migration in NaCl of the negative-ion vacancy in the pair consisting of coupled positive- and negative-ion vacancies (Fig. 1). He used the Born-Mayer theory of ionic crystals with the modifications introduced by Mott and Littleton. The migration of the negative-ion vacancy is presumably the barrier for diffusion of the pair. It will be recalled that these investigators[18] derived values of 0.51 ev and 0.56 ev for the energy of migration of isolated positive- and negative-ion vacancies with this method. The observed value for the positive-ion vacancy is between 0.78 and 0.98 ev. By analogy with the cases of KCl and NaBr, discussed in the preceding paragraphs, we might suppose that the experimental values for negative-ion vacancies would be between 0.5 and 1.0 ev larger. In spite of these relatively large calculation errors, Dienes believes that the result he obtained for the activation energy for migration of a pair, namely, 0.375 ev is somewhat more accurate on a relative scale because the pair is neutral and long-range polarization terms do not play as important a role as in the case of the isolated vacancies. The drop in the activation energy for the pair, in comparison with the single vacancies, occurs because the missing positive ion lowers the barrier opposing the movement of a negative ion into the negative-ion vacancy, as Huntington first pointed out. The contributions to the activation energy from electrostatic, polarization, repulsive, and miscellaneous second-order terms are as follows:

Electrostatic	+1.330 ev
Polarization	−0.730
Repulsive	+0.110
Second order	−0.335
Total	+0.375 ev

We see that a variety of effects enter into the final value. Unfortunately the repulsive term, which along with the electrostatic term, is most reliably handled in the Born-Mayer method, is smaller than the polarization and second-order terms, which are probably given less accurately. In any case, the analysis makes it seem likely that the activation energy for migration of the pair is in the vicinity of 0.5 ev. If we assume that the coefficient of the Boltzmann factor in the expression for the jump frequency of the pair is 10^{14} sec^{-1}, we conclude that the jump frequency is near 10^6 sec^{-1} at 300°K, that is, is far larger than the corresponding quantity for positive- or negative-ion vacancies. On the other hand, the jump frequency should be negligibly small compared with 1 sec^{-1} at 100°K, the actual value being less than 10^{-4} sec^{-1}.

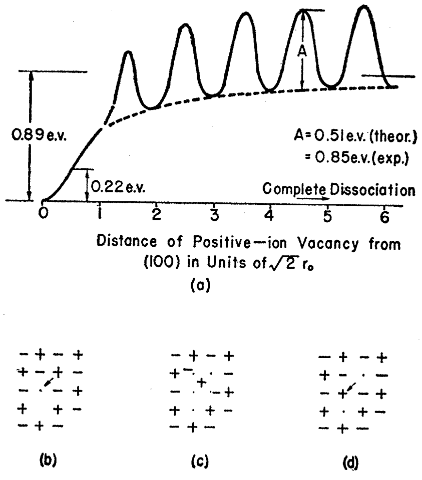


FIG. 9. The upper diagram (a) shows the profile of the energy surface for dissociation of a pair of vacancies of opposite sign in NaCl. Figures (b), (c), and (d) below show the first stages of dissociation in the direction for which the upper curve is valid. Figure (b) represents the normal configuration, of lowest energy, whereas (c) and (d) represent successive stages in which the vacancy is removed in the (110) direction. It may be seen that configuration (d) is entirely unstable relative to (b).

Reitz and Gammel[17] have employed the same technique to determine the energy required to dissociate the pair into isolated vacancies in NaCl and have obtained 0.89 ev, which is remarkably close to the value of about 0.98 ev one estimates from the expression $e^2/k_s r_0$ for the interaction energy of point charges of magnitude e separated by a distance r_0 in a continuous medium of dielectric constant k_s.

Figure 9(a) shows the energy profile for continuous dissociation of the pair. The abscissa gives the distance of separation of the constituents in units of the separation of nearest like ions in the normal lattice. It is interesting to note that there is no energy minimum at the point corresponding to displacement of one of the vacancies to the first like-neighbor position Fig. 9(d), that is, to the position 1.0 in the units used in the figure. The first minimum appears at the next like-neighbor position in the same direction. In other words, if a free positive- and a free negative-ion vacancy wander until they achieve the configuration 9(d) in Fig. 9, they will automatically be drawn into nearest-neighbor positions [configuration (b) of Fig. 9]. It is also interesting to note that the activation energy barrier decreases by an appreciable fraction as the positive-ion vacancy approaches the negative, even for distances larger than unity in the diagram.

Although Reitz and Gammel and Mott and Littleton employed somewhat different values of the repulsive functions, both pairs of investigators obtained very nearly the same value for the energy necessary to remove a positive ion from the lattice. Reitz and Gammel obtained 4.75 ev, whereas Mott and Littleton obtained

---

[34] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).

4.62 ev. This is to be compared with the value of 4.65 ev determined by Bassani and Fumi (Sec. 6).

Rittner, Hutner, and du Pré[35] have extended the method of Mott and Littleton by treating the polarization of the lattice around isolated vacancies more completely. Mott and Littleton regarded the lattice as if a continuous dielectric medium beyond a certain set of neighbors of the vacancies. In the most evolved form of this procedure they treated the first four shells of ions as discrete and the remainder as if part of a continuum. Rittner, Hutner, and du Pré extended the number of shells treated as discrete and improved the consistency of the calculations in other respects. In the best case considered by Mott and Littleton the *purely polarization* energies required to remove isolated positive and negative ions from the lattice are 2.53 and 1.53 ev, respectively. In their corresponding best cases, the other investigators found 2.52 ev and 1.56 ev, which differ remarkably little from the previous results. This agreement shows that the Mott-Littleton procedure converges rapidly, at least in cases in which the configuration is highly symmetrical.

It is perhaps worth noting at this point that Brauer[36] has carried out a detailed investigation of the heat of solution of TlCl in both NaCl and KCl with the use of ionic theory and has found that this energy is endothermic to the extent of 1.47 ev per molecule in NaCl whereas the corresponding value is only 0.25 ev in KCl. In other words, one would expect TlCl to be appreciably more soluble in KCl than in NaCl. For example, it may be estimated that 10^{22} Tl ions will dissolve in one mole of KCl at 1000°K, whereas the corresponding number is 10^{20} for NaCl. The relative ease with which Tl dissolves in KCl is intimately related to the fact that the ionic radius of Tl^+ is more nearly like that of K^+ than of Na^+. It may be added that experiments on the activation of fluorescence in the alkali halides with Tl bear out the conclusion concerning relative solubility derived by Brauer.

Several investigators have examined the extent to which electrons may be self-trapped in the alkali halides by the mechanism proposed by Landau.[37] The most careful analysis of the principles involved in self-trapping has been given by Fröhlich, Pelzer, and Zienau,[38] who have pointed out that self-trapping becomes impossible if the time required by the electron to traverse its orbit is long compared to the relaxation time of lattice polarization over atomic distances. This time, which is about 10^{-13} sec, can be estimated from $k\theta/h$, where θ is the characteristic temperature, and k and h are Boltzmann's and Planck's constants. Under these conditions, the polarization cloud associated with ionic displacement will follow the electron instead of acting as a center for its orbital motion. One would expect self-trapping in the opposite extreme, namely, when the orbital frequency of the electron in the self-trapped state is large compared with the lattice vibrational frequency.

Pekar[39] examined the energy of the self-trapped state on the assumption that the lattice could be treated as a continuous dielectric medium. He obtained an expression for the binding energy of the self-trapped state that varies from one crystal to another only through the factor $(1/k_0-1/k_s)$, where k_0 is the high-frequency dielectric constant, determined from the refractive index in the visible region and k_s is the static dielectric constant. His relation yields the value 0.32 ev for the binding energy in NaCl. Markham and the writer[40] carried out a more detailed calculation for this crystal, taking the discreteness of the lattice into account explicitly, and found that the energy of self-trapping is 0.13 ev. The energy of the light quantum required to free the self-trapped electron by direct ionization was estimated to be 0.68 ev. Both methods of calculation lead to values of the orbital frequency several times larger than the lattice vibrational frequency. However the two frequencies are sufficiently close that the existence of self-trapped electrons must be regarded as marginal. In the case of LiF, the calculated values of the energies of self-trapping and of the light quantum needed to free the electron are about twice as large as for NaCl, namely, 0.3 ev and 1.6 ev, so the situation is slightly less marginal.

Thus far no experimental observer has found an effect that can be remotely associated with self-trapping.[41]

Lee, Low, and Pines[42] have carried out an important examination of the influence of the coupling between the lattice vibrations and electrons on the motion of the latter. This work, which is based upon techniques developed to treat the coupling between mesons and other particles, particularly nucleons, extends more rudimentary work of a similar kind by Fröhlich, Pelzer, and Zienau[38] and Pekar.[39] Similar calculations have been carried out almost coincidently, with equivalent results, by Fröhlich.[43] Attention was focused on the coupling of the electron with longitudinally polarized vibrational modes in the optical band, in which ions of opposite sign move in opposite directions, since the latter modes have an oscillating electrical field associated with them. The parameter which provides a measure of the strength of the coupling

---

[35] Rittner, Hutner, and du Pré, J. Chem. Phys. **17**, 198 (1949); Hutner, Rittner, and du Pré, J. Chem. Phys. **17**, 204 (1949).

[36] P. Brauer, Z. Natürforsch. **7a**, 372 (1952).

[37] L. Landau, Physik. Z. Sowjetunion **3**, 664 (1933).

[38] Fröhlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).

[39] S. Pekar, J. Phys. U.S.S.R. **10**, 341, 347 (1946); Zhur. Eksptl. i Teort. Fiz. **19**, 796 (1949).

[40] J. J. Markham and F. Seitz, Phys. Rev. **74**, 1014 (1948).

[41] W. H. Duerig, Phys. Rev. **86**, 565 (1952).

[42] T. D. Lee and D. Pines, Phys. Rev. **88**, 960 (1952); Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953).

[43] This work was reported by H. Fröhlich in the abstracts of Sections B and C of the International Conference of Applied Physics (IUPAP meeting, Kyoto, Japan, September 1953) page 84. See, also, the paper by Toyozawa, Inui, and Uemura, Progr. Theoret. Phys. Japan **9**, 563 (1953); **10**, 57 (1953).

is the dimensionless quantity,

$$\alpha=\frac{e^2}{2nc}\left(\frac{2mc^2}{\hbar\omega}\right)^{\frac{1}{2}}\left(\frac{1}{k_0}-\frac{1}{k_s}\right), \tag{1}$$

in which e, m, $\hbar$, and c have their usual connotation, ω is the vibrational frequency of the longitudinal mode of highest quantum energy, and k_0 and k_s are the high-frequency and static dielectric constants, respectively. In a crystal such as NaCl, for which ω is about 4.8×10^{13} sec^{-1} and $\hbar\omega$ is about 0.03 ev, α is about 5.2 The investigators conclude that their work has more than qualitative worth for values of α in this range.

The calculations center about the development of wave functions which involve both the electron and the polar modes and describe a correlated motion of the two. The phonon cloud is, of course, the quantum analog of the classical polarization one expects about a charge in a polar crystal. The approximations employed in developing the wave function rest on the assumption that the polar waves present are not correlated with one another, but only with the electron. The lattice is treated as a dielectric continuum since the dimensions of the polarization cloud are large compared with the atomic spacing, moreover the electron is treated as if free in the starting approximation.

The effective mass of the electron, as determined by interaction with the lattice vibrations, and calculated from the curvature of the energy *versus* wave number curve of the electrons near the ground state, is found to have the value

$$m^*=m(1+\alpha/6), \tag{2}$$

when the electron energy is small compared with $\hbar\omega$. Thus the influence of the phonon atmosphere should not be an order of magnitude greater than that of the lattice potential, for the coefficient of m in (2) is in the vicinity of 2 for most of the alkali halides. For example, it is 1.9 in the case of NaCl.

The ground state of the electron in the crystal is lowered as a result of the phonon atmosphere. The amount of the lowering is found to be $-\alpha\hbar\omega$, which is -0.16 ev in the case of NaCl. This is of the same order as the energy of self-trapping calculated by Markham and the writer and is somewhat larger, in absolute magnitude, than the energy computed by Fröhlich, Pelzer, and Zienau and Pekar.

The mean number of phonons in the atmosphere about the electron is given by the expression,

$$N=\tfrac{1}{2}\alpha\left(1+\frac{\epsilon}{2\hbar\omega}\right), \tag{3}$$

in which ϵ is the energy of the electron relative to the ground state, that is, is $\mathbf{P}^2/2m^*$, where $\mathbf{P}$ is the momentum. Thus for values of ϵ of the order of $\hbar\omega$ or less and values of α of the order of 5, N lies between 1 and 10.

Low and Pines[44] have employed the foregoing approximation, in conjunction with extensions due to Schwinger, to compute the scattering of electrons by longitudinally polarized phonons in the optical branch of the vibrational spectrum. They consider essentially elastic collisions in which the electron encounters a phonon and both are deflected, the particles suffering momentum change but no energy shift. This is a double process, analogous to the scattering of light by electrons, when viewed from the standpoint of conventional perturbation theory. Apparently Herring (unpublished work) was the first investigator to point out that this double process is more important than the single processes, in which the electron absorbs or emits phonons, precisely because of the strong coupling which makes perturbation theory inaccurate. He showed that when an electron absorbs a phonon of the optical band, the phonon is re-emitted so rapidly that the energetic state of the electron can be regarded as virtual. The techniques employed by Low and Pines permit evaluation of the double process without use of perturbation theory.

The resulting expression for the mobility is

$$\mu_e=(1/2\alpha\omega)e/m(m/m^*)^2 f(\alpha)\exp(\hbar\omega/kT) \tag{4}$$

in which the various quantities have their previous meaning, and $f(\alpha)$ is a slowly varying function of α which is about 1.25 for magnitudes of α between 3 and 6. The result is valid for magnitudes of the electron energy small compared with $\hbar\omega$, that is, for values of T small compared with the characteristic temperature, if the electrons are in equilibrium with the lattice vibrations, and for values of α not large compared with unity.

The expression (4) represents a generalization of that derived by Herring with intuitive use of conventional perturbation theory in the present strong-coupling case. The formal addition to his result is the factor $f(\alpha)$, which approaches unity in the limit of weak coupling, when α is small compared with unity and perturbation theory becomes valid. Since $f(\alpha)$ actually is only about 1.25 in the range of α of practical interest for the alkali halides, this work shows that Herring's manipulation of perturbation theory did not introduce radical errors.

Still further, expression (4), exclusive of the coefficient $f(\alpha)$, is just three times smaller than the mobility derived by Fröhlich and Mott[45] for the case in which the energy of the electron is small compared with $\hbar\omega$ by considering single processes, that is, by treating absorption of phonons and using perturbation theory. The high degree of similarity is not accidental, for the process treated by Fröhlich and Mott is the

---

[44] F. E. Low and D. Pines, Phys. Rev. **91**, 193 (1953).

[45] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 476 (1939). See, also, footnote 23.

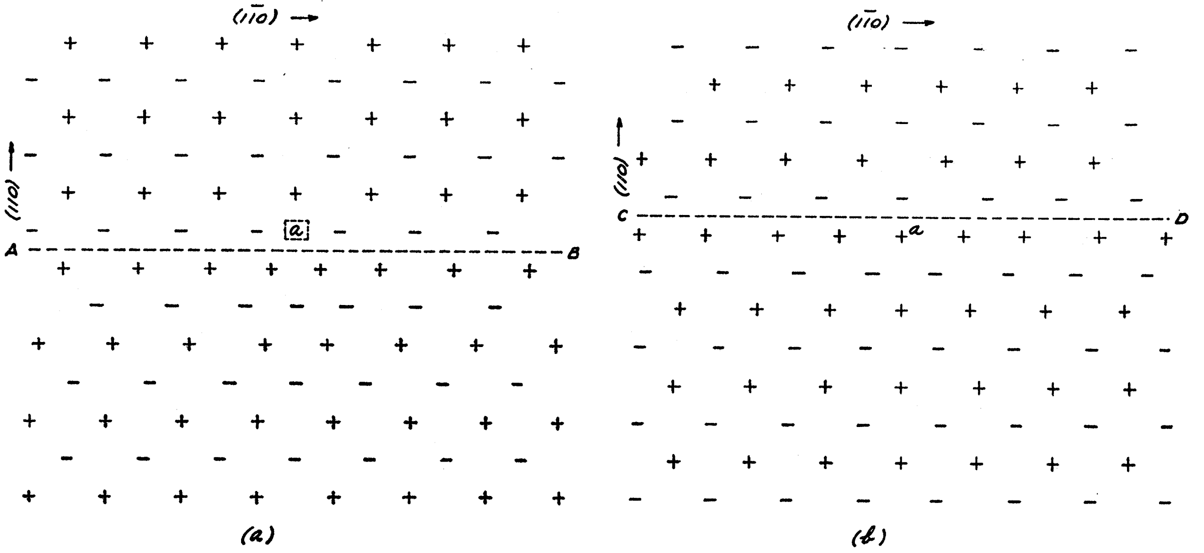


FIG. 10. The cross section of a Taylor-Orowan dislocation in the NaCl lattice in a plane normal to the dislocation line. It is assumed that the dislocation line jogs from one plane to the next at the point where the planar cut intersects the line. The slip plane is normal to the (110) direction and the slip direction is (1$\bar{1}$0). The two halves of the figure face one another on a (001) plane at the position of the jog, so that the slip plane jumps from the line *AB* to the line *CD*. The incipient halogen-ion vacancy *a* (in square) in Fig. (a) faces the positive ion *a* in Fig. (b).

first virtual step in the double process considered by Herring.

Toyozawa[46] has treated the cloud of electron polarization which accompanies an electron moving through a crystal by a method similar to that used to discuss polarons. However, we shall defer a discussion of this to Sec. 12, which deals with excitons.

10. The Experiment of Gyulai and Hartly

In 1928 Gyulai and Hartly[47] demonstrated that the conductivity of NaCl, measured at 39°C, is enhanced by a factor of the order of hundreds immediately after substantial plastic strain in the range of ten percent. This effect has been confirmed qualitatively by Stepanow[48], and appears to be beyond reasonable doubt. The increase in conductivity observed by Gyulai and Hartly decays in the course of about twenty minutes near room temperature. However, a new pulse can be stimulated by inducing further plastic flow.

The writer[5] has interpreted this effect in terms of an electrolytic current associated with the generation of positive- and negative-ion vacancies during plastic flow, presumably as a result of the motion of the dislocations responsible for the ductility of the salts. The positive-ion vacancies are sufficiently mobile at the temperatures employed by Gyulai and Hartly that they should be able to migrate to the negative-ion vacancies and produce uncharged pairs in the course of minutes, thereby removing the source of the extra carriers. Unfortunately, the investigators do not quote the initial value of the electrical conductivity of the specimens, so it is only possible to infer that about 10^{18} pairs of vacancies per cc are produced by a strain of the order of ten percent. This interpretation is in agreement with the observation that crystals which have been deformed plastically darken more easily under x-irradiation than well annealed and undeformed crystals. As we shall see in more detail in Sec. 28, it is probably easier to form color centers from the debris produced by clustering of vacant lattice sites than in the relatively perfect lattice. It is also in good accord with the evidence that vacant lattice sites are produced in metals during plastic flow.

Tyler[49] has suggested that the effect observed by Gyulai and Hartly may be associated, at least in part, with the freeing of electrons by the motion of dislocations. Since free electrons are presumed to have a higher mobility than positive-ion vacancies, under these circumstances, fewer will be needed to provide the observed enhancement of conductivity. In support of this possibility, Tyler has called attention to work of Gyulai and Boros, later than the foregoing, carried out on colored and uncolored specimens of KCl and KBr at stresses nearer the threshold of plastic flow than those employed by Gyulai and Hartly. More sensitive methods of measuring conductivity were also employed. Under these circumstances currents which decayed much more rapidly than those observed by Gyulai and Hartly were found. The currents were about twice larger for the colored than the uncolored

---

[46] Y. Toyozawa, Progr. Theoret. Phys. Japan **9**, 677 (1953). The writer is deeply indebted to Dr. Toyozawa for a more detailed account of this work (to be published).

[47] Z. Gyulai and D. Hartly, Z. Physik **51**, 378 (1928); Z. Gyulai, Z. Physik **78**, 630 (1932).

[48] A. W. Stepanow, Z. Physik **81**, 560 (1933).

[49] W. W. Tyler, Phys. Rev. **86**, 801 (1952).

specimens. The writer is inclined to the opinion that the effect obtained at low applied stresses is fundamentally different in nature from that observed at high stresses, when the crystal is deformed by as much as ten percent. It would be very desirable, however, to have all the measurements repeated in the light of our present knowledge of the properties of the alkali halides.

Figure 10[5] shows the cross section of a Taylor-Orowan or edge-type dislocation in the NaCl lattice for a plane normal to the line of the dislocation. It is assumed in the figure, for illustrative purposes, that the line of the dislocation, that is the edge of the "extra" half-plane represented by the edge dislocation, jogs by one ionic distance at the plane through which the section is made, the direction of the jog being normal to the slip plane or the Burgers vector. In the case illustrated, the crystal is compressed below the horizontal slip plane and is in tension above this plane, as a result of the presence of the extra half-plane. The last ion on the edge of the extra half-plane at the position where this edge jogs downward [Fig. 10(b)] is positive in the case shown, so that it lacks a neighboring negative ion in the direction normal to the page, that is, in the plane of Fig. 10(a). The writer has referred to a jog of this type, in the case in which the last ion in the extra row on the extra plane is positive, as an incipient negative-ion vacancy, for a normal negative-ion vacancy may be created by taking a negative ion from a normal site in the lattice and adding it to the edge of the plane at the jog, that is, at the point enclosed by the square in Fig. 10(a). Since the extra row at the edge of the extra plane will then end with a negative ion at the position of the jog, it can be regarded as terminating with an incipient positive-ion vacancy. Evidently, jogs of this type represent excellent sources and sinks of positive- and negative-ion vacancies, which we may expect to have distributed throughout the volume of the crystal, assuming it possesses the normal density of dislocations. Nabarro[50] has shown that the average energy required to generate vacant lattice sites at dislocations is the same as that required to generate them by taking ions from normal sites to incompleted rows on the surface, provided the dislocations are reasonably straight. This principle is valid if the Burgers vector associated with the dislocation is an allowed lattice translation and if one considers additions of entire unit cells both to the jog in the dislocation and to the surface of the crystal. That is, the principle is true for the alkali halides if applied to the production of separated pairs of vacancies of opposite sign.

At the present time we do not know whether the vacant lattice sites produced when dislocations are set in motion during plastic flow are generated one by one at jogs in the moving dislocations during the motion, or whether large numbers are generated at once when the moving dislocation encounters obstacles.

The principle that dislocations may act as sources or sinks for vacant lattice sites is one of the most important additions to the store of concepts in the field dealing with imperfections in crystals discovered since 1946. Unfortunately, we are not yet familiar with the range of restrictions which should be placed upon the use of this principle. Experiments[51] in metallic systems show that there are circumstances in which vacant lattice sites, present in excess concentration, prefer to condense so as to form voids in the lattice, rather than to add in a simple and direct way to jogs on the edge of long edge dislocations. The metallic systems studied have, essentially without exception, the face-centered cubic structure. Ideal edge dislocations in this lattice, having a Burgers vector equal to the shortest allowed translation, may split into two partial dislocations, having Burgers vectors which are not allowed translations and which are connected by an area possessing incoherence similar to that at a twin interface. Connected partial dislocations of this kind cannot accept or produce vacant lattice sites with the same ease as dislocations which are not split. Thus the restrictions on the precipitation of vacancies, observed in the face-centered metals, may be uniquely applicable to these metals and not to crystals such as the alkali halides in which the energy of the twin interface connecting partial dislocations is probably much too large to permit splitting under conditions near equilibrium.

IV. ADDITIONAL STUDIES OF ELECTRONIC STATES IN UNCOLORED CRYSTALS

11. Electron Density in Pure Salt

Witte[52] and his colleagues have extended the work of Peters[52] on the determination of the density of the valence electrons in the alkali halides with the use of Fourier analysis and measured x-ray intensities using several hundred orders of the diffraction spectrum. This work has confirmed the simple ionic model for the ground state of NaCl to a remarkable degree. For example, it shows that the charges of neighboring halogen ions do not overlap appreciably in the (110) direction in a (001) plane containing the usual square array of positive and negative ions. There is, however, a small degree of overlapping, which presumably is important for the transmission of holes through the lattice, in portions of the $(1\bar{1}0)$ plane containing rows of halogen ions. This overlap does not occur along the

---

[50] F. R. N. Nabarro, Report of a Conference on the Strength of Solids, Proc. Phys. Soc. (London), Suppl. p. 75, (1948).

[51] See, for example, the survey by the writer, Acta Metallurgica **1**, 355 (1953).

[52] Krug, Wagner, Witte, and Wölfel, Naturwiss. **40**, 599 (1953). This publication stresses the observations of density in the square nets represented by (100) planes. The writer is indebted to Professor Witte for an informal account of more extensive work, dealing with other planes, which presumably will be published at a later date. C. Peters, Elektrochem. **46**, 436 (1940). See, also, Brill, Grimm, Hermann, and Peters, Ann. Physik **34**, 393 (1939); Brill, Hermann, and Peters, Ann. Physik **41**, 37 (1942).

lines containing such rows but in regions displaced from these lines. In other words, the electronic distribution about a given negative ion is not perfectly spherical but is distorted in such a way as to project in directions other than (100) and (110) relative to the center of the ion. Presumably a series development of the wave functions comparable in accuracy to that of the x-ray analysis would be required to provide a theoretical description of comparable accuracy based entirely on the Schrödinger equation.

12. The Fundamental Absorption Band. Exciton Waves

The extensive work[53] on the fundamental absorption bands of the alkali halides by Hilsch and Pohl and their co-workers, Schneider and O'Bryan, and, more recently, by Apker and Taft shows that these bands possess several peaks which are most clearly resolved at low temperatures. There are tails associated with these peaks which extend on either side. Almost nothing is known about the high-energy tail since it lies in a region that is difficult to explore optically in all crystals. In contrast, it is known that the low-energy tail is sensitive to temperature and to the state of perfection of the crystal. Moreover it is known that no photoconductivity is observed if light is absorbed in the long-wavelength tail, provided the crystal is uncolored. Experiments of Ferguson[54] cast doubt upon this conclusion, but the recent work of Apker and Taft[55] shows with little uncertainty that his specimens probably had received sufficient radiation to possess F centers which were at least indirectly responsible for the photocurrents (see Sec. 40).

Recently Hartman, Siegfried, and Nelson[56] have undertaken a new study of the fundamental absorption bands of NaCl and KCl and other alkali halides in the range from 950A to 1700A, placing more emphasis upon the short-wavelength region than previous investigators. They have employed evaporated films and have restricted the measurements to room temperature in the initial studies. The preliminary results of these investigations suggest that the absorption bands show much more structure on the high-energy side than earlier work indicated. For example, the observers have found a peak near 1100A in NaCl and one near 1000A in KCl, both of which were apparently unresolved in previous work. The same pattern of structure has been found in measurements of reflectivity. There seems to be little doubt that much of this structure lies in the region of the spectrum that should be ascribed to jumps to the ionization states of the crystal. The transition from exciton to ionization levels does not appear to be distinguished by a sharp change in the quality of the absorption spectrum.

It is now generally concluded that excitons are produced by irradiating the crystals in the tail and the first peak on the long-wavelength side of the fundamental bands. In effect, the halogen ions are excited and the excitation is propagated from one ion to the next. The various peaks in the fundamental band are assumed to be associated with different states of excitation or ionization of the halogen ions, whose wave functions are affected by the crystalline aggregation. It is not known precisely at what point in the spectrum the excitation states cease and the ionization states, in which the electron and hole are not bound to one another, start. Presumably this point occurs about 1 ev higher than the first peak on the long-wavelength side of the band in a crystal such as KCl, for one would expect the energy of dissociation of the electron and hole to be of magnitude $R/2k_0^2$, where R is the Rydberg energy (13.54 ev) and k_0 is the high-frequency dielectric constant of the crystal. This energy is slightly larger than 1 ev for crystals such as NaCl and KCl, and near 1 ev for others.

Dexter[57] has attempted to determine the oscillator strength associated with the first two peaks on the long-wavelength side of the fundamental band in NaCl under the assumption that the peak of lowest energy is associated with an exciton state and the second belongs to the ionization continuum. He selected wave functions for the $3p$ electrons in the ground state of Cl^- having the following radial component:

$$\varphi_{3p}=\mathrm{C}r[\exp(-r/A)-23.2\exp(-r/B)]. \qquad (1)$$

Here $A=a_0/1.1$ and $B=a_0/8$, where a_0 is the Bohr radius. The exciton wave functions were represented as the product of a hydrogen-like function times a function $g(r)$ possessing the periodicity of the crystal. The damping length of the hydrogenic function was chosen to be $3a_0$ for distances close to the halogen ion and k_0a_0 for larger distances, k_0 as previously being the high-frequency dielectric constant of the crystal. The continuum functions were chosen to be hydrogen-like.

Dexter found, using these wave functions, that the ratio of the absorption coefficient at the lowest-energy peak to that for the next highest peak is 1.6, whereas the observed ratio is almost exactly 1.0 for both NaCl and KCl. About 4.7 times as much of the intensity at the second peak, assumed to be in the ionization continuum, arises from the d states as from the s states. The oscillator strength per electron associated with the first, or exciton, peak is found to be 0.07, in contrast with the value of 0.55 per electron for the total band found by Mayer on the basis of a semiempirical analysis of the optical dispersion produced by the band. Dexter estimates that about a third of the total strength of

---

[53] See the review by R. W. Pohl, Physik. Z. **39**, 36 (1938); E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937); L. Apker and E. Taft, Phys. Rev. **81**, 698 (1951).

[54] J. N. Ferguson, Phys. Rev. **66**, 220 (1944).

[55] L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951).

[56] Hartman, Siegfried, and Nelson, work in progress, Cornell University.

[57] D. L. Dexter, Phys. Rev. **83**, 435 (1951).

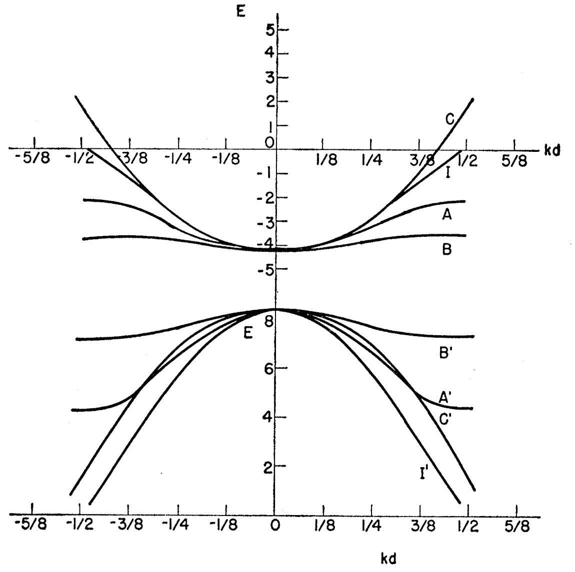


FIG. 11. The energy of exciton waves as a function of wave number (after Heller and Marcus). The upper family of curves is for excitons for which the electric dipole moment is normal to the direction of propagation, whereas the lower family is for polarization parallel to the wave-number vector. k is the wave-number vector and d is $(2n_0)^{-\frac{1}{3}}$ where n_0 is the density of ions contributing to the exciton propagation. The energy is expressed in units of $\mu^2 n_0$, where μ is the electric dipole moment of the excited state. Curves A, B, and C in the upper diagram are for k vectors in the (100), (110), and (111) directions, respectively. The same is true for curves A', B', and C' in the lower diagram. Curves I and I' are for integral approximations in which the excitons behave isotropically. In the model described here excitons produced by photons, which would have essentially zero wave number, will lose energy during scattering until their energy reaches the lowest point on curve C' [parallel polarization and k in (111) direction].

the band is associated with the first peak, so that 0.18 is the appropriate value to compare with his calculated one. Thus there is a discrepancy of about three.

One may conclude that Dexter's procedure is in general semiquantitative agreement with the facts, however, the agreement is not sufficiently good to furnish unambiguous proof that the second peak lies in the ionization continuum.

Heller and Marcus[58] have extended the theory of exciton propagation in a way that is important for the alkali halides. In the primary work on the topic, Frenkel[59] and, subsequently, Slater and Shockley,[59] related the ease of propagation of excitons to the overlap of the excited-state wave functions on neighboring atoms. Heller and Marcus have shown that the propagation may be exceedingly good even if the overlap is small, the coupling originating in the dipole-dipole terms of the interaction Hamiltonian which are responsible for the van der Waals interaction in second-order perturbation theory. When one of the atoms in the lattice is excited to a state which has a large oscillator strength relative to the ground state, there is a strong dipole coupling between this excited atom and neighboring identical atoms which are in the ground state. This coupling permits the energy to migrate.

The dipole coupling has been used by Cario and Franck[60] and by Foerster[60] to explain the radiationless transfer of energy from an isolated atom or complex to another atom or complex sufficiently remote that the charge distributions of the two do not overlap. The requirements on the transfer in such a case are: (1) The available energy in the first center must correspond to the separation of the ground state and excited state in the second, that is, the possible emission spectrum of the first center must overlap the absorption spectrum of the second; (2) The oscillator strengths for the emissive transition of the first center and the excitive transition of the second must be comparable to unity; (3) The center must be separated by a distance not larger than 50A when condition (2) is satisfied. The probability of the transition falls off as the inverse sixth power of the separation. The case treated by Heller and Marcus is very different from that of the well-isolated centers, for the ions in a salt are separated by only a few angstrom units. Moreover, the system has the translational symmetry of the lattice, so that one expects solutions of the Schrödinger equation which describe moving waves of excitation, completely analogous to Frenkel's exciton waves. If k is the propagation, or wave-number, vector of such a wave which may range over the points in a Brillouin zone for the crystal, the investigators distinguish between two interesting cases in a cubic crystal, namely, those in which the induced dipole moment is parallel and perpendicular to k. Waves of the second type will be generated by absorption of light if the polar modes of lattice vibration do not intervene since the electric vector is perpendicular to the propagation vector for light quanta. In this important case, the initial propagation vector of the exciton will be the same as the corresponding vector for the light quantum. An exciton of the second type could become converted to one of the first type, and vice versa, as a result of scattering collisions with phonons or other lattice imperfections.

The excitons which are perpendicularly polarized are found to have an energy which increases with wave number for all prominent directions of propagation [e.g., (100), (110), and (111)] in a simple cubic lattice [Fig. 11]. Thus the "effective mass" of the exciton is positive. The converse is true for excitons which are polarized parallel to the propagation vector (Fig. 11), therefore they should behave as if they have negative mass.

The magnitude m^* of the effective mass of the excitons is given by the relation

$$m^* \cong mR_0/f_{n0}a_e. \qquad (2)$$

---

[58] W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

[59] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931); Physik. Z. Sowjetunion **9**, 158 (1936); J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

[60] G. Cario and J. Franck, Z. Physik **17**, 202 (1923); T. Foerster, Ann. phys. **2**, 55 (1948). This topic has been extended recently by D. Dexter and J. Schulman, J. Chem. Phys. (to be published).

Here m is the electronic mass, f_{n0} is the oscillator strength connecting the ground state and excited state, a_e is the equivalent Bohr radius for the excited atom, and $R_0=(3\pi/4n_0)^{\frac{1}{3}}$, where n_0 is the atomic density. Thus m^*/m should be near unity if f_{n0} is near unity and if a_e is comparable to the interatomic separation. Both conditions are satisfied for the alkali halides.

The calculations of Heller and Marcus leave little doubt that the excitons in the alkali halides are quite mobile, however, it is important to ask if there is good experimental evidence for the ability of excitons to migrate about the crystal. Such evidence is almost exclusively indirect at the present time for a very good reason. If we assume that the maximum lifetime of an exciton in the alkali halides is 10^{-8} sec, corresponding to the emission of dipole electromagnetic radiation, the total distance which the exciton could expect to migrate in one lifetime would be about 0.1 cm, since it would move with the same velocity as a thermal electron, namely, 10^7 cm/sec. This distance should not be in a straight line, however, for the exciton is presumably scattered strongly as a result of interaction with the oscillational modes of the crystal. If we assume the mean free path for such scattering is of the order of atomic dimensions, say 10^{-7} cm, we readily find that the radial distance the exciton migrates from its initial point of origin is about 10^{-4} cm. Thus, at best, one would have to investigate phenomena on a scale at the limit of ordinary microscopic resolution to detect a spatial separation between the points where the exciton is created and dies.

Actually the lifetime of a free exciton may be much less than 10^{-8} sec. No one has observed a strong characteristic luminescence associated with absorption in the fundamental band. This suggests either that the exciton almost inevitably transfers its energy to another imperfection in a time appreciably less than 10^{-8} sec, or that it becomes self-trapped in such a way that the configurational coordinates associated with the minimum of the excited state lie outside the parabolic energy *versus* nuclear coordinate curve associated with the excited state. If the exciton had a lifetime of 10^{-8} sec, it would pass through about 10^7 ions during its existence. Thus it would have unit probability of meeting any impurity atom or other imperfection which affects at least one atom in 10^7 in the lattice. Such a density would be lower than that of typical impurities in typical specimens of the alkali halides employed at present and is generally believed to be comparable to the density of atoms immediately adjacent to dislocation lines. For this reason the writer is inclined to the view that excitons transfer their energy to imperfections before they have an opportunity to radiate and that the absence of a fundamental luminescent radiation does not imply self-trapping in a radiationless state.

Smakula's[61] observation that one may produce F centers with unit quantum efficiency by irradiating in the tail of the fundamental absorption band *without altering the shape of the tail of the band* supports this view. The quantum yield is unity for the range of production of F centers extending to a density of about 10^{14} per cc, and falls for higher densities. These experiments appear to show that the excitons migrate from the place where they are produced to places where they may generate F centers during the initial stages of irradiation. They leave the region where they are generated unaltered, on the average, for the tail of the fundamental absorption band is not changed as a result of the production of F centers.

In this connection, Markham has pointed out to the writer that the amount of coloration achieved in Smakula's work is independent of the wavelength of irradiated light. Since some of the wavelengths are absorbed very near the surface, the results imply that the excitons may migrate to greater depths.

As was remarked at the end of Sec. 9, Toyozawa[46] has treated the cloud of electronic polarization which accompanies an electron moving through a crystal by a method similar to that used by Lee, Low, and Pines to discuss the polarization by lattice displacement. In Toyozawa's case the particles in the polarization cloud are excitons rather than phonons. He considers a somewhat simplified model in which the oscillator strength is localized in one band of exciton levels for which the energy states are given by the parabolic relation

$$E_e=\left(\epsilon+\frac{\hbar^2\mathbf{w}^2}{2m_e}\right)n_w. \tag{3}$$

Here ϵ is the energy of the bottom of the exciton band relative to the ground state of the system, $\mathbf{w}$ is the wave-number vector of an exciton, m_e is the exciton mass, and n_w is the number of excitons of given wave number. For simplicity, it is assumed that at most only one exciton of a given type is present in the lattice, that is, that the n_w are zero or unity. The coupling between the electron and excitons is assumed to be proportional to the amplitude of the exciton wave functions at the position of the electron, the coupling coefficient being a constant relating ϵ and the high-frequency dielectric constant of the crystal.

Toyozawa finds that the energy of a conduction electron in the lattice can be expressed in the form

$$E_c(\mathbf{P})=-\epsilon_s+(1/2m_c)\mathbf{P}^2+\cdots \tag{4}$$

in which $\mathbf{P}$ is the wave-number vector of the electron and its associated exciton cloud, ϵ_s is the self-energy of the electron arising from polarization, and m_c is the effective mass of the electron plus polarization cloud. Only the terms quadratic in $\mathbf{P}$ are shown in a somewhat crude approximation in which the wave-number

---

[61] A. Smakula, Z. Physik **63**, 762 (1930).

vector of the excitons is assumed to extend to infinity. ϵ_s and m_c are determined by the relations

$$-\epsilon_s = -\alpha\nu\epsilon,$$
$$\frac{1}{m_c} = \left(1 - \frac{\alpha\nu^3}{6}\right)\frac{1}{m_f}. \tag{5}$$

Here m_f is the mass of the electron in the crystal when electronic polarization is neglected, and the parameters α and ν are given by the relations

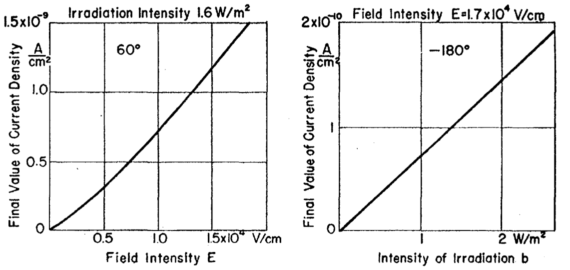
$$\alpha = \frac{1}{2}\left(1 - \frac{1}{k_0}\right)\frac{e^2 u}{\epsilon},$$
$$\nu = \left(\frac{m_e}{m_f + m_e}\right)^{\frac{1}{2}} \tag{6}$$

in which u is defined in terms of ϵ through the relation

$$\hbar^2 u^2 / 2m_f = \epsilon. \tag{7}$$

Since ν is near unity and α is between 0.5 and 1.0 for most crystals, the polarization energy is an appreciable fraction of ϵ and hence is not negligible. However the corrected mass m_c does not differ greatly from m_f.

Toyozawa has employed the formalism which leads to the foregoing results to discuss the interaction between free excitons and trapped electrons, in particular transitions in which the trapped electron accepts the energy associated with the entire exciton. He considers a somewhat simplified, but practically interesting, system consisting of a crystal containing hydrogen-like impurity atoms for which the ionization energy is ϵ_t and computes the lifetime of an exciton when the density of the impurties is specified. Since the exciton should lose its "kinetic" energy very rapidly after being formed, he assumes that the interaction involves primarily excitons of very long wavelength. If the parameters for the crystal are $k_0 = 2$, $m_c = m$, $\epsilon = 6$ ev and if there are 10^{15} impurity atoms per cc, the lifetime of an exciton is found to be 3×10^{-9} sec. Toyozawa considers this to be somewhat too short, compared with the situation for an actual alkali halide crystal having the same parameters, because all of the oscillator strength is assumed to be localized in one exciton band, and suggests that 10^{-7} sec is a more reasonable value to consider for an alkali halide containing 10^{15} F centers per cc. Actually, we have seen above, in connection with Dexter's calculation of the oscillator strengths, that about a third of the oscillator strength is associated with the first-exciton peak, so that Toyozawa's initial estimate of a lifetime near 10^{-9} sec actually may be more nearly correct for the density of impurities assumed.



(a) (b)

FIG. 12. The two diagrams show the saturation current density observed during x-irradiation of KCl at the two temperatures indicated (after Harten). The left-hand curve is given as a function of field intensity for *fixed* irradiation intensity, whereas the right-hand curve is given as a function of irradiation intensity for *fixed* field intensity. The reader should note that the irradiation intensities are given in watts per square *meter*, whereas the field intensities are given in volts per centimeter.

