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Bleaching Properties of *F* Centers in KBr at 5°K†

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The bleaching properties of *F* centers in KBr have been investigated experimentally at 5°K and 78°K. The stability of *F* centers towards bleaching is dependent on the temperature and mode of formation. Those produced by additive coloration are stable; those produced at room temperature by x-rays bleach slightly; those produced at 78°K by x-radiation show some bleaching; while those produced at 5°K by x-radiation show a large initial instability. Some tentative theoretical conclusions are made.

I. INTRODUCTION

THE nature of the *F* center which forms in alkali halide crystals is well established.[1] The *F* center results from the trapping of an electron in a negative-ion vacancy, and has a ground state and a single excited state. The gap between the excited state and the conduction band is small (about 0.15 ev in KBr) so that at room temperature the electron easily escapes from the excited level. However, at 5°K the thermal energy of the lattice is too small to produce the transition and the center should not be destroyed by light absorption.

These properties are observed in KBr additively colored with excess potassium. In KBr colored by x-rays, the *F* band bleaches when exposed to light. The extent and nature of this process depends on the temperature at which the crystal was x-rayed.

The paper begins by considering the explanation by Mott and Gurney[1] of Glaser's[2] photoconductivity data. This theory forms the basis of our interpretation. Next the experimental details will be described. Following this the bleaching data will be presented and finally, a summary of the results will be made.

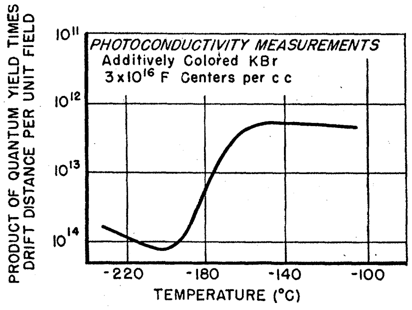

FIG. 1. Photoconductivity as a function of temperature in additively colored KBr. Curve taken from Glaser, reference 1. (The increased thermal range caused by thermal ionization of F' centers is not shown.)

II. ENERGY LEVEL DIAGRAM FOR AN *F* CENTER IN KBr

Glaser's[2] photoconductivity data on additively colored KBr is reproduced in Fig. 1. Two regions of $\eta\omega$ should be noted (η is the ejection probability per quantum absorbed and ω is the electron drift distance per unit electric field). Below -190°C this product decreases with increasing temperature. This is known as the colloidal range since the photoconductivity seems to be the result of colloidal particles which form in additively colored crystals. One would not expect this region to appear in the case where the coloration was produced by x-rays. The second region occurs at temperatures above -190°C where the product rises to a plateau. If we associate the change in the curve as being due to changes in η, (i.e., ω is independent of temperature), we may apply the theory of Mott and Gurney[3] to obtain the thermal activation energy ϵ_t to ionize an excited *F* center. A simplified energy level diagram is shown in

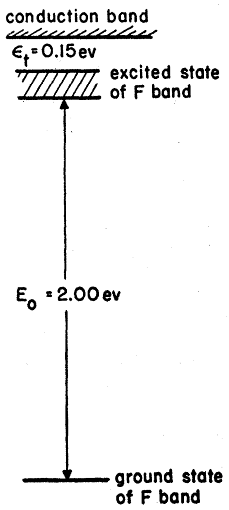

FIG. 2. Energy level diagram of an *F*-center in KBr. The energy at the half-height of the *F* band on the red side is taken as the lower level of the excited state; the energy on the violet side as the upper level. ϵ_t is the thermal ionization energy obtained from the theory of Mott and Gurney and the measurements shown in Fig. 1.

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* Now at Zenith Radio Corporation, Research Div. 6001 W. Dickens Avenue, Chicago, Illinois.

[1] Some reviews of the field are R. W. Pohl, Proc. Phys. Soc. (London) **49** (extra part) 4 1937, or Physik. Z. **39**, 36 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford Press, New York, 1940), Chap. 4; and F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[2] G. Glaser, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl **3**, 31 (1937).

[3] See reference 1, pp. 133 and 160. η was assumed to have a value of unity at -150°C. This is sufficient to determine the thermal ionization energy.

