

Photoconductivity in Crystals

A. L. HUGHES, *Washington University, St. Louis*

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I. INTRODUCTION

THE particular phase of photoconductivity to be discussed in this article is that dealing with the electrical conductivity imparted to certain insulating crystals when suitably illuminated. It is worthy of note that the attention of the many American investigators working in the field of photoelectricity has been focused almost exclusively on the surface photoelectric effect; photoconductivity, an equally interesting aspect of photoelectricity, has been ignored.¹ Much of what is known about photoconductivity in crystals is due to the brilliant and systematic work of Professor Pohl and his associates at Göttingen. The fact that many of the researches of this school are published in the *Göttingen Nachrichten*, a journal which is not accessible to many American physicists, is an additional justification for writing this summary of the present status of photoconductivity in insulating crystals.

Photoconductivity touches on many other fields of physics. It is closely related to certain optical properties of the crystals. It is an important source of information for data on crystal structure, its results are particularly significant for the division of the properties of crystals into "structure sensitive" and "structure insensitive" properties. This is confirmed by the frequent reference to photoconductivity in the London Conference on the Solid State held in

¹ The only exception appears to be F. C. Nix, *Phys. Rev.* **47**, 72 (1935).

1934.² It provides a sort of model of a "diluted" metal, i.e., a solid containing enough free electrons to conduct, but not so many as to make it too opaque for optical measurements. Finally it provides plenty of perplexing results which, up to the present, have not been satisfactorily explained in terms of the theories of the crystalline state now available, and should therefore be a stimulus to their improvement. In this respect it is a typical "structure-sensitive" phenomenon. In photoconductivity we have still another illustration of the constant shift of emphasis in the development of a branch of science. Ten years ago, the principal goal was the understanding of how electrons were separated photoelectrically by the absorption of quanta; today photoconductivity is looked upon rather as one means of approach to the solution of the problem of the nature of a crystal.

II. SUMMARY OF RESULTS OBTAINED BEFORE 1932

In view of the fact that full accounts³ of the state of our information about photoconductivity up to 1932 are available, we shall give here only a summary of these results insofar as they are needed to explain the terminology and methods referred to in succeeding sections. The conductivity of a crystal is measured by applying

² *International Conference on Physics*, Vol. II. "The Solid State of Matter" (Cambridge University Press, 1935).

³ A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena*, Chap. VIII (McGraw-Hill, 1932); F. C. Nix, *Rev. Mod. Phys.* **4**, 723 (1932).

voltages to it by means of suitable electrodes (such as graphite or platinum pressed on to opposite faces), the current being registered by a quick acting electrometer. (A wide range of currents may be measured by shunting the electrometer by one of a set of high resistances varying from 10^6 to 10^{11} ohms.) The current may be studied as a function of one or more of the following variables: applied voltage, the intensity of the light, its frequency, the temperature and previous history of the crystal. Gudden and Pohl made a very significant advance when they recognized that, in general, in an illuminated crystal, a *secondary current* may often co-exist with the *primary photoelectric current*. In contrast with the primary photoelectric current, the secondary current is characterized by strong hysteresis effects. The primary photoelectric current is the direct result of the absorption of quanta within the crystal. The secondary current is the result of an increase (usually progressive) in the conductivity of the crystal resulting from the passage of the primary photoelectric current. In certain cases it may exceed the primary photoelectric current by a thousandfold or more and so completely obscure it. (A very instructive account of experiments on the development of secondary currents has been given recently by Lehfelddt.)⁴ In general, the primary photoelectric current increases with the applied voltage and, with some crystals, a saturation current can be obtained when the applied voltage is sufficiently high. When saturation is obtained the charges separated photoelectrically move all the way towards the electrodes; below saturation the field is insufficient to drive them the whole way to the electrodes. It has been found that quantum equivalence is obtained in certain diamond and zincblende crystals, i.e., an electron and a corresponding positive charge are separated and move to their respective electrodes for each light quantum absorbed. The primary photoelectric current is made up of two parts: the *electron primary current*, which is associated with the movement of electrons towards the anode, and the *positive primary current*, which is due to the motion towards the cathode of the positive charges left behind wherever an electron is set

free by the absorption of a quantum. When both flow simultaneously we have the full primary photoelectric current. Under certain conditions (e.g., low temperature, nearly perfect lattice), only the electron primary current is found: the positive charges remain fixed and build up a positive space charge. The crystal is now said to be "excited," for its properties have been changed temporarily. Its absorption spectrum has been altered slightly; it absorbs more strongly on the long wave-length side of the absorption band than before. It has acquired a temporary photoelectric sensitivity to red and infrared light, but this sensitivity lasts only long enough to allow as much current to pass as was associated with the electron primary current. We may think of the positive charge left behind whenever the absorption of a quantum releases an electron as being set free by the long wave-length radiation. The positive charge may also be made free to move, merely by warming the crystal. To avoid trouble arising from the building up of a space charge it is the custom to flood the crystal with red and infrared light along with the photoelectrically active light. It is not to be supposed that positive ions, as such, move towards the cathode; it is the *location* of the positive charge which slips back towards the cathode. This may be thought of as the neutralization of the positive charge by an electron moving to it from a nearby place in the lattice leaving a new positive charge nearer the cathode, which in turn slips back still further towards the cathode by a repetition of this process. A complete absence of the positive primary current is to be found only under rather unusual conditions; the general rule is that there is some spontaneous flow along with the electron primary current. In such cases the flow persists after the light is cut off and the electron primary current has thereby ceased, until the positive space charge disappears. At a sufficiently high temperature, or when the crystal is exposed to red and infrared light, the two parts of the primary photoelectric current flow together. Because of the peculiar way in which the positive charges move towards the cathode without actual bodily transfer of ions, the phenomenon is often referred to as supplementation, substitution, replacement, or "ersatz" conductivity.

⁴W. Lehfelddt, Gött. Nachr. No. 42, 263 (1933); No. 14, 171 (1935).

Hilsch and Pohl⁵ have studied the photoconductivity in naturally colored rocksalt at various temperatures. In a certain piece at 100°C the current started at a value of 4×10^{-9} amp. and then fell within about 10 sec. to a value of 2×10^{-9} amp. The initial value represents the true photoelectric current appropriate to the applied voltage, the end value is due to polarization set up because of the positive charges left behind at the centers. The final value of the current corresponds to a balance between the electrons released photoelectrically moving towards the anode and their replacement by other electrons set free thermally or photoelectrically. The "replacement" electrons constitute the positive primary current. That the polarization persists for an appreciable time is shown by an experiment in which the applied field is removed when the light is cut off, and then, 30 seconds later, the light is turned on again causing a current to flow in the *opposite* direction. If the experiment is repeated at 220° there is no drop in the value of the current from the initial value. At this temperature the electrolytic current which flows in the dark is quite appreciable. This means that polarization does not build up because the large ionic conductivity allows the positive primary current to flow at its full value. Polarization occurs only when the mechanism for compensating the positive charges is inadequate.

De Boer⁶ proposes the following picture of the mechanism of the positive primary current. In a photoconducting crystal are to be found numerous centers from which photoelectrons can be separated. The first result of illuminating a crystal with suitable light is to set free a number of electrons. These travel in the direction of the electric field until they are caught in a defect or irregularity in the lattice. They move over a certain distance which, while small compared with the dimensions of the crystal, is large in comparison with the average distance between the centers. This first displacement of these electrons constitutes the electron primary current. The electrons are bounded more loosely to the lattice irregularities, the "excitation" centers, at which they are caught, than to the original centers. Consequently they can be set free from the "excitation" centers by infrared quanta which do not have enough energy to set them free from the original centers. If now it be postulated that, on the

average, the electron set free from an excitation center by the absorption of a quantum of infrared light has to travel the same distance to get to one of the original centers as that traveled by the electron originally released from it, then it is seen that the positive primary current and the electron negative current must be equal. This explanation breaks down, however, when we consider the case when saturation of the electron primary current is obtained⁷ for then all the electrons set free are driven all the way to the anode and there are none left in the crystal to account for the positive primary current in the way contemplated by de Boer. Even when we are far from saturation and no electrons escape from the crystal, it is by no means clear why the average displacement of a photoelectron from an original center should be the same as the subsequent displacement from an excitation center to an original center left charged.

The conductivity imparted to crystals by light is electronic in character. Most "insulating" crystals conduct in the dark when raised to a sufficiently high temperature, but the conductivity is electrolytic in nature. Electrolytic conductivity is associated with the transport of matter to the electrodes which can be observed with sufficiently high currents.⁸

Gudden and Pohl found photoconductivity in two very different types of crystals which they termed idiochromatic and allochromatic crystals. In the former, the crystals exhibit photoconductivity when chemically pure and when, regarded as single crystals, they are perfect, or nearly perfect. Diamond and zincblende are such crystals. In allochromatic crystals, no photoconductivity can be detected when the crystal is pure. Photoconductivity is the result of the addition of foreign atoms, i.e., atoms which do not belong to the regular lattice, or is a result of physical changes effected by certain agencies. Alkali halide crystals are outstanding illustrations. The photoconductivity of many allochromatic crystals has been investigated with great thoroughness in the last five years; very little attention, on the other hand, has been paid to idiochromatic crystals.⁹

⁷ See, for instance, Gudden and Pohl's work in which saturation electron primary currents were followed by practically equal saturation positive primary currents (Hughes and DuBridge, *Photoelectric Phenomena*, p. 295).

⁸ For comments on electronic and electrolytic conductivity, see B. Gudden and W. Schottky, *Phys. Zeits.* **36**, 717 (1935).

⁹ For work on idiochromatic crystals, see F. C. Nix, *Phys. Rev.* **47**, 72 (1935), and R. Robertson, J. J. Fox and A. E. Martin, *Phil. Trans. Roy. Soc.* **232**, 463 (1934).

⁵ R. Hilsch and R. W. Pohl, *Zeits. f. Physik* **87**, 78 (1933).

⁶ J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, 1935).