13. The Production and Migration of Electrons and Holes

Free electrons and holes may be produced in the alkali halides by irradiating them with energetic ionizing radiations such as x-rays, cathode rays, or alpha particles. The available experimental evidence, to be summarized, indicates that the hole current is inseparably smaller than the electron current when an electrostatic field is applied to the crystal being irradiated. Apparently the displacement distance of the holes is less than one-tenth that of the electrons in typical specimens. Fortunately, there are experiments, to be discussed in Secs. 30 and 33 which show that holes actually are mobile in the alkali halides.

Harten[62] has investigated the currents induced in both clear and colored alkali halides during x-irradiation at various temperatures. He employed thin crystals of KCl, of the order of 0.3 mm thick, and irradiated with x-rays in the range between 0.2 and 1A which have an extinction coefficient of approximately 0.85 mm^{-1}. Thus only about 25 percent of the x-rays were absorbed in the specimens when irradiated through the thin dimension. Electrodes were placed on the faces through which the x-rays penetrated and fields extending to 15 000 volts/cm were applied across the specimens. The x-ray intensities employed were in the range of 1.6×10^{-4} watt/cm^2.

It was found, over the temperature range from −180°C to 60°C, that the current induced by the irradiation behaves in the same qualitative manner. The current falls continuously from its value at the start of irradiation and eventually attains a saturation limit. The relative magnitude of the drop varies from about 3.5 at 60°C to a factor nearer 20 at −180°C. Moreover, the time required to attain saturation is much smaller at high temperatures, being about 6 minutes at 60°C and 175 minutes at −180°C.

The production of F centers during the irradiation was also investigated. Although this is a topic which will be discussed in more detail in Sec. 28, the basic conclusions may be listed here: The density of F centers

---

[62] H. U. Harten, Z. Physik **126**, 619 (1949); Nachr. Akad. Wiss. Göttingen **1950**, 15 (1950).

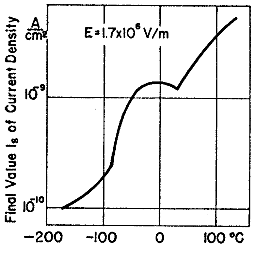


Fig. 13

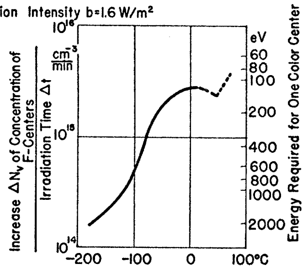


Fig. 14

FIG. 13. The saturation current observed by Harten as a function of temperature for fixed field intensity. Note that the field intensity is given in volts per *meter* in this diagram and that the irradiation per unit area is given in units of watts per square *meter*.

FIG. 14. The energy required to form an *F* center by x-irradiation as a function of temperature (after Harten). The scale on the right gives the energy per *F* center in electron volts, whereas that on the left gives the increase in density of *F* centers per minute for fixed intensity of irradiation.

rises monotonically with irradiation and eventually reaches a saturation value characteristic of the temperature and the intensity of irradiation. The saturation level is attained more rapidly at high temperatures than at low; however, the saturation level is higher at low temperatures. Interestingly enough a much longer time is required to attain saturation of the density of *F* centers than to attain saturation of the current. For example, saturation of darkening requires about two hours at 60°C, in contrast with the 6 minutes required for saturation of current.

There does not seem to be accurate information on the extent to which the curves relating darkening are sensitive to cold work and to impurities. It is well recognized that plastic flow increases the darkenability, however this observation is usually restricted to qualitative observations. It is possible that the effect is confined principally to the initial period of time where the rate of darkening is greatest, or it may extend over the entire range. Hummel[63] has shown that the rate of darkening is very sensitive to the presence of divalent ions. For example, the addition of $CaCl_2$ to KCl increases the rate of darkening over the entire range of observation, at least at room temperature.

Figures 12(a) and 12(b) show the saturation current as a function of field intensity and x-ray intensity at two of the temperatures employed, namely, 60°C and −180°C, respectively. It may be seen that both curves are nearly linear, the first having a slight upward curvature. Figure 13 shows the saturation current as a function of temperature for a field intensity of 17 000 volt/cm, whereas Fig. 14 displays the initial rate of production of *F* centers as a function of temperature. The scale on the right-hand side of this figure gives the energy in ev required to form a single *F* center. It may be seen that this energy is about 120 ev at room temperature and rises to about 2000 ev at liquid nitrogen temperature. There is evidence for cusped minima in the curves of Figs. 13 and 14 near room temperatures. These figures probably cannot be regarded as universal curves from a quantitative viewpoint since the influence of impurity content and previous history is not completely known.

Harten concludes that the energy required to produce an electron-hole pair by ionizing radiation must lie between the ionization threshold, near 10 ev, and the energy of about 120 ev required to produce an *F* center. He notes that if one assumes 50 ev is required per pair, it is possible to estimate that the value of the displacement per unit field lies between 10^{-8} and 10^{-9} cm per volt/cm, which is close to the values observed in additively colored crystals.

In a subsequent investigation, Harten[62] employed a very similar experimental arrangement with notable refinements in the electrometer system which permitted him to observe currents for times of the order of seconds under conditions in which the total irradiation is so small that no more than 3×10^{14} *F* centers per cc are formed. Figure 15 shows the displacement distance per unit field intensity as a function of temperature for three specimens. Specimen *a* was uncolored, specimen *b* contained 3×10^{15} *F* centers per cc produced by x-irradiation, and specimen *c* contained 3×10^{17} *F* centers per cc introduced additively. It may be seen at once that the displacement distance is diminished by the presence of *F* centers, in accordance with the view that the *F* centers act as traps for the conduction electrons, forming *F′* centers. In both cases there is a break in the curve at −80°C, the temperature

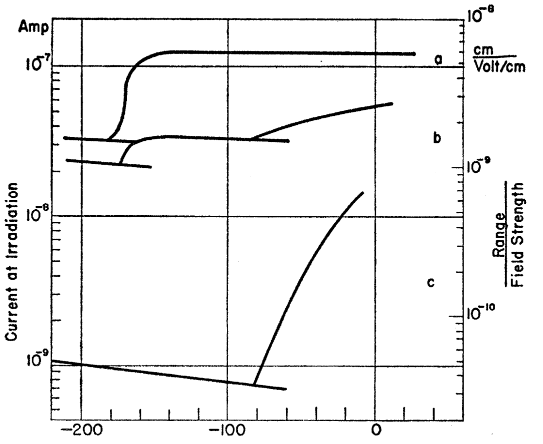


FIG. 15. The displacement distance per unit field strength as a function of temperature for three specimens of KCl, as determined by measurement of current during x-irradiation (after Harten). Specimen (*a*), which gives the greatest *Schubweg*, was uncolored. Specimen (*b*) contained 3×10^{15} *F* centers per cc produced by x-irradiation, whereas (*c*) contained 3×10^{17} *F* centers per cc introduced additively. The breaks which occur at about −80°C in specimens (*b*) and (*c*) are caused by the decomposition of *F′* centers at higher temperatures. The breaks in the vicinity of −200°C in (*a*) and (*b*) are believed to be associated with divalent impurities (see text). The scale on the left gives the current during radiation.

---

[63] H. Hummel, thesis, Göttingen University, 1950.

at which F' centers cease to be stable for the period of time of the order of seconds, involved in the measurements. The ranges increase at higher temperatures indicating that the F centers no longer act as effective traps.

The curves for both specimens *a* and *b* display knees at a temperature in the vicinity of −150°C. In both cases the displacement distance drops steeply at lower temperatures to a new plateau, which terminates at about −170°C. Harten has demonstrated that this break and the steep rise at higher temperatures may be accentuated by adding divalent ions such as Ca^{++} and Sr^{++}. He concludes that these ions trap and hold the conduction electrons at temperatures below −170°C and that the break at −170°C occurs when the temperature is sufficiently high that the trapped electrons regain their freedom during the time of measurement as a result of thermal ionization. According to this view the normal crystal possesses sufficient divalent ions as impurities to provide the break at −170°, a plausible assumption.

We may consider the alternative possibility that the steep rise which starts at −170°C is associated with the freeing of holes rather than electrons. Harten's results alone do not appear to allow one to exclude this possibility. The issue could presumably be settled by seeing if the corresponding rise appears in the photocurrent stimulated by light lying in the F band in additively colored crystals containing comparable amounts of divalent impurity. Holes would play no role in this experiment. Actually, experiments on the counting of pulses produced by alpha particles in NaCl, to be described later in this section, seem to make it safe to conclude that Harten's hypothesis is the correct one. If the rise starting at −170°C were associated with the freeing of holes, we would have to conclude that holes are responsible for most of the current above this temperature, the ratio of hole to electron current being at least five over the range of temperature above −150°. Experiments with alpha pulses in NaCl show, instead, that the electron current actually is at least five times larger than the hole current at 0°C. Hence, if NaCl and KCl behave reasonably alike in this respect, we may conclude that the rise at −170°C in KCl is to be associated with the freeing of electrons.

It seems attractive to assume that the units involving divalent ions which trap and retain free electrons below −170°C are associated pairs of divalent ions and positive ion vacancies. This, however is purely conjectural.

Granting that the major features of the three curves in Fig. 15 are to be associated with the behavior of electrons, we apparently must conclude that the hole current is small, contributing features which lie within the scatter of the experimental points shown. This would imply that the hole current is not greater than ten percent of the electron current over the range shown. We shall return to this point in Secs. 30 and 33.

It is worth noting that none of the curves in Fig. 15, in particular, curve *c* for an additively colored crystal, possesses a knee near −130°C of the type observed when colored crystals of KCl are irradiated in the F band. This supports the view that this knee and the steep fall in $\eta\omega/E$ which occurs at temperatures below it arise from a rapid decrease in η, the quantum efficiency for generating free electrons from F centers. The currents produced in darkened and undarkened crystals by x-rays should arise primarily from ionization of the bulk material and be unaffected by the stability of excited F centers.

Witt[64] has extended the preceding measurements by investigating pulses induced by alpha particles. Unfortunately, the work was carried out with sodium chloride instead of potassium chloride, so that the two types of measurement do not form a completely contiguous system. The observations were made on slabs of crystal 1 mm thick and about 1 cm on an edge. Thin electrodes of silver were placed on the large faces for applying a potential. As in Harten's experiments, the radiation was directed through the electrodes. Alpha particles of ThB, having energies of 8.8 and 6.6 Mev were used. These particles have a range of about 0.03 mm in NaCl. Thus they penetrate only a fraction of the thickness of the specimen. Electric fields in the vicinity of 175 000 volt/cm were applied. The observations were made at 0°C.

It will be recalled that the thermally increased range does not start until about 20°C in NaCl, so that these measurements were made in the region of temperature in which F' centers are stable.

Well-defined counts were observed in uncolored specimens, the magnitude of the pulses being about five times the electronic noise background in the best case. Moreover, counts were observed only when the electrode through which the alpha particles entered was the cathode. In other words, only electron pulses were found. We can conclude that the range for holes is not larger than 0.2 times that for electrons, for the noise background was relatively high.

Although the peak intensity of the electric field was chosen so that the *Schubweg* of the electrons, namely, 0.07 mm, would be essentially equal to the thickness of the crystal in the clear specimens, the size of the pulses varied linearly with field strength over a wide range. An analysis of the number of electrons in each pulse which reach the electrode at the highest field shows that about 600 ev is expended by the alpha particle in producing an electron which arrives at the anode. This conclusion stands in marked contrast with the results for x-rays, for Harten estimated that only about 50 ev was required to produce a free electron in his experiments. A similar effect, namely, a tenfold drop in the efficiency of producing electron pulses, has been

---

[64] H. Witt, Z. Physik 128, 442 (1950).

observed by van Heerden[65] and Jaffe,[66] who studied pulses in silver chloride and liquid methane when they shifted from beta to alpha particles. The first of these investigators concluded, with good justification, that the ionization along the track of an alpha particle is so intense that a field of the order of 100 000 volt/cm is not sufficient to separate all the electrons from the holes. In effect, the electrons are caught in a potential trough coincident with the trajectory of the particle and only a fraction near the edge succeed in escaping. This trough is much shallower for beta particles, for the density of ionization is much lower.

Witt darkened the crystals with x-rays and observed diminution of the pulse size as darkening increased. The pulses reached the level of noise, that is, decreased by a factor of five, when 9×10^{15} *F* centers per cc were present. Figure 16 shows the variation of the pulse size with the concentration of *F* centers.

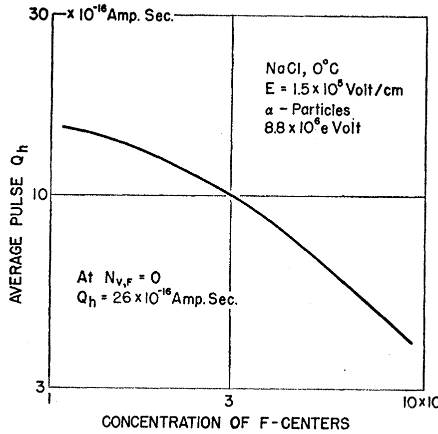


FIG. 16. The variation of the size of ionization pulses obtained in NaCl under α particle bombardment as a function of the concentration of *F* centers in the specimens. The legend in the lower left-hand quadrant gives the pulse size when no *F* centers are present.

V. ADDITIVELY COLORED CRYSTALS

14. Introduction

Specimens of the alkali halides colored by the addition of a stoichiometric excess of alkali metal have occupied a special position in the study of the color centers in the alkali halides. Perhaps the most important reason for this is the relative stability of the coloration, for it is associated with the presence of a specific chemical agent, namely, the excess metal. Thus one may coagulate the centers under appropriate conditions, but cannot bleach them entirely without transporting material throughout the specimen. In contrast, crystals colored by ionizing radiations can be bleached by providing conditions which allow electrons and holes to annihilate one another.

Additively colored crystals possess additional virtues. For example, they make it possible to study complexes in which only electrons and vacancies are involved, that is, in which holes are absent. Thus they permit the separation of effects associated with such complexes from those arising from *V* centers. The stability of the coloration in additively colored crystals made it feasible to demonstrate that *F′* centers are formed as a result of adding a second electron to an *F* center by studying quantum yields in the conversion from *F* to *F′* centers. In addition, additively colored crystals have several advantages in the study of photoconductivity outside the region of fundamental absorption. First, the photoelectrons are not annihilated, but merely trapped. Second, the photocurrents appear to behave in a much more "ideal" manner. For example, Glaser[67] has found that the thermally increased range, observed at temperatures where *F′* centers are not stable, is appreciably longer in crystals colored additively, either by electrolysis or by heating in the vapor, than in crystals darkened by x-rays (See Fig. 1 of reference 67). A part of the longer range may be associated with the absence of *V* centers, where the electrons can be annihilated; however, it is also possible that the bottom of the conduction band is much smoother in additively colored crystals than in crystals darkened by x-rays because the former are homogeneously *n* type instead of being mixed *n* and *p* type. That is, one would not expect to find *n-p* junctions, even in incipient form, in crystals which are colored additively to such a degree that the excess of alkali metal dominates any other agent which may act as donor or acceptor.

On the debit side, it should be mentioned that a reasonably pure *F* band can be obtained in additively colored crystals containing a high concentration of excess metal only by quenching them from temperatures well above room temperature, such as 400°C in the case of KCl. Unless the crystals are quenched, at least a fraction of the centers appear in the form of aggregates or precipitates. It is not known to what extent the properties of the crystals are altered as a result of this quenching procedure, which is undoubtedly accompanied by thermal stresses and the associated plastic flow. The electrical and photolytic properties of the silver halides are exceedingly sensitive to the type of anneal the crystals receive and one may expect at least a degree of this behavior in the alkali halides.

It may be mentioned at start that there have been a number of experimental observations centering about the behavior of the *F* band as a function of temperature and pressure. This work has recently been summarized by Jacobs[68] in connection with an account of his own high-pressure investigations. The reader is referred to this source for an account of the topics.

---

[65] P. J. van Heerden, dissertation, University of Utrecht, 1945.

[66] J. Jaffe, J. phys. 5, 263 (1906).

[67] G. Glaser, Nachr. Akad. Wiss. Göttingen **1937**, 31 (1937); see, also, G. Glaser and W. Lehfeldt, Nachr. Akad. Wiss. Göttingen **1936**, 91 (1936); H. Rögener, Nachr. Akad. Wiss. Göttingen **1940**, 219 (1940).

[68] I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

{*Note added in proof.*—The reader's attention is called to the paper by Shamovsky, Rybakova, and Gosteva [Doklady Akad. Nauk, SSSR, **91**, 67 (1953)] on a proposed mechanism of additive coloring of the alkali halides.}

Among other advances made with the use of additively colored crystals, the following merit attention.

15. Decrease in Density as a Result of Additive Coloring

Witt[69] has extended the measurements of Estermann, Leivo, and Stern[15] on the changes in density which accompany the introduction of F centers. This group of investigators studied the change of density of crystals of KCl which were darkened inhomogeneously by x-rays and found a close correlation between the number of F centers and the decrease in density. The change in density was determined by measuring the temperature at which the crystals would float in a liquid of comparable density but having a greater expansion coefficient.

In contrast, Witt measured the changes in turning rate of much larger crystals immersed in a liquid of nearly equal density after about half the volume of the specimens had been additively colored by electrolytic means. The crystals were pivoted horizontally about an axis passing nearly through the center of gravity and were mounted at the start of the experiment in such a way that they would turn through 180° about this axis as a result of the buoyant forces. Measurements were made on specimens of KCl having 3.2×10^{17} and 3.4×10^{18} F centers per unit volume, as determined optically. The densities of F centers determined from the changes in mass density on the assumption that one halogen-ion vacancy is introduced for each F center were 4.9×10^{17} and 6.1×10^{18}, respectively. The deviations are in the same directions in the two specimens but are regarded as lying within the experimental error.

Measurements closely related to the foregoing, carried out by Sakaguchi and Suita[70] on crystals darkened by x-rays, will be described in Sec. 32.

It is important to emphasize once again, as the writer did in the 1946 review (Sec. VI), that the observed decreases in crystal density which accompany the formation of F centers do not alone provide a proof of de Boer's model of the F center, for the decreases could conceivably be associated merely with an increase in the average lattice spacing of the specimens. This issue could be settled only by simultaneous measurement of changes in density and lattice parameter. Such measurements would provide means of determining the change in the product ρv_c, where ρ is the density of the crystal and v_c is the volume of the unit cell, which is directly related to the number of vacancies produced. Apparently no investigator to date has taken the measurement of lattice parameters in the colored alkali halides seriously.

In this connection it may be remarked that there now seems to be general agreement[71] that measurements of the x-ray diffraction peaks of crystals containing randomly distributed imperfections determine through the Laue-Bragg relations the true average lattice parameters in such crystals. This was first questioned by Miller and Russell, and was subsequently subject to considerable theoretical analysis by these investigators and by Eshelby and Teltow, all of whom conclude that the initial work of Miller and Russell contained an error.

16. Coagulation of F Centers

R and M bands appear when crystals containing dispersed F centers are irradiated with light in the F band at temperatures near to room temperature. These are shown in Fig. 17 for the case of KCl. As discussed in Sec. 2, the writer proposed models for the R and M bands in the 1946 review (Fig. 2). Although the M band was first observed by Ottmer[72] in 1928, its role was not appreciated until Molnar undertook a general survey of the coloration accompanying the F band in additively colored crystals in the period prior to 1940. The writer and his associates introduced the term "M band" in recognition of Molnar's contribution.

By coincidence, Petroff,[73] engaged in research in Pohl's laboratory during the war, carried out an investigation very similar to Molnar's which was not published until 1950. He emphasized the region of the absorption spectrum between 4000A and 10 000A (3.0 ev and 1.0 ev) and discovered independently the R_1, R_2, and M bands, which were named E, D, and C. His absorption measurements were made at liquid nitrogen temperatures, so that excellent resolution was obtained. In addition to the bands mentioned, he discovered a band farther to the infrared, which he termed G. This was discovered independently by Burstein and Oberly,[74] who termed it the N band, in crystals darkened by x-rays. The peak of the N band lies at about 1.3 ev in KCl, that is, at about 9700A. Still further, he discovered evidence for two other bands, termed A and B, which have not been observed generally and which may be idiosyncrasies of the particular specimens he employed. The A band (Fig. 17) lies on the long-wavelength side of the F band and overlaps with it, although the two are separable. The B band overlaps the F band extensively. Its presence is implied by broadening of the latter. Both the A and B bands appear at early stages during irradiation of the

---

[69] H. Witt, Nachr. Akad. Wiss. Göttingen **1952**, 17.

[70] K. Sakaguchi and T. Suita, Technol. Repts. Osaka Univ. **2**, 177 (1952).

[71] P. H. Miller, Jr., and B. R. Russell, J. Appl. Phys. **23**, 1163 (1952); **24**, 1248 (1953); J. D. Eshelby, J. Appl. Phys. **24**, 1249; **25**, 255 (1954); J. Teltow, Ann. Physik **12**, 111 (1953).

[72] R. Ottmer, Z. Physik **46**, 798 (1928).

[73] S. Petroff, Z. Physik **127**, 443 (1950).

[74] E. Burstein and J. J. Oberly, Phys. Rev. **76**, 1254 (1949); **79**, 903 (1950).

crystal with light in the F band. For example, they occur at the end of two minutes of irradiation at room temperature, under conditions in which about 60 minutes are required to develop the R, M, and N bands (Fig. 17).

It seems wisest at the present time to set the A and B bands aside and assume that they are characteristic of Petroff's specimens rather than of the alkali halides in general. Further research may make it necessary to revise this judgment. The Göttingen workers believe that these bands occupy an important genetic relationship in the formation of the other bands.

None of the preceding work, nor any to be described below, is in contradiction with the models of the R and M bands presented in 1946. It still seems reasonable to suppose that these bands are associated with small aggregates of electrons[75] and vacancies, as shown in Fig. 2. Moreover, it still seems reasonable to suppose that these aggregates are formed by the ionization of F centers with light and the transport of the halogen-ion vacancies produced in this way to F centers in the form of mobile pairs of vacancies (See Sec. 9). In the early stages of this process, the photoelectrons are trapped and retained, at least briefly, either by F centers or by other traps such as divalent impurities. However, once R_1 and M centers have been formed by the union of F centers and halogen-ion vacancies or paired vacancies, the latter should act as more effective traps.

The N center should be associated with a unit containing three halogen-ion vacancies, according to this scheme, for the R and M centers exhaust the possibilities obtainable with two halogen-ion vacancies. For example, it could be a neutral center consisting of three F centers or an R_2 center to which a neutral pair of vacancies has been attached. Or it could be a positively charged center obtained by adding a halogen-ion vacancy to an R_2 center or a neutral pair to an R_1 center.

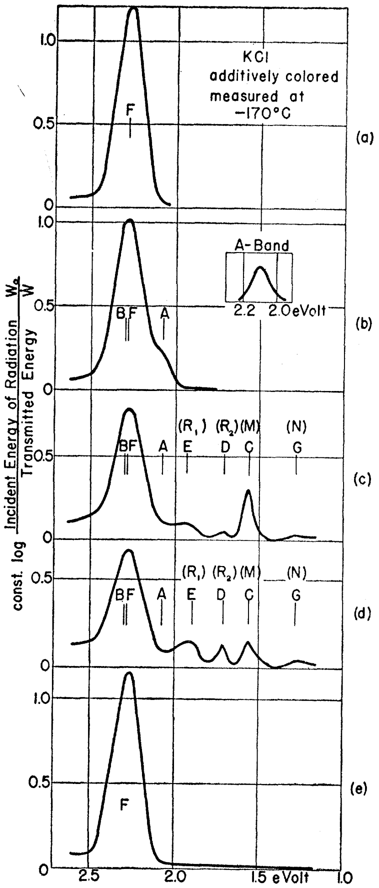


FIG. 17. A sequence of absorption measurements on a specimen of KCl subject to irradiation with F light at room temperature (after Petroff). The absorption measurements were made at -170°C for maximum resolution. Curves (a), (b), (c), and (d) correspond to successive stages of irradiation. The E, D, C, and G bands shown in (c) correspond, as indicated, to the R_1, R_2, M, and N bands employed in this article. Curve (e) shows the state attained after the specimen is warmed to the neighborhood of 500°C and quenched, following the attainment of the state corresponding to (d). The A and B bands have not been observed by other investigators to the present time and are not given a prominent position in this article.

Inui, Uemura, and Toyozawa[76] have computed the wave functions and energies of the low-lying states of the M center on the assumption that the model proposed by the writer is correct. The wave functions were constructed with the use of linear combinations of s and p atomic functions of the alkali metal atoms, distributed over the eight alkali metal ions neighboring the three vacancies in the hypothetical M center. The orbital degeneracy of the atomic p state is lifted entirely because the symmetry of the center is very low (C_{2v}). There are four types of state which can occur, namely, one which has the symmetry of the configuration and into which the s state of the atom is transformed, and three which reverse signs when subject to appropriate combinations of the symmetry elements of the configuration. The three atomic p functions of given total quantum number are transformed into the latter.

---

[75] Professor Yoichi Uchida and his colleagues at the University of Kyoto have observed a new set of bands, which they have termed the K bands, in crystals of NaCl darkened at 450°C by drawing an electron current from a sharp cathode. The new bands lie at 2950A. Photoconductivity and luminescence are stimulated at room temperature by irradiating with light absorbed in the K band. During such irradiation the band bleaches in part and F centers are formed. The K band may be restored by heating to 400°C. The investigators point out that the K band possesses many of the properties that one might expect of F_2 or F_2^+ centers, which the writer has previously associated with the R bands. Inasmuch as the R bands have been observed in a number of independent laboratories, whereas the K band has not yet been explored widely, it seems wisest at this time to continue with the previous identification of the R centers and to leave the origin of the K band an open matter for further investigation. The writer is deeply indebted to Professor Uchida and his colleagues for a number of stimulating discussions of the field of color centers during the meetings of the International Union of Pure and Applied Physics held at Kyoto in September, 1953. See abstracts of Secs. B and C of this meeting, page 93. See also, Uchida, Ueta, and Nakai, J. Phys. Soc. Japan 6, 107 (1951).

[76] Inui, Uemura, and Toyozawa, Progr. Theoret. Phys. Japan **8**, 355 (1952).

TABLE I. Energies of the first three levels of the M center for LiCl and NaCl (in ev, after Inui, Uemura, and Toyozawa).

	Level			Difference		Observed M peak
	A_1	B_1	B_2	A_1-B_1	A_1-B_2	
LiCl	-4.86	-2.76	-1.45	2.10	3.41	1.90
NaCl	-5.63	-3.90	-1.45	1.73	4.17	1.72

The lowest level, designated as A_1 by the investigators, has the symmetry of the configuration. The next lowest level, according to the calculations, is that going with a wave function which retains its sign when reflected in the plane containing the three vacancies (Fig. 2) and reverses it when reflected in that plane normal to this which passes through the positive-ion vacancy and bisects the angle connecting this vacancy and the two halogen-ion vacancies. The function reverses its sign when the system is rotated through 180° about an axis which lies in the plane of the three vacancies, passes through the positive-ion vacancy, and bisects the angle between the two halogen-ion vacancies. This level is designated as B_1. The third level considered, designated as B_2, retains its sign on reflection in that plane, normal to the plane containing the three vacancies, which bisects the angle between the two halogen-ion vacancies. It reverses sign under the action of the other symmetry plane and the 180° rotation already described. A fourth possible function, designated as A_2 and not treated in detail by the workers, reverses its sign under reflection in the planes but retains its sign under the twofold rotation.

The Hamiltonian operator for the system was chosen as the sum of the electronic kinetic energy terms and the potentials of each of the ions in the positions neighboring the vacancies. Spectroscopic data was employed for determining the energies of the atomic functions which appear as linear combinations in the composite wave functions. The fields of the ions were treated as Coulomb-like in evaluating interaction integrals which involve two or more centers simultaneously. The ions were assumed to occupy the positions they do in the perfect lattice.

Table I shows the calculated energies of the states designated as A_1, B_1, and B_2 for LiCl and NaCl, along with the differences in energy between the ground state and the first two excited states. The absolute values of the electronic levels, which are determined relative to the ionized states of the atoms present, are probably not as reliable as the differences in energy. There is in fact remarkable agreement between the observed positions of the M peak and the difference A_1-B_1. In the case of NaCl, the difference A_1-B_2 represents a transition which should fall on the high-energy side of the F band. It would be very interesting to know if the M band that can be produced in additively colored NaCl possesses a companion band in the near ultraviolet, neighboring 3000A. In contrast, the transition A_1-B_2 for LiF would lie nearer the visible, according to the calculations.

It has been known for several decades[5] that the darkening produced in the alkali halides by ionizing radiations bleaches in the regions where slip occurs during plastic flow. Jacobs,[68] in a series of experiments devoted primarily to a study of the influence of pressure upon the F band, has demonstrated that a transformation of the same type does not occur in additively colored crystals when deformed by uniaxial strain at room temperature. If electrons are freed by the migration of dislocations, they return to halogen-ion vacancies at the end of the process.

17. Colloids

Investigations closely related to the foregoing have been carried out by Scott[77] and his co-workers, who studied the changes induced in additively colored crystals of KCl, KBr, KI, and NaCl by both light and heat. Their work is distinguished by the use of specimens containing a wide range of variation of concentration of F centers, namely, from about 10^{17} to 10^{19} centers per cc, and use of temperatures which are normally avoided, namely, those in the range from 300°C to 500°C.

Before this work on aggregation is described in detail, it should be pointed out that similar, although more qualitative, studies have been made on additively colored crystals of NaCl in the past, and a number of very definite conclusions have been drawn for such specimens:

(a) Siedentopf[78] found that additively colored NaCl containing atomically dispersed F centers, which is yellow in color, turns blue after being annealed at temperatures in the vicinity of 400°C. Visual inspection with an ultramicroscope reveals the presence of small colloidal particles of sodium in specimens which have been annealed sufficiently long and which absorb most strongly in the red end of the spectrum.

(b) Gyulai[79] showed that the blue coloration observed in specimens of natural rock salt duplicates the blue obtained in additively colored NaCl, thereby demonstrating that the colloidal particles of metal observed in the natural specimens are composed of sodium. He also studied the photoconductivity produced by irradiating in the absorption bands of the colloidal particles and concluded that such conductivity arises as a result of emission of electrons from the metal into the salt. Mott and Gurney have employed these

---

[77] A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950); Scott, Hrostowski, and Bupp, Phys. Rev. **79**, 346 (1950); A. B. Scott and W. A. Smith, Phys. Rev. **83**, 982 (1951); Scott, Smith, and Thompson (as yet unpublished); F. E. Theisen and A. B. Scott, J. Chem. Phys. **20**, 529 (1952); A. B. Scott, J. Phys. Chem. **57**, (1953).

[78] H. Siedentopf, Physik. Z. **6**, 855 (1905). Apparently one of the earliest investigations of additively colored crystals is that of H. Rose, Pogg. Ann. **120**, 1 (1863).

[79] Z. Gyulai, Z. Physik **35**, 411 (1925); **37**, 889 (1926).

results, in conjunction with the work function of the alkali metals having a vacuum interface, to estimate the position of the bottom of the conduction band relative to the exterior of the crystal. They obtained a value of −0.5 ev.

Gyulai has also observed that KCl will darken more deeply than NaCl during additive coloring *without* the formation of colloidal absorption bands. In other words, it is easier to develop the *F* band in KCl without developing the auxiliary bands on the long-wavelength side associated with the colloid. This point will merit further comment in connection with the work of Scott and his associates.

(c) Savostianova[80] has applied the Mie theory[81] of the scattering of light by metallic spheres to the case of particles of metallic sodium embedded in NaCl. The optical constants of the metal measured by Duncan and Duncan and by Morgan[82] were employed in these calculations. Although Ives and Briggs[83] have since obtained better values, the older measurements are adequate for the calculations. Figure 18 shows the total extinction coefficient as a function of wavelength, calculated by Savostianova, for colloids of various sizes in a specimen of NaCl possessing one part in 10^6 by volume of metallic Na. The curve for zero particle size, which has its maximum at 5500A, corresponds to the limit in which the particles are much smaller than the wavelength of light. The *F* band for NaCl peaks near 4700A, so it lies well to the left of the family of curves shown. It may be seen that the peak of the extinction curves shifts to longer wavelengths as the particle size increases. Figure 19 shows the extinction coefficient for total scattering of light in all directions for the colloids of various size as a function of wavelength. It may be seen that the extinction coefficient for scattering is only a small part of the total for particles under 300A in size. With use of the theoretical extinction curves, shown in Fig. 18, and measured curves obtained both from natural and additively colored crystals of NaCl, Savostianova has concluded that the full range of colloidal size employed in the calculations can be achieved in this salt.

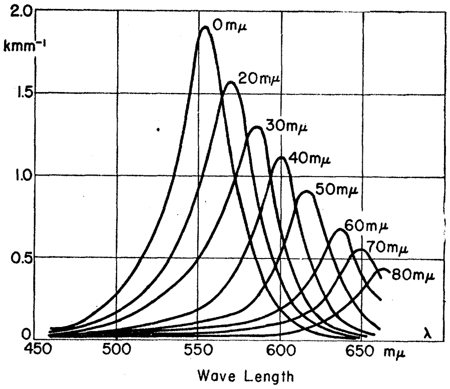


FIG. 18. Extinction curves for absorption calculated from the Mie theory by Savostianova for a specimen of NaCl containing one part per million by volume of metallic sodium. The particles are assumed to be spheres having the diameter given with each curve.

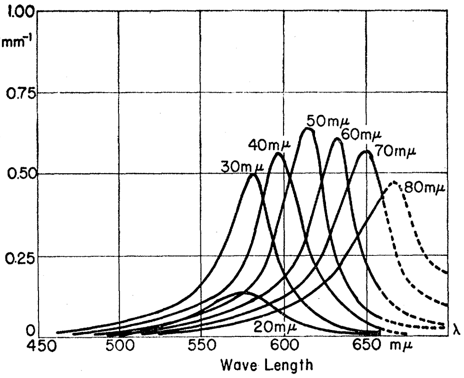


FIG. 19. Extinction curves for scattering equivalent to those of Fig. 18 (after Savostianova).

(d) Mollwo[84] examined the absorption bands in additively colored crystals of NaCl for various times of annealing in what may be termed an extension of Savostianova's work. He demonstrated that the *F* band is distinct from the family of colloidal bands and that the peaks of the latter shift to longer wavelength with increased annealing, in accordance with the notion that the colloids grow during annealing at temperatures between 250°C and 500°C. For example, the peak was observed to shift from 5700A to 6200A on heating from 300°C to 450°C. However the peak could not be shifted beyond 6500A. Mollwo has estimated that the colloids obtained by heating to 350°C are about 200A in size whereas those obtained by heating to 450°C are 500A. At temperatures as high as 700°C the colloidal bands vanish and are replaced by the *F* band. This indicates that the colloids are soluble in the crystal, or, in turn, that they are formed by coagulation of the *F* centers under conditions of supersaturation.

Mollwo also demonstrated that crystals containing large colloids, whose diameter is comparable to or larger than $\lambda'/2\pi$, where λ' is the wavelength of light in the salt, become dichroic if the crystal is sheared plastically. This result demonstrates that the colloids are elongated in the direction of shear during plastic flow so that light polarized parallel to the direction of shear is scattered differently from that polarized normal to this direction.

It may be remarked in this connection that E. Rohloff [Z. Physik **132**, 643 (1952)] has studied the same type of dichroism in rolled specimens of silver chloride con-

---

[80] M. Savostianova, Z. Physik **64**, 262 (1930).

[81] G. Mie, Ann. Physik **25**, 377 (1908); R. Gans, Ann. Physik **37**, 881 (1912).

[82] R. W. Duncan and R. C. Duncan, Phys. Rev. **1**, 294 (1913).

[83] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **26**, 238 (1936); **27**, 395 (1937).

[84] E. Mollwo, Nachr. Akad. Wiss. Göttingen **1932**, 254 (1932).

taining photolytically produced colloids of silver. The results indicate that *all* the spherical colloidal particles are deformed to essentially the same elliptical shape when the crystal is strained. The average eccentricity developed is nearly the same as that to be expected if a sphere were subject to the same strain as the crystal. This result has remarkable features, for the colloids are smaller than the normal spacing between slip bands in plastic crystals, and one might have expected the spheres to be deformed either much or little depending upon their proximity to a slip line. Further examination of such dichroism in the alkali and silver halides may shed valuable light upon the mechanism of plastic flow.

It is interesting to note that the area under the extinction curve computed by Savostianova for particles of smallest size (Fig. 18), is considerably larger than one would expect for the corresponding density of F centers in NaCl on the basis of Smakula's analysis, assuming the oscillator strength for the F center is unity. The result may be expressed in the following way. The density of excess Na considered by Savostianova would correspond to 2.6×10^{16} F centers per cc. The width of the curve for smallest size in Fig. 18 is 400A, or 0.16 ev. If the F band were this narrow, the magnitude of the extinction coefficient at the peak of the absorption curve would be 0.5 mm^{-1} for the corresponding number of F centers, provided we assume the oscillator strength is 1.0. Actually the peak of the curve for smallest size in Fig. 18 is 1.9 mm^{-1} or about four times larger. This result is valid, of course, only if the particles are sufficiently large that the bulk optical constants can be employed.

To return to the work of Scott and associates, the following results may be noted:

(a) The investigators have concluded that the type of aggregation which can be produced at room temperature with the aid of light alone is greatly limited, probably to the R, M, N, and similar bands. If one combines light and heat, temperatures under 100°C being apparently adequate for KCl, it is possible to obtain a broad band, which Scott, Hrostowski, and Bupp have termed the R' band. This is probably a combination of the other bands just named and additional aggregates. Initially the investigators placed great emphasis on the R' band, regarding it as a form of progenitor of the colloidal band. Subsequent work disclosed its highly composite character and has made it appear less interesting than the true colloid band which is much narrower, when the colloids are homogeneous, and which can ke produced by heat alone at somewhat higher temperatures.[85] For example, if an additively colored crystal of KCl which has been quenched to room temperature from above 500°C and as a result contains dispersed F centers, is raised to 300°C, the F band will decrease in intensity and the colloid band will grow in relatively pure form, provided light is excluded. An equilibrium state is attained in about ninety minutes in KCl. The rate of attainment of equilibrium increases with increasing temperature.

In all of the work carried out by Scott and his coworkers on KCl, KBr, KI, and NaCl, the colloid bands produced by annealing additively colored crystals have been of that ultimate smallness for which light scattering is negligible, that is, for which the diameter is small compared with $\lambda'/2\pi$. It is not clear why this limitation appears in the specimens, but presumably is associated with the density of nuclei for colloids and is typical of the crystals employed.

(b) The F band never vanishes completely at temperatures above 300° C in the additively colored crystal employed in the work, even when equilibrium is attained. On the contrary, its intensity at equilibrium, as determined by measuring the area of the F band, is independent of the amount of excess alkali metal in the particular specimen, to within an experimental error of about 7 percent. The equilibrium density does depend upon the temperature at which the equilibrium is attained, increasing with increasing temperature. The absorption measurements are usually made at room temperature after quenching the crystal from the temperature where equilibrium is attained. In brief, the colloid centers observed by these investigators behave as if they constituted a liquid or solid phase of the excess alkali metal. The F centers which are at equilibrium with the colloid centers behave in turn as if they constituted a monatomic vapor in equilibrium with solid or liquid phase. Scott, Smith, and Thompson have found, in fact, that the equilibrium density of F centers varies with temperature in the same manner as the vapor pressure of a gas in equilibrium with its solid or liquid. Values of the heats of vaporization ΔH_c are listed in Table II. The measurements are less reliable for NaCl than for the potassium salts because the F centers in equilibrium with the colloid centers at a high temperature tend to "condense" more readily in NaCl during the quenching.

Figure 20 shows the equilibrium relation between the F band and the colloid band for KCl at five temperatures. Specimens having essentially equal concentrations of excess alkali metal (about 5×10^{17} atoms per cc) were used for these measurements. It will be seen that the ratio of the F band to the colloid band in-

TABLE II. Equilibrium heat of F centers and colloidal centers (after Scott, Smith, and Thompson).

Crystal	ΔH_c(kg cal per mole)	ΔH_c(ev per center)
KCl	8.0±0.3	0.35
KBr	11.4±0.4	0.50
KI	9.0±0.3	0.39
NaCl	9 ±2	0.39

---

[85] See the paper by R. T. Platt and J. J. Markham, Phys. Rev. **92**, 41 (1953) for a discussion of what earlier investigators termed the "erregt" state, probably related to the development of the R' band.

creases with increasing temperature. The second band nearly vanishes above 450°C, presumably because the solid or liquid phase has completely "evaporated." This effect has been observed qualitatively in NaCl by Mollwo but evidently can be subject to much more reproducible analysis.

(c) The total area under the *F* and colloid bands is not constant. In fact, if one starts with a crystal containing only *F* centers and converts these principally to colloid centers by heating to equilibrium at 300°C, the area under the colloid band which develops may be "very much greater" than that under the initial *F* band. This indicates that the aggregated phase is much more effective in attenuating the incident light beam than the dispersed *F* centers are. The result appears to be at least qualitatively similar to that pointed out in connection with Savostianova's extinction curves, which show that small colloidal particles are more effective than the equivalent number of *F* centers in attenuating the incident light.

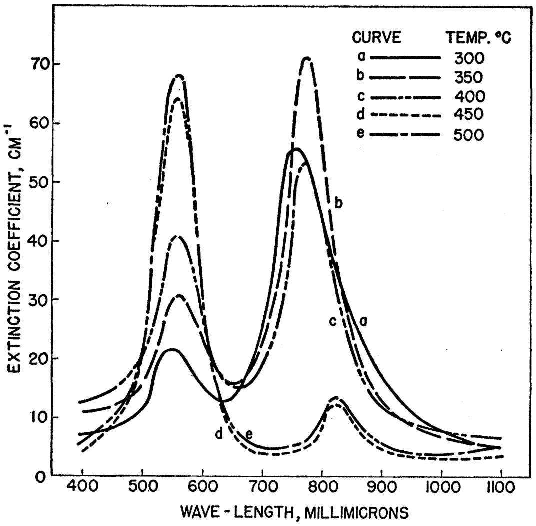


FIG. 20. The equilibrium relation between the *F* band and the colloid band in KCl at five temperatures (after Scott and associates). It may be seen that the *F* band grows at the expense of the colloid band as the temperature increases to 500°C. The specimens used in this work had approximately 5×10^{17} *F* centers per cc. The *F* band is on the left.

It would be valuable to have quantitative measurements of the change in area under the extinction curve when *F* centers are transformed to colloid centers. Such observations could be used to test alternately appropriateness of the use of the Lorentz correction in Smakula's treatment of the dispersion of light by *F* centers or the use of the optical constants of the bulk metal in the calculations of the extinction produced by the colloidal particles.