Fig. 2. These two figures indicate that an electron cannot escape from the excited state at 5°K and that the fraction which escape at 78°K is very small.

Glaser has measured the photoconductivity in KCl crystals colored (1) by K vapor, (2) by the dissociation of KH molecules which have been built into the crystal, (3) by x-rays, and (4) by a pointed cathode. The general features of Fig. 1 hold in every case. The gap between the excited level and the conduction band seems to depend slightly on the mode of production, i.e., the thermal activation energy for additively colored KCl is 0.11 ev while for x-rayed KCl is 0.13 ev. Variations between samples of crystals are possible and we do not know what causes the change of 0.02 ev. Nevertheless Glaser's data indicate that the energy level diagram shown in Fig. 2 applies approximately to all F centers in KBr irrespective of their mode of formation.

From Figs. 1 and 2 one must conclude that F light creates excited F centers. At 5°K the thermal energy is insufficient to ionize this state so that no electrons are released to the conduction band. This indicates that the explanation of the data to be presented cannot be given in terms of the migration of electrons through the conduction band.

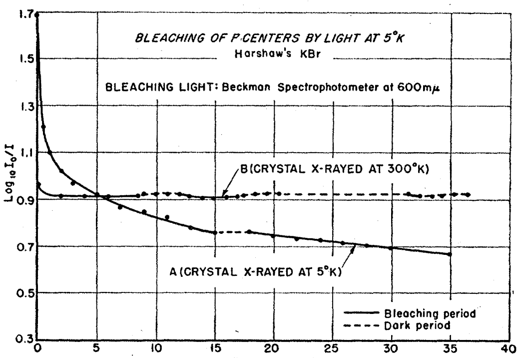

Fig. 3. Decay curves of the F band at 5°K when exposed to F light.

III. EXPERIMENTAL PROCEDURE

The experimental procedures were similar to those described previously.[4,5] The KBr crystals were obtained from three sources. One was from the Harshaw Chemical Company. The purity of this sample has been discussed previously.[5] The second specimen was a large single crystal grown by J. Schulman of the Naval Research Laboratory. The third sample were Harshaw crystals additively colored with potassium by A. B. Scott of the Oregon State College.

Qualitative spectroscopic analyses made by S. Zerfoss of the Naval Research Laboratory, of the Schulman and Harshaw samples did not indicate any major difference. (It will be recalled that the spectroscopic analyses are only approximate.) An absorption band at 285 mμ appears in the untreated Schulman crystal.

The ionic conductivity of Schulman's crystal however, is exceptionally low.[6] This indicates that the concentration of divalent impurities is smaller in Schulman's samples. This fact and the method of preparation leads us to believe that Schulman's samples are purer than the Harshaw samples in spite of the appearance of the 285 mμ-band.[7]

All the bleaching was done with the Beckman Model DU Spectrophotometer using a slit width of 2 mm. At 600 mμ, the peak of the F band at 5°K, this slit width corresponds to a band pass of about 20 mμ. At 750 mμ, the wavelength used for bleaching the F' centers, the band pass was about 30 mμ. Throughout these experiments no corrections were made for the variation of coloration with depth.

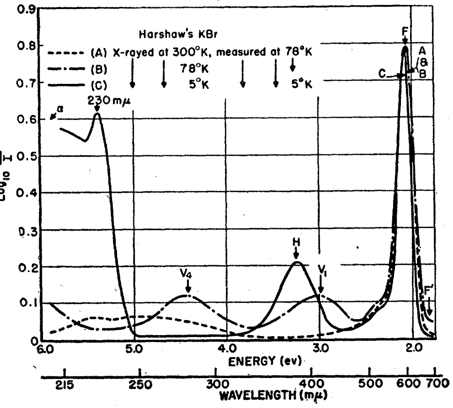

Fig. 4. Absorption spectra of Harshaw KBr crystal x-rayed at 300°, 78° and 5°K.

IV. RESULTS AND INTERPRETATIONS

1. The General Phenomena

Our experiments on additively colored KBr indicate that no bleaching occurs at 78°K and 5°K with our light source. This agrees with the model shown in Fig. 2. The F centers produced by x-radiation, however, bleach at both temperatures. Figure 3 shows the bleaching properties at 5°K of two Harshaw crystals, one x-rayed at 5°K and the other at 300°K.