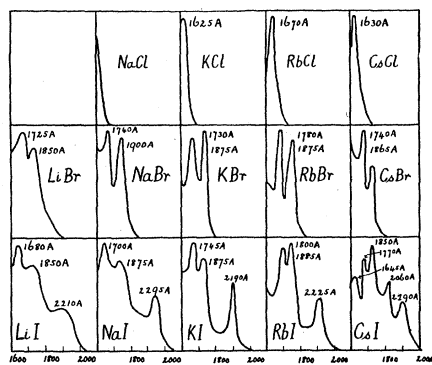


FIG. 1. Characteristic absorption bands of alkali halide crystals.

III. ABSORPTION BANDS IN ALKALI HALIDE CRYSTALS

Crystals of pure alkali halide salts are characterized by an almost complete absence of absorption in the near ultraviolet, the visible, and far into the infrared.¹⁰ In the far ultraviolet, each alkali halide crystal has a very strong characteristic absorption band, almost metallic in its opacity. In the chlorides there is a single peak close to 1650Å; in the bromides, there is one close to 1880Å and another at a shorter wavelength (Fig. 1). When light is absorbed in this characteristic absorption band, there is no trace of any resulting photoconductivity. The high value of the absorption coefficient shows that a great many atoms in the lattice are capable of absorbing the light in this region, and so it is justifiable to take the view that such absorption is associated with the transfer of an electron from any negatively charged halogen ion in the regular lattice to a nearby positively charged alkali ion. The details of this process are outside the scope of this paper, except for this, that this type of absorption is not accompanied by any electrical conductivity. This is in accord with the view that, as a result of absorption, the electron moves only from one ion to the next one, a distance too small to give any measurable current. The lack of any observable permanent

¹⁰ R. Hilsch and R. W. Pohl, *Zeits. f. Physik* **59**, 812 (1930). Absolute determinations of the absorption coefficients have been made by G. Bauer, *Ann. d. Physik* **19**, 434 (1934).

change in the crystal suggests that the electron returns to its original position in a very short time, otherwise an appreciable number of neutral atoms would be formed in the crystal and so change its absorption spectrum.

Absorption in this characteristic absorption band is to be regarded as a "structure-insensitive" phenomenon, in contrast to those absorptions about to be described which are "structure-sensitive" phenomena.

The characteristic absorption band has a long wave-length foot extending into the near ultraviolet. This does not show up in Fig. 1 because the absorption in the foot is about a million-fold less than in the band itself. When a crystal is made containing one part of KNO_3 to 100,000 parts of KBr , the long wave-length foot is altered somewhat in shape and is more pronounced and so it is natural to attribute the long wave-length foot in this case to the foreign matter which is presumably located at the irregularities in the lattice. Absorption here may be regarded as the displacement of a rather loosely bound electron from a foreign atom. In the case of a supposedly pure salt, we may perhaps postulate foreign atoms to account for the long wave-length foot, but an alternative view is to suppose that the electrons may be more easily separated from atoms situated at the irregularities in the lattice, the flaws, or the internal surfaces, than from atoms inside the small units in which the lattice is perfectly regular. Such a view receives support from several experiments, among which may be cited this one.¹¹ The absorption coefficient for the long wave-length foot in a presumably pure crystal can be increased several times merely by applying suitable stresses to the crystal and then removing them. There can be no question here of increasing the number of foreign atoms inside the crystal but it is easy to believe that after the stresses have been applied the crystal will contain more internal cracks, flaws, etc., than before.

Some crystals of alkali halide salts can be made, or found, with a visible coloration due to colloidal particles of the metal dispersed throughout the crystal. Rocksalt containing colloidal particles has a blue color. The shape and location

¹¹ E. Rexer, *Phys. Zeits.* **36**, 602 (1935); see also J. Boros and Z. Gyulai, *Zeits. f. Physik* **96**, 355 (1935).

of the absorption band changes with the size of the particles.¹² When light is absorbed in this band, the crystal acquires a conductivity. Electrons are released photoelectrically from the surfaces of the colloidal particles and, under an electric field, are displaced in the lattice.

Perhaps the most interesting photoconducting colored crystals, and certainly the most extensively studied, are those which show no trace of colloidal particles. If the color is due to foreign matter it must be dispersed in atomic form. With this type of coloration, rocksalt is yellow and potassium bromide is blue. To avoid committing ourselves too far at this point as to the origin of this coloration, we shall follow Pohl and simply refer to the sources of this type of coloration as "color centers" or "*F* centers." These color centers can be produced in a variety of ways, shortly to be described. They give a remarkably simple absorption band, which is conveniently referred to as an *F* band (Fig. 2). The location of the band is determined by *d*, the spacing of the lattice according to the formula

$$\nu_{\max}d^2 = \text{const.} \quad (1)$$

When adjusted so that their maxima coincide, the curves for the different alkali halides show a remarkable superposability (Fig. 3). The bands become narrower as the temperature is reduced, but the total area remains the same, indicating that the number of absorbing centers remains unchanged. When light is absorbed in this band, the crystal becomes conducting.

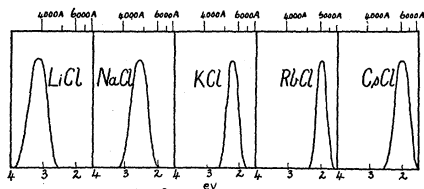


FIG. 2. *F* bands in alkali halide crystals.

¹² Colloidal particles are produced in rocksalt, for example, by heating it in sodium vapor at 760°. The sodium enters and is dispersed in atomic form. The atoms coagulate into colloidal particles if the crystal is held for some time between 300° and 500°. Rapid cooling from 760° prevents the formation of colloids. E. Miescher, *Gött. Nachr.* No. 47, 329 (1933); E. Mollwo, *Gött. Nachr.* No. 6, 79 (1934).

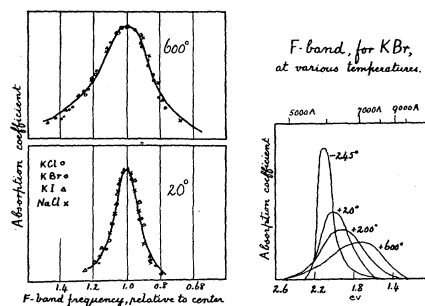


FIG. 3. Superposability of *F* bands for various alkali halide crystals and effect of temperature on the shape of the *F* band.

It will be shown later that *F* centers are associated with a stoichiometric surplus of alkali metal in the crystal. The *F* bands of the various sodium halides occur at different places in accord with Eq. (1); i.e., the lattice spacing is the determining factor. This is in marked contrast to the absorption spectra obtained when sodium is dissolved in molten NaCl, NaBr, or NaI, for here it is found that the absorption band is unaffected by the kind of molten salt in which the metal is dissolved; its location is determined solely by the nature of the metal.¹³ The center of the absorption band, which is approximately 2.0 volts wide, is to be found on the long wave-length side (0.5 eV separation) of the position of the resonance line of the metal in the vapor phase. This suggests that the spectrum of the surplus metal dissolved in the molten salt is effectively that of the metallic vapor, but displaced and much broadened by the proximity of the molecules of the solvent. But when the molten salt is cooled and changes to the crystalline state, one obtains the *F* bands with their significantly different character depending directly on the crystal spacing and not at all on the nature of the surplus metal.

Recently Pohl and his collaborators have discovered that under certain conditions, still another absorption band, this time in the ultra-violet, can be induced in an alkali halide crystal. This they call the *U* band (Fig. 4) and they attribute its origin to *U* centers. When light is absorbed in this band, no photoconductivity is observed, but the interesting thing is that absorption of light in the *U* band uses up the *U* centers and replaces them by *F* centers, that is to say, the crystal becomes colored, and when exposed to visible light it is conducting. The *U* bands resemble the *F* bands in that they have a simple bell-like shape, in that they become narrower as

¹³ E. Mollwo, *Gött. Nachr.* No. 18, 203 (1935).

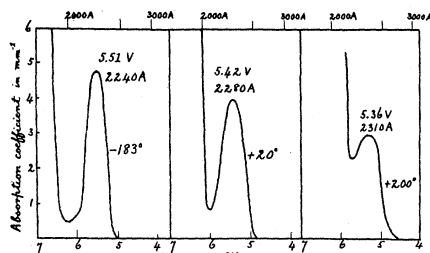


FIG. 4. *U* bands in KBr at different temperatures.

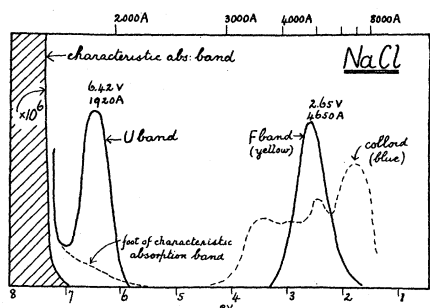


FIG. 5. Relative positions of the characteristic absorption band, the *U* band, the *F* band, and the band due to colloidal particles.

the temperature is lowered, and in that there is a simple relation between the position of the maximum and the value of the grating constant,

$$\nu_{\max} \cdot d^2 = \text{const.},$$

which is the same relation as for the *F* band, except for the value of the numerical constant.

The various absorption bands which have been found in alkali halide crystals are collected together in Fig. 5.

IV. PRODUCTION OF *F* CENTERS

We shall now enumerate the ways in which the coloration corresponding to the *F* band, can originate, or be induced: 1. Crystals are often found in nature with this type of coloration, i.e., the *F* centers are already present. 2. By exposing perfectly transparent crystals of rocksalt, or any alkali halide, to x-rays, they become colored with *F* centers. 3. By exposing them to ultra-

violet light the *F* centers are formed. The ultraviolet light must belong to the long wave-length foot of the characteristic absorption band. Light within the absorption band itself cannot penetrate into the crystal, it is so strongly absorbed in the surface layers. 4. The same bands may be induced by exposing a crystal at a sufficiently high temperature to the vapor of the alkali metal, usually the metal of the positive ion in the crystal, though it seems to be immaterial which alkali metal is used. This is called "additive" coloring. 5. By driving electrons into a warmed crystal from a pointed cathode pressing against it. 6. By absorbing ultraviolet light in the *U* bands of the crystal, if the crystal has been prepared or treated so as to contain *U* centers.

It is an interesting and significant thing that the *F* bands produced in such a variety of ways are identical in shape and location.

