COLOR CENTERS PRODUCED BY X-RAYS AT LOW TEMPERATURES

IN ALKALI HALIDE CRYSTALS

By
William H. Duerig

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CHAPTER I

INTRODUCTION

In attempting to solve any complicated problem, the simplest aspects are treated first in the hope that their solution will direct the way to the solution of the more complicated phases. An outstanding example of such a procedure is the position of the work on the hydrogen atom in the field of quantum mechanics. The methods which finally were successful in treating this atom have been extremely fruitful in extension to the more complicated systems. In solid state physics, the various phases of work on the alkali halides can be likened to the hydrogen atom development in that it is hoped to be a fundamental approach to an understanding of the physics of solids. Since the solid is an array of atoms, even the most basic approach can be generally expected to be far more difficult than that of the hydrogen atom. Hence the study of this group of solids of the simplest structure, face-centered cubic, is made up of many parts with the hope that eventually the solutions of these individual aspects may be synthesized into a complete picture, from which a firm approach to the more complicated solids may be made. For these reasons a tremendous amount of valuable work has already been accomplished on the various properties of the alkali halides.

Of the many phenomena studied in the alkali halides, e.g., plastic properties, electrolytic conductivity, photoconductivity, ultraviolet and infrared absorption, one of particular interest is that of the

production of color centers. Perhaps the main reason for the attention is the relation of these color centers to the electronic processes and the various imperfections present in the crystals. Imperfections[1] are responsible for many of the known properties of solids, e.g., luminescence, electrolytic conductivity, plasticity, etc., and thus the study of color centers is highly desirable since it may lead to further knowledge of these imperfections and the role they play in the structure of solids.

This dissertation will deal primarily with that phase of color centers in which electron and hole trapping occurs within the crystal during irradiation by x-rays at low temperatures.

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[1] F. Seitz, Conference on Physics of Ionic Crystals, University of Illinois, October 1951, has listed six primary imperfections now known to exist in solids. These are phonons, electrons and holes, excitons, vacant lattice sites and interstitial atoms, foreign atoms in interstitial or substitutional positions and dislocations.

CHAPTER II

BACKGROUND AND THEORY

A. Structure and Properties of Alkali Halides

Single crystals of the pure alkali halides many pounds in weight

can be grown artificially. Natural crystals of sodium chloride have

been found in many parts of the world. These crystals of the pure

alkali halides possess properties such as good cleavage, transparency

from the far ultraviolet (around 150 to 180 mμ for most) to the far

infrared (from about 10μ to 100μ) and electrolytic conductivity at

high temperatures. At the transmission limits the crystals exhibit

extremely high absorption coefficients similar to metals. The ultra-

violet absorption is due to the excitation of the electronic orbits of

the ions and the infrared absorption to the vibration of the ions.

Other properties include the fact that they are good insulators and

do not exhibit photoconductivity or luminescence under radiation from

the infrared to the ultraviolet unless certain imperfections are present

in the crystal.

The alkali halide crystals are composed of a face-centered cubic

array of highly electro-positive alkali ions and highly electro-negative

halogen ions. Hence the binding energy is mainly electrostatic. Homo-

polar binding also occurs to a small degree, since the electrons in the

outer shell of the negative ions are shared with the surrounding positive

ions. When the ions move close together, overlap forces come into play

and the ions repel one another.[1]

The alkali halide crystals become colored when subjected to a number of processes. This was recognized as far back as 1863 by Rose[2] who colored rocksalt and KCl by heating them in sodium and potassium vapor and by Goldstein[3] in 1896 who colored rocksalt by irradiating it with cathode rays. At present this coloration has been found to be produced in the crystals by the following methods:

(1) Exposure to radiations including x- and γ-rays, β and α particles and neutrons.

(2) Heating in an alkali metal vapor not necessarily that of the alkali halide being heated.

(3) Application of a pointed cathode to the crystal held at high temperatures (400° to 800°C), i.e., electrolysis.

This coloration is due mainly to a single absorption band called the F-band, after Pohl's naming of the absorbing centers causing the band, the Farbzentren or color centers. These processes also create other absorption bands which shall be discussed later, but the major effort of the early workers in the field, i.e., Pohl's group in

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[1]A summary is given of the structure and cohesive forces in ionic crystals in F. Seitz, Modern Theory of Solids, McGraw-Hill, New York: 1940.

[2]H. Rose, Ann. Physik and Chemie 120, 15 (1863).

[3]E. Goldstein, Zeit. f. Instrumentkunde 16, 211 (1896).

Göttingen[1] and Przibram's group in Vienna,[2] was the study of the F-band. This experimental study proved extremely fruitful, for the presently accepted nature of the F-center as proposed by de Boer[3] and further studied by Mott and Guerney[4] and Seitz[5] is largely based on the experimental results of these groups. These workers and many others have since examined the effects of a number of other color centers and their relation to the crystal properties.

To understand the problems undertaken in this dissertation, it is advisable to review this previous work in detail. This will be done in the following manner.

First, the study of the characteristics of the F-center and the experiments leading to a formulation of its exact nature will be given. This point is emphasized here because the model for the F-center is used extensively as a basis for the evaluation of other color centers formed by the above mentioned processes.

Next, the other color centers occurring in the range of room temperature will be described since they have a bearing on the centers produced

[1] R. W. Pohl, Proc. Phys. Soc. (London) 49 (extra part), 3 (1937). This paper gives an excellent summary of the work of this school through 1937.

[2] K. Przibram, Z. Physik 20, 196 (1923); 41, 833 (1927), 68, 403 (1931), 102, 331 (1936). These papers provide a summary of the work of the Vienna school through 1936.

[3] J. H. de Boer, Recueil des Trav. Chem. d. Pays Bas 56, 301 (1937).

[4] N. F. Mott and R. W. Guerney, Electronic Processes in Ionic Crystals, p. 111 (Oxford, 1940).

[5] F. Seitz, Revs. Modern Physics 18, 384 (1946).

at low temperatures. This will be followed by a discussion of these
color centers formed at low temperatures. This work is included since
it establishes the pattern into which the color centers found in the
experiments for this dissertation must fit.

Since a knowledge of the processes which occur during radiation
bombardment can play an important role in the understanding of color
center formation, these will be discussed next. Emphasis is placed here
on the existence or creation of ion vacancies, for this problem is funda-
mental in the occurrence of F- and other centers.

As a basis for understanding these processes, the study of the growth
rates of certain of the color centers when the crystals are continuously
exposed to a high energy radiation such as x-rays will then be discussed.

Finally, two associated points will be described. These are the
impurity problem and the existence of the self-trapped electron. Since
color centers can be produced by impurity atoms present in the crystals,
the interpretation of any experimental data should be done with this
point foremost in mind. The existence of a self-trapped electron has
been studied theoretically by several workers with different assumptions
and results. This center might be considered as an addition to the
problem of color center formation.

B. The F-Center

1. Characteristics of the F-Center.

The F-center absorption band has a bell shape for all the alkali
halides as can be seen for a number of crystals in Fig. 1. Its width

and the position of its maximum are quite temperature dependent down to about $180^\circ C$, below which there is little change (see Fig. 2). The wavelength on the ultraviolet side corresponding to one-half the maximum absorption constant is apparently independent of temperature, however. This consistent bell shape and temperature dependence led Smakula[1] to assume a number N_o of identical absorbing centers per unit volume which could be treated as the individual oscillators in classical dispersion theory as causing the F-band. Applying this theory he arrived at the following expression for the number of centers:

$$N_o = \frac{1}{f} \; \frac{9 \; mc}{2e^2 h} \left(\frac{e}{300}\right) \frac{n'}{(n'^2 + 2)^2} K_m W = 1.31 \times 10^{17} \frac{1}{f} \frac{n'}{(n'^2 + 2)^2} K_m W,$$

where f = oscillator strength for centers,

   n' = index of refraction of the pure crystal at band maximum,

   K_m = absorption constant for band maximum (cm^{-1}),

   W = half-width of band in ev,

   m = electron mass,

   e = electron charge,

   h = Planck's constant,

   c = velocity of light.

The oscillator strength has been measured experimentally only for KCl,[2]

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[1]A. Smakula, Z. Physik 59, 603 (1930).

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

its value being .81.[1] Since only one absorption peak is observed, it is expected that all of the optical strength of the oscillators is centered in this band. Thus f is usually taken to be about unity for the alkali halides. K_m is the constant defined by

$$I = I_o \exp [-K_m d]$$

where I is the intensity of light transmitted, I_o the intensity of the incident light and d the thickness of the crystal. The number of centers necessary to make the crystal appear colored to the eye is about 10^{14} cm^{-2}.

A further property of the F-centers observed is that crystals possessing an F-band become photoconductive when illuminated in the F-band. This photoconductivity is dependent on temperature, decreasing with temperature as shown in Fig. 3 for KCl.[2]

Other properties include the bleaching of these centers. In the region of room or higher temperatures, the F-centers in x-rayed crystals

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[1] A. Scott and W. Smith, Phys. Rev. 83, 982 (1951) have examined Kleinschrod's work and conclude that because of his lack of certain measurements, his value for the oscillator strength in KCl is very doubtful, and in fact concluded it safer to use the value 1. However, F. Seitz, Rev. Modern Phys. 18, 384 (1946) discusses the oscillator strength in relation to Pick's data and appears to confirm Kleinschrod's work.

[2] G. Glaser, Nachr. Acad Wiss. Göttingen II, 31 (1937).

WAVE-LENGTH (Mμ)
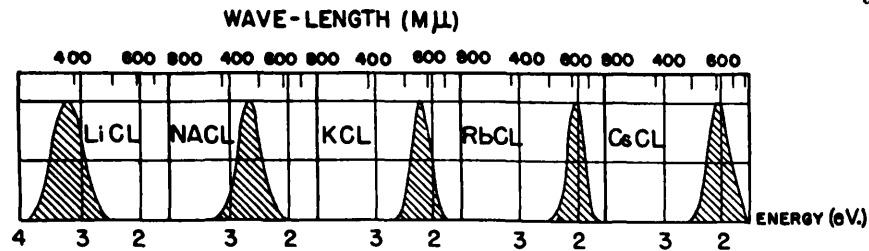
Fig. 1 THE F-BAND FOR SEVERAL ALKALI LALIDES (AFTER POHL).
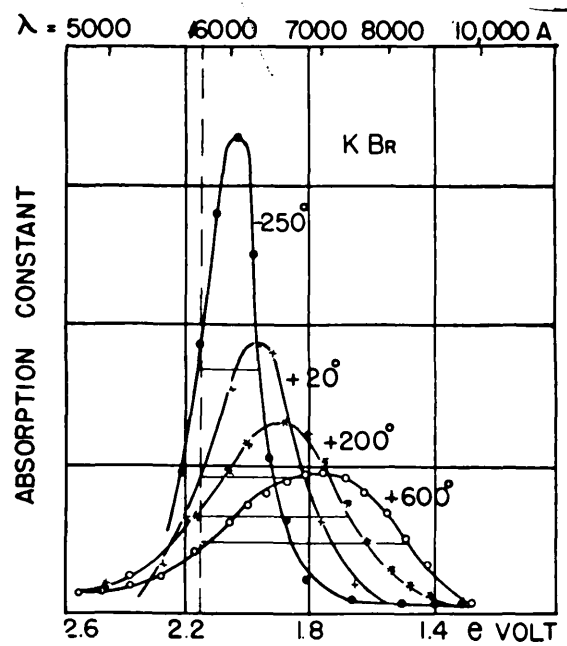
Fig. 2 THE DEPENDENCE OF THE WIDTH OF THE F-BAND UPON TEMPERATURE (AFTER POHL).
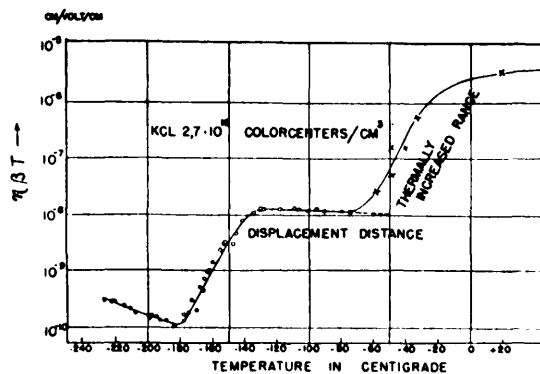
Fig. 3 THE DEPENDENCE OF THE PHOTO CURRENT PER UNIT FIELD INTENSITY UPON TEMPERATURE (AFTER GLASER).

readily bleach with light. These centers can also be bleached[1] by

high temperatures with an accompanying luminescence, as was noted very

early by Przibram.[2] F-centers produced by additive coloring will not

fully bleach at high temperatures but form colloidal groups. They can

be swept out of a crystal, however, by application of an electric field

at high temperatures.[3] This sweeping out is visible and from this the

mobility can be achieved.

The rate at which the centers build up under radiation was measured

in rocksalt by Belar[4] for various γ -ray dosages from a radium source.

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[1] It is important to note here that the thermal and optical activation
energies for a given color center are considerably different. This
phenomenon is explained by the Franck–Condon principle which is discussed
by N. Mott and R. Guerney, Electronic Processes in Ionic Crystals, p. 16
(Oxford, 1940). When a photon removes an electron from the color center,
it does so before the surrounding ions can move, i.e., the action occurs
in a medium with a dielectric constant of only the high frequency
(frequencies above lattice vibrations of 10^{12} per second) component.
After the electron has left the center, the ions in that region move to new
positions of equilibrium, giving out energy in the process. Thus the
crystal attains a new energy level in that locality. The thermal
activation energy is the difference between the two equilibrium energy
states of the crystal, one with the electron trapped at the center and
the other with the electron removed to the conduction band. Thus the
thermal activation energy will always be lower than the optical activa-
tion energy.

[2] K. Przibram, Z. Physik 20, 196 (1923).

[3] R. W. Pohl, loc. cit.

[4] M. Belar, Wien. Ber. 135 II, 189 (1926).

She found the amount of coloration to reach a limiting value after about a year, the limiting value being dependent on the size of the source. Fig. 4 gives her curve of the limiting value of coloration versus the intensity of radiation. This saturation effect will be discussed in detail later.

2. The Relation of the F'-Band to the F-Band.

Early workers[1] noted that when the F-band in NaCl was irradiated with light in the F-band, another band is excited as a long wavelength tail of the F-band (see Fig. 5). Further it was noted that this process was reversible in that irradiation of the long wavelength tail bleached it and rebuilt the F-band with almost 100 per cent efficiency at room temperature, i.e., it was a reversible process.[2] Although considerable experimental work was done on this effect, it was not until Pick[3] investigated it thoroughly in KCl and KBr that its relation to the F-band could be formulated.

As can be seen in Fig. 5, the excited band in NaCl is not very distinct, and as will be shown later might even be confused with other bands. Fig. 6 shows the corresponding band in KCl which was produced by irradiating the F-band of an additively colored crystal with F-band light at $80°K$ and the crystal lowered to $20°K$ for the absorption measurement. Here the excited band is quite distinct and because of its relation to

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[1]Z. Gyulai, Z. Physik 33, 251 (1925); B. Gudden and R. W. Pohl, Z. Physik 31, 651 (1925).

[2]K. Przibram, Z. Physik 102, 33 (1936) shows, however, that stressing the NaCl decreases this reversibility until at a stress of 5000 kg/cm^2, it is almost 90 per cent irreversible.

[3]H. Pick, Ann. Physik 31, 365 (1938).
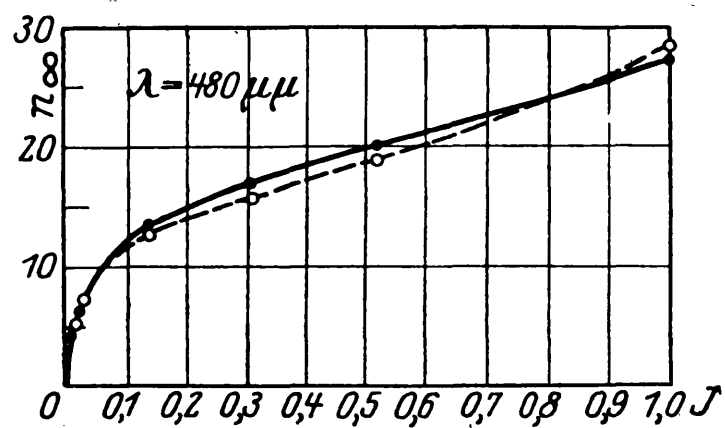
Fig. 4   THE DEPENDENCE OF THE LIMITING VALUE OF THE F-BAND vs RELATIVE r-RAY
INTENSITY (AFTER BELAR).
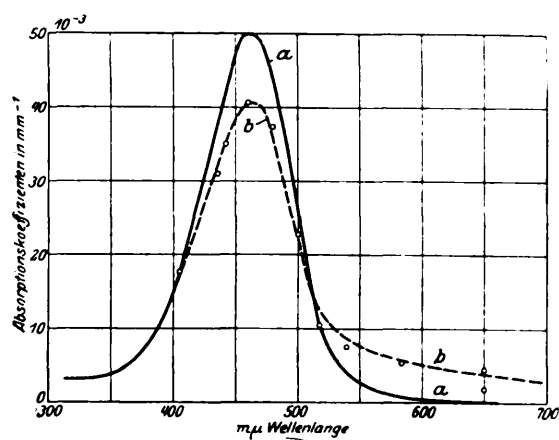
Fig. 5   THE BAND TO THE INFRARED OF THE F-BAND EXCITED IN NaCl BY F-LIGHT
(AFTER GYULAI).

the F-band has been named the F'-band.

Pick's work[1] showed that the quantum yield of the reactions F → F' and F' → F varied with temperature from nearly zero to a maximum of 2. That is, at the proper temperature every incoming photon in the F-band destroyed two F-centers and created one F'-center. Likewise at another temperature every photon in the F'-band (any wavelength within the F'-band will work) created two F-centers for each F'-center destroyed. This indicated that an F'-center is created by adding a unit of charge to the F-center. Fig. 7 gives the quantum yield versus temperature for these two reactions in KCl from Pick's data. Each of the points of these two curves represent the initial slope of curves of the number of F- or F'-centers created versus the amount of irradiation. These curves are shown in Fig. 8 and as can be seen, the slope changes rapidly at the lower temperatures indicating a dependency on the relative number of F- and F'-centers present at any time.

3. Model of the F-Center.

The experimental data stated above were sufficient to postulate that an F-center is an electron trapped in a Coulomb field. The series of arguments leading to this conclusion have been clearly set forth by Seitz.[2]

There are three possible means of obtaining a Coulomb field in a crystal (see Fig. 9). Hence, it now became a matter of determining

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[1] H. Pick, Ann. Physik 31, 365 (1938), 37, 421 (1940).

[2] F. Seitz, Revs. Modern Phys. 18, 384 (1946).
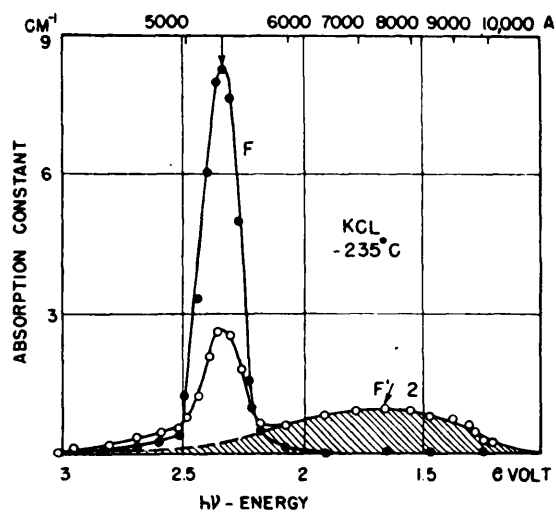
Fig. 6   THE BAND TO THE INFRARED OF THE F-BAND EXCITED BY F-LIGHT IN KCl
(AFTER PICK).
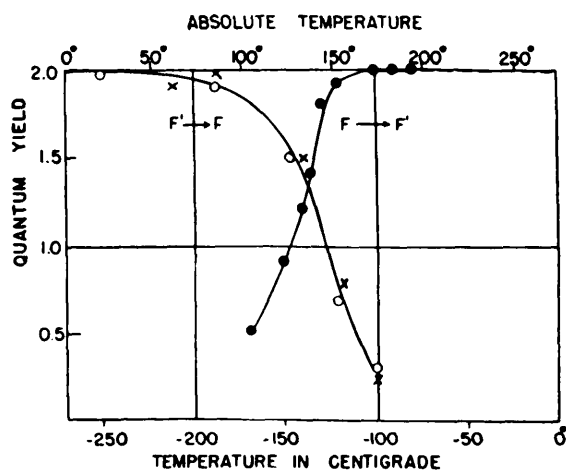
Fig. 7   THE DEPENDENCE OF THE QUANTUM YIELD OF THE REACTIONS F'→F AND F→F'
UPON TEMPERATURE (AFTER PICK).

which of the three was responsible for the trapping of an electron to form an F-center.

One of the possible ways of a Coulomb field arising in a crystal is by a self-trapped electron. Landau[1] proposed the F-center as this electron trapped in the field which it has created itself by polarization of the lattice in its vicinity. This trapping might occur if an electron, moving through the lattice, remains near an ion site long enough for its field to displace the surrounding ions as shown in Fig. 9. The time must be greater than the period of the ion vibrations, i.e., greater than 10^{-12} seconds, for such a displacement and although this means a very small velocity for the electron, statistically a number of them will have this range of velocities.

A second possibility is the Coulomb field that arises in the crystal from the charge of an interstitial ion trapping an electron, as seen in Fig. 9.

The third proposal is that of de Boer.[2] Here an electron is trapped in the Coulomb field arising at a lattice point from which the negative ion normally occupying it is missing[3] (see Fig. 9).

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[1]L. Landau, Z. Phys. Sowjet. $\underline{3}$, 664 (1933).

[2]de Boer, loc. cit.

[3]Both interstitial ions and ion vacancies should occur in crystals as natural phenomena. It can be shown that the presence of a number of these defects in the crystal lattice is required for the free energy (F = E - TS) of the crystal to be a minimum (see J. Frenkel, Z. Physik $\underline{35}$, 652 (1926) and C. Wagner and W. Schottky, Z. Physik Chem. (B) $\underline{11}$, 163 (1930)). Expressions for the number of these defects as a function of temperature are given in N. F. Mott and R. W. Guerney, Electronic Processes in Ionic
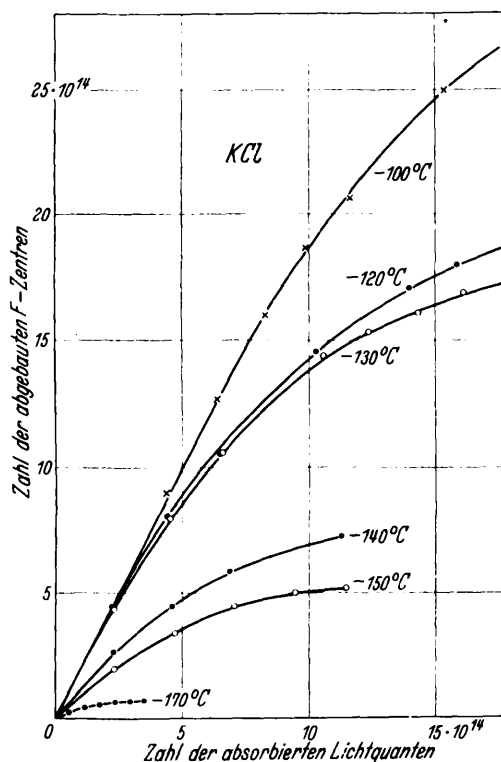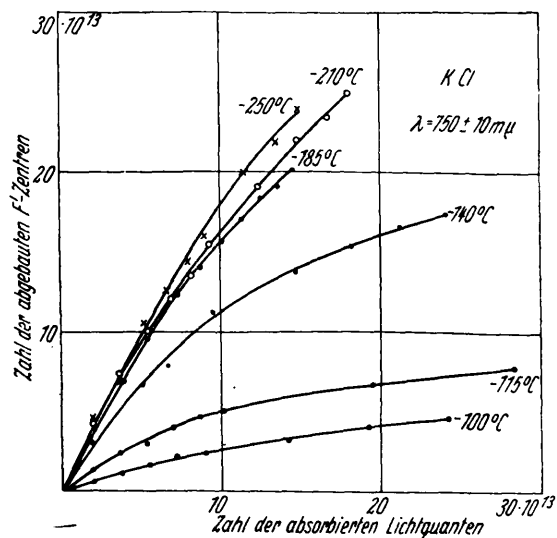
Fig. 8   THE DEPENDENCE OF THE NUMBER OF F OR F' CENTERS CREATED UPON TOTAL
RADIATION (AFTER PICK).

INTERSTITIAL ION   **VACANCY**   **SELF-TRAPPED ELECTRON**

(a)   (b)   (c)
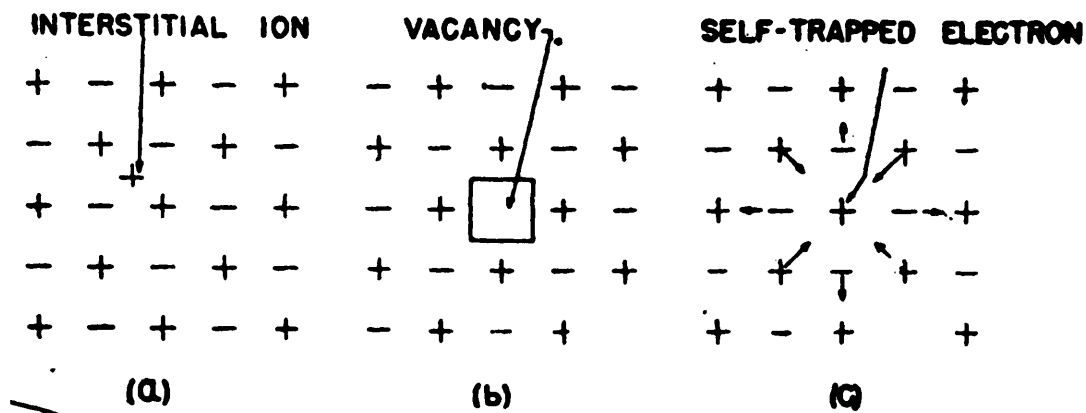
Fig. 9   THE THREE WAYS OF OBTAINING COULOMB FIELDS THAT MIGHT TRAP AN ELECTRON
(AFTER SEITZ).

The proper choice for an F-center of these three trapped electrons, i.e., the self-trapped electron, the electron trapped at an interstitial site and the electron trapped at a negative ion vacancy, was arrived at by a number of theoretical arguments, using experimental facts for substantiation. The interstitial defects require considerable energy for formation and in fact calculations show the number of interstitial defects to be negligible compared to the number of ion-vacancy defects. The energy required to form a self-trapped F-center by heating in the alkali vapor is calculated to be more than 1 ev greater than that to form an F-center composed of an electron trapped at a negative-ion vacancy. Hence this latter case of an electron trapped at a negative-ion vacancy has been established as the correct model of the F-center. Thus, the F'-center is two electrons trapped at a negative-ion vacancy.[1]

Crystals, Ch. II (Oxford, 1940). High concentrations of the order of 10^{18}cm^{-3} of these defects will occur only near the melting points of the crystals.