The temperature of the irradiation is of great importance in determining the susceptibility to bleaching.

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[4] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421 (1952).

[5] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

[6] Private communication. The conductivity measurements were made by Dr. H. W. Etzel.

[7] Because of the uncertainty of the role that impurities play in coloration phenomena it was desirable to compare the crystals used in these experiments with those employed at Göttingen University. Crystals furnished by Prof. R. W. Pohl were analyzed spectroscopically. The crystals were not so pure as those used here. However, Prof. Pohl has stated that crystals of higher purity than those made available for analysis have been grown in Göttingen.

For convenience, the following abbreviations will be adopted: *X*-5 for the crystal x-rayed at 5°K, *X*-300 for the crystal x-rayed at 300°K, etc. In Fig. 3, *X*-5 shows a large amount of initial bleaching and no definite saturation. There is no recovery in the dark. The *X*-300, however, shows a much smaller amount of bleaching, a definite saturation, and a small but measurable amount of recovery in the dark. After the recovery, one may rebleach the crystal and again obtain a definite saturation. Evidently, there is a considerable difference between the *X*-300 and *X*-5 crystals which also shows up in the optical absorption spectra of these crystals.

The structure of the absorption bands formed during x-raying depends on the temperature of irradiation. Figure 4 shows the absorption spectra of Harshaw crystals for various irradiation temperatures. The difference in absorption measuring temperature is of little importance. The only structure observed to the red of the *F* band is the *F*′ band in *X*-78. The radical changes occur to the violet. The *X*-300 crystal has a violet structure about which little is known. The structure has been partially resolved by Dorendorf.[8] The *X*-78 crystal has an *F*′ band due to the association of two electrons with a negative-ion vacancy; a well-developed V_1 band, which is believed to be caused by a hole attached to a positive-ion vacancy;[9] and a V_4 band of unknown origin. From Martienssen's[10] measurements we know that an α and a β band occur beyond the wavelength range of the Beckman. The *X*-5 crystal has a prominent *H* band which Seitz[11] has suggested may be due to the trapping of a hole at a vacancy pair and a band at 230 mμ of unknown origin. Similarly to *X*-78 it has an α and a β band. According to Delbecq, Pringsheim and Yuster[12] an α band is associated with the creation of an exciton next to a negative-ion vacancy, and a β band arises from a similar process which occurs next to an *F* center.

Figure 5 shows the spectra of a Schulman *X*-5 measured at 5°K. The crystal was then warmed to 78°K and remeasured. Comparison of Fig. 5 with previous work done in a similar manner on Harshaw KBr[5] shows that the 230 mμ band (see Fig. 4) is not observed in the Schulman sample. The other essential features seem to be preserved. From these data it appears likely that the 230 mμ band is due to some impurity which occurs in the Harshaw but not in the Shulman sample.

A difference between the Harshaw and Schulman samples is found in NaCl as well as in KBr. Figure 6 shows the absorption of a Schulman NaCl which has been x-rayed and measured at 5°K. Previous work[5] indicates that with Harshaw NaCl a small *F*′ band (hardly measurable) may form during x-radiation of NaCl at 5°K. The large *F*′ band of Fig. 6 points to a distinct difference between the two materials. Speculations on the formation of lattice vacancies suggest that the production of *F*′ centers occurs when the concentrations of α centers (negative-ion vacancies) is small.[13]

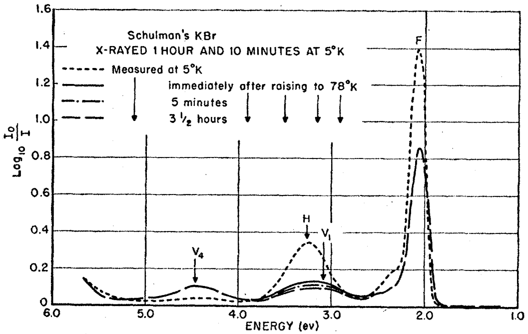

FIG. 5. Absorption spectra of KBr x-rayed at 5°K and subsequently raised to 78°K. The crystal was prepared by Dr. Schulman.