It is perhaps worth emphasizing that it is not *necessary* that the areas under the *F* band and under the colloid bands, when plotted as functions of energy, be equal in order to preserve oscillator strength. Both centers interact with the surrounding dielectric medium and derive a part of their optical properties from this interaction. As Smakula's equation relating the area of the absorption band of the *F* center to the number of *F* centers shows, the dielectric properties of the salt play an important role in the relationship. The two types of center are basically different and are imbedded in the matrix in dissimilar ways. For example, the single electron of the *F* center presumably overlaps an appreciable number of ions surrounding the halogen-ion vacancy, whereas the electrons in a colloidal particle may belong much more specifically to the speck of metal which has a relatively well defined boundary and can be treated as a separate phase.

TABLE III. Wavelength of peak of extinction band for small colloids (after Scott, Smith, and Thompson)

Crystal	Wavelength at Peak Calculated	Observed
KCl	7300A	7750A
KBr	7600	8500
KI	8000	8850
NaCl	5180	5650

(d) The investigators have repeated the calculations of the absorption curves for small colloids, in the case in which $\lambda'/2\pi d$ is small compared with unity, using optical constants of Ives and Briggs suitably extrapolated to cover the range of interest. The values of the wavelengths associated with the peaks in absorption are given in Table III. The total density of excess metal in the specimens is not known accurately enough to compare the calculated amplitudes of the extinction coefficients; however, the positions of the peaks and the shapes of the curves are given fairly closely by the theory as is shown in the table. The value of the wavelength at the peak of the extinction coefficient calculated by Savostianova with the use of the optical constants of Duncan and Duncan is 5500A. The deviations between observed and calculated values probably lie within the experimental error of the optical constants used in the latter.

(e) A minimum value for the size of the particles responsible for colloidal bands can be inferred from the observation that the density of *F* centers in equilibrium with the particles is independent of the total amount of excess metal to within about 7 percent, in the range of concentration up to about 10^{18} atoms per cc. It follows that there must be at least ten metal atoms involved in each particle. Careful observations with an electron microscope of replicas of the specimens revealed no structure above 50A in size which could be correlated with the colloids. The investigators conclude that the particles studied in this work must be less than 50A in size. Thus they are probably between 10A and 50A in diameter and contain between 10 and 1000 atoms.

(f) In additively colored crystals of KI heated for long periods in potassium vapor prior to quenching (more than 90 hours at 600°C), the F band was converted to a new band which appears at shorter wavelengths. This new band is at 6500A whereas the F band is at 6950A and the colloid band at 8850A. Since the new band is observed only in specimens having a relatively low concentration of excess metal, namely, 2.25×10^{17} per cc, it is not unlikely that it is associated with a contamination which goes into solution in the long heating process.

(g) The investigators found that the colloid band is not preceded by the appearance, in measurable amounts, of the R_1, R_2, or N bands when F centers are converted into colloids. On the other hand, the M band is usually present even in crystals quenched from very high temperatures in which the colloid band is absent.

(h) Irradiation in the colloid band does not lead to strong photoconductivity, that is, with a quantum yield close to unity. Moreover, the photosensitivity curve extends more broadly over the spectrum than the extinction peak, as if only a small fraction of the latter were directly involved in the production of photoelectrons. In this respect photoemission from the colloid particles resembles that from metallic surfaces. The shape of the colloid band remains almost unaltered when the crystals are cooled from room temperature to liquid nitrogen temperature.

The observation that the R and N bands are not found in the transition from F to colloid centers at temperatures above 300°C implies that the first two types of center are not stable above this temperature. A simple calculation shows that this is what one would expect if the energy of association of R and N centers is not larger than 0.5 ev (11.5 kg cal per mole). On the other hand, the neutral vacancy pair has an association energy nearer 1.0 ev and should be stable in the range from 300°C to 500°C. This probably explains the existence of M centers at room temperature during a wide variety of conditions, for the M centers can be formed during the quenching process by the combination of the roving pairs and F centers.

TABLE IV. Selected calculations from the book by Mott and Gurney.

Thermal dissociation energy of F center (ev) (page 143, Mott and Gurney)		
NaCl	1.89	
KCl	1.95	
KBr	1.78	
Heat of solution of alkali metal atoms in crystals (ev) (theoretical: page 146, Mott and Gurney; experimental: Rögener and Mollwo)		
	Calculated	Observed
NaCl	−0.05	(0.0)
KCl	−0.18	−0.10
KBr	−0.48	−0.25
Work functions, or energies required to extract electron from bottom of conduction band (ev) (page 97, Mott and Gurney)		
NaCl	0.53	
KCl	0.07	
RbCl	0.40	
KBr	0.70	

The mechanism by which the F centers coagulate is relatively obscure at the present time. Theisen and Scott have examined the rate of diminution of the F band during the formation of colloid centers in KCl. They conclude that the reaction is approximately bimolecular and that the activation energy for the process is in the vicinity of 10 kg cal per mole, that is, about 0.43 ev per atom. One might anticipate a larger activation energy if the F centers migrate directly to the colloidal particles, for we saw in Secs. 7 and 8 that the activation energy for migration of a negative-ion vacancy in KCl is probably nearer 1.5 ev. The activation energy for the unassisted migration of an F center presumably would be at least as large. Similarly, one might expect a larger activation energy for the process if the F centers first decompose into halogen-ion vacancies and free electrons, the former migrating relatively easily in the form of a pair. Mott and Gurney[86] have estimated the binding energy of the electron on the F center from the migration of F centers during electrolytic darkening and have obtained a value of 1.95 ev for KCl (see Table IV). However, it may not be necessary for the F center to be ionized more than once, so that this relatively slow process is not a bottleneck at the temperature range of interest. Theisen and Scott have demonstrated, however, that the disappearance of the F band is accelerated by application of light in the F band, in the range of temperature where colloids form. This problem evidently merits more consideration.

We saw (Table II) that the energy ΔH_c required to form an F center from a colloid center in KCl is about 8 kg cal per mole, or about 0.35 ev per F center. The energies for the other alkali halides are comparable. From these values one may estimate the energy required to sublime an alkali metal atom from a colloid center into the monatomic vapor phase. We shall make this estimate under the assumption that the colloid centers of unknown size join the lattice of the alkali halide continuously. Consider the following cycle:

(a) A pair of separated positive- and negative-ion vacancies is formed by plucking two ions from typical positions in the lattice and taking them to infinity. The energy required is $V_{+}+V_{-}$, where V_{+} and V_{-} are the energies required to form positive- and negative-ion vacancies.

(b) An alkali metal atom is taken from a colloid center to infinity and replaced by the positive and negative ions removed from the lattice in step (a) in order to maintain continuity. The energy required is Q_c-S_I, where Q_c is the energy required to sublime an alkali metal atom under the conditions of continuity and S_I is the average energy required to sublime a free pair of ions from the surface of the lattice, that is, the

---

[86] N. F. Mott and R. W. Gurney, reference 4, p. 141 ff.

heat of sublimation of the salt to the state of free gaseous ions.

(c) The alkali metal atom is ionized. An energy I_M is required.

(d) The electron is placed in the halogen-ion vacancy created in step (a), thereby forming an F center; the positive ion is placed in the positive-ion vacancy created in step (a). The energy required is $-\varphi_F-V_+$, where q_F is the energy required to remove an electron from an F center and carry it outside the crystal. V_+ was defined in step (a).

The result of these four steps is the formation of an F center from an alkali metal atom in the colloid-center under conditions of continuity. Thus we have

$$\Delta H_c=Q_c+V_--S_I+I_M-\varphi_F. \tag{1}$$

Now $V_--S_I+I_M-\varphi_F$ is the energy W_F required to form an F center from an alkali metal atom in the vapor about the crystal.[86] This energy has been measured by Rögener[87] for KCl and KBr and has been analyzed by Mott and Gurney in terms of the electron affinity of the crystal and the energy required to take an electron from an F center into the conduction band (Table IV). The values for KCl and KBr determined by Rögener are -0.10 ev and -0.25 ev, respectively, whereas the corresponding values determined by Mott and Gurney from a cycle involving consideration of the migration of F centers in electrostatic fields are -0.02 and -0.30 ev. Thus in the cases of KCl and KBr

$$Q_c=\Delta H_c-W_F\begin{matrix}\cong 0.35+0.10=0.45\text{ ev (KCl)}\\ \cong 0.50+0.25=0.75\text{ ev (KBr)}.\end{matrix} \tag{2}$$

These values of Q_c should be contrasted with the heat of sublimation of atomic potassium from the pure metal, namely, 0.98 ev. It is doubtful if the difference, of the order of 0.5 ev in the case of KCl, can be the result of error in measurment of ΔH_c or W_F. Apparently we must conclude that the average energy of cohesion of the potassium atoms in the cluster corresponding to the typical colloid center in KCl is not over half the cohesive energy in the bulk metal. The deviation is less in the case of KBr but is still in the same direction.

Values of W_F having accuracy comparable to those of Rögener are not available for KI and NaCl. Mollwo,[88] however, has given a comparison of the density of F centers and of atoms in the vapor over a range of temperature for all of the crystals considered in Table II. The comparison for KI is of relatively little value, although it indicates that $-W_F$ is probably larger for KI than for KCl and suggests thereby that the deviation between Q_c and the heat of sublimation of the metal may be no worse in this case than that for KBr. On the other hand, Mollwo's comparison for NaCl shows that the densities in the vapor and crystal are very nearly equal, hence the value of W_F is very close to zero. Thus if the value of ΔH_c given in Table II for NaCl is correct, the deviation between Q_c and the heat of sublimation for metallic sodium, namely, 26 kg cal per mole or 1.1 ev, is much greater than for the potassium halides. In this connection, it is interesting to note that Mott and Gurney obtained a positive theoretical value for W_F in the case of NaCl, namely 0.23 ev (Table IV).

Three factors could conceivably contribute to the differences in heats of sublimation.

(a) The surface of the cluster is in intimate contact with the salt. One might expect this influence in itself to increase the cohesive energy of the cluster since the atoms on the surface of the cluster would be more stable if bounded by crystal than by vacuum. Moreover, there is no reason why this influence should be greatly different for the various crystals.

(b) The atoms in the cluster may be under high hydrostatic pressure and hence less stable than at atmospheric pressure. The molar volume of potassium metal is 45.5 cc, whereas the corresponding volume for KCl is 37.7 cc. Thus the metallic cluster would be compressed by about 18 percent if it occupied the volume of the molecules of KCl which are replaced. Assuming potassium retains its normal compressibility for this degree of compression, we may estimate that the decrease in cohesive energy of the metal would be about 800 cal per mole or about 0.035 ev per atom. Since the compressibility of potassium probably does not vary by more than a factor of three over the range of compression of interest, if the cases of lithium and sodium[89] can be used as analogs, it seems safe to conclude that the compressional energy is inadequate to account for the difference between Q_c and the heat of sublimation of the normal metal. It may be noted in this connection that the molar volume of KBr is more nearly equal to that of potassium than is the case for KCl (i.e., 43.5 cc for KBr, in comparison with 45.5 for K). Hence the compressional factor would be relatively negligible in this case. Moreover, the molar volume of metallic sodium is 23.4, in comparison with the value of 27 for NaCl. Thus the situation would be entirely reversed for NaCl, which seems to show the largest deviation.

(c) The number of atoms in the cluster comprising the colloid center may be relatively small, and therefore the surface energy may be comparable to the energy of cohesion. This can be true if the clusters contain a very small number of particles, that is, a number not appreciably larger than 10, the lower limit estimated by Scott and his associates. Assuming the clusters have the properties of the bulk metal, we find that the diameter of the particles would have to

---

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

[88] E. Mollwo, Z. Physik **85**, 56 (1933).

[89] See, for example, the discussion of the work of Bardeen and Bridgman in the book by the writer, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 374.

be 6A corresponding to about 2 atoms if the energy of surface tension is to lower the cohesive energy per atom by as much as 0.4 ev, the magnitude of the deviation in KCl. This calculation is based on use of a value for the surface energy of potassium of 86–97 ergs per cm^2. The value[90] of the surface tension of metallic sodium is somewhat larger, namely 192 ergs per cm^2. It follows that this source of energy would be only slightly larger in NaCl than in the other salts for particles of the same size, provided the vacuum values of the surface energy for the bulk metal may be employed in this calculation.

The latent heat of fusion is too small to explain the deviation in terms of the presence of an amorphous rather than the crystalline state, at least for particles sufficiently large that the bulk properties may be employed. For example, the heat of fusion is only 0.025 ev per atom in metallic potassium.

To summarize, the most reasonable of the possible suggestions for explaining the low values of the energy required to form F centers from the colloidal particles is to assume that the latter are quite small, containing not appreciably more than ten atoms. This possibility has not been turned into a detailed quantitative explanation but seems to be most nearly in agreement with the facts available at present.

[*Note added in proof.*—At the time proof was being read, the writer received a draft of a manuscript from A. B. Scott searching more deeply for the source of the discrepancy. Scott has proposed that the preceding analysis contains two major errors which, taken together, provide a good explanation of the deviation. First, the surface energy of the cavity of the salt should be included as well as the surface energy of the metal. This correction would not in itself alter the results qualitatively since the surface energy of (100) planes of the alkali halides are not greatly different from those of the alkali metals (e.g., the surface energy for NaCl is about 150 ergs/cm^2). On the other hand, Scott proposes that, at least for small colloids, the number of metal atoms in the cavity is substantially smaller than the number of positive ions removed. In effect, he concludes that there is a large surface energy of misfit between the metal and salt and, in fact, the cavity must be large in order to keep the energy of misfit relatively small. Pairs of positive- and negative-ion vacancies condense along with the F centers during the stages of colloid precipitation presumed to be of interest in connection with the experiments of Scott and his associates. The surface energy of misfit accounts for the low "heat of vaporization" of the colloids. If this viewpoint is correct, the heat of vaporization of the F centers should increase as the particles become larger during sufficiently long anneals.]

It was remarked in connection with the review of the older work on the formation of colloidal particles in NaCl that colloids form more easily in this salt than in the potassium salts. Scott and his associates have confirmed this fact. On the other hand, the older work also seemed to demonstrate that it is possible to obtain large colloids of metal in sodium chloride. It would be valuable to determine the heat of formation of F centers from colloids of this type, since the preceding discussion indicates that the value should be larger than that found by Scott, Smith, and Thompson.

18. Large Concentrations of *F* Centers

Buckel and Hilsch[91] have developed a technique for obtaining evaporated layers of the alkali halides and other salts that contain a large excess of metal in widely dispersed form. This method is based on simultaneous evaporation of the salt and the metal from heated containers with subsequent condensation of the mixed vapor upon a surface at a low temperature, such as 90°K. Kaiser[92] has applied this technique to the alkali halides, condensing the salt and alkali metal simultaneously. In this way he has obtained specimens containing a stoichiometric excess of alkali metal in the vicinity of 10 percent.

The remarkable feature of this work is that the absorption spectra of the evaporated films, when measured at the low temperature at which they are formed, indicate the presence of large concentrations of F, R, and M centers. In the case of KCl, which has been studied most extensively to date, the density of F centers, as determined from the area under the F band with the use of Smakula's equation, does not exceed 1.1 percent even when more metal is present. Figure 21 shows the absorption spectra in three cases in which the mole fraction of excess potassium is 0.005, 0.015, and 0.07. The upper curves represent the absorption spectra immediately after the films are formed, whereas the lower curves show the spectra after two hours of standing. The F and M bands are particularly prominent and it requires little imagination to visualize the R bands. The change in each absorption spectrum as a result of standing implies that diffusion is occurring, presumably on an atomic scale, even at liquid nitrogen temperatures.

The position of the F band in the evaporated layers is displaced in the direction of short wavelengths relative to the positions for normally colored crystals containing a mole fraction of the order of 10^{-5} F centers. This displacement is 120A (i.e., from 5480A to 5360A) for the entire range of concentration studied in the evaporated films. The constancy of the shift indicates that it is primarily related to the imperfec-

---

[90] The best values of the surface tensions for potassium and sodium seem to be those of L. A. Quarterman and W. L. Primak, J. Am. Chem. Soc. **72**, 3035 (1950) and F. E. Poindexter and M. Kernaghan, Phys. Rev. **33**, 837 (1929). The writer is indebted to A. B. Scott for this information, which supplants that provided by the American handbooks in common use.

[91] W. Buckel and R. Hilsch, Z. Physik **131**, 420 (1952).

[92] R. Kaiser, Z. Physik **132**, 482 (1952).

tions in the evaporated films rather than to the high concentration of metal. The magnitude of the shift is far less surprising than the relative constancy of the band, for one must conclude that the *F* center is affected relatively little even when the lattice is so imperfect that there is nearly unit probability that the second shell of halogen ions surrounding a given halogen-ion vacancy has a flaw in it. This must be the case, for example, when the density of *F* centers is as high as 1 percent and the density of other imperfections is presumably even higher. In fact, it seems fairly safe to conclude that the essential characteristics of the *F* band are determined by the electron in the halogen-ion vacancy, the first shell of six alkali metal ions and the next shell of twelve halogen ions. Apparently the more distant environment has only secondary influence.

Figure 21 shows another interesting feature. The relative area under the *F* band decreases in comparison with that under the companion bands on the red side, that is, the *R* and *M* bands, as the concentration of excess metal increases. This supports the view that the *R* and *M* bands are aggregates of *F* centers and vacancies which have greater probability of occurring the higher the density of alkali metal.

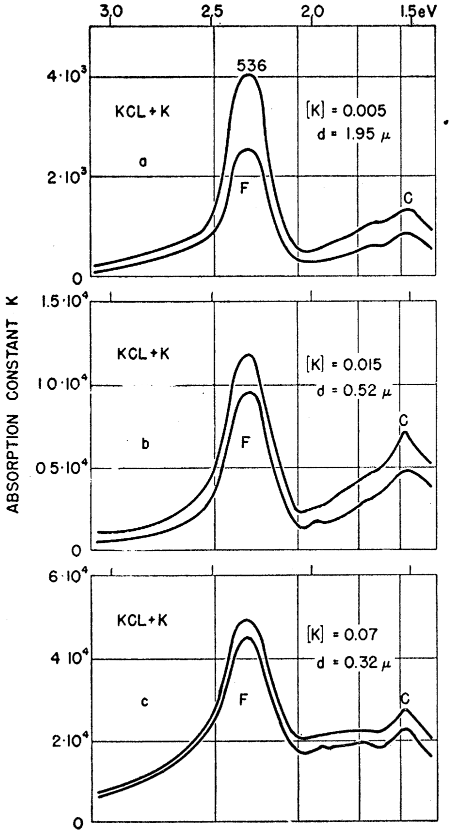


FIG. 21. The absorption spectra of evaporated specimens of KCl containing excess potassium (after Kaiser). The fraction of excess potassium increases from 0.005 to 0.07 in going from (*a*) to (*c*). The *F*, *R*, and *M* bands are clearly resolvable (the latter being designated as *C*). The quantity *d* shown in the upper right-hand corner of each figure is the thickness of the film. The upper curve in each of the three panels was made immediately after evaporation whereas the lower one was made after two hours of standing at liquid nitrogen temperature. All measurements carried out at liquid nitrogen temperature (see text).

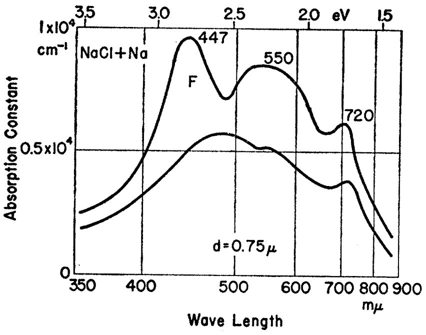


FIG. 22. Diagram similar to those shown in Fig. 21 for NaCl with excess Na. The colloid band at 550 mμ appears in this case as well as the *F* and *M* bands (after Kaiser).

Films that are condensed at liquid hydrogen temperature exhibit the *F* band, much as those condensed at liquid nitrogen temperature; however, the absorption on the red side, particularly that arising from the *M* band, is relatively more prominent than in corresponding specimens prepared at the higher temperature. Since the *M* band presumably is formed by combination of an *F* center and a neutral vacancy pair the experiments at hydrogen temperatures suggest that the density of vacancy pairs is greater in the films formed at the lower temperature and that a larger fraction of the potassium atoms are, as a result, incorporated as *M* centers. The bands formed at hydrogen temperatures do not vary with time if the specimens are maintained at that temperature, in contrast with those formed at nitrogen temperature.

Films prepared by evaporation at room temperature show no striking evidence of the *F* band. However, an entirely new band appears in the vicinity of 4380A at higher concentrations of metal. Kaiser offers the suggestion that this arises from colloidal potassium located outside the cyrstals.

Phenomena similar to those observed in KCl have been found in NaCl and KBr. Interestingly enough, there is evidence for the presence of colloids of sodium in the specimens of NaCl+Na formed at 90°K. In particular the peak near 5500A, which is associated with small colloids, is found (Fig. 22). This peak is also found in specimens of KCl which have been condensed at room temperature with excess Na. Since KCl and NaCl have almost the same index of refraction, one would expect colloids of Na in KCl to have almost the same optical properties as colloids of the same size and shape in NaCl.

It is interesting to observe that Delbecq has studied the absorption spectra of evaporated and thin cleaved layers of KI at temperatures extending as low as

$-190°C$ [J. Chem. Phys. (to be published)]. Two bands were found in the vicinity of the first peak of the fundamental band of relatively perfect crystals in the layers evaporated at low temperatures. One of these peaks, with its maximum at 2130A, appears to be a somewhat broadened version of the first peak of the fundamental band of KI, whereas the second, which occurs as a shoulder on the low-energy side of the first, lies in the vicinity of the α band (Sec. 24), as if it is associated with halogen ions near vacancies or voids. Both bands merge into a single band peaked at 2142A when the specimen is warmed to room temperature, as if much of the disorder vanishes. The two peaks can also be merged into a single broad band having a maximum at 2165A by irradiating for a period of the order of one-half hour at temperatures near $-135°C$ with light absorbed in the original peaks. The new peak is about 1.5 times broader than the first fundamental peak in a relatively perfect specimen. The effect is not observed at $-190°C$, although a peak near the α band can be developed by irradiation.

A similar, more or less complete, diffusing of the first fundamental band is not found when single crystal wafers are given the same type of irradiation. Instead, a very strong version of the α band appears. This may be produced at liquid nitrogen temperature but is much stronger when the specimen is at $-135°C$.

The results suggest that exciton production has a very strong disordering effect upon crystals, particularly at temperatures in the vicinity of $-135°C$. Interestingly enough, Delbecq did not observe appreciable production of F centers in the specimens of KI under the conditions of radiation employed. We shall return to a discussion of these measurements in Sec. 37.

19. Photoconductivity and Hall Effect in Additively Colored Crystals

Additively colored cyrstals irradiated in the F band possess four distinct ranges of photoconductive behavior when the measured quantity $\eta\omega/E$ is regarded as a function of temperature (Fig. 23). Here η is the quantum efficiency for freeing the photoelectron and ω/E is the distance by which the free electron is displaced in unit field strength.

(a) Between a temperature T_α, at the lower limit of present observations near 1°K, and a temperature T_β, which depends upon the particular specimen and is near $-200°C$ in a typical case for a well-quenched crystal, the photocurrent varies slowly with temperature and is presumably derived from electrons ejected from colloidal aggregates of F centers. This statement is true with the provision that F' centers be absent, for the photocurrents derived from F' centers may dominate at very low temperatures if the latter are present, at least for the range of wavelengths in which the F' band is appreciable. On the whole there does not appear to have been any extensive study of the dependence of photoconductivity in the colloidal range upon wavelength and other variables. If present suppositions are valid, the quantum efficiency should be small compared with unity and the wavelength response should be similar to that observed by Gyulai and others at higher temperatures in crystals having a high density of colloidal particles.

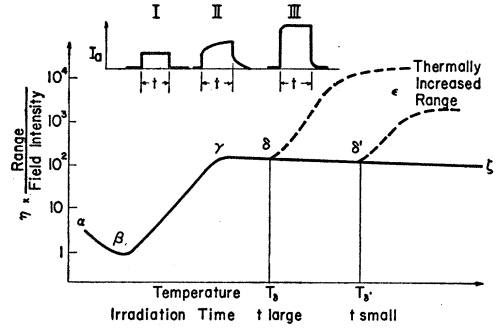


FIG. 23. Typical behavior of the photocurrent of an additively colored alkali halide crystal as a function of temperature. Colloidal particles presumably supply the photoelectrons in the range $\alpha-\beta$. The quantum efficiency for freeing photoelectrons from F centers rises to unity in the range from β to γ. δ is the temperature at which the decomposition of F' centers becomes important during the time of measurement. This temperature rises from T_δ in a static measurement to $T_{\delta'}$ in a rapid measurement (after von Gericke). The inset shows the typical time-dependence of the photocurrent.

(b) The colloidal range is terminated relatively abruptly by a steeply rising portion of the photoconductivity curve which extends from T_β to a temperature T_γ at which there is a knee with negative curvature. Although the curve is continuous at T_β, the slope varies very rapidly in well-quenched specimens. As emphasized earlier, the knee at T_γ appears to be an intrinsic property of the F centers, little dependent upon other imperfections in the lattice. The absorption associated with the main part of the F band presumably raises the electron to a discrete, bound state from which it can escape only if the temperature is sufficiently high to induce thermal ionization. Since the alternative to thermal ionization is a return to the ground state by light emission or by a radiationless process, one would expect the lifetime of the excited state to be less than 10^{-8} sec, the lifetime for the radiative transition under all conditions if this picture is correct.

(c) The photoconductivity curve decreases relatively slowly with increasing temperature between the knee at T_γ and a temperature T_δ which depends both upon the crystal and the time of observation. In this range the electrons freed from the F centers are captured by other F centers to produce F' centers, which are stable during the time of measurement.

(d) Above T_δ, the F' centers decompose into F centers and free electrons during the time of observation and the photoconductivity curve rises as a result of the extended range.

von Gericke[93] has measured the photocurrent for very short periods of time in the range of temperature above T_β, placing particular emphasis on the region between T_β and T_δ. Whereas previous "fast" measurements required of the order of 0.1 sec, with the exception of some observations made by Flechsig on NaCl at 30°C in times of the order of 10^{-4} sec, von Gericke carried out measurements from -180°C to room temperature in times as short as 10^{-6} sec. His conclusions are as follows:

(a) The time required to initiate the primary current is less than 2×10^{-5} sec in KCl in the range from T_β to T_γ, that is, in the steeply rising region between the colloidal range and the knee where the quantum efficiency is sensitive to temperature. The knee is at -140°C in KCl and the measurements extend between -180°C and this temperature.

(b) The photocurrent in NaCl rises to its primary saturation value in less than 5×10^{-6} sec at 30°C. This temperature is just below T_δ for measurements made much more slowly, that is, measurements made over times of the order of 1 sec.

(c) Observations of the time dependence were made in the range above -80°C for periods varying between 1.5×10^{-6} and 10^{-4} sec in KCl, for which T_δ occurs at about -100°C when measurements are made for durations of the order of 1 sec. The current remains primary, that is, becomes flat after the initial rapid rise, in the temperature region from -80°C to $+20$°C for observation times of the order of 10^{-4} sec but shows evidence of the extended range at higher temperatures. In other words, the F' center is stable for about 10^{-4} sec at 20°C and has a shorter life at higher temperatures. The current is primary for a time of the order of 5×10^{-6} sec at 100°C.

The three values of T described in (c) and the associated lifetimes τ of the F' center can be fitted to an expression of the form

$$\tau=\tau_0\exp(\epsilon/kT),$$

in which ϵ is the binding energy of the electron released from the F' center. One readily finds $\epsilon=0.42$ ev and $\tau_0=10^{-11}$ sec. The value of τ_0 is not reliable to a factor better than 100, whereas ϵ is probably reliable to about 20 percent.

Taken as a whole, von Gericke's observations serve to confirm the accepted picture of the origin of the photoconductivity without extending it in a radical way.

Redfield[94] has devised a technique for measuring the Hall coefficient in photoconducting NaCl at low temperatures under conditions in which the light is pulsed so that polarization effects are made small. The method has many unique features including the very important one that the Hall emf is balanced by an externally applied and controlled field. Hence it is not necessary for a relatively large charge induced by the Hall field to build up and compensate for this field. Crystals darkened both additively and by x-irradiation were employed.

The mobility measured at 82±2°K is 260±30 cm²/volt-sec, whereas the value at 200°K is 40±20 in the same units. The relatively large experimental error arises from unsteadiness in the resistivity of a conducting layer on one face of the plate-like specimens employed to establish an electrostatic gradient along this face. The value of the mobility at 80°K calculated with Eq. (4) of Sec. 9, derived by Low and Pines, is 90 cm²/volt-sec for NaCl if one assumes that m is the electronic mass.

J. R. MacDonald and J. E. Robinson (as yet unpublished work at Argonne National Laboratories) have devised an alternating current method for measuring the Hall voltage in photoconducting crystals and have applied this to additively colored sodium chloride at room temperature. They have obtained a value of 12.5 cm²/volt-sec, which they believe is accurate to about five percent. [*Note added in proof.*—See the papers by J. R. MacDonald, Phys. Rev. **85**, 381 (1952); **90**, 364 (1953); **91**, 412 (1953); **92**, 4 (1953)].

20. Photoconductivity in the *M* Band

Barth[95] has investigated the photocurrent obtained by irradiating in the M band. Additively colored specimens of KCl containing of the order of 5×10^{16} F centers per cc were irradiated with light in the F band until the M band at 8200A developed, whereupon the photocurrent was studied as a function of temperature for light absorbed near the center of the M band. Such studies are complicated somewhat by the fact that the F band possesses a tail in the vicinity of the M band which contributes appreciably to the photocurrent, even though the absorption associated with the F band is small relative to that of the M band. Actually the photocurrent is very nearly proportional to the absorbed energy for a range of concentration of M centers near 5×10^{16} per cc as long as the crystals are irradiated with light near the center of the M band. It follows that absorption in the M band is responsible for most of the photoconductivity in the M region.

A comparison of the photocurrents near room temperature for light absorbed in the F band and in the M band shows that the product of the quantum efficiency for freeing electrons and the range of the electrons (i.e., the product $\eta\omega/E$ of Sec. 2, paragraph 5) is about 10.5 times larger for the F than for the M band. Unfortunately, F' centers are not stable near room temperature in KCl, so that the range varies somewhat erratically from one specimen to another. We may conclude that η is near 0.10 for the M band,

---

[93] V. O. von Gericke, Nachr. Akad. Wiss. Göttingen **1950**, 1.

[94] A. Redfield, Phys. Rev. **91**, 244, 753 (1953).

[95] C. Barth, Z. Physik (to be published).

for the quantum efficiency η is assumed to be unity at room temperature for KCl when light is absorbed in the F band, and it seems safe to assume that ranges are equal for electrons released by quanta absorbed in either center.

The quantum efficiency for bleaching the M band with light absorbed in this band is not known, however, Pick (private comment) has expressed the opinion that it is not above 0.1 and may actually be smaller. In this connection, Barth has noted that the R and N bands may be developed by irradiating in the M band as well as in the F band.

The product $\eta\omega/E$ was evaluated as a function of temperature for the M band in the range from about −140°C to room temperature. Barth subtracted the photocurrent observed in a crystal containing only F centers, when irradiated near 8200A, from the corresponding current for a crystal possessing the M band and corrected for the difference in absorbed radiation. The results show that the photocurrent associated with the M band exhibits the extended range found when light is absorbed in the F band at temperatures above about −80°C. This is not surprising, for the density of F centers is much higher than that of M centers and we should expect the F centers to be the natural traps for free electrons at temperatures below −80°C. Thus the photocurrent should show a rise whenever the F' centers become unstable. The measurements of the photocurrents are not sufficiently accurate to determine whether a second sharp drop occurs below about −130°C, as is found for the photocurrent from the F band.

There is a possibility that the radiation absorbed by the M centers is transferred to the F centers by a radiationless process involving the resonance of electric dipoles (see Sec. 12). In this case the photoelectrons would be emitted by the F centers and one would expect a drop in η below −130°C, as when light is absorbed directly by the F centers.

21. Luminescence in the *F* Band

Ghormley and Levy[96] have carried out a sequence of measurements of luminescence in crystals containing F centers. The most interesting part of this work, from the standpoint of the present section of this review, deals with a search for luminescence stimulated by absorbing light in the F band. Crystals of KCl colored additively by electrolysis were irradiated in the F band at 25°C and at −196°C and the emission spectrum was investigated from 2300A to 12 000A. A band which peaks somewhere on the long-wavelength side of 10 000A was observed at both temperatures, the intensity being somewhat higher at the lower temperature. It is possible that this is the characteristic luminescence of the F band.

The same emission band was found at −196°C on specimens of KCl darkened at room temperature with γ rays.

The measurements on additively colored crystals of KCl were extended by studying the glow curve obtained when F' centers, produced at liquid nitrogen temperatures by irradiating in the F band, are bleached by warming the specimen to room temperature. Since the F' centers eventually revert to F centers by ejection of an electron which is captured by a halogen-ion vacancy, one expects phosphorescence in the infrared if the peak near 10 000A described above is the characteristic radiation of an F center. Radiation beyond 6000A was detected with an infrared sensitive photomultiplier. This observation proves, incidentally, that the characteristic luminescence does not lie in the visible part of the spectrum. The phosphorescent glow exhibited peaks at five temperatures during the warming process. One of the largest of these occurred between −100°C and −50°C and is presumably associated with decomposition of F' centers. The origin of the others is unknown; however, the complexity of the glow curve gives one a feeling of insecurity in a simple interpretation of the results.

Somewhat similar measurements were carried out with LiF darkened with x-rays. In this case the specimens were irradiated in the M band, which appears near 4500A, and luminescent peaks were observed at 7000A and 10 000A. The investigators conclude that the peak at 7000A arises from the M centers, whereas the other is probably characteristic of the F center formed by bleaching of the M center.

In contrast with the foregoing work, Klick (as yet unpublished investigations) has searched for luminescence in specimens of LiF darkened at 4°K with x-rays and in specimens of additively colored KCl. Both crystals were irradiated in the F band at 4°K. The concentration of F centers was of the order of 5×10^{17} per cc or less. In the case of LiF, the spectrum was searched between 5200A and 20 000A, whereas the range between 6500A and 20 000A was explored in KCl. No luminescent radiation was detected that could be ascribed to a quantum efficiency as great as 3 percent.

Luminescence observed in irradiated specimens of KCl will be described further in Sec. 30.

{*Note added in proof.*—S. I. Pekar [Zhur. Eksptl. i Teort. Fiz. **22**, 641 (1952)] has considered the theory of luminescence of the F bands and concluded such luminescence should exist. The outstanding experimental evidence does not seem to favor this viewpoint.}

22. Study of *F* Centers with Spin Resonance

A very important addition to the study of F centers has arisen from the discovery by Hutchison[97] and his

---

[96] J. A. Ghormley and H. A. Levy, J. Phys. Chem. **56**, 548 (1952).

[97] C. A. Hutchison, Phys. Rev. **75**, 1769 (1949); C. A. Hutchison and G. A. Noble, Phys. Rev. **87**, 1125 (1952). Other early resonance studies are those of E. E. Schneider and T. S. England, Physica, **17**, 221 (1951) and M. Tinkham and A. F. Kip, Phys. Rev. **83**, 657 (1951).

associates that the alkali halides containing F centers possess spin resonance absorption lines which can be associated with the unpaired electrons in the F centers. The static paramagnetism of F centers was observed before the war by Jensen;[98] however the study of the resonance absorption has provided a much deeper insight into the structure of the F center. Most of the interpretive work in this area has been carried out by Kip and Kittel, who with their co-workers Tinkham, Kahn, Abrahams, Levy, and Portis have extended[97,99] and analyzed the experiments.

The resonance absorption peaks exhibit two important characteristic properties which reflect upon the structure of the F center:

(1) *Shift of g Factor*

The g factor which determines the splitting of energy levels per unit magnetic field, and which should be 2.0023 for a free electron, actually is 1.995 ± 0.001, thereby differing by the amount $\Delta g=-0.007$ from the free value. Kahn and Kittel have concluded that this deviation arises from the coupling of the electron with an appreciable component of orbital momentum. Such a coupling is not explicable if one assumes that the lowest state of the F center is almost exclusively s type, as would be true if the central field approximation for treating this center were accurately valid.

Kahn and Kittel[99] have calculated the shift in g factor on two assumptions. First, the normal state of the F center is describable in terms of a wave function which is centered at the midpoint of the halogen-ion vacancy and is a mixture of s- and g-type functions conditioned by an electrostatic field which deviates from spherically symmetric form; second, the wave function is a linear combination of atomic alkali metal functions centered about the six alkali metal ions neighboring the vacancies. In the second case the atomic functions were taken to be linear combinations of the s and p orbitals to take account of the polarization of the atoms induced by the presence of the vacancy.

The spin orbit coupling term, which together with the mixing of s-type functions with the other types determines the shift in g factor, was taken to have the form

$$\lambda \mathbf{L}\cdot\mathbf{S},$$

in which $\mathbf{L}$ and $\mathbf{S}$ are the orbital and spin angular momentum operators and λ is a coupling parameter. λ was evaluated in rather different ways in the two approximations. In the first case, it was estimated by assuming that the g function is chiefly concentrated about a circle passing through four of the positive ions surrounding the vacancy and that the electron moves on the average in a simple Coulomb field of the form e^2/r, where r is the radial variable measured from the center of the vacancy. This gives an exceedingly weak coupling constant for the g function, of the order of 0.1 cm^{-1} in wave-number units, as one might expect from the weak field employed. The actual value for KCl was about 0.8 cm^{-1}. In the second case, the coupling constant was chosen by employing the multiplet splitting in the alkali atoms. This leads to a value of about 38 cm^{-1} in the case of potassium.

Kahn and Kittel found that they could obtain a reasonable value of Δg in the first case only by assuming that the ground state is almost pure g function. In the writer's opinion this conclusion is somewhat too radical. Since the electron spends at least half its time near the six neighboring alkali metal ions, it would probably have been more reasonable to assume that the coupling constant λ is nearer the value for the metal atoms, that is, nearer 38 cm^{-1} than 0.8 cm^{-1} in the case of potassium. If this is done, the observed shift in the g factor can be explained on the assumption that the ground-state wave function of the F center is about equally divided between s and g function centered about the middle of the vacancy.

The wave function constructed by selecting sums of linear combinations of atomic s and p functions over the six neighboring alkali metal ions, when taken in combination with the value of λ derived from the atomic data, gives the proper value of Δg if the atomic functions are nearly equal admixtures of s- and p-type orbitals.

In the writer's opinion, the two approaches, based upon wave functions centered in the vacancy and wave functions constructed by taking linear combinations of the atomic functions, have about equal merit. The first should contain nearly equal admixtures of s- and g-type functions, whereas the second should have nearly equal admixtures of atomic s- and p-type orbitals. The relatively low value of λ employed in the first case accounts for the large component of g function required.

In this connection Dexter and Krumhansl[100] have demonstrated that a great deal of the weakness of the centrally-symmetric wave function derived from the continuum model is only apparent. This function $f(r)$ may appropriately be regarded as the coefficient of the Bloch-type function u_0, associated with the bottom of the conduction band in a development of the wave function ψ for the bound electron of the F center in the form

$$\psi=f(r)u_0(r). \tag{1}$$

---

[98] P. Jensen, Ann. Physik **34**, 161 (1939). See also the paper of C. V. Heer and J. Rauch, Phys. Rev. **90**, 530 (1953) which indicates that Curie's law is not obeyed when the density of F centers is near 10^{19} per cc.

[99] A. H. Kahn and C. Kittel, Phys. Rev. **89**, 315 (1953); Kip, Kittel, Levy, and Portis, Phys. Rev. **91**, 1066 (1953); C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953); A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[100] D. L. Dexter, Phys. Rev. **93**, 244 (1954); J. A. Krumhansl, Phys. Rev. **93**, 245 (1953). The writer is deeply indebted to the authors for the opportunity of reading prepublication versions of their manuscripts.

The development (1) is rigorous, within the one-electron scheme, only when $f(r)$ varies slowly over one unit cell of the lattice. On the other hand, the wave function (1) is a better approximation to the true solution than $f(r)$ alone even when $f(r)$ is distributed only over a small number of unit cells. Proper use of continuum wave functions within this framework requires knowledge of the properties of $u_0(r)$, particularly if one is interested in the behavior of ψ near the nucleus, as is important in the resonance problem. This knowledge is, unfortunately, available[101] only for HF, LiF, and NaCl at the present time.

Krumhansl has constructed a wave function of the type (1) for the case of an F center in NaCl with the use of techniques reviewed in the next section, in order to demonstrate that it is possible to obtain a reasonable description of the behavior of ψ near the alkali metal ions bordering the vacancy. As a test, he considered the half-width of the resonance peak to be discussed in the next part of this section rather than the shift in g value. ψ was assumed to be a solution of the Schrödinger equation for a simple potential well within the vacancy, whereas it was assumed to be of the composite form (1) outside the well, $f(r)$ being a solution of the Schrödinger equation with the potential $-e^2/k_0r$. Although $f(r)$ varies smoothly near the alkali metal ions, u_0 does not and guarantees that ψ will have an amplitude in the immediate vicinity of the nucleus comparable to that in the free neutral atom. Krumhansl determined this amplitude on the assumption that it bears the same ratio to the magnitude of $f(r)$ at the edge of the simple potential well that the value in the free atom does to the amplitude of the wave function near its maximum at about 3.5 a_0. In this way he found that the value of ψ^2 at the positive ions is 0.666×10^{-24} cm^{-3}, in contrast with 5.09×10^{-24} cm^{-3} for the free atom. This amplitude gives a value of 280 oersteds for the half-width of the F-center resonance [see (2) following] in comparison with the observed value of 162 oersteds, so that it appears to be in error on the high side by no more than a factor of two. Since there are six neighboring Na ions, the total amplitude of ψ^2 near the nuclei as computed by Krumhansl is $6\times0.666\times10^{-24}$ cm^{-3}= 4.0×10^{-24} cm^{-3}. If this is decreased in the ratio $162/280=0.58$ to bring about closer agreement with experiment, the result is 2.3×10^{-24} cm^{-3}, which is just about one-half the value of 5.09×10^{-24} for the neutral free atom.

To summarize, the centrally symmetric wave function is capable of giving the proper magnitude of the hyperfine interaction when used appropriately in a function of the type (1). Presumably it also can give a reasonable account of the shift in g value, since the wave function has a mixture of s and p character near the nuclei.

It is interesting to note that the total value of the density of the wave function of the electron in the F center at the six Na$^+$ ions is about half the value of the 3s function in a free atom. The electron in the crystal is not only dispersed over six alkali metal ions but is also dispersed more widely through space.

(2) *Breadth of the Resonance Band*

Hutchison and Noble[97] observed that the width of the spin resonance absorption lines in KCl containing F centers is much greater than one would anticipate from spin-spin interactions between different centers. The observed width at half-maximum is about 56 oersteds, for a specimen containing about 10^{18} F centers per cc, whereas the width calculated with the use of magnetic dipole-dipole interaction between centers is about 0.1 oersted. Moreover the observed shape of the line is Gaussian, whereas the shape expected from dipole coupling is of the Lorentz form, common in dispersion theory.