Absorption of light within the *F* band by a colored crystal may result in (a) excitation, (b) bleaching, or (c) in formation of colloidal particles.¹⁴ These are not exclusive, for example, cases are known where (a) and (b) occur together. When excitation occurs, the *F* band broadens out on the long wave-length side. Flooding with infrared light removes the excitation and the band resumes its original shape. One may think of excitation as a process whereby an electron is removed from an *F* center by the absorption of a quantum and moves a little way until it gets loosely bound at an irregularity in the lattice. Here it may be thought of as part of an excitation center from which it can be easily moved. Thus infrared light can set it free, and so it returns to the original, or some other *F* center. Bleaching occurs when the electrons set free are caught by neutral halogen atoms, converting them into ions to which the electrons are bound strongly, thus accounting for the fact that bleaching is an irreversible process while excitation is reversible. At room temperature excitation is found in NaCl crystals, bleaching in KBr crystals, according to Umrath.¹⁴ In strongly colored NaCl absorption of light within the *F* band leads also to a coagulation of the *F* center into colloidal particles.¹⁴

¹⁴ W. Umrath, Dissertation (Göttingen, 1933).

V. CONDUCTIVITY IN CRYSTALS CONTAINING F CENTERS

We now turn to a consideration of the photoconductivity associated with the F bands. The electrical arrangement for investigating this is very simple (Fig. 6). The crystal is mounted between two electrodes. A potential difference is supplied by a suitable battery and the current measured by a quick acting electrometer shunted by a high resistance. In the dark the crystal is a good insulator, provided that the temperature is not too high, but when it is illuminated by any light which is absorbed within its F band, it becomes conducting. In many cases, the current falls off as time goes on because of a growing polarization within the crystal which tends to annul the applied field. The explanation is that whenever a quantum of light within the F band is absorbed, it sets free an electron which travels in the direction of the applied field for a short distance until it gets caught in some obstacle such as a crack, or flaw, or internal surface in the lattice. When this has been going on for a sufficient time the crystal becomes electrically polarized as a result of the separation of the electrons from their original locations, where positive charges are left behind. The F band of the crystal is now flattened and broadened, particularly to the long wave-length side. The crystal is said to be "excited." The "excitation" can now be removed by warming the crystal or by flooding it with red and infrared light.

These results suggest that, when electrons have been released from the F centers, they are caught at other places where the binding energy is so small that infrared light, or even the heat motion of the lattice due to moderate temperatures, can set them free. In the absence of an

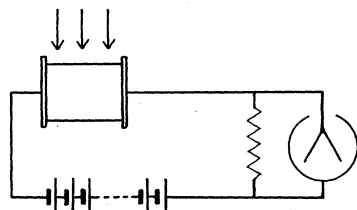


FIG. 6. Experimental set-up for measuring photoconductivity.

electric field, they then wander back to the original F centers, thereby removing the excited state.

There is a noteworthy difference in the behavior of F centers with regard to an electric field according to the manner of their production. When a crystal is colored as a result of 2 or 3 (see beginning of Section IV), the application of an electric field to the crystal produces a current indicating that electrons are set free and move. This happens only if the temperature of the crystal is sufficiently high (above about 250° for NaCl, 180° for KCl, etc.). At the same time the color fades away, leaving the crystal colorless. This is known as "bleaching." Different results are obtained when the coloration is produced as in 4, 5, or 6. In these cases the application of an electric field (provided, as always, that the temperature is high enough) produces a current, indicating the movement of electrons, but now the colored region moves bodily across the crystal into the anode, leaving the crystal colorless.¹⁵ In the case of 6 the intensity of the colored region diminishes as it moves with the field, indicating a return of some of the F centers into invisible U centers as the electrons move towards the anode. It is possible to account for the difference in behavior between the F centers of 2 and 3 and those of 4 and 5 in this way. In 2 and 3, the F centers are created in the crystal by exposure to ultraviolet light and to x-rays, respectively, a process which does not disturb the one to one relationship between the metal and halogen atoms, but which may be supposed to remove electrons from certain halogen ions leaving them neutral. The electrons set free become loosely attached at various suitable places, forming F centers. Provided that the temperature is high enough, an electric field causes these electrons to move, and sooner or later they are recaptured by the neutral halogen ions to which they are strongly bound, thus restoring the condition existing before the coloration was produced and accounting for the bleaching. In cases 4 and 5, no such effect can happen since there are no neutral halogen atoms to capture the electrons. The electrons keep on moving intermittently towards the anode, and at all places at which

¹⁵ R. Hilsch and R. W. Pohl, *Gött. Nachr.* No. 52, 406 (1933); A. D. v. Lüpke, *Ann. d. Physik* 21, 1 (1934).

they stop temporarily they form F centers. Hence the coloration moves across the crystal into the anode. This explanation is consistent with the fact that in cases 4, 5, and 6 there is a stoichiometric surplus of metal atoms over halogen atoms, whereas such is not the case in 2 and 3.

The method of coloring a crystal by driving electrons into it—listed as method 5 in Section IV—deserves special attention. A crystal is mounted between a flat anode and a pointed cathode. On heating the crystal in a small electric oven and applying several hundred volts difference of potential, a cloud is seen expanding from the pointed cathode, as shown in Fig. 7, which moves over towards the anode and in a few seconds fills the whole crystal. When the crystal is cooled to room temperature, the cloud is yellow in NaCl, violet in KCl, and blue in KBr. In all cases, the absorption bands are identical in location and shape with the F bands already described. If the field is reversed the cloud draws away from the new cathode and the boundary moves towards the new anode. In fact, we have now something closely resembling a cathode dark space, which, however, unlike the dark space in a gas, can be made to expand or contract merely with the passage of the current. Potential measurements also show another similarity. The field is greater in the clear space than in the colored space, which is thus analogous to the positive column in a gas discharge.

Pohl's hypothesis is that the colored cloud obtained in this way is associated with the penetration of electrons into the crystal. F centers arise whenever these electrons are bound to the internal surfaces or defects in the lattice. It is not every kind of cathode which will give the electron cloud.

A heated transparent alkali halide crystal conducts electrolytically; we must think of the positive metal ions as moving up to the cathode and there being neutralized by electrons from the cathode. Conditions are altered when special kinds of electrodes are used. A sharply pointed cathode provides a high local field enabling electrons to pass right into the crystal so that the current is now being carried by electrons in the crystal, moving away from the cathode, as well as positive ions moving to the cathode and

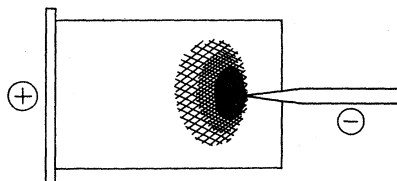


FIG. 7. Colored cloud due to electrons from a pointed cathode. (The shading attempts to represent the smooth decrease in depth of color.)

negative ions moving away from it.¹⁶ A cathode which has been "anodically polarized" will also act as a source of electrons penetrating into the crystal. An experiment which illustrates this is the following. A transparent crystal is provided with two electrodes, one a flat platinum sheet in intimate contact with the crystal and the other a layer of graphite. With the graphite as cathode and the platinum as anode, a current—the usual electrolytic current—passes through the heated crystal which remains transparent. On reversing the current and so making the platinum the cathode, a cloud, whose absorption spectrum is that of the F band, is now observed to grow out of the cathode.

Let us suppose that the coloration is produced by mobile electrons which somehow form F centers. It is possible to estimate that visible clouds must be associated with electron densities of the order of 10^{17} electrons per cc. But one cannot simply put down 10^{17} electrons in a cc, for the repulsive forces would give pressures corresponding to a million atmospheres or so. There must be some compensating motion of positive or negative charges. Thus, as the cloud moves towards the anode there may be a compensating movement of halogen ions such that the electrons displace an equal number of Cl ions. The conductivity associated with the electron cloud is illustrated by an experiment in which a clear KCl crystal is heated to 675° and a voltage of 2000 applied to it between a pointed anode and a plane cathode.¹⁷ A steady electrolytic current flows through it and no change in color is to be noticed. The field is reversed and now the point becomes the cathode and a visible cloud grows out of it into the crystal. The current

¹⁶ R. W. Pohl, *Kolloid-Zeitschrift* 71, 257 (1935); *Zeits. f. Metallkunde* 26, 217 (1934).

¹⁷ R. W. Pohl, *Zeits. f. Metallkunde* 26, 217 (1934).

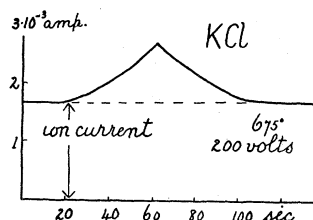


Fig. 8. Showing superposition of an electron current on the ion current.

increases as the cloud grows, and if the direction of the current be reversed, the excess current diminishes and finally we get the initial pure electrolytic current when the cloud shrinks back again into the cathode (see Fig. 8). At the lower temperature of 390° , the electrolytic current is much smaller, of the order of 25 microamp. On driving in the cloud the current rises until it reaches a value of 40,000 microamp. when the cloud reaches all the way across the crystal and colors it uniformly. While the front boundary of the cloud is advancing, we must suppose that enough Cl negative ions move ahead so as to make room for the on-coming electrons and keep the crystal neutral or nearly neutral. Once the cloud stretches uniformly all the way across, the ions are no longer involved, for just as many electrons leave the crystal at one electrode as enter it at the other. We now have a picture which is very similar to that of a metal, in fact the crystal colored in this manner may be regarded as a much "diluted" metal. In a clear rocksalt crystal there will be just as many positive sodium ions as there are negative chlorine ions. In a colored crystal, this balance is upset, i.e., there is a stoichiometric surplus of Na atoms. There may be N Na ions, n electrons, and therefore $N - n$ Cl ions.¹⁸ If the Cl ions could be completely replaced we should have N sodium positive ions arranged in a lattice with N free electrons, that is to say, ordinary metallic sodium. As it is, the colored crystal represents something in between the two extremes of a pure

¹⁸ It may be of interest to point out that the surplus of metal atoms is brought about in a slightly different way when F centers are made by heating the crystal in an alkali metal vapor and when they are made by driving electrons into the crystal from a pointed cathode. In the first case, metal atoms are actually added to the crystal; in the second case the electrons presumably drive out a corresponding number of halogen ions.

metal with nothing but positive Na ions and electrons on one hand, and a rocksalt crystal containing equal numbers of positive Na ions and negative Cl ions, and nothing else on the other. To be sure, the colored crystal is much closer to the clear crystal than it is to the metal, for even under the most favorable circumstances it has not yet been possible to bring into the crystal more than one electron for every hundred thousand or so ions already present. In this sense, we understand why Pohl refers to the crystal as a diluted metal, for unless the temperature is high enough to bring in the electrolytic current, the conductivity of a uniformly colored crystal is electronic exactly as it is in a metal.