As the temperature is lowered, the mobility of these defects decreases rapidly. In the region of room temperature and below, these defects should be entirely immobile for all practical purposes as has been experimentally observed by H. Etzel and R. Maurer, J. Chem. Phys. 18, 1003 (1950). Thus cooling a crystal rapidly from temperatures near the melting point (usually termed "quenching") should "freeze" a number of these defects into the crystal.

[1]F. Seitz, Revs. Modern Phys. 18, 384 (1946) presents a detailed account of the arguments leading to these conclusions.

C. Other Color Centers Produced in the Range of
Room Temperature and Above

A number of other color centers have been produced by the various methods in the alkali halide crystals in the range of temperature from room temperature and above.

1. The M- and R-bands.

Molnar[1] and Ottmer[2] found that when the crystals are x-rayed at room temperature an absorption band forms to the infrared side of the F-band. This band, named the M-band, also occurs if the F-band is irradiated with F-light at room temperature.[3] Irradiation of the M-band with M-band light bleaches it and builds the F-band back up, although not to 100 per cent of its former value.

The difference apparently goes into the making of two additional bands, called the R_1 and R_2 bands. These R-bands, situated between the F- and M-bands, cannot be bleached with light.[1] Fig. 10 shows these bands for NaCl, the spectra of NaCl being also given at -180°C to bring out the bands more sharply. It is surprising that these bands were not fully studied by the previous workers, since, as was discussed earlier, the F'-band was obtained in NaCl by irradiation in the F-band. This work of Molnar's places some doubt perhaps on the F → F' reaction in NaCl because of the similarity of the shape and position of the R-bands and F'-band

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[1] J. Molnar, Ph.D. Thesis, M.I.T., 1940.

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

[3] St. Petroff, Z. Physik 127, 443 (1950)

(compare Fig. 5 and Fig. 10). Since the F$\rightleftharpoons$F' reaction is 100 per cent reversible and the R-bands do not bleach, however, there seems but little chance that the F'-band is not correctly described in NaCl. The R- and M-bands cease to appear at temperatures much lower than room temperature, e.g., the F'-band in KCl and KBr occurring instead.

Seitz has proposed models for the M- and R-bands.[1] He suggests the M-center to be an F-center combined with a pair of vacancies.[2] The R_1-band is proposed as being caused by a pair of F-centers, i.e., a pair of halogen vacancies with two captured electrons, and the R_2-band by a pair of halogen vacancies with one captured electron. Seitz likens the situation of R-bands to diatomic molecules in that photo-electrons are not released when light is absorbed. The model of the M-center indicates it to be an anisotropic in structure and hence it might have a preferred direction for absorption of light. Seitz[3] described an experiment of Ueta whereby M-centers were bleached with polarized light until no further bleaching was possible. Then changing the degree of polarization bleached further M-centers, indicating that there is an anisotropic nature to this center.

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[1] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[2] It should be pointed out here that vacancies may occur in pairs, quartets or even higher aggregates in the crystal and the action of electrons on these groups is to break them up and rearrange them. At room and higher temperatures the mobilities of these pairs and higher aggregates is supposedly sufficient for centers of the M and R type to be quickly formed.

[3] F. Seitz, Conference on Physics of Ionic Crystals, University of Illinois, October, 1951.

Petroff's work although done in 1944 was not published until 1950. His investigation of these M- and R-centers was quite extensive and his data is in agreement with Seitz's models for these centers.

2. **The N-Band.**

Burstein and Oberly[1] report still another center beyond the M-center toward the infrared which has been named the N-center. This center, also observed by Petroff and Molnar, requires exposure of heavily x-rayed or additively colored crystals to white light. Aggregates of the M or R type have been proposed as models for this center but more experimental facts are required.

3. **The V_2- and V_3-Bands.**

To the ultraviolet of the F-band a number of other bands have been produced. Mollwo[2] found several bands formed far in the ultraviolet by heating KBr and KI in their halogen vapors. Since this is apparently very difficult to do without the formation of colloids, results in other crystals have not been obtained. The first model proposed for these centers was the analogy to the F-center, i.e., a hole trapped about an alkali-ion vacancy. If these V-bands shown in Fig. 11 are caused by such a model, then it would be natural to expect x-raying the crystals to produce similar bands. X-rays should create both holes and electrons, and, since there should be positive (alkali ion) vacancies incipient in the crystal, the holes should diffuse until they become trapped at these vacancies.

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[1] E. Burstein and J. Oberly, Phys. Rev. **76**, 1254 (1949).

[2] E. Mollwo, Ann. Physik **29**, 394 (1937).
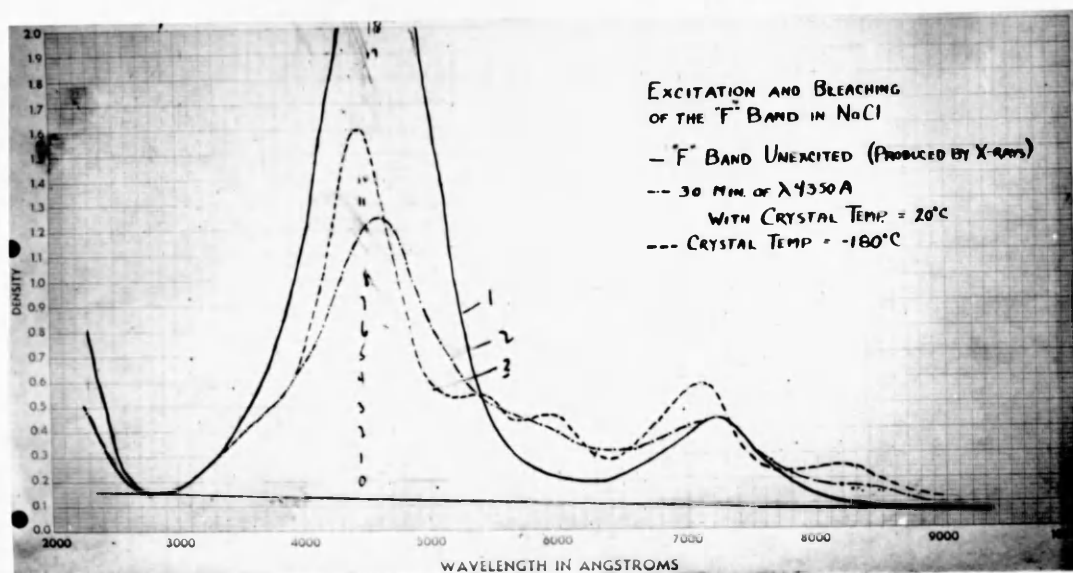
Fig. 10 THE M- AND R-BANDS PRODUCED IN NaCl BY x-RAYS AND LIGHT IRRADIATION
(AFTER MOLNAR).
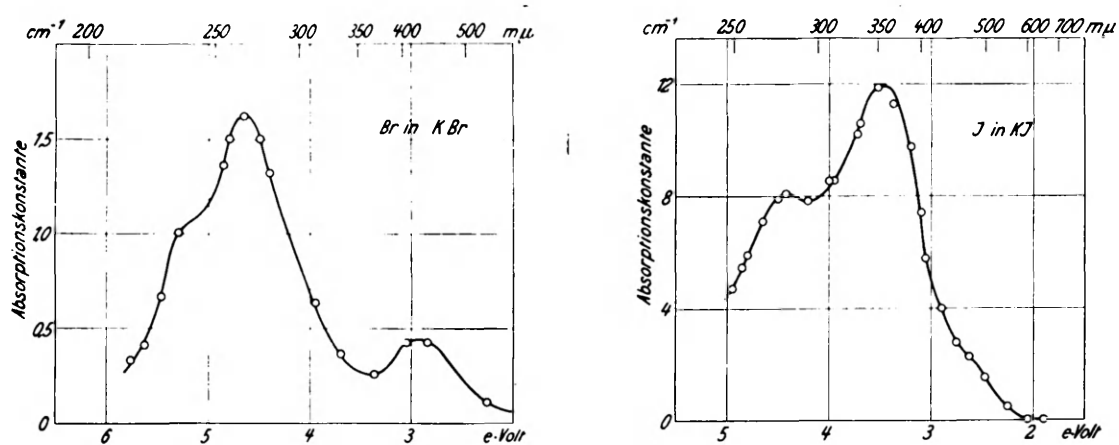
Fig. 11 THE V-BANDS OCCURRING IN KBr AND KI HEATED IN THEIR RESPECTIVE HALOGEN
VAPOR (AFTER MOLLWO).

Alexander and Schneider,[1] and later Casler, Pringsheim and Yuster[2]
x-rayed a number of crystals at room temperature and compared the ultra-
violet absorption spectrum with Mollwo's data of Fig. 11. V-bands oc-
curred in KBr in fair agreement with the two peaks farthest to the ultra-
violet. It was found, however, that these bands could not be per-
manently bleached with V-light, for after such bleaching, they grow back
to their former value in several days. Further, bleaching the F-band
with F-light, a process which should release electrons which could com-
bine with the trapped holes to neutralize the V-centers, caused the V-
band (designated V_2) nearest the F-band to bleach, but the other (V_3)
was unchanged. Similar V-bands were formed in KCl and NaCl[3] but not
in KI.

On the basis of this work Seitz[4] proposed a model for the V_2- and
V_3- centers similar to that of the R-bands, i.e., a pair of positive-
ion vacancies to which one or two holes are trapped. The previous
model of a hole trapped at one positive-ion vacancy is proposed for the
V_1-band which appears only at low temperatures and will be discussed
later.

4. Other V-Bands.

Dorendorf[5] has observed other V-bands produced with x-rays in KCl

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

[2] R. Casler, P. Pringsheim and P. Yuster, J. Chem. Phys. 18, 1564 (1950).

[3] A tabular summary of the various bands will be given for these crystals in Section V.

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

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

and KBr at room temperature (V_5, V_6, V_7 in Fig. 12) and has made a study of the temperature dependence of the various bands between $90°K$ and $350°K$. Further studies of these bands will be required before models may be proposed for them.

5. The α - and β -Bands.

Delbecq, Pringsheim and Yuster[1] recently observed two new bands in KI appearing to the far ultraviolet of the F-band (see Fig. 13). Both bands occur on the steep slope of the first fundamental absorption band as can be seen in Fig. 13. These bands have not been observed previously in other crystals since they would be in the vacuum ultraviolet region and thus inaccessible to measurement on the usual spectrophotometer.

The farthest ultraviolet band, the β -band, appears at room temperature in both x-rayed and additively colored crystals and its height is reported as proportional to the height of the F-band.

The α -band is very weak at room temperature. It forms on x-raying at temperatures below that of dry ice ($195°K$) and decays rapidly on warming to room temperature. It can also be formed below this temperature in additively colored crystals or increased in size in x-rayed crystals by bleaching the F-band.

From their work it has been proposed by Delbecq, Pringsheim and Yuster that the β -band is the first fundamental absorption band that has been perturbed by the presence of F-centers, i.e., the valency

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[1]C. Delbecq, P. Pringsheim and P. Yuster, J. Chem. Phys. 19, 574 (1951).
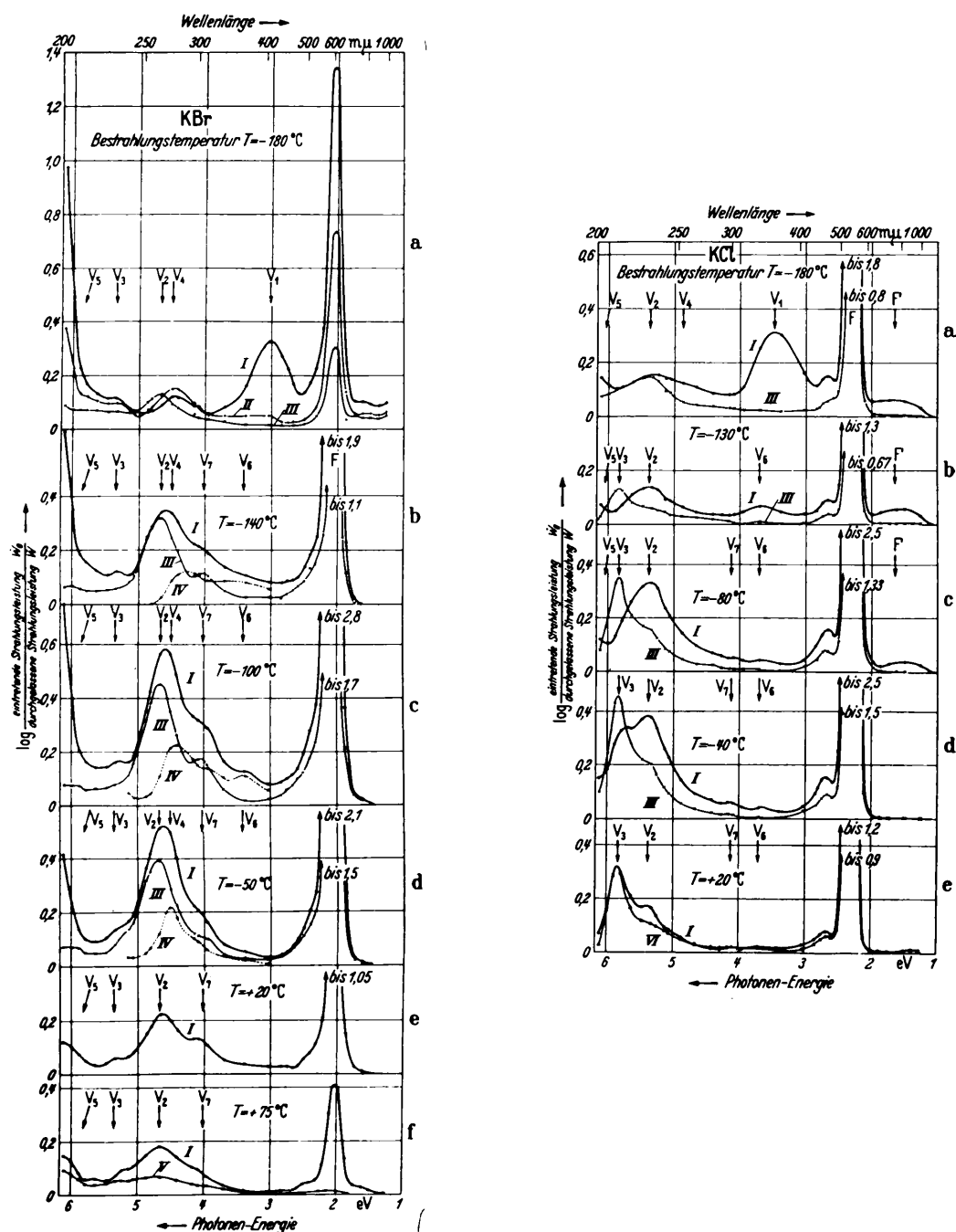
Fig. 12 THE BANDS PRODUCED IN KBr AND KC1 AT VARIOUS TEMPERATURES BY x-RAYS.
ALL CURVES MEASURED AT -180°C.

I. After x-raying at stated temperature. II. After short rise
to -140°C. III. After raising to 20°C for two hours. IV.
Decrease in absorption caused by raising to 20°C (curve I less
curve III). V. After irradiation with light of λ >550 mμ for
1/2 hour. VI. After 48 hours at 20°C. (after Dorendorf).

electrons of the halide ions surrounding the F-center undergo a perturbed
transition. The α -band is proposed likewise to represent a perturbing
of the electrons, this time only by the presence of the negative-ion
vacancy itself. Since the α -band is in part unstable at room temperature,
it is supposed that these vacancies have sufficient mobility at this
temperature to diffuse through the lattice until they combine with positive
vacancies to form pairs, quartets, and higher aggregates of vacancy
clusters.

Martienssen[1] x-rayed KBr at 20°K and 90°K and observed what appears
to be the α -band (see Fig. 14). By additive coloration he also pro-
duced β -bands in both KBr and RbBr comparable in height with the F-band.
This work confirms the observations in KI and presents a strong argument
in favor of the explanation proposed by Delbecq, Pringsheim and Yuster.

D. Color Centers at Low Temperatures

The lifetime of a color center at any temperature T is given approxi-
mately by the equation

$$\tau = v^{-1} \exp [E/kT]$$

where v is the lattice vibrational frequency of approximately 10^{12} per
sec and E is the thermal activation energy. This equation has been
arrived at by modification of the Arrhenius equation used in chemical
kinetics. Theoretically it has no rigorous derivation pertaining to

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[1] W. Martienssen, Naturwiss 38, 482 (1951) and work to be published
in Z. Physik.
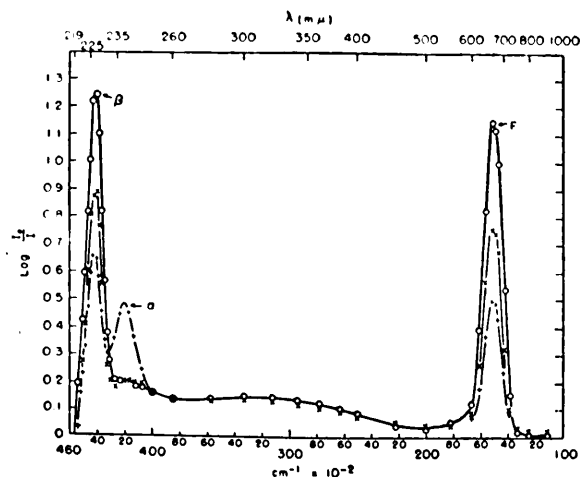
Fig. 13 KI x-RAYED 20 MINUTES AT ROOM TEMPERATURE 0-0-0. AFTER 75 HOURS IN
DARK AT ROOM TEMPERATURE x-x-x. AFTER BLEACHING WITH F-LIGHT FOR
35 MINUTES AT -195°C +-+-+. ALL MEASUREMENTS MADE AT -195°C
(AFTER DELBECQ, PRINGSHEIM AND YUSTER).
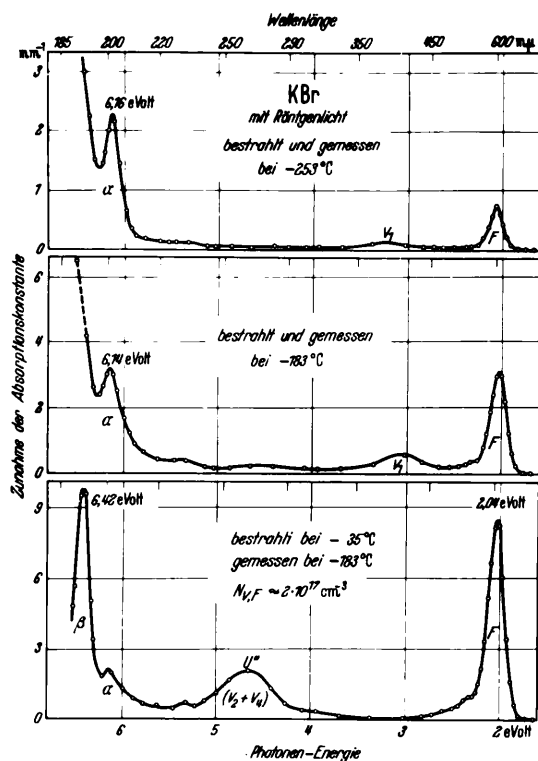
Fig. 14 ABSORPTION CURVES OF KBr x-RAYED AT 20°K, 190°K AND 238°K
(AFTER MARTIENSSEN).

electrons trapped in solids.

Several of the centers formed at low temperatures have already been mentioned. The F'-band in KCl and KBr is stable only well below room temperature.[1] These centers can be produced by irradiation of the F-band with F-light, by x-raying the crystal[2] and by almost any other method which releases large numbers of electrons in the crystal at the proper temperature when it contains F-centers. From the quantum yield curve for the reaction F→ F' for KCl seen in Fig. 7, it might be expected that the F'-band would not be formed at very low temperatures. Dutton, Heller, and Maurer[3] report the absence of the F'-band in KCl x-rayed near liquid helium (4.2°K) temperature, confirming this work for KCl. Why the F'-bands apparently form only within a selective temperature range has not been explained.

The V_1-band proposed by Seitz as a hole trapped at a positive-ion vacancy occurs upon x-raying only near liquid nitrogen temperature (77.2°K). Whether it occurs at lower temperatures is not known. Other V-bands occurring at higher temperatures apparently do not occur upon x-raying at 90°K as can be seen from Dorendorf's data in Fig. 12.

At least two possibilities are apparent to explain why some centers do not form below certain temperatures. One is that the capture cross section of the center for a hole or an electron depending

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[1] H. Pick, Ann. Physik 31, 365 (1938), 37, 421 (1940).

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

[3] D. Dutton, W. Heller, and R. Maurer, Phys. Rev. 84, 363 (1951).

on its affinity, varies with temperature. A second is that other centers with much larger capture cross sections for the same particle become stable at the lower temperatures and compete for the particles so successfully that few are trapped at the centers seen at higher temperatures. Probably both of these processes and possibly others play a part in the formation of color centers during x-raying.

In addition to the α -band formed at low temperatures, an interesting band to the infrared of the F-band has been observed in LiF by Pringsheim and Yuster.[1] This broad band to the infrared of the F-band shown in Fig. 15, occurs on x-raying at $77\,^{\circ}K$, and bleaches at $138\,^{\circ}K$ with considerable blue luminescence while the F-band decreases only about 50 per cent. If this band is irradiated at $77\,^{\circ}K$ with light within its band, it almost completely bleaches although the F-band is unaffected. Hence the band is certainly not an F'-band although it might be attributed to self-trapped electrons. Further, it reaches a saturation value after continued x-irradiation while the F-band continues to grow. Hence it might also be due to an impurity center. However, in this case the size or saturation value should vary widely among different crystals. It would be interesting to observe if such a band exists in other crystals at low temperature.

The self-trapped electron center should also exist only at very low temperatures. This center will be discussed in a later section.

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[1]P. Pringsheim and P. Yuster, Phys. Rev. 78, 293 (1950).
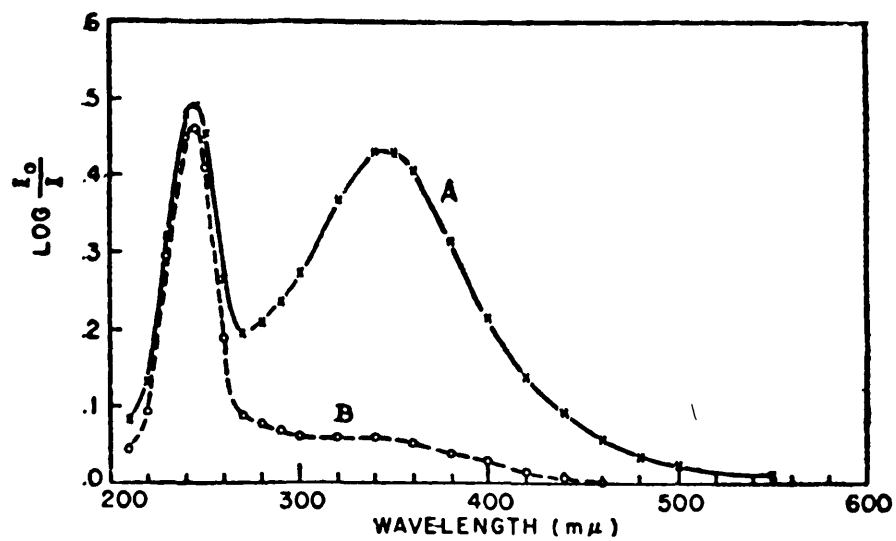
Fig. 15 ABSORPTION SPECTRUM OF LiF x-RAYED AT 78°K (CURVE A). AFTER BLEACHING
1 HOUR AT 78°K WITH LIGHT OF λ = 3650 (CURVE B).
(AFTER PRINGSHEIM AND YUSTER).

E. Formation of Color Centers by High Energy Irradiations

1. Processes Occurring During Irradiation.

A number of processes may occur during the exposure of a crystal to radiation such as x-rays. Some of these might be listed as follows:

a. Electrons are raised to the conduction band.

b. Positive holes are created in the filled band where the electrons have been raised to the conduction band.

c. Both electrons and holes diffuse through the crystal until they either recombine or are trapped by one of the several imperfections to form color centers.

d. The color centers are destroyed by the radiation and resulting high energy particles, again freeing the electrons and holes.

e. Positive and negative-ion vacancy imperfections are created either by a diffusion process from the surface of the crystal or by a local diffusion away from a dislocation.

f. Clusters of vacancies "frozen" into the crystal may be broken up forming single-ion vacancies.

From the experimental evidence on the build up of F and F'-centers, it appears certain that free electrons and holes occur during the x-radiation. The trapping processes are far from being solved, even at room temperatures where a great deal of work has been done. The occurrence of vacancies and other imperfections is also a major problem, and one in which the evidence is seemingly in conflict.

2. The Existence of Ion Vacancies.

For this problem of the existence of ion vacancies, the following

experimental evidence can be considered.

a. F-center concentrations greater than 10^{18} cm^{-3} are obtainable by x-rays in single alkali halide crystals. Densities of 10^{19} cm^{-3} have been obtained in thin evaporated layers.[1]

b. Estermann, Leivo and Stern[2] measured the change in the density of KCl at room temperature before and after x-radiation. They employed a floatation method and observed that for x-rayed crystals containing about 5×10^{17} cm^{-3} F-centers (measured optically) a decrease in density of about one part in 10^{4} had occurred. This decrease would correspond to about 10^{18} cm^{-3} F-centers and vacancies, in close agreement with the optical measurement. This suggests that most of the vacancies had diffused into the crystal during x-raying. Rough estimates of the mobility of vacancies diffusing as neutral pairs indicate that such diffusion may be marginally possible at room temperature.[3]

c. Etzel and Maurer[4], Wagner and Hantelmann[5], and Kelting and Witt[6] have calculated from conductivity measurements the number of incipient vacancies present in the crystals below about 500°C to be of the order

[1] L. Apker and E. Taft, Phys. Rev. 79, 964 (1950).

[2] I. Estermann, W. Leivo and O. Stern, Phys. Rev. 75, 627 (1949).

[3] F. Seitz, Revs. Modern Phys. 18, 384 (1946).

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

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

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

of 10^{17} to 10^{18} cm^{-3} and independent of temperature. Breckenridge[1] found a similar value by dielectric loss measurements in NaCl.

d. Seitz[2] has pointed out that the jog in a Taylor type dislocation may be regarded as the site of an incipient ion vacancy which should have a charge of $\pm$ e/2. Hence it might trap a hole or an electron to form a V-or F-center which might then diffuse away from the dislocation jog. In well annealed crystals, however, Seitz[3] apparently estimates the density of incipient vacancies to be as low as 10^{15} cm^{-3}.

(e) The α-band, which has been interpreted[4] as due to the presence of ion vacancies, does not appear in uncolored KI, but does occur in KI x-rayed below -80°C indicating that the vacancies have been created by the x-rays. This is true for KBr as well.

Which of the two possibilities, i.e., large numbers of incipient vacancies accounting for F-center growth or negligible numbers of incipient vacancies with production of most vacancies by x-rays, is correct is still in doubt. Since F-centers can be produced at liquid helium temperature[5] where the possibility for diffusion is remote,

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[1] R. Breckenridge, J. Chem. Phys. 16, 959 (1948).

[2] F. Seitz, Revs. Modern Phys. 23, 328 (1951); Phys. Rev. 80, 239 (1950).

[3] As reported by D. Dexter and W. Heller in Phys. Rev. 84, 377 (1951).

[4] C. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. 195 74 (1951).