Kip, Kittel, Levy, and Portis[99] have concluded that the observed breadth and shape are a consequence of the fact that the electron in the F center spends a large portion of its time about the alkali metal ions neighboring the vacancy. As a result its spin magnetic moment is coupled with the nuclear moment much as in a free atom. This coupling accounts for the hyperfine structure of the atomic spectral lines, which is greatest for s electrons since they spend the largest fraction of their time near the nucleus. The investigators emphasize that the hyperfine structure expected in the crystalline case is not as simple as in the free atom, for the spins of the six alkali metal ions neighboring the vacancy may be oriented in a wide variety of ways. For example, K^{39} and K^{41}, the most abundant potassium isotopes, have spins of $\frac{3}{2}$ and, as a result, possess four possible spin orientations. Thus there are $4^6=4096$ possible arrangements of the spins on all six alkali metal atoms having variable interactions with the electron.

The investigators found that they could account for both the width and shape of the resonance line on the basis of the hyperfine interaction and a wave function constructed by taking linear combinations, summed over the six ions, of the superposition of atomic s- and p-type orbits determined by Kahn and Kittel from the calculation of Δg described above. The Gaussian shape is a consequence of the Gaussian distribution of the total nuclear spin of the six ions. It was concluded, from the observed breadth, that the atomic combinations employed are about 60 percent s type.

The supposition that the hyperfine interaction is the source of the breadth was confirmed by measurements made with specimens of KCl enriched in K^{41}. The ratio of the magnetic moment of K^{41} to that of K^{39} is 0.550 so that one would expect the resonance line to be narrower in the material containing the enriched isotope. In actual fact, it was found that the width is only 36 ± 2 oersteds in a specimen made of potassium which contains more than 99 percent K^{41}, whereas the

---

[101] See, for example, the book by this writer *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

width is 54±2 for a specimen having the natural abundance (93.08 percent K^{39} and 6.91 percent K^{41}). While the shift in width is in the proper direction, one would have expected a value of only 31 oersteds if the electrons interacted only with the nuclei of the six neighboring alkali ions. The investigators conclude from the discrepancy that the electrons spend a fraction of their time about the halogen nuclei, which are not affected by the change in isotopic concentration of the potassium ions. The relative density of the electron cloud in the immediate neighborhoods of the positive and negative ions is estimated to be about 6.

At the time this is written, early results on NaCl and KBr are also available. The shifts in g are very closely the same as in KCl, whereas the half-widths are 162 and 146 oersteds, respectively. The larger widths can be explained to a reasonable degree of approximation with use of the measured hyperfine constants for Na and Br in conjunction with the assumption that the electrons are distributed between the neighboring alkali metal and halogen ions in much the same way as in KCl.

The outstanding conclusion to be drawn from this work, as far as the theory of color centers is concerned, is that the electrons in the F centers belong to the ions of the lattice in a very real way and are not confined entirely to the vacant lattice space. The interaction between the electron and the ions is sufficiently great that the former cannot be treated exactly as if it moved in a central field. Moreover the electron is not so strongly localized on a single ion that one can use simple atomic s functions in describing its behavior. These conclusions are not surprising; however, it is fortunate such beautiful and powerful tools are available for justifying them.

Schneider[102] has reported early results of similar resonance experiments on specimens of LiF darkened by x-rays and presumably containing both F- and V-type centers. The absorption spectrum observed consists of a Gaussian peak, corresponding to a positive shift in g value, superimposed upon a sharp spectrum containing 19 equally spaced peaks possessing nearly equal intensity. Schneider has proposed tentatively that the broad peak arises from the V bands, whereas the sharp series is to be associated with the F band. It seems wisest to hold opinions in abeyance until this topic has been subjected to further study.

In so far as the resonance experiments indicate that the electron associated with the F center overlaps the surrounding positive and negative ions appreciably, they cast doubt on the appropriateness of Smakula's use of the Lorentz correction for the local field in determining the dispersion of light by F centers, for this correction can be used rigorously only when the polarizable units do not overlap. Presumably the correction to Smakula's equation would be in such a direction as to weaken the local field and thereby reduce the effective refractive index of the medium. Thus the values of the oscillator strengths to be associated with the F bands would have to be raised accordingly. Since the oscillator strengths accepted at the present time are fairly near to unity (e.g., 0.81 for KCl), it appears that the correction cannot be more than twenty percent or so.

It is interesting to consider another aspect of the foregoing work. The interpretation of the Gaussian width of the resonance band is in excellent accord with the vacancy model of the F center, for this model predicts at once that the electron associated with the F center should be shared equally by the six metallic ions surrounding the halogen vacancy. Can alternative models of the F center be excluded on this ground? As far as the writer is aware the only serious competitor to de Boer's model for the F center is the unit consisting of an alkali metal atom in an interstitial site. The most likely interstitial sites would be the eight $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$-type positions in the unit cube. The most powerful arguments against this model stem from the view that Schottky-type imperfections play a more natural role than interstitial imperfections because of the higher energies required to form the latter—a view that is abundantly supported by the existing body of electrolytic measurements in uncolored crystals. It is also true that the density measurements of Estermann, Lievo, and Stern and others support the de Boer model even though the associated measurements of lattice parameter are absent. Nevertheless, none of the existing experimental "proofs" of the vacancy model is completely closed in the logical sense and one may rightfully ask if the interstitial model can be eliminated by consideration of the magnetic resonance phenomena involving F centers.

An alkali metal ion at the interstitial position described above would be surrounded tetrahedrally by four other metal ions at a distance $r_n=\sqrt{3}r_0/2$, where r_0 is the nearest neighboring distance in the perfect crystal. It would also be surrounded tetrahedrally by negative ions. If the electron associated with the interstitial ion spent a much larger fraction of its time near this ion than near the four neighboring ions, the hyperfine interaction of the electron would be principally with the nucleus of this ion. Thus the resonance spectrum would show quartet structure, the peaks corresponding to the cases in which the nuclear spin of $\frac{3}{2}$ is oriented in four possible ways relative to the applied magnetic field when the electron spin undergoes transitions, if the magnetic field employed in the resonance measurements is sufficiently strong to break down the hyperfine coupling, as is the case in the observations dealing with F centers. The hyperfine interaction of the electron with more distant nuclei would broaden each of the quartets into Gaussian form; however, the quartet pattern would be resolvable if the interaction with the interstitial nucleus predominated. Since the

---

[102] E. E. Schneider, Phys. Rev. **93**, 919 (1954).

observed resonance pattern does not show this structure, we may conclude either that the interstitial model is incorrect or that the electron does not prefer the central nucleus, if the interstitial model actually obtains.

A simple theoretical analysis shows that the electron would probably have almost equal probability of being found at the nucleus of the interstitial ion or any one of the four nearest neighbors, whence the absence of the quartet structure does not rule out the interstitial model. Consider the case of NaCl for example. Here $r_0=5.3\ a_0$, so that the distance r_n from the interstitial ion to the neighboring ions, in the undistorted lattice, is 4.5 a_0. The electron would have no difficulty in bridging the distance if the potentials at the nuclei arising from the rest of the lattice are nearly the same, for the separation of sodium atoms in the metal is nearly twice as large. The interstitial ion is at a position of zero potential in the perfect unpolarized lattice. In contrast, the four neighboring sodium ions, occupying normal lattice positions, are at regions where the Madelung potential is -8.9 volts when the interstitial ion is absent. The interstitial ion raises the potential to -2.9 volts, so that the energy of an electron at one of the neighboring ions, arising from the field of other ions, is 2.9 ev. This value evidently is valid only when the polarization of the lattice is neglected. If we assume that the ions behave like spheres occupying spherical voids in a dielectric continuum of dielectric constant k_0, the potential near the interstitial ion is lowered by the amount $V_p=-e(1-1/k_0)/(r_n/2) = -6.7$ ev as a result of the polarization of the surrounding electron cloud, provided we assume that the spherical cavity associated with the interstitial ion has the radius $r_n/2$. Actually the potential energy of an electron near the interstitial ion is raised by an amount more nearly equal to $-eV_p/2$ since the electronic polarization of the lattice will relax more rapidly than the electron trapped to the interstitial ion. (See the viewpoint of Krumhansl and Schwartz discussed in the next section). Hence the electrostatic energy of the electron near the interstitial ion lies between about 3.4 and 6.7 ev, exclusive of the energy term arising directly from this ion. Electronic polarization will screen the surrounding positive ions from the field of the interstitial ion. If the continuum model is used, the potential near the neighboring ions is the Madelung potential plus e/k_0r_n, corresponding to an electron energy of about 5.5 ev, instead of the value 2.9 ev computed for unscreened charges. The potential energy of an electron which is at the ion is probably somewhat lower because its polarization charge neutralizes partly that arising from the field of the interstitial ion. In summary, the potential terms to be added to the ion core fields at the interstitial ion and the four neighbors as a result of the environment, appear to be very nearly equal and about -3 volts. For comparison, it may be added that the potential at a distance $r_n/2$ from a bare sodium ion in a vacuum is about -12 volts, which is much larger than the uncertainties in the additional terms.

Thus it appears that the electron associated with the interstitial atom actually would be more or less equally divided between the intersitital ion and its four neighboring metal ions. In this connection it may be added that about 20 percent of the electronic charge of the 3*s* electron on a neutral sodium atom lies inside the sphere of radius $r_n/2=2.25\ a_0$. Presumably a large part of the electronic charge associated with the interstitial atom would be distributed within the five spheres of radius 2.25 a_0 associated with the interstitial ion and its five neighbors.

One of the features of the ground-state electronic function for the interstitial center which would distinguish it from the wave function of the vacancy center is its tetrahedral symmetry. Thus the most prominent harmonic constituents would have *s* and *f* symmetry rather than *s* and *g* symmetry. Since the *f* function has odd parity, whereas *s* and *g* functions have even parity, one might hope for a decisive test on the basis of parity. The writer, however, has not been able to devise a suitable test.

23. Theoretical Study of the *F* Center

There have been a number of theoretical analyses of the properties of the *F* center. Work of this kind is particularly valuable when carried out in connection with experimental work such as that on the spin resonance spectrum described in the previous section. However, it also has its own merits.

As mentioned in the previous section, one of the methods of determining a wave function for the electron in the *F* center is to employ an effective potential field which is centered in the middle of the halogen-ion vacancy to compute what might be termed a molecular type of orbital that is distributed throughout the vacancy and extends to the neighboring ions. This procedure is particularly simple if the potential field is centrally symmetric, for then the Schrödinger equation is separable in spherical polar coordinates. It was employed first for the *F* center problem by Tibbs[103] in work described in the book of Mott and Gurney. He assumed that the electronic potential is Coulomb-like from infinity to a limiting radius and is constant inside this radius. The Coulomb-like term was chosen in the form $-e^2/k_0r$, where e is the electronic charge, r is the radius vector from the center of the vacancy, and k_0 is the high-frequency dielectric constant valid when the ions are fixed. The limiting radius was determined under the condition that the Coulomb potential there be equal to the potential estimated at the center of the vacancy by taking account of the missing ion and the polarization of the lattice. This potential yields an energy of about -3.0 ev for the 1*s* state and an energy of about -0.6 ev for the 2*p* state obtained

---

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

by direct optical transition from the 1*s* state in the case of NaCl. Thus the energy of excitation is about 2.4 ev whereas the energy associated with the center of the *F* band, which should arise from the transition, is 2.7 ev.

Simpson[104] sought to improve upon Tibbs calculations and employed a field which is Coulomb-like at large distances but terminates in a square well whose radius was estimated to be about 5.0 a_0 from the work of Mott and Littleton. The energies and mean radii of the 1*s* and 2*p* states for this potential, as determined with use of a variational procedure, are given in Table V.

TABLE V. Values of the energies of the states of *F* centers (after Tibbs, Simpson, and Krumhansl, and Schwartz).

	NaCl Energy (ev) Tibbs	 Simpson	 Krumhansl-Schwartz	Mean Radius (a_0) Simpson
1*s*	−3.0	−3.2	−3.85	3.0
2*p*	−0.6	−1.0	−1.23	5.6
2*p*−1*s*	2.4	2.2	2.62	
Observed *F* Absorption			*2.7*	
		KCl		
1*s*			−3.18	
2*p*			−0.82	
2*p*−1*s*			2.36	
Observed *F* Absorption			*−2.3*	

It may be seen from Table V that most of the 1*s* electron is inside the square well of radius $5a_0$ assumed by Simpson, whereas the 2*p* electron is about half inside, at least for the state obtained by direct transition without a change in nuclear coordinates. These results, when taken in combination with the work on spin resonance, indicate strongly that Simpson's procedure represents a significant oversimplification of the actual situation, traceable to oversimplification of the potential employed. Although the average radial distribution may not be greatly in error, the potential must exhibit strong deviations from a constant value inside $r=5a_0$ if the ground state is a nearly equal mixture of *s* and *g* type.

Simpson has also attempted to estimate the thermal ionization energy of the electron in the 2*p* level. This requires determination of the change in polarization energy, first when the system comes into equilibrium in the 2*p* state and second when the electron is free. Simpson assumed that the equilibrium configuration for the 2*p* state does not differ by very much from that for the 1*s* state and ascribed most of the reduction of the 1.0 ev needed to free the electron in the 2*p* state optically (see Table V) to adjustment of polarization of the ionized state. He estimated that the energy recovered in this way is 0.55 ev so that the thermal ionization energy from the 2*p* level is 0.45 ev. This is probably too high by a factor of at least 5 and demonstrates the difficulty of estimating the energy associated with redistribution of nuclei from first principles even in the relatively simple ionic lattice.

Krumhansl and Schwartz[105] have subjected the models employed by Tibbs and Simpson to a critical analysis and have suggested a change in the depth of the potential well employed by the latter which would have the effect of increasing the spacing between the 1*s* and 2*p* electron. The basis for this change is as follows. Assume that a negative ion has been removed from the lattice; then the Madelung potential at the center of the vacancy is $\alpha e/d$, where α is the Madelung constant, e is the absolute value of the electronic charge, and d is the nearest-ion spacing. However, the actual potential at this position is lower because the surrounding medium is polarized. In considering the *F* center, it is assumed that the distant ions remain at their normal positions since the unit is neutral. On the other hand, when the electron is far away, during the course of its motion, the positive charge will induce electronic polarization in the lattice. If one assumes that the vacancy can be represented by a positively charged cavity in a continuous dielectric medium, as was first suggested by Jost, the potential in the cavity arising from this polarization field is $-e(1-1/k_0)/R$, where k_0 is the high-frequency dielectric constant and R is the radius of the cavity. Tibbs and Simpson assume that this negative term should be added to the Madelung potential in evaluating the depth of the well inside the vacancy with their models.

Krumhansl and Schwartz point out that the procedure followed by Tibbs and Simpson is equivalent to assuming that the electronic polarization of the lattice cannot follow the motion of the electron associated with the *F* center so that the polarization field is regarded as fixed in determining the potential of the electron in the cavity. Actually, the natural frequency associated with the electron in the *F* center is appreciably less than that of the electrons of the bulk material so that the electronic polarization of the crystal should be able to shift as the electron moves. If this shift is assumed to take place adiabatically, the addition to the Madelung potential is reduced to one-half the value assumed by Tibbs and Simpson. The influence of this decrease is greater on the 1*s* function, which is strongly localized within the cavity in this approximation, than it is upon the 2*p* function. The changes in energy are shown in Table V.

Whatever advantages this increase in the precision of the analysis may have, it alone does not improve those features of the wave function of the ground state which are important for understanding the magnetic resonance absorption of the *F* center; for the Krumhansl-Schwartz model will pull even a larger fraction of the electronic charge into the cavity where the field is most reasonably assumed to be spherically symmetric and slowly varying. As we saw in the last section, it is

---

[104] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[105] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953).

TABLE VI. Energy of the F band in the approximations treated by Inui and Uemura (in atomic units. 1 atomic unit=27.1 ev).

Approximations:
I. Vacancy treated as point charge in continuum.
II. Vacancy treated as uniform sphere in continuum.
III. Large molecule approximation, nearest neighbors only.
IV. Large molecule approximation, influence of more distant neighbors included.

	LiF	LiCl	LiBr	LiI
I.	0.122	0.067	0.063	0.053
II.	0.091	0.076	0.073	0.065
III.	0.217	0.170	0.155	0.135
IV.	0.157	0.127	0.116	0.105
Experimental	*0.180*	*0.115*	*0.101*	*0.086*

necessary to assume that the continuum-type wave functions are forms of the function $f(r)$ appearing in Eq. (1) of that section in order to begin discussing the resonance properties in a satisfactory way. Krumhansl's calculations, discussed in connection with this equation, show that this procedure actually leads to results that are reasonable semiquantitatively.

Kubo,[106] Nagamiya,[107] and Pincherle[108] have also employed the spherical approximation, however, we shall devote attention to the more comprehensive work of Inui and Uemura.[109] These investigators have carried out a very careful analysis of wave functions and energies for the F center employing both the centrally symmetric approximation of the type studied by Tibbs and Simpson and the scheme, based upon use of linear combinations of the atomic orbitals of the alkali metal atom, which Kip, Kittel, Levy, and Portis found helpful in discussing the spin resonance. Most emphasis was placed upon the second procedure which they term the "large molecule approximation."

The investigators determined the energy of the 1s and 2p functions in the centrally symmetric approximation with the assumptions that the field of the vacancy can be represented by a point charge and by a uniformly charged sphere imbedded in the dielectric. The second procedure is evidently similar to that used by Simpson. The principal differences lie in the nature of the wave functions employed in the variational procedure and in the value of the radius at which the simple Coulomb potential is terminated. The radius was selected to be the nearest interionic distance, which is 5.32 a_0 in NaCl, and should be compared with the value of 5.0 used by Simpson.

The large molecule approximation was treated in two stages. The calculations were restricted to the lithium halides for simplicity. In both stages the atomic wave functions were chosen to be analytic approximations of the Hartee 2s functions for Li. Moreover, the Hartee potential of the ion core was also approximated analytically. Attention was focused on the six alkali metal ions neighboring the vacancy. The wave functions considered were taken as linear combinations of the six atomic functions for these ions so that the secular equation for the problem is six dimensional. The Hamiltonian operator was chosen to be the sum of the electronic kinetic energy and a sequence of potential energy terms arising from the ions. The two stages of approximation mentioned represent different ways of including the potential field of the ions more distant than nearest neighbors in the approximate Hamiltonian operator. The two lowest roots of the secular equation derived from this operator were evaluated by methods common to the Heitler-London procedure and were associated with the ground and first-excited states of the F center.

Table VI contains a list of the calculated results for the spacing between ground and excited state in the four approximations used, attention being limited to the lithium halides. The implications of the four procedures are indicated in the key to Table VI. The experimental values for the energy associated with the maximum of the F band are obtained with the use of Ivey's[110] interpolation equation

$$\lambda_F = 703d^{1.84},$$

where λ_F is the wavelength of the maximum in Angstrom units and d is the distance between nearest ions in the same units.

As the writer commented in the previous section, the two principal methods of approximation have comparable quality on the whole, although a given one may be preferable to use in treating a given problem.

Attention may be called here to the work of Muto[111] on the coupling between the electronic states and the lattice vibrational waves. He has employed this coupling to discuss the dependence of the breadth and maximum position of the F band upon the temperature. This problem has also been investigated by Inui and Uemura.[112]

The properties of the hypothetical center consisting of an interstitial alkali atom in an alkali halide crystal were discussed briefly at the end of the last section (Sec. 22). It was pointed out that the electron is probably distributed more or less equally over five metallic ions. Simpson has discussed the same center with the use of the spherically symmetric continuum theory, assuming that the field of the interstitial ion can be described with the use of a point charge which is screened by polarization of the medium, the screening being a function of radius. This model appears to work very well for the silver halides, for the calculated radii of the 1s type orbits are 7.4 a_0 and 8.3 a_0 in the case of the chloride and bromide. Thus, the radii are

---

[106] R. Kubo, J. Phys. Soc. Japan **3**, 254 (1948).

[107] T, Nagamiya, J. Phys. Soc. Japan **7**, 358 (1952).

[108] L. Pincherle, Proc. Roy. Soc. (London) **A64**, 648 (1951).

[109] T. Inui and Y. Uemura, Prog. Theoret. Phys. Japan **5**, 252 (1950).

[110] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

[111] T. Muto, Prog. Theoret. Phys. Japan 4, 181, 243 (1949).

[112] T. Inui and Y. Uemura, Prog. Theoret. Phys. Japan **5**, 395 (1950).

appreciably larger than the spacing of nearest neighbors. On the other hand, the radius of the 1*s* orbit for the case of NaCl is found to be 3.8 a_0, which is very close to $r_n=4.5a_0$. Hence only the crudest features of the center are described in the spherical approximation. Incidentally, Simpson finds that the optical ionization energy of the center is 1.52 ev.

24. The α and β Bands

While probing the absorption spectrum, in the vicinity of the fundamental absorption band, of potassium iodide crystals which had been colored both additively and by x-irradiation, Delbecq, Pringsheim, and Yuster[113] made a remarkable discovery which has provided a valuable new tool for the study of color centers in the alkali halides. We shall emphasize the aspects of their work which have to do with additively colored crystals in the present section and discuss more general aspects later in the article.

In brief, they found that an additively colored crystal, containing primarily *F* centers, possesses an absorption peak just on the edge of the fundamental absorption band which can be closely associated with the *F* band. This peak, which is termed the β band, is shown at the left-hand side of Fig. 24. It does not appear in an uncolored crystal. The β band diminishes in proportion to the diminution of the *F* band, if the crystal is irradiated in the *F* band in such a way as to transform a substantial fraction of the *F* centers into *F′* centers. At the same time, a new peak, termed the α band, appears just to the long-wavelength side of the β band and grows in proportion to the *F′* band. The α band disappears and both the *F* band and β band are re-established with their original intensity if the crystal is heated so as to decompose the *F′* centers.

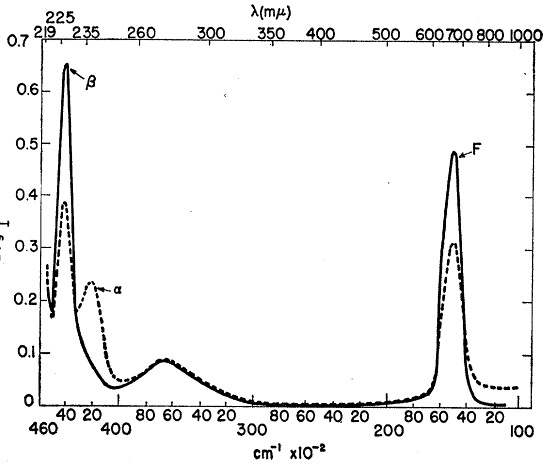


FIG. 24. The relationship between the *F*, *F′*, α, and β bands in an additively colored crystal (after Delbecq, Pringsheim, and Yuster). The continuous curve shows the absorption spectrum on the long-wavelength side of the fundamental band in an additively colored specimen of KI. The *F* and β bands appear alone. If the specimen is irradiated in the *F* band to generate the *F′* band (to right of *F* band) both the *F* and β bands decrease and the α band, previously absent, grows (dashed curve). The peak near 2700A is not relevant.

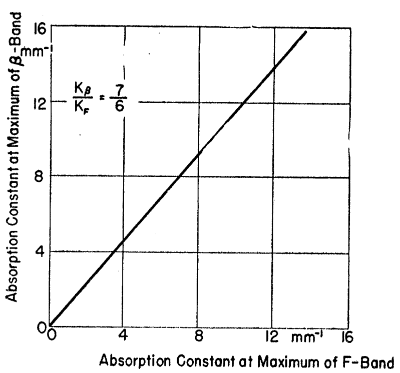


FIG. 25. The linear relationship between the peak intensity of the β band and *F* band found by Martienssen in KBr.

One may conclude from this experiment alone that the β band is intimately connected with the *F* center since the latter is assumed to be the prominent imperfection introduced by additive coloring. On the other hand, there is ambiguity concerning the origin of the α band, for in converting *F* centers to *F′* centers, one produces halogen-ion vacancies, unoccupied by electrons, as well as *F′* centers. Either of these imperfections could be responsible for the α band. Fortunately crystals, colored at low temperatures by x-rays, which have a negligible amount of *F′* absorption show the α band prominently. Hence it may be concluded that the α band is associated with a halogen-ion vacancy and that the *F′* band has no auxiliary band, which is detectable, analogous to the α band and β bands.

These conclusions, first drawn for KI, have been amply confirmed by additional work carried out both at Argonne Laboratories and at Göttingen.[114] For example, the α and β bands have been observed and studied in KCl, KBr, and RbCl as well as KI. Figure 25 shows the degree of proportionality found between the intensities at the peaks of the β and *F* bands for a range of concentration of *F* centers. Figure 26 shows the positions of the peaks of the α and β bands as well as of the first and second maxima in the fundamental absorption band for a number of crystals. The vertical scale indicates the crystal type, whereas the horizontal scale is energy. It can be seen that there is a close correlation between the position of the α and β bands and the first maximum of the fundamental absorption band, designated by I_a in Fig. 26.

What electronic changes take place during absorption in the α and β bands? Since both bands occur on the edge of the fundamental absorption band and evidently are closely connected with the processes

---

[113] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952).

[114] W. Martienssen, Z. Physik **131**, 488 (1952); W. Martienssen and R. W. Pohl, Z. Physik **133**, 153 (1952); W. Martienssen, Nachr. Akad. Wiss. Göttingen **1952**, 111.

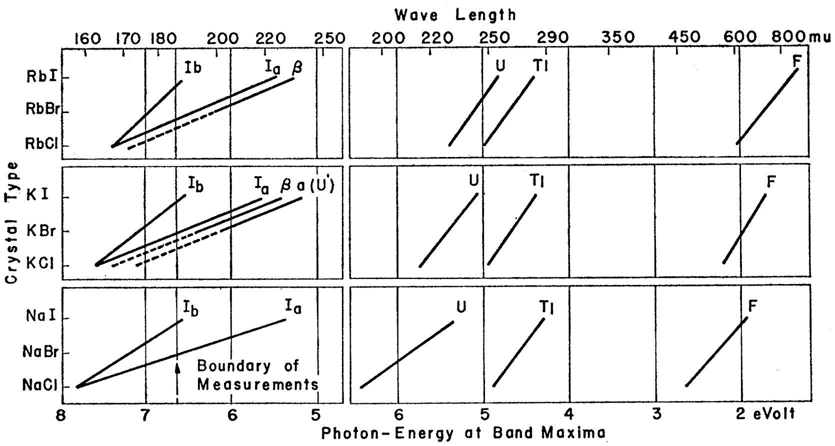


FIG. 26. The positions of the peaks of a number of absorption bands in the alkali halides. The horizontal scale expresses the energy of the photons associated with the peak position. The vertical scale represents different alkali halide crystals of a homologous family. I_a and I_b are the positions of the first two peaks of the fundamental band. α and β are the positions of the α and β bands, known well only for some potassium and rubidium salts. The other lines, to the right, refer to the positions of the U bands, thallium absorption bands, and F bands.

which occur during absorption in the long-wavelength side of the fundamental band, we may conclude safely that both imperfection-induced bands are associated with excitation of electrons on the halogen ions to fairly well-defined higher levels, not present in the perfect crystal. It is reasonable to assume that an electron on the halogen ions is excited to these bound levels when absorption occurs in the α and β bands, for both the F center and the halogen-ion vacancy can bind an electron not present initially. Or, expressed in another way, an exciton which is trapped at the lattice imperfection is produced, the excited electron being more stable than in the perfect crystal because of the attractive potential fields occurring near the halogen-ion vacancy and the F center.

What becomes of the hole associated with the exciton when the electron is bound to the lattice defect? It seems fairly safe to assume that the hole remains part of the complex. In the first place, the F center is neutral so that one would expect both the electron and hole associated with the exciton produced by absorption in the β band to find a state in which all particles are bound. This state would necessarily lie in an ionization continuum of the entire system, for the energy absorbed in the β band is greater than the energy required to ionize the F center by a factor of the order of two. Thus the state attained in this way should be susceptible to autoionization. In point of fact, Apker and Taft[115] have observed a type of photoelectric emission from thin films of the alkali halides that can be associated with this autoionization process in a fairly unambiguous way (see Sec. 40).

The halogen-ion vacancy, in contrast with the F center, has a positive charge, so that it will attract the electron associated with the exciton but repel the hole. Thus the question of whether the hole decides to remain bound or become free, as a result of excitation in the α band, rests upon the result of competition between the attractive force exerted by the electron and the repulsive Coulomb force associated with the vacancy. In general, as the existence of negative ions shows, correlation effects permit the electronic system to do more than compensate for unfavorable Coulomb terms arising from ions, so that we should expect the hole to remain bound in the state achieved by absorption in the α band. This point of view is strongly supported by two auxiliary facts associated with the α band. First, the band is narrow, like the F band, rather than broad like the F' band, as if it arises from a transition between two discrete states. Second, absorption in the α band stimulates a lively, blue fluorescence, which presumably is associated with an optical transition from the excited to the ground state. We would expect a temperature dependent phosphorescence of the bimolecular type, instead of fluorescence, if the hole were made free and recombined with the electron only after wandering about the crystal.

Dexter[116] has examined the oscillator strengths of the α and β bands to be expected on theoretical grounds if the models described above are correct. He assumed that in both cases a $3p$ electron on one of the halogen ions surrounding the vacant site is excited, the hole remaining in the vicinity. He approximated the radial wave function for the $3p$ electron in the manner,

$$\varphi_{3p}=r[\exp(-r/A)-C\exp(-r/B)], \tag{1}$$

in which r is the radial distance from the chlorine nucleus, $A=a_0/1.1$, $B=a_0/8$, $C=23.2$. The unit of distance a_0 is the Bohr radius.

The wave function associated with the electron in the normal F center was taken to have the form

$$\varphi_F=g\exp(-r/\gamma_F), \tag{2}$$

in which r is the distance from the center of the vacancy. This assumption follows the procedure of Tibbs,[117] who treated g as a function of r. For simplicity, Dexter regarded g as a constant and gave γ_F the value k_0a_0, where k_0 is the high-frequency dielectric constant of the crystal (2.25 for NaCl which was treated as a

---

[115] E. Taft and L. Apker, J. Chem. Phys. **20**, 1648 (1952).

[116] D. L. Dexter, Phys. Rev. **83**, 1044 (1951).

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

typical example by Dexter). Tibbs found this value of γ_F to be a good approximation for large values of r.

The F center produced immediately upon excitation in the α band is not the same as the normal F center because the nuclear configuration does not have time during excitation to adjust from the arrangement present before excitation. Since the potential at large distances from a negative-ion vacancy is $e/k_s r$, where k_s is the static dielectric constant (5.62 for NaCl), Dexter selected the corresponding wave function to be

$$\varphi_F{}^* = g\exp(-r/k_s a_0). \tag{3}$$

Similarly, Dexter selected wave functions for the F' centers of the form

$$\varphi_{F'} = g\exp(-Zr/a_0), \tag{4}$$

where

$$Z = (z - 5/16k_0) \tag{5}$$

in which z is the effective charge on the halogen-ion vacancy, taken as $1/k_0$ in atomic units. The value of Z is derived from the well-known variational treatment of the problem of two electrons moving in a Coulomb field.

With use of these wave functions, Dexter found the following values of the oscillator strengths for the α and β bands in NaCl:

$$f_\alpha = 1.89, \qquad f_\beta = 0.612. \qquad \text{(NaCl)}$$

In order to test the sensitivity of the results to the particular values of the parameters chosen, Dexter varied both γ_F and Z. He found that the oscillator strengths were fairly stable. For example, f_β varies from 0.612 to 0.680 if γ_F is changed from 2.25 to 3.0 for $Z = 1/3.27$, the accepted value. Similarly, f_β changes from 0.605 to 0.544 if Z changes from 1/3.00 to 1/5.62 for $\gamma_F = 2.25$. By comparison, f_α has the values 1.23 and 1.22 when k_s in (3) is given the values of 3 and 7.3, respectively, instead of the value 5.62.

The conclusion that f_α and f_β are near unity, rather than much smaller as one might guess at first hand from the small overlap between the $3p$ wave function and those associated with F, F^*, and F', stems from the fact that many electrons contribute to the transition. Any one of the 72 $3p$ electrons in the twelve halogen ions surrounding the halogen-ion vacancy may participate in the transition. Similarly, the conclusion that f_α is of the order of twice f_β arises from the fact that the electron jumping into the halogen-ion vacancy may ignore the spin of an electron already present, as is not the case for the transition involved in the β band.

It is very difficult to compare the half-widths of the α and β bands either with one another or with that of the F band at a standard temperature, such as −180°C, because the first two overlap, when both are present, or overlap the tail of the fundamental band. It seems safe to conclude, however, that the widths of all three bands are the same to better than a factor of two. Thus the height of the peaks of the absorption bands give a relative measure of the product of the oscillator strength and the density of centers. Martienssen[114] has found that in the case of KBr the ratio of the height of the β band to that of the F band is about 1.16 over a tenfold range of extinction coefficient (Fig. 25). Since the oscillator strength of F centers in KBr is presumably in the vicinity of 0.8, in analogy with KCl, we may conclude that the corresponding oscillator strength for the β band is also near unity. These estimates are in good qualitative accord with Dexter's analysis of the oscillator strength of the β band, although they leave much to be desired from a quantitative standpoint.

Table VII contains additional information obtained by Martienssen from two additively colored crystals. The specimen contains very few F' centers after irradiation with infrared light so that the α band is weak. On the other hand, an appreciable part of the β band is replaced by the α band after absorption of light in the F band. However, the fall in the peak of the β band does not equal the rise in peak of the α band, as may be seen from the last column of the table which contains the sum of the previous two columns. Thus we must conclude that f_β actually is somewhat larger than f_α, if the α and β bands have the same width, in contradiction with Dexter's results. It does not seem safe to carry this conclusion very far at the present time. It is certain, however, that the wave function of the electrons in the F center produced by excitation in the α band avoids the halogen ions much more than (3) indicates to be the case (see Sec. 22), so that the overlap of φ_{3p} and φ_{F*} is not as great as Dexter's procedure implies. The corresponding drop in the overlap of φ_{3p} and $\varphi_{F'}$ would not be as great because the wave functions of the negatively charged F' center are certain to be more diffusely distributed than φ_{F*}.

Does any other center of the type of general interest in the theory of colored alkali halides possess an absorption band analogous to the α and β bands? In considering this problem, we may note that the F' center does not have such a band and for the following evident reason: The F' center is a saturated electronic system; any electron added to it would have to be promoted to the $2s$ state, if we regard the normal state of the electrons in the F center as being of the $1s$ type. The additional energy of promotion is prohibitive. This tells us that we might not expect to find such an absorption peak for the F_2 center (R center formed by union of two F centers) since here too the excited

TABLE VII. Absorption constants at peaks of F, β, and α bands in additively colored KBr. (Absorption in units of mm^{-1}.)

After irradiation with	F band (6110A)	β band (1930A)	α band (2020A)	$\alpha+\beta$
Infrared	5.10	6.3	0.44	6.74
	4.89	6.21	0.54	6.75
F light	2.47	3.3	2.26	5.56
	2.40	3.10	2.38	5.48

electron would be promoted. On the other hand, there seems to be no obvious reason why the M center and the F_2^+ center (R center formed of union of an F center and a halogen-ion vacancy) could not have peaks analogous to the β band. The density of both these centers, however, is usually small compared with the density of F centers. Thus, since the β band already lies close to the fundamental band, such peaks may be difficult to resolve, even if they exist.

We might also expect divalent impurity ions, such as Ca^{++} and Sr^{++}, which presumably can accept and bind an electron in much the same way as a halogen-ion vacancy, to possess absorption bands at the edge of the fundamental band.

Does the neutral pair of vacancies possess a "Greek" band? At first sight this appears to be plausible, however, there are good reasons for believing that the band does not exist. Apparently an electron would be very weakly bound to the pair, for otherwise we might expect to find centers corresponding to such combination, formed by union of F centers and the positive-ion vacancies always present as a result of divalent impurities. Moreover, we shall see in subsequent sections that the hole is very weakly bound to a free positive-ion vacancy and hence should be even more weakly bound to the pair. Thus the exciton formed at the pair would presumably gain little if any stability from the presence of the pair. At most we might expect pairs to add to the distortion of the edge of the fundamental band.

It would be very interesting to examine the absorption in the region of the Greek bands in clear crystals which have been deformed plastically. The experiment of Gyulai and Hartly (Sec. 10) suggests that free positive- and negative-ion vacancies are formed by plastic flow and that these will combine at room temperature. It would be interesting to see if the α band appears immediately after plastic flow and if this band disappears as the ionic conductivity induced by plastic flow falls.

VI. CRYSTALS CONTAINING A STOICHIOMETRIC EXCESS OF HALOGEN

25. Mollwo's Work

Mollwo[118] demonstrated in 1937 that it is possible to impregnate KBr and KI with an excess of halogen and thereby introduce a sequence of absorption bands in the ultraviolet which are members of what have since been termed the V bands (Fig. 4). This work shows that there is a close correspondence between the properties of crystals containing excess halogen and those containing excess alkali metal, although there are striking differences, apart from the shift in wavelength of the absorption bands. The most notable features are as follows:

(a) Mollwo did not succeed in coloring the chlorides with excess chlorine in spite of the fact that he used pressures in the vicinity of 100 atmospheres and temperatures near 700°C. He concluded that either chlorine is not soluble, or it does not diffuse sufficiently rapidly at the temperatures employed. It is interesting to speculate briefly on this point. The simplest way for an excess of halogen to diffuse into the crystal is to have vacant metal-ion sites and holes migrate from the surface into the interior, the metal ions and electrons produced thereby interacting with the halogen atoms at the surface and building new layers of alkali halide crystal. Since both metal-ion vacancies and holes are very mobile, it seems most likely that coloration is not observed in chlorides either because the solubility is very small or because the activation energy for the reaction at the surface is excessive. This will be discussed in more detail below.

(b) The concentration of halogen in the crystals was determined by measuring the total charge in excess of the purely electrolytic charge which would flow in absence of the color center when the halogen is removed with use of an electrostatic field at high temperature. This technique proved to be more reliable than one using the area under the absorption bands (Fig. 4), although the results obtained from the two methods are roughly proportional. Mollwo concluded from a comparison of the two methods that the oscillator strength associated with the absorption bands in KBr is of the order of 0.1 to 0.2, whereas that in KI is nearer unity. In any event, the concentration of halogen in the crystal varies directly with the first power of the pressure of the *diatomic* halogen gas, in contrast with the intensity of the F bands for additive coloring with excess metal, which varies as the first power of the pressure of the *monatomic* gas. This indicates that the bands shown in Fig. 4 are presumably to be associated with centers containing *pairs* of positive-ion vacancies. At the present time the two poorly resolved peaks shown in Fig. 4 are termed the V_2 and V_3 peaks and are believed to be associated with units consisting of two positive-ion vacancies with one and two holes, respectively, analogous to the R_1 and R_2 centers observed in crystals containing excess alkali metal. The small peak near 3 ev in Fig. 4 is probably not a volume imperfection since it is not found in specimens darkened by x-rays (see Part VII). Figure 27 shows the solubility of Br_2 in the crystal as a function of both temperature and the pressure of Br_2 in the vapor. It may be seen that the relative solubility of the gas in the crystal is less than 10^{-3} even at 700°C. The heat of solution of the gas in the crystal is found to be -1.2 ev per molecule in KBr. The corresponding value for I_2 in KI is -0.8 ev. These are to be contrasted with the values of $+0.10$ ev and $+0.25$ ev per atom found by Rögener for potassium in KCl and KBr, respectively.

{*Note added in proof.*—L. M. Shamovsky [Doklady Akad. Nauk SSSR **91**, 229 (1953)] has proposed a

---

[118] E. Mollwo, Nachr. Akad. Wiss. Göttingen **1935**, 215; Ann. Physik **29**, 394 (1937).

mechanism for the formation of V centers from the vapor.}

26. Models of V Centers

It should be mentioned that Mollwo recognized the diatomic nature of the centers responsible for the V_2 and V_3 bands in his original work but did not attempt to propose specific models. In 1950 the writer[119] and Nagamiya[120] suggested models involving positive-ion vacancies and holes independently. In particular, the writer suggested that the most prominent band observed by Mollwo, namely V_2, is to be associated with the unit consisting of two vacancies and one hole, whereas the V_3 center is to be associated with the unit consisting of two vacancies and two holes, analogous to a halogen molecule embedded in a void in the crystal. Nagamiya focused attention on the second center and discussed some of its properties. Since 1950 much more information has accumulated concerning the properties of the V_2 and V_3 centers. The writer has decided, as a result of the present analysis, that the original models for the two centers should be inverted, that is the assignment should be that given in Fig. 28 instead of that proposed in 1950. The new assignment has many advantages over the old which will appear as we proceed. In particular the neutral diatomic pair, namely, the V_2 center of Fig. 28, is now assumed to be responsible for the dominant peak in Mollwo's absorption spectrum.

Arguing by analogy with specimens containing excess alkali metal, we might expect to find the four centers, designated by V_1, V_2, V_3, and V_4 in Fig. 28, in crystals containing excess halogen. V_1 is the analog or the antimorph of the F center, whereas V_4 is the analog of the M center. As we shall see in the next section, absorption spectra which the writer has associated with the V_1 and V_4 centers have been observed in specimens of the alkali halides irradiated with x-rays at liquid nitrogen temperatures. Both these bands vanish if the crystals are warmed to room temperature; thus they could not have been observed by Mollwo, who restricted observations to room temperature. It may be added that the V_2 and V_3 bands shown for KBr in Fig. 4 are also observed in the specimens irradiated with x-rays.

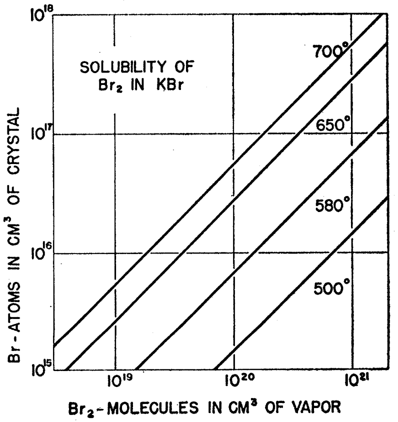


FIG. 27. Isotherms of solubility for Br_2 in KBr. It may be seen that the solubility varies linearly with the concentration of Br_2 in the vapor (after Mollwo).

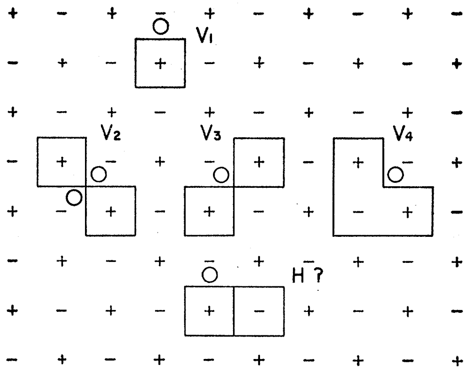


FIG. 28. Proposed models of the V centers. V_1 is assumed to be the antimorph of the F center, consisting of a hole plus a positive-ion vacancy, whereas V_2 and V_3 are the antimorphs of the R centers. It is suggested that V_3 is the negatively charged unit consisting of one hole and two positive-ion vacancies, which should repel electrons that do not overlap the hole distribution. V_4 is the antimorph of the M center. It is possible that the H band observed by Duerig and Markham originates from a hole trapped at a pair of neutral vacancies.