Let us turn back to the case where we start with a crystal full of color centers and apply a field, using such electrodes that electrons do not pass from the cathode into the crystal. The colored region will then move into the anode until it disappears. To maintain electrical neutrality in the crystal, we may suppose that within the colored patch there is a surplus of positive sodium ions, or a deficit of negative chlorine ions, or perhaps a combination of both. These move according to the laws of electrolysis. Consequently the colored patch cannot move faster than do the compensating ions. This viewpoint is very neatly supported by measurements of the mobility of a small isolated colored patch, or electron cloud, through a clear KCl crystal.¹⁹ At temperatures below about 680° the cloud became diffuse, the front boundary corresponding to the fast-moving electrons and the rear boundary to the slow moving electrons. Above 680° , the cloud kept together as though all the electrons constituting it move at exactly the same speed (Fig. 9). Studies of the electrolytic

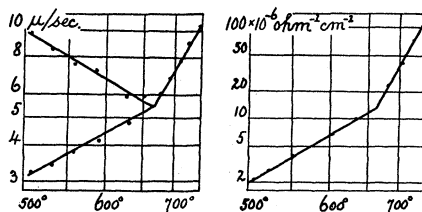


Fig. 9. Comparison of the mobility of electrons with the electrolytic conductivity at different temperatures.

¹⁹ O. Stasiw, Gött. Nachr. No. 50, 387 (1933).

conductivity show a decided break at the same temperature. Above this point, all the ions in the lattice take part equally well in the process of conduction, below it, only the more loosely bound ions at the internal surfaces contribute. There is probably a wide dispersion in the speeds of ions slipping along internal surfaces because these are presumably non-uniform and vary widely in character. One thinks of the conductivity at the higher temperature as being a "structure-insensitive" phenomenon, and that at the lower temperature as a "structure-sensitive" phenomenon.²⁰ The electrons, while potentially capable of moving at considerable speeds, cannot move any faster through the crystal than the ions associated with them, and so their observed mobility is conditioned by movement of the ions. (At high temperatures the speeds of individual ions have a relatively small range, hence the electron cloud keeps together; at lower temperatures the speeds of the individual ions that take part have a wide range, hence the wide dispersion in the electron speeds.)

If the colored cloud extends uniformly from one electrode to the other and if the cathode is of the type from which electrons pass into the crystal, the electrons move from the cathode into the crystal, through it, and finally pass out into the anode, thus not requiring any compensating movement of ions, just as in a metal. However, when the cloud is localized in part of the crystal, then there must be a compensating movement of ions to keep the crystal electrically neutral.²¹

The mobility of the electrons constituting a color patch in a clear crystal can be measured by observing the rate at which it moves in a given field.²² The mobilities in various alkali halides are shown in Fig. 10. The values of the mobility fit the formula

$$v_T = v_0 \exp(-\epsilon/kT), \quad (2)$$

²⁰ W. Lehfeldt (Zeits. f. Physik 85, 717 (1933)) presents evidence for the view that, whereas at high temperatures, all the ions in a crystal take part in the conductivity giving what may be called the "characteristic" or "high temperature" conductivity of the crystal, at lower temperatures the conductivity is that resulting from the movement of a relatively few ions free to move along the cracks and internal surfaces. This is the "Storleitung" which may perhaps be called the structure-sensitive conductivity.

²¹ R. W. Pohl, Phys. Zeits. 35, 107 (1934).

²² O. Stasiw, Gött. Nachr. No. 50, 387 (1933). See also A. Smakula, Gött. Nachr. No. 4, 55 (1934); O. Stasiw, Gött. Nachr. No. 12, 147 (1935); E. Mollwo, Gött. Nachr. No. 6, 81 (1934).

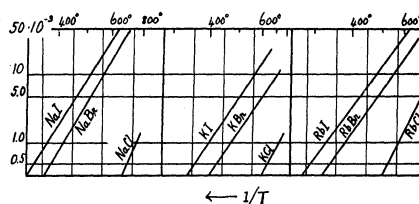


FIG. 10. Mobilities of electrons in various alkali halide crystals at different temperatures. Values are in cm/sec. for fields of 1 volt/cm (Smakula).

where v_T is the mobility at the temperature T and v_0 a constant which turns out to be of the order of the mobility of electrons in metals. ϵ has a value a little below 1 ev.

VI. CONCENTRATION OF COLOR CENTERS IN CRYSTALS

The next point to be discussed is the connection between the optical absorption of a colored crystal and the number of F centers, when these are produced by driving in electrons. Each electron driven in is associated with one F center, or constitutes an F center, when we consider it as bound somehow within the crystal.

If one starts with a colored crystal and applies a field to it by means of electrodes which do not drive in more electrons, then the cloud is slowly driven out of the crystal into the anode. The measured current falls off with the time and finally drops to a constant value, as shown in Fig. 11, when the cloud disappears. The constant value represents the electrolytic current while the shaded area represents the total charge carried by the electrons forming the cloud. On dividing by " e " the total number of electrons may be found. Having thus determined the number electrically, we proceed to consider how it may be found optically.

Let us assume that these electrons, insofar as they are bound loosely to the lattice, constitute F centers. If each be regarded as a simple oscillator then the general dispersion formula leads to this result,²³ that the number of oscillators and therefore the number of electrons involved in the absorption in a color band is

$$N_0 = 1.3 \times 10^{17} K H n / (n^2 + 2)^2,$$

²³ E. Mollwo and W. Roos, Gött. Nachr. No. 8, 107 (1934); A. Smakula, Zeits. f. Physik 59, 603 (1930).

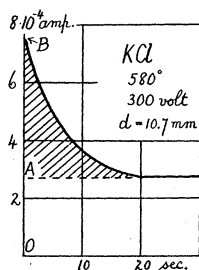


FIG. 11. Showing decrease in conductivity as the electron cloud is driven out of the crystal.

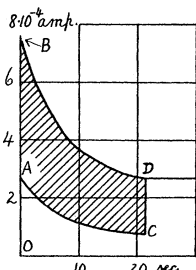


FIG. 12. Illustrating true division of observed current between electrons and ions.

where n is the refractive index in the middle of the band,

K is the absorption coefficient in the middle of the band,

H = half value width of the band (in ev).

It was found that the number of electrons obtained electrically agreed with that obtained optically to within a few percent. This is probably too good an agreement, for the exact value of the numerical constant in the optical formula differs according to the nature of the assumptions made in deriving it. However, the fact that the two values are substantially identical, pending further detailed analysis, strongly supports the view that the electrons which take part in the conductivity are also those responsible for the type of coloration under discussion. Concentrations between 10^{17} and 10^{18} electrons per cc have been obtained in alkali halide crystals exposed to K or Na vapor at temperatures between 400° and the melting point.²⁴

Closer analysis, by Mollwo and Roos, shows that the method just described of computing the number of electrons, or F centers, from the shaded area in Fig. 11, requires correction.²³ It was tacitly assumed in this method that the electrolytic current has the same value in the clear part of the crystal as in the colored part (Fig. 13). Let V be the total potential fall across the crystal. The currents i_i and i_e carried by the ions and by the electrons when the crystal is uniformly colored are equal to V multiplied by the corresponding conductivities c_i and c_e . When the crystal is completely clear the current is carried by the ions alone and we have $i_i = c_i V$. When the crystal

²⁴ E. Mollwo, Zeits. f. Physik 85, 56 (1933).

is colored uniformly from cathode to anode, the current is

$$J = i_i + i_e = (c_i + c_e)V. \quad (3)$$

(There is an assumption here that the presence of the color centers is without influence on the ionic conductivity.) Hence the fraction of the current carried by the ions is $c_i/(c_i + c_e)$ of the total current. This means that in the completely colored crystal OA represents the electrolytic current and AB the electron current (Fig. 11). Now as the field drives the colored portion into the anode leaving a clear part behind (Fig. 13), the division of the current, in the colored portion, between ions and the electrons will still be in the ratio of c_i to c_e . Hence Fig. 11 must be replaced by Fig. 12. Here the ordinate of any point on AC is always $c_i/(c_i + c_e)$ of the corresponding point on BD . The area representing the charge conveyed by the electrons is $ABDC$, which turns out to be approximately twice as great as the area ABD previously considered to represent the charge carried by the electrons. We have therefore a more accurate method of deducing the value of the number of electrons in a color cloud from measurements of the charge associated with it. It is possible to set up expression for i_i and i_e as follows. The total potential drop V is made up of two parts, V_1 , the drop across the clear part, and V_2 , that across the colored part. Hence

$$V = V_1 + V_2$$

and clearly

$$V_1/V_2 = (x/c_i)/(c_i + c_e)/(d-x). \quad (4)$$

From this we get

$$V_1 = [(c_i + c_e)x/(c_i d + c_e x)] \cdot V$$

and

$$V_2 = [c_i(d-x)/(c_i d + c_e x)] \cdot V. \quad (5)$$

The field is evidently greater in the clear part of the crystal. The current J which flows in the clear part of the crystal is made up of two parts, i_i and i_e , in the colored part. We then have

$$i_i = [c_i^2 A/(c_i d + c_e x)] V \quad \text{and} \quad i_e = [c_i c_e A/(c_i d + c_e x)] V, \quad (6)$$

where A is the area of cross section. These two equations tell us how the two components of currents diminish as the length of the clear portion of the crystal increases, and moreover it is seen that $i_i/i_e = c_i/c_e$ in agreement with what we used previously.

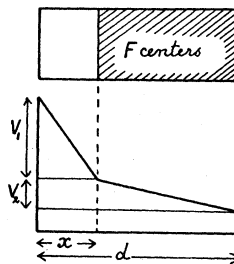


FIG. 13. Voltage drop in a partly colored crystal.