The data on NaCl suggest that the α centers are created less readily in Schulman's sample than in the Harshaw sample. The α band has not yet been studied in NaCl[10] so that its concentration cannot be measured directly. Two reasons for the lower concentration suggest themselves. If the Nabarro-Seitz mechanism[13,14] is responsible for the production of negative-ion vacancies, one must assume that there are less Seitz jogs in Schulman's crystals as a result of different growth techniques. If purity is a basic factor in the growth rates of *F* centers, then the difference in purity of these samples may account for the *F*′ band. This problem has recently been reviewed by Schulman[15] and

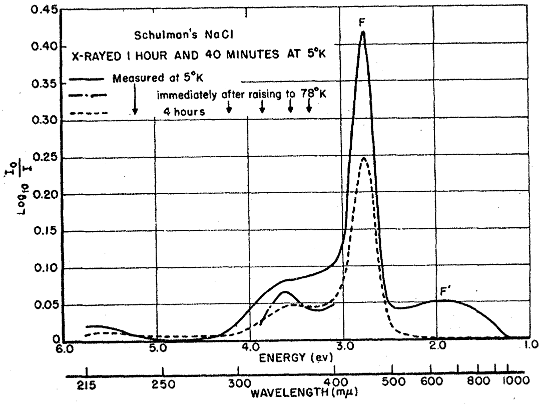

FIG. 6. Absorption spectra of NaCl x-rayed at 5°K and subsequently raised to 78°K. The crystal was prepared by Dr. Schulman.

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[8] H. Dorendorf, Z. Physik **129**, 317 (1951).

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

[10] W. Martienssen, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. 111 (1952).

[11] F. Seitz, Phys. Rev. **89**, 1299 (1953).

[12] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951).

[13] J. J. Markham, Phys. Rev. **88**, 500 (1952).

[14] F. Seitz, Phys. Rev. **80**, 239 (1950).

[15] J. H. Schulman (to be published).

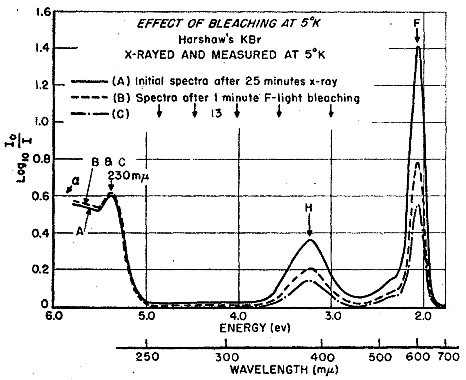

FIG. 7. Absorption spectra of Harshaw KBr x-rayed at 5°K and subsequently bleached with *F* light.

his study indicates that impurities have an effect on the coloration rate.

If one releases electrons to the conduction band during bleaching, the difference between the properties of *X*-5 and *X*-300 could be accounted for in terms of the variations in the hole centers shown in Fig. 4. Figure 2 indicates, however, that this explanation is questionable An alternate mechanism will be offered when the data are presented in detail.

2. X-Radiation at 5°K

Figure 7 shows what effect the bleaching of *F* centers in an *X*-5 crystal has on the other centers. The *H* band diminishes along with the *F* band but the 230 mμ and α bands increase. The overlap of the 230 mμ and α bands is such that one cannot be certain whether the increases are caused by a change in concentration of both centers or only one. No *F′* band was detected during these measurements. Further studies of these effects are shown in Figs. 8–10. Figures 8 and 9 show the percentage remaining centers in a Harshaw crystal.

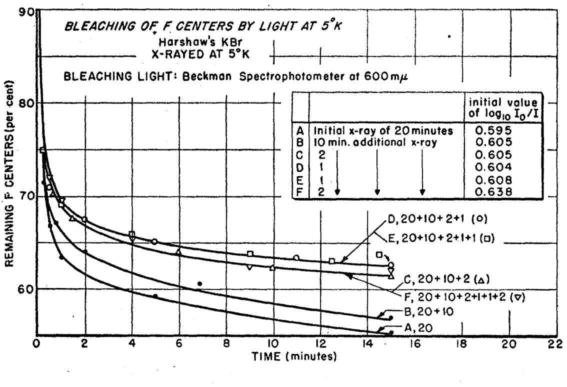

FIG. 8. Bleaching of the *F* band in Harshaw KBr after repeated x-ray exposures. Curve *C* represents a crystal that was initially x-rayed for 20 minutes, bleached for 15 minutes, exposed to x-rays for 10 minutes and again bleached for 15 minutes. Finally it was exposed to x-rays for 2 additional minutes, and Curve *C* describes the third bleaching.