[5] D. Dutton, W. Heller and R. Maurer, Phys. Rev. 84, 363 (1951).

further questions are raised. It has been suggested[1] that the x-ray
photons may dissipate most of their energy in very short-lived local
heating of the crystal, making possible momentary high temperatures over
a region of the radius of several lattice sites. Thus the local tempera-
ture could be high enough to permit diffusion of the vacancies for very
short distances. Since the energy would be removed from the region in
probably less than 10^{-9} sec., this diffusion could only occur for a very
small distance.

Dexter and Heller point out[2] that the trapping of electrons at dislo-
cation jogs and the subsequent diffusing away of the F-center may result
in a lengthening of the dislocation line and thus a decrease in crystal
density. This process could be in agreement with the density observa-
tions of Estermann, Leivo and Stern. At the same time it would permit
F-center production at low temperatures if the center remained in the
very near vicinity of the dislocation jog since further diffusion would
not appear possible at low temperatures.

F. Formation or Growth Rates of Color Centers by High Energy Irradiations

1. Dependence of Form of Growth Curves on the Various Processes.

Another possibility for the understanding of the processes occurring
during x-radiation is the study of the growth rates of the various centers
under various conditions. For example, if x-raying produced no vacancies

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[1] I. Estermann and S. Foner (private communication).

[2] D. Dexter and W. Heller, Phys. Rev. 84, 377 (1951).

at all and the F-centers are formed only by filling the incipient
vacancies, then it would be expected that the F-band would grow rapidly
during the early x-raying and then gradually reach a limiting value after
nearly all vacancies have trapped electrons. This saturation value should
represent an equilibrium between the number of F-centers being destroyed
by x-rays, hole capture and other collision processes and the number
being re-created per unit time. If the temperature is such that F'-
bands are stable, then these should subract from the maximum number of
F-centers.

If, on the other hand, the number of incipient vacancies is negligibly
small but many are created by the x-rays, then the growth-rate curves
should possess a different shape, dependent on the number of incipient
vacancies. For example, if there are 10^{14} to 10^{16} cm^{-3} isolated in-
cipient vacancies and the x-rays produce additional vacancies at a fairly
constant rate, then the shape of an F-growth curve should be such that the
initial portion is quite steep, indicating the combination of filling the
incipient vacancies and those created. Then the rest of the curve should
change to a smaller but fairly constant slope. This curve also should
eventually reach a limiting value when the number of F-centers and vacan-
cies approaches some value limited by the crystal structure and destruc-
tion rates.

Obviously the above growth rate discussion is simplified since the
number of possible processes occurring during x-raying is greater than
included there. However, experiments designed to observe specific effects
in these growth processes might prove very fruitful in obtaining a general

understanding of the phenomena.

2. Experiments Pertaining to Growth Rates of Color Centers.

Unfortunately, little has been done so far in this direction. The following list summarizes what has been done experimentally which pertains to these growth processes. While only Harten and Smakula used x-rays, the other experiments can contribute to an understanding of growth rates during x-raying.

(a) Przibram[1], Belar[2], and Urbach[3] describe experiments in which natural NaCl and KCl were exposed to the radiation from a radium source. They found the F-center coloration to reach a limiting value, the magnitude of which was dependent on the intensity of radiation as shown in Fig. 4. Further, if after the limiting value had been reached at one intensity, the F-center concentration built up to a new limiting value as shown in Fig. 16 if the intensity was suddenly increased.

(b) Smakula[4] measured the growth rate of the F-centers in a number of crystals irradiated with ultraviolet in the first fundamental absorption band at room temperature and $190^\circ K$. This irradiation creates excitons[5] which move through the crystal. If they collide with an

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[1] K. Przibram, Z. Physik 20, 196 (1923).

[2] M. Belar, Wien. Ber. 135 II, 189 (1926).

[3] F. Urbach, Wien. Ber. 135 II, 149 (1926).

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

[5] An exciton is understood to be an excited state of an electron in the lattice. This excited state is below the conduction band and may transfer or jump from atom to atom within the solid. The mechanisms for the dissipation of this exciton are not fully understood beyond the

imperfection such as an ion vacancy, they may form an F-center with the help of the lattice vibrations. The growth curves are shown in Fig. 17. Especially important are the curves for KBr since three wavelengths of the irradiation were used, 203 mμ being on the edge of the fundamental absorption band and 199 and 193 mμ being well into this band which is shown in Fig. 18 as well as that for other of the alkali halides. The 193 mμ photons will be absorbed in a thin layer, i.e., a small fraction of a millimeter, on the surface of the crystal. The 199 mμ photons should penetrate considerably more, while the 203 mμ photons should penetrate well over a millimeter.

Several observations can be made from these curves. The rate of F-center production is very high for a few seconds and then sharply drops to a very small value. The ordinates are the total number of centers obtained per unit area. The actual concentration in terms of number per cm^3 can not be obtained since the depth of coloration d used in Smakula's formula is not known. The total number of centers is a function of the wavelength of irradiation although enough wavelengths were not taken to obtain a quantitative variation. Lowering the temperature apparently lowers the total number of F-centers produced for a given uv exposure.

(c) The limiting value of F-centers produced by excitons may be explained by an experiment of Apker and Taft[1]. They have shown that when

possibilities of its emitting light, creating phonons or colliding with imperfections. See F. Seitz, The Modern Theory of Solids, McGraw-Hill Book Company, Inc., New York: 1940, and N. Mott and R. Guerney, Electronic Processes in Ionic Crystals, Oxford: 1940.

[1] L. Apker and E. Taft, Phys. Rev. 79, 964 (1950), 82, 814 (1951).
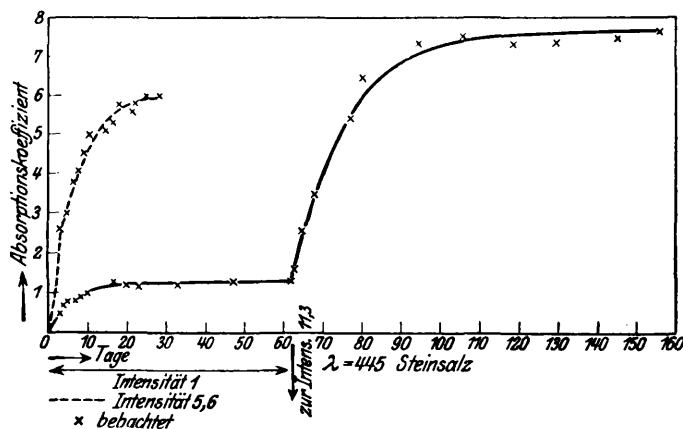
Fig. 16   INCREASE IN F- ABSORPTION WITH INCREASED r-RAY INTENSITY AFTER SATU-
RATION HAS BEEN REACHED AT A LOWER INTENSITY (AFTER PRZIBRAM).
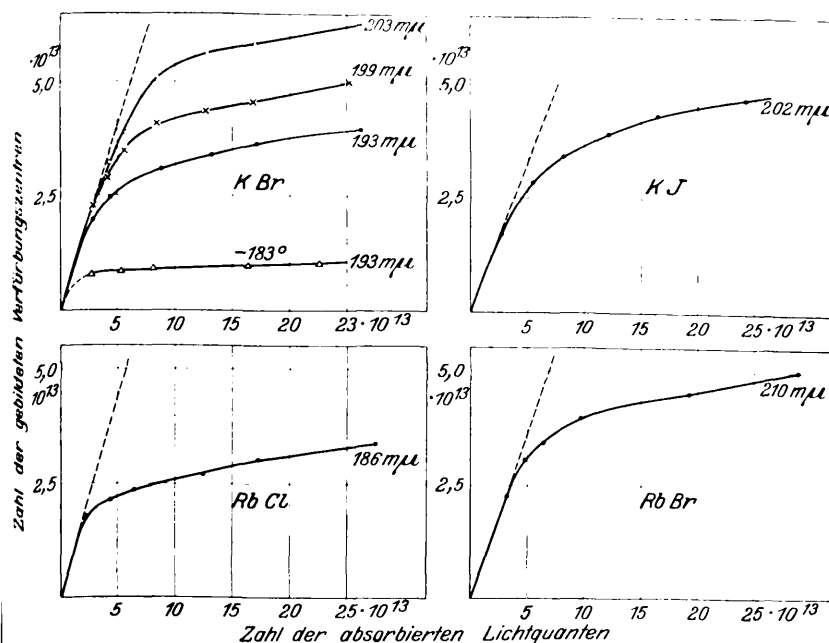
Fig. 17   GROWTH OF NUMBER OF F-CENTERS PER UNIT AREA PRODUCED BY ULTRAVIOLET
IRRADIATION ON THE LONG WAVE LENGTH SLOPE OF THE FIRST FUNDA-
MENTAL ABSORPTION BAND (AFTER SMAKULA).
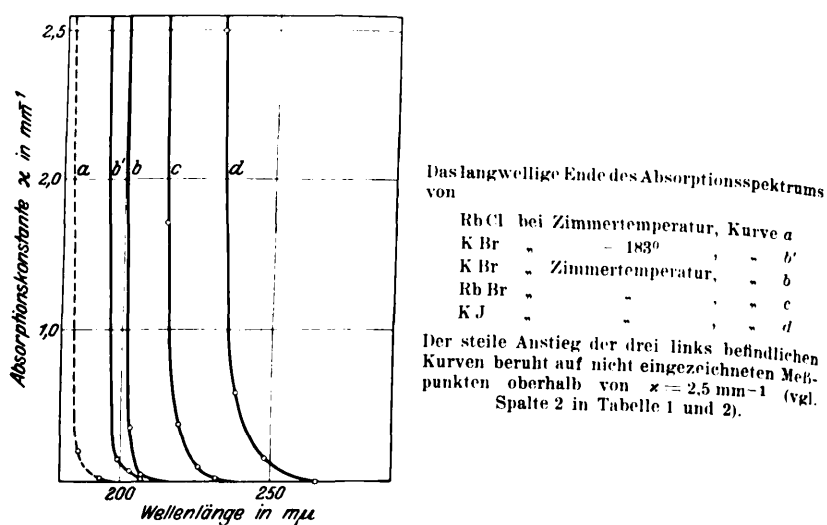
Fig. 18   LONG WAVE LENGTH SIDE OF THE FIRST FUNDAMENTAL ABSORPTION BAND FOR
SEVERAL ALKALI-HALIDES (AFTER SMAKULA).

a thin evaporated layer of KI or RbI containing large concentrations of

F-centers is irradiated in the first fundamental band, electrons are re-

leased from the F-centers by collisions with excitons, the electrons ac-

quiring sufficient energy to penetrate the potential barrier of the sur-

face and leave the crystal to cause a photo-electric effect. Hence,

excitons may destroy as well as create F-centers. It might be expected

that a similar destruction would occur for V-centers.

(d) Harten[1] has run an excellent set of growth-rate curves in x-rayed

KCl at temperatures from -180°C to $+60^\circ$C. These are shown in Fig. 19.

He also measured the current occurring during this irradiation and found

it to reach a limiting value whose magnitude is dependent on temperature

(see Fig. 20). The arrows in both Figs. 19 and 20 indicate the point

where the current reached a limiting value.

Several observations can be made on these curves. The overall growth

rate of F-centers increases as the temperature is lowered below $+60^\circ$C

until it reaches a maximum somewhere between -20°C and -75°C below which

it decreases. This further decrease in rate apparently becomes small

below -110°C. Reference to Dorendorf's data in Fig. 12 shows how the

various bands occur at different temperatures. The occurrence of certain

of these bands probably affects the growth of the F-band. The mobility

of the various imperfections also changes with temperature and this may

further affect the rate, at least in the range of $+60^\circ$C to -20°C.

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[1]H. Harten, Z. Physik 126, 619 (1949).
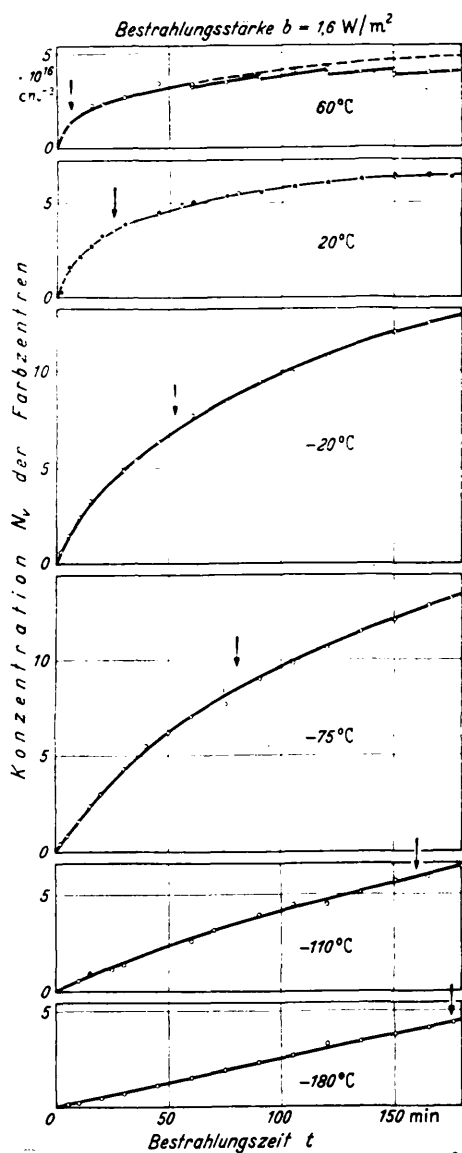
Fig. 19
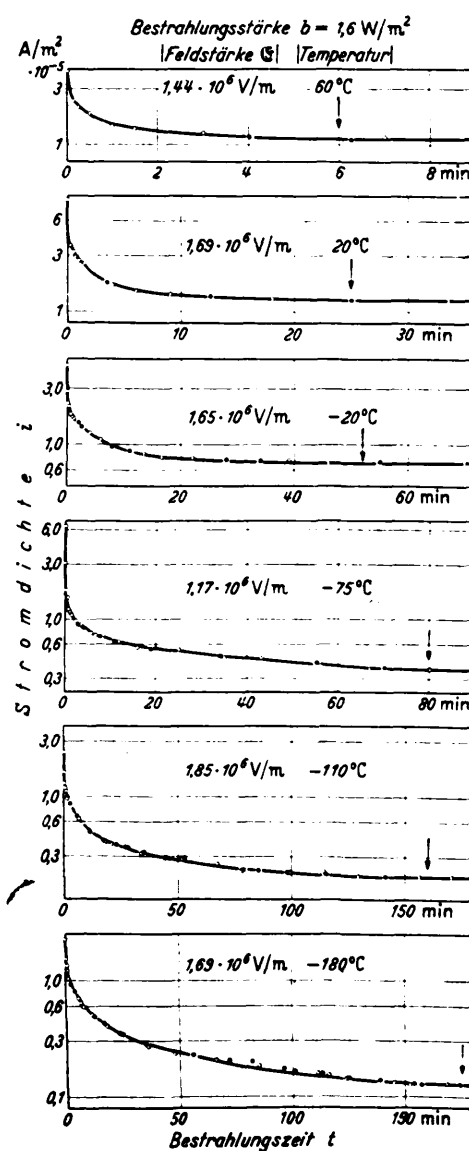
Fig. 20

Fig. 19 GROWTH OF F-BAND AT VARIOUS TEMPERATURES UNDER IDENTICAL x-RAY CONDITIONS
(AFTER HARTEN).

Fig. 20 PHOTO CURRENT VERSUS x-RAY TIME AT VARIOUS TEMPERATURES (AFTER HARTEN).

The limiting value of the current and its relation to the knee in the F-center growth rate curves might be indicative of more than one process occurring in the generation of F-centers, i.e., the first part of the curve might be due to filling of isolated incipient vacancies and that after the knee due to the constant production of vacancies by the x-rays.

Harten observed a further interesting point. He found that at + 15°C the number of F-centers produced has a limiting value, independent of the number of centers present in the crystal before the x-raying is started. This is shown in Fig. 21, where curve a starts with a greater number of F-centers than the limiting value, but the number actually decreases under x-rays to the limiting value which would be obtained starting with a crystal with no F-centers present. Curve b starts with less than the limiting value of F-centers and the number increases under x-radiation until the limiting value is reached.

That this limiting value is fixed at this temperature is most surprising. It might indicate an equilibrium between the creation and destruction of F-centers and ion vacancies. The F-centers might be destroyed by holes, photons and electrons and the ion vacancies, by diffusion to the surface, clustering or collision with interstitial ions. The investigation of such equilibrium situations at other temperatures is necessary before further discussion is possible.

Harten ran all his growth rate curves with the same KCl crystal, bleaching the color centers between each curve by heating the crystal to 350°C and keeping it at this temperature for 5 minutes. This technique gave reproducible growth-rate curves.

Bestrahlungsstärke $b = 1.6 \, \text{W}/\text{m}^2$
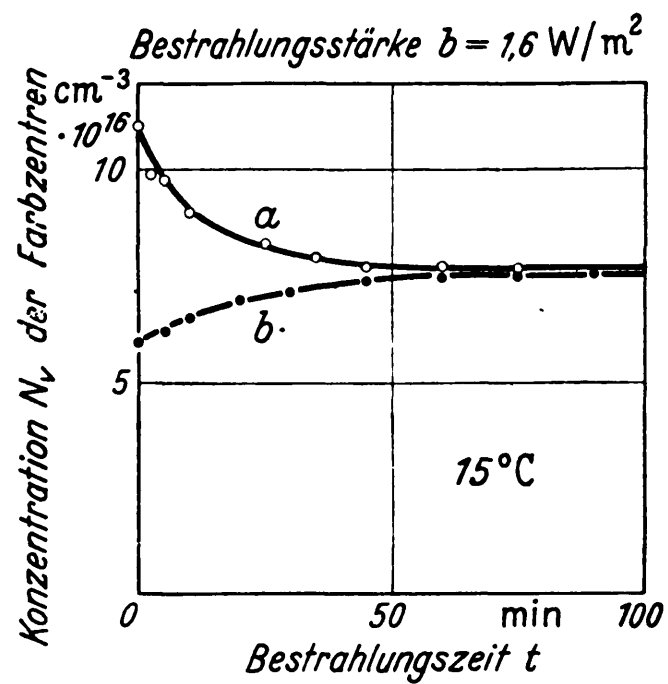
Fig. 21 F-CENTER CONCENTRATION vs x-RAY TIME AT +15°C. CURVE(a) WITH A HIGHER
CONCENTRATION THAN THE LIMITING VALUE AND CURVE(b) WITH A LOWER CON-
CENTRATION (AFTER HARTEN).

(e) Hummel[1] has observed that KCl crystals containing divalent Ca

ions acquire higher F-center concentrations under γ -rays than pure

crystals do. Further, the density of the color centers increases with

increasing amounts of Ca present in the crystal. Smakula[2] added Tl to

NaCl and observed an increased growth rate of the F-band by x-rays with

amounts of the order of .0025 to .05 mol per cent added to the melt.

However, his experiments may not have been so carefully controlled as

necessary to confirm that this mono-and tri-valent impurity aids F-

center production.

3. Further Discussion of the Growth Rate Experiments.

A similarity to be noted among these experiments is the limiting value

of the F-center concentration. This saturation at room temperature occurs

for all of the radiations employed, i.e., γ - and x-rays and ultraviolet.

In each case the incident radiation probably either directly destroys F-

centers or produces particles which destroy them as Apker and Taft have

shown for excitons.

The balance between the destruction and creation of F-centers has been

shown to depend on temperature by Harten. At least part of this balance

is due to the stability of the various other centers. As can be seen

in Dorendorf's work, Fig. 12, the F'-, V_1- and certain other V-bands are

not stable at room temperature. Thus there will be a different number of

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[1]H. Hummerl, Thesis, Göttingen University (1950).

[2]A. Smakula, Z. Physik 59, 603 (1930).

free holes and electrons present in the lattice at room temperature than
at low temperatures. That such a difference can affect the F-center
production rate has been proposed by Seitz[1]. He suggests that the increase
in F-centers observed in Hummel's work is due to the capturing of holes by
the divalent ion sites, thus eliminating some of the destroyers of F-
centers. Similarly, when the temperature of x-raying is above that for
the stability of V_1-centers, _more_ free holes will be present in the
lattice to destroy F-centers.

The thermal energy of the lattice may also affect this balance between
creation and destruction of F-centers. When the temperature is high
enough, diffusion of certain imperfections may be possible. For example,
at room temperature when an F-center is destroyed by a hole, the result-
ing negative-ion vacancy may be able to diffuse through the lattice far
enough for it to be destroyed. This destruction of the vacancy might
merely be its return to the jog of the Taylor dislocation from whence it
originally came. Or perhaps a permanent destruction might occur by an
interstitial negative ion diffusing into the vacancy. At any rate the
number of ion vacancies available to form F-centers may be lowered at
the higher temperatures.

A combination of these types of effects and others is probably
responsible for the wide variation in the F-center growth with tempera-
ture. To synthesize these discussions into a model for the processes

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[1]F. Seitz, Phys. Rev. 83, 134 (1951).

a crystal undergoes during irradiation such as x-ray bombardment is not yet possible. They do point the way, however, for experiments which should be performed if this synthesis is to be made more possible.

G. The Self-Trapped Electron

Although the self-trapped electron has been ruled out as the model for the F-center, its existence might still be possible. Mott and Guerney[1] made one of the first calculations of the binding energy of a self-trapped electron. Their work, entirely of a classical nature, was very rough and yielded a binding energy of several electron volts. This high an energy would indicate a very stable center although none was found which might be construed as this center by the early workers. Later Pekar[2] calculated the binding energy using a self-consistent field method and obtained a value of .32 for NaCl.

Two detailed calculations making use of quantum mechanical methods have been recently carried out. The first of these was done by Markham and Seitz[3]. They treated the dielectric medium as being discontinuous. The field created by the displacement of the lattice in the vicinity of the self-trapped electron was assumed to be a sawed-off Coulomb field. A self-consistent method was used, i.e., the field determined by the wave function displaces the ions in the vicinity of the electrons, this

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[1] R. W. Guerney and N. F. Mott, Proc. Phys. Soc. (London) 49 (extra part), 32 (1937).

[2] S. Pekar, J. Phys. USSR 10, 341, 347 (1946).

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

polarization of the lattice determines the field which traps the electron, and this field determines the wave function. Actual values for the thermal and optical activation energies for a self-trapped electron in NaCl were found. In addition, it was found that the electron was smeared out spherically over several lattice sites. Hence, it was concluded that self-trapped electrons might be observed as stable centers at very low temperatures.

Frohlich, Pelzer and Zienau[1] also carried out a detailed calculation of slow electrons in ionic crystals. They assumed the dielectric to be a continuous medium, however, with a single vibrational frequency for long longitudinal polarizational waves. They found the electron to exist with equal probability at any point in the crystal. Further, their calculations show that the energy difference of states for these electrons hardly differs from that for free electrons, although the overall conduction band is lowered because of interaction with the lattice. Thus self-trapped electrons should never exist except as levels in the conduction bands. In this case they would diffuse through the crystal much as the free electron until they either recombined with holes or became trapped at other centers, for example at negative-ion vacancies to form F-centers. Hence they should not be experimentally observable.

H. Effect of Foreign or Impurity Atoms

Color centers can be produced by the presence of impurity or

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[1] H. Frohlich, H. Pelzer and S. Zienau, Phil. Mag. 41, 221 (1950).

foreign atoms in the alkali halides. The importance of this subject is illustrated by the work of Hilsh and Pohl[1] in the U-band. This band was reported as an intrinsic band, i.e., one resulting from imperfections in a pure crystal such as a combination of lattice vacancies and electrons or holes. It was discovered later, however, that this band was caused by a hydrogen impurity. The H-ions apparently replace the halogen ions in the lattice as deduced from the fact that the lattice constant decreases as the amount of hydrogen in the crystal increases. The fact that impurity atoms and colloids could cause color centers in the alkali halides was already well established, when the U-band was found. Hence this work illustrates how easily the experimentalist can go astray in interpretation of color centers.

F-center concentrations of 10^{16} cm^{-3} produce visible absorption bands, but since there are 10^{22} ion sites per cm^3, this represents only one F-center per 10^6 ion sites. Hence if the centers occurring at impurity ions absorb light, then impurity concentrations as low as one in 10^6 may also cause visible absorption bands. A great many of the early papers deal with the effect of adding specific impurities, such as thallium, to the crystal since they cause phosphorescence in certain cases. Although many workers mention the possibility of impurities interfering with studies of color centers, none discuss the problem of obtaining really pure alkali halide crystals for study. In fact, although many papers state the amount of impurity added to the melt of the crystal, only one paper[2] has been found

[1] R. Hilsch and R. W. Pohl, Nachr. Akad. Wiss. Göttingen, Math-physik Kl. 322 (1933).

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

which gives a quantitative analysis of the impurities present in a crystal. Since the crystal melt rejects impurities during growth[1], the quantity added to the melt will not be the amount in the crystal, and all previous work is therefore only qualitative. Further, since the work deals with only a few impurities under special conditions, little can be obtained quantitatively on the effect of impurities. A review of the literature does result in the realization that impurity concentrations of less than one part in 10^4 will result in extensive color center bands. Hence any work must be considered with that fact foremost in mind. Only one early paper[2] has been found that goes into detailed experiments of the effects of x-raying crystals with added impurities. In this particular paper Tl and Pb were added to KCl, KBr and NaCl and several of the impurity color center bands examined under varying amounts of x-rays.

It should be pointed out that impurities affect other properties in addition to the absorption bands. The conductivity is apparently a function of impurity content also, as well as luminescence and phosphorescence. A separate bibliography is presented at the end of this dissertation covering papers which discuss the effects of impurity or foreign atoms in alkali halides.

The actual processes of color-center production by impurity additions are many-fold. Foreign ions may occur interstitally or substitutionally

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[1] R. McFee, J. Chem. Phys. 15, 856 (1947).

[2] A. Arsenjeiva, Z. Physik 57, 163 (1929).

in the lattice and, depending on the degree of their affinity, will be able to trap electrons or holes. These trapped charges should undergo transition with light absorption giving rise to a line spectrum leading to a series limit[1], broadened of course by the lattice vibrations into an actual band.

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[1] N. F. Mott and R. W. Guerney, Electronic Processes in Ionic Crystals, Oxford: 1940, p. 102.

CHAPTER III

SUGGESTED PROBLEMS

A. Experimental Search for the Self-Trapped Electron in the Alkali Halides

The calculations of Markham and Seitz discussed in Chapter II-H for the self-trapped electrons in NaCl gave, for the highest approximation, a thermal activation energy E_t of .13 ev and an optical activation energy E_o of .68 ev. From the expression for the lifetime of such a center, given approximately by $\nu^{-1} \exp [E_t/kT]$ where ν is of the order of 10^{12} to 10^{13} sec^{-1} [1] self-trapped electrons in NaCl should have a lifetime long enough to be observed only at temperatures in the range of liquid helium.

The optical activation energy corresponds to a wavelength of 1.8 μ . Hence, if these calculations are correct, when an NaCl crystal is cooled to this low temperature range and electrons are released within the crystal by x-raying, it would be expected that an absorption band should occur somewhere in the infrared spectrum of the crystal due to the self-trapping of these electrons at lattice sites. Care would be necessary to avoid the optical bleaching of the centers before the spectrum was completely obtained.