The V_3 center pictured in Fig. 28 possesses an excess negative charge because the hole present in it neutralizes only one of the positive-ion vacancies. As a result, this center should repel a wandering free electron, the energy of repulsion being $e^2/k_s r$, in which e is the electronic charge, k_s is the static dielectric constant, and r is the radial distance of the electron from the center. At room temperature the thermal energy of an electron is of the order of 0.025 ev. Since k_s is in the neighborhood of 5 for a typical alkali halide, we see that the closest distance of approach of the electron would be near 50A at this temperature. The distance would be greater at lower temperatures. In consequence, free electrons should experience difficulty in annihilating the holes associated with V_3 centers. It follows by analogy that a free hole would experience difficulty in annihilating the electron associated with the R_1 center shown in Fig. 2.

We shall see in Sec. 29 that the V_3 band found in crystals colored by x-rays actually appears to resist bleaching under conditions in which free electrons are present in the lattice, whereas the V_2 band does not. This is one of the strongest pieces of evidence to support the models proposed in Fig. 28. It should be emphasized, however, that the basis for these models is, at present, not nearly so good as that supporting the models presented in Fig. 2 for the F-type centers. This

---

[119] F. Seitz, Phys. Rev. **79**, 529 (1950).

[120] T. Nagamiya, J. Phys. Soc. Japan **7**, 358 (1952). Previous publication in Japanese in Busseiron Kenkyu, March, 1950.

aspect of V band theory is still in its rudimentary stages at present.

Mollwo's[118] observation that both V_2 and V_3 centers occur in the crystals is remarkable and somewhat mysterious. It should be mentioned, however, that the specimens were subject to special treatment after being additively colored with halogen. Following impregnation at high temperatures and pressures, the crystals were cooled at a normal rate to room temperature. The absorption band found in one of the specimens at this stage was quite irregular and is ascribed to the presence of colloidal aggregates since, at least in the case of the iodide, the band resembles the absorption spectrum of finely divided iodine crystals. To obtain curves of the type shown in Fig. 4 the crystals were heated to 600°C in air and quenched to room temperature in carbon tetrachloride. The results suggest in a rather vague way that V_2 centers, that is, what are in effect halogen molecules in solution, are produced overwhelmingly during the initial heating in the presence of halogen gas. The units precipitate to form colloids of halogen during the subsequent slow cooling. These aggregates are redissolved and other centers are formed during the heating and quenching process. If V_3 centers were present in appreciable quantities during the initial heating, it would be necessary to account for the state of the extra hole responsible for balance of charge. This hole would contribute to the entropy of the dissolved system if it were free and one might expect the solubility to vary as the square root of the pressure of halogen gas, much as if two V_1 centers were formed.

27. Energy of Solution

The energy of solution of the halogen in the crystal may be discussed in terms of the following cycle:

(a) Remove two positive ions from the crystal, thereby forming two positive-ion vacancies. An energy $2V_+$ is required.

(b) Remove two electrons from the top of the filled band and take them out of the crystal, thereby creating two holes. An energy $2H$ is expended. H is the work required to form one hole and presumably is the sum of the energy P needed to form a pair and the energy χ required to remove an electron from the conduction band to the outside of the crystal.

(c) Dissociate one of the halogen molecules to form two halogen atoms. An energy D is required.

(d) Add the two electrons removed in step (b) to the halogen atoms. An energy $-2A$ is required, where A is the electron affinity of the halogen atom.

(e) Combine the halogen ions and positive ions and add them to the surface of the crystal in typical positions. An energy $-2S$ is required, where S is the energy of sublimation of a pair of ions from the surface.

(f) Combine the two positive-ion vacancies and the two holes to form a V_2 center. An energy $-V_2$ is required. This term presumably cannot be neglected even if the halogen is dissolved at high temperatures, for Mollwo's experiments indicate it to be sufficiently large that V_2 centers are formed as the major equilibrium product. We apparently must assume that the energy needed to form V_3 centers from the two vacancies and one of the holes and to bind the extra hole at another, unknown, position is essentially the same as V_2, if V_3 centers actually occur.

Only a partial list of the energies appearing in this cycle is available, even if we are willing to restrict attention to differences for a pair of substances such as KCl and KBr, instead of requiring absolute values. Values for these two materials are as follows:

(a) Mott and Littleton have estimated that V_+ is 4.47 ev and 4.23 ev for KCl and KBr, respectively. These are based on lattice calculations.

(b) The writer estimates, from an analysis of the position of the edge of the fundamental absorption bands, that H is about 0.8 ev larger for KCl than for KBr. Absolute values are not accurately known since the limit of the exciton spectrum is uncertain.

(c) The dissociation energies of Cl_2 and Br_2 are 2.47 ev and 1.97 ev, respectively.

(d) The electron affinities of Cl and Br are 3.83 ev and 3.65 ev.

(e) The energy of sublimation to the state of free ions is 7.17 ev for KCl and 6.81 for KBr.

(f) Essentially nothing is known about the energy of dissociation of the V_2 and V_3 centers into their components; however, they would seem to possess binding energies in the vicinity of 1 ev if they remain undissociated at temperatures near 1000°K, as Mollwo's results suggest.

The difference ΔE in the heat of solution of Cl_2 and Br_2 in KCl and KBr, respectively, is found to have the value

$$\Delta E(\mathrm{KCl},\mathrm{KBr}) = 1.54 \text{ ev} - \Delta V_2$$

per molecule, if we combine the foregoing values of the constituents in the cycle. ΔV_2 is the difference in the energy of dissociation of the V_2 centers. Since we know little at present about this quantity, it is not possible to say whether the energy required to form a hole is the most important bottleneck in inhibiting the solution of the halogens.

Nagamiya[120] has carried out a cyclic calculation closely related to the foregoing. In effect, he dissociates a gaseous halogen molecule into atomic constituents, introduces these into the normal halogen positions of a neutral quartet of vacant lattice sites and then allows the halogen atoms to assume the normal spacing they possess in the free molecule, thereby regaining, by assumption, the energy of dissociation of the molecule. The energy required to form the quartet is calculated by adding the energy required to form two positive-and two negative-ion vacancies, all separated from one another, to the simple (negative) electrostatic energy of attraction of the four when arranged in the quartet configuration. The vacancies are regarded as point charges at normal lattice positions in calculating the electrostatic energy of the quartet. Lattice polarization is taken into account by treating the crystal as a continuous dielectric medium. The corresponding energies of formation of the diatomic center (termed V_2 in this review, but V_3 by Nagamiya, and by the writer, in 1950) are listed in Table VIII.

The energies of free vacancies, in the second column, are theoretical values obtained by the method of Mott and Littleton. They are unquestionably low. For example, the experimental value for KCl, discussed in Sec. 5, is $2\times 2.4=4.8$ ev. However the method evidently has value as a means of extrapolating from the bromide and iodide to the chloride. It suggests that the energy of solution of the chloride should be only slightly larger than that of the bromide.

Alexander and Schneider[121] have found that V centers can be produced to the exclusion of F-type centers in KCl by darkening the crystals with x-rays and removing the F centers by electrolysis with a strong electrostatic field. Both F type and V centers are produced in the darkening process; however, a field of the order of 2000 volts per cm, in combination with irradiation in the F band, apparently is adequate to remove the F centers and leave pure V centers. The investigators used crystals of the order of $10\times 5\times 1$ mm in the work so that normal-sized specimens can apparently be treated in this way.

Uchida and Ueta[122] have reported preliminary results on the properties of V centers formed additively in NaI and KI, either by heating in iodine vapor or by passing a current from a pointed anode into the crystal. They have found two peaks in KI at 3650A and 2980A, which appear to coincide with the main peaks observed by Mollwo. A third peak appears at about 2600A. This, however, is found only in crystals darkened by heating in the vapor. The investigators conclude that the third peak may not arise from V centers. The ratio of the intensities of the peaks observed at 2650A and 2980A is independent of the absolute intensity of the bands and the way in which they are formed. It is concluded, as a result, that both peaks probably arise from a single center. The peaks may be bleached by irradiating with light in the near-ultraviolet portion of the spectrum. They are replaced by a broad absorption band extending from the tail of the fundamental absorption band to the near ultraviolet. The original bands may be regenerated by heating the crystals to 250°C.

TABLE VIII. Energy of formation of neutral diatomic V center (V_2) (in ev, after Nagamiya).

Crystal	Energy of free vacancies	Electrostatic energy of quartet	Total	Observed
KCl	4.16	−2.5	1.7	
KBr	3.84	−2.4	1.4	1.2
KI	∼3.3	−2.1	∼1.2	0.8

The observation that the V centers may be formed by electrolytic means with the use of a sharp anode provides additional evidence for the view that they are the result of the appropriate combination of holes and positive-ion vacancies.

Glasner and Tompkins,[123] as a result of a study of regularities in the positions of the bands associated with the color centers in the alkali halides, have proposed models which, in some cases at least, are at strong variance with those employed in this article. For example, they propose that the V_1 band is associated with an isolated positive-ion vacancy and that the β band is associated with an isolated negative-ion vacancy. They suggest that the α band is to be associated with an aggregate of vacancies. It is very difficult to fit their interpretation of the system of centers into the general pattern of experimental material available. For example, one would not expect to find the β band varying linearly with the concentration of F centers in additively colored crystals if it is associated with isolated negative-ion vacancies. Similarly, one would expect to find the V_1 band in uncolored crystals containing divalent impurities if it is associated with positive-ion vacancies alone.

The writer believes that further experimental study of crystals containing excess halogen has been deferred far too long and that these materials should be reexamined in the light of our present knowledge of the properties of the alkali halides. It would be particularly interesting to know if V_1 centers can be produced by suitable quenching to low temperatures, or if the V_2 or V_3 centers can be converted to V_1 centers by irradiation with x-rays at a suitable temperature.

VII. PROPERTIES OF CRYSTALS COLORED ABOVE 50°K

A great deal of important research has been carried out on the properties of crystals which have been darkened by x-rays at nitrogen temperatures, as a result of the general availability of liquid nitrogen and x-ray sources. This work will be summarized in the present section. Special attention will be devoted to investigations at helium and hydrogen temperatures in the next section since such work has disclosed phenomena not found at higher temperatures.

---

[121] J. Alexander and E. E. Schneider, Nature 164, 653 (1949).

[122] Y. Uchida and M. Ueta, see abstracts of Sections B and C of the meeting of the International Union of Pure and Applied Physics, Kyoto, Japan, September 1953, p. 93. See also Y. Uchida and Y. Naki, J. Phys. Soc. Japan 8, 795 (1953).

[123] A. Glasner and F. C. Tompkins, J. Chem. Phys. 21, 1817 (1953).

28. Absorption Bands; Darkenability

Studies of the absorption bands of crystals darkened by x-rays have yielded a wealth of information, particularly in the ultraviolet where the V bands are situated. In some respects this work was anticipated by the work of Molnar before the war, however, the great majority has been carried out since 1946 at a number of laboratories in Europe, Japan, and the United States. It is perhaps worth mentioning again that the extensive research on additively colored crystals prior to the war provided an essential link in the interpretation of the later work by permitting a clear separation of bands derived from F centers and the V bands.

We have already mentioned, in Part IV, Harten's measurements on the rate of production of F centers by x-rays over a range of temperature. Essentially coincident with this, Burstein and Oberly explored the visable and infrared portions of the spectrum of KCl and NaCl darkened at $-190°C$ and discovered the N band, which had been missed by Molnar. This lies at about 9700A in KCl. As remarked in Sec. 16, Petroff had observed this band during the war in additively colored crystals in which partial aggregation had been induced by irradiating with light lying in the F band (see Fig. 17); however, his measurements were not published until 1950.

The most important extensions of prior information were made in the ultraviolet portion of the spectrum in connection with the resolution of the V bands and the α and β bands, described in Sec. 24. The outstanding exploratory work on the V bands was carried out by Casler, Pringsheim, and Yuster[124] and by Dorendorf,[125] the latter, in the main, confirming and extending the very valuable work of the former group. These investigators found that if crystals are irradiated at room temperature, or are irradiated at liquid nitrogen temperature and warmed to room temperature, one obtains the V_2 and V_3 bands observed by Mollwo in crystals containing an excess of halogen (Fig. 4). This point had actually been verified independently by Alexander and Schneider.[121] Figure 29 shows the overlapping V_2 and V_3 bands, obtained at room temperature in KBr by Casler, Pringsheim, and Yuster and by Schneider and Alexander, and provides a comparison with the results obtained by Mollwo.

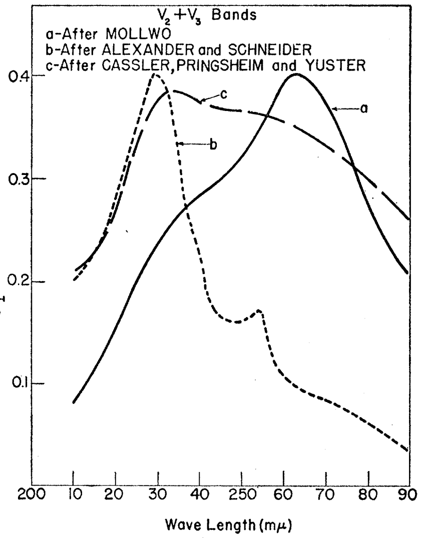


FIG. 29. The envelope of the V_2, V_3 bands observed by three different investigators. Curve a, due to Mollwo, is for a crystal containing excess halogen, whereas the other two are obtained from crystals darkened with x-rays.

What is more exciting, however, the Argonne group observed a new band, now termed V_1, when they irradiated at liquid nitrogen temperatures. It is responsible for a large part of the absorption in the ultraviolet when measurements are made near liquid nitrogen temperature, but it vanishes if the crystal is heated above $-100°C$. This band and the changes in absorption induced by warming the crystal to $-80°C$ are shown in Fig. 30 for KCl, which is fairly typical of the alkali halides. The V_1 band peaks near 3600A in this case, and near 4100A in KBr. It may be seen that a second absorbing region is evident in the portion of the spectrum below 3000A. This region may be resolved into the V_2 band, which peaks near 2300A and a band, designated as V_4 by Dorendorf, which peaks near 2540A. The V_4 band, like the V_1 band, vanishes when

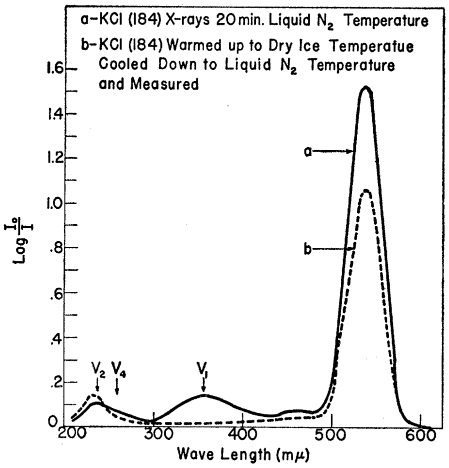


FIG. 30. The V_1 band produced by Castler, Pringsheim, and Yuster by irradiating KCl with x-rays at liquid nitrogen temperature (full curve). This vanishes when the specimen is warmed to room temperature (dashed curve). The intensity of the F band diminishes at the same time. There is also a shift at the ultraviolet end of the spectrum, indicating that the V_4 band diminishes and the V_2 band grows.

---

[124] Casler, Pringsheim, and Yuster, J. Chem. Phys. 18, 887, 1564 (1950).

[125] H. Dorendorf, Z. Physik 129, 317 (1951). See, also, H. Dorendorf and H. Pick, Z. Physik 128, 166 (1950).

the crystal is warmed to dry ice temperature. Figure 30 also shows that the F band decreases during warming to dry ice temperature, whereas the absorption in the region of the V_2 and V_3 bands increases.

Figure 31 illustrates a sequence of absorption measurements made by Dorendorf on specimens of KCl held at various temperatures between $-180°C$ and $20°C$ during irradiation. In each case the measurement was made at $-180°C$ in order to obtain high resolution. Moreover, each specimen was raised to room temperature after initial observation; following this it was again cooled to $-180°C$ and a new measurement was made. The second absorption measurements are also shown.

TABLE IX. Position and widths of the principal V bands in KCl and KBr (in angstroms and ev, after Dorendorf).

	V_1	V_2	V_3	V_4
	3560	2300	2120	~2540A
KCl	3.48	5.37	5.83	~4.87 ev
	0.73	0.5	0.35	ev (Half-breadth)
	4100	2650	2310	2750A
KBr	3.02	4.67	5.35	4.50 ev
	0.7	0.6	0.45	~0.4 ev (Half-breadth)

It can be seen in Fig. 31 (a), which depicts a specimen darkened initially at $-180°C$ where the V_1 band is clearly visible, that the process of heating to room temperature removes the V_1 band and presumably all of the V_4 band. The F band drops and the F' band disappears entirely. The V_3 band is initially very weak and the V_2 band appears to change very little. The V_1 and V_4 bands are not present in specimens irradiated at the higher temperatures. Most of the changes obtained on heating appear to be associated with the freeing of electrons from the F' centers or possibly other F-type centers. The greatest change in the V bands resulting from the warming step is the growth of the V_3 band and the fall of the V_2 band. This is precisely what we would expect if the models of the V_2 and V_3 centers are as shown in Fig. 28. The electrons released from the F' centers may annihilate one of the holes associated with the V_2 centers, transforming them into V_3 centers; however, the latter will resist bleaching since they are negatively charged.

We shall see in Sec. 30, in describing work of Dutton and Maurer, that the V_4 band bleaches at about $-27°C$ in KBr during warming, whereas the V_1 band bleaches at about $-158°C$. Thus the two centers have rather different stability for thermal decomposition.

It is appropriate to mention at this point that Casler, Pringsheim, and Yuster found that electrons freed photoelectrically from F centers at room temperature with the use of F light bleach V_2 centers with high efficiency, whereas V_3 centers are little affected if at all. This work supports the view that the holes in V_3 centers resist annihilation by free electrons, whereas those in V_2 centers are much more susceptible.

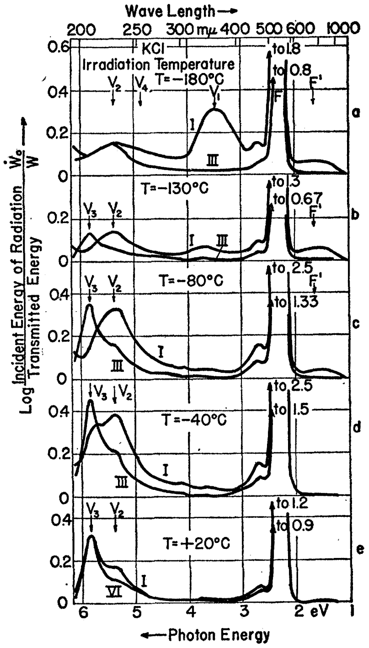


FIG. 31. The V bands produced in KCl when irradiated with x-rays at various temperatures. The curve I in each panel shows the absorption spectrum immediately after irradiation, whereas curve III shows the spectrum after the specimen was raised to room temperature. All measurements were made at liquid nitrogen temperature to achieve maximum resolution. In this material the V_3 band grows on warming, whereas the other bands decrease (after Dorendorf).

Dorendorf has made a similar series of measurements for KBr. The results are about the same, on a relative scale, with two important exceptions: The V_4 band is much closer to the V_2 band in KBr; the relative amplitudes of the V_2 and V_3 bands are initially the reverse of those found in KCl, and, in fact, are the reverse of those found by Casler, Pringsheim, and Yuster (Fig. 29), thus resembling on the whole the amplitudes found by Mollwo[118] (Fig. 4). One may conclude that the initial ratio of the two bands depends upon the history of the specimen.

Although the same terminology, namely, V_1, V_2, V_3, and V_4 is used to designate the V bands observed in KCl and KBr, it is not completely certain at the present time that the lattice imperfections responsible for the individual bands actually are equivalent in the two cases. The V_1 band is sufficiently unique that there seems to be little doubt that this has the same origin in the various crystals in which it has been observed; however, a degree of uncertainty remains in the other cases.

Table IX contains the principal facts about the V bands for KCl and KBr, as tabulated by Dorendorf.

Dorendorf[125] observed relatively strong absorption on the high-energy side of the four V absorption bands discussed above and designated the corresponding region by V_5. This absorption is probably associated with the α and β bands, and will be discussed independently below. He also observed a pair of relatively small peaks on the long-wavelength side, which he termed V_6 and V_7. These peaks do not appear to have been observed generally and it is best to set them aside until it is demonstrated that they are not characteristics of the particular specimens used.

The writer[119] proposed that the center responsible for the V_1 band is the antimorph of the F center (Fig. 28), in keeping with the view that the V_2 and V_3 centers have diatomic character. Although these assignments are still conjectural, they seem to be in agreement with the facts which are available at the present time. Initially, it was suggested that the V_1 band vanishes when the crystals are heated above $-100°C$ because of a high intrinsic mobility the positive-ion vacancy might possess at this temperature, in spite of the fact that it has a hole attached to it. Subsequent work by Dutton and Maurer[126] makes it appear certain, however, that the V_1 center decomposes by evaporation of the hole, which either is annihilated at an F-type center, or is captured by a V_3 center to form a V_2 center. As we saw above, there is unambiguous evidence that the freeing of electrons from F-type centers, particularly the F and F' centers, leads to the growth of the V_3 band at the expense of the V_2 band, as we should expect from the models proposed in Fig. 28. Unfortunately the evidence concerning the nature of the changes produced in the V_2 and V_3 bands when the V_1 band vanishes on heating is not very precise at the present time. The V_3 band appears to be small in most cases after low-temperature irradiation, and both it and the V_2 band are somewhat obscured by the V_4 band. On the whole, however, Dorendorf's work, particularly that on KBr, supports the view that the V_3 band diminishes and the V_2 band grows when the V_1 centers dissolve on warming.

It may be added that the V_3 center should exhibit spin paramagnetism if the model proposed in Fig. 28 is correct, for it has only one hole associated with it, whereas the V_2 center should be diamagnetic.

An alternative to the assignment of models for the V centers shown in Fig. 28 assumes that the V_4 band arises from the antimorph of the F center, that is from the center designated as V_1 in Fig. 28, and that the V_1 band is to be associated with a center which is the antimorph of the F' center, that is, contains two holes and a single positive-ion vacancy. This association would be in keeping with the observation that the V_1 band bleaches at a temperature not radically different from that of the F' center, whereas the V_4 center persists to higher temperatures. The strongest objections to this asignment arise from the fact that the V_1 band does not possess other attributes of the F' band. It has a bell-type shape, more nearly like that of the F band. Moreover, work of Teegarden and Maurer,[127] to be described later (Sec. 33) shows that the photoconductive yield of holes, when the V_1 centers are irradiated with light in the V_1 band, is small, in contrast with the situation for the F' centers. Conversely, the V_4 centers possess a relatively high yield. To summarize, the V_1 band behaves very much as if it were the result of a transition between two discrete levels, rather than like the F' band which behaves like the result of a transition from a discrete level to an ionization continuum. At the time this is written, the writer is inclined to the view that the antimorph of the F' center exists only at very low temperatures, if at all.

The association of the V_4 band with the antimorph of the M center is a plausible relation if there is a close qualitative correspondence between the F- and V-center systems. Ueta, studying absorption with polarized light, has demonstrated very convincingly that the M center has the low symmetry of the configuration shown in Fig. 2. These measurements will be described in the next section. It is possible that a similar investigation could be made with V_4 centers, perhaps in a case such as KCl where the V_4 band is moderately well separated from the V_2 band.

Among the various bleaching experiments on x-ray darkened crystals, which will be reviewed in the next section, there is an investigation by Dorendorf[125] which merits discussion here. He darkened a specimen of KCl at room temperature until it contained a prominent F band and a V-type band which was probably the result of superposition of V_2 and V_3 bands. The crystal was then irradiated at room temperature with light from an incandescent lamp, filtered so that only radiation having wavelength greater than 5000A was incident on the specimen. The F band was bleached entirely with a quantum yield not appreciably smaller than unity. The V_2 band subsided, perhaps completely; however, most if not all the V_3 band remained. There was no evidence of an F-type band to wavelengths as long as 9000A. The results obtained in this experiment appear to be almost unique in bleaching experience, as we shall see in the next section, for the F band usually resists complete bleaching if visible light alone is used. The simplest explanation to offer in the present case is that a fraction of the electrons freed from the F centers, sufficient to compensate for the holes in the V_3 band, migrated from the crystal, leaving it with a stoichiometric excess of halogen. In effect, the initial x-irradiation might be said to have decomposed a part of the alkali halide, producing what can be regarded as alkali metal and halogen centers (F and V centers). A part of the former migrates from the specimen during irradiation, combines with another agent, perhaps oxygen from the air, and leaves an excess of halogen in the specimen in the form of V_3 centers. Since the latter are negatively charged, according to the picture presented here, the negative-ion vacancies associated with the original F centers should remain in such number as to preserve neutrality.

Schneider[128] and his co-workers have investigated

---

[126] D. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953). See, also, Dutton, Heller, and Maurer, Phys. Rev. **84**, 363 (1951).

[127] K. Teegarden and R. J. Maurer (to be published).

[128] E. E. Schneider, *Photographic Sensitivity* (Butterworth Scientific Publications, London, 1951), p. 13; Grant, Hesketh, and Schneider (to be published); also, D. F. Grant, thesis, University

the darkening and bleaching of KCl at room temperature and have come to a number of interesting conclusions. We shall discuss the darkening here and defer bleaching to the next section. This group restricted attention to temperatures at and above room temperature and placed particular emphasis on the relatively low level of darkening in which no more than 5×10^{17} F centers are produced per cc. They found that the darkening increases relatively rapidly at start under x-ray bombardment and then attains a constant rate of increase which is retained throughout the range studied. In KCl the initial rate of darkening is so rapid that only 18 ev is required to form one F center, although the equilibrium energy in the linear portion of the range is about 53 ev. These results are remarkably different from those of Harten, described in Sec. 13 (see Fig. 14). He found that the energy required to form an F center in KCl near room temperature is somewhat above 100 ev, even in the initial range. Schneider employed two intensities, differing by a factor of ten; however, the results were not highly sensitive to intensity for KCl. Moreover, the highest intensity used was about the same as Harten's, namely, *ca* 10^{-4} watt/sec.

Schneider has compared the results obtained by his own group for KCl with earlier work of Leitner[129] using natural NaCl and irradiation by x-rays, β rays, and γ rays. About 40 ev was required to produce an F center with x-rays of intensity comparable to those employed by Schneider and associates under optimum conditions, whereas the value in the steady-state linear range was several times this. The efficiency differed relatively little for x-rays and for β rays of one hundredth the intensity. In contrast, about 2000 ev was required to produce an F center with γ rays.

The highly erratic nature of these results suggest that either chance impurities or the mechanical history of the specimen plays an enormous role in determining the efficiency of coloration at room temperature. It is interesting to note that the highest efficiency observed by Schneider in the case of KCl is only about three times lower than that attained by Smakula[61] irradiating in the tail of the fundamental band.

As we have remarked earlier in this section, Schneider and his associates also observed a somewhat poorly resolved version of the V_2-V_3 absorption (Fig. 29).

The quantum efficiency very close to unity observed by Smakula during the initial stages of darkening is difficult to understand on any ground unless one assumes that the halogen-ion vacancies involved are present initially either fully formed or as units relatively weakly attached to a dislocation, possibly as incipient vacancies.[130] It is possible that a small number of vacancies are produced by the mechanical strain incident to handling the specimens and that they capture electrons from the excitons generated during irradiation in the fundamental band, producing F centers and free holes. If this point of view is accepted, it is necessary to assume that any current associated with the free holes is sufficiently small, relative to normal electronic photocurrents produced in the alkali halides, that it would not have been detected in the experiments of Hilsch and Pohl which led to the conclusion that a negligible photocurrent is produced by irradiation in the fundamental band. This seems to be a perfectly reasonable assumption since Teegarden and Maurer have concluded that the displacement distance of a free hole is only a few percent of that of a free electron in typical specimens, possibly because holes have a low mobility.

It is worth emphasizing again, that Hummel[63] has demonstrated that the addition of $CaCl_2$ to KCl enhances the darkenability of this salt at room temperature. Etzel[131] has shown that NaCl is also "sensitized" by $CaCl_2$, both the F-type and V-type centers being generated more readily at room temperature. Interestingly enough, NaCl is not sensitized by additions of $CdCl_2$. Etzel has suggested that this difference originates in the possibility (see Sec. 6) that the positive-ion vacancies introduced by the divalent cadmium ions are entirely associated at room temperature and hence act as poor traps for holes, whereas the positive-ion vacancies introduced by divalent calcium are not associated and, as a result are available to assist in the formation of V centers. This explanation has much merit if further work shows that the V centers which can be formed are particularly resistent to bleaching by free electrons, as the V_3 center proposed in Fig. 28 would be.

Schulman[132] has recently summarized the experimental evidence concerning the influence of impurities upon darkenability and has suggested that they may play three independent roles: (1) They may accentuate mismatch when the lattice is formed and increase the density of dislocations; (2) they may enhance the density of vacancies available for the trapping of electrons and holes, just as the divalent ions enhance the density of positive-ion vacancies; and (3) they may act as traps for electrons and holes. He has also suggested that the ideally pure crystal may not darken under the action of ionizing radiation since the impurities are essential catalysts for the process. The writer is inclined to believe that dislocations alone should be adequate catalysts; however, it would be exceedingly desirable to carry out investigations on crystals far purer than any now available.

There is another possible influence of divalent additions which may be important at temperatures near room temperature where normal diffusion is appreciable. It has been emphasized previously that the positive-ion vacancies may assist negative-ion vacancies to

---

of Durham, Durham, England (1950); R. V. Hesketh, thesis, University of Durham, Durham, England (1953).

[129] I. Leitner, Sitzber. Akad. Wiss. Wien **145**, 407 (1936).

[130] F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

[131] H. W. Etzel, Phys. Rev. **87**, 906 (1952).

[132] J. H. Schulman, J. Phys. Chem. **57**, 13 (1953).

migrate by forming pairs. Thus the positive-ion vacancies introduced along with the divalent additions may help to disperse the negative-ion vacancies formed from the dislocations by the action of the absorbed radiation and thereby enhance darkenability. This action evidently would be effective only at temperatures where the positive-ion vacancies are not tightly associated with the divalent ions. At the time this is written the writer is inclined to give more credence to such an interpretation of the influence of divalent additions on darkenability than any of the others. If it is correct, the sensitization relative to pure crystals should diminish at low temperatures where the positive-ion vacancies are immobile.

Cunnell and Schneider[13] have found that specimens of NaCl and KCl quenched from 750°C darken more rapidly than unquenched specimens, the darkening ratio varying between 1.07 and 1.25 in typical cases. It seems reasonable to suppose that the quenched crystals exhibit many of the same properties as those deformed plastically[5] and that the enhanced darkenability is the result of the generation and migration of dislocations.

Work of Markham and his associates, described in Part VIII, indicates that purer crystals of the alkali halides actually darken somewhat more slowly than less pure crystals, even at helium temperatures, however, a relatively complete story on this topic is not yet available. It is interesting to note that divalent additions *de*sensitize the silver halides in which interstitial silver ions migrate to trapped electrons to form the latent image. The additional positive-ion vacancies introduced with the divalent ions will suppress the number of interstitial silver ions.

It is also interesting to call attention, at this point, to the work of Hacskaylo, Groetzinger, Otterson, and Schwed[133] on the sensitization of specimens of NaCl induced by passing an electrolytic current. The crystals were electrolyzed in the vicinity of 600°C without introducing permanent *F* centers. In some cases, an electrolytic current which did not produce darkening was passed through the specimens. In others, the crystals were first darkened with a pointed cathode and then uncolored by reversing the current so as to remove the cloud. It was found in both cases that the regions subject to electrolysis darkened much more readily and much more permanently under x-ray bombardment than other portions of the specimen. Measurements made concurrently show that the uncolored crystals subject to electrolysis exhibit a drop in mass density of the same order of magnitude as crystals darkened electrolytically or darkened by x-rays without electrolysis. On the other hand, the crystals first subject to electrolysis and then darkened with x-rays showed much greater decreases in mass density, as if much greater concentrations of *F* centers were produced.

The investigators ascribe the sensitization to the introduction of "precursors" which they assume are a superconcentration of negative-ion vacancies, matched by an equal number of positive-ion vacancies. Actually, one might expect at most to form clusters or small pores of vacancies which are readily converted to *F*-type and *V*-type centers by the introduction of large numbers of carriers. Still further, it is perhaps only necessary to assume that the dislocation pattern inside the crystals is disturbed as a result of the electrolysis, many more incipient vacancies being produced, in order to explain the sensitization. The initial electrolysis was carried out in air, thus providing a chance that chemical changes, such as the introduction of oxide, could account both for the changes in density and the changes in darkenability.

In subsequent work Hacskaylo and Otterson[133] examined with considerable care the *p*H of solutions in which the crystals of NaCl treated in various ways had been dissolved. They came to the conclusion that the clear crystals containing precursors possess of the order of 3×10^{17} excess neutral Na atoms per unit volume in a form which does not give the normal *F* band, or an associated coloration. The excess metal is accompanied by an almost equal increase in crystal volume. The density of excess metal in the clear electrolyzed crystals is almost equal to the density in crystals darkened electrolytically in such a way as to produce permanent *F* centers. Still further, crystals darkened with x-rays showed the presence of excess sodium, if they were not subject to a bleaching anneal, irrespective of whether they were irradiated in the virgin state, in the clear electrolyzed state, or the colored electrolyzed state. The amount of excess sodium increased, in sequence, in each of the three cases, for fixed irradiation, and was accompanied by an almost proportional increase in crystal volume. The crystals which are clear before irradiation show no retention of the excess sodium if they are bleached by heating to 400°C. It is far from clear in just what form the excess metal resides in the lattice in the clear electrolyzed crystals.

The investigators suggest that essentially free chlorine is produced in the crystals darkened by x-rays and that this does not react with the aqueous medium when the crystals are dissolved, so that only the complementary *F* centers affect the *p*H of the solution. This view was supported by measurements of the concentration of "free" chlorine in the solutions obtained by dissolving crystals. Presumably the halogen remains in the crystal and combines with the *F* centers when the x-rayed crystals are annealed at 400°C. To exclude the possibility that the effects were the result of a reaction with atmospheric air or water during electrolysis or irradiation, some of the experiments were carried out in dry helium without producing a significant difference.

---

[133] M. Hacskaylo and G. Groetzinger, Phys. Rev. **87**, 790 (1952), M. Hacskaylo and D. Otterson, J. Chem. Phys. **21**, 552 (1953); Hacskaylo, Otterson, and Schwed, J. Chem. Phys. **21**, 1435.

The magnitude of the scale of effects observed in this work is somewhat disconcerting since it lies in the range of interest for much of the work on darkening with x-rays. One can only hope that the observations will be repeated in another laboratory so that independent checks may be obtained.

In connection with this discussion of the influence of imperfections on the darkenability of the alkali halides, it is interesting to note that Przibram[134] and his colleagues have found that the darkening produced by cathode rays at room temperatures passes through a maximum as a function of time. The maximum darkening corresponded to an average volume density of *F* center of 4.58×10^{19} per cc in NaCl and 2.85×10^{19} per cc in KCl in the layer penetrated by the radiation. Apparently the disorder produced in the lattice structure by the bombardment eventually lowers the attainable density of *F* and *V* centers, perhaps as a result of the generation of a high concentration of clusters of vacancies which permits the electrons to tunnel relatively freely from one position to another.

Although many of the most important facts concerning the α and β bands were related in Sec. 24, a few additional comments should be made. Actually these bands were first discovered by Delbecq, Pringsheim, and Yuster[113] as a result of investigations on crystals of KI colored by x-rays. Such work suggested studies with additively colored crystals, and, in conjunction with the latter, eliminated the possibility that the α band is to be associated with an F' center, for the x-rayed crystals exhibit a strong α band even when the number of F' centers is negligible. Taken as a whole, this investigation leaves little doubt that the α band is to be associated with the vacant halogen site, as described previously.

The observation that the α band is strong in crystals irradiated with x-rays shows that many halogen-ion vacancies, unassociated with *F*- or *V*-type centers, are formed during x-irradiation. We are led to the conclusion that one of the important influences of ionizing radiations is the production of vacant lattice sites in quantities well beyond the number which serve as traps for electrons and holes. This is the important, characteristic "solvent action" of ionizing radiations which the writer discussed in the 1946 review.

Martienssen[114] amplified the work on the Greek bands, using both additively colored and irradiated specimens. He showed that they occur in a variety of crystals, as should be expected if the initial interpretation is correct. He also demonstrated, to relatively high precision, that the intensity of the β band is strictly proportional to that of the *F* band (Fig. 25), again as is to be expected if the basic picture is valid.

In addition to furnishing this important confirmatory evidence, however, Martienssen added two new basic facts:

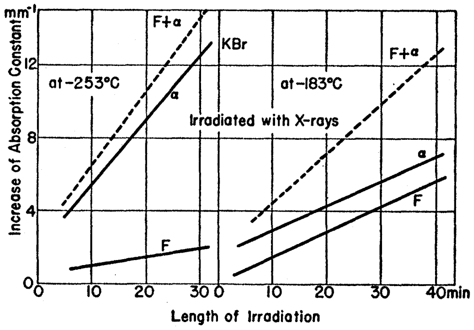


FIG. 32. The growth of the *F* band and α band in KBr with time of irradiation with x-rays (after Martienssen). The diagram on the left is valid for irradiation at liquid hydrogen temperature, whereas that on the right is valid for liquid nitrogen temperature. In this specimen the α band grows more rapidly at the lower temperature although the growth of the sum of both bands (dashed curve) is about the same at the two temperatures. It is to be noted that the curves do not extrapolate linearly to the origin.

(a) The relative magnitude of the ratio of the α band to the *F* band increases as the temperature at which irradiation is carried out decreases. Figure 32 shows the increase in the value of the extinction coefficient as a function of time for the peaks of the α and *F* bands in the range of time in which these vary linearly. The right-hand curve corresponds to a specimen irradiated at liquid nitrogen temperature, whereas its partner was obtained by irradiating at liquid hydrogen temperature. The same x-ray intensity was used in both cases. The rate of increase of the α band is sufficiently more rapid at -253°C that there is a small over-all gain in the "total" absorption obtained by adding intensities at both peaks even though the *F* band increases less rapidly at the lower temperature. Since the measurements of the Argonne workers indicate that the peak absorption for the α centers is somewhat less per center than for the *F* centers, we seem led to the conclusion that the total production of centers of both types is not appreciably more slow at the lower temperature. In any case there may be many more vacant sites than *F* centers. We may estimate from the intensity of irradiation, namely, 5×10^{-4} watt/cm^2, that about 1200 ev is required per center produced if we assume that the "total" extinction coefficient of 12 mm^{-1}, corresponding to about 23 minutes of irradiation at the lower temperature, represents the production of about 4×10^{15} centers per cm^2 in the layer about 0.1 mm thick in which the x-rays employed by Martienssen are absorbed in KBr. Approximately the same value is valid at liquid nitrogen temperature where the total number of centers produced in given time is almost the same. Moreover, about twice as much energy, namely, $\sim$2000 ev, is needed to produce an *F* center at liquid nitrogen temperature. This value is very close to that found by Harten for KCl at the same temperature (Fig. 14).

(b) Martienssen has found that the α band may be

---

[134] K. Przibram, Sitzber. Akad. Wiss. Wien. **135**, 202 (1926), and following; Z. Physik **130**, 269 (1951).

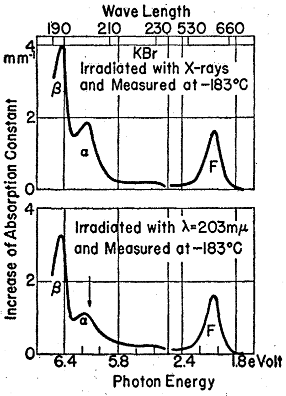


FIG. 33. Bleaching of the α band in KBr when the crystal is irradiated with light absorbed in this band (after Martienssen). The upper diagram shows the α, β, and F bands immediately after the specimen is darkened with x-rays, whereas the lower diagram shows the effect of irradiation with light quanta on the α band. Martienssen states that the efficiency of bleaching is low.

bleached at $-183°$C with light absorbed in the band itself. Figure 33 shows the effect for KBr in which the α band has been produced at $-183°$C by irradiation with x-rays. The quantum yield for the bleaching process is low; moreover, there is a characteristic luminescence of unknown quantum efficiency associated with absorption in the band.

This discovery is remarkable in view of the fact that there is essentially unambiguous evidence to show that the α band is associated with absorption of light by the halogen ions around a halogen-ion vacancy. The bleaching of the band implies that the vacancies migrate as a result of absorption of successive light quanta and change their character from isolated units to a state in which they are bound in more complex imperfections, such as pairs or other aggregates, which do not possess the α band. Since the α band centers at about 6.2 ev and since the absorption process could lead to luminescence in the visible or near-ultraviolet part of the spectrum with unit quantum efficiency, it is possible that only about 3 ev of the total energy absorbed is expended in stimulating lattice vibrations. The total energy could be divided into two portions which are released, respectively, both just after the absorption act and just after the transition back to the ground state. On the other hand, a much larger amount of energy may appear in the form of lattice vibrations in the second step, that is an amount presumably much nearer 6 ev, if the luminescent efficiency is much less than unity. It seems most plausible now to assume that the diffusion of the halogen-ion vacancy is the result of these point "thermal spikes" which raise the vibrational temperature near the vacancy to a very high value for a short period of time, of the order of 10^{-12} sec, and permit the vacancy to diffuse about one atomic distance.

We may attempt to estimate the temperature required if the vacancy is to jump once each time it absorbs a quantum, using the assumption that the temperature endures for a time $\tau = 10^{-12}$ sec. The probability for a jump is

$$p_- = \nu_{0-}\tau \exp(-\epsilon_-/kT),$$

where ν_{0-} is the coefficient of the Boltzmann factor in the expression for the jump frequency of the negative-ion vacancy (see Secs. 4, 7, and 8) and ϵ_- is the activation energy for the jump. We shall also assume that $\nu_{0-}\tau$ is about 100 and that ϵ_- is 1.2 ev for KBr, in keeping with Schamp's measurement for NaBr (see Eq. (1), Sec. 7). It follows that kT must be about 0.26 ev, corresponding to $T = 3000°$K. Now the negative-ion vacancy has six positive and twelve negative ions as its nearest neighbors. If we assume that these participate equally in the initial thermal spike and that the average thermal energy of each is $3kT$, the total energy of the neighbors is about 14 ev when kT has the value given above. Although this is more than twice the energy of the quantum absorbed in the α band, the general agreement is about as close as one could expect with use of the simple reasoning and estimates made, provided most of the energy of the quantum actually is available for conversion to thermal vibrations. Thus, if this simple model is at all valid, it is necessary to assume that the quantum yield of luminescent radiation is not close to unity and that most of the absorbed energy is expended in producing lattice vibrations.