In Fig. 8 the curves seem to depend on the length of the last x-raying interval. The shape of the curve which gives the percentage of the remaining *H* centers is similar; however, the fraction remaining is considerably larger.

Figure 10 shows that bleaching also occurs in a Schulman crystal. The percentage bleached is greater although the spectroscopic analysis and absence of the 230 mμ band indicate the Schulman crystal is more nearly perfect. In this case the curves do not depend on the last x-raying interval. Further tests are needed to show under which conditions, if any, the last x-raying interval determines the shape of the percentage curve.

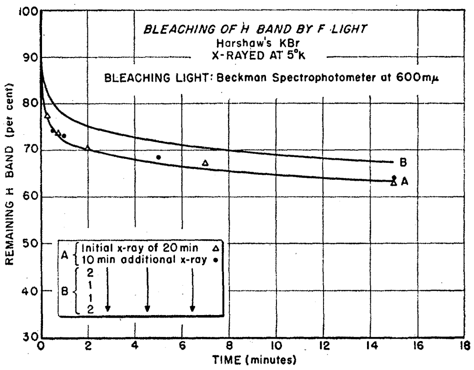

Fig. 9

FIG. 9. Decay of the *H* band in KBr as a function of time of bleaching of the *F* band.

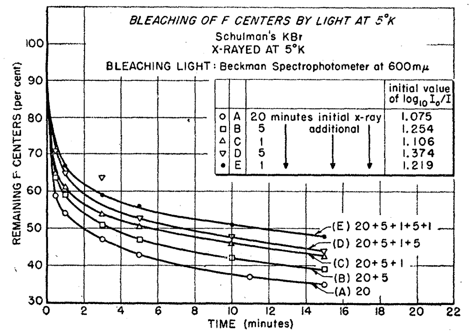

FIG. 10. Bleaching of the *F* band in KBr after repeated x-ray exposures. The crystal was prepared by Dr. Schulman.

Two additional observations have been made:

(a) After x-raying at 5°K, the decay rate in the dark of the *H* band is extremely small.

(b) Attempts were made to bleach the 230 mμ band and the *H* band. The 230 mμ band was not affected by a two-minute exposure in the Beckman. The band pass of the Beckman with a slit width of 2 mm at this wavelength is about 3 mμ. The *H* band seemed to bleach very slightly in an eight-minute exposure. In this case the band pass is 20 mμ wide.

It is impossible to interpret fully the above data. It seems, however, opportune to consider briefly what may be happening. It is believed that the x-rays produce free electrons and holes as well as generate vacancies in the lattice. The generation of vacancies seems to be produced by a mechanism proposed by Nabarro and extended by Seitz.[13,14] In the simplest form of this theory one assumes that the "extra half plane" associated with a Taylor dislocation has a jog in it. This jog may capture an electron or a hole or even an exciton. This process generates a local thermal spike which results in some ionic diffusion.[11] It is believed that this may cause ions to diffuse into the jog, leaving vacant sites behind near the boundary of the "extra half plane." As this process continues the plane builds up but leaves many vacancies in a region around the boundary of the original "extra half plane."

Since the alkali halides have positive and negative charges, neutrality requires a pair of half-planes instead of single planes. Most probably the Nabarro-Seitz mechanism produces a high concentration of vacancy pairs along certain planes. Thus, the extra planes associated with a Taylor dislocation determine layers in the crystal where there is a high concentration of vacancy pairs as well as individual vacancies. The thickness of the layer and hence the vacancy concentration is determined by the ability of the imperfections to diffuse away from the "extra planes." It is estimated that when an α center captures an exciton the energy liberated produces a thermal spike of a temperature 400° above ambient.[11] Thus, the diffusion of the vacancies would be much greater when the crystal is x-rayed at 300°K than when x-rayed at a lower temperature. At 5°K the generated vacancy pairs can trap electrons to form F centers (the positive vacancy diffusing away) or holes to form H centers.