The fact that the *front* boundary of a color cloud becomes diffuse while the *rear* boundary remains sharp follows from the foregoing equations or from the fact that the field is smaller in the colored part than in the less conducting clear part. If any electron tends to lag behind the rear boundary of a colored cloud it falls into a region where the field is stronger and drives it forward into the cloud. Hence the boundary is kept sharp. The same argument will likewise explain why a front boundary tends to become diffuse. It is of interest here to point out two formal analogies. First, the sharpness or diffuseness of the boundary between two differently colored electrolytes has been explained on similar lines. Second, the clear region and colored region correspond to the Crookes dark space and the positive column, insofar as the relative magnitudes of the fields are concerned.

We have seen that a consistent interpretation of the phenomena can be had if we suppose that within the cloud there are electrons which can move in a field. But these electrons are not so completely free as the electrons in the metal. In the first place there is a wide region in the infrared over which the crystal is still transparent, which is not found in metals or even to be expected in an idealized diluted metal. Also the existence of a color band in a definite region of the spectrum indicates a preferential binding. The picture of the situation then is this. An electron is for a moment bound to a part of the lattice, probably at some internal surface, crack, or flaw. The heat motion of the crystal sets it free intermittently, and so in the presence of a field it is displaced a short distance towards the anode until it is stopped at another irregularity. Sooner or later, heat motion again releases it and it slips away a little further on its stop-and-go journey to the anode. During each stop, where it is bound to the lattice it is in a condition to absorb a quantum of light. Hence the part of the crystal containing the electrons is colored. It is clear that the higher the temperature, the more easily do these electrons move. At room temperatures, absorption of light sets the electrons free, but because there is no ion current present, a polarization builds up which tends to annul the applied field.

One may think of the nature of the color centers, or *F* centers, in a different way, although it is not in conflict with picturing them as electrons loosely bound here and there in the crystal. If we take a crystal of clear rocksalt and another which is colored in the way we have just discussed

and dissolve them both in water, the solution of the first is neutral and that of the second is alkaline. This then is clear proof that there are more sodium atoms than chlorine atoms in the colored crystal. Again, if a well-colored crystal be heated to a sufficiently high temperature in a vacuum, the color will disappear and sodium will be found condensed on the walls of the container. Again, when the *F* band is obtained by "additive" coloring, i.e., by exposing the clear crystal to the metal vapor at high temperatures, it is natural and proper to think, of the neutral atoms penetrating into the crystal. The evidence from all three sides is fairly conclusive that the phenomenon of the *F* band is associated with surplus metal atoms in the crystal. But it is not certain that the surplus metal atoms, as such, are the color centers. One may also equally well hold that the surplus atoms are dissociated into positive ions and electrons, and consider the electrons to be actively concerned in the color centers, the function of the positive ion merely being a secondary one, to provide electrical neutrality in the crystal.

One piece of evidence for thinking of the color centers as electrons rather than as particular neutral atoms is the following: The *F* band is precisely the same whether one colors the crystal by exposure to sodium vapor or to potassium vapor.²⁵ The function of the metal would seem to be merely to provide a compensating positive charge, the binding that is involved in the color band is that between the electron and the internal surfaces, and not that within the metal atom by which the electron is introduced.

The electron constituting an *F* center is probably to be found at an internal surface or flaw in the crystal. Since, after all, the internal surface is itself made up of the ions of the lattice, one may, if one wishes, think of the electrons as being tied loosely to the nearest positive ion, thus giving us back a neutral atom as an *F* center. The two points of view which are to be found in the literature are not in conflict. Which of the two one adopts is largely a matter of convenience in terminology.

Investigations have been made on the maximum attainable concentrations of *F* centers in NaCl, additively colored by exposure to the metal vapor²⁶ and in fluorite (CaF₂) colored by

²⁵ Z. Gyulai, *Zeits. f. Physik* 37, 889 (1926).

²⁶ E. Mollwo, *Zeits. f. Physik* 85, 56 (1933).

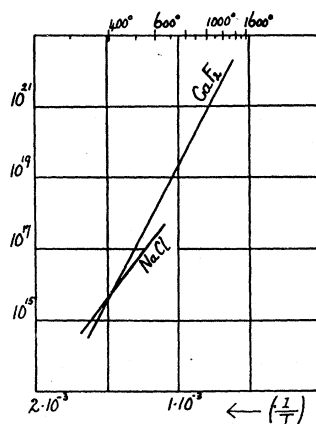


FIG. 14. Concentration of color centers, or electrons, in NaCl and in CaF_2 at different temperatures.

driving electrons in from a pointed cathode.²⁷ The results are shown in Fig. 14. The concentrations appear to be an exponential function of the reciprocal of the temperature. In the case of fluorite it is possible to go as high as 1500°C and there the concentration of color centers reaches 10^{22} per cc. Crystals with such concentration are noticeably less dense than normal crystals, a result which is consistent with the view that the incoming electrons displace the same number of fluorine ions.

The *diffusion* of color centers in a crystal has been investigated by Stasiw.²⁸ The procedure is briefly as follows: A flat crystal uniformly filled with F centers is raised to a suitable temperature for a certain interval of time and then cooled. As a result of diffusion the uniform distribution has been replaced by one in which the concentration falls off from the center to the faces. The gradient of concentration is measured by slicing the crystal into thin sections and measuring the absorption coefficient of each section. For KCl the diffusion constant D varies from 9.4×10^{-5} cm²/sec. at 755° to 5.7×10^{-7} cm²/sec. at 490° . Stasiw showed that when the temperature of the crystal was above 700° the mobility v and diffusion coefficient D are related by the simple formula

$$v = De/kT, \quad (6)$$

²⁷ E. Mollwo, *Gött. Nachr.* No. 6, 79 (1934).
²⁸ O. Stasiw, *Phys. Zeits.* **36**, 737 (1935).

a formula long known in the theory of the motion of ions in gases. At lower temperatures this does not hold, however. It can be expected to hold only so long as nothing impedes the motion of the electrons. If the motion of the positive charges—which must move with the electrons to maintain electrical neutrality—becomes sluggish, then theory shows that the above equation is to be replaced by

$$v = Dv_+ / (v_+kT/e - D), \quad (7)$$

where v_+ is the mobility of the positive charges moving in the crystal. v_+ is not the same thing as v_+' , the mobility of individual metal ions, but is equal to it multiplied by the ratio of the number of metal ions moving in the crystal to the number of electrons.²⁹ It is therefore possible to use the relation to calculate the mobility v_+ of the positive charges from the experimental values of v and D , as has been done by Stasiw. At moderate temperatures (below 700°) the advance of the electrons is retarded by the sluggishness of the associated positive charges. Above 700° the positive charges no longer retard the electrons and the speed with which they move now depends simply on the ratio of the intervals during which they move freely to those during which they are bound temporarily here and there as F centers.

Thermoelectric potentials in crystals containing color centers have been measured by Stasiw.³⁰ Color centers are introduced into the middle portion of a long crystal of KCl cut so as to have a rectangular cross section. In contact with the platinum electrodes which are pressed against the two ends are to be found two water-cooled crystals (Fig. 15). The "junctions," 1 and 2, are

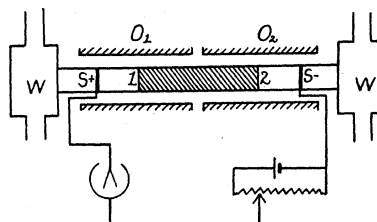


FIG. 15. Arrangement for measuring thermoelectric potentials set up when junctions between colored and clear crystal are heated to different temperatures.

²⁹ See O. Stasiw, ref. 19, also *Gött. Nachr.* No. 12, 151 (1935).

³⁰ O. Stasiw, *Gött. Nachr.* No. 17, 199 (1935).

maintained at different temperatures by two ovens, O_1 and O_2 . If the temperature of one junction be maintained at 700° and that of the other be varied between 700° and 400° , an e.m.f. is developed, which for a 270° temperature difference, when the concentration of F centers is 1.2×10^{18} per cc, amounts to 0.4 volt. The results can be interpreted in terms of Nernst's theory of diffusion potentials according to which the registered e.m.f., V , is the difference of two e.m.f.'s, V_1 and V_2 , developed at each junction. Each of these depends upon the *difference* between the mobility of the electrons and that of the positive charges. So long as a junction is below 700° a difference between the mobilities exists, as we have seen in the previous paragraph, and consequently a thermoelectric e.m.f. can be developed. But if both junctions are at different temperatures *above* 700° , no thermoelectric e.m.f. appears, in accordance with the view that when the positive charges move as quickly as the electrons no diffusion potential can be set up.

VII. THE POSITIVE PRIMARY PHOTOELECTRIC CURRENT

In Section II it was mentioned that the positive charge left behind at a place in a crystal from which an electron was set free by the absorption of a light quantum, may or may not move towards the cathode. If the conditions are favorable to its motion it was pointed out that we must not think of an ion moving bodily through the crystal, but rather of electrons advancing in the sequence 1, 2, 3, \dots , thus shifting the location of the positive charge (Fig. 16).

We have seen that one way of introducing an electron cloud, which behaves like the electron primary current, into a crystal is to bring a surplus of metal atoms into it by heating it in metal vapor. Recently Mollwo³¹ has shown that introducing a surplus of *halogen* atoms provides a means of making visible the *positive primary cur-*

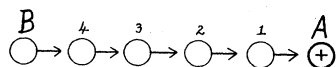
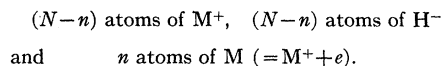


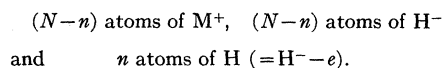
FIG. 16. Illustration of the mechanism of the positive primary current whereby the location of the positive charge slips back from A to B .