There are, however, factors which may mitigate the diffusion process and make it possible for migration to occur for much lower temperatures. For example, the activation barrier for motion of the vacancy from one site to the next may be much less than 1.2 ev in the excited state of the system, so that there is an appreciable probability that the vacancy will shift to a neighboring position during the adjustment which occurs immediately after absorption, even though the temperature is much less than 3000°K. If we assume that about one quarter of the total energy, or 1.5 ev, becomes available to stimulate oscillations in this step, the energy associated with the thermal spike is about 0.1 ev for each of the 18 nearest neighbors. Hence it corresponds to a temperature nearer 300°K if the energy is distributed equally among the vibrational degrees of freedom. Actually, the equipartition principle may not be valid during the critical period of time.

It would be valuable to have an experimental determination of the quantum efficiency of the luminescence. It would also be valuable to know if the α band produced at helium or hydrogen temperatures can be bleached at such temperatures by irradiating with light in the α band.

Table X gives the positions of the peaks of the α and β bands for a number of crystals.

TABLE X. Positions of peaks of α and β bands for several crystals (in ev, after Martienssen).

	NaBr	KBr	KI	RbBr	RbI
α band	6.23	6.15	5.21	6.04	5.16
β band		6.44	5.48	6.31	5.40

One of the interesting features of Martienssen's observations of the decay of the α band under irradiation with light absorbed in this band is the fact that it does not seem to be accompanied by a decrease in the intensity of the F band. If, as we have supposed, the decrease in intensity of the α band is the result of migration of halogen-ion vacancies, we might expect some of the vacancies to join F centers and convert them to R centers. The evidence suggests that the vacancies prefer to join other imperfections. It is conceivable that the negative-ion vacancies join positive-ion vacancies preferentially as a result of the Coulomb attraction so that a negligible number of F centers are lost. This would imply, in turn, that the Coulomb attraction is sufficient to influence the course of migration and that the local temperatures in the thermal spikes required to stimulate appreciable migration are not more than a few tenths of an electron volt, even though the spikes do not endure for more than a few oscillation times.

In a study to be published shortly, Duerig has investigated the generation of color centers by x-rays in KCl and KBr at 78°K both in the dark and in the presence of light which bleaches the F' band. He found that the F band rises more rapidly in the presence of bleaching light than in the dark. Moreover, one may pass in a quasi-reversible manner from the "light" to the "dark" curve giving darkening as a function of time of x-irradiation by turning off the F' bleaching light for several minutes during x-irradiation. One may also pass in the reverse direction by turning on the light after a period in the dark. In other words, the time of x-irradiation of a given specimen at a given temperature appears to determine the potential number of F and F' centers in a way that is independent of the ratio of the number of such centers actually present. This ratio may be altered by illuminating coincidentally with light absorbed by the F' centers. Or expressed in another way, it appears that the number of vacancies present in a given specimen is determined primarily by the conditions of the x-ray irradiation and not by the way in which the vacancies are occupied by electrons and holes.

It is of interest, in connection with the discussion of the bleaching in the next section, to note that Duerig found that the specimens could be returned to essentially their virgin condition by raising them to room temperature after x-irradiation in the presence of a strong incandescent light.

There are several observations on the influence of darkening on the mechanical properties of the alkali halides which have bearing on the role played by dislocations. Podaschewsky[135] demonstrated in 1936 that darkening at room temperature increases the yield stress of NaCl several fold. The effect persists even after bleaching with light at room temperature. Li,[136] who called the writer's attention to this work, subsequently showed that the effect also occurs in the silver chloride and is a volume rather than a surface effect.

Frankl and Read[137] have studied what is presumably a closely related effect. They have investigated the internal friction of plastic origin, discovered by Read,[138] in single crystals of NaCl both before and after irradiation with x-rays and following bleaching. The decrement of the undarkened specimens is in the range of 10^{-3} for strain amplitudes near and below 10^{-6}. The decrement can be increased several fold, however, by increasing the strain amplitude. In fact the amplitude of vibration attainable in the experiments with undarkened specimens was limited by the rise in internal friction. This rise in internal friction is inhibited by irradiation, so that the decrement can be made almost independent of amplitude. The x-rays employed were produced with a tube operating at 40 kv and 20 ma. The lowering of decrement was clearly evident at the end of 2 minutes and complete in 20 minutes. Although the bulk of the x-rays are absorbed in a thin surface layer, the crystals were darkened lightly throughout, presumably because of the harder component present. The effect was not determined primarily by the surface darkening, for the same results were found when a thin crystal of NaCl was used as a filter and when the heavily darkened surface layer was dissolved.

The decrement, measured at room temperature, of specimens which were darkened and bleached at liquid nitrogen temperatures without being warmed to room temperature prior to bleaching does not show a significant decrease. On the other hand, specimens darkened at liquid nitrogen temperatures and bleached at room temperature behave qualitatively like those darkened and bleached at room temperature.

The internal friction observed by Frankl, like the plastic flow studied by Podaschewsky, presumably originates in the stress-induced motion of dislocations which is inhibited by the products of darkening when they have an opportunity to diffuse. It seems clear that the F centers alone are not the hardening agent, for the decrease in decrement persists even after bleaching if the process is carried out at room temperature. Moreover, diffusion is essential since the effect is not observed in the specimens darkened and bleached at low temperatures.

Frankl has proposed that the positive-ion vacancies produced during darkening migrate to dislocations and pin them sufficiently tightly that they are unable to dissipate vibrational energy. It seems more reasonable to the writer to suppose that the locking is caused by clusters of vacancies of both signs which condense near dislocations both during irradiation and subsequent bleaching at room temperature. Isolated positive-ion

---

[135] M. N. Podaschewsky, Physik. Z. Sowjetunion 8, 81 (1935).

[136] Y. Li, Acta Metallurgica 1, 455 (1953).

[137] D. R. Frankl and T. A. Read, Phys. Rev. 89, 663 (1953); Also, D. R. Frankl, thesis (unpublished).

[138] T. A. Read, Phys. Rev. 58, 371 (1940); Trans. Am. Inst. Mining Met. Engrs. 143, 30 (1941); F. Seitz and T. A. Read, J. Appl. Phys. 12, 100 (1941).

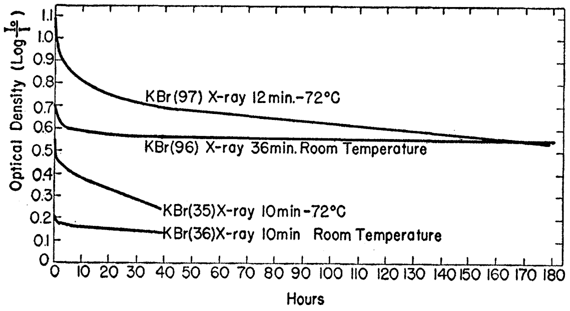


FIG. 34. Thermal bleaching of F centers in KBr produced by x-irradiation at various temperatures (after Casler, Pringsheim, and Yuster). The bleaching occurs at room temperature. It may be seen that the rate of bleaching decreases with time. The darkening attains a limiting value which depends upon the specimen and the conditions of irradiation. In general the crystals darkened at the lower temperature bleach more rapidly for a given initial level of darkening.

vacancies cannot form clusters and presumably would migrate along the dislocations until they meet jogs where they may join incipient negative-ion vacancies. It is difficult to believe that they would have a strong pinning effect at such positions, whereas clusters of both types of vacancy could form major locking units. The fact that specimens darkened and bleached at low temperatures do not exhibit the decrease in decrement suggests that the vacancies produced at low temperatures do not migrate far. Either they become reincorporated into the source, presumably a dislocation, during bleaching or they remain dispersed and do not inhibit the motion of the dislocation.

The density of F centers in the bulk of Frankl's specimens was probably not above 10^{16} per cc. It would be interesting to know if the internal friction is unaffected when the specimen is darkened much more heavily at liquid nitrogen temperature and bleached before being warmed to room temperature.

29. Bleaching

The bleaching of specimens of the alkali halides which have been darkened by ionizing radiation is a topic which has been the subject of interest for a number of decades. An appreciable portion of the definitive work was carried out by Przibram[134] and his co-workers in the 1920's. Bleaching, or partial bleaching, may be accomplished by application of heat, by light absorbed by one of the bands, particularly the F band, or by both agencies in combination with relatively weak irradiation with ionizing radiations.

A general qualitative feature of bleaching, regardless of the temperature at which the darkening has occurred, is that it occurs rapidly at first and then becomes increasingly difficult. For example, Fig. 34 shows a typical set of bleaching curves obtained by irradiating KBr at -78°C and at room temperature and studying the subsequent changes in F absorption as a function of time. These are typical thermal bleaching curves. It may be seen that the quantitative details of the process are strongly dependent upon the particular specimen under observation.

On the whole there has been essentially no quantitative work on the relative strengths of the F-type and V-type bands during bleaching. Such measurements would, however, probably be of little value until the oscillator strengths of the various centers are known at least semiquantitatively. Both the F and V bands decrease simultaneously in most cases investigated. The former do not vanish completely unless the latter also do, as one might expect from the supposed complementary nature of the two types of center. Dorendorf's experiment, described in the last section, on the optical bleaching of the F-type bands in a specimen of KCl darkened at room temperature with quantum yield near unity and without complete bleaching of the V_3 center, appears to be a very notable exception to this rule. More studies of this type would appear to be valuable.

It has become a moderately widespread practice to describe the rather great difference between the high initial rate of bleaching and the slow terminal rate by stating that there are "soft" F centers which are easy to bleach and "hard" F centers which persist. Oberly and Burstein have gone so far as to suggest that this difference represents an actual physical or chemical difference in the makeup of the F centers involved. The writer is inclined to discount this proposal at the present time and search for other sources of the persistence of F centers. Although the work of Kaiser[92] and the other investigators at Erlangen, described in Sec. 18, shows that the F band is surprisingly insensitive to relatively large amounts of imperfection, it is difficult to believe that so many features of the hard and soft centers, such as the shape of the F band, would be left unaltered if the two centers possessed strikingly different atomic configurations. Above all, the writer would like to emphasize that no phenomena observed in conjunction with additively colored crystals have made it necessary to assume essentially different types of F centers. It seems most reasonable at present to assume that the differences in properties of irradiated crystals ascribable to soft and hard centers stem either from the possibility that the crystals contain both F centers and a mixture of two or more types of V center which are well separated from one another but which are not necessarily distributed uniformly, or from the possibility that the centers are produced in highly localized regions, such as near the edges of Taylor-Orowan dislocations, and are sufficiently close to one another that some of the electrons can tunnel to holes, particularly when the electrons are raised to an excited state. It is likely that both factors play a role, the first being more important at temperatures near and above -190°C and the second at very low temperatures (discussed in the next section).

It is too much to hope that any theory of bleaching will explain quantitatively the available information concerning bleaching, for most data have been gathered under conditions in which many important factors, such as the nature and concentration of impurities and the distribution of V centers, are unknown. At best one may hope for something slightly better than a qualitative analysis which can be used to guide additional experiments which are undertaken.

There is one guiding principle which presumably can be used with safety in a large part of the discussion of thermal bleaching. The activation energies for freeing electrons thermally into the conduction band from typical F centers in crystals such as NaCl, KCl, and KBr are so large that this process can be discarded as a contribution to bleaching at any temperature near or below room temperature. Mott and Gurney have shown that the energies required to ionize F centers thermally are 1.89 ev, 1.95 ev, and 1.78 ev in each of the three crystals just named (see Table IV). While these values were determined somewhat indirectly from an analysis of the migration of clouds of F centers in strong electrostatic fields, they are in good agreement with the stability of F centers in additively colored crystals at room temperature. We may infer that the relaxation time τ for freeing an electron by thermal means is much larger than 10^7 sec (86 days) at temperatures near or below room temperature, if we make the assumption that the coefficient ν_0 of the Boltzmann factor in the expression

$$1/\tau = \nu_0 \exp(-\epsilon_F/kT), \qquad (1)$$

where ϵ_F is the activation energy for freeing the electron from the F center, is not larger than 10^{14} sec. This conclusion does not imply that an electron may not tunnel from the ground state of an F center to a state in another center which is sufficiently close, but it does exclude the possibility that the electron will wander freely through the conduction band as a result of thermal excitation.

Casler, Pringsheim, and Yuster[124] have made a very valuable contribution to the theory of bleaching by showing that an important component of the bleaching that occurs when crystals of KCl and KBr which have been irradiated at liquid nitrogen temperatures are warmed above −100°C is associated with disappearance of the V_1 band produced at the lower temperature. These observations, when taken in conjunction with the measurements of Dutton and Maurer (described in the next section) which show that holes are released from the V_1 centers at the time they vanish, lead to the conclusion that at least part, if not all, of the portion of the F band which vanishes during warming does so because the holes annihilate electrons. The rate of bleaching decreases when the easily available holes from the V_1 centers are exhausted. The V_4 band also vanishes during the rise in temperature, although at a later point, and presumably furnishes additional holes. The remainder of the holes which survive the initial irradiation process presumably are tied in V_2 and V_3 centers and possibly other "minor" centers of the V type, which are more or less stable than the V_1 and V_4 centers.

This work shows how exceedingly important it is to understand the properties of the V centers in much more detail than we do at present if we are to have further insight into bleaching at temperatures above liquid nitrogen temperatures.

Schneider[128] and his co-workers have examined the rate of thermal bleaching of F centers in KCl in the temperature range between room temperature and about 160°C. Presumably V_1 and V_4 centers are not present during this process. They have found that the relaxation time for bleaching the soft and hard centers can be fitted by expressions of the form (1) in which the appropriate activation energies are 0.61 and 0.31 ev, respectively. The corresponding values of ν_0 are 0.6 sec^{-1} and 0.31 sec^{-1}. The parameters are remarkable in two ways: The activation energies are relatively small, being comparable to the energies for freeing holes from V_1 centers, whereas the frequency factors are far less than 10^{13} sec^{-1}, as one might expect for the simple process of freeing a hole. It seems almost useless to speculate on the mechanism until more information concerning the behavior of the V centers present is available. The low value of the frequency coefficient suggests that the rate-limiting step is one which involves many repetitions of a single process.

Schneider also studied optical bleaching in KCl at room temperature and found a fast process which acts with a quantum efficiency near unity and has a frequency of about 1.7×10^{-3} sec^{-1}, apparently determined by the light intensity used, which is independent of temperature within the limitations of the experiment. There is also a slow process which has an activation energy of 0.25 ev and a frequency of 2.5×10^{-4} sec. The fast process seems to correspond to the capture of a photoelectron by a V center, presumably V_2, which possesses a hole that can be annihilated without an activation energy.

The slow process, on the other hand, implies either that some of the F centers cannot be ionized easily when in the excited state, requiring an activation energy of 0.25 ev instead of a value nearer 0.075 ev estimated by Mott and Gurney,[139] or that the free electrons can join with one of the V centers, presumably V_3, only if an activation energy is furnished by thermal quanta. The second possibility seems the more reasonable to the writer at the present time. In fact, the observed activation energy is close to the value we might expect if the conduction electron must overcome the repulsive electrostatic field which is associated with the V_3 center if our model is valid (Fig. 28). We saw in the last section that an electron having a thermal energy of 0.025 ev, corresponding to the mean of the Maxwell

---

[139] N. F. Mott and R. W. Gurney, reference 4, page 133.

distribution at room temperature, should be able to approach only to a distance about 50A from a V_3 center in a typical alkali halide. In contrast, an electron having an energy of 0.25 ev should be able to approach to a distance of about 5A, which presumably is adequate for annihilation of the hole. The available evidence seems to support this view of the "hard" step although the evidence is fairly fragmentary.

If further experimental work demonstrates, by chance, that the V_3 center has the configuration now assigned to V_2 (Fig. 28), whereas the V_2 band arises from a center with an entirely different structure, there is another avenue which may be used to provide an explanation of the stability of the V_3 band in the presence of free electrons. The center designated as V_2 in Fig. 29 is equivalent to a neutral halogen molecule imbedded in a void in the crystal. Since the equilibrium spacing of the chlorine atoms in Cl_2 is 1.99A, in contrast with the value of 4.44A for the spacing of Cl^- in KCl, it is possible that the equilibrium spacing of the halogen atoms to which the holes are attached in this neutral center is much smaller than the equilibrium spacing of Cl^- ions in the crystal. The corresponding equilibrium configuration of nuclear coordinates could conceivably be one for which the energy of the neutral center plus a free electron is lower than the energy of the center obtained by having the electron annihilate one of the two holes. An activation energy sufficient to distort the V_3 center to the region of coordinates where the order is reversed would have to be furnished before annihilation could occur. As remarked previously, there seems to be no need for invoking this possibility since the charge associated with the V_3 center proposed in Fig. 28 is adequate to account for its stability.

It should be added that Casler, Pringsheim, and Yuster[124] have examined the influence of temperatures as high as 200°C on the behavior of the V bands obtained in KCl by x-irradiation. Unfortunately, the absorption measurements were made at room temperature so that the V_2 and V_3 bands were poorly resolved. The results support the view, however, that the V_2 band bleaches first whereas the V_3 band resists bleaching most strongly.

There is another phenomenon which may contribute to the progressive increase of resistance to bleaching, particularly at low temperature where ionic migration is negligible, namely, the development of local space charges which prevent electrons or holes from migrating over the distances necessary to permit annihilation of carriers of opposite sign. Suppose, for example, that the distributions of F-type and V-type centers differ somewhat so that there are regions in which one or the other predominates by an amount of the same order of magnitude as the average density. We should not expect such unbalance when the centers are formed at low temperatures, where ionic diffusion is almost negligible, but it could conceivably occur at room temperature.

To deal with a specific model, suppose that the bleaching agent frees electrons which proceed to annihilate the holes bound in various V-type centers. Initially the electrons will combine with holes near to the regions where the former are released; however, the crystal will eventually be left with "islands" in which one of the two types of center predominates. Such islands would correspond to the regions in which the concentrations were unequal initially. From this point onward bleaching will continue only if the electrons freed from the F-type centers can diffuse to the regions where the V-type centers are concentrated. However, localized space charge may inhibit such migration. For simplicity, let us assume that the islands are spheres of radius r_s, containing an unbalanced charge ne, where e is the electron unit of charge, which is uniformly distributed through the sphere. Let us also assume that the potential is zero at the periphery of the spheres. A sphere containing F-type centers will become positively charged as a result of the loss of electrons. Hence the energy of an electron will be lower at the center of the sphere than at the periphery. For the configuration assumed, the difference in energy is

$$ne^2/2k_sr_s, \qquad (2)$$

where k_s is the static dielectric constant. This is of the order of 1 ev, and hence large compared with kT, if

$$n \sim r_s/r_0, \qquad (3)$$

where r_0 is the spacing between nearest neighboring ions. If we assume in addition that the density of charge in the sphere is αn_F, where n_F is the mean density of F centers and α is a constant near unity, we also have the relation

$$n \sim \alpha 4\pi r_s^3 n_F/3. \qquad (4)$$

The quantities (2) and (4) are equal for values of n_F near 10^{16} per cc if

$$r_s/r_0 \sim 10^3. \qquad (5)$$

In summary, if unbalanced charge densities of the order of n_F can occur in islands of mean radius r_s, as a result of nonuniform distributions of F-type and V-type centers, the mobile carriers will become trapped within the islands in which they originate as soon as $r_s/r_0 \sim 10^3$, for normal densities of centers. Thus the development of local space charge may inhibit complete bleaching of color centers.

We may observe that nonidentical distributions of F and V centers imply regions which are predominantly n and p type and hence the presence of at least incipient n-p junctions prior to bleaching. Wannier[140] apparently was the first to point out the possible importance of such junctions in affecting photocurrents. The bleaching process described in the previous paragraph would lead to the accentuation of these junctions since carriers leave regions of opposite charge and go to

---

[140] G. Wannier, Phys. Rev. 76, 438 (1949).

regions of the same charge until the differences in potential become sufficiently great to prevent the transfer.

Oberly and Burstein[141] have examined the photocurrents produced in KCl and KBr during the bleaching of x-rayed crystals by irradiation in the F-type bands. They have observed photocurrents associated with illumination in the F, R, M, and N bands and have found that the magnitude of the current resulting from irradiating in the F band drops more rapidly than the absorption coefficient of light during bleaching. This is exactly what one would expect if the range of the electrons were limited by the development of n-p junctions. The average electrostatic fields appearing in the specimens used were probably of the order of 5000 volts per cm, which would correspond to a *Schubweg* of about 10^{-4} cm in additively colored crystals. Thus the results of these studies are consistent with the notion that the *Schubweg* decreases to a value of the order of 10^{-5} cm after the intensity of the F band is reduced by a factor of two.

It should be added that the investigators do not discuss the polarization field in their specimens. There is also a reasonable possibility that this field changed during irradiation and decreased the driving field.

Oberly[141] has studied the change in photoresponse with decreasing temperature in specimens of KCl darkened by x-rays and held at temperatures in the range from room temperature to -190°C. The response was studied in the F, R, M, and N bands, as well as in the shoulder on the short-wavelength side of the F band (the K band in Fig. 3), which Burstein and Oberly have termed the L band. As the temperature dropped, the photoresponse of all bands decreased, the decline being greatest for those at longer wavelengths. The investigator has concluded that the thermal energy required to free electrons from the excited states of the various centers increases as the peak of the absorption band shifts to the red. At -185°C only the K band provides a strong photoresponse, the density of F' centers, being negligible. Oberly concludes that the K band should be associated with excitation either to the highly excited bound states of the F center or to the ionization states. The crystal was bleached somewhat with F light at room temperature after the x-ray treatment in order to develop the R, M, and N bands.

Oberly also examined specimens which had been bleached at -115°C after being darkened with x-rays and found that the photoresponse at -190°C is much the same as in the specimens treated at room temperature. F' centers were present in the specimen bleached at the lower temperature, however, and contributed a peak in the photoresponse in the region near 10 000A.

Alexander and Schneider[121] have investigated the absorption in the region of the V_2 and V_3 bands when crystals, darkened by x-rays at room temperature, are irradiated with light absorbed both by these bands and by F centers. The investigations were carried out with crystals of KCl. Since the absorption coefficients were studied at room temperature, the V_2 and V_3 centers were not clearly resolved. The general conclusions drawn were as follows:

(a) The initial decrease in the F band occurs with quantum efficiency near unity when the bleaching is carried out with F light. During this phase the V bands decrease relatively slowly; most of the drop in the F band is associated with formation of the R and M bands. The F band stabilizes in a later stage, the quantum efficiency for the decrease approaching a value nearer 0.005. The rates of decrease in F and V bands are comparable in this stage. These conclusions seem to fit in with the work of other investigators.

(b) The V absorption decreases without an associated drop in the F-type bands when the crystals are irradiated in the V bands. On cessation of the ultraviolet irradiation, the V absorption begins to recover and regains its original value in several days. The investigators do not provide details of the wavelengths employed in this irradiation. The results are exceedingly interesting, however, for they imply that either the V_2 or the V_3 center possesses a metastable excited state from which the system slowly returns to the ground state. Presumably the holes are not freed during the irradiation and are not able to annihilate the electrons associated with the F-type centers, as occurs when the V_1 centers decompose during warming from very low temperatures. These observations are highly intriguing and merit more detailed attention. It would appear that the metastable state is characteristic of the V_3 center since it predominated in the specimens studied by these investigators.

(c) The bleaching of F and V centers may be greatly accelerated by irradiating in both bands simultaneously. In a vague way, these results suggest that a free electron may combine readily with the metastable V centers, so that the V_3 centers lose their resistance to bleaching. It seems useless to speculate further on these results until the experimental picture is more complete.

30. Release of Charge During Warmup

Dutton and Maurer[126] have studied the current produced in specimens of KCl and KBr which have been irradiated at liquid nitrogen temperatures when the crystals are raised to higher temperatures and absorption bands such as V_1 and F' bleach. The experiments were performed in such a manner that the applied field presumably was constant during the measurements. Absorption measurements over a range of wavelengths from about 9000A (1.1 ev) to 2200A (5.5 ev) accompanied the observations of current. On the whole the technique applied is somewhat reminiscent of the "glow-curve" measurements of phosphorescence (see Fig. 35); however, the charge current, rather than

---

[141] J. J. Oberly and E. Burstein, Phys. Rev. **79**, 217 (1950); J. J. Oberly, Phys. Rev. **83**, 228 (1951); **84**, 1257 (1951).

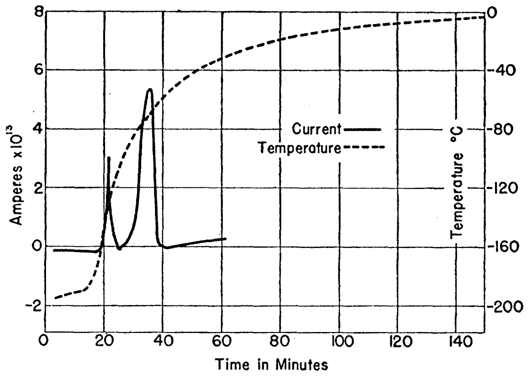


FIG. 35. Typical current "glow curve" studied by Dutton and Maurer. A run for KCl is shown. The dashed curve shows the variation of temperature of a particular specimen with time (right-hand scale), whereas the full curve shows the current. The peak observed earliest is that associated with the vanishing of the V_1 band and is assumed to arise from a flow of holes. The second peak is associated with the bleaching of the F' band.

luminescent radiation, is observed. About 5×10^{15} color centers of a given kind bleached in a given run.

The principal conclusions drawn from this work are as follows:

(1) The V_1 band vanishes on warming to about $-158°C$ in KBr and $-145°C$ in KCl if the crystals have been darkened at $-183°C$. A current pulse is observed during this disappearance. Neither the V_1 band nor the current pulse is observed in KBr if the crystal is darkened at $-156°C$. Thus the charge is assumed to be released from the V_1 centers. The F band diminishes at the same time, indicating that the moving charges are holes which combine with bound electrons on F-type centers. We apparently must conclude that a V_1 center decomposes into a positive-ion vacancy and a free hole at a relatively low temperature if the model of the V_1 center shown in Fig. 28 is correct. From estimates of the density of color centers and the currents observed, the investigators have conluded that the displacement distances for the holes are smaller than those for free electrons under the same conditions.

(2) There is evidence, principally for KBr, that the V_3 band diminishes and the V_2 and possibly V_4 bands grow during bleaching of the V_1 band. The diminution of the V_3 band and growth of the V_2 band is explained readily with the models of the corresponding centers proposed in Fig. 28 on the assumption that the negatively charged V_3 centers capture some of the holes and are converted into V_2 centers. The changes in the V bands other than V_1 are less clear in KCl because of the limitations of the spectroscope employed in the work.

(3) A second current pulse occurs when KBr is raised to the vicinity of $-130°C$ and KCl is raised to $-68°C$. These pulses are attributed to the freeing of electrons from F' centers, for most of the F' band bleaches in the two crystals at this temperature. Moreover, the thermally increased range starts at about these temperatures in additively colored crystals. It is interesting to note that the F' band does not decrease exponentially with time, but changes from "soft" to "hard" character after the initial decrease. One might expect the F' band in an additively colored crystal to decay according to a bimolecular type of law, in contrast with an exponential type, because the number of vacant halogen-ion sites diminishes at the same rate as the number of F centers. In contrast, it might be supposed that electrons freed in crystals darkened by x-rays would have had less difficulty in finding sinks other than F centers. Apparently those factors, discussed in the previous section, which inhibit the ability of electrons freed by light to combine with holes are operative when F' centers are decomposing.

(4) The V_4 band of KBr bleaches near $-27°C$ with the release of charge and light. The F band decreases at the same time, but no strong change is observed in the V_2 or V_3 band. The results imply that holes are released from the V_4 center during its disappearance. The peak current is larger, in comparison with the size of the absorption band, when the V_4 band vanishes than when the V_1 band does. This could mean either that the range of holes is greater at the higher temperature or that the oscillator strength for the V_4 centers is low relative to that of the V_1 centers.

(5) A large current peak is observed at $-48°C$ in KBr. It could not be correlated with any change in absorption in the spectral range studied other than a drop in the F band. The observation implies that holes are released from an unknown trap when the temperature is near $-48°C$. If the trap contributes to the absorption spectrum, the band is either diffusely distributed or lies outside the spectral range covered in the experiments.

(6) Each of the current pulses is accompanied by the release of luminescent radiation. In the case of KBr most of the light is transmitted by a filter which cuts off below 3800A. Table XI contains a list of the main frequency limits. Approximately 10^{13} light quanta are emitted with each peak. This number is probably about 100 times smaller than the number of centers

TABLE XI. Characteristics of conductivity and luminescence peaks for KBr and KCl (after Dutton and Maurer).

Temperature of peak	Absorption band showing principal change	Calculated trap depth	Luminescence
		KBr	
$-158°C$	V_1 band	0.23 ev	($\lambda>5500A$)
$-130°$	F' band	0.29	($\lambda<3800A$)
$-88°$	?	0.38	($\lambda>5500A$)
$-48°$	?	0.46	Observed
$-27°$	V_4 band	0.50	($\lambda<5500A$)
		KCl	
$-145°C$	V_1 band	0.26	Observed
$-68°$	F' band	0.42	Observed
$-36°$	?	0.49	Observed

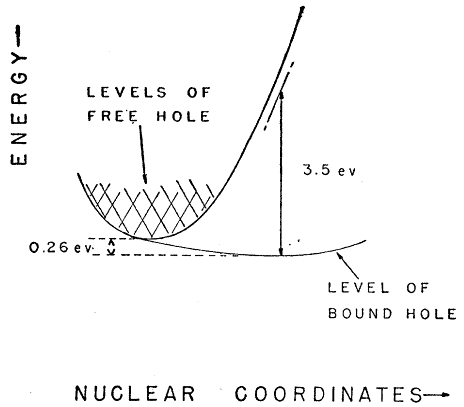


FIG. 36. Proposed energy level and configurational coordinate diagram for the V_1 center. The ground state has a very shallow trough with a minimum occurring for positions of the nuclei relatively far from those for the normal lattice. The thermal ionization energy is assumed to be 0.26 ev in the case of KCl. Presumably the first excited state possesses a minimum at a position which assures a high probability that the system will return to the ground state at temperatures where the V_1 center is thermally stable.

which disappear when one of the peaks diminishes. Thus the quantum efficiency for the luminescence probably is not near unity. A glow peak which does not correspond to a current peak is observed in both KBr and KCl. This occurs at $-36°C$ in KCl and at $-90°C$ in KBr. On the whole the observations of luminescence do not appear to add substantially to the picture of the processes; the glow appears to be incidental.

(7) Several runs were made on specimens of KCl using liquid helium as a coolant. The electrical measurements showed a large current pulse which appeared during warming from helium temperatures to $-190°C$. The current peak associated with disappearance of the V_1 band was observed at $-145°C$, but that at $-68°C$, associated with dissolution of the F' centers, was not found, in keeping with the observation that the F' band was essentially absent in the crystals darkened at helium temperatures. In contrast, the F band was somewhat larger for given irradiation than in specimens darkened at liquid nitrogen temperature. We shall return to this topic in the next part of this review which deals with other observations at very low temperatures.

(8) In one case a crystal of KBr was irradiated at $-156°C$. The V_1 band was essentially absent, and the V_2 and V_4 bands were relatively strong. The current peak at $-160°C$, associated with the V_1 band, was not observed during warming; however the peak at $-130°C$, associated with vanishing of the F' band, was about 20 times larger than in specimens irradiated at $-183°C$ under otherwise similar conditions. In contrast, a current peak having no counterpart in the specimens darkened at lower temperatures was found at $-90°C$. Electric breakdown prevented further measurements.

(9) An attempt was made to determine the sign of the carriers produced in each current peak by darkening a thin layer of the crystal and observing the magnitude of the pulses produced in cases in which the the field is in opposite directions. The experiments did not yield positive results, presumably because the displacement distance was less than the thickness of the darkened layer in the specimens.

Table XI contains a list of the temperatures at which the currents or luminescent peaks were observed in this work, along with estimates of the activation energies required to stimulate the processes responsible for the peaks. The final column shows the region of the spectrum in which most of the radiation appears.

Perhaps the outstanding result of the work is the conclusion that V_1 centers, which absorb light quanta of the order of 3 ev or more in both crystals, decompose at temperatures as low as 120°K. The estimated activation energies for dissociation shown in Table XI indicate that the process requires less than 0.3 ev in the two cases, that is, the thermal dissociation energy is approximately ten times smaller than the optical excitation energy of the centers. Apparently the configurational energy diagram of the V_1 center has the characteristic form shown in Fig. 36, the ground state being very shallow and the excited states rising very steeply in the vicinity of the minimum of the ground state. The relative shallowness of the ground state agrees with the observation that the V_1 band is broad in comparison with the F band at low temperatures (see Fig. 30).

Ghormley and Levy[96] have measured phosphorescent glow curves for specimens of KBr and LiF darkened with γ rays at nitrogen temperatures (see Sec. 21). In the case of KBr, which is of interest for comparison with the work of Dutton and Maurer, peaks were observed at $-150°C$, $-70°C$, and $-10°C$. The temperatures correspond moderately well to three of the temperatures listed in Table XI for KBr. The wavelengths of the emitted light do not correspond very well, however. The radiation emitted at $-150°C$ possessed peaks at 3200A and 5000A, that emitted at $-70°C$ possessed a single peak at 5000A, whereas that emitted at $-10°C$ had peaks at 2900A and about 4500A. Only the last case appears to fit in with the results listed in Table XI. It seems futile to push interpretation of the luminescent spectra very far.

An interesting type of "temperature-independent" phosphorescence was observed at liquid nitrogen temperatures in specimens of LiF, KBr, and NaCl darkened with gamma rays at low temperatures. It was found, for example, that the specimens emitted radiation when maintained at constant temperature near $-196°$. The rate of emission could be increased by raising the temperature, however, the rate was restored essentially to its old value when the temperature was re-established at $-196°C$. The investigators sug-

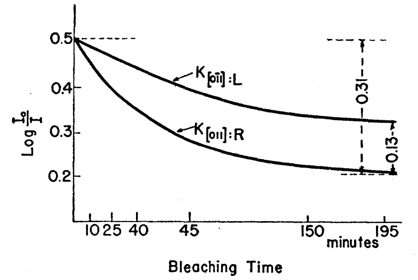


FIG. 37. Variation of the extinction coefficients of the *M* band for light polarized in the $(0\bar{1}1)$ and (011) directions when the *M* band is bleached with light polarized in the second direction (after Ueta). The coefficient falls more rapidly for light polarized in the same direction as the bleaching radiation, showing that the *M* center does not have cubic symmetry and that there are at least two types of *M* centers when viewed from the standpoint of light polarized in (110)-type directions.

gest that the emission is associated with tunneling of electrons to holes. On the other hand, it could be characteristic of any process in which only a small fraction of the reactants is consumed in the excursion to higher temperatures.

31. Bleaching of *M* Centers with Polarized Light

Ueta[142] has carried out a revealing series of experiments with polarized light. He darkened a single-crystal specimen of KCl with x-rays in such a way as to produce a prominent *M* band and examined the change in absorption within the *M* band for light traveling in the $(\bar{1}00)$ direction and polarized in either the (011) or $(0\bar{1}1)$ direction after bleaching with light polarized in one of these two directions. He found that the decrease in absorption is always greatest for light polarized in the same direction as the bleaching radiation (Fig. 37). An experiment of the same type carried out with the *F* band instead of the *M* band would have revealed no difference in absorption for light polarized in either direction. The conclusion to be drawn is that the *M* center possesses lower than cubic symmetry. There are at least two essentially different types of *M* center for light polarized in the (011) direction, whereas all *F* centers are equivalent since they have cubic symmetry.

Ueta's result is in excellent qualitative accord with the model of the *M* center proposed in Fig. 2, for this has the symmetry of the crystal class C_{2v}. Naturally, Ueta's measurements do not furnish a unique proof of this model, but indicate that it is qualitatively reasonable.

{*Note added in proof.*—Professor E. E. Schneider has called my attention to a weak dichroism observed by S. Nikitine [Compt. rend. **213**, 32 (1941); **216**, 730, 758 (1943); J. phys. **3**, 203 (1942)] after bleaching *F* centers, produced by x-rays, in NaCl and KCl. This effect appears to be an order of magnitude smaller than that observed by Ueta.}

32. Expansion of Lattice during X-Ray Darkening

Sakaguchi and Suita[70] have investigated the change in volume of KCl, KBr, and NaCl during x-irradiation at room temperature by an ingenious method which permits continuous observations during the darkening process. The specimens studied were employed as the base for one electrode of a condenser, which was fastened to the crystal. The expansion of the crystal during irradiation alters the capacity of the condenser and permits relatively direct determination of the dimensional changes. The capacity of the condenser was measured by alternating current means. The diameter of the circular electrodes was 5 cm and the gap was taken to be about 1 mm in a typical case. Studies were made in cases in which the specimens were irradiated both parallel and perpendicular to the normal to the condenser plates.

The expansion of the crystal starts as soon as the irradiation begins and varies linearly for an initial period of about an hour for typical intensities. Eventually the expansion saturates and approaches an asymptote. The x-rays employed were sufficiently hard to penetrate for distances of the order of tenths of a millimeter; however, darkening was observed to depths of about 0.7, 0.65, and 0.45 cm in specimens of KCl, NaCl, and KBr, respectively. The increase in linear dimensions is of the order of 3×10^{-5} cm in a typical case. The expansion would correspond to the production of about 1.2×10^{18} vacancy pairs per cc in the typical case at saturation if this were the principal source of volume change. The estimated density of *F* centers agrees with this value to within about thirty percent. There is a chance that the expansion observed had its origin in factors other than the mere production of *F* centers, for the experiments were carried out at room temperature in air. For example, the salt may have decomposed, producing porosity and alkali metal oxide. It would be valuable to have the work extended under somewhat different conditions, for example, at lower temperatures and in a vacuum.

Figure 38 shows the averaged values of the expansion

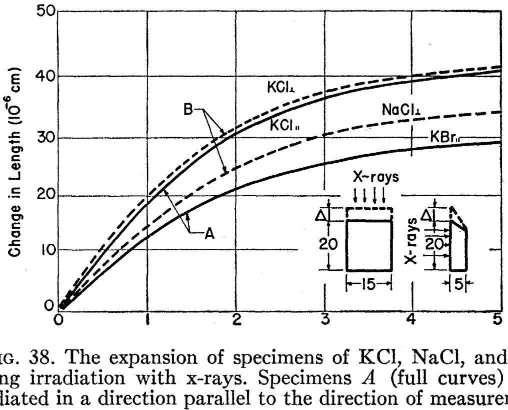


FIG. 38. The expansion of specimens of KCl, NaCl, and KBr during irradiation with x-rays. Specimens *A* (full curves) were irradiated in a direction parallel to the direction of measurement, whereas specimens *B* were irradiated in the normal direction (after Sakaguchi and Suita).

---

[142] M. Ueta, J. Phys. Soc. Japan **7**, 107 (1952).

of the specimens measured as a function of time. The full curves, designated by A, correspond to specimens irradiated parallel to the normal of the condenser plates whereas the dashed curves, labeled B, correspond to specimens irradiated in the perpendicular direction.

This very valuable investigation would appear to dispose of the notion that, in cases of this type, a substantial part of initial darkening takes place with the use of vacancies or vacancy clusters already present and hence without an expansion of the specimen. If the measurements may be taken at their face value, the expansion varies linearly with time when the average density of color centers in the darkened region is as small as 10^{16} per cc. It is possible, of course, that existing pores are dissolved during the entire darkening process and that a fraction of the darkening does not require the development of new porosity. This would require a careful comparison of the total density of centers of all types employing vacancies and the change in volume of the crystal.

One of the great virtues of the technique developed by Sakaguchi and Suita is that it can, in principle, be applied at any temperature. Thus it should make the determination of density changes at low temperatures possible and open areas not accessible to direct means, such as those employed by Estermann, Leivo, and Stern.

33. Photoconductivity in the V Bands

Teegarden and Maurer[127] have studied both the efficiency with which the V_1 band may be bleached and the photocurrents induced by irradiating with light in and near the V_1 band for both KCl and KBr. The work is still in progress at the time this review is being prepared, so that the principal conclusions can be presented only in a tentative manner.

The quantum yield for bleaching the V_1 centers in KCl with light absorbed by this band is in the vicinity of 0.05 at $-185°C$. This result is remarkably low in view of the small activation energy Dutton and Maurer obtained for freeing the holes thermally. Apparently the first-excited state is very close to the ground state for a range of the nuclear coordinates near the minimum of the former, whence the transition back to the ground state occurs with a fairly high probability.

The photocurrent, or rather the product of the hole range per unit field and the quantum efficiency of freeing a hole, is very low in the vicinity of the V_1 band, relative to the value farther in the ultraviolet, near the V_2, V_3, and V_4 bands, for both KCl and KBr. In fact the photocurrent in the part of the optical spectrum where this band has its peak is relatively insensitive to the extent by which the V_1 band has been bleached previously by heat. The investigators conclude that the V bands farther to the ultraviolet are probably much better photoelectric sources of holes than the V_1 bands. A semiquantitative study of the photocurrents obtained from these bands in KBr indicates that the yield is perhaps five times larger at $-133°C$ than at $-185°C$ in a specimen darkened with x-rays at $-100°C$.

The investigators have attempted to set a lower limit on the *Schubweg* of the holes freed by light in the V_1 band relative to the *Schubweg* of electrons freed from F centers in KCl at liquid nitrogen temperatures. They assume that the quantum yield for freeing holes is 0.05, whereas the corresponding yield for electrons in the F band, at $-185°C$, is 0.1. This yields a lower limit for the ratio of *Schubwegs*, for it is not certain that the bleaching of V_1 bands by the action of light, which occurs with quantum efficiency 0.05, actually requires the freeing of holes. Tunneling may play an important role if the orbital radius of the excited state of the hole is so large that the distribution function overlaps into regions of the crystal where there is a substantial number of F-type centers, or other centers which may accept a hole. In any case, Teegarden and Maurer conclude that the ratio is not less than 1/25. Dutton and Maurer attempted a similar comparison on the assumption that all the V_1 centers contribute free holes when bleached by warming. The corresponding ratio is found to be nearer 1/6 for KCl darkened by x-rays if one compares the *Schubweg* of electrons measured at $-120°C$, as determined from Glaser's photoconductive measurements, with the *Schubweg* of holes at $-145°C$, as determined from the bleaching of the V_1 band. The quantum yield for freeing holes should be about four times smaller than that for bleaching V_1 centers with light if the difference between this ratio and the value of 1/25 derived previously is to be taken seriously.

VIII. PROPERTIES OF CRYSTALS COLORED AT HYDROGEN AND HELIUM TEMPERATURES

Whenever one investigates a well-known physical system, with its associated problems, under new physical conditions such as in a new range of temperature, some of the problems are greatly simplified and many uncertainties are removed. On the other hand, entirely new problems and complications may arise as well. These may make the initial issues seem relatively simple. The extension of research on color centers in the alkali halides to the hydrogen-helium range appears to exhibit some of this characteristic behavior, although it must be admitted that the field is still insufficiently explored to permit extensive generalizations. Perhaps the most simple and effective experiment carried out in this range is that of Domanic[143] on the measurement of photocurrents in crystals containing F' centers when irradiated in the F' band at hydrogen temperatures. This work shows that the F' centers are capable of yielding photoelectrons at very low temperatures as a result of irradiation in the main band. Moreover it supplies important evidence to confirm the

---

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

view that the F' center has the characteristics of a negative ion.