The photoconductivity data quoted previously[3] and the shape of the F band, which to a first approximation is independent of the method of production,[16] suggest that the model shown in Fig. 2 applies to X-5. We, therefore, do not release electrons from the excited state to the conduction band in these experiments. In bleaching, one excites F centers in regions where the concentration of hole centers is high. The electron may tunnel from the excited state to a neighboring H center, causing annihilation of both itself and the hole. This would explain the rise in the absorption in the far ultraviolet where the α band is located. The decrease in the bleaching efficiency occurs as the closest H and F centers are destroyed.

The above explanation is the simplest that can be given which preserves the fairly well established theory of the F center and the most reasonable mechanism for its generation during x-radiation. Further, the calculation of Simpson[17] shows that the Bohr radius of the excited state of the F center is 3A compared to 1.6A for the ground state. This lends support to the suggestion, since the electron in the excited state has a lower and narrower hill to go through.

3. X-Radiation at 300°K

Figure 11 shows the bleaching which occurs when one x-rays KBr (Schulman) at 300°K and lowers it to 5°K. We shall first describe the left-hand side of the curve. There a sizable initial bleaching occurs which seems to approach a saturation after 10 minutes. In the dark there is a measurable recovery which takes of the order of an hour to occur. These effects have been observed in both Harshaw and Shulman X-300 KBr at 78° and 5°K. The magnitude of the effect seems to be independent of the temperature or the source of the material. The only difference that has been noticed is that a very definite saturation occurs in the Harshaw sample after 2 minutes.

It was difficult to establish directly if any bands besides the F band were bleached or created during the experiments. If F' centers were formed, their concentration was too small to be determined by direct measurement although there was a small increase in absorption in the F' region.

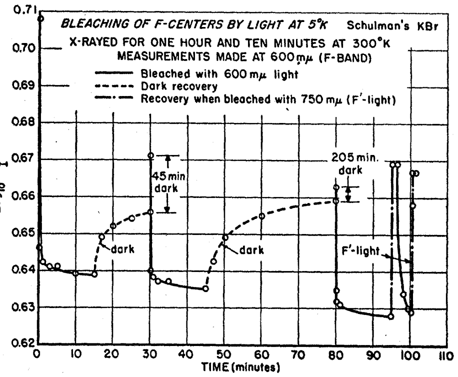

Fig. 11. Bleaching and recovery in dark of the F band in KBr. The crystal was prepared by Dr. Schulman.

It is to be stressed that X-300's recovery after bleaching eliminates the possibility that one is dealing with a thermal ionization process. The lifetime of this type of process should be determined by an equation of the type $A \exp(b/T)$, where A and b are constants. At 78°K the lifetime must be of the order of 100 sec (time for the F center to recover). If one assumes that A is as large as 10^{-8}, then $e^{b/T}$ is of the order of 10^{10}. At 5°K this would make the lifetime so long that no bleaching would be observed. This argument is based on classical statistics.

The dark recovery suggests that tunneling is again involved. If all the electrons were trapped at hole centers, one would expect annihilation and no recovery in the dark. The following explanation suggests itself. Consider two F centers which are close to each other,

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[16] Mador, Markham, and Platt, Phys. Rev. **91**, 1277 (1953).

[17] J. H. Simpson, Proc. Roy. Soc. (London) **197**, 269 (1949).

perhaps several lattice sites apart.[18] We excite one of them and the following reaction occurs:

$$F_{ex}+F \xrightarrow[\text{(minutes)}]{\text{(by tunneling)}} F'+V_-, \tag{1}$$

where F is an F center in the ground state, F_{ex} is an excited F center, F' is an F' center, and V_- is a negative-ion vacancy. We assume that this reaction occurs by tunneling, and Fig. 11 indicates that it takes a matter of minutes to approach completion. On the other hand, the dark recovery may be a result of the following reaction:

$$F'+V_- \xrightarrow[\text{(hours)}]{\text{(by tunneling)}} 2F. \tag{2}$$

If the F' centers formed by (1) are anything like the F' centers studied by Pick,[19] they should be completely stable at 5°K relative to thermal dissociation of an electron to the conduction band. Figure 11 suggests that it takes about an hour for reaction (2) to occur. Since the ground state of the F' center is considerably lower than that of the excited F center one would expect the barrier for reaction (2) to be greater than the barrier for reaction (1). This agrees with the observed relative rates of the reactions.