³¹ E. Mollwo, Gött. Nachr. No. 20, 215 (1935).

rent, the compensating or "ersatz" current. A crystal of potassium iodide is exposed to iodine vapor at 600° . The crystal becomes deeply colored. If cooled slowly the color is turbid, indicating the presence of colloidal particles which can be removed by heating the crystal to 600° and quickly quenching it. When free of colloidal particles the color is a clear green. Just as there is no connection between the absorption spectrum of a crystal into which surplus metal atoms have been introduced and that of the metal vapor, so the absorption spectra of free iodine and of potassium iodide crystals containing surplus iodine have nothing in common. On heating the crystal to between 400° and 600° and applying an electric field, the colored part moves to the *cathode*, thus behaving like a cloud of F centers except that it moves in the opposite direction. The conductivity is largest when the cloud fills the crystal and least after it has been driven out by a field. The mobility at 450° is of the order of 2.6×10^{-4} cm/sec. in a field of 1 volt/cm. Electrical and optical methods (employed exactly as was described previously for F centers) gave 1.2×10^{17} and 1.7×10^{17} centers/cc, respectively, for a crystal at 455°C . In the normal crystal the iodine atoms occur always as negative ions, equal in number to the positive metal ions. If there is any excess iodine it must be present as neutral atoms. We have seen previously, when considering an alkali halide crystal MH containing an excess of the metal M , that we could think of the surplus metal either as being made up of neutral atoms or as positive ions associated with a like number of electrons, according to the following scheme:



In similar fashion we can think of the same crystal with an excess of halogen as follows:



Here the " $-e$ " is to be interpreted as a missing electron, i.e., a sort of fictitious positive charge, and it is this positive charge which slips back to the cathode as indicated in Fig. 16, where we see that the mechanism is actually effected by the motion of electrons. No positively charged par-

ticle, as such, moves. In recent years, work on semi-conductors has led to the notion of "surplus" and "defect" conductors. Crystals with an excess of metal are typical "surplus" conductors; conductivity results from the motion of the nearly free electrons associated with the F centers. These experiments of Mollwo bring out very clearly that the conductivity of a crystal with a halogen in excess is the result not of the straightforward motion of the electrons towards the anode, but rather the result of the motion of what might be called an "electron hole," or a region with a defect of electrons, which thereby acts like a positive charge. The positive primary current, the mechanism of which is essentially the same thing as that studied by Mollwo, is to be considered as an example of "defect" conductivity.

VIII. FORMATION OF U CENTERS

We shall now consider a new type of absorption band discovered within the last three years in Pohl's laboratory.³² This is the U band already referred to. It is located in the ultraviolet on the long wave-length side of the characteristic absorption band of the crystal. We shall first mention how a U band can be produced in a crystal and then discuss its properties.

One way is to heat a crystal for a long time, at a high temperature, in the vapor of the metal.³³ The crystal soon becomes colored all the way through because of the formation of F centers, but another change is going on which is not immediately apparent. After prolonged heating in the vapor a section is cut from the crystal across the middle. If this is examined in visible light, it shows the characteristic visible coloration, due to F centers, except for the border which is somewhat more transparent. If now a picture is taken of the crystal by means of transmitted ultraviolet light, it is found that the center is transparent while the border is opaque. The thing that is new is the appearance of the absorption in the ultraviolet. This is called the U band, and it is postulated that it arises from U centers. Suppose that the crystal is again heated at a high

temperature, but now without the metal vapor. The crystal becomes completely transparent in the visible, which means that the F centers responsible for the color have evaporated out. Examined in ultraviolet light, the border has become wider, showing the slow diffusion of the U centers towards the interior of the crystal. A second method³⁴ and one which gives a more uniform distribution of U centers throughout this crystal is this. A small crystal is held on the surface of the molten salt. From a pointed cathode pressing into the solid crystal, electrons are driven into the crystal. The anode is somewhere at the bottom of the molten salt. By controlled cooling the crystal is allowed to grow while the current is continuously flowing. Such a procedure results in a crystal full of U centers as well as F centers. What presumably happens is that at the boundary between the solid crystal and the molten salt, many of the electrons moving out from the crystal combine with the metal ions coming into it and so we have neutral metal atoms frozen, so to speak, in the growing crystal.

From a consideration of the methods of producing U centers, it is clear that they, like the F centers, are due to a stoichiometric surplus of metal atoms in the crystal, a view which is borne out by an experiment which shows that a perfectly clear crystal containing U centers shows an alkaline reaction on solution. However, the fact that the U band and F band differ in location, and the fact that F centers move in an electric field whereas U centers do not, indicate that they must, in some way, be different. Although U centers are produced easily in a growing crystal into which electrons are driven, it is possible to produce them to a lesser degree occasionally in ordinary crystals.³⁵ In such cases it is possible to see both the cloud of F centers and the cloud of U centers grow out of the pointed cathode. (To see the U cloud, ultraviolet light is projected through the crystal on a fluorescent screen.) If, at 700°, after driving in a known number of electrons from the pointed cathode, one reverses the field, thus driving the F centers out, one recovers only 60 percent of the electrons. This means that 40 percent in this case were im-

³² R. Hilsch and R. W. Pohl, *Gött. Nachr.* No. 46, 322 (1933).

³³ R. Hilsch and R. W. Pohl, *Gött. Nachr.* No. 52, 406 (1933).

³⁴ R. Hilsch and R. W. Pohl, *Gött. Nachr.* No. 9, 115 (1934); A. D. v. Lüpke, *Ann. d. Physik* 21, 1 (1934).

³⁵ A. D. v. Lüpke, *Ann. d. Physik* 21, 1 (1934).

mobilized in U centers. It can also be shown that there are only a limited number of "places" available in the crystal at which U centers can form.

Some unpublished experiments by Kleinschrod have shown that, in a given crystal, the number of places available for U centers is limited. In KCl, the concentration of U centers remained almost unchanged at approximately $5 \times 10^{16}/\text{cm}^3$, while the number of F centers was increased from $9 \times 10^{16}/\text{cm}^3$ to $115 \times 10^{16}/\text{cm}^3$ by exposure of the crystal to the metal vapor. However, by driving the F centers out by heating in the absence of metal vapor, and then producing them again by heating in the presence of the metal vapor and repeating this sequence many times, the number of U centers in another crystal was increased from $19 \times 10^{16}/\text{cm}^3$ to $120 \times 10^{16}/\text{cm}^3$. This suggests that the number of U locations can be increased sixfold by driving F centers in and out repeatedly, a process which evidently produces the physical changes which increase the number of possible U centers. The formation of U centers is clearly a structure sensitive phenomenon.

IX. EQUILIBRIUM BETWEEN U AND F CENTERS

A crystal containing U centers may be perfectly transparent in the visible if the F centers created along with them are driven out by a field, or by evaporation. The crystal is now clear but is very different from the usual transparent crystal in this respect. If the crystal be warmed it is found that the crystal becomes more and more colored, i.e., U centers change into F centers. If it is cooled slowly enough to insure equilibrium at all times, the crystal fades or the F centers disappear and change back into U centers. The process can be repeated time and again. It is found that the relation governing the equilibrium $U \rightleftharpoons F$ is of the familiar form: $\exp(-E/kT)$, where E is of the order of 1.1 volts. These remarks apply only when the crystal is not in an electric field. If the crystal is in an electric field, the electrons, or the F centers if we desire to avoid too precise a specification, are displaced. The interesting thing now is that the U centers cannot be reproduced again, nor can they be restored by driving in a fresh supply of electrons. The changing of U centers into F centers

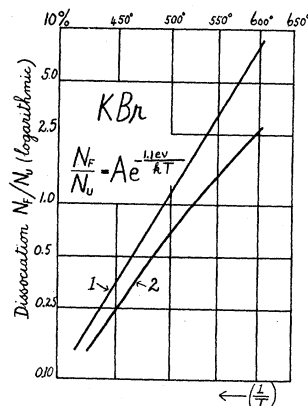


FIG. 17. Dissociation of U centers into F centers as a function of the temperature. Concentration of U centers: $1.3(10)^{16}$ per cc for curve 1, $16(10)^{16}$ for curve 2.

and the shifting of the latter by an electric field is an irreversible process. The U absorption band has disappeared for good.

Hilsch³⁶ has recently studied the thermal equilibrium between U and F centers in KBr. The numbers of U and F centers are obtained from measurements on the absorption bands. As the crystal, initially containing only U centers, is heated, it remains colorless until about 400° , above which the color due to the F band becomes more and more noticeable. The degree of dissociation of U centers into F centers is shown in Fig. 17 for two different U -center concentrations. The ratio of the number of F centers to the number of U centers is found to fit the formula

$$N_F/N_U = A \exp(-E'/kT), \quad (8)$$

where E' is 1.1 ev. If this be regarded as a bimolecular reaction E' is half the heat of reaction. (This relation was established by Wilson and by Fowler.)⁴¹

The formula may be derived as follows. Suppose that the difference in energy between the F and U band, the F being the higher, is E . Let P_F and P_U be the number of places in each band in which an electron may be found. Let N_F be the number of electrons found in the F level at a temperature T . These have come from the U level, and if we suppose that at zero temperature all the places in the U level were occupied, then the number left in the U level at temperature T is $P_U - N_F$. Equilibrium occurs when

³⁶ R. Hilsch, Phys. Zeits. **36**, 735 (1935).

the free energy $\phi(N_F)$ is a minimum. We have

$$\phi(N_F) = N_F E - TS. \quad (9)$$

where S is the entropy and E and T have been defined before. For equilibrium

$$(\partial/\partial N_F)\phi(N_F) = 0 = E - T(\partial S/\partial N_F). \quad (10)$$

But $S = k \ln W$, where W is the thermodynamical probability. The thermodynamical probability for the distribution of N_F electrons among P_F places and of $P_U - N_F$ electrons among P_U places is

$$W = (P_F! / N_F! (P_F - N_F)!) \cdot (P_U! / N_F! (P_U - N_F)!).$$

Then by using Stirling's theorem, we get

$$\ln W = -\ln N_F^{N_F} / (P_F - N_F)^{P_F - N_F} (P_U - N_F)^{P_U - N_F}.$$

On inserting this in Eq. (10) we get

$$N_F = [(P_F - N_F)(P_U - N_F)]^{\frac{1}{2}} \exp(-E/2kT). \quad (11)$$

This explains why the 1.1 eV mentioned previously is only half the heat of reaction. Also it shows that if $\ln N_F$ be plotted against $1/T$ one should get a straight line if the expression under the radical can be treated as a constant. This is the case so long as N_F is small in comparison with the number of available places in either level. Fig. 17 shows that this is true when the number of U centers is $1.3 \times 10^{16}/\text{cm}^3$, but not when it is $16 \times 10^{16}/\text{cm}^3$. One may infer therefore that in the latter case the number of electrons transferred to the F level is no longer negligibly small in comparison with the places available.