The most extensive program at the lower temperature range has been that of Markham[144] and his associates, particularly Duerig, although several very important investigations have been carried out by others, particularly by Martienssen.[114] We shall discuss all of this work by considering two principal categories, namely, the F-type and V-type bands.

34. *F*-Type Bands

The F band may be formed with characteristic intensity and properties by x-raying crystals at hydrogen and helium temperatures. The process is somewhat slower than at higher temperatures; however, there appears to be no essential qualitative difference. Figure 32, which was discussed earlier, shows the variation of the intensity of the F band of KBr as a function of time of irradiation with x-rays at both −253°C (20°K) and at −183°C as determined by Martienssen. It may be seen that the rise is linear in both cases, but is more rapid at the higher temperature. The curves do not extrapolate linearly to the origin but have a greater slope at low intensities. The α band, associated with a halogen vacancy, is also observed to grow during irradiation. The intensity of this band as a function of time is shown in the same figure. As was remarked in Sec. 24, Martienssen found that the α band grows more rapidly at the lower temperature and in such a way that the sum of the intensities of the two bands increases in almost the same way at the two temperatures. We obtain the interesting conclusion that the total number of F centers and isolated halogen-ion vacancies increases at about the same rate in KBr at hydrogen and nitrogen temperatures, at least under the conditions of irradiation employed, for the widths and oscillator strengths of the two bands are about the same as far as can be discerned from existing data (see Sec. 24). As emphasized earlier, this result seems to imply that the x-radiation has about the same potentiality for producing isolated vacant sites at the two temperatures; the extent to which they are occupied by electrons to form F centers is determined by secondary characteristics of the irradiation process.

Duerig and Markham have investigated a number of properties of the F centers formed at low temperatures on a variety of crystals from different sources. Figure 39 shows the growth of the F band in a typical specimen of NaCl as a function of time when irradiation occurs at 5°K. The behavior is closely the same as that found by Martienssen. The F bands produced in this way resemble those produced at higher temperatures and by additive coloring very closely. However, there are quantitative differences which appear to be well beyond the limits of error. A striking feature of the results is that the bands produced at helium temperatures are somewhat narrower than those produced at higher temperatures. Table XII shows typical data for NaCl on which the greatest variety of measurements has been made. The quantity λ_m is the wavelength of the maximum of the band, whereas λ_v and λ_r are the values of the wavelengths of the violet and red edges of the band at half-maximum. While the shifts are only about one percent in the greatest cases, and hence relatively small compared with those observed by Kaiser in evaporated and additively colored deposits, they do indicate that the F centers are formed in different environments in the different crystals under different conditions. On the whole, the specimens used by Duerig and Markham appear to give narrower F bands than those of other investigators at the helium and nitrogen ranges, perhaps because the crystals are more homogeneous chemically and physically. The results of all investigators seem to be comparable at room temperature; possibly the influence of thermal vibration masks all other sources of imperfection at this and higher temperatures.

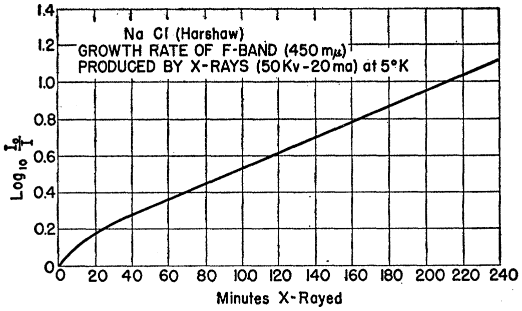


Fig. 39. The growth of the F band in NaCl during x-irradiation at 5°K (after Duerig and Markham).

Differences comparable to those given in Table XII are also found for KCl and KBr, the bands determined by Duerig and Markham being narrower than those measured by Mollwo,[145] mainly with additively colored crystals. The first pair of investigators note that some of the bands observed by Casler, Pringsheim, and Yuster[124] are nearly the same as their own.

The average densities of color centers attainable at 5°K with relatively short times of irradiation are comparable in NaCl, KCl, and KBr. For example, the darkening in the colored layers is estimated to correspond to 1.6, 1 and 1×10^{18} F centers per cc at the end of 15 minutes for the three crystals in the order mentioned under conditions in which the x-ray tube was operating at 50 kv and 20 ma.

Duerig and Markham did not always find more rapid growth of the F band at nitrogen than at helium

---

[144] J. J. Markham, Phys. Rev. **88**, 500 (1952); W. H. Duerig and J. J. Markham, *ibid* p. 1043; J. J. Markham, J. Phys. Chem. **57**, 26 (1953); R. T. Platt and J. J. Markham, Phys. Rev. **92**, 40 (1953); Markham, Platt, and Mador, Phys. Rev. **92**, 597 (1953). Also as yet unpublished thesis of W. H. Duerig. See also the paper by Mador, Markham, and Platt, Phys. Rev. **91**, 1277 (1953) concerning the width of the F band formed in different ways and measured at 78°K.

[145] E. Mollwo, Z. Physik **85**, 56 (1933).

temperatures, as Martienssen observed in the case of KBr. For example, the specimens of NaCl employed in the work appeared to be an exception. More rapid darkening was found at the lower temperature in most other cases, however, including KBr. It is not possible to state whether the more rapid growth of the F band at lower temperatures is balanced by a slower growth of the α band for they did not study the growth of the α band.

As remarked at several points in the preceding sections, the rate of darkening is controlled by factors such as the impurity content or the dislocation pattern which are only crudely understood at the present time.

Neither the R nor the M bands have been observed in any of the specimens darkened at helium or hydrogen temperatures. On the other hand, the F' band is found as a relatively weak satellite in both NaCl and KBr, although it has not yet been observed in KCl. The investigations on KBr indicate that the magnitude of the F' band increases relative to that of the F band with increasing intensity. Thus the F' band could not be separated when the x-ray tube was operating at 20 ma and 50 kv, but it became evident when the current was 48 ma.

Markham, Platt, and Mador[144] have made measurements on crystals from a variety of sources, extending from commercially available specimens to specially purified materials prepared by Schulman at the Naval Research Laboratory. There is evidence that the purer materials darken somewhat more slowly even at low temperatures. In addition, the F' band was found to be more highly developed in the purer specimens of NaCl, as if there were fewer halogen ion vacancies present in total to trap electrons when the density of F centers attains a given level, that is, as if the ratio of the α band to the F band were smaller than in the relatively impure materials. It would be valuable to have data for crystals containing additions of divalent impurities.

35. V-Type Bands

Whereas the observations on the F-type bands produced at very low temperatures exhibit a pristine type of simplicity, the observations on the V-type bands show more complexity. As noted previously, the α band appears prominently. The β band is also present (see Fig. 40), however, it has not been studied as carefully as the α band and may possibly display structure not found in additively colored crystals or in specimens darkened at higher temperatures. This additional structure may arise from clusters or centers not produced at higher temperatures.

TABLE XII. Values of λ_v, λ_m, and λ_r for the F band in NaCl under various conditions (in angstroms, after Duerig and Markham). λ_m = wavelength at maximum. λ_v, λ_r = wavelengths of violet and red edges at half-maximum.

Origin	λ_v	λ_m	λ_r
1. X-ray at 5°K, measured at 5°K[a]	4260	4500	4710
2. Probably additive, measured at 20°K[b]	4260	4540	4820
3. X-ray at 5°K, measured at 78°K[a]	4270	4510	4730
4. X-ray at 78°K, measured at 78°K[a]	(Same as 3)		
5. Probably additive, measured at 78°K[b]	4260	4550	4830
6. X-ray at 300°K, measured at 78°K[c]	(Same as 5)		
7. X-ray at 300°K, measured at 300°K[a]	4220	4650	5060
8. Probably additive, measured at 300°K[b]	(Same as 7)		

[a] Duerig and Markham, reference 144 (see, also, Mador, Markham and Platt, reference 144).
[b] E. Mollwo, reference 145.
[c] P. Molnar, thesis, Massachusetts Institute of Technology (unpublished).

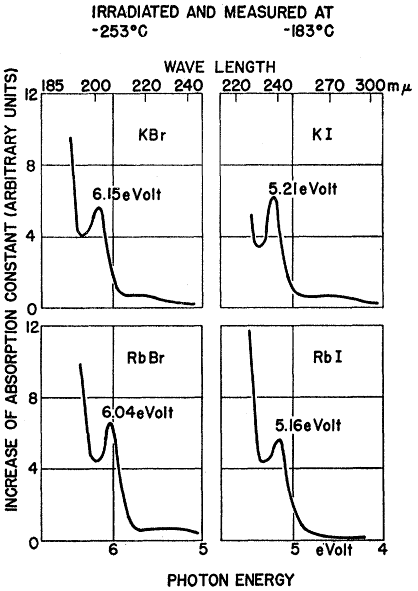


FIG. 40. Absorption spectra in the region of the α and β bands in specimens of several crystals irradiated at liquid hydrogen and nitrogen temperatures (after Martienssen). The prominent peak is the α band, whereas most of the rise on the short-wavelength side of this peak is in the vicinity of the β band. It is not known whether the β band appears alone or is accompanied by absorption associated with other centers.

The region covering the V_2, V_3, and V_4 bands was not studied in NaCl because it lies outside the range of the spectroscope employed in the work. Similarly, the V_3 band was not studied in KCl. In the second case, a very small band was observed at 2550A. This seems to correspond closely with the V_4 band observed by Dorendorf at higher temperatures but is sufficiently obscure that the identification is not reliable. The V_2 band, which is at 2300A in KCl, is not found in the specimens irradiated at 5°K, when observed at that temperature (Fig. 41). KBr exhibits no striking evidence of the V_2 and V_3 bands, both of which would have been amply covered by the spectrograph; however, there is evidence of a weak band which may be identified rather roughly with the V_4 band. The observed peak is at about 2850A, whereas the V_4 band found by Dorendorf is at 2750A. The investigators found a band at 2300A in KBr which was not found in specially purified material. It apparently is not characteristic of the pure crystal and may be set aside for purposes of the present discussion.

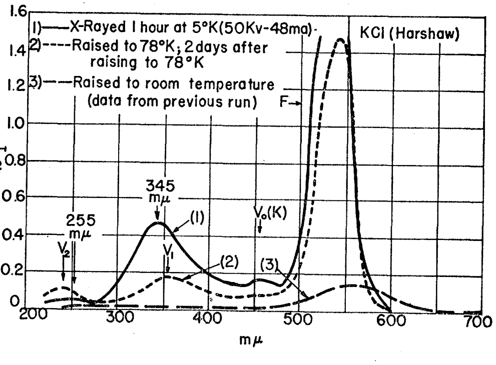


FIG. 41. Absorption spectra of a specimen of KCl irradiated at liquid helium temperature and subsequently raised to 78°K and to room temperature. It may be seen that the band at 345 mμ drops as a result of warming to liquid nitrogen temperature, whereas the V_2 band grows. The K band appears prominently. The band at 345 mμ differs from the V_1 band, peaking farther to the violet (after Duerig and Markham).

The K band (Fig. 3) is shown prominently in Fig. 41. Duerig and Markham designated this by V_0 in their initial work, since in many ways it behaves somewhat like a V-type band; for example, it decreases when F' centers are bleached with F' light. This drop, however, is probably a consequence of the extension of the F' band on the blue side of the F band[146] (Fig. 42). The absorption in the region of the K band drops when the F' center is bleached even in cases in which the F' centers are converted into F centers. As a result, it appears to the writer that it is more conservative at the present time to retain the viewpoint that the K band is associated with transitions to the higher discrete states of the F center, as first proposed by Mott and Gurney. It is possible that the higher excited states are perturbed more than the first-excited state by the environment of the F centers when other imperfections such as vacancies or other F centers are nearby and that some of the variations in the relative intensity of the K band in crystals darkened at low temperatures can be ascribed to variations in the local density of such imperfections. Markham has expressed concurrence with this viewpoint at the time this article is being written (see the comments on the K band in Sec. 2).

The greatest difference in properties at helium and nitrogen temperatures is observed in the vicinity of the V_1 band. It is not possible to say whether V_1 actually occurs at helium temperature; however if it does it is masked in all three crystals by a strong band, designated as H by Duerig and Markham, which covers the same general region as the V_1 band but has its peak farther to the ultraviolet (Fig. 43). The wavelengths of the maxima of the H and V_1 bands are compared in Table XIII.

The H band bleaches almost completely when the crystals are heated to 78°K, although a small "hard" component remains at the end of twenty minutes, probably bleaching slowly (see Fig. 43). It is replaced by the V_1 band, which inevitably appears, and by a relatively small component of the V_2 or V_4 band. The first of these is most prominent in KCl and the second in KBr. A large part of the F band vanishes during this transition.

It is interesting to note, in connection with the vanishing of the H band, that Dutton and Maurer[126] (Sec. 30) made several measurements of the current pulses observed when a specimen of KCl darkened at liquid helium temperatures was warmed from such temperatures to room temperature. They found a large burst of charge during the transition to −183°C, presumably as a result of the bleaching of the H band. Moreover, they found no evidence of the band at −68°C associated with the bleaching of the F' band. Optical measurements at liquid nitrogen temperatures did not reveal the F' band.

Figure 41 shows the absorption spectrum of KCl after irradiation at 5°K and after being raised first to liquid nitrogen temperature and then to room temperature. The specimen was held at 78°K for two days before measurements were made. The disappearance of the H band during the first warming and of the V_1 band during the second is clearly evident. Figure 43 shows, in greater detail, the absorption in the region of the V_1 and H bands of KBr just after a specimen is warmed from 5°K to liquid nitrogen temperature and after it is held for twenty minutes. The slow subsidence of the H band is evident.

36. Bleaching

Markham, Platt, and Mador[144] have found that the F band produced at helium temperatures will bleach

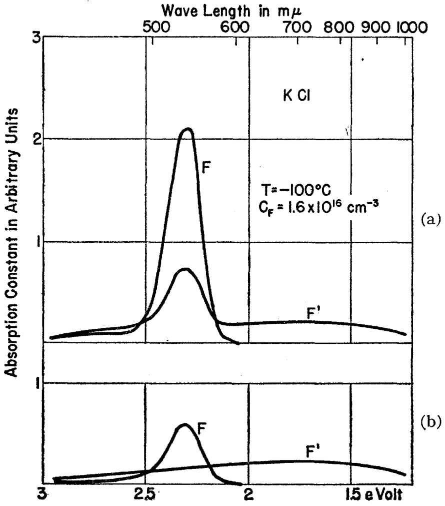


FIG. 42. Resolution of the F and F' bands in KCl (after Pick). The F' band appears when the additively colored crystal is irradiated with light in the F band at −100°C [diagram (a)]. Diagram (b) shows the resolution of the F and F' bands. It may be seen that the latter extends to the short-wavelength side of the former.

---

[146] H. Pick, Ann. Physik 37, 421 (1940).

if held at that temperature even in the absence of light. Such bleaching, which is of the order of a few percent, is detectible over a period of one hour after the end of irradiation, that is, over a period of time comparable to the initial irradiation. This inherent instability can be accelerated greatly, and the bleaching extended, by irradiating with light in the *F* band. Such irradiation presumably does not ionize the *F* centers, but raises them to the first excited state. One may apparently conclude that the electrons are able to bleach more easily from the excited state than from the ground state. The existence of such bleaching processes implies that measurements of the number of *F* centers, and presumably of other centers, is strongly dependent upon the history of the specimen after irradiation. It would be interesting, for example, to know the history following irradiation of Martienssen's specimens on which the data of Fig. 32 were obtained.

It seems most reasonable to asume that the *F* centers bleach both in the dark and as a result of irradiation in the *F* band at helium temperatures because the electrons are able to tunnel to holes, probably associated with *V* centers. This assumption implies in turn that the centers produced at helium temperatures must be relatively close together, so that the mechanism of generation leads to relatively dense arrays of *F*-type and *V*-type centers.

It is sufficient, for the present discussion, to employ Simpson's model[104] of the *F* center (Sec. 23) in order to obtain an estimate of the distribution of the electron in the normal and excited state. He has found that the mean radius of the charge distribution is 3.0 a_0 or 1.6A for the 1*s* or ground state, and 5.6 a_0, or 3.0A, for the 2*p* state, attained by excitation with light in the *F* band. The attenuation of the wave function of the ground state is such that the electron density drops by a factor of 10^{20} in a distance of about 25A. This means that the electron would find itself near another center which it could join or at which it could be annihilated about once in 10^6 sec if the second center is at a distance of 25A. Similarly an electron in the first-excited state, with a lifetime of 10^{-8} sec or less, will have unit probability of meeting a similar center within this lifetime if the center is at a distance less than 13A. In other words, the hypothesis of tunneling described above seems to require[147] that a large fraction of the *F* centers have *V* centers, or other centers which may provide bridges, in a distance lying in the range from 10 to 30A. This limit is attained if the densities of centers achieve values in the range from 10^{19} to 10^{20} in the darkened regions and if the *F* and *V* centers are more or less uniformly distributed relative to one another in such regions. Since Duerig and Markham have found that the average density in the darkened layer of their specimens is nearer 10^{18} *F* centers per cc, it would seem to follow that the coloration is not uniformly spread, but is localized in regions constituting of the order of a few percent or less of the darkened volume. It would be interesting to know if such concentrations of darkening can be observed under a strong microscope.

TABLE XIII. The wavelengths of the peaks of the V_1 and H bands at 5°K (values in angstroms, after Duerig and Markham).

Crystal	V_1	H
NaCl	3450	3300
KCl	3560	3450
KBr	4100	3800

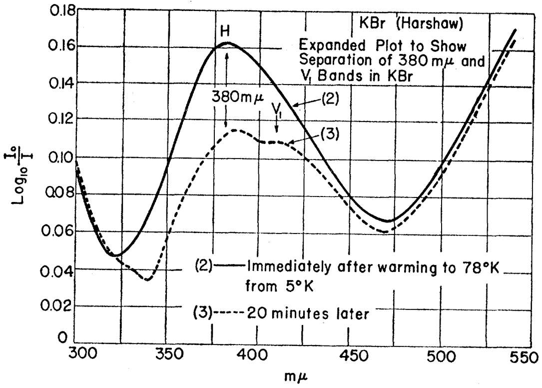


FIG. 43. Expanded plot of the V_1 region in KBr (after Duerig and Markham). The full curve shows the absorption spectrum just after the crystal has been warmed from liquid helium to liquid nitrogen temperature, whereas the dashed curve shows the absorption spectrum twenty minutes later. It is clear that the *H* peak and the V_1 peak are different.

(*Note added in proof.*—Markham has pointed out to the writer that calculations based upon the direct tunneling process *overestimate* the likelihood of the tunneling transition in cases like that considered here because they do not account for the fact that the two electronic states have different energies. Not only must tunneling occur, but the electronic state must change in such a way that excess electronic energy is carried away. Thus such transfers require the emission of either light quanta or phonons. Markham is extending this investigation. The corrections presumably will be in such a direction as to decrease the distance at which tunneling can occur in the times of interest.)

Markham, Platt, and Mador have also found, in certain specimens of crystal darkened at helium temperatures, that a portion of the *F* band can be converted into the *F'* band by irradiating in the *F* band. This was observed after a large part of the *F* band had bleached, presumably by tunneling of electrons to holes, and a type of stability had been attained. If the crystal containing *F'* centers was left in the dark, the *F'* band decayed with restoration of the *F* band. This restoration could be accomplished more rapidly by ir-

---

[147] The writer is indebted to D. L. Dexter for a discussion of the radius within which tunneling is highly probable. The values given above for the *F* center in the normal state are about two times larger than initial estimates made by the writer. The change is a result of discussion with Dexter.

radiating with light in the F' band. The process of conversion from F to F' centers and back again could be carried out a number of times without major diminution of the over-all strength of the F band. It would appear in this case that the F centers responsible for the effect lie so close to other F centers that the electrons associated with them can transfer to other F centers, converting the latter into F' centers, when raised to the first excited level. The transferred electrons subsequently tunnel back to the vacant sites produced by the first process, restoring the F centers, if the specimen is in the dark. It is not yet clear what occurs when the F' centers are irradiated with light in the F' band. One might expect this process to free the extra electrons, for they presumably may make a transition to the ionization states even at liquid helium temperatures. Since the F band is restored even in this case, it appears that the free electrons are recaptured by vacant lattice sites, perhaps because the V centers present will not accept them.

Crystals darkened at 78°K and room temperature will also bleach, although to a lesser extent, when irradiated at 5°K with F light. In these cases about half the darkening lost is recovered after the first bleaching. Almost all is recoverable in successive bleachings. Presumably only about half the electrons associated with the bleached F centers are annihilated during the first bleaching in such cases, whereas the remainder join other F centers to form F' centers, and may tunnel back to halogen-ion vacancies. Taken as a whole, the bleaching experiments carried on at 5°K imply that the F and V centers are very close and intimately mixed in the specimens darkened at helium temperatures. Under these circumstances bleaching occurs primarily by annihilation. In contrast, the F-type and V-type centers which survive the original irradiation with x-rays seem to be more completely separated from one another in the specimens darkened with x-rays at higher temperatures. Neighboring centers are still sufficiently close, however, that the electrons may tunnel to them from excited F centers.

Incidentally, the investigators found that they could not convert the F centers in additively colored crystals to F' centers at helium temperatures. Presumably the centers are much more diffusely distributed in such specimens, so that tunneling cannot occur during the brief time in which the F center is excited.

37. Formation of Color Centers

How are the color centers formed at low temperatures? Since thermal diffusion is negligible at hydrogen and helium temperatures and since the porosity associated with the vacancies belonging to the color centers presumably is not present prior to irradiation, it is simplest to assume that the vacant lattice sites are generated at dislocations as a consequence of very high temperatures, attained at the dislocations during irradiation, and are made to diffuse as a result of similar thermal spikes. The writer would like to propose that the excitons generated during irradiation are adequate for producing the high temperatures necessary for both processes. It is only necessary to assume that excitons travel through the crystal until they meet dislocations or vacancies and become trapped at such positions, expending their energy in the stimulation of a highly localized burst of lattice vibration. For example, a small number of atoms at the edge of a dislocation could receive a total of 6.7 ev of vibrational energy by this mechanism. As we saw in connection with the analysis of the migration of halogen ion vacancies as a result of thermal spikes (Sec. 29), energies of this magnitude are adequate to explain the stimulation of typical rate processes. It is possible that the free electrons and holes created by ionizing radiations play an important role in the generation of vacancies at helium and hydrogen temperatures; however, it does not seem necessary to make this assumption. There is sufficient similarity between the generation of color centers at helium and nitrogen temperatures that it appears adequate to assume the same mechanism can operate at both temperatures. Smakula[61] and Apker and Taft[55] have shown that color centers can be produced at liquid nitrogen temperatures by irradiation in the fundamental band alone, that is, with the use of excitons alone. The coloration produced in this way at these temperatures seems to be much the same as that produced by ionizing radiations, although it must be admitted that the average density was much lower in Smakula's case. Hence, in lieu of experiments to the contrary, it appears reasonable to conclude that excitons could be effective at still lower temperatures.

Martienssen's[114] observations on the bleaching of the α band with light absorbed in this band forms a very convincing link in justifying the foregoing reasoning. It is worth noting that we should not expect coagulation of vacancies similar to that implied in Martienssen's experiments if the crystal receives radiation in the fundamental band itself instead of radiation absorbed in the α band alone. The latter will presumably raise the temperature around isolated halogen-ion vacancies exclusively and leave them unaffected once they have joined an aggregate which does not possess an α band. On the other hand, free excitons, produced by irradiation in the fundamental band itself, presumably, can interact with clusters of vacancies and dislocations as well as with isolated vacancies. Hence they will have the effect of raising the entire complex of imperfections which are genetically related to vacancies to high transient temperatures, at least in local regions, and tend to generate a gas of isolated vacancies within the solid. It is not unreasonable to suppose, however, that some simple clusters, particularly neutral pairs of vacancies, will form in the process. Whenever a positive- and a negative-ion vacancy find one another within a few atom distances they will exert a strong attraction and, if sufficiently close, may join without the requirement of a thermal activation energy (see Fig. 9).

The thermal spikes produced at the vacancies by excitons may, of course, cause vacancies to migrate and hence diffuse away from the region of origin.

Figure 44 shows schematically the essence of the foregoing process. The extra half-plane of ions associated with a typical edge dislocation is indicated by the rectangle whose long axis is in the vertical direction. As vacant lattice sites are "evaporated" from it by the thermal energy supplied by excitons, this half-plane extends downward (dashed rectangle). It is to be emphasized that this extension is not minor if current estimates of the density of dislocations are correct. According to present views, about 10^{15} atoms per cc are immediately adjacent to dislocation lines. Hence the edge of the average dislocation must "climb" through about 1000 atomic distances in generating 10^{18} vacancies per cc. In other words, the darkening process should have a major influence on the dislocation pattern.

Delbecq's observation that light absorbed in the first fundamental band of evaporated deposits of KI produces a diffuse broadening of this band, discussed at the end of Sec. 20, suggests that the process described here whereby vacancies are generated from dislocations, and presumably cracks, by excitons can fill the entire crystal with vacancies and vacancy clusters in a practically observable time (10^3 sec) if the ambient temperature is above -135°C. The intrinsic importance of the limiting temperature is not obvious; however, it seems plausible to assume that at this point ambient temperature begins to aid vacancies which are created near appropriate imperfections by thermal spikes to diffuse to other parts of the crystal. This, for example, may be the point at which the vacancy pairs in KI become sufficiently mobile to diffuse for distances of the order of 1μ in a time of the order of 10^3 sec, as would be the case if the activation energy for such diffusion in KI were between 0.25 and 0.30 ev. Dienes' calculated value for NaCl is 0.375 ev (Sec. 9), so a value near 0.25 ev for KI is not unreasonable. It would be interesting to study the influence of radiation under conditions producing the type of disorder observed by Delbecq on specimens which are additively colored by addition of excess alkali metal or excess halogen. Perhaps V_2 and V_3 centers can be converted into V_1 centers under these conditions.

Granting that the thermal spikes derived from excitons are adequate to produce vacant lattice sites, the extension of reasoning that is needed to account for generation of color centers does not appear great. In the first place, there will be many free electrons and holes in crystals bombarded with ionizing radiations; it is only necessary to have these captured by the appropriate vacancies. Moreover, since the binding energy of a negative-ion vacancy for an electron is probably somewhat larger than the binding energy of the electron and hole in an exciton, it is quite possible, as proposed by Dexter and Heller,[148] that excitons have an appreciable probability of decomposing into F centers and free holes on colliding with halogen-ion vacancies. A fraction of the holes formed in this way could subsequently produce V centers by combining with positive-ion vacancies. Acceptance of this process would not explain how light in the fundamental band can produce F centers with a quantum yield of unity; however, this is true only for very low yields, of the order of 10^{13} or 10^{14} F centers per cc, which may be accomplished by a highly specialized mechanism. For example, the excitons may be decomposed, with capture of an electron, at a small number of negative-ion vacancies produced by plastic flow incident to handling the specimens.

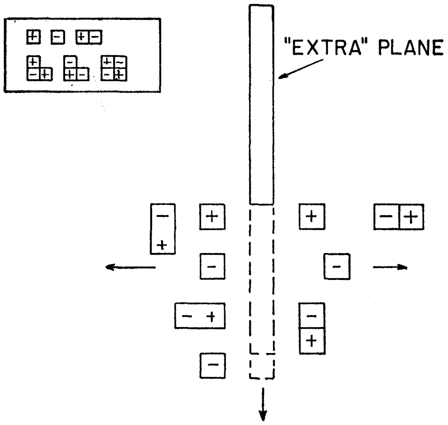


FIG. 44. Schematic representation of the production of vacancies at a Taylor-Orowan dislocation. The vacancies "evaporate" as a result of thermal spikes at the edge of the dislocation and diffuse away when they are able to absorb additional energy producing thermal spikes. The edge of the dislocation moves downward as a result of the loss of vacancies. The upper left-hand panel (inset) shows clusters which may be expected as a result of this process.

It is interesting to estimate the distance which the vacancies diffuse from the source during x-irradiation. The measurements of Harten at liquid nitrogen temperature (Fig. 14), and similar measurements by Martienssen (Sec. 28) at liquid hydrogen temperature, show that an average energy of the order of 2000 ev is required to form an F center at low temperatures. Somewhat less may be required to form a vacancy. If we postulate that this energy is divided into units of about 10 ev, each of which may raise the environment of a vacancy to a temperature sufficient for it to jump one atomic distance, the average vacancy may make 200 jumps during the period of irradiation, as a result of thermal spikes. The radial distance R which the vacancy diffuses from the source as a result is given by

$$R = 2r_0(n/6)^{\frac{1}{2}},$$

where r_0 is the spacing of nearest neighbors and n is the number of jumps. The factor 6 arises from the fact

---

[148] D. L. Dexter and W. H. Heller, Phys. Rev. 84, 377 (1951).

that the jump can occur in 12 different directions, of which 8 give contributions $\pm r_0$ along one of the (100) directions. R is about 40A when n is 200.

The value of the distance R calculated in the preceding paragraph implies that very high densities of vacancies can be achieved near the sources. Suppose, for example, that the source is an edge dislocation which climbs a distance large compared with R. The density of vacancies in the layer of width $2R$ on either side of the surface through which the dislocation has climbed is near 10^{21} per cc. This density is diminished if the dislocation has strong screw character[149] or is predominately screw type, for the density given above should be multiplied by the ratio of edge-to-screw character.

In this connection, the writer has had the pleasure of seeing preliminary results of calculations by H. B. Huntington and Mrs. J. D. Apker which indicate that the screw dislocation may be energetically more stable than the edge dislocation in sodium chloride. This suggests in turn that the source dislocations in well annealed specimens of the alkali halides may be predominantly of screw type.

Dexter (unpublished work) has emphasized the difficulties of supposing that the sources of F centers are pure isolated edge dislocations unless one assumes that the vacant lattice sites produced at such dislocations by irradiation can diffuse from the point of origin by a distance much larger than 50A. He has shown that the influence of the compressive stresses around a typical edge dislocation on the absorption spectrum of an F center closer than 50A is so great that one should expect marked broadening and displacement of the F band in experiments of the type carried out by Duerig and Markham, in contradiction with the actual observations which show that the spectrum obtained during low-temperature irradiation is, if anything, narrower and more well defined than that in additively colored crystals having a much lower density of F centers. Dexter employed values of the pressure shift of the F band measured by Burstein, Oberly, and Davisson in determining the importance of compressive stresses near the edge dislocation. His expression for the energy of the center of the F band in KCl, as a function of the position of the center relative to the dislocation line, is

$$E = 2.21 + 0.92(\sin\omega/r) \text{ (in ev)}.$$

Here 2.21 ev is the energy in the undistorted lattice, r is the radial distance from the line in angstrom units, and ω is the dihedral angle between the slip plane and the plane through the dislocation line and the F center. The second term, representing the influence of the dislocation, is of the same order as the experimental error of the best observations, for all values of ω, only when r is greater than 50A.

Since the most elementary calculation of the number of times a vacancy may jump after being produced at a dislocation during irradiation has led us to the conclusion that the diffusion distance of the average vacancy is appreciably less than 50A, we must conclude either that the elementary calculation is incorrect or that the predominant sources are not simple isolated edge dislocations. Either the sources are primarily screw type, and hence[149] induce relatively small dilatation or they are closely bound groups of edge dislocations, like small-angle boundaries, which do not produce appreciable distortion at distances larger than a few atomic distances. In the second case, the wall would presumably be one in which the dislocation lines are so close that the angle of disorientation is of the order of a degree. It would not be surprising to find the dislocation sources tied into such clusters, for the specimens on which measurements are made usually are well annealed so that the dislocation pattern should have achieved some quasi-equilibrium state. Evidently this problem merits much more detailed consideration.

Martienssen has found that a prominent α band which was produced at -253°C in RbBr with ten minutes of x-irradiation, and which was completely stable at that temperature, bleached somewhat when the specimen was warmed to -183°C (Fig. 45). It bleached even further on warming to -100°C. The specimen contained a negligible number of F-type centers so that the decrease in the α band cannot be ascribed to the fact that the halogen-ion vacancies capture electrons freed during the warming. Since an isolated halogen-ion vacancy should have negligible thermal mobility at any of these temperatures, it appears necessary to assume that some of those negative-ion vacancies which have positive-ion vacancies particularly close by draw the latter to them at the higher temperatures with the aid of the relatively small thermal fluctuations available and form pairs, which do not possess the α band.

According to the viewpoint presented here, the relative difficulty of producing F' centers at helium

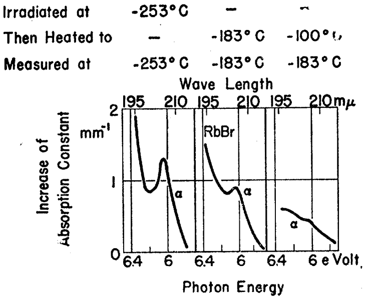


FIG. 45. The bleaching of the α band produced in RbBr at -253°C when the crystal is raised to -183°C and -100°C. The absorption measurements were made at -253°C for the left-hand panel, whereas the measurements were made at -183°C in the other two cases. The diminution of the α band on warming implies that the isolated halogen-ion vacancies are joined by other vacancies to form clusters which do not possess the α band (after Martienssen).

---

[149] The writer is indebted to Dr. R. Thomson for a number of informative discussions of the properties of dislocations in the alkali halides possessing strong screw character.

temperatures, in comparison with liquid nitrogen temperatures, could originate in the possibility that the vacancies are more closely packed when generated at the lower temperature, perhaps because a small but critical amount of thermal energy for diffusion is not available. The distance required for the bleaching of F' centers by tunneling is more closely matched as a result. Higher intensity of x-irradiation may stimulate the dispersal of the vacancies and hence aid the stabilization of all centers relative to bleaching by tunneling.

38. Nature of H centers.

What are the H centers? The writer would like to propose that they arise from holes trapped at neutral vacancy-pairs, the hole in each center of this type being associated with the halogen ions adjacent to the positive-ion vacancy in the pair. The binding energy of a hole and an isolated positive-ion vacancy is so small, about 0.23 ev in KBr, that we should not expect the hole to exert sufficient repulsive force on the negative-ion vacancy in the pair to eject the latter. On the other hand, we should expect it to have a small attractive interaction with the pair. In contrast, an electron makes much better use of the field of a negative-ion vacancy than a positive-ion vacancy does, the energy of dissociation of an F center being about twice that of the pair of vacancies. Hence we should expect the electron to eject the positive-ion vacancy from a pair by at least a few interatomic distances and form an isolated F center and an isolated positive-ion vacancy. The hole should be less stably bound to the pair than to an isolated positive-ion vacancy. Thus it should be released from the pair during warm up at a much lower temperature than from the vacancy. The holes freed in this way will wander about until they meet F centers, where they are annihilated, or until they find stable traps. The most satisfactory traps are isolated positive-ion vacancies or clusters consisting of two positive-ion vacancies and a negative-ion vacancy. Both will exert a Coulomb attraction on the hole. V_1 and V_4 centers are formed in the two cases. We would not expect pairs of positive-ion vacancies to be present because of their electrostatic repulsion. In consequence, essentially no V_3 centers should form as a result of the freeing of holes from H centers. On the other hand, any V_3 centers present initially could be converted into V_2 centers. As remarked previously, the H band is sufficiently broad and prominent that it is difficult to say whether the V_1 band has appreciable intensity after the initial irradiation. It should be present, according to the picture proposed here, for there should be an abundance of isolated positive-ion vacancies and some of them should capture holes.

It is also formally possible that the H band arises from a positively charged center which is the antimorph of the F' center. It is not evident, however, why the majority of positive-ion vacancies should prefer to capture two holes.

Duerig[144] has noted that the V_2 band increases in KCl when the H band is bleached by raising the temperature of the specimen from 5°K to 78°K. In contrast, the V_4 band increases in KBr. This difference suggests that the centers associated with the V_2 band in KCl and the V_4 band in KBr are identical. A reassignment of band designations may be appropriate in at least one of these crystals. On the whole, the behavior of the bands at higher temperatures does not seem to justify such a conclusion at the present time; however, the issue remains open for further consideration.

IX. THE SURFACE PHOTOELECTRIC EFFECT

39. Introduction

Apker and Taft[150] have carried out a very illuminating series of experiments on the photoelectric ejection of electrons from the alkali halides, particularly KI and RbI. This research has thrown penetrating light upon some of the events which transpire when the crystals are irradiated in the region of fundamental absorption and has focused new interest on the problems relating to excitons in crystals. The investigators have presented an excellent review of their own work in the symposium volume, *Imperfections in Nearly Perfect Crystals*,[150] to which the reader is referred. A brief summary of the work, slanted toward the matters of interest in this paper, will be presented here.

The research was carried out between room and liquid nitrogen temperatures on evaporated deposits prepared at room temperature. All available information, such as that carried out during the war on dark-trace tubes and the work of Hilsch and associates on additively colored deposits, indicates that the properties of evaporated layers are in the main typical of those of the bulk alkali halides, at least as far as the characteristics of color centers are concerned. On the other hand, the investigators found evidence that the outer surface of their layers contained a stoichiometric excess of halogen in certain cases, probably because of decomposition of the salt in the evaporator during the early part of the evaporation cycle. This was first discovered by indirect means as a result of analyses of the measurements made by Hebb.[151] To compensate, some of the later deposits were made in a low vapor pressure of the alkali metal (e.g., 10^{-7} mm of Rb) in order to obtain data from specimens having a complementary composition, that is, excess alkali metal near the surface. The properties of the stoichiometric composition may be inferred with high reliability from a comparison of the two types of specimen.

---

[150] See footnotes 47 and 100. Also, E. Taft and L. Apker, Phys. Rev. **83**, 479 (1951); E. Taft and L. Apker in ***Imperfections in Nearly Perfect Crystals***, Edited, W. Shockley, Chairman (John Wiley and Sons, Inc., New York, 1952), p. 246.

[151] M. H. Hebb, Phys. Rev. **81**, 702 (1951).

40. Summary

A summary of the work is as follows:

(a) No significant photoelectric current is observed with photon energies less than 5 ev if the deposit is stoichiometric and has not been subject to prior irradiation with electrons or with light in the fundamental absorption band. However, photoelectrons will appear at energies below 3.0 ev if the deposit is treated in a manner which is known to produce *F* centers. Equivalent results have been obtained with specimens darkened with cathode rays, general ultraviolet radiation, and light lying in the fundamental band. Figure 46 shows the yield, in photoelectrons per quantum, as a function of photon energy at room temperature in the case of KI. There is a well-defined yield of about 10^{-8} electrons per photon near 2 ev. The observed yield rises to a plateau in the vicinity of 10^{-4} electrons per photon just above 4 ev. The threshold for the plateau is presumably near 3.0 ev. A similar rise and plateau are found in RbI. This part of the yield curve is relatively insensitive to temperature. Apker and Taft conclude that the long-wavelength portion of the yield, including that in the plateau, arises from electrons which are ejected from *F* centers directly to the free electron states by the photons and have sufficient kinetic energy to overcome the barrier at the surface which represents the transition from the bottom of the conduction band to the zero of potential outside the specimen. The center of the *F* band is at about 1.7 ev in KI and at 1.6 ev in KBr. Even though free electrons are produced by irradiating in the *F* bands, they do not have sufficient energy to escape from the crystal. The investigators conclude that an additional 1.9 ev is required if they are to emerge outside the crystal; however, since more energy is required to ionize the electron directly, rather than excite it to an upper discrete level and permit thermal fluctuations to complete the freeing process, not all the 1.9 ev is required to overcome the surface barrier.

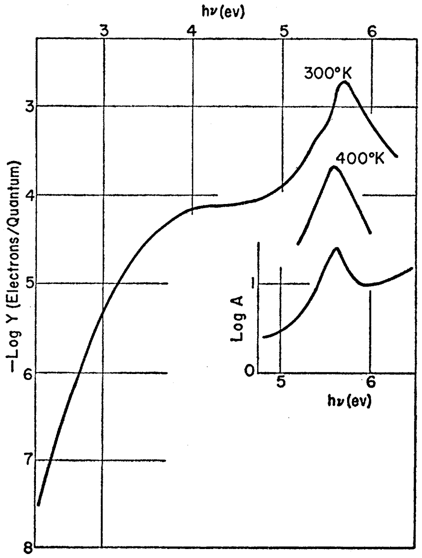


FIG. 46. The photoelectric yield as a function of wavelength for an evaporated specimen of KI which has been sensitized by previous irradiation in the fundamental band (after Apker and Taft). The peak near 5.5 ev coincides with the first fundamental peak of the salt. The complete curve was obtained at 300°K, as indicated, whereas the portion shown below it was measured at 400°K. The inset shows the relative absorption coefficient at 300°K as a function of photon energy, on the same horizontal scale, to illustrate the coincidence of peaks.

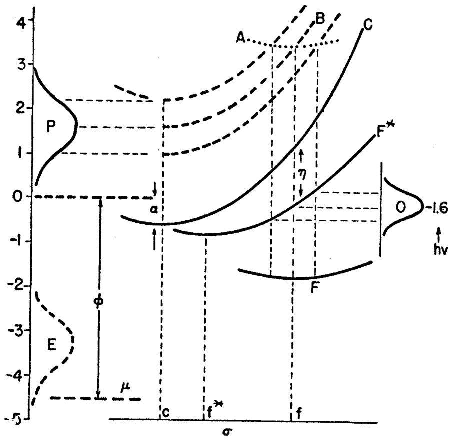


FIG. 47. Energy-level diagram for a specimen of RbI containing an *F* center, proposed by Apker and Taft. The vertical energy scale is in electron volts. The horizontal axis represents configurational coordinates σ. The lowest full curve represents the energy surface for the crystal containing an *F* center in the ground state. The next full curve shows the energy when the *F* center is raised to the first-excited state. The distribution of intensity in the *F* band, which peaks at 1.6 ev is illustrated on the right-hand side of the diagram. Curve *C* represents the lower edge of the ionization continuum. The abscissa points f, f^*, and c represent the values of σ at which these three curves have their minima. The dashed curves *B* represent ionization states in which the electron has various kinetic energies. The dotted curve *A* is parallel to *F* and pictures the ionization states which can be attained by vertical transitions, in accordance with the Franck-Condon principle. The distribution curve *P* on the right shows the spectrum of electron energies to be expected from direct photon ionization of the *F* center with monoenergetic light quanta which induce the transition from curve *F* to *A*. The quantity α is the electron affinity of the crystal, that is the energy required to remove an electron from the bottom of the conduction band. The dotted curve *E* shows the apparent depth from which the photoelectrons in the distribution *P* originate.

The investigators conclude from the photoelectric efficiency in the plateau that the cross section for photoionization of the *F* center is about 10^{-18} cm^2. This is in good agreement with theoretical estimates of the cross section based on use of a hydrogen-like model of the *F* center and the assumption that a total oscillator strength of the order of 0.1 is associated with the ionization continuum.