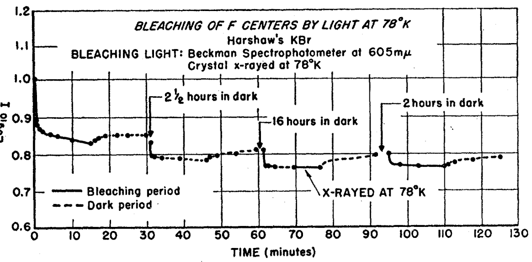

FIG. 12. Bleaching and recovery in dark of the F band in Harshaw KBr.

F' centers are readily subjected to optical bleaching at any temperature. This leads to the reaction

$$F'+V_- \xrightarrow[\text{(seconds)}]{\text{(by } F' \text{ light)}} 2F. \tag{3}$$

The difference between (2) and (3) is in the rate. To study the above hypothesis the data shown on the right-hand side of Fig. 11 were taken. The difference in rates between (2) and (3) is clearly shown.

The optical recovery shown in Fig. 11 is as complete as the dark thermal recovery. This is a little surprising in view of Duerig's growth rate data at 78°K.[20] These data indicate that a sizable fraction of the electrons released optically from an F' center end up in hole centers, causing an annihilation of the hole. One may suggest two possible reasons for this difference: (a) The V centers formed at room temperature in KBr do not trap electrons as readily as the V bands formed at 78°K or (b) the proximity of F' centers and V_- centers is such that an electron released from an F' center does not wander through the lattice but is immediately retrapped by the neighboring negative-ion vacancy. Test, on X-78 could partially resolve this question.

The saturation to bleaching which is observed may be due to a combination of two effects: (a) the number of pairs of close F centers may diminish after the first minutes of F light irradiation, or (b) the F and F' bands overlap so that back reaction (3) occurs in addition to (1). Probably both effects enter into this problem.

Reaction (3) has been tested in Harshaw's X-300 at 78°K. The results are very similar to the one given in Fig. 11.

4. X-Radiation at 78°K

One bleaching run was made on an X-78 Harshaw crystal at 78°K. The results are shown in Fig. 12. The graph indicates that one has a combination of two effects. The lack of saturation during the first 15 minutes of bleaching is similar to the behavior of X-5. The dark recovery is similar to X-300 and the behavior after the second cycle resembles this crystal completely. This suggests that immediately after irradiation there is tunneling to both F and hole centers. There seems to be only a limited number of close hole centers, however, so that after a period of bleaching the properties of the X-78 crystal approach the properties of the X-300 crystal. The layers of vacancies at 78°K have a thickness between the values at 5° and 300°K.

V. SUMMARY

The summary will be divided into two parts. The first presents the actual data, while the second gives a tentative interpretation. The following experimental facts seem to be established for KBr.

1. The F band in additively colored KBr cannot be bleached at 5° and at 78°K.
2. The F band in crystals which have been colored by x-rays bleach at 5° and at 78°K. The stability depends on the temperature of x-radiation. Between the limits of 5° and 78°K it does not depend on the temperature of bleaching. The following statements can be made regarding the behavior.

(a) The F centers formed by x-raying KBr at 5°K bleach up to 65 percent. During this process a large fraction of the H centers disappear. No recovery is observed in the dark. A small amount of bleaching by H light has been observed. The 230 $m\mu$ band cannot be bleached.

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[18] This may arise by a quartet of vacancies (two positive and two negative) capturing two electrons and dissociating into two F-centers and two positive-ion vacancies. Positive-ion vacancies have a high mobility at room temperature, a jump frequency of one per second in KCl. See Seitz, reference 1, pp. 402 and 404.