If such an experiment resolved an absorption band in the infrared, it should be possible to prove that electrons are present in the centers

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[1] See F. Seitz, _Modern Theory of Solids_ (McGraw-Hill Book Company, Inc., New York, 1940), discussion on Specific Heats of Solids.

be about 10^6 seconds, long enough for it to be easily observable. This might also occur in NaF and KF where $\left(\dfrac{1}{K_o} - \dfrac{1}{K}\right)$ is .407 and .375 respectively. Thus a similar experiment for these crystals at 78°K as proposed above for NaCl at 4.2°K might also prove successful. For LiF, Markham and Seitz predict a band in the visible or near infrared to be produced by self-trapped electrons.

If the approaches of Pekar and Markham and Seitz are reasonably correct, such experiments should resolve absorption bands which might be attributed to stable self-trapped electron centers. If these absorption spectra are not observed, this will not mean for certain that these centers do not exist, for they may exist as Fröhlich's theory concludes, i.e., in lower states in the conduction band. Or since the self-trapping wave functions indicate the electron to be smeared out over many lattice sites, very small activation energies might cause it to move from lattice site to site and thus diffuse through the crystal until it is trapped at a more stable center, e.g., F center. Even at 4.2°K the lattice vibrations might provide sufficient energy for such diffusion, although this seems unlikely.

Since the approach of Markham and Seitz is fundamentally different from that of Fröhlich's in that a discontinuous dielectric medium is assumed by Markham and Seitz, while a continuous dielectric medium with a single vibrational frequency for the longitudinal polarization waves is considered by Fröhlich, an experimental study of the problem might be of help in indicating which approach is more valid. Further, this problem has far-reaching effects in that the theoretical bases and

methods are employed extensively in treating electronic processes in dialectrics, such as dielectric break down.

B. Study of the Color Centers Produced by X-Raying Alkali Halides
   Held at Liquid Helium Temperatures

As was discussed in Chapter II-D, the self-trapped electron is not the only center whose thermal activation energy is so small that it can exist only at low temperatures. Some of the F'- and V-centers are good examples of these. There are also centers which are created at higher temperatures which do not occur at the lower temperatures. A good example of these is the M- and R-bands. It is important to know if further centers can be formed at temperatures below 77.3°K which, with the exception of Dutton, Heller and Maurer's[1] photo-conductivity work and Martienssen's work[2] in KBr, is the lowest temperature at which color center data has been published for x-rayed alkali halides. Of course a similar statement holds for the question as to whether any of the bands formed at 77.3°K or higher will not occur at lower temperatures.

The answer to these experimental questions of color centers at very low temperatures may be able to help in a formulation of the structure of the centers formed at these and higher temperatures, and also assist in the postulation of the exact processes that occur when the alkali halides are irradiated with energies such as those of x-rays.

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[1] D. Dutton, W. Heller, and R. Maurer, Phys. Rev. 84, 363 (1951).

[2] W. Martienssen, Naturwiss. 38, 482 (1951).

This problem is related by the experimental requirements to that posed above in (A). The alkali halides must be cooled to the 4.2 $^{\circ}$K range, and while at this temperature x-rayed and their absorption spectrum measured. The effects of increasing x-ray dosage, the stability of the color center bands formed and the effects of warming the crystals to higher temperatures after the x-raying are some of the experimental phases necessary to achieve some of the answers to the problem of color centers at very low temperatures.

Of course the question of whether or not F-centers occur under x-raying at liquid helium temperature is in itself important since at this very low temperature any extensive diffusion of ions and vacancies probably can not occur.

Further, since there are several possible ways of forming an F-center, i.e., by an electron captured at an isolated incipient vacancy, at the incipient vacancy caused by the jog in a Taylor type dislocation, or at vacancies produced through the action of the x-rays, it is possible that the shape (half-width) may be different for F-centers formed at low temperatures. Petroff and Oberly[1] have proposed different types of F-centers to exist but this work is insufficient to form any complete conclusions.

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[1] St. Petroff, Z. Physik 127, 443 (1950) and J. J. Oberly, Phys. Rev. 84, 1257 (1951).

C. Growth Rates of the F-, F'- and Certain of the V-Bands by
X-Rays under Different Conditions

The problems posed in (A) and (B) are such that work on them may

also pertain to an understanding of some of the processes occurring

during x-rays discussed in Chapter II-E and -F. Experimental studies

pertaining to particular phases of growth rates such as the work of

Harten, Przibram, and Smakula already discussed are also necessary. A

problem in this category is the study of the growth rates of the F-,

F'- and certain of the V-centers at 78°K x-rayed under different light

bleaching conditions.

If a KCl or KBr crystal is x-rayed in the dark at 78°K, the F'-band

will appear, as might have been predicted from Pick's[1] quantum yield

data. Surprisingly enough experimental verification of this manner of

producing the F'-band was not published before Dorendorf[2], and he

merely labelled the band on a graph but did not mention it in his text

(see Fig. 12). If the accepted structure of the F'-band is correct,

i.e., 2 electrons captured at a negative-ion vacancy, then the fact that

it can be produced during x-raying may permit a study of the effect it

has on the growth of the F- and V-trapping centers. For when the

crystal is x-rayed while F'-light is incident upon it, then all F'-

centers will be destroyed as rapidly as they are made and thus the F- and

certain V-bands should have growth rates that are different from when the

F'-band is not bleached. The V-band caused by a hole captured at a

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[1]H. Pick, Ann. Phys. 37, 421 (1940).

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

positive vacancy should be destroyed by electrons and possibly other trapped hole (or holes) centers. Thus, this experiment could present a relationship amongst these bands, and give further insight to the manner of vacancy production and presence.

CHAPTER IV

EXPERIMENTAL PROCEDURE

A. Acquisition and Handling of the Alkali Halide Crystals

Crystals of a number of the alkali halides may be obtained commercially from the Harshaw Chemical Company, Cleveland, Ohio, and the Optovac Company, Boston, Massachusetts. These include LiF, NaCl, NaI, KF, KCl, KBr, and KI. Others must be grown privately. This can be done by sealing a quantity of pure material under high vacuum in a chemically clean silica tube, placing the sealed tube in a furnace, and, after the material is fully melted, slowly cooling it to room temperature. The NaF used in these experiments was grown in this manner for the author by Dr. Zerfoss of the Naval Research Laboratory. An alternate way of growing these crystals is by the Kryopolus Method.

The crystals used were cleaved from large crystals to pieces about 15 x 15 x 1.5 mm. Some of the alkali halides are very slightly hygroscopic, LiF, NaF, and NaCl falling in this category. Exposure to ordinary air does not readily fog their surfaces. Others, such as KCl, KBr, and KI are only mildly hygroscopic and should not be exposed to the atmosphere for longer than necessary. To insure clear surfaces free of dissolved water, the large crystals were removed from the desiccator in which they were stored only when a crystal for an experiment was required. Then a piece twice the required thickness (about 2 or 3 mm) was cleaved from the large crystal with a light

mallet.[1] Then this piece was cleaved in half and the freshly cleaved face mounted in the cell (to be described) so that it faced the x-ray beam. The cell was then immediately evacuated so the time the newly cleaved face was in contact with the air was usually less than five minutes.

The other alkali halides are quite hygroscopic, some, like KF, to such a degree that unless they are cleaved in a perfectly dry atmosphere, their surface will become instantly fogged. The dry atmosphere can be achieved only with a good dry box using liquid N_2 as a desiccant. Another method of cleaving such extremely hygroscopic crystals is to do it under a liquid such as benzine from which all the water has been removed by adding sodium metal. Since the alkali halides are not soluble in benzine, the benzene will evaporate from the cleaved surface after it has been mounted in the cell and evacuated.

B. Purity of the Alkali Halide Crystals

As has already been noted, impurity atoms in the crystal can cause color centers which may be confused with those occurring only in a pure crystal. Since the degree of purity of the commercial crystals is not available, Dr. Zerfoss of the Naval Research Laboratory and Dr. Scribner of the National Bureau of Standards were kind enough to run spectroscopic analyses of the crystals employed. The results are presented in table I.

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[1]Cleaving the thick piece first was necessary since thinner pieces would shatter rather than cleave cleanly from the large crystal. By halving each time, samples as thin as .5 or .6 mm can be obtained.

TABLE I. Spectroscopic impurity analysis of several alkali halide crystals

Element	NaCl					KCl		KBr			NaF
	Harshaw NRL	Harshaw NRL	Harshaw NBS	Harshaw NBS	Optovac NRL	Harshaw NRL	Harshaw NBS	Harshaw NRL	Harshaw NBS	Pilot Chemical NRL	Zerfoss NBS
Ag	FT	-	FT	-	-	-	-	FT	-	-	-
Al	W	W	FT	FT	W	T	FT	W	FT	W	-?
As			-	-			-		-		-
Au			-	-			-		-		-
B			-	-			-		-		-
Ba			-	-			-		-		-
Be			-	-			-		-		-
Bi			-	-			-		-		-
Ca	-	-	VW	VW	M	T	VW	-	VW	-	W
Cb			-	-			-		-		-
Cd			-	-			-		-		-
Ce	-	-	-	-	-	-	-	-	-		-
Co			-	-			-		-		-
Cr			-	-			-		-		-
Cs			-?	-?			-?		-		-
Cu	T	-	-?	-?	FT	-	-?	T	-	-	T
Fe	T	W	T	T		T	T	FT	T	FT	T
Ga			-	-			-		-		-
Ge			-	-			-		-		-
Hf			-	-			-		-		-
Hg			-	-			-		-		-
In			-	-			-		-		-
Ir			-	-			-		-		-
K	-	-	-	-	-	VS	VS	VS	VS	VS	W
La			-	-			-		-		-
Li	-	-	T	T?	FT	-	-	-	T	-	T
Mg	-	-	T	T	FT	-	T	-	T	-	T
Mn			-	-			-		-		-?
Mo			-	-			-		-		-
Na	VS	VS	VS	VS	VS	T	W	FT	W	W	VS
Ni			-	-	FT		-		-		T
Os			-	-			-		-		-
P			-	-			-		-		-
Pb			-?	-?			-		-		-
Pd			-	-			-		-		-
Pt			-	-			-		-		-
Rb	-	-	-	-	-	-	T	-	T	-	-?
Rh			-	-			-		-		-
Ru			-	-			-		-		-
Sb			-	-			-		-		-
Sc			-	-			-		FT		-
Si			FT	FT			FT		-		-?
Sn			-	-			-		-		-
Sr	-	-	-	-	T	-	-	-	-	-	-?
Ta			-	-			-		-		-
Te			-	-			-		-		-
Th			-	-			-		-		-
Ti			-	-			-		-		-
Tl			-	-			-		-		-
U			-	-			-		-		-
V			-	-			-		-		-
W			-	-			-		-		-
Y			-	-			-		-		-
Zn			-	-			-		-		-
Zr			-	-			-		-		-

Definition of Symbols: VS—greater than 10%; S-1.0 to 10%; M-0.1 to 1%; W-0.01 to 0.1%; VW-0.001 to .01%; T-and FT 0.001 to 0.001%; - not detected.

Because of calibration difficulties these impurity figures cannot be considered to better than a factor of 10. Unfortunately, only 55 of the elements can be observed by this technique and detection of the remaining elements in quantities of less than 1 part in 10^4 is not readily possible by other means. As can be noted, 7 of the impurities occur in quantities greater than 1 part in 10^6 and these could produce a considerable number of extraneous effects. These impurity analyses were discussed with many of the workers in this field at the University of Illinois Conference on the Physics of Ionic Crystals, including F. Seitz and R. Pohl, and with R. Hilsch at the Bureau of Standards' Low Temperature Conference. It was the unanimous opinion that crystals of much higher purity must be obtained before all the presently known data can be fully acceptable. This view is readily justified when it is realized that an impurity content of even 1 part in 10^6 represents 10^{16} per cm^3 imperfections in the lattice and color center concentrations of the order of 10^{15} per cm^3 are visible.

There are at least two possible attacks to this impurity problem. One would be to induce known amounts of each of the impurities occurring in quantitites greater than 1 part in 10^6 and observing the color center spectrum produced in each crystal. This method would be extremely tedious since great care would be necessary with each crystal grown to insure that only one impurity was dominant.

The second method and the fundamentally desirable one is that of attempting to grow an exceptionally pure crystal, i.e., one with no impurities greater than 1 part in 10^6. This method involves two

factors. First, the acquisition of highly pure raw material and second, the growth of a crystal using this material. The raw material may be purified by repeated recrystallization and filtering through molecular filters after the use of various precipitants such as ammonium sulfide.[1] Since foreign-ion rejection from the melt occurs during the growth process[2], this will further purify the crystal. In fact several remelting and regrowth cycles, each time using only the purest portion of the previous melt may be necessary. Of course, only the purest of silica can be used for the crucible and its surface must be thoroughly cleansed with an agent such as pure hydrofluric acid. If such a crystal is grown and the spectroscopic analysis of the 55 or so elements now possible indicates a purity of the magnitude discussed above, one might be reasonably safe in assuming that the other 40 odd elements were present to no greater degree than that for those actually observed.

This impurity problem has been circumvented in this paper in a manner similar to that of several previous workers[3] with the exception that a majority of the actual impurities were determined. Most experiments were repeated with crystals of the same alkali halide with small

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[1]R. Hilsch (private communication).

[2]R. McFee, J. Chem. Phys. 15, 856 (1947).

[3]See for example St. Petroff, Z. Physik 127, 443 (1950). He compared his results with KCl crystals taken from the clean part of the melt to those from the dirtiest part of the melt and since they were in agreement, assumed that impurities were not responsible.

variations in impurity content and the results compared. Results among different alkali halides were also compared. This procedure gives at least some physical basis on which to substantiate the results.

C. Cooling the Crystals - the Low Temperature Optical Cell

1. Principle of Cell Design.

In order to perform the experiments proposed in Chapter III, several factors had to be taken into account. First it was necessary to cool the crystal to liquid helium temperature in a manner permitting the crystal to be x-rayed and then its absorption spectrum measured, from the ultra-violet to the far infrared. Further, since long x-ray exposures, wide spectrum range measurements, and stability-with-time observations adding up to many hours of operation for a single run are required, the apparatus for cooling the crystal, called a low temperature optical cell (or cryostat), must be capable of containing the liquid helium coolant for this period. Finally, the cell must be easily portable since the use of several instruments during one run is necessary.

Since the alkali halides conduct heat in the region of 4.2°K about as well as copper at room temperature thermally[1] bonding the crystal to a surface at 4.2°K should be sufficient to cool the entire crystal to nearly that temperature. This fact was employed in the design of the cell by attaching a copper crystal holder to a container of liquid helium, all of which was suspended in a vacuum and shielded from room temperature radiation by interposing a liquid N_2 cooled shield between.

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[1]W. J. de Haas and T. Biermasz, Physica $\underline{4}$, 759 (1937).

The edges of the crystal were clamped to the crystal holder.

A number of low temperature cells are described in the literature[1], but none of them lend themselves fully to the above described requirements. Hence, it was necessary to design a cell incorporating features which would permit these requirements to be met. The cell built is depicted in Fig. 22, and it has proved satisfactory in most respects. The maximum outer body diameter of the cell is six inches permitting a reasonable liquid helium capacity. The cell is narrowed at its lower end, however, so that the sample is only one inch from the outside, room-temperature windows. The liquid helium container and sample holder are connected to the body of the cell through an arrangement incorporating a sylphon bellows allowing vertical displacement of the sample, in reference to the outside windows, without breaking the vacuum.

2. Construction of the Cell.

The cell consists of three sections: (1) outer vacuum jacket, including appropriate windows; (2) liquid nitrogen container and radiation shield; (3) liquid helium container and sample holder. The three sections are pictured disassembled in Fig. 23.

The top flange plates which support each of the sections overlap so that they may be bolted together with "O" rings (Fig. 22) between to make vacuum-tight seals. A common vacuum is maintained between sections.

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[1]Fleschig Zeit. f. Phys. 36, 605 (1926); H. O. McMahon, R. M. Haines, and G. W. King, J. Opt. Soc. Am. 39, 786 (1949); and P. D. Johnson and F. J. Studer, Phys. Rev. 82, 976 (1951).
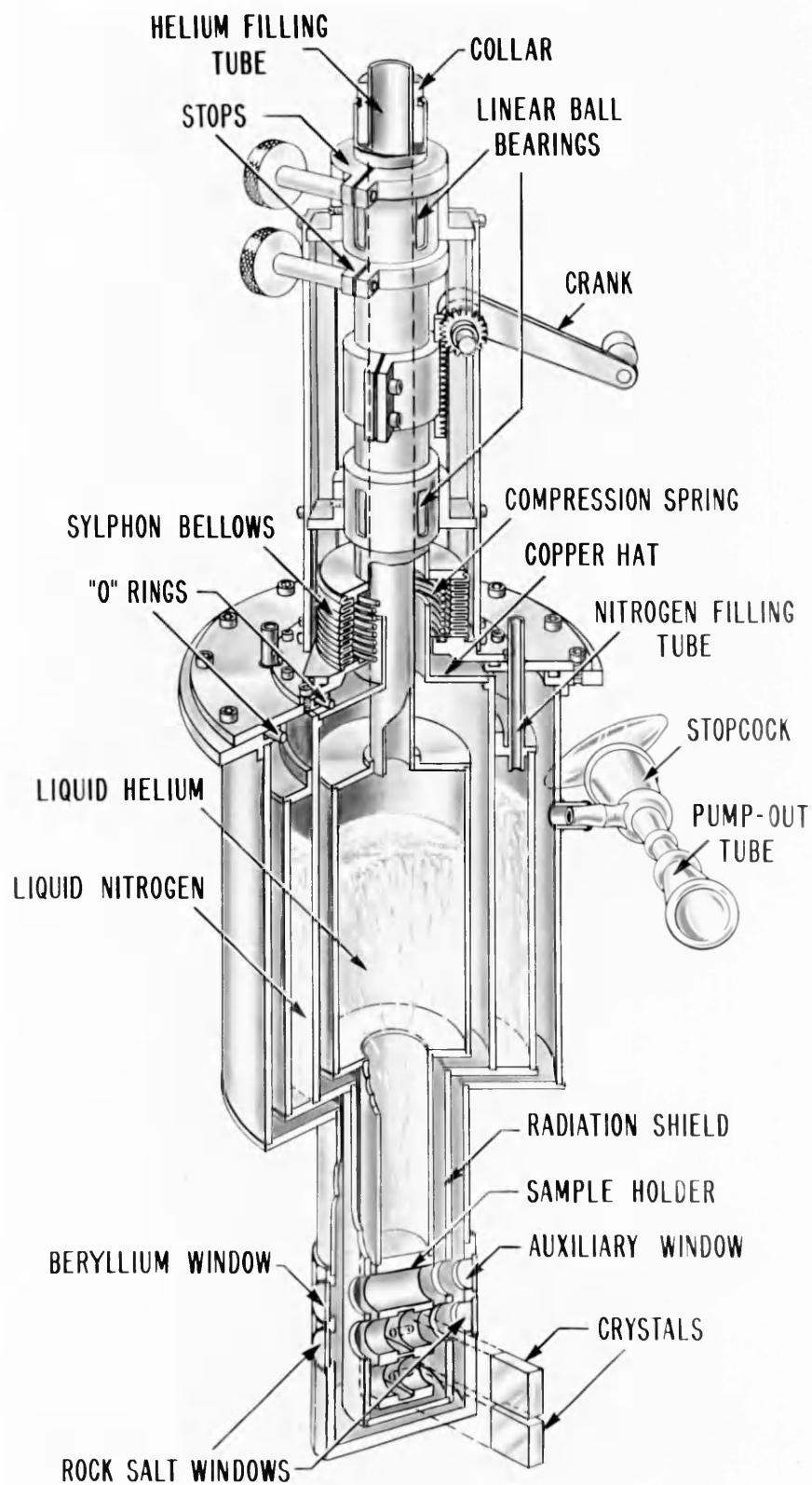
Fig. 22 CUT-AWAY DRAWING OF LOW TEMPERATURE OPTICAL CELL.

Fig. 23 DISASSEMBLED CELL, LEFT TO RIGHT; OUTER VACUUM JACKET, LIQUID N_2
CONTAINER AND RADIATION SHIELD, LIQUID He CONTAINER AND SAMPLE
HOLDER.   RADIATION SHIELD FOR HELIUM VESSEL FILLING TUBE
IN FOREGROUND.

A pumpout line through a stopcock is provided by which the cell can be evacuated and then sealed off.

The liquid helium container of 1-liter capacity is suspended from a 5/8" O.D., 0.028" wall stainless steel tube, 17" long which is soldered to a collar at the top. Concentric with the support tube and separated by a vacuum is a 1" stainless steel tube whose lower end terminates at a sylphon bellows. This latter tube is guided in two linear ball bearings and by means of the crank and rack and pinion assembly the helium container can be raised or lowered. Within the bellows is a coiled compression spring to lessen the work required to extend the bellows, which is under atmospheric pressure during operation. A total vertical displacement of the liquid helium container of about 2" has been achieved with this arrangement.

The low heat of vaporization of liquid helium, 4.93 cal/gm[1] necessitates a high degree of thermal isolation of the helium vessel. A low heat input by conduction is achieved through the use of the long 18-8 stainless steel tube, its thermal conductivity being about 0.039, 0.032 and 0.001 cal/cm/sec/°C at 298°, 77°, and 4°K, respectively.[2] This marked drop in conductivity at low temperatures is particularly advantageous since the temperature profile through the tube length is lowered by heat exchange of the tube with the effluent helium gas.

[1] A. Wexler, Westinghouse Research Laboratories Scientific Paper 1558 (1951).

[2] J. E. Zimmerman, Thesis, Carnegie Institute of Technology (1951).

Radiation losses have been minimized by reducing the emissivity through copper plating[1], and by designing the cell so that the liquid helium vessel "sees" nothing warmer than $77^{\circ}K$, except for the radiation through the windows. A small metal disc shown in the foreground of Fig. 23 is suspended from the top (by a thin stainless steel rod) two-thirds of the way into the helium vessel filling tube. The disc is cooled by the exit helium gas and prevents radiation being funneled in by this path.

The upper part of the liquid helium container and a portion of the filler tube are shielded from room temperature by means of the copper "hat". On assembly, this "hat" falls into place on an extension of the liquid nitrogen vessel and rests in that position without making contact with the helium container.

The liquid nitrogen container is suspended from the top plate by two filling tubes with two additional support rods (not shown) displaced at 90° from the filling tubes for added rigidity. The lower end of the assembly is a heavy-walled copper heat shield which, through cooling by conduction, is effectively at $77^{\circ}K$. The heat shield at its lower end is drilled out in accordance with the window design.

The body of the outer can is of 0.040" wall stainless steel to reduce the weight of the assembly. At the lower end seats have been machined to which the various windows are sealed with baked Glyptal.

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[1]A. Wexler, Westinghouse Research Laboratories Scientific Paper 1558, page 20 (1951).

With the exceptions noted above, brass was used in the construction.
All joints were silver-soldered. Wherever possible tubes were butted
against oversize end plates which were turned down to size after soldering.
All low temperature radiating surfaces were copper-plated and polished to
a high reflectivity. Whenever possible during construction, sub-assem-
blies of the sections were leak-tested by pressurizing them to about 30
psi and submerging under water. A mass spectrograph helium leak
detector was employed (and was almost indispensable) in leak testing the
assembled cell. Total machine shop time was approximately 150 man-hours.

3. Operation of the Cell.

To operate, the cell is evacuated at a vacuum bench through the
ground glass joint to a pressure of about 10^{-4} mm. The liquid nitrogen
container is filled through an insulated tube. For precooling, liquid
nitrogen is also added to the helium container till liquid just begins
to collect. At this point, if the cell is vacuum tight, the pressure
should drop below 10^{-5} mm. The stop-cock is then closed and the cell
is removed from the vacuum line. After boiling away any liquid nitrogen
remaining in the helium container, it is filled directly from a Collins
Liquid Helium Cryostat. About one liter of liquid helium is required
for precooling.

Since NaCl is only slightly hygroscopic and its transmission
extends from about 170 mμ $\underline{1/}$ to well beyond 15μ it makes an ideal
window material for the cell. Hence, the two lower windows were fitted

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$\underline{1/}$E. G. Schnider and H. M. O'Bryan, Phys. Rev. 51, 293 (1937).

with pieces of carefully cleaved NaCl about 1.5 mm thick and baked on with glyptal. One of the upper windows was a .5 mm thick beryllium disc for x-raying, and the other a quartz disc to permit bleaching the crystal with light simultaneous to x-raying it.

Two slots are available in the crystal holder so that two different samples may be studied in one run. The upper hole in the crystal holder is provided as a blank. This is necessary since the per cent transmission of a crystal is measured by comparing the light incident on a light detector, e.g., photocell with and without the crystal in the light path. In order to x-ray the crystal the crank is turned until the desired crystal is in line with the Be window.

Some difficulty is encountered in making thermal contact between the crystals and sample holder. Silicone grease loaded with #325 mesh silver dust, silver conducting paints and soldering with indium have been employed for thermal bonding and bring the crystal to about 5° to $8^{\circ}K$. Other methods are being sought for better bridging this interface. A gold-cobalt alloy versus copper (or constantan) thermocouple[1] was employed to measure the temperature with the junction inserted in a hole drilled in the middle of the crystal. When liquid N_2 was used as the coolant, the crystals were brought very close to $78^{\circ}K$ as measured by a constantan copper thermocouple.

The helium vessel has a large moment of inertia and small lateral rigidity by virtue of its suspension from the top by the long thin

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[1] W. H. Keesom and C. F. Matthijs, Physica 2, 623 (1935).

stainless steel tube. This results in vibration of the crystal holder with amplitudes up to 1/8" when the vessel is raised or lowered or when the cell is moved. However, the vibration damps out in a matter of seconds.

The level of liquid He in the container has been most satisfactorily determined by lowering into the vessel a 200 ohm, $\frac{1}{2}$ watt carbon resistor connected to an ohmeter. When the resistor encounters the liquid, the resistance increases sharply to approximately 10 K ohms. The operating time remaining for any given amount of liquid can be evaluated by measuring the rate of helium gas evolved with a gas flow meter. For a qualitative measure of the gas flow rate and a sign of when the liquid helium is exhausted, a simple bubbler has been satisfactory.

A single filling of one liter of liquid helium has lasted for over 20 hours. If the cell is properly vacuum tight, the liquid helium container serves as the vacuum pump and thus the cell need not be returned to the external pump-down system at any time during the run, making the cell completely portable.

When several consecutive runs were to be made as in the growth-rate experiments and the crystal had to be bleached by heating to 200 or 300°C, this was done by inserting an electric heater in the form of a 100 watt cal-rod. The temperature was measured with a thermocouple. Since the heating was necessary only for two or three hours, the outside of the cell remained at room temperature as long as a good vacuum was maintained in the cell.

D. X-Raying, Bleaching and Measurement of the
Absorption Spectrum of the Crystals

1. General Method.

After a crystal had been cooled to liquid helium in the cell, its

per cent transmission I_o was measured from 210 mμ to 1200 mμ on a

Beckman Spectrophotometer Model DU (see Fig. 24) and from 1200 mμ to

the infrared absorption limit of the crystal or 15 μ , whichever was

less, on a Perkin-Elmer Infrared Spectrophotometer using a Golay

detector.[1] For the self-trapping experiments the spectral region of

1.2 μ to 3.3 μ was also measured on a rapid scanning spectrophotometer.[2]

The cell was then mounted as in Fig. 25 on a Picker X-ray Diffrac-

tion Unit using a Macklett No. C-524A molybdenum target x-ray tube with

a maximum rating of 50 kv and 50 ma, and a thin beryllium window. With

the cell in position the crystal was about 1 3/16 inches from the x-ray

window. For the growth rate experiments the x-ray voltage was kept

constant by manual adjustment of a variac connected to the input.