The rate at which F centers change into U centers when equilibrium is upset was measured in this way. The crystal was heated to a suitable temperature and then numerous F centers were produced by a short exposure to ultraviolet light, thus disturbing the thermal equilibrium between U and F centers. The rate at which the color faded to the equilibrium state gave a measure of the rate at which F centers pass back into U centers. The time taken for the F -center concentration to fall to half its initial value varies from 90 sec. at 375° to 2.0 sec. at 625° .

There is another way of producing the F color band in a clear crystal, when it contains these U centers, and that is to illuminate it with ultraviolet light in the U band. The crystal then becomes colored because of the creation of F centers, and measurements show that this comes about at the expense of the U centers (Fig. 18).^{36a} There are certain interesting phenomena here. If the crystal is kept at liquid air temperature, absorption of ultraviolet light in the U band of the crystal does not lead to the formation of F

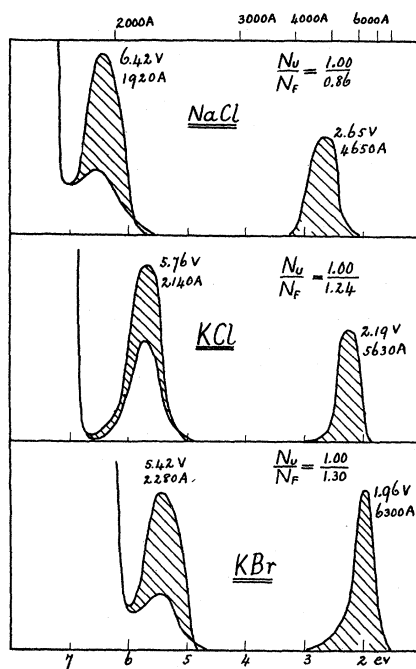


FIG. 18. Showing formation of F centers at the expense of U centers. The shaded area F grows at the expense of the shaded area U .

centers, but, as the temperature is raised, the efficiency of conversion of U centers into F centers increases until, at 500° for KBr , one attains full quantum equivalence. That is to say, for every quantum of ultraviolet light absorbed in the U band, one U center changes into an F center. It is necessary to emphasize that this quantum equivalence relation occurs only when the temperature is sufficiently high. It is as though the electron were set free from the center by the absorbed quantum, but at low temperatures it falls back immediately, while at high temperatures the motion of the atoms in the lattice allows it to escape and become an F center elsewhere.

New measurements have been made recently by Hilsch and Pohl.³⁷ A clear crystal containing

^{36a} R. Hilsch and R. W. Pohl, Gött. Nachr. No. 48, 322 (1933).

³⁷ R. Hilsch and R. W. Pohl, Gött. Nachr. No. 9, 115 (1934); 19, 209 (1935).

nothing but U centers is exposed to ultraviolet light falling within its U absorption band and becomes colored because of the formation of F centers. The total number of U quanta absorbed is measured. Then by measurements on the new F band it is possible to compute the number of F centers produced. (The method has been described in Section VI.) The yield is defined as the ratio of F centers produced to the number of quanta absorbed in the U band. This method cannot be employed above about 150° in KBr because, at higher temperatures, the F centers change back to U centers at a rate which interferes with measurements of the constants of the F band.

In the previous paragraph we saw that when the F and U centers were in thermal equilibrium the lower the temperature the fewer were the F centers. This refers to real equilibrium. It is possible to disturb this equilibrium by exposing the crystal to ultraviolet light which increases the number of F centers at the expense of the U centers. But the situation immediately after illumination is not one of equilibrium, for the excess F centers begin to disappear. The rate at which they return to the equilibrium value diminishes rapidly with the temperature (the values are given earlier in this section) so that at room temperature we can understand why the F centers produced at the expense of the U centers are almost permanent, even though there is no true thermal equilibrium.

To obtain the yield at higher temperatures, Hilsch and Pohl used a different method.³⁷ Light whose wave-length lay within a U band of the crystal was allowed to fall on a limited portion of the crystal. Suitable measurements gave the total number of quanta absorbed. The number of F centers was inferred from the value of the saturation photoelectric current. The basic idea is that each quantum absorbed replaces a U center by an F center, which we have seen it to be regarded as an electron bound rather loosely to an internal surface. At sufficiently high temperatures the electrolytic current which flows in

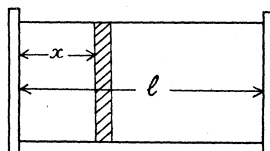


FIG. 19. Measurement of efficiency of conversion of U centers into F centers, by absorption of light in U band. Illumination is limited to shaded area.

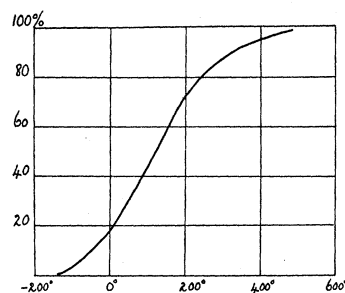


FIG. 20. Yield of F centers per quantum absorbed in the U band as a function of temperature.

the dark is considerably greater than the photoelectric current superposed on it when the crystal is illuminated. When these conditions obtain, it is found that the excess current, which is obtained on illumination and so can be called a photoelectric current, is saturated with a field of the order of 30 to 100 volts/mm. The experiments were carried out by illuminating a narrow strip of the crystal at right angles to the direction of the field at a distance x from the cathode (Fig. 19). If N be the number of electrons set free photoelectrically per second and which arrive at the anode (since the current is saturated), then the current is

$$i_s = Ne(1 - d/2l - x/l), \quad (12)$$

where d is the width of the strip and l the length of the crystal. The value of N , obtained by putting in experimentally determined values of i_s , d , x and l , is assumed to be identical with the number of F centers produced per second, and so the yield can be found at the higher temperatures. The way in which the yield has been measured at lower temperatures has already been described. The complete yield curve for this photochemical production of F centers from U centers is shown in Fig. 20 and can be fitted to the formula

$$\eta = 1 - [1 - \exp(-\epsilon/kT)]^A, \quad (13)$$

where A is 7 or 8 and $\epsilon = 0.085$ ev. Practically full quantum equivalence is obtained in KBr when the temperature is over about 500° .

Eq. (13) may be established as follows: Hilsch and Pohl postulate that an electron is set free from a U center which has absorbed a quantum and so can form an F center elsewhere, if one of the atoms near the U center has greater energy than ϵ , and so can exchange places with the electron

and liberate it. The probability that an atom has energy greater than ϵ is $\exp(-\epsilon/kT)$, and so the probability that it does *not* have this energy is $1 - \exp(-\epsilon/kT)$. If there are A atoms in the vicinity of the U center, the probability that no one of them has energy exceeding ϵ is $[1 - \exp(-\epsilon/kT)]^A$. Hence the probability that one (or at least one) atom *does* have energy greater than ϵ is

$$1 - [1 - \exp(-\epsilon/kT)]^A.$$

This is the probability of the electron changing places with an atom, and so being free to become an F center here or elsewhere.

Several years ago Pohl pointed out the close connection between certain phenomena in photoconducting crystals and the formation of the latent image in photography. The recent discovery of how to introduce U centers into crystals permits a rather interesting illustration of this. Suppose that we are provided with a transparent crystal containing U centers. Now allow ultraviolet light belonging to the U band to fall on the crystal through a stencil. In a few seconds, the parts illuminated by the ultraviolet light become visibly colored, yellow for rocksalt, blue for potassium bromide. If an electric field be now applied, the colored patches can be driven out of the crystal, which is again transparent. If, after this, the whole crystal be illuminated with the ultraviolet light, it will become colored in those parts which had not been previously exposed. In the parts which had been previously exposed, the U centers were used up to give F centers which were then removed by the electric field, and so there were no U centers in these parts to be affected during the second exposure to ultraviolet light. Pohl's view is that there is no essential difference between the photochemical production of color centers in large alkali halide crystals and the production of the latent image in an ordinary photographic emulsion. In the latter case, color centers are produced, but since the crystals are so tiny the coloration is invisible, and hence the term latent image. With large silver bromide crystals, properly illuminated, the latent image is visible.

X. PHOTOCONDUCTIVITY IN DIAMOND AND RED MERCURIC IODIDE

Robertson, Fox, and Martin have studied the photoconductivity in many diamonds.³⁸ The

³⁸ R. Robertson, J. J. Fox and A. E. Martin, Phil. Trans. Roy. Soc. **232**, 463 (1934).

photoconductivity differs widely from specimen to specimen. However, it seems possible to separate them into two classes. In class I we have diamonds which show surprisingly little photoconductivity. These diamonds are characterized by an ultraviolet cut-off at 3000A and by an infrared absorption band at 8μ , in addition to the usual infrared bands. Diamonds belonging to class II show considerable photoconductivity. They have no infrared absorption band at 8μ and they are transparent as far as 2250A. The authors confirmed the work of Pohl and Gudden in that for illumination by wave-lengths between 2400A and 5000A the yield tended towards quantum equivalence. This was provided that the diamonds had not been previously exposed to light of wave-length 2300A, a treatment which produces an effect not hitherto recorded. After a diamond has been exposed to 2300A it shows a conductivity in the dark which diminishes as time goes on. If a diamond, after being exposed to 2300A, is then examined for photoconductivity in the region 2400A to 5000A, it is found that initially a much *larger* response is obtained than if the diamond had not been "activated" by exposure to 2300A. In a short time, however, the yield for 2400A to 5000A drops to its normal value and the induced dark current disappears. But if, after being exposed to 2300A, it is then subjected to red and infrared light (5000A to 9000A), a very large response is obtained which is practically permanent. (The results are shown in Fig. 21.) This is a remarkable result, for it appears (although it is not explicitly stated), that the total charge transported during the longer wave-length illumination may be many times larger than that associated with the electron

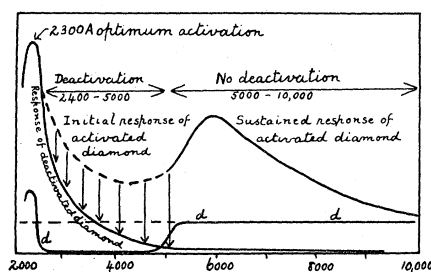


FIG. 21. Photoconductivity in a diamond.

primary current. This would seem to prevent our identifying the effect due to infrared light as the positive primary current for this can never exceed the electron primary current. There appears to be no obvious explanation for this effect.