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

[20] W. H. Duerig, thesis, Unversity of Maryland (1952).

(b) Ten percent of the *F* centers formed by x-raying KBr at 300°K can be bleached by *F* light at 5° or at 78°K. Over half of the bleached centers are rebuilt in the dark after several hours. After the dark recovery, one may bleach the *F* band again. If one shines F' light on a bleached crystal, it recovers in a few seconds. The changes in the F' absorption band were too small to directly establish its presence.

(c) About 20 percent of the *F* centers can be bleached in a crystal x-rayed at 78°K. There is a partial recovery in the dark, the fraction recovered being less than the previous case. After this crystal has been put through the cycle of bleaching and dark recovery several times, it behaves similarly to a crystal x-rayed at 300°K.

It is to be stressed that no qualitative calculations on tunneling have been made as yet. Some idea of the order of magnitude of the distance the electron can tunnel through would be very helpful in interpreting the above data. Photoconductivity measurements at 5°K would undoubtedly throw a great deal of light on the mechanisms of bleaching. Nevertheless, the following interpretation of the above data is offered: These data indicate the tunneling from one imperfection to another occurs if the distance is small. This tunneling can cause significant and readily measurable effects. These experiments suggest that the color centers are not distributed uniformly throughout the crystal but have a relatively high concentration in certain layers. The concentration of imperfections in these layers depends on the temperature at which the crystal is x-rayed. Higher concentrations are obtained at lower temperatures. If the Nabarro-Seitz production hypothesis is correct, the location of high concentrations is determined by the distributions of dislocations.

ACKNOWLEDGMENT

The authors would like to express their appreciation to Dr. J. H. Schulman and Professor A. B. Scott for their crystals and to Professor F. Seitz and Dr. W. H. Duerig for their helpful discussions of the theoretical problems of this paper.

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An Augmented Plane Wave Method for the Periodic Potential Problem

J. C. Slater*
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A new method is proposed for solving a periodic potential problem in which the potential can be approximated as a constant outside spheres surrounding the atoms, spherically symmetrical within the spheres. We set up unperturbed functions consisting of a plane wave outside the spheres, joined continuously and with continuous derivative to functions derived from the spherical problem within the spheres. These spherical solutions are linear combinations of eigenfunctions of Schrödinger's equation within the spheres, subject to the boundary conditions that the logarithmic derivative of the function of each l value at the surface equals the logarithmic derivative of the corresponding Bessel function in the expansion of the plane wave, thereby insuring continuity of the derivative of the wave function over the sphere if the function itself is continuous. The coefficients in the expansion within the spheres are determined by demanding that the expectation value of the energy of the wave function be stationary when the coefficients are varied. The secular equation connected with this variation problem can be solved exactly, leading to wave functions having the general character of orthogonalized plane waves. A linear combination of such functions is then used to build up an approximate solution of Schrödinger's equation. It is shown that the tightly-bound states are handled quite differently from the conduction band, and that the treatment of the conduction band can well resemble the free-electron approximation, thereby perhaps explaining the empirical success of the free-electron approximation for the conduction electrons in metals. The method can be extended to a case where the potential does not have the simple behavior postulated, by treating the difference between the actual potential and the postulated form as a perturbation.

1. GENERAL FORMULATION OF THE METHOD

THE solution of the wave-mechanical problem of an electron moving in a three-dimensional periodic potential of the type found in a crystal as treated by a self-consistent field method is an important part of the theory of solids. No existing approximate solution is completely satisfactory, and we present in this paper a new method having certain advantages over each of the existing approximations. The method is directly applicable to a problem in which the potential is spherically symmetrical within spheres surrounding the various nuclei, and is constant in the region between the spheres, which are assumed not to overlap, though we shall later show how to extend it to more general potentials.

For such a potential, it has been generally assumed that the wave function in the region between spheres could be well approximated by a superposition of a relatively small number of plane waves. On the other hand, such a wave function behaves very badly in the neighborhood of the atoms. Herring[1] has suggested the method of orthogonalized plane waves, by which one adds to each of these plane waves a set of atomic func-

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[1] C. Herring, Phys. Rev. **57**, 1169 (1940).