Regulation to within 0.4 per cent was achieved by this technique.

The x-ray current was also kept constant by manual adjustment to within

2 per cent. After x-raying the crystal, the transmission I was again

measured on the spectrophotometers.

2. Measurement of Spectrum from 210 to 1100 mμ on the Beckman
Spectrophotometer.

A special cell-holder housing was built for the Beckman so that the

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[1]This detector makes use of the motion of a diaphragm caused by
changes in the pressure of a gas due to the incident light energy from
the monochromator.

[2]R. Bullock and S. Silverman, J. Opt. Soc. Am. 40, 608 (1950).

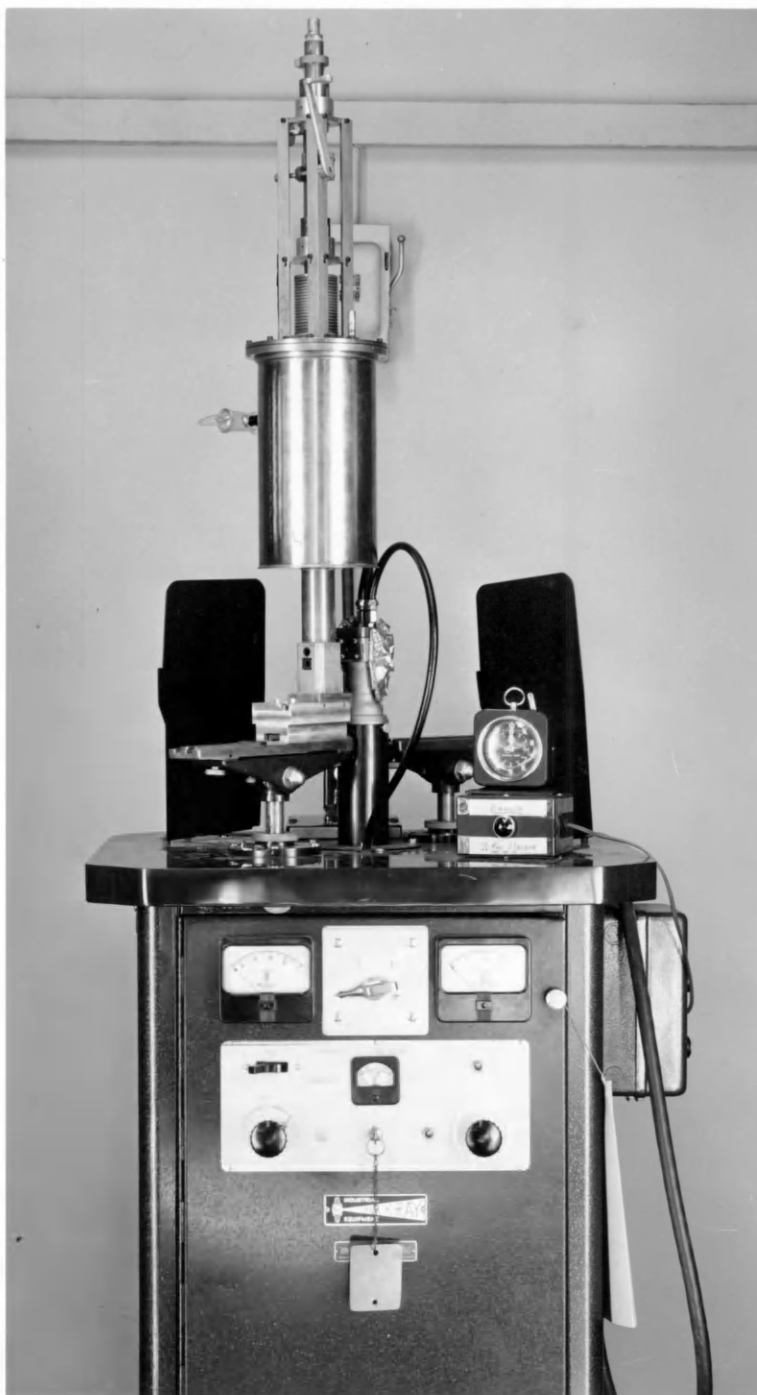Fig. 24   LOW TEMPERATURE CELL USED WITH BECKMAN SPECTROPHOTOMETER.

Fig. 25 LOW TEMPERATURE CELL MOUNTED ON x-RAY UNIT.

cell could be placed between the exit slits of the quartz-prism mono-
chromator and the photocell with a position accuracy of .02 inches.
In order to make a per cent transmission measurement, the vacant hole
in the cell holder is lowered with the crank into line with the two
NaCl windows. This is done by first adjusting the upper stop with a
special positioning bar, permitting an adjustment of the stop to about
.01 inches.[1] The smallest slit opening necessary was then used to
obtain a zero balance of the instrument photocell current for any given
wavelength. Then the lower stop is adjusted so that when the crystal
holder is raised the desired crystal will move into line with the windows.
Then a potentiometer, calibrated to read the per cent transmission
directly, is adjusted until the instrument is again balanced.

The ultraviolet spectrum is obtained with a hydrogen discharge lamp
source and the visible with a tungsten lamp. By using minimum slit
openings the resolution obtained is very satisfactory for determining
the fine details of the absorption band structures. The spectral band-
width used in the experiments was about 11 $\overset{o}{A}$ in the range 210 to 300 mμ
and about 25 $\overset{o}{A}$ from 300 to 1100 mμ . This was obtained from the data
of Haendler[2] who calculated the spectral band width as a function of wave-
length and slit opening.

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[1] A set of these position bars was made for all positions required of
the cell holder, i.e., placing either crystal in front of the NaCl win-
dows or the x-ray window in addition to the above-mentioned blank hole
position. Since the variation in length of the overall helium vessel
and tube was considerable with the temperatures employed, a separate set
of these positioning bars was made for liquid helium, liquid nitrogen and
room temperature measurements.

[2] H. Haendler, J. Opt. Soc. Am. 38, 417 (1948).

With the above accuracies of positioning the cell in the Beckman holder and adjusting the crystal holder stops, the per cent transmission readings could be repeated to better than ± 0.5 per cent transmission. This accuracy is constant over the entire range of per cent transmission, the error being caused by the above positioning and the ability of the operator to adjust the wavelength dial and balance the instrument. Once the cell is in place and the stops adjusted, readings could be repeated to better than ± 0.3 per cent transmission. For readings of less than 10 per cent in the growth rate curve experiments, several readings were taken and an average of these used.

In all but the growth-rate curve experiments the ± 0.3 per cent repeatability was the important accuracy figure, for it is required to differentiate the position and shape of the absorption bands. This accuracy is unnecessary in determining the absolute number of centers. Other factors of much larger magnitude, to be discussed shortly, affect this number.

3. Measurement of Spectrum from 1 to 15 μ on the Perkin-Elmer Spectrometer.

The operation with the Perkin-Elmer Spectrometer is very similiar to that of the Beckman, except that it employs an automatic recording device. With this unit the light from the globar source is chopped 13 times per second by a rotating shutter, then passed through the cell and into the monochromator, using an LiF or NaCl prism, and thence to the Golay detector. The ac signal from the Golay is amplified, rectified and recorded on a Brown pen recorder. The spectrum is slowly swept by means of rotating the prism from a motor driven shaft,

wavelength calibration points from a ratchet mechanism on the drive shaft being recorded simultaneously with an extra pen. Here again two runs are made, one before x-raying to measure I_o, and the other after x-raying to measure I.

Because the inherent noise level in the overall system is of the order of 2 to 3 per cent, and the stability is about 2 per cent, individual points can be taken from the pen record with an absolute accuracy of about 4 or 5 per cent. However, this instrument was used only to look for an indication of any absorption bands in the infrared and as such would be able to discriminate a band of only 3 or 4 per cent absorption (i.e., 100 per cent less the per cent transmission) change. Hence, even as weak an absorption band as that would be quite distinguishable on the record.

Because of the nature of the detectors used for the infrared detection in the Perkin-Elmer, it was necessary to place the cell in front of the globar light source rather than at the exit slits of the monachromator. This was occasioned by the fact that if the cell were placed in front of the detector it radiated so strongly to the liquid helium temperature surfaces inside the cell that it became unstable. An entirely new detection technique would be required to make this possible. Placing the cell directly in front of the light source presented the possibility that any trapped color centers might be bleached before their spectrum was obtained. For this reason the spectrum was run as rapidly as possible, but this still entailed approximately 10 minutes.

4. <u>Measurement of the Spectrum from 1 to 3.5 μ on the Rapid</u>
   <u>Scanning Spectrometer.</u>

The rapid scanning spectrometer solved this problem in the region
of 1 to 3.5 μ. With this device the reflecting mirror behind the prism
is vibrated at about 120 cycles per second and by the use of a semi-
conductor detector, such as lead selenide which has a photo response
time of the order of 100 kilocycles, the entire spectrum can be ob-
served on a cathode ray oscilloscope 120 times per second.

A special light tight housing was built for the cell between the
Nernst Glower light source and the entrance slits to the monochromator.
An ordinary camera shutter was built into the housing on the light
source side and a tube in line with this shutter installed on the other
side leading to the entrance slits. Then the crystal could be raised in
line with the cell windows which were in line with the shutter and exit
tube without any light falling on it. The shutter of a Polaroid Land
Camera viewing the oscilloscope was opened and then the shutter in front
of the crystal opened for about 1/50 second, during which time two
complete spectra were photographed. Thus one complete spectrum was
obtained within 1/100 second after the light from the Nernst Glower
source first contacted the crystal almost eliminating the possibility of
bleaching before observation.

In spite of the rapid sweep rate the detector and amplifying system
had high enough frequency response to provide a sufficient system band-
width so that absorption bands of only 4 to 5 per cent absorption and
less than 0.1 μ in width could be resolved. This data was obtained by
observing materials (e.g., frozen acetone) which had narrow, weak

absorption bands in the region the spectrometer covered.

5. **X-Raying and Bleaching the Crystals.**

A cell holder was also built for the Picker x-ray unit, designed so that the cell could be positioned with an accuracy of better than .05 inches in front of the x-ray tubes beryllium window. Again such accuracy was necessary only in the growth rate curve experiments where the cell was mounted and removed many times during a single run. A positioning bar again permitted the crystal under observation to be raised to a position in line with the cell's beryllium window with an accuracy of better than .01 inches.

With the exception of the F'-bleaching experiments proposed in Chapter III-C, the crystal was kept in the dark during x-raying by the thin lead sheet wrapped about the base of the cell and the x-ray tube.

For the F'-bleaching work the lead sheet was peeled back to expose the quartz window opposite the cell's beryllium x-ray window. A 250 watt projector bulb was mounted 2 inches from this quartz window and the proper Corning glass filters[1] placed against the window so that only F'-light could reach the crystal during x-raying. The x-rays and bleaching light were turned off and on together.

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[1] For KCl a combination of Corning Glass Color Filters 2-58 and 2-64 were used. This insured a very sharp cut-off of light below 650 $m\mu$ and good transmission of light from 670 $m\mu$ out to 2.7μ . For KBr a combination of Filters 2-64 and 7-57 giving a cut-off below 680 $m\mu$ were used.

6. __Measurement of Absorption Coefficient and Number of F-Centers.__

In order to conform with the usual practice, all data will be given

in terms of $\log_{10} I_0/I$ where

$$I_o = \text{per cent transmission of crystal before x-raying;}$$

$$I = \text{per cent transmission of crystal after x-raying.}$$

Thus $\log_{10} I_0/I$ is proportional to the actual absorption coefficient ob-

tained from Lambert's formula

$$I = I_o e^{-Kd}$$

given in Section III. Since the x-rays do not color the crystal uni-

formly but rather penetrate a short depth in an exponential fashion,

it is very difficult to obtain d. Dorendorf[1] gives the depth at which

the coloration is $\frac{1}{2}$ its maximum as 0.2 mm for KCl and 0.8 mm for KBr

which had been x-rayed in a similar manner to the crystals used for

this paper. By x-raying the crystals at room temperature and then

cleaving them perpendicular to the x-rayed face into very thin slices

which were then placed under a traveling microscope, the half depth of

coloration could be estimated. After 30 minutes x-rays (50 kv-30 ma) the

following half depths were measured:

KCl   .06 mm.

KBr   .08 mm.

NaCl .07 mm.

When the value of the per cent transmission after x-raying I

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

falls below two per cent, the error of $\pm$ 0.5 per cent occurring in the Beckman measurements will cause larger errors in $\log_{10} I_o/I$. In certain cases, e.g., growth rates of F-band, it is important to obtain the value of $\log_{10} I_o/I$ for the F-band when I is considerably less than 2 per cent. . In these cases the half-width measurement was used. This is possible because the half-width (width at the points of one-half the maximum of $\log_{10} I_o/I$) of the F-band is constant at any given temperature. Thus an accurate half-width value would first be obtained for small F-bands, i.e., for values of I much larger than two per cent. Then the points on both sides of the large F-band maximum whose value is to be obtained are carefully plotted on a suitably large graph to which the known half width can be applied, giving the value for $\frac{1}{2} \log_{10} I_o/I$. Repeated checks of this method on small F-bands (I less than 2 per cent) showed it to be accurate to about 3 per cent of $\log_{10} I_o/I$.

CHAPTER V

RESULTS AND CONCLUSIONS

A. Experimental Search for the Self-Trapped Electron
in Alkali Halide Crystals

1. Results and Discussion of Experiments.

The infrared absorption spectra of NaCl, KCl, KBr, NaF and KF were
examined at $5^\circ K$ $\underline{1/}$ and that of LiF at $78^\circ K$. The choice of these par-
ticular alkali halides was based on their availability and on the calcu-
lations and experiments of previous workers. In every run absorption
bands were observed in the region to the ultraviolet of the F-band but
none can be definitely attributed to self-trapped electrons as will be
discussed in Chapter V-B. The runs made for each crystal, the method
of obtaining the absorption spectrum for the region noted and the
observed bands are given in Table II. (The F- and ultraviolet bands are
not included here but will be discussed in Chapter V-B).

The broad band at 2.7 μ appearing in the first run of NaCl was
never duplicated in any of the four succeeding runs. The detector
circuit of the Perkin-Elmer spectrometer was exceptionally noisy and
unstable during the first run. This coupled with the fact that 2.3 μ
is also the peak of the globar infrared source used on the Perkin-Elmer

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[1]This figure will be used throughout to signify the approximate
temperature of a crystal when liquid helium was used as the coolant
in the low temperature cell.

Table II. Summary of Runs Made in Search for Absorption Band Related to Self-Trapped Electrons

Crystal	Date of Run	Temp.	X-Ray Time Intensity	Measuring Instrument Used for Various Spectral Regions		Bands Observed
NaCl #1	6/14/51	5°K	45 min. 50 kv-20 ma and 140 min.	210-1200 mμ 1 - 3.1 μ	Beckman Perkin-Elmer	Broad band peaking at 2.27 μ
NaCl #2	8/29/51	5°K	3 1/2 hrs. 50 kv-20ma	210-1200 m μ 1 - 5 μ	Beckman Perkin-Elmer	No bands to infrared of F-band
NaCl #3	9/6/51	5°K	4 hrs. 50 kv-20 ma	210-600 m μ 1 - 15 μ	Beckman Perkin-Elmer	Possibly a very slight F'-band. No other bands.
NaCl #4	12/12/51	5°K	2 1/2 hrs. 50 kv-48ma	210-600 mμ 1 - 3.2 μ 1 - 6 μ	Beckman Scanner	Possibly a very slight F'-band. No other bands.
NaCl #5	12/20/51	5°K	1 hr. 50 kv-48 ma	210-600 mμ 1 - 3 μ	Beckman Scanner	Possibly a slight F'-band more apparent than previous runs. No other bands
KCl #1	5/4/51	5°K	30 min. 50 kv-20 ma	210-1200 m μ	Beckman	No bands to infrared of F-band
KCl #2	8/30/51	5°K	106 min. 50 kv-20ma	210-1200 m μ 1 - 15 μ	Beckman Perkin-Elmer	No bands to infared of F-band
KCl #3	12/20/51	5°K	1 hr. 50 kv-48 ma	210-600 m μ 1 - 3 μ	Beckman Scanner	No bands to infrared of F-band
KBr #1	9/26/51	5°K	1 hr. 50 kv-20 ma	210-1200 m μ 1 - 15 μ	Beckman Perkin-Elmer	No bands to infrared of F-band
NaF #1	4/20/51	78°K	20 min. 50 kv-20ma	610-1200 m μ	Beckman	Broad band to infrared of F-band peaking at 600 mμ
NaF #2	9/7/51	5°K	1 hr. 50 kv-20 ma	210-1200 mμ	Beckman	Broad band to infrared of F-band peaking at 650mμ which decays slowly at 5°K
KF #1	9/26/51	5°K	3 hrs. 50 kv-20 ma	210-1200 m μ 1 - 6 μ	Beckman Perkin-Elmer	No bands formed to infrared of F-band
LiF #1	5/27/51	78°K	20 min. 50 kv-20 ma	210-1200 mμ 1 - 5 μ	Beckman Perkin-Elmer	Broad band to infrared of F-band peaking at 345 mμ.

spectrometer could account for this result. If there were a band of this nature in this region, the Rapid Scanning Spectrometer would certainly have detected it in the other runs. Hence it is concluded that no bands appear in NaCl at 5°K to the infrared of the F-band with the exception of the possible F'-band, to be discussed later.

A similar conclusion can be made for KCl, KBr and KF at 5°K, not even an F'-band being observed to the infrared of the F-band.

The broad band appearing in NaF at 5°K and 78°K and in LiF at 78°K is seen in Figs. 26, 27 and 15. From its shape, position and bleaching effects, this band is apparently caused by the same center in both crystals. Since Markham and Seitz estimate a band possibly in the visible spectral region that is stable at 78°K for self-trapped electrons in LiF, it is important to examine the experimental data on this band in both LiF and NaF. From the work of Pringsheim and Yuster[1] the following data are available on this band in LiF:

(1) When LiF is x-rayed or subjected to 1-Mev electrons at 78°K a broad band at 345 mμ appears with intensity comparable to that of the F-band.

(2) While the F-band is about .65 ev wide (width at half amplitude) this band is about 1.2 ev wide.

(3) With increasing x-rays the 345 mμ band approaches saturation while the F-band continues to grow.

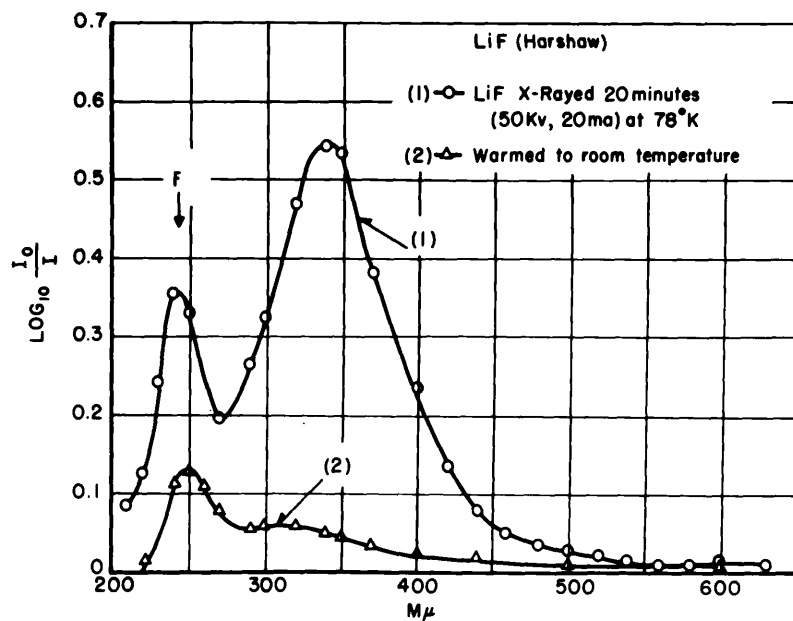[1] P. Pringsheim and P. Yuster, Phys. Rev. 78, 293 (1950).

Fig. 26

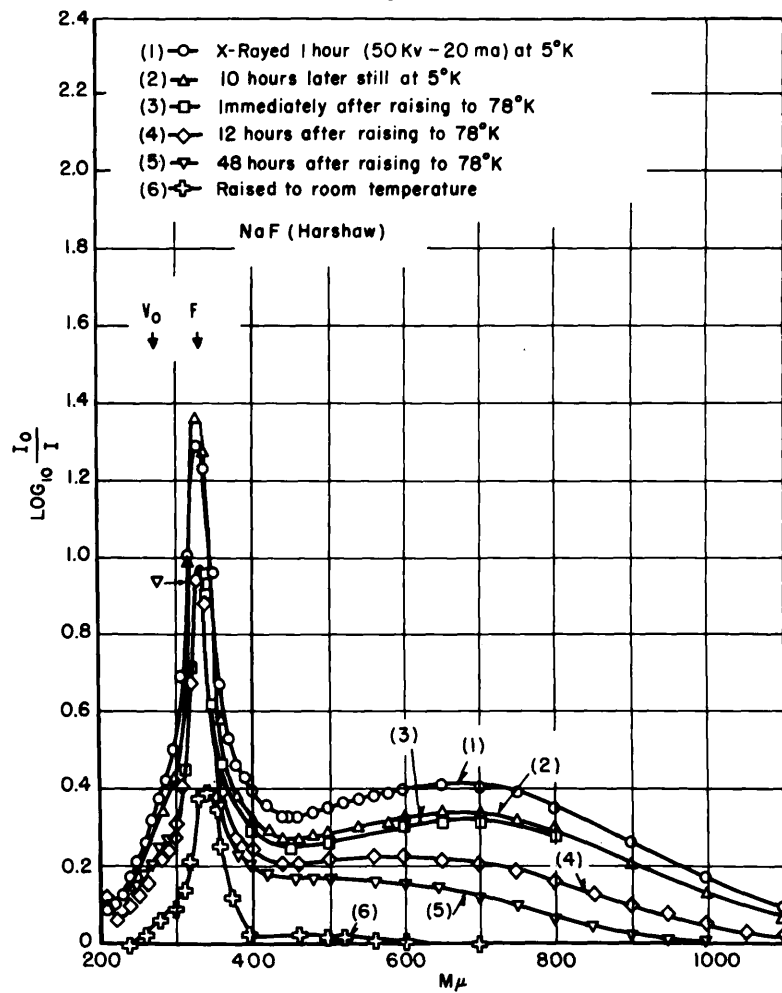Fig. 27

(4) Warming to room temperature bleaches the 345 mμ band with a burst of luminescence at 138°K and the F-band is diminished to about 50 per cent of its initial intensity at 78°K.

(5) The 345 mμ band can be bleached with light within its band at 78°K while the F-band remains unaffected during the bleaching. If the crystal is now warmed to room temperature, there is very little luminescence.

(6) In a heavily bombarded crystal after the 345 mμ band has bleached and the crystal is at room temperature, a band forms at 620 mμ which then bleaches to form a band at 445 mμ which is very stable at room temperature.

In addition to these observations, the work done on LiF at 78°K for this dissertation (see Fig. 26) shows that the 345 mμ band can become considerably more intense than the F-band at 78°K. Also on warming to room temperature, the F-band does not decrease to 50 per cent but only to about 70 per cent of its former value if the difference in half width of the F-band at 78°K and 293°K is taken into account. Finally, when the 345 mμ band has bleached at room temperature a small band around 320 mμ appears to remain, indicative of an F'-band, although this band has not been found previously in LiF.

The author has found that for NaF (see Fig. 27):

(1) 50 kv x-rays produce a broad absorption band at 5°K peaking at 670 mμ with a half width of about 2.0 ev.

(2) The 670 mμ band decays slowly at 5°K while the F-band remains nearly constant.

(3) Warming from 5°K to 78°K results in a further decrease of the 670 mμ band and a 22 per cent reduction of the F-band, not making any correction for a change in half width since the half widths are unattainable in the presence of the broad 67° mμ band.

(4) This band continues to decay at 78°K with no measurable effect on the F-band. As the band bleaches at 78°K a broad second band at 500 mμ becomes apparent.

(5) Upon warming to room temperature the rest of the 670 mμ band bleaches at a temperature near 218°K leaving the 500 mμ band which is stable at room temperature. The F-band decreases to about 53 per cent of its value at 78°K and 30 per cent of its original value at 5°K correcting only for the change in half width at room temperature and 78°K.

Several possibilities for the model of the center causing the broad band in both LiF and NaF at low temperature can be eliminated. The fact that the F-band is unaffected by the bleaching of this band eliminates the possibility of its being an F'- or trapped-hole center. If it were an F'-center, the F-band would increase with its bleaching. If it were a trapped-hole center, the released holes would bleach the F-band.[1]

It would seem then most probable that this band is caused by a center (other than an F') at which one or more electrons are trapped. The width of the band is not suggestive of the numerous impurity bands

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[1] See R. Casler, P. Pringsheim and P. Yuster, J. Chem. Phys. 18, 1564 (1950) where bleaching of the V_1-band in KCl by either light or thermal action release holes which bleach the F-band. This will be discussed further in the succeeding sections.

which are usually much narrower as a review of the literature will
reveal.[1] Further, such a trapping center would have almost zero
mobility at low temperatures and this would not account for the slow
decay of the band in NaF. Unfortunately, it is not certain that the
light required to take readings on the Beckman did not cause some or
all of the bleaching. Therefore, this decay cannot be relied on and
further experiments are required to substantiate it.

One difficulty in understanding these broad bands in LiF and NaF
is their apparent lack of effect on the F-band when they bleach.
While trapped holes and an F'-center seem unlikely as the model, if
electrons are released, some of them should fill incipient negative-
ion vacancies and thus increase the F-band. This would be true unless
no incipient vacancies are present after several minutes of x-raying.
Hence, it has not been definitely established whether or not this is
a self-trapped electron band, although this is probably one of many
possibilities.

2. Conclusions.

The absence of any bands in NaCl, KCl and KBr at 5°K suggests that
if the self-trapped electron exists, it diffuses easily through the
lattice, even at 5°K. Thus, the binding energy would not be greatly
affected by the mean location of the electron, i.e., it can jump from
a position of minimum binding energy to another even at these low
temperatures, as suggested by Markham and Seitz.[2] Perhaps at lower

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[1] See Impurity Bibliography, Appendix 1.

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

temperatures one might be able to freeze the electron at a lattice point long enough to be observed. In any event, the results appear to provide a strong justification for disregarding the lattice structure of the crystal above 5°K as was done by Fröhlich, Pelzer and Zienau.[1]

The broad bands in LiF and NaF will require a considerable amount of further experimentation before any model can be ascribed to them. The effect on them of irradiating the F-band with F-light appears to be a possibly profitable experiment, since the electrons released from the F-centers might be captured in the centers forming these broad bands. In any event there is so little evidence to indicate the nature of these bands that the conclusions in the previous paragraph seem very justifiable for the general case.

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[1] H. Frohlich, H. Pelzer and S. Zienau, Phil. Mag. 41, 221 (1950).