Nix has investigated a peculiar effect in crystals of red mercuric oxide.³⁹ These crystals lose their conductivity on aging. At the same time there is a progressive change from the mono- to the polycrystalline fibrous state. Crystals which have lost much of their photoconductivity regain it after a short exposure to an electric field.

XI. CONCLUDING REMARKS

The preceding sections summarize the more important advances which have been made, during the past few years, in the field of photoconductivity of crystals. Most of the information gained has come chiefly from an intensive study of the properties of *F* and *U* centers. Yet, while a vast amount of useful information has been acquired, it must be admitted that we do not have a clear-cut rational theory describing precisely what happens in photoconductivity. At best we have merely working hypotheses, as Professor Pohl, the leader in the field, has often emphasized. The characteristics of photoconductivity leave no doubt but that it is to be regarded as one of the "structure-sensitive" phenomena. It is well known that interpretation of "structure-sensitive" phenomena is in a far more primitive state than that of "structure-insensitive" phenomena. For example, we have no theory in the structure-sensitive domain which compares in precision and completeness with that dealing with the analysis of crystal structure by x-rays—a typical structure-insensitive field. Thus the absence of a comprehensive theory of photoconductivity is typical of the group of phenomena to which it belongs.

The presence of *F* and *U* centers is, as we have seen, associated with a stoichiometric surplus of metal atoms in the crystal, i.e., the crystal is no longer made up of exactly equal numbers of metal atoms and halogen atoms. (This is true at least for *F* centers produced by methods 4, 5, and 6, listed in Section IV, but there is no definite evidence as to those produced by methods 1, 2,

and 3.) It does not follow, however, that the centers must necessarily be neutral metal atoms. In Pohl's view the surplus atoms occur as positive metal ions and electrons dissociated from each other, at least for the case of *F* centers. The behavior of *F* centers is consistent with the view that they are electrons bound more or less loosely to the flaws, faults, or internal surfaces in the crystal, the positive ions serving merely to offset the negative space charge which would result from electrons alone. As has been implied previously, *U* centers resemble *F* centers in that they are associated with a stoichiometric surplus of metal atoms, but differ from them in that their binding energy is considerably larger. Pohl states that not enough is known about *U* centers to enable one to state precisely what they are; he has suggested on one or two occasions that they may be neutral atoms (to which the valence electron is bound rather strongly) lodged here and there in the lattice. De Boer offers the suggestions that *F* centers occur when alkali metal atoms are adsorbed on negative ions situated at internal surfaces in the crystal, while *U* centers occur when the atoms are adsorbed on positive ions found at internal surfaces.⁴⁰

In view of the success of the quantum mechanics approach in almost every field of atomic physics, it is desirable to state briefly what has been accomplished in describing photoconductivity in the terminology of quantum mechanics. As this article is concerned chiefly with experimental results, only a brief outline will be given; for fuller theoretical treatment the reader is referred to various writers on the subject.⁴¹ The energy level scheme for a crystal consists of broad bands within which electrons may be found. Each band can accommodate a certain maximum number of electrons; thus a band may be completely filled, partially filled, or completely empty. Bands may be separated from each other by forbidden areas, which is to say

³⁹ J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, 1935), p. 281.

⁴¹ A. H. Wilson, *Nature* **130**, 913 (1932); *Proc. Roy. Soc.* **151**, 274 (1935); R. H. Fowler, *Proc. Roy. Soc.* **140**, 502 (1932); **141**, 56 (1933); R. W. Gurney, *Proc. Roy. Soc.* **141**, 209 (1933); B. Gudden and W. Schottky, *Phys. Zeits.* **36**, 717 (1935); F. Hund, *Phys. Zeits.* **36**, 725 (1935); P. Tartakowsky, *Zeits. f. Physik* **96**, 191 (1935); G. Liandrat, *Thèses* (Masson et Cie., Paris, 1935); A. F. Joffé, *Conductibilité électrique des isolants solides et des semi-conducteurs* (Hermann et Cie., Paris, 1934).

³⁹ F. C. Nix, *Phys. Rev.* **47**, 72 (1935).

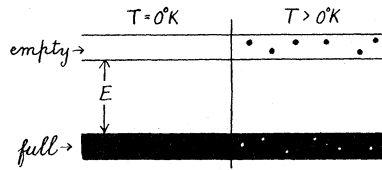


FIG. 22. Energy level diagram for an insulating crystal showing surplus and defect conductivity at $T > 0^\circ\text{K}$. (Gudden and Schottky.)

that electrons cannot exist within the crystal with energy values lying inside these areas. Conductivity is interpreted in this manner. If an applied electric field moves an electron and so does work on it, its energy is increased in continuous steps. If then the electrons lie within a band which is only partially filled, there are empty levels in the band which can accommodate the electron as its energy is altered. Such a crystal conducts. If, however, the band be completely filled, there are no levels within it to which the electron with its added energy can be transferred; the crystal is now an insulator. An electric field can impart energy to an electron only in continuous steps, hence the electron cannot be transferred from a full band to an empty band across a forbidden region. A crystal with a forbidden region between a full band and an empty band is therefore an insulator (Fig. 22). Electrons may pass across the forbidden area when the temperature is raised or, under certain restrictions, when quanta of sufficient energy are absorbed. The number of electrons in the upper band, which is empty at 0°K , is proportional to $\exp(-E/kT)$, where E is half the energy difference between the two bands and T the temperature. Since there are now electrons in a band which has places for a great many more, the crystal is conducting. The conductivity depends on the number of electrons in the upper band, and so it is evident that the greater E is, the higher must be the temperature before appreciable conductivity can be obtained.

In addition to this conductivity arising from the movements of electrons towards the anode, which is sometimes known as "surplus" conductivity, we have also a "defect" conductivity arising from the movement of the "electron holes" left in the full band. These electron holes behave like positive charges and so move towards the

cathode. A motion of electron holes would resemble a positive primary current.

When we have surplus conductivity, directly involving the motion of electrons, we should expect to get the normal (negative) Hall effect predicted by the simple classical theory. This is found in some conductors, but there are many cases in which an anomalous (positive) Hall effect, i.e., one with the sign reversed, occurs. Such an effect was inexplicable from the classical point of view, but is a natural consequence of the application of quantum mechanics to defect conductivity. When a crystal is additively colored by introducing metal atoms which, as we have seen, provide a means of introducing electrons, we have an example of surplus conductivity. When it is colored by introducing halogen atoms which can be thought of as carriers for the electron holes we have a case of defect conductivity. However, we shall see the scheme represented by Fig. 22 is too simplified to describe what goes on in a photoconducting crystal.

Pure alkali halide crystals do not become conducting until quite a high temperature is obtained, and the evidence is that the conductivity then obtained is ionic in character. Thus we have no evidence for the existence of electronic conductivity in these crystals. This points to the conclusion that the energy separation E between the full band and the empty band is considerable. Electronic conductivity has been found only in colored crystals, i.e., in crystals containing F centers, and then only when the temperature is moderately high or when the crystal is illuminated by light absorbed within the F band. This leads to the view that the electrons in the F centers are to be found in localized energy bands (implying that there is no continuous connection between them). These are located a short distance below the empty band. The energy level scheme for a colored crystal is shown in Fig. 23. The value of E' is of the order of the energy in the quantum of radiation absorbed in the F

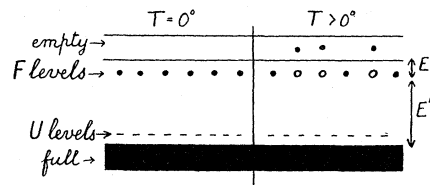


FIG. 23. Energy level diagram for a photoconducting crystal showing localized levels corresponding to F centers and those corresponding to U centers (when present). (Gudden and Schottky.)

band. Fig. 3 shows that it is of the order of 2 ev for KBr at low temperatures. When U centers are present, they, like the F centers, are to be regarded as localized energy levels. Since it takes a quantum of energy E'' —approximately equal to 3.5 ev according to Fig. 18—to replace a U center by an F center, the U levels are placed as shown in Fig. 23. Absorption in the long wavelength foot of the characteristic absorption band likewise results in F centers and so we could place the corresponding localized levels in the vicinity of the U levels.

Gurney has argued that the transitions between U and F levels, in either direction, cannot be direct but must take place from one to the other through a transition to a level *higher* than both of them. This is done to avoid a conflict with thermodynamical reasoning which states that there is no possibility of having direct upward transitions highly probable and at the same time having direct downward transitions highly improbable, which is evidently the case for a crystal in which the color is retained permanently. (Gurney actually considered the formation of F centers when light is absorbed in the long wavelength foot of the characteristic absorption band. At the time he wrote his paper, U centers had

not been discovered. The argument applies equally well to U centers.)

The most elaborate scheme of energy levels for an alkali halide crystal is that proposed by Tartakowsky,⁴¹ who makes use of evidence from many sources to put it together. In none of the schemes hitherto proposed can all the energy levels be located with reasonable certainty, nor can reasons be given why transitions occur between some but not between others. It must be acknowledged that the various attempts to give a description of photoconductivity in the language of quantum mechanics of crystals have not passed beyond the tentative state; we are far from having a rational theory accounting quantitatively for the principal phenomena and suggesting new lines of investigation.

I am very much indebted to Professor R. W. Pohl for sending reprints of many articles which were not accessible to me. I take this opportunity of thanking my colleague, Dr. C. Zener, for the derivations of Eqs. (11) and (13) and for discussions of various problems which came up from time to time in the preparation of this paper. I wish also to acknowledge assistance from the Fund given by the Rockefeller Foundation to Washington University for research in science.