Figure 47 shows a more complete energy level diagram, constructed by Apker and Taft on the basis of a scheme proposed by Herring, to bring together the data for RbI in a consistent manner. The vertical axis is energy expressed in electron volts and the horizontal axis σ represents the configurational coordinates around the F center. The zero of energy is chosen to be the zero of potential outside the specimen and is marked for a range by the horizontal dotted line. The heavy line F represents the energy surface for the normal state of the F center, whereas F^* represents this surface for the first excited state, to which the electron is raised by absorption in the F band. The small diagram on the right shows the distribution of intensity in the F band, centered at 1.6 ev on the scale of the diagram. Curve C represents the energy surface of the ionized state of the F center, that is, of the state in which the electron is free and a negative-ion vacancy remains. α is the height of the barrier which retains conduction electrons in the crystal. Apker and Taft term this the *electron affinity* of the crystal. The energy η is the excess energy required to ionize the F center directly in place of raising it to the discrete level F^*. The minimum of F occurs for the values of the configurational coordinates designated by f, whereas those for F^* and C occur at the coordinate values f^* and c. The dashed curves at the top of the diagram are parallel to C and correspond to states in which the electron is freed with an energy in excess of that barely needed to produce ionization. It is assumed that the variation of these levels with configurational coordinates is independent of the kinetic energy of the electron and hence is the same as for C. The dotted curve A, which cuts across the dashed curves, is parallel to F and represents the energy of the system if the electron on the F center receives 4.99 ev from a photon or other source. The difference in energy between the minima of F and of C represents the energy required to ionize the F center thermally and is about 1.3 ev. Similarly, the corresponding difference for F^* and C is the relatively small energy required to ionize the excited F center thermally. The curve P on the left-hand side represents the distribution in energy of the electrons which have been excited from the F centers with 4.99 ev. As we shall see below, this distribution is measured experimentally relative to the zero of energy on the left-hand scale. It is determined, within the framework of the diagram, by projecting points on the dotted curve A along curves parallel to C to the value of σ where C has its minimum. The dotted curve E, at the lower left-hand side of the diagram, shows the apparent depth from which the photoelectrons originate.

The investigators assume that η is about 1 ev in the case of RbI. Then, from measurements of the distribution curve P, they infer that α, the electron affinity, is about 0.7 ev. This is consistent with estimates for other alkali halides by Mott and Gurney which lead to values under 1 ev. The assignment of this value to η also carries the implication that the transitions to continuum levels of the F band start on the short-wavelength side of the K band associated with the F band (Fig. 3), which is consistent with the view that the K band arises from transitions to discrete levels of the F band above the first excited state.

(b) Referring again to Fig. 46, we note that the photoelectric efficiency increases in the range beyond about 4.5 ev as the energy of the photons enters the range of the first fundamental absorption peak, and, in fact, passes through a peak which is coincident with the latter. The inset shows the absorption coefficient in the fundamental band. Experiments show that the position of the peak in photoelectric efficiency shifts to shorter wavelengths at low temperature, in correspondence with the shift of the absorption peak. The conclusion to be drawn is that the energy absorbed in the fundamental band and expended in the production of excitons is dissipated, at least in part, by ejecting electrons from F centers with sufficient energy to permit them to leave the solid. The extinction coefficient for the incident light is so great near the peak of the absorption curve that the quanta travel a mean distance of only about 2×10^{-6} cm.

In the initial work carried out on RbI at liquid nitrogen temperature, the peak associated with photoelectric emission exhibited structure which was not found in the fundamental absorption band at the same temperature and which was attributed initially to possible optical interference effects. Subsequent work showed that the structure actually has the following interpretation:

(1) A peak which occurs at about 5.5 ev in KI and about 5.4 ev in RbI has been associated with the β band in these salts. It will be recalled that the β band is currently identified with the excitation of a halogen ion adjacent to an F center (Sec. 24). Since the excited state of this system, attained by stimulation of the β band, should lie in the continuous spectrum, we should expect the system to exhibit autoionization, that is, we should expect internal conversion to take place with ejection of an electron. This process apparently accounts for a "resonance peak" in the photoelectric effect. It evidently is closely related to the ejection of electrons from F centers by normal excitons.

(2) A type of "self-reversal" was observed in some specimens at the very peak of the absorption curve, where the mean free path for absorption of the incident quanta is least. This decrease has been associated unambiguously with the presence of a surface layer nearly devoid of F centers. The thickness of this layer is nearly equal to the depth of penetration of light quanta having energies at the peak of the absorption curve. In other words, most of the light quanta were absorbed in regions where there were few F centers in the specimens showing the effect. The self-reversal was greatly decreased, and even eliminated entirely, by employing layers deposited in the presence of the alkali metal. Photoelectric efficiences as high as 0.04 electrons per quantum have been observed at the peak of the absorption curve under these conditions. The dead layer is also absent in some of the deposits made

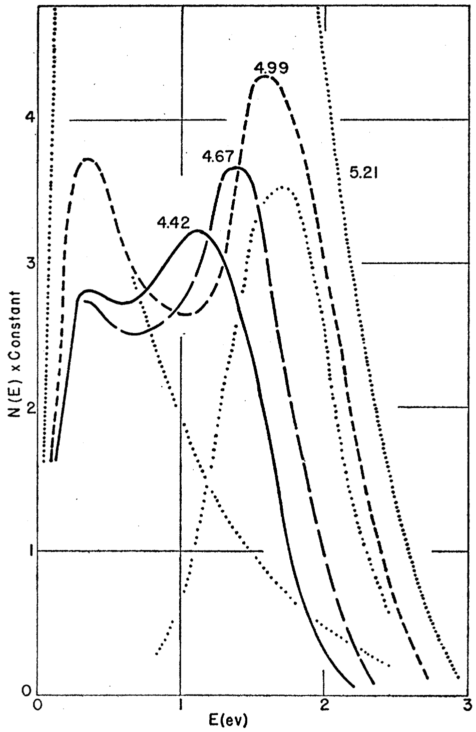


FIG. 48. The distribution in energy of photoelectrons in RbI produced with light quanta of the energies shown (in ev). The *s* and *f* components give separate peaks, which are resolved in detail for the case of photons having 4.99 ev. The maximum of the *f* peak shifts to the right with increasing photon energy, whereas the maximum of the *s* peak does not change (after Apker and Taft).

without excess alkali metal. Particular attention has been given to these specimens.

(c) The energy distribution of the photoelectrons is strikingly different in the region of photon energy where the quanta ionize the *F* centers directly and in the region at shorter wavelengths where the energy is transferred to excitons initially. In the first range, the energy distribution is dominated by a peak of Gaussian form which has a half-width of about 1 ev and whose maximum shifts to higher energy in direct proportion to the energy of the quanta employed (Fig. 48). This peak, which has been designated the *f* peak (*f* for fast), appears to originate in the manner of the distribution designated by *P* in Fig. 47. In contrast, the energy distribution in the region of fundamental absorption is dominated by a peak, termed the *s* peak (*s* for slow), which rises very steeply to a maximum at about 0.3 ev and then falls, more or less exponentially, to a tail which terminates rather sharply. The terminal energy of this tail appears to be proportional to the absorbed energy. The evidence leaves little doubt that the *s* peak is frequently associated with electrons which have been ejected from *F* centers by excitons. Apparently the electron in the *s* distribution carries little memory of the energy of the photon absorbed in producing the exciton but is influenced most strongly by the fact it was freed by an exciton.

There is a component of the *s* peak in the photoelectric distribution of RbI obtained at room temperature for quantum energies as low as 4.42 ev. The fundamental absorption peak extends toward long wavelengths at this temperature and the production of excitons is probably not negligible throughout the plateau region shown in Fig. 46. The investigators report, however, that the *s* band has been observed in RbBr under conditions in which exciton production must have been negligible.

Two explanations have been given of the fact that the *s* peak is essentially independent of the energy of the absorbed light quantum. Hebb[151] has proposed that most specimens contain a dead layer on the surface so that the photoelectrons are produced at considerable depth, near 10^{-6} cm, and lose most of their energy on the way to the surface. The writer has suggested that the excitons lose all of their excess kinetic energy before interacting with an *F* center, and, in fact, even those produced with minimum possible energy, concomitant with the selection rules for optical absorption, lose some energy because transitions occur to states of higher wave number which have lower energy (see Fig. 11). Thus they transmit even less energy to the electrons on the average than light quanta having energies in the plateau range near 4.5 ev do. In fact only one electron in 25 obtains enough energy to escape under these conditions, in the best circumstances. At the present time the second explanation seems to be the most reasonable, for the characteristic *s* peaks have been observed in specimens prepared in the presence of excess alkali metal, in which the dead layer should be very small. Such a conclusion implies that excitons come to equilibrium in traveling about 1000 atomic distances, for the density of *F* centers is of the order of 10^{19} per cc, or one part in 10^3, in many of the specimens studied. This is not unreasonable if the mean free path for inelastic collisions is of the order of one atomic distance.

It should be emphasized again that Hebb[151] carried out a careful theoretical analysis of the diffusion and aging of excitons and photoelectrons in the absorbing layer before the existence of the dead layer had been demonstrated by direct experiment with additively colored specimens. He decided that the phenomenon of self-reversal of the photoelectric yield, observed near the peak of the absorption curve and described above, could be explained only on the basis of a dead layer. In fact he concluded that such layers must be of the order of 140A thick in some of the specimens of RbI employed in early experiments.

(d) It was noted in (a) that no significant photocurrents are observed for photon energies less than 5 ev if the crystals are clear and stoichiometric initially.

---

[151] M. H. Hebb, Phys. Rev. 81, 702 (1951).

In constrast, the typical photocurrent appears if the specimen is irradiated in the fundamental band for a period of time, the yield growing continuously with time. Figure 49 shows, for example, the growth of the yield as a function of time for KI when the specimen is irradiated at 300°K with quanta having 5.66 ev of energy. In this case the quanta generate excitons which serve two purposes, namely, to produce F centers and to eject electrons from these centers. Eventually the yield curve saturates, presumably because a limiting density of F-type and V-type centers is attained. Such a limiting yield had been observed in connection with studies of dark-trace screens bombarded with cathode rays and was noted by the writer in the 1946 review. The limiting average density was established at about 10^{19} F centers per cc. A similar limit has been found in the surface layers of specimens darkened with soft x-rays. As remarked in the introduction, the writer has ascribed this limit to a condition in which electrons are able to tunnel to holes. Apker and Taft have concluded that the same limit is attained in the layers darkened with light in the fundamental band by comparing the properties of such layers with those darkened with cathode rays. Since the thickness of the darkened layer is of the order of 10^{-6} cm when the darkening is achieved with light near the center of the fundamental band, it follows that the surface density of F centers in these layers reaches a limit of about 10^{13} per cm^2. This is below the limit which can be ascertained by direct observation, although Smakula has measured surface densities as low as 5×10^{13} per cm^2.

The darkening *versus* time curve shown in Fig. 49 was obtained at room temperature, as noted in the foregoing. Somewhat similar curves have been obtained at liquid nitrogen temperatures, however, the investigators have tended to avoid darkening at temperatures below 300°K because the deposits behave as if they contained complex aggregates of color centers. This effect might bear more thorough investigation. It would also be valuable to know if F centers can be generated at hydrogen or helium temperatures by the action of excitons alone.

The monotonically decreasing curve in Fig. 49 shows the fall in photoelectric yield which occurs if the darkened specimen is raised to 400°C. Presumably the F centers bleach as a result of heat. It will be noted that a small residual yield, about a tenth of the original, persists at the end of fifty minutes.

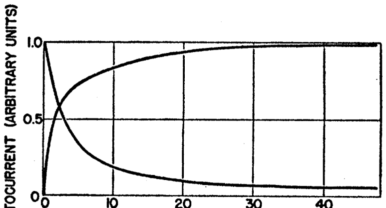


FIG. 49. The growth and decay of photocurrent in KI as functions of time (after Apker and Taft). The growth curve was obtained by irradiating with quanta of energy 5.66 ev at 300°K. This presumably follows the growth of density of F centers. The decay curve was obtained by raising the crystal to 400°C, at which temperature the F centers bleach.

(e) Taft and Apker have also observed photoelectric emission of electrons from F' centers in RbI. A specimen containing F centers, presumably produced by additive coloring, was irradiated with photons of energy 1.9 ev at 85°K. Initially no photoelectric yield was observed at this energy. After continued irradiation, however, the yield curve developed a new shoulder extending to energies as low as 1.6 ev. This shoulder could be removed by heating the specimen to room temperature or by irradiating with 1-ev photons which are known to lie in the F' band of RbI. All these facts leave little doubt that the irradiation with 1.9-ev photon generates F' centers which provide a new source of photoelectrons.

The long-wavelength threshold of the F' band does not seem to be known for the iodides; however, it is probably near to and not higher than 0.8 ev if one may extrapolate from the results for KCl and KBr presented by Pick. Since photoelectrons are ejected by 1.6-ev light quanta, the results imply that the electron affinity is near 0.8 ev, in close agreement with the value of 0.7 ev discussed in (a).

X. CRYSTALS CONTAINING FOREIGN ATOMS

The studies of colored alkali halide crystals obviously may be expanded in interesting and important ways by adding foreign atoms. At the present time only a relatively small amount of such work has been carried out in this intriguing area. This is fortunate in one sense, for a great deal has been gained by concentrating upon the properties of pure crystals. For completeness, we shall give a very brief survey of the coloration effects related to three important classes of foreign additions, namely, mixed crystals, the alkali metal hydrides, and the alkaline earth halides. The last of these three topics, which is currently receiving much well-deserved attention at the hands of Italian investigators, merits particular note because it provides further insight into the influence of additions which have played a critical role in unraveling electrolytic phenomena.

We shall not include a survey of the theory of the alkali halides containing additions of thallium halides, for most of the studies of this mixed system have not been concerned with the production of F-type or V-type bands. However, attention should be called to the extensive theoretical work of Williams[152] on the emission and absorption bands associated with the thallous ion and to the interesting measurements made by Yuster and Delbecq[153] on the absorption spectrum of KI containing additions of TlI.

---

[152] F. E. Williams, J. Phys. Chem. **57**, 44 (1953).

[153] P. H. Yuster and C. J. Delbecq, J. Chem. Phys. **21**, 892 (1953).

41. Mixed Crystals

The simplest manner in which to contaminate one of the alkali halides is, when possible, to add to it another alkali halide which is soluble in the first. Two simple types of "alloys" may be formed in this way, namely, those containing mixed alkali metals and those containing mixed halogens. Among the interesting systems of this type which have been studied, KCl−RbCl and KCl−KBr have received particular attention. Both systems form over the entire range of the constitutents. Other mixed systems on which information is available are NaCl−KCl, NaBr−NaCl, and KBr−RbCl. The first of these forms a mixed crystal for only a part of the range of composition, whereas the other two are completely miscible.

Gnaedinger,[154] who did the pioneer work in this field devoted particular attention to the F band produced by x-irradiation. Measurements of the positions and half-widths of the F bands were made. Interestingly enough, some of the crystals, such as a 50KBr−50RbCl crystal could not be darkened effectively with x-rays.

The KCl−RbCl system proved particularly amenable to investigation and was studied in greatest detail by Gnaedinger. He found that the position of the peak of the F band shifts continuously as the composition of the mixed crystal is varied from one limit to the other. This rule is valid both at room temperature and at liquid nitrogen temperature. On the other hand, the half-breadth of the F band increases as one approaches the 50–50 composition range from either pure crystal limit. The "extra" half-width obtained from alloying is about the same at nitrogen temperature as at room temperature. Gnaedinger has pointed out that the continuous shift of the center of the F band shows that the average environment of a halogen-ion varies continuously as the composition is varied. The extra width implies, however, that this environment is not the same throughout a specimen of given composition, different halogen vacancies having somewhat different arrays of alkali metal ions among the neighboring positions. Since the maximum extra width is only about fifteen percent of the width of the F band in one of the pure constituents at liquid nitrogen temperature, the effect of the variation of environment in a specimen of given average composition is not great.

Gnaedinger carried out a theoretical analysis of the shape of the F band for special compositions on the assumption that the breadth arises from the superposition of bands arising from halogen-ion vacancies having different environments within the given alloy. It was assumed that the ratio of half-breadth to maximum frequency for each of the component bands is the same as the invariant ratio found for pure crystals. In addition, it was assumed that the peak of a given component band is determined by the average number of alkali ions of each kind among the six neighboring positions. The best agreement between experiment and theory possible within this framework was not obtained if it was also assumed that the relative numbers of the various possible arrays of positive-ion vacancies are determined purely by the statistical number of combinations leading to each array. Instead, it was found preferable to assume that the arrays possessing a higher density of Rb ions are favored, presumably because the larger ions are relatively more stable near the vacancies.

An attempt was made to demonstrate the presence of the composite bands by irradiating on one side of the band of a mixed crystal to see if that side of the band would bleach preferentially. The development of M and R bands masked any shift which may have occurred.

Gnaedinger also investigated the F band in a crystal of KCl−KBr containing a 50 molar percent ratio of each constituent and found the same type of additional width observed in the KCl−RbCl system.

Still further, he studied the F band in a crystal of KCl containing ten mole percent of NaCl, which did not seem to form a completely mixed system, and in a specimen of NaCl containing seventeen percent of NaBr. In the first case, the peak of the F band appeared to be on the short-wavelength side of that of pure KCl rather than on the side nearer the peak of the F band in NaCl. The NaBr−NaCl system seems to show the same large half-breadth found in the other mixed systems and apparently offers a good case for further work.

The foregoing work was supplemented by an investigation by Miessner and Pick,[155] who studied the V bands, as well as the F band, in the KCl−RbCl and KCl−KBr systems. The specimens were darkened at liquid nitrogen temperature as well as at room temperature. Moreover, the KCl−KBr system was darkened additively. The investigators confirmed both the continuous shift and the increase in half-width of the F band for intermediate compositions in both systems.

The V_1 band is almost invariant throughout the range of composition in the KCl−RbCl system, whereas it shifts continuously from the KCl to the KBr value in the mixed KCl−KBr system. In contrast with the F band, however, the greatest shift in the position of the V_1 band in the latter system occurs near the end phases of pure KCl and KBr. Less than twenty percent of the shift occurs between the compositions containing 20 and 80 percent of KBr in KCl. Still further, almost half the total shift occurs during addition of the first 20 percent of KBr. The conclusion to be drawn is, apparently, that the V_1 center, like the F center, derives its properties as the result of some average distribution of the hole over the six halogen ions neighboring the positive-ion vacancy. Either the distribution of ions in the system is most stable when the Br ions have a

---

[154] R. J. Gnaedinger, J. Chem. Phys. **21**, 323 (1953).

[155] G. Miessner, Z. Physik **134**, 576 (1953); H. Pick, Z. Physik **134**, 604 (1953).

higher than average tendency to cluster about this vacancy, so that the influence of this ion is felt comparatively strongly when only a small amount is present, or the holes prefer to spend their time on the Br ions even in the Br-poor end of the diagram. The situation is somewhat reversed at the Cl-rich end of the composition range, for reasons which are not entirely obvious since Cl^- is smaller than Br^- and possesses a higher electron affinity.

The other V bands, which presumably are a result of aggregation, behave differently from the V_1 band in one important respect. Whereas they differ little throughout the KCl−RbCl system, they do not shift continuously in the KCl−KBr system. Instead, the set of bands associated with the chloride diminish in intensity as the bromide is added, and the bands associated with the bromide increase. Both band systems are present and completely resolvable in intermediate ranges of composition. In other words, the V bands, other than V_1, behave as if they originated in centers whose properties are critically determined by a small number of halogen ions, regardless of the total number of ions involved. This seems to be in agreement with the notion that two halogen ions become greatly displaced from the normal equilibrium positions of the perfect lattice in forming the V_2 and V_3 centers and the holes involved spend most of their time on this pair. For reasons which are not clear, but which may be related to the advantages possessed by a resonating system, the members of the pair prefer to be the same. An effect of this type is not demonstrated by the free molecules, for the binding energies of Cl_2, BrCl, and Br_2 are 2.481, 2.26, and 1.97 ev, in the order given.

The KCl−KBr system possesses a minimum in melting point for the composition containing about 75-mole percent KBr. Schulze[156] has demonstrated that the ionic conductivity of the mixed crystals system is highest for this composition at any given temperature. Although the results do not permit the separation of the mobility from the density of carriers, they suggest strongly that the density of vacancies reaches its maximum at any given temperature for this "eutectic" composition.

42. Additions of Alkali Metal Hydrides

A new absorption band,[157] termed the U band, appears relatively far in the ultraviolet when the hydride of a given alkali metal is added to the corresponding halide. For example, it occurs at 2280A in KBr. This band was studied extensively at Göttingen prior to the war and much of the basic work was reviewed by Pohl in 1938. The theoretical side of this research was covered in turn by Mott and Gurney.[158] In brief, the appropriate model for the U center appears to consist of a negatively charged hydrogen ion H^- occupying substitutionally the position of a halogen ion. Thus the alkali metal hydride forms a simple substitutional alloy with the halide, the hydrogen ion having its characteristic absorption band. Photoelectrons are not produced by irradiation in the U band.

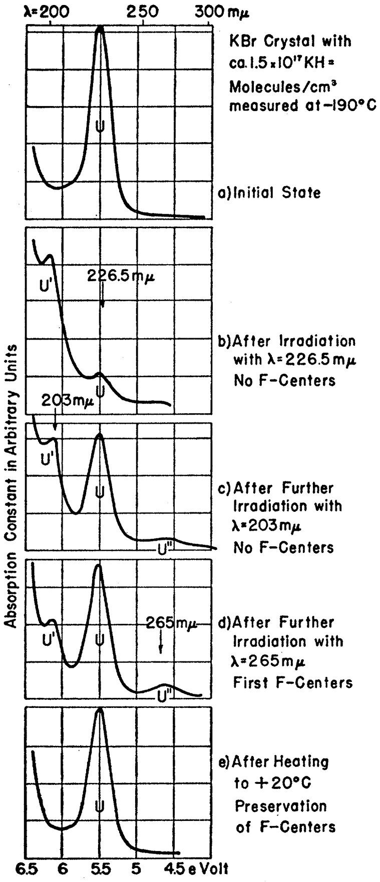


FIG. 50. Transformation of the U band at −190°C (after Thomas). Diagram *a* shows the U band produced by adding KH to KBr. *b* demonstrates the development of the U' band (α band) by irradiating with photons absorbed by the U band at liquid nitrogen temperature. On further irradiation in the U' band (diagram *c*) some of the U band is restored and the U'' band appears. F centers may be generated by irradiating in the U'' band (*d*). The original U band may be restored by raising the specimen to room temperature. In (*e*) read: "Preservation of U centers" instead of "Preservation of F-centers."

At sufficiently high temperatures, for example above −100°C in KBr, there is a significant probability that the U center will be converted into an F center as a consequence of irradiation with light in the U band. The quantum efficiency is about 5 percent at −100°C, however, it rises to 100 percent near 600°C. Mott and Gurney concluded that the excited state of the U center is metastable as a result of crossing of the crystalline Franck-Condon levels and that a hydrogen atom may escape from the center in the metastable condition, leaving an F center. No evidence has arisen to contradict this picture in the range of temperature for which it was proposed.

Thomas[157] showed in 1940 that an entirely different process occurs at temperatures below −100°C when the crystal is irradiated in the U band. The U band bleaches as at higher temperatures and with increasing efficiency as the temperature is lowered. The efficiency reaches a plateau below −200°C. In place of the F band, however, a new band appears on the short-wave-

---

[156] H. Schulze, thesis, Göttingen University, 1952.

[157] See the review article by Pohl, reference 53; also H. Thomas, Ann. Physik 38, 601 (1940); W. Martienssen, reference 114.

[158] Reference 4, p. 147 ff.

length side of the U band (Fig. 50). This was designated the U' band by Thomas, but has since been identified with the α band by Martienssen.[114] The conclusion to be drawn from this is, apparently, that the entire H^- ion has an appreciable probability, of the order of 0.4 under the optimum conditions, of escaping from the halogen site when in the excited state and leaving a vacancy. No absorption spectrum which can be associated with the H^- ion in its new position has been detected, but observation has not yet been extended into the infrared.

The simplest explanation to offer is that the excited H^- ion, being transformed into an essentially different chemical species as a result of the excitation, prefers to be surrounded differently by halogen ions and moves from a substitutional to an interstitial position several lattice spacings from the original site. It may, for example, take up a position where it is surrounded tetrahedrally by four halogen ions with which it may form a resonance-stabilized system, the electronic state remaining excited.

A portion of the U band may be restored by irradiating the crystal in the α band produced by the original irradiation in the U band. It may be restored entirely by raising the temperature to +20°C. The restorative influence of irradiation in the α band indicates that the hydrogen atom has not migrated far from the vacancy and can be induced to migrate back under the action of the thermal spike and the electronic changes which result from irradiation in the α band.

U centers may be converted into F centers by irradiating the crystal containing the hydride with x-rays at room temperature. The F centers produced in this way are more stable than those generated by x-rays in pure salt and, in fact, resemble somewhat those produced additively. This phenomenon has been studied by Pick and Martienssen[159] in specimens of KCl containing amounts of U centers ranging between about 1×10^{17} and 2.5×10^{18}. The specimens were irradiated with 50-kv x-rays. The curves representing the generation of F centers as a function of the absorbed x-ray energy rise steeply and eventually saturate when over ninety percent of the U centers have been converted. The crystals containing various amounts of hydride form a homologous system in the sense that the curves relating concentration of F centers to irradiation can be brought to coincidence if the ratio of the density of F centers to the *initial* density of U centers is employed as a parameter. Even further, if the energy efficiency

$$E=dW/dn_F,$$

where W is the absorbed x-ray energy per unit volume and n_F is the density of F centers, is plotted as a function of n_F/n_{U0}, where n_{U0} is the intital density of U centers, the data for all specimens satisfy the simple relation

$$E=E_0\exp(\alpha n_F/n_{U0}).$$

Here E_0 and α are constants over the range of n_F/n_{U0} from zero to about 0.9. The value of E_0, which represents the initial energy required to convert a U center to an F center, is about 35 ev. The energy attains a value near 90 ev at about 80 percent of saturation.

The conversion from U to F centers can occur in several simple ways. First, a hole may annihilate one of the electrons on the U center; the hydrogen atom may diffuse away from the vacancy and be replaced by an electron. Second, an exciton may ionize the U center and the processes following capture of a hole be repeated. Third, an exciton may excite the U center to the state attained by irradiating in the U band, after which a hydrogen atom diffuses away. The experiments with light show that the quantum yield is about 20 percent for KBr when quanta lying in the U band are employed at room temperature. Since the efficiency is probably lower for KCl and since at least 7 ev is required to produce an exciton, it seems very doubtful that the last of these mechanisms is the principal one. Moreover, we do not know if an exciton can ionize a U center, so that the second mechanism is questionable. Thus the first of the three seems most likely at present, although the other two may contribute a share.

The diminution of the efficiency for producing F centers, as the density of such centers increases, shows that other processes compete for the energy. The homologous nature of the decrease in efficiency, depending as it does principally upon the ratio n_F/n_{U0}, shows quite clearly that the F centers produced are the competing agent. Thus, over the ranges of concentration of U centers considered, these experiments seem to demonstrate that the holes and electrons wander until they find either a U center, an F center, or a negative-ion vacancy produced during the irradiation. Unfortunately the same conclusion cannot be drawn for excitons since we do not know whether they play a role. It would be very interesting to examine the quantum efficiency of production of F centers from U centers with light in the tail of the fundamental band in the range of concentration studied here. Such experiments would provide convincing evidence that the excitons wander until they meet U centers if the efficiency is the same as for light quanta absorbed in the U band.

The homologous behavior of the system of crystals containing U centers was found to disappear in the specimens studied when the density of U centers dropped appreciably below 1×10^{17} centers per cc. For example, the energy required to produce an F center initially became appreciably higher than 35 ev. Presumably imperfections other than U centers begin to absorb an increasingly large fraction of the energy

---

[159] W. Martienssen and H. Pick, Z. Physik **134**, 309 (1953).

transmitted to the crystal by the x-rays as the density of U centers falls below this critical value.

43. Additions of Divalent Chlorides

An entirely new set of absorption peaks[160] lying in the visible portion of the spectrum, termed the Z bands, can be produced by introducing divalent ions into the alkali halides. The bands were discovered in additively colored crystals by Pick and studied extensively by him and by Heiland and Kelting. More recently, the subject has been approached with renewed precision and imagination by a group of Italian investigators, Bassani, Camagni, Chiarotti, Fumi, and Giulotto,[19,161] who promise to transform it into one of the major areas of color center research. As remarked in the introduction to Part X of this review, this is highly appropriate since the influence of divalent additions on the alkali halides has been one of the key subjects in the evolution of our knowledge of the field.

The writer summarized the early work in 1951 and presented a possible interpretation of the effects observed. The reader is referred to this paper for a relatively complete review; only the broad outlines will be presented here. Subsequent research has focused sharper attention on speculative aspects of this interpretation and has permitted further inferences. It is to be hoped that these investigations will continue.

If the additively colored crystals of KCl containing divalent halides are annealed and quenched to room temperature in the conventional manner, the F band, with its center at 5400A at -215°C, appears as in a normal crystal. If, however, a specimen is irradiated in the F band, this band diminishes and a band termed Z_1 appears just on the long-wavelength side, centering near 5900A at -215°C. The new band evidently is the result of capture of the photoelectron liberated from the F center by a divalent ion. The writer has proposed that the Z_1 center is the neutral unit consisting of a divalent ion, occupying a positive-ion position substitutionally, and an electron. Thus it is analogous to an F center, the positive charge originating in a doubly charged positive-ion instead of in a halogen-ion vacancy. It is assumed that the positive-ion vacancy which was initially associated with the divalent ion migrates away, possibly to join the negative-ion vacancy left behind by the electron. The Z_1 centers cannot be reconverted into F centers by irradiating with light in the Z_1 band at least near room temperature. Apparently the first-excited state of the Z_1 center is much more stable than that of the F center, perhaps because there is much less room for ionic displacement in the first case so that the minima of the Franck-Condon curves of all levels occur for more nearly the same values of the configurational coordinates.

Some of the Z_1 band is reconverted into the F band if the crystal containing both the F and Z_1 band is heated to a temperature near 110°C, but the majority is converted into an entirely new band, termed Z_2, which lies still farther to the red, centering near 6100A at -215°C. A further portion of the F band can be converted into Z_1 centers with light in the F band and a part of these can be transformed into Z_2 centers by heating to 110°C. Thus the Z_2 band can be built up in stages. The writer has proposed that the Z_2 center is the result of union of a Z_1 center and a neutral pair of vacancies, so that it bears the same relation to the Z_1 center that an M center does to an F center.

The Z_2 band may be bleached entirely by heating the crystal above 200°C, in which case the F band reemerges as in the original crystal.

Both bands diminish and the F' band and a new type of band, termed Z_3, appears if the crystal is cooled to -90°C and irradiated in either the F or the Z_2 band. The Z_3 band has much the same form as the F' band although it lies on the blue side of the Z_2 band and evidently is associated with a negatively charged unit, like the F' center. It seems simplest to assume that the Z_3 center is a Z_2 center which has captured a second electron. The Z_2 band, like the F band, should be a source of photoelectrons according to this picture of the state of affairs. Unfortunately photoconductive measurements have not been made.

Sodium chloride containing strontium or calcium exhibits properties somewhat different from potassium chloride. When additively colored crystals containing Sr are quenched, both the F band and a band, which is probably Z_2, appear. This result is in accordance with the models proposed above if we assume that the divalent ions are much more mobile in NaCl than in KCl and that a fraction of the ions and the associated positive-ion vacancies diffuse to F centers during the quenching procedure to form Z_2 centers. The experiments also show that the Z_2 band of NaCl can be bleached at room temperature by light in the Z_2 band to form the F band and a band which is probably Z_1. The result suggests that the positive and negative-ion vacancies diffuse away in the form of pairs when the Z_2 center in NaCl loses its electron. The photoelectrons combine both with the divalent ions which are left behind, to form Z_1 centers, and with the pairs to form F centers. Presumably the Z_3 centers are not stable at room temperature.

Pick has also found that when crystals of undarkened NaCl containing divalent ions are irradiated with x-rays at room temperature they develop the F band but not any of the Z bands. However, if the darkened crystals are subsequently irradiated with light absorbed in the F band, the F band diminishes and the Z_1 band appears, much as in additively colored crystals of KCl containing divalent ions.

---

[160] H. Pick, Ann. Physik **35**, 73 (1939); Z. Physik **114**, 127 (1939); G. Heiland and H. Kelting, Z. Physik **126**, 689 (1949); F. Seitz, Phys. Rev. **83**, 134 (1951).

[161] Camagni, Chiarotti, Fumi, and Giulotto, Phil. Mag. (to be published). The writer is deeply indebted to Dr. Fumi for detailed correspondence concerning this work prior to publication.

Camagni, Chiarotti, Fumi, and Giulotto[161] have studied the properties of crystals of KCl containing $SrCl_2$ which were darkened both additively and by x-irradiation at room temperature. They found that the F band, not the Z bands, is developed most prominently as a result of irradiation, just as in NaCl. The Z_1 band develops in both cases when the darkened crystal is irradiated with the 5461A line of a mercury arc, which lies in the region where the F and Z_1 bands overlap. Moreover, the F band appears predominantly when the additively colored crystals are quenched to room temperature, in accordance with the earlier work. The two bands appear to attain a limiting ratio in additively colored crystals, with the Z_1 band eventually predominating, as if there may be a slow reconversion of Z_1 centers to F centers under the action of light, or as if the F centers eventually become "hard" to bleach. The Z_1 band grows initially under illumination with the mercury light in x-rayed crystals, however, both it and the F bands eventually bleach, after attaining a limiting ratio not unlike that in the additively colored crystals.

The investigators also determined both the quantum efficiency for the generation of Z_1 centers from F centers and the oscillator strength of the Z_1 band by studying the initial diminution of the F band in additively colored crystals. The results obtained for the two quantities are, respectively,

$$\eta_{Z,F}=0.15 \text{ and } f_{Z1}=0.84.$$

The second quantity is very close to the oscillator strength for the F center, namely 0.81, and supports the view that the Z_1 center is very similar to the F center.

The Italian workers have proposed that the limitation on the production of Z_1 centers is determined by the fact that only unassociated divalent ions have an appreciable cross section for capturing electrons and that the number of such ions changes very slowly with time at room temperature because of the magnitude of the dissociation energy. If we assume that the activation energy for the rate of dissociation is the sum of the activation energy for migration of free positive-ion vacancies (about 0.85 ev according to the discussion of Sec. 4) and the energy of association (about 0.2 ev, according to the calculations of Bassani and Fumi discussed in Sec. 6), we would expect the relaxation time for attainment of equilibrium between associated and dissociated divalent ions to be of the order of hours at room temperature. Hence the density of unassociated ions should be relatively static during the periods of irradiation. The proposal that the cross section for permanent capture of electrons by the associated divalent ions is small compared with that of unassociated ions is alo in excellent agreement with Harten's observation (Sec. 13) that electrons form units with divalent additions which become unstable near liquid nitrogen temperatures. It would seem that Harten's traps are associated pairs of divalent ions and positive-ion vacancies.

On the basis of this hypothesis, the assumption that the saturation of the Z_1 band is determined by the density of unassociated divalent ions, and knowledge of the amount of divalent addition, the investigators are able to estimate the fraction of unassociated ions and hence the association energy of positive-ion vacancies. They obtain a value of 0.3 ev for Sr^{++} in KCl, which is to be compared with the value of 0.2 ev calculated by Bassani and Fumi. They also find that the cross sections for capture of electrons by negative-ion vacancies and unassociated divalent ions are very nearly equal, as might be supposed from the close similarity of the F and Z_1 centers.

It would seem to follow that the preferred production of F centers during x-irradiation stems from the fact that the density of unassociated divalent ions in the crystal is small compared with the density of negative-ion vacancies produced by the x-rays, at least by the time at which the darkening is sufficiently great to measure accurately. One would not expect this to be true at start of irradiation since the density of free negative-ion vacancies should be negligible. It would be interesting to know if traces of the Z_1 band are apparent in very weakly darkened specimens. In any case, it is clear that conclusions dealing with the interpretation of the new experiments are highly speculative.

Fumi (private communication) has informed the writer that complete conversion from the F to the Z_1 band can be achieved in additively colored crystals in which the density of F centers is much smaller than the density of divalent additions. In such cases, presumably the density of unassociated divalent ions exceeds the density of F centers.

One of the intriguing aspects of these observations is that the initial efficiency of conversion from F to Z_1 centers appears to be near a tenth rather than unity in additively colored crystals. The investigators suggest that such crystals contain an excess of halogen-ion vacancies. This point bears deeper investigation since such an excess is not found in crystals relatively free of divalent ions. A comparable effect is not observed during the conversion of F centers to F' centers in crystals which have received a very similar treatment.

XI. SUMMARY

(1) Significant advances have been made in our understanding of the imperfections appearing in uncolored alkali halides. The Schottky-Wagner theory of the defects responsible for electrolytic transport has been confirmed by experimental work from many sources and seems irrefutable at this time. Diffusion measurements, however, have disclosed deviations from the Einstein relation between electrolytic conductivity and diffusion coefficient in NaCl and KCl which are poorly understood at present. It appears that one or more neutral carriers contribute appreciably

to the diffusion in suitable temperature ranges; experimental information concerning the nature of these is fragmentary.

(2) There is now little doubt that excitons are produced by irradiating an alkali halide in the first fundamental band and that they may migrate and transfer their energy to imperfections in the lattice. The best experimental work on this problem, namely that of Apker and Taft, centers about the use of evaporated films. It would be very valuable if attention could be returned to the study of phenomena associated with production and migration of excitons in single crystals, both pure and intentionally contaminated. Crystals containing *U* centers, which can be transformed into *F* centers under suitable conditions, and crystals containing luminescent-activating ions, such as thallium, may provide interesting subjects for study with light absorbed in the fundamental bands.

(3) Redfield's observation, based on measurement of the Hall coefficient, that the mobility of electrons in the alkali halides is in the vicinity of 100 cm^2/volt-sec at liquid nitrogen temperatures, and hence lies in the general range expected on theoretical grounds, has removed one of the outstanding uncertainties and has opened a rich field for both experimental and theoretical study. Our knowledge of the behavior of free holes is still very unsatisfactory, however, and may become clearer only when studies of the *V* bands have been extended, for it appears that the hole pulses arising from the passage of ionizing radiations through pure, uncolored crystals are too small to be studied.

(4) Understanding of the nature of the *F*-type centers has advanced since 1946 without the need for any radical changes in viewpoint. The model of the *F* center proposed by de Boer has withstood the test of time and remains an anchor-point in the theory. The model of the F' center introduced prior to 1940 seems equally secure. The models of the centers formed by coagulation of *F* centers with light, proposed by the writer in 1943, still seem acceptable and are supported by more extensive measurements. The colloidal bands, brought back into prominence by Scott and his coworkers offer an interesting avenue for further research. Studies of the spin resonance of electrons in *F* centers have provided deeper insight of the extent to which the wave functions are influenced by the ions bordering the halogen-ion vacancy.

(5) Important new information on the *V* centers has become available. It now seems highly likely that the V_1 center is the counterpart or antimorph of the *F* center. The V_1 center has remarkable properties for, although it seems to dissociate at relatively low temperatures into a hole and a positive-ion vacancy, it does not seem to be a very efficient source for producing holes by photoelectric means. The V_2, V_3, and V_4 bands are probably the result of absorption of light in coagulates of vacancies and holes, analogous to the *R* and *M* bands, however the models proposed are highly tentative. On the whole the *V* centers appear to depend in a much more erratic way upon the history and chemical composition of the specimens than the *F*-type centers do. The study of *V* centers may be aided appreciably by renewal of investigations with specimens containing a stoichiometric excess of halogen, following the older work of Mollwo. It is possible that new levels of purity will have to be achieved before further significant advances are made in the study of *V* centers. One may hope that the holes in *V* centers will provide measurable spin resonance absorption.

(6) We still do not possess critical experimental information on the factors which influence the darkenability of the alkali halides when exposed to x-rays in spite of observations extending over many years. There is little doubt that impurity atoms, such as divalent ions, and plastic strain are important, but the experiments are tantalizingly qualitative. The writer has proposed that the extensive darkening which can be induced at temperatures at and below liquid nitrogen temperatures involves the production of vacancies from dislocations by thermal spikes which occur at the dislocations when excitons die near them. *F* centers are formed when the halogen-ion vacancies created in this way capture electrons, either by trapping free electrons or decomposing excitons which wander nearby. V_1 centers are formed when positive-ion vacancies capture free holes. Smakula's old observations show that excitons are capable of producing darkening at nitrogen temperatures. It would be good to carry out similar measurements at helium or hydrogen temperatures with crystals of varying purity. It is possible that the dimensional changes induced by formation of vacancies at low temperatures can be measured at such temperatures with the use of special techniques, such as the condenser technique developed by Sakaguchi and Suita.

(7) Crystals darkened at helium-like temperatures are, on the whole, much like those darkened at nitrogen temperatures. There is strong evidence, however, that the *F*-type and *V*-type imperfections are very densely packed in localized regions, attaining concentrations near 10^{20} centers per cc. Such regions should cluster mainly about the surfaces swept out by the dislocations which climb as vacancies evaporate. Microscopic observations with resolution on the scale of 1 micron may make it possible to discern these areas.

(8) The mechanisms which contribute to the properties observed when irradiation-darkened crystals are bleached are not very well understood. The rather qualitative experimental information available is used as a basis for suggesting several factors which probably enter into the process. It is proposed that the V_3 center, which apparently resists combination with electrons freed from *F* centers, is a negatively charged unit consisting of one hole and two positive-ion vacancies. There appears to be incontrovertible evidence that the electrons associated with *F* centers formed at

helium temperatures can annihilate holes attached to other centers by tunneling. This process is accelerated by raising the electron to the first excited state.

(9) The experiments of Apker and Taft, on the electrons ejected from alkali halide layers by photons, have added an important chapter in our understanding of exiton-induced processes and have furnished data from which a fairly complete energy level diagram may be constructed for *F* centers in the alkali halides most amenable to this type of investigation.

(10) Until the present time, experiments concerning color centers in crystals containing additional agents have played a secondary role in the development of the subject. It is probable, however, that the point has been reached where appropriately chosen investigations with treated materials may furnish much key information. Recent work on *F*-type and *V*-type centers in mixed crystals of KCl—RbCl and KCl—KBr has cast an interesting light on the properties of such centers. Similarly, work on the conversion of *U* centers to *F* centers under x-irradiation has made it clear that a large part of the energy transferred to the crystal by x-ray quanta is able to migrate extensively through the lattice before being dissipated.

It is a pleasure for the writer to express his gratitude to a number of colleagues who have subjected an early draft of this manuscript to careful criticism and have proposed numerous additions and corrections, many of which are incorporated in the final text. He would also like to express particular thanks to those investigators who permitted him to read unpublished notes and manuscripts and to include relevant material from such work. Finally, he wishes to acknowledge the fact that support provided to the solid state group at the University of Illinois by the U. S. Office of Naval Research, the Office of Scientific Research of the Air Research Development Command, the Office of Ordnance Research, the U. S. Atomic Energy Commission, and the National Science Foundation played an important role in making this contribution possible.