B. Study of Color Centers Produced by X-Raying Alkali
Halides at Liquid Helium Temperatures

The crystals x-rayed at 5°K were NaF, KF, NaCl, KCl and KBr. The

F-band in NaF and KF is too close to the ultraviolet limit of the

Beckman Spectrophotometer to determine any significant V-band structure

beyond the band which usually occurs on the short wavelength tail of the

F-band.[1] The ultraviolet bands in NaCl, KCl and KBr are sufficiently dis-

placed toward the red, however, so that many of them could be measured

on the Beckman.

In addition to the formation and growth of the ultraviolet bands, the

growth and wavelength of the peak and half-width points of the F-band at

5°K are important as was briefly mentioned in Chapter III-B.

The observations made on the color centers formed by x-raying NaCl,

KBr and KCl at 5°K will be presented in the following manner. The results

for each crystal will be given in separate sections, each starting with a

table of the presently known bands, including the wavelength maximum and

temperature at which they were measured. A reference will be given with

each band which is not intended to exclude the fact that other workers

have observed it but is meant to be a lead reference. The new bands found

by x-raying at 5°K are also included in the tables. Since their exact

nature is not definite, some of them will be labeled H-bands for their

occurrence at liquid helium temperatures. The rest will not be labeled

at all, but will be described only by their wavelength at 5°K. Follow-

ing the tables, a description of the experimental results will be given.

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[1]For convenience this band will be called the V_0-band. See Figs. 19
and 20 for its appearance in KCl and KBr.

After the results have been given for each crystal a special set of experiments will be described for KBr. These are intended to give further evidence on the nature of some of the H- and V- bands as well as the growth processes occurring during x-raying. These experiments evolved from the initial results in NaCl, KCl and KBr which are described below.

1. Experimental Results and Conclusions for NaCL.

Table III. Wavelengths of the Maximum of
Various Bands Observed in NaCL

Band Name	$V_3^{1/}$	$V'^{1/}$			$V_1^{1/}$	$F^{2/}$	$F'^{4/}$	$R_1^{3/}$	$R_2^{3/}$	$M^{3/}$
Wavelength mμ	210	223	260	330	345	454	510	540	595	710
Temperature	Room	Room	5°K	5°K	80°K	20°K	140°K	90°K	90°K	90°K

Careful measurements have been made on the F-band so that the peak and half-widths are well known. For NaCl at 20°K Mollwo[2] presents the following data for the F-band produced at room temperature:

$$\lambda_v = 426 \text{ m}\mu$$

$$\lambda_m = 454 \text{ m}\mu$$

$$\lambda_r = 482 \text{ m}\mu$$

[1] R. Casler, P. Pringsheim and P. Yuster, Phys. Rev. 18, 1564 (1950).

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

[3] J. P. Molnar, Ph.D. Thesis, M.I.T., 1940.

[4] A. Smakula, Z. Physik 59, 603 (1930).

λ_m is the wavelength at the peak of the F-band. λ_v is the wavelength on the ultraviolet side of λ_m and λ_r the wavelength on the infrared side where $\log_{10} I_0/I = \frac{1}{2} \log_{10} I/I_{max}$. Mollwo's values agree with the measurements at $90^\circ K$ of Molnar.[1] Flechsig[2] has measured at $90^\circ K$ the F-band produced at room temperature by x-rays in natural and synthetic NaCl. All values of λ_v agree very well; however, Flechsig's value of $\lambda_r (505$ mμ) on synthetic crystals disagrees with the one given above.

Figure 28, curve 1, shows the absorption spectrum of a Harshaw NaCl crystal which has been exposed to x-rays (50 kv-48 ma) at $5^\circ K$ for two hours. The effects of raising the crystal to $78^\circ K$ after this exposure are also shown in this figure. The following conclusions can be made:

(a) An F-band comparable in size with those produced at $78^\circ K$ and higher temperatures appears at $5^\circ K$ with the following values:

$$\lambda_v = 426 \text{ m}\mu$$

$$\lambda_m = 450 \text{ m}\mu$$

$$\lambda_r = 471 \text{ m}\mu$$

The values of λ_v and λ_{max} agree with previous measurements but λ_r disagrees and the difference is too large to be ascribed to experimental error. Four other separate runs also using Harshaw NaCl produced spectra substantiating Fig. 28. On three of these, the x-ray tube was run at 50 kv-20 ma and in the other at 50 kv-48 ma. The variation of the λ's between the runs is less than 1 mμ and the average

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[1]Molnar, loc. cit.

[2]W. Flechsig, Z. Physik. 36, 605 (1926).

value has been given above.

(b) In Fig. 29, $\log_{10} I_o/I$ is plotted against time of exposure to
x-rays. Similar data taken on the other runs support this data. These
curves should be compared with similar curves given by Harten[1] and in the
next section (C) at higher temperatures.

(c) In NaCl the F'-band is difficult to detect since the F-band
overlaps it. In three runs at 20 ma, no indication of an F'-band ap-
peared. The runs at 48 ma, however, indicate a rise on the infrared
side of the F-band. This might be interpreted as an F'-band which
appears when the intensity of x-radiation is high.

(d) The M- and R- bands do not appear.

(e) A broad well-defined band forms at 330 $m\mu$ which is not the
V_1-band. The V_1-band is produced by x-raying at 78°K, and is much
narrower (see item h below).

(f) A band has been measured at 260 $m\mu$. A second weak band may
form at 230 $m\mu$ although the data does not establish this band con-
clusively.

(g) The data suggests the possibility of a band between the F-band
and the 330 $m\mu$ -band. The band would correspond to the V_o-band which
will be described in KCl.

(h) Heating to 78°K causes the 330 $m\mu$ band to disappear and the V_1-
band to appear. When measured immediately after warming to 78°K, the
absorption maximum of the V_1-band has grown higher than the 330 $m\mu$

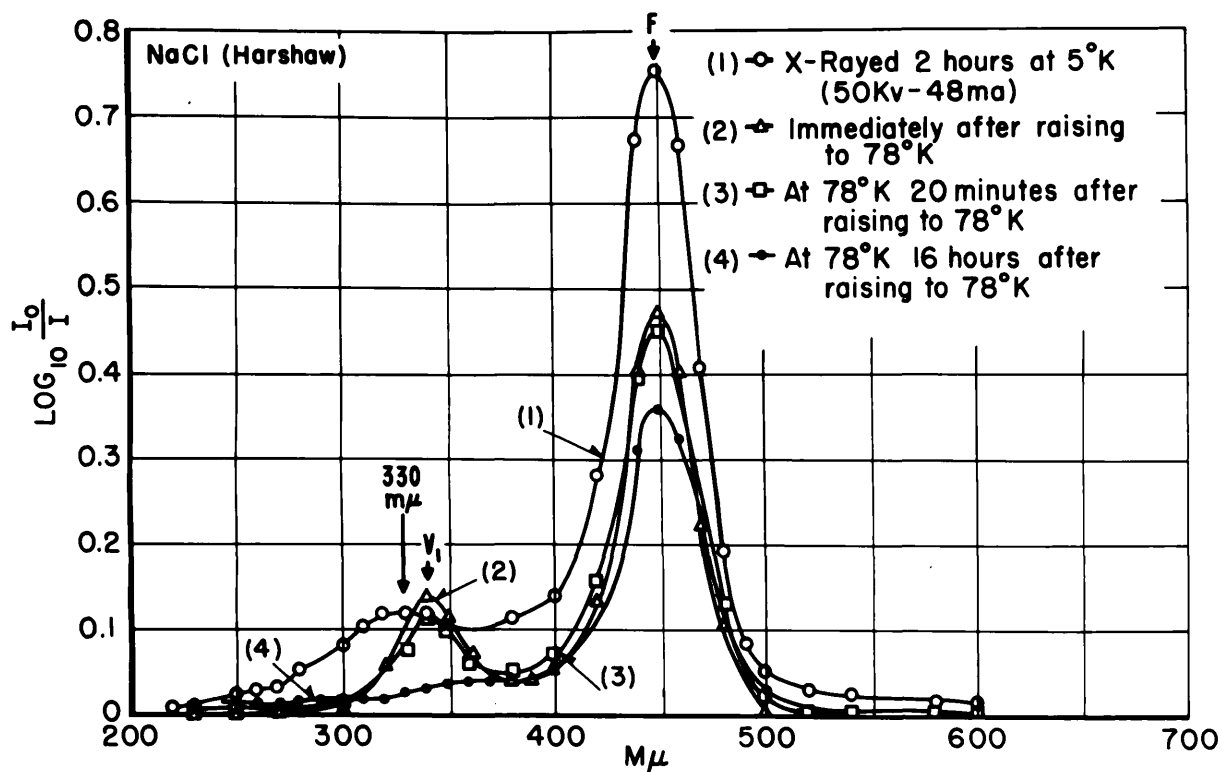[1]H. Harten, Z. Physik. <u>126</u>, 619 (1949).
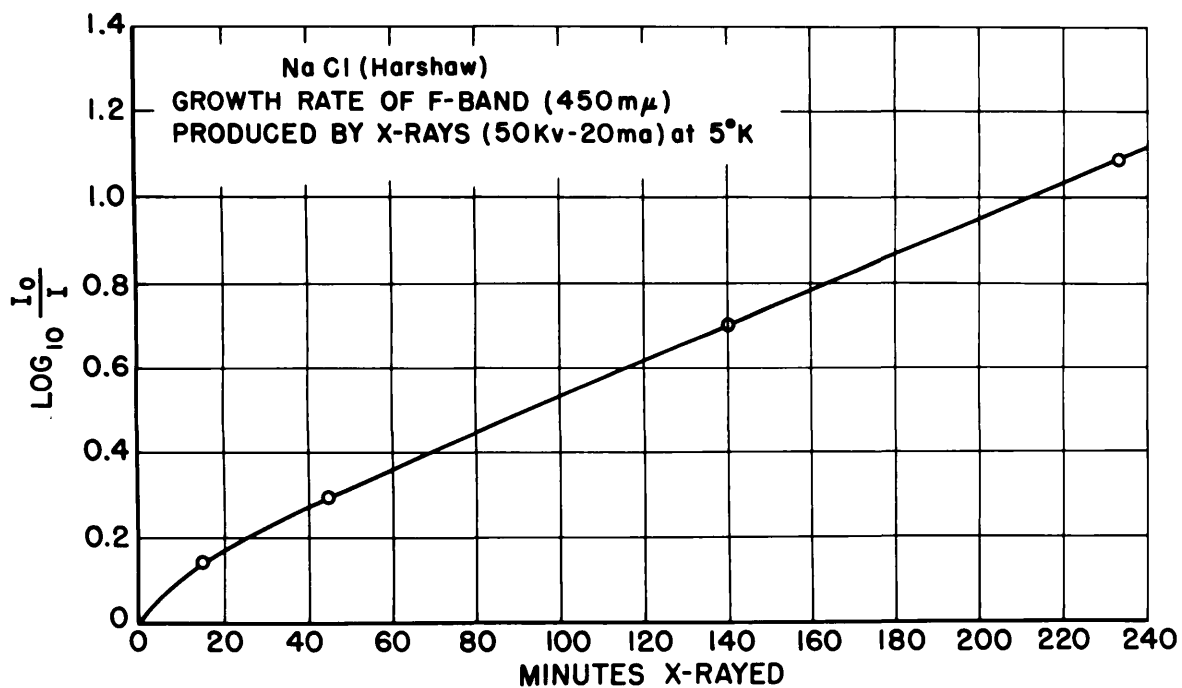
Fig. 28

Fig. 29

band was previously. With this occurrence the number of F-centers[1] is reduced to about 60 per cent of its previous value at $5°K$ (curve 2 of Fig. 28).

(i) The effect described in (h) occurs immediately after warming to $78°K$ and is followed by a gradual bleaching of both the V_1- and F-bands until the V_1-band is gone (curves 3 and 4 of Fig. 28). The F-band is now reduced to about 48 per cent of its previous value at $5°K$ and no further changes occur.

(j) Warming to $78°K$ causes a small change in the width of the F-band, i.e.,

$$\lambda_v = 427 \ m\mu$$

$$\lambda_m = 450 \ m\mu$$

$$\lambda_r = 473 \ m\mu$$

Crystals x-rayed initially at $78°K$ have, within the accuracy of the author's measurements, the same values of λ_v and λ_r. Mollwo's values

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[1]This difference in the number of F-centers is obtained from Smakula's equation given in Chapter II-B. Since nothing changes on warming to $78°K$ but the half-width W and the absorption constant K_e, the ratio of the number of centers at $5°K$ to the number at $78°K$ is simply

$$\frac{N_o(5°K)}{N_o(78°K)} = \frac{W(5°K) \times K_e(5°K)}{W(78°K) \times K_e(78°K)} \ ,$$

where all the W's and K_e's can be determined from Fig. 28.

at 90°K for F-centers produced at room temperature are:

$$\lambda_v = 426 \text{ m}\mu$$

$$\lambda_m = 455 \text{ m}\mu$$

$$\lambda_r = 483 \text{ m}\mu$$

Molnar's measurements at 90°K on F-centers produced at room temperatures agree with Mollwo's values. The author x-rayed these same crystals at room temperature obtaining:

$$\lambda_v = 422 \text{ m}\mu$$

$$\lambda_m = 465 \text{ m}\mu$$

$$\lambda_r = 506 \text{ m}\mu$$

in excellent agreement with Mollwo's data at room temperature. Apparently this difference in width is real and consistent.

(k) The number of F-centers occurring after four hours of x-rays (50 kv-20 ma) at 5°K was calculated from Smakula's formula to be about 1.5×10^{18} cm^{-3}. The value 0.07 mm given for d in Chapter IV-D(5) was used. In addition f $= 0.7$, $W_{5^{\circ}K} = 0.27$ ev and n' $= 1.5$ were used.

2. Experimental Results and Conclusions for KCl.

Table IV. Wavelength of the Maximum of the Various Bands Obtained in KCl

Band Name	$V_5^{1/}$	$V_3^{1/}$	$V_2^{1/}$	$V_4^{1/}$	H_2	$V_7^{1/}$	$V_6^{1/}$	H_1
Wavelength mμ	200	212	230	254	255	300	334	345
Temperature	90°K	90°K	90°K	90°K	5°K	90°K	90°K	5°K

Band Name	$V_1^{1/}$	$V_0^{1/}$	$F^{2/}$	$R_1^{3/}$	$R_2^{3/}$	$F'^{4/}$	$M^{3/}$	$N^{5/}$
Wavelength mμ	356	455	550	670	720	750	815	930
Temperature	90°K	90°K	28°K	Room	Room	170°K	Room	80°K

Mollwo's[6] values for the F-band at 28°K are

$$\lambda_V = 515 \ m\mu$$

$$\lambda_m = 540 \ m\mu$$

$$\lambda_r = 560 \ m\mu$$

The value of λ_m and λ_r shift to the infrared with rising temperature but λ_V is apparently constant below 78°K.

The absorption spectrum of a Harshaw KCl crystal which was exposed to x-rays (50 kv-48 ma) at 5°K is shown in Fig. 30, curve 1. Curve 2

[1] H. Dorendorf, Z. Physik 129, 317 (1951). The V_0 band appears when KCl is x-rayed but not when it is colored in a vapor.

[2] Mollwo, loc. cit.

[3] Molnar, loc. cit.

[4] H. Pick, Ann. Physik 31, 365 (1938) and 37, 421 (1940).

[5] E. Burstein and J. J. Oberly, Phys. Rev. 76, 1254 (1949).

[6] Mollwo, loc. cit.

of this figure shows the effect of raising the crystal to 78°K, and

curve 3 to room temperature. Two other runs were made with KCl

at 5°K which substantiate the data. The following conclusions can be

made:

(a) An F-band comparable in growth rate with those produced at 78°K

and higher temperatures appears at 5°K with the following values:

$$\lambda_V = 518 \text{ m}\mu$$

$$\lambda_m = 540 \text{ m}\mu$$

$$\lambda_r = 557 \text{ m}\mu$$

Unfortunately, only one run was made in which it was possible to obtain

the half-width points at 5°K.

(b) There are no indications of any band structure (F', R_1, R_2 and

M) to the infrared side of the F-band.

(c) Two distinct ultraviolet bands are formed. The predominant

band at about 345 mμ is not the V_1-band but is distinctly separate.

It has been labeled H_1. This distinction is not so obvious in KCl as

it is in KBr, as will be seen in the later discussions. The H_1-band in

KCl appears to have a considerably higher growth rate at 5°K than the

V_1 does at 78°K.

The V_o-band appears here as it does at higher temperatures. A

very small band is indicated at about 255 mμ which is 20mμ to the red

side of the V_2-band and has been labeled H_2. It is not at all certain

that the H_1 and H_2 bands in KCl are caused by the same centers as the

260 mμ and 330 mμ bands in NaCl. Because of their relative positions

in the spectrum of both crystals, however, and the effect on subsequent

warming to $78^{O}K$, there might be some justification for this connection.
Since the so-called V_1-band grows on warming to $78^{O}K$ while entirely
different bands grow in KCl and KBr under the same conditions, doubt is
cast on whether the ultraviolet bands of NaCl have been correctly labeled.
The measurements did not extend far enough to the ultraviolet to measure
V_3.

(d) On warming to $78^{O}K$, the H_2 band apparently disappears and a
band at 238 mμ appears, quite clearly the V_2-band from both its shape
and position, with over twice the height of the small H_2 mμ band it
replaces. It is assumed that a band does not shift to the violet on
warming. Although the above values are only approximate, it is believed
that the difference between 225 mμ and 238 mμ is real.

The H_1-band disappears on the warming to $78^{O}K$ and leaves the usual
V_1-band at 356 mμ . The V_0- and F-bands are reduced to about 45 per
cent of their values at $5^{O}K$ by this warming to $78^{O}K$.

(e) The F-band attains the following values on raising to $78^{O}K$:

$$\lambda_v = 516 \text{ mμ}$$

$$\lambda_m = 540 \text{ mμ}$$

$$\lambda_r = 563 \text{ mμ}$$

The value of λ_r is considerably less than the value obtained by creating
the F-band by x-rays at room temperature or heating in the alkali vapor
and then cooling to $78^{O}K$. For example, Mollwo[1] obtains the following

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[1]Mollwo, loc. cit.

values for the F-band at 90°K produced at room temperature:

$$\lambda_v = 515 \text{ m}\mu$$

$$\lambda_m = 548 \text{ m}\mu$$

$$\lambda_r = 571 \text{ m}\mu$$

Molnar's values[1] are in agreement with Mollwo's.

The author x-rayed KCl at 78°K and obtained the same values as those for the crystal warmed to 78°K after x-raying at 5°K. Casler, Pringsheim, and Yuster's[2] data are also in agreement with this. As with NaCl this difference in width of the F-band seems real and consistent.

(f) After 15 minutes of x-rays (50 kv, 20 ma) at 5°K the F-center density was calculated to be about 1.0×10^{18} cm^{-3}, when d = 0.08 mm, F = 0.81, n' = 1.46, and $W_{5^{\circ}K}$ = 0.188 ev.

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[1] Molnar, loc. cit.

[2] Casler, Pringsheim and Yuster, loc. cit.

3. Experimental Results and Conclusions for KBr.

Table V. Wavelength of the Maximum of Various Bands in KBr.

Band Name	V_3[1]	V_2	V_4[1]	H_2	V_7[1]	V_6[1]	H_1	V_1[1]
Wavelength mμ	230	231	265	275	285	308	362	380	410
Temperature	5°K	90°K	90°K	90°K	5°K	90°K	90°K	5°K	90°K

Band Name	V_0	F[2]	F'[3]	R[4]	R'[4]	M[4]	N[5]
Wavelength mμ	530	602	700	730	795	895	1090
Temperature	5°K	28°K	170°K	90°K	90°K	90°K	Room

Mollwo's data taken at 28°K on the F-band in KBr are:

$$\lambda_v = 570 \text{ m}\mu$$

$$\lambda_m = 602 \text{ m}\mu$$

$$\lambda_r = 628 \text{ m}\mu$$

Further, λ_v does not change with temperature, but λ_m and λ_r shift to the infrared with increasing temperature.

The absorption spectrum of a Harshaw KBr crystal x-rayed at 5°K is given in Fig. 31, curve 1. Curves 2 and 3 of this figure show the effects

[1] Dorendorf, loc. cit.

[2] Mollwo, loc. cit.

[3] H. Pick, Ann. Physik 37, 421 (1940).

[4] Molnar, loc. cit.

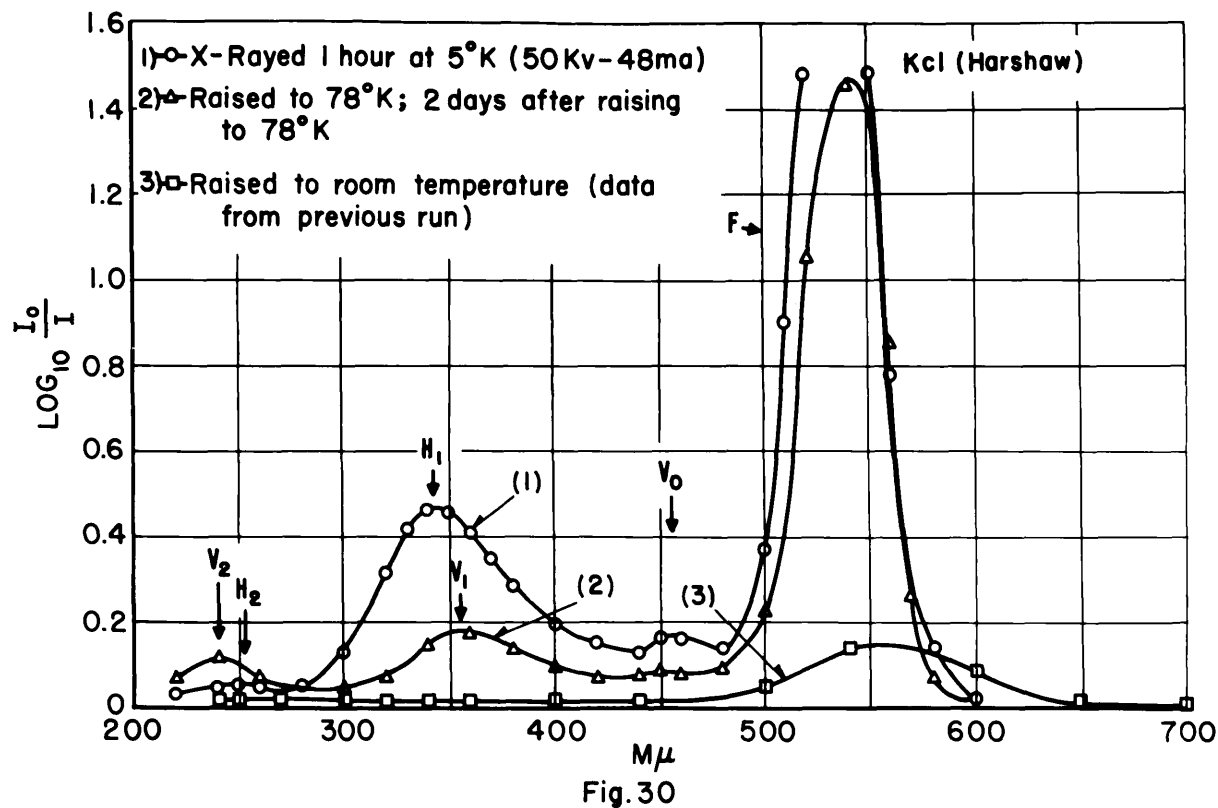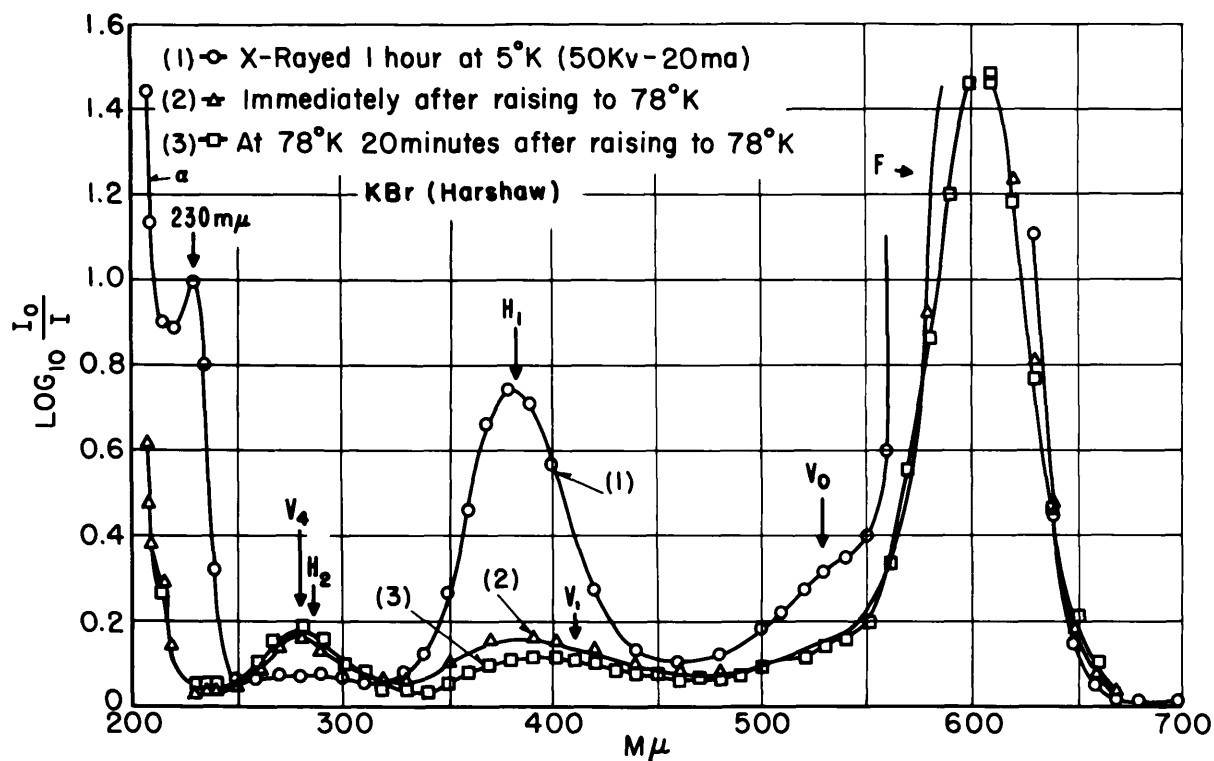[5] Burstein and Oberly, loc. cit.

Fig.30

Fig.31

of raising the crystal to $78\,^{o}$K. The following conclusions can be made:

(a) A large F-band appears at 5°K. It has the following values at this temperature:

$$\lambda_v = 577 \text{ m}\mu$$

$$\lambda_m = 602 \text{ m}\mu$$

$$\lambda_r = 624 \text{ m}\mu$$

These figures are within 0.5 mμ of the values obtained on a second run at 5°K. Thus the band is narrower than Mollwo's at 28°K. The large difference in the λ_v found here and that given by Mollwo is difficult to understand since λ_v is essentially constant with temperature. Perhaps there is a difference in monochromator calibration.

(b) The R- and M-bands do not appear

(c) Whether or not the F'-band appears is highly questionable. A very slight trace appears in the two runs made, but nothing definite can be said.

(d) Several bands appear to the ultraviolet of the F-band. A narrow band appears at 230 mμ . It apparently is of considerable height and is well formed although it appears on the infrared side slope of another very large band, probably the α-band from Martienssen's[1] data as can be seen in Fig. 14. While the 230 mμ band occurs at the same point as V_3 (231 mμ) as reported by Dorendorf[2], it is probably

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[1] W. Martienssen, Naturwiss. 38, 482 (1951)

[2] Dorendorf, loc. cit.

not the same, since the V_3^- band is stable well above 78°K. It is possible of course that if it is the V_3-band, it is bleached by the release of holes or electrons by another band, although this appears unlikely as will be discussed in the next part describing the special KBr experiments.

At 285 mμ a weak band forms that corresponds to the H_2-band in KCl.

A large band arises at 380 mμ that corresponds to the H_1-band in KCl and as will be shown is definitely not the V_1-band.

A slight rise to the ultraviolet side of the F-band at 530 mμ indicates the V_0-band. This rise also appears in additively colored crystals.[1]

(e) On warming to 78°K, the V_0^-, H_1^- and F-bands decrease considerably. It is impossible to determine whether the band to the far ultraviolet, i.e., probably the α-band, is changed.

The H_2-band at 285 mμ apparently disappears and a band at 278 mμ, undoubtedly the band usually labeled the V_4-band, appears with over twice the height of the one it replaces. The effect is the same as was discussed above for KCl, with the exception that in KCl, it was the V_2-band which grew on warming. From this result it appears that either the V_2^- or the V_4^- band has been misnamed in KBr, for the analogy of the band structure at 5°K and the effect of raising to 78°K for these two crystals is quite clear from Figs. 30 and 31. For the sake

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[1] Martienssen, loc. cit.

of convention, however, the 280 mμ band occurring in KBr will continue

to be called V_4.

The H_1-band decreases rapidly on warming to $78^\circ K$, and as can be seen

in the expanded plot of Fig. 32, curve 3, after twenty minutes at $78^\circ K$

the V_1-band becomes distinct from the H_1-band. Unfortunately, points

were not taken after twenty minutes on this particular run, but on a

subsequent run to be described (see Fig. 33), the H_1-band disappears

completely after about two hours at $78^\circ K$, the V_1-band remaining.

It should be further noted that the decay of the H_1-band at $78^\circ K$ is

accompanied by a further bleaching of the F-band; this suggests that

it may be releasing holes which then combine with the F-centers to destroy

them.

(f)   After warming to $78^\circ K$, the F-band acquires the following values:

$$\lambda_v = 576 \ m\mu$$

$$\lambda_m = 605 \ m\mu$$

$$\lambda_r = 632 \ m\mu$$

These are in excellent agreement with the values obtained by x-raying

the crystal initially at $78^\circ K$.

Again a disagreement arises with Mollwo's data for a crystal in which

an F-band formed at room temperature is measured at $90^\circ K$. His values at

$90^\circ K$ are

$$\lambda_v = 573 \ m\mu$$

$$\lambda_m = 609 \ m\mu$$
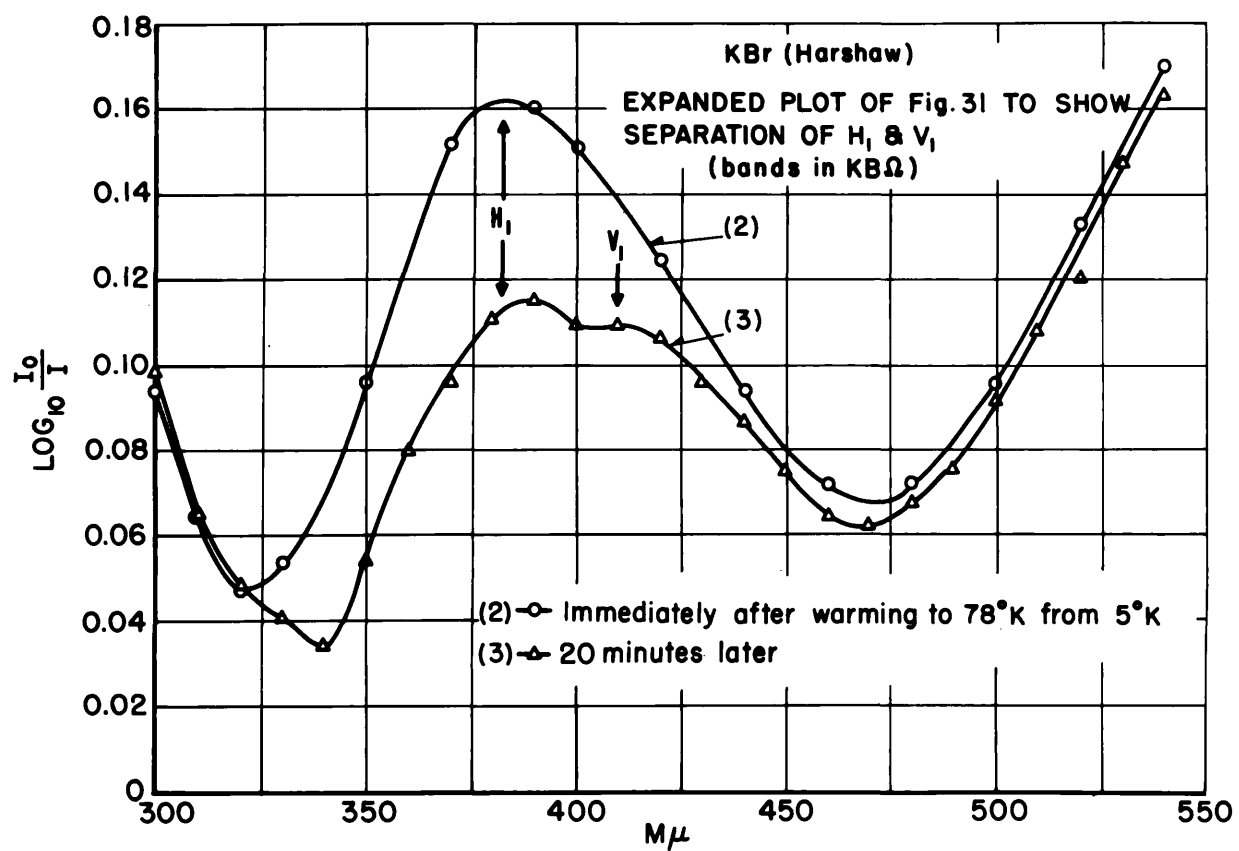
$$\lambda_r = 639 \ m\mu$$

Fig. 32

Thus a consistent difference occurs in the F-band shape for all three crystals NaCl, KCl and KBr. It is always narrower when originally produced and measured at low temperatures than when it is produced at room or higher temperatures and measured at low temperatures.

(g) A surprising effect was noted at 5°K. After a spectrum was obtained the crystal was allowed to remain in the dark for four hours. A slight bleaching of the order of 6 per cent of the H_1-, H_2-, V_o- and F-bands occurred between the points for the spectrum taken immediately after x-raying at 5°K and four hours later at 5°K. No further bleaching occurred in a subsequent period of eight hours in the dark at 5°K after the four hour period. In the second run of KBr at 5°K a similar bleaching occurred after 20 minutes in the dark. This effect will require further work to be proved, however.

(h) After 15 minutes of x-rays (50 kv-20 ma) at 5°K the F-center density was calculated to be about 1.1×10^{18} cm^{-3}, when d = 0.06 mm, f = 0.9, n' = 1.52, and $W_{5^\circ K}$ = 0.16 ev.

4. Additional Experiment in KBr.

In order to be sure that the H_1-band is separate from the V_1-band as is strongly suggested by curve 3 of Fig. 32, an additional run was made in KBr. Hence a KBr crystal was first x-rayed at 78°K until a fairly large V_2-band was established. The crystal was then lowered to 5°K and the spectrum again observed. After this it was x-rayed further at 5°K and then raised back to 78°K.

In addition a second KBr crystal that was the other cleavage half of the crystal used in the above experiment was installed in the other slot

in the crystal holder of the cell. It was mounted in the same fashion

to be described in the growth-rate experiments of Section C of this

chapter, i.e., the side or face x-rayed was in contact before cleavage

with the side of the crystal x-rayed in the above experiment. As will

be shown, the growth rates of the F-band for two such crystals will be

the same to better than 1 per cent when x-rayed under identical condi-

tions. Thus the F-band growth rate of the first crystal x-rayed at 78°K

could be compared with that of the second x-rayed at 5°K.

The results of these two runs are shown in Figs. 33 and 34. The

following conclusions can be made:

(a) As can be seen in Fig. 33, there is little difference in the

maximum of the V_1-band between 78°K and 5°K, it being 410 mμ at 78°K

and about 409 mμ at 5°K. However, on further x-raying at 5°K, the H_1-

band appears at 385 mμ , masking the V_1-band. On warming to 78°K, the

H_1-band can be seen to bleach rapidly, leaving the V_1-band after $2\frac{1}{2}$ hours.[1]

Thus, the H_1-band is definitely a distinct band.

(b) In addition, the V_4-band exhibits a remarkable behavior. It

disappears on x-raying at 5°K (curves 2 and 3 of Fig. 33) and reappears

on warming back to 78°K (curve 4 of Fig. 33). In fact, if curve 3 of

Fig. 33 is compared with curve 1 of Fig. 31, it is difficult to realize

that the crystal in Fig. 33 was first x -rayed at 78°K for 41 minutes

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[1]The final height of the V_1-band at 78°K (curve 4 of Fig. 33) is
slightly less than its value at 78°K before it was lowered to 5°K (curve
1 of Fig. 33) because curve 1 was made with an F'-band present and curve
4 with the F'-band bleached. As will be seen in Section C of this
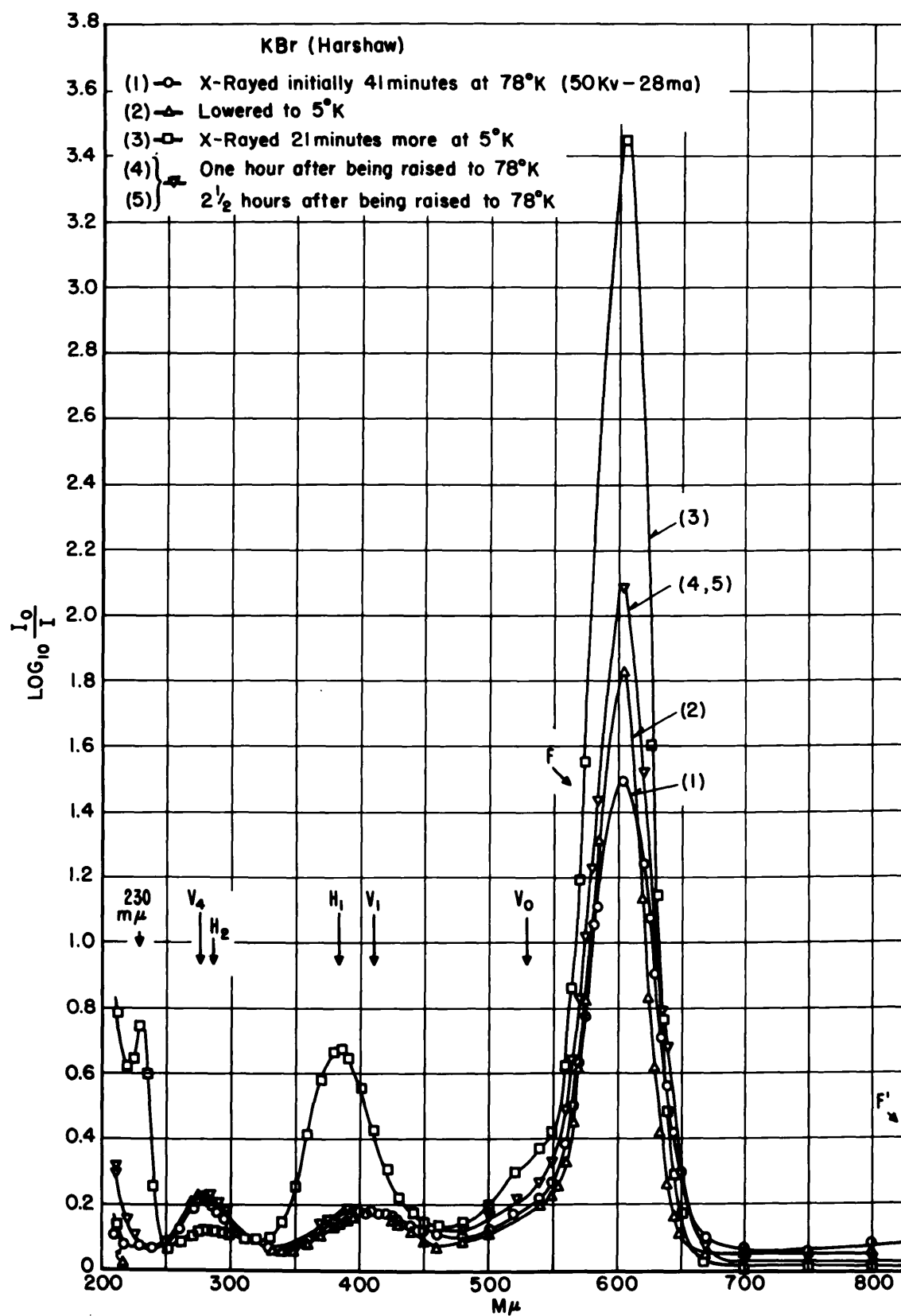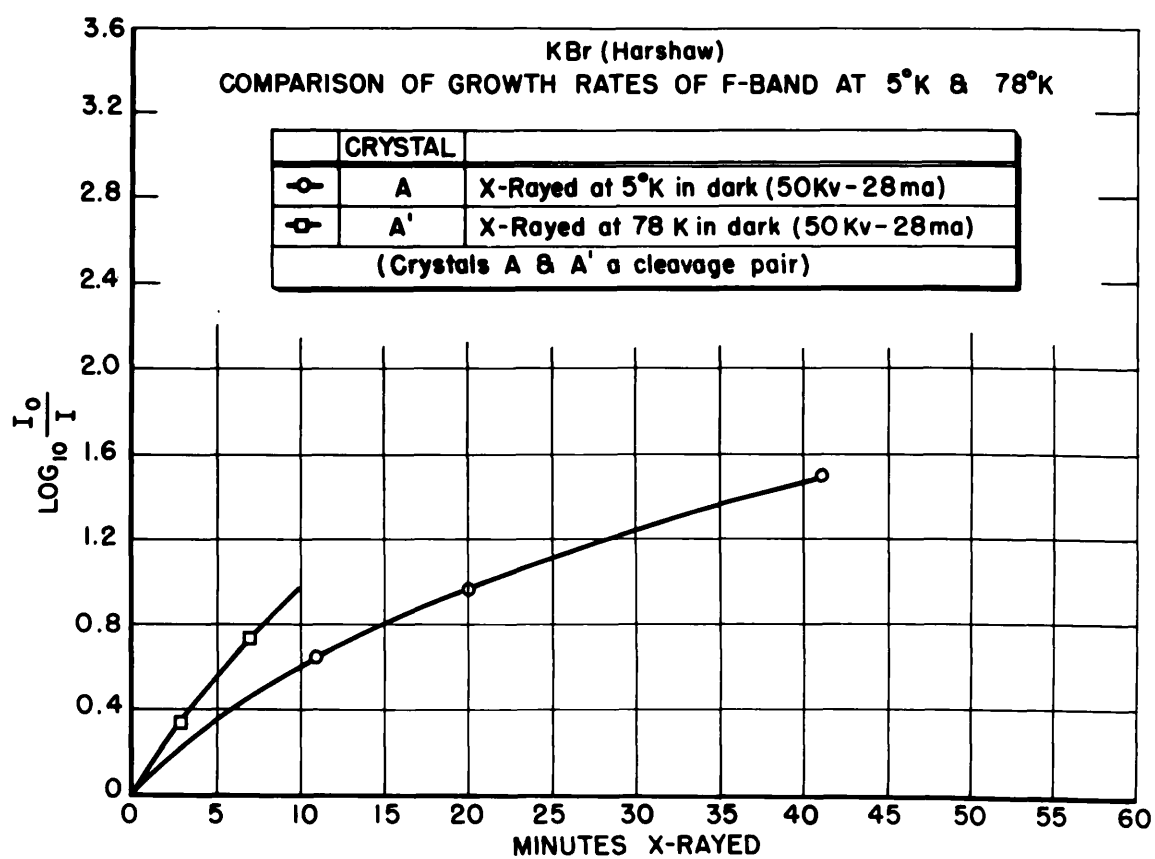chapter, the V_1-band always has a lower value without the F'-band present
at 78°K.

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Fig. 33

KBr (Harshaw)

COMPARISON OF GROWTH RATES OF F-BAND AT 5°K & 78°K

	CRYSTAL	
◆	A	X-Rayed at 5°K in dark (50Kv-28ma)
◆	A'	X-Rayed at 78 K in dark (50Kv-28ma)
(Crystals A & A' a cleavage pair)		

Fig. 34

before being lowered to 5°K and x-rayed 21 minutes more.

(c) It was noted that the 230 mμ band bleached completely below 78°K when the crystal slowly warmed to 78°K.

(d) In order to make a comparison of the number of F-centers produced at 78°K and 5°K from Fig. 34, two corrections must be made. First, curve 1 at 78°K was produced in the dark, i.e., an F'-band was permitted to occur. However, the number of F-centers which would have occurred if the F'-centers were not present can be accurately obtained from similar F-band growth curves for KBr at 78°K given in the next section (Fig. 43). Second, the number of F-centers present, as calculated from Smakula's formula given in Chapter II-B, is dependent on the half-width. From the above data of λ_v and λ_r for KBr at 78°K and 5°K the ratio $W_{5^\circ K}/W_{78^\circ K}$ is about 0.845. Using this ratio, the ordinate value of 0.737 after 7 minutes of x-rays at 5°K in Fig. 44 should be reduced by 0.845, giving 0.623. This value can then be compared with the value of 0.460 at 7 minutes for the 78°K curve corrected to 0.520 to include the F'-centers. Thus, the number of F-centers produced after 7 minutes of x-rays at 5°K is about 20 per cent greater than the number produced in the same time at 78°K.

About the same figure is found if the number of centers produced after 21 minutes extra of x-rays at 5°K (curve 3 of Fig. 33) is compared with the number of centers which would have been produced if the extra 21 minutes of x-rays had been continued at 78°K rather than 5°K. (This extrapolation of the growth at 78°K is concluded from the growth-rate data of the next section for KBr, see Fig. 44).

C. Growth Rates of F-, F'-, and Certain V-Bands in X-Rayed Alkali Halides at 73°K

1. Experimental Technique.

In order to obtain growth-rate curves of the various centers which could be quantitatively compared with and without the F'-band present, the reproducibility of growth rates in the same crystal had to be established. Two techniques were attempted for these experiments.

In one a crystal about 3 mm thick was cleaved in half and each of the faces in contact before cleaving x-rayed under the same conditions. As can be seen in Figs. 35 and 36 an agreement to within 1 per cent is achieved in KCl and KBr at 78°K. The same technique was tried with NaCl at room temperature and agreement to within 5 per cent was obtained. While this technique would be extremely useful for comparison experiments in which one crystal was permanently changed by the experimental conditions, e.g., possibly quenching or additive coloration, the second technique was found to be even better for these growth-rate experiments.

Here the KBr crystals were warmed to room temperature in the cell after each x-raying at 78°K and irradiated with light from a tungsten source for several hours. KCl had to be warmed to about 250°C under the light to bleach out a band at 290 mμ which appears on warming to room temperature after x-raying at 78°K. KCl was also run, however, with only room temperature bleaching with identical results to the 250°C bleaching. With such a technique the growth curves were reproducible to within 0.5 per cent, as Harten[1] has shown for KCl.

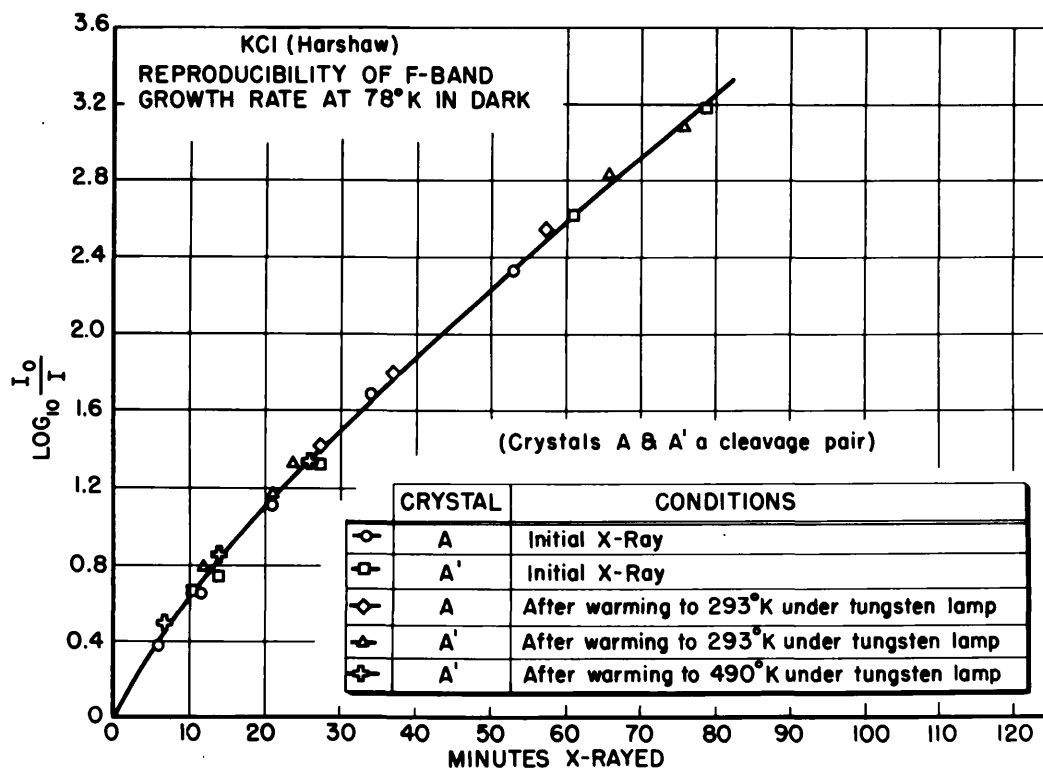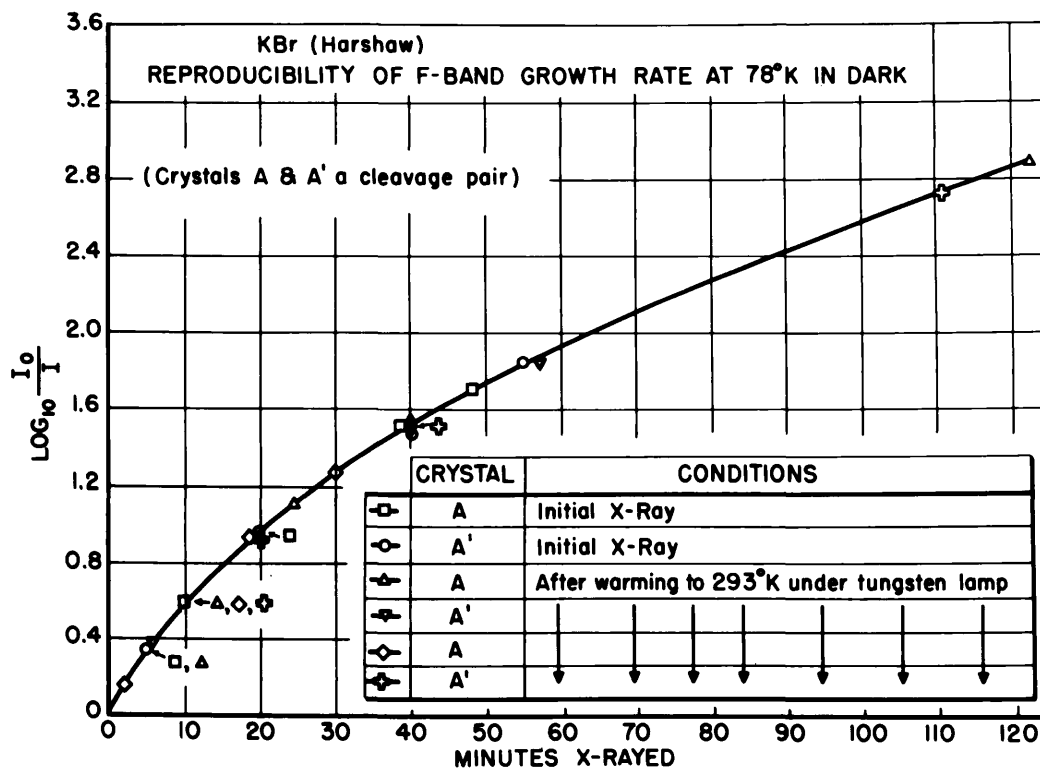[1] H. Harten, Z. Physik 126, 619 (1949).

Fig. 35

Fig. 36

The bands appearing after x-raying KCl and KBr in the dark at 78°K are shown in Figs. 37 and 38. These are in agreement with the work of Dorendorf[1] (see Fig. 12) and Casler, Pringsheim and Yuster.[2] The bands are labeled in the convention discussed in Chapter II. In addition, the effect of bleaching the F'-band on the various bands is presented.

The growth rate of each of these bands was obtained at constant x-ray intensity of 50 kv-28ma, first with the crystal in total darkness and then with all conditions exactly the same except the crystal was irradiated with F'-light during x-raying. Then the crystal was initially x-rayed under identical conditions in the dark for a number of minutes and then x-rayed further under the F'-light. Similarly the crystal was x-rayed under F'-light initially for a number of minutes and then x-rayed further in the dark.

2. Experimental Conclusions.

The results of these experiments are shown in Figs. 39 through 45. The growth rate of each of the bands in KCl and KBr under the various conditions is shown. The following conclusions can be made:

(a) The shape of the growth curves for the F-, F'-, V_o-, and V_1 bands is similar. In KBr their initial slope is quite steep, decreasing quite rapidly to a fairly constant slope after about 30 to 40 minutes.

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

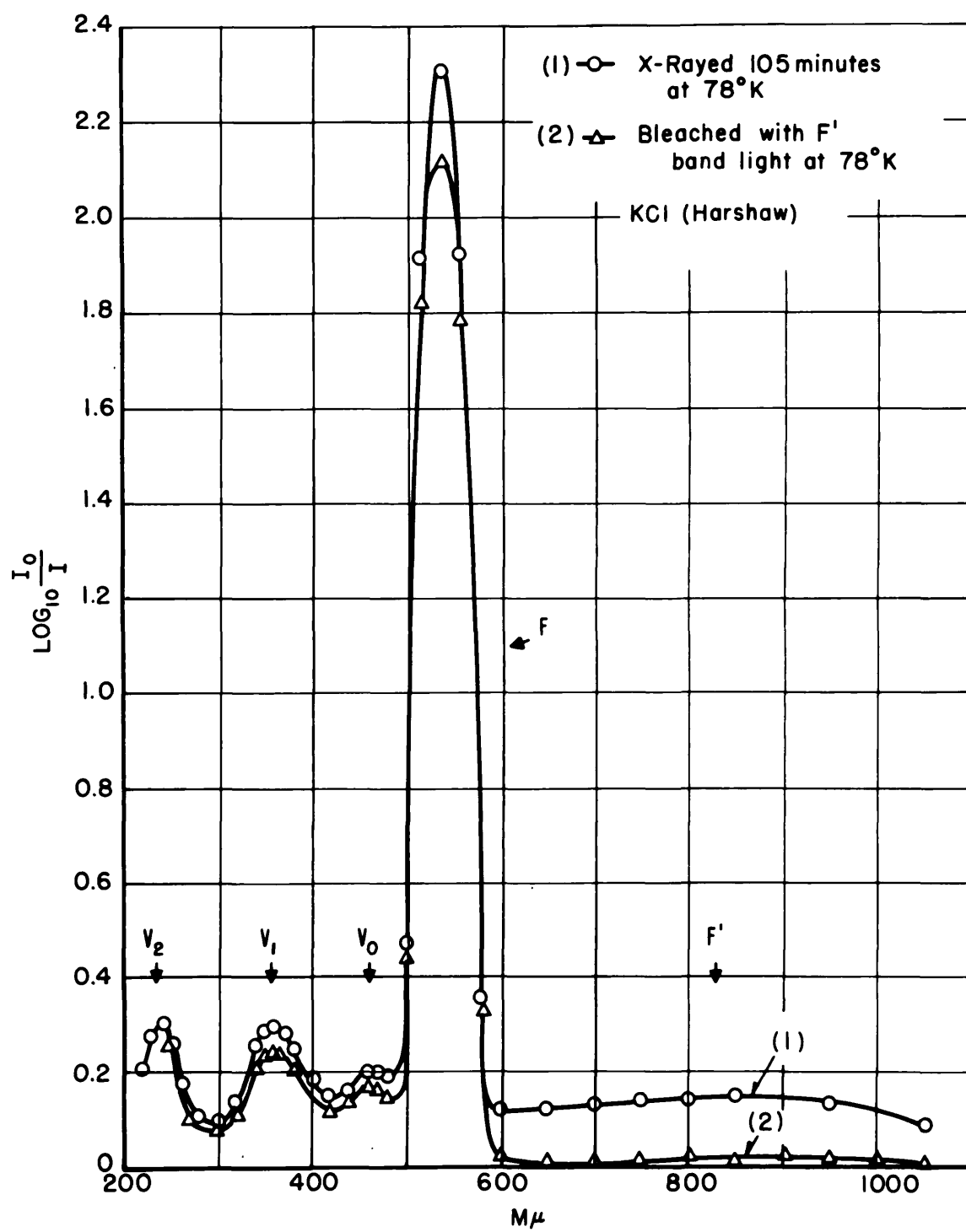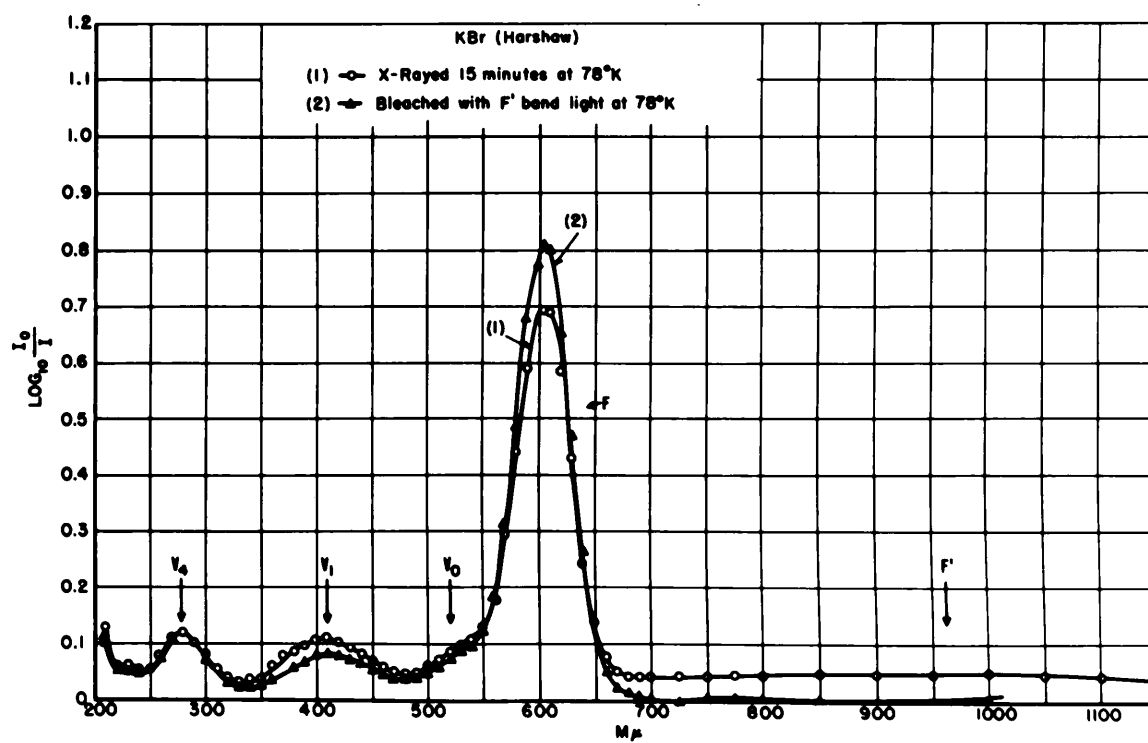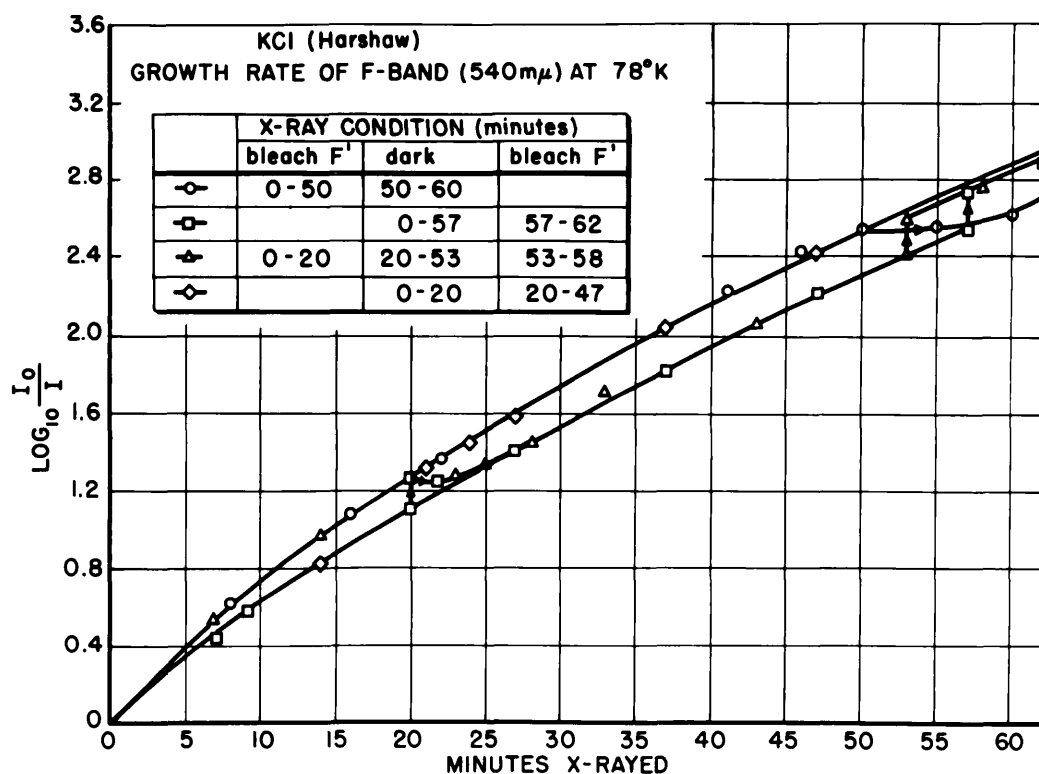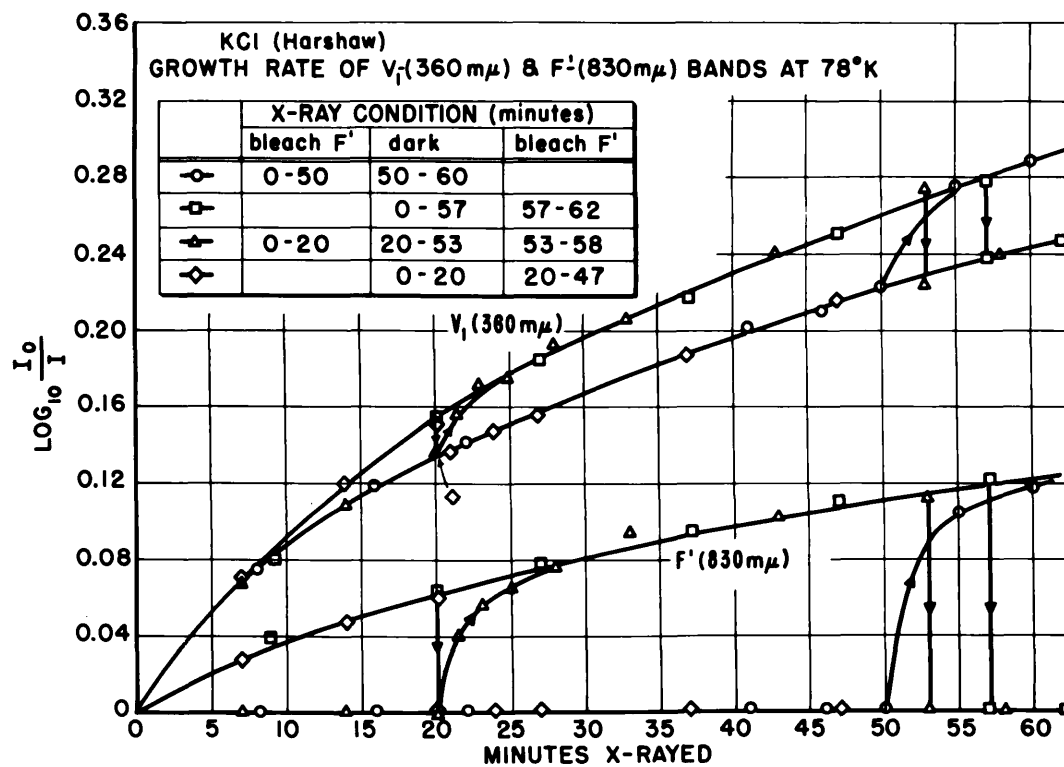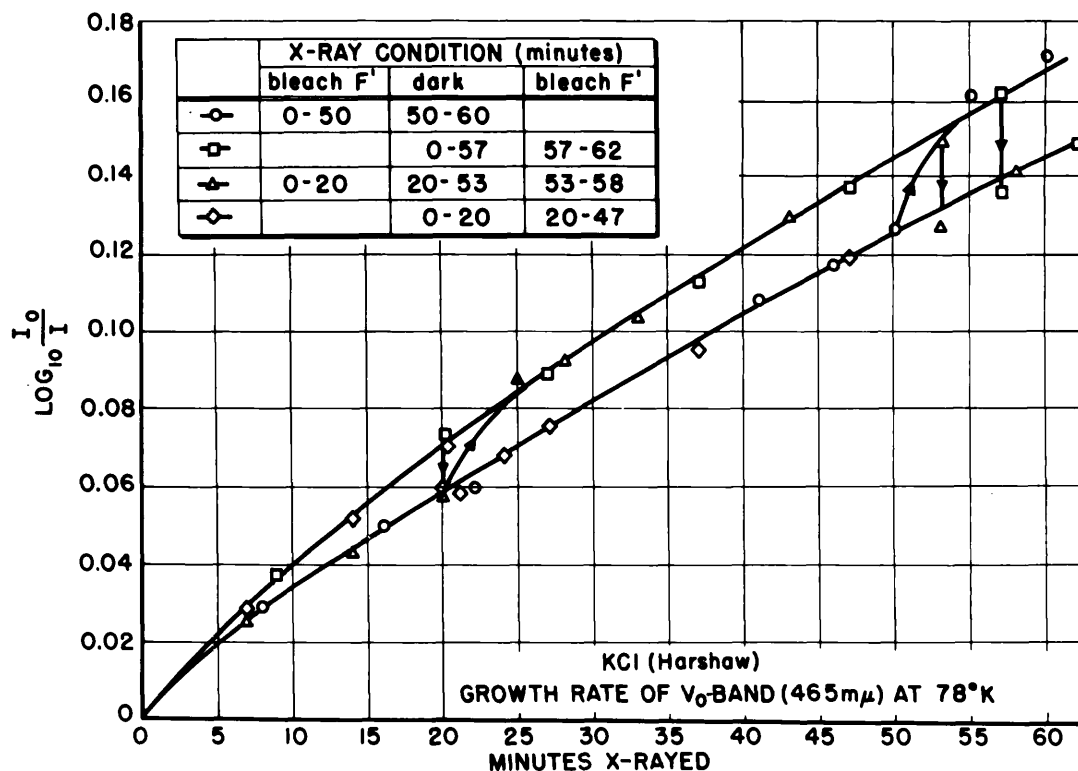[2] R. Casler, P. Pringsheim and P. Yuster, J. Chem. Phys. 18, 1564 (1950).

Fig. 37

Fig. 38

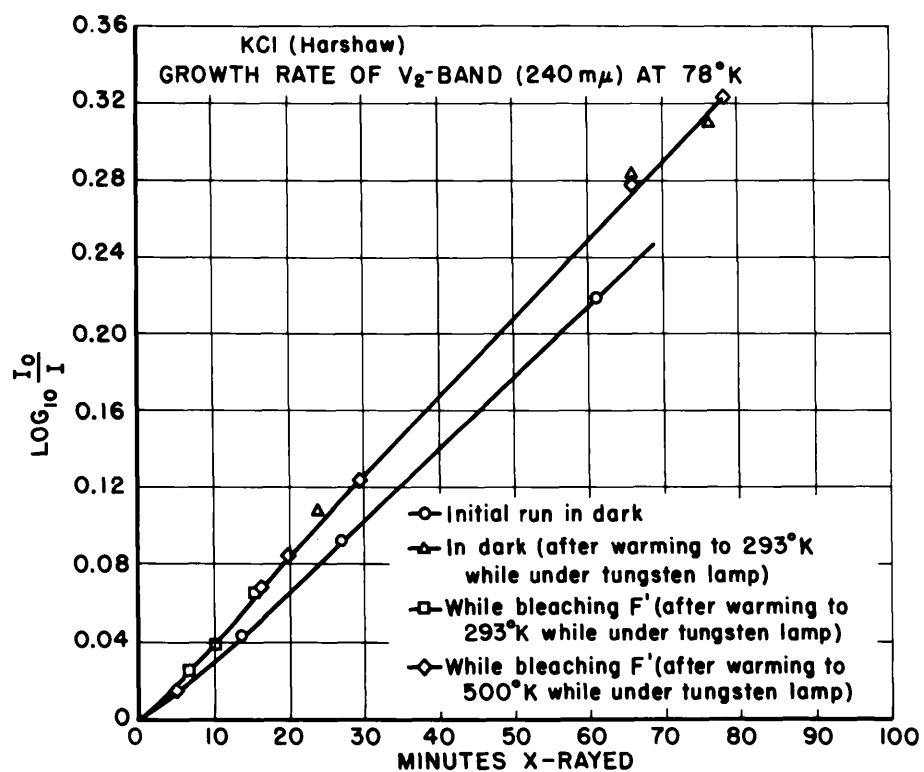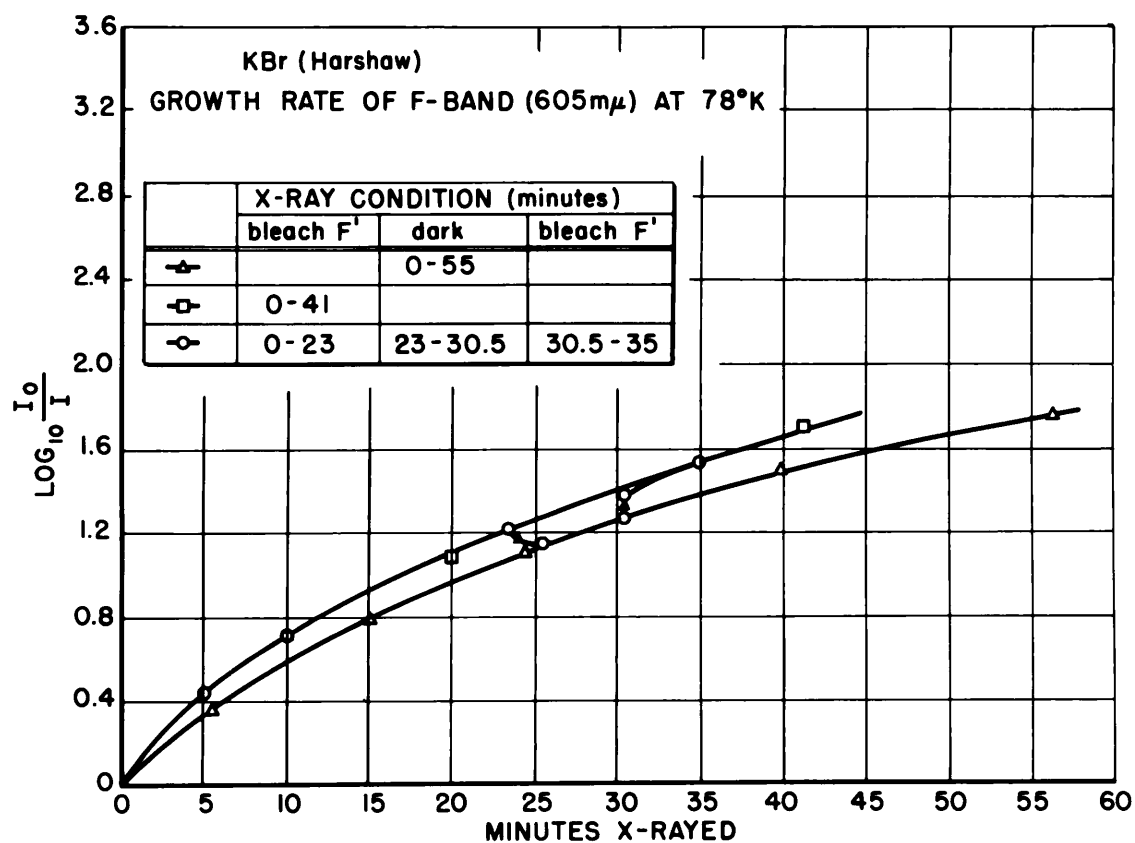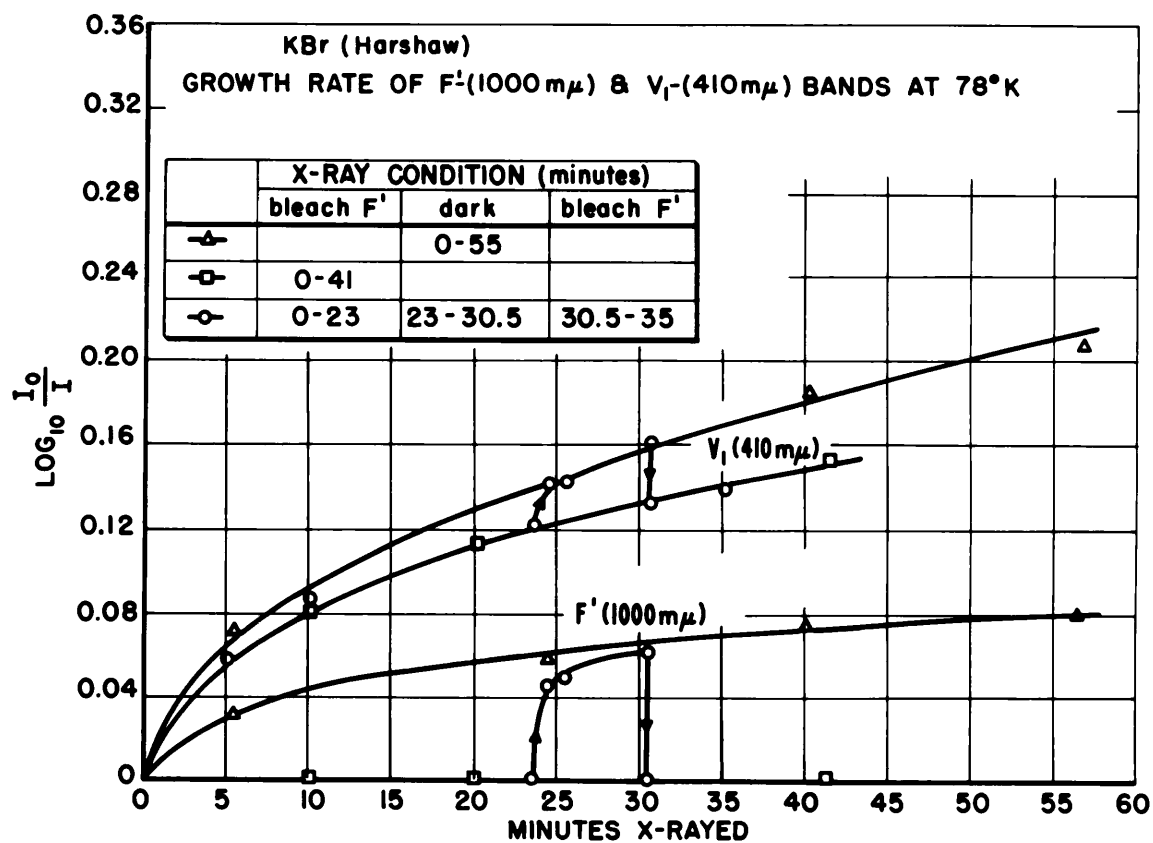Fig. 39

Fig. 40

Fig. 41

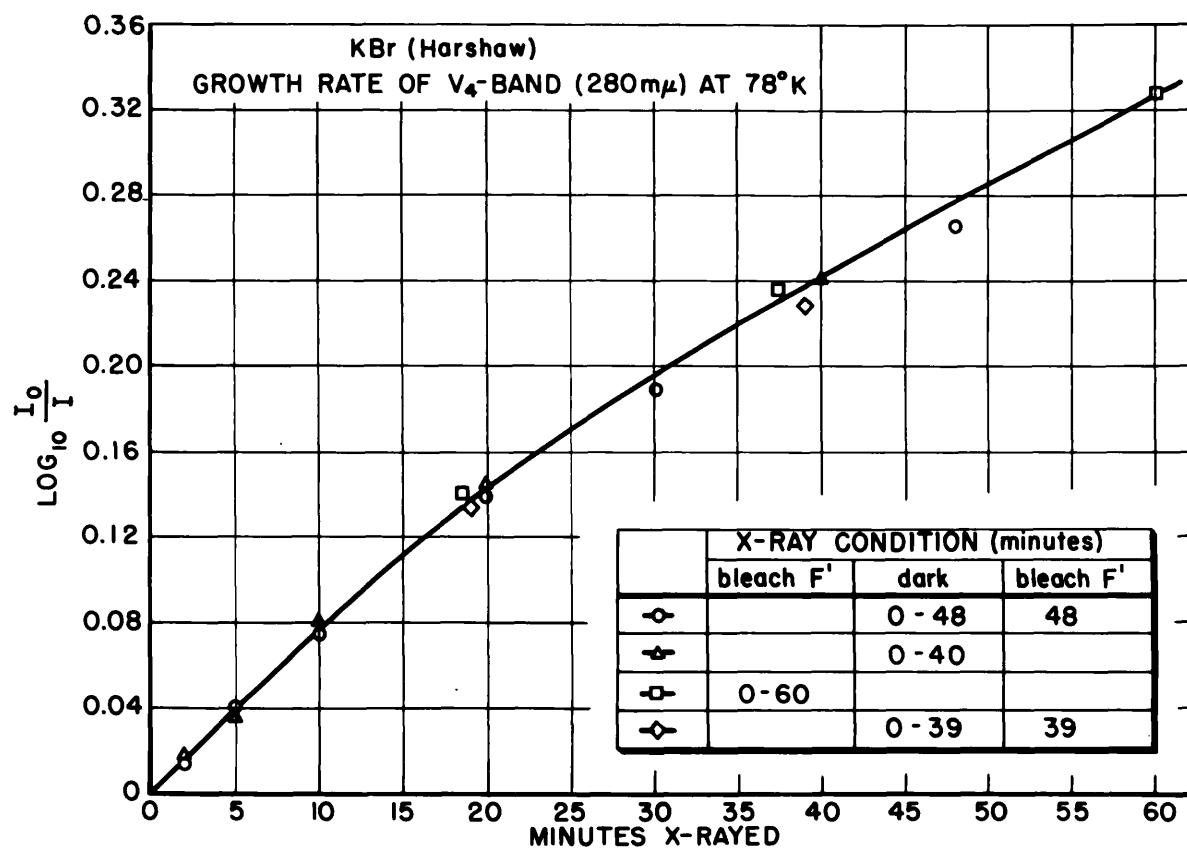
Fig. 42

Fig. 43

Fig. 44

Fig. 45

In KCl a similar effect is noted except that the slope is less steep and changes much less with time of x-raying.

(b) The V_2-band grows at a nearly constant rate in both KCl and KBr, independent of whether the crystal is in the dark or the F'-band is being bleached.

(c) When the crystal is x-rayed in the dark a lower number of F-centers are present at any given total time of irradiation than when the crystal is x-rayed while the F'-band is being bleached.

(d) A larger number of V_1- and V_0- centers are present at any given time when the crystal is x-rayed in the dark than when the crystal is x-rayed while the F'-band is being bleached.

(e) If the crystal is x-rayed initially in the dark for any number of minutes and then the F'-bleaching light is turned on, the number of F'-, F-, V_0- and V_1- centers present at any subsequent x-raying time is exactly the same as if the F' bleaching light had been on during the entire time of x-raying.

(f) If the crystal is x-rayed initially with the F'-band being bleached by F'-light and then at any time the F'-band bleaching is stopped, the number of F-, F'-, V_0- and V_1-centers present after a short subsequent x-raying time is the same as if the crystal had been x-rayed in the dark throughout the entire x-raying period.

(g) The change in the number of F'-, F-, V_0- and V_1- centers occurring at any time during F'-bleaching to the number present for the crystal in darkness is very rapid, the number of F-centers actually decreasing until the other curve is reached.

(h) The change from F'-bleaching to darkness and vice versa may be made any number of times during the x-raying with the growth rates always quickly changing from one fixed curve to the other.

(i) Warming to room temperature after the crystal has had of the order of 10^{18} cm^{-3} F-centers created at 78°K by x-rays[1] and bleaching with white light is sufficient to restore the crystal entirely to its initial condition before x-raying, that is, at least as far as the further build-up of the F-, F'-, V_o-, and V_1- color centers are concerned.[2] Higher heating is required to bleach the V_2 band.[3]

3. Special Observations.

Several observations may be made from these experimental conclusions:

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[1]After 60 minutes of x-rays (50 kv-28 ma) at 78°K, the F-center density in KCl reaches about 2.4×10^{18}cm^{-3}, using the values d = 0.08 mm, n' = 1.46, $W_{78^{\circ}K}$ = 0.202 ev and f = 0.81. Similarly for KBr after 110 minutes of x-rays (50 kv-28 ma) at 78°K, the F-center density reaches about 2.6×10^{18} cm^{-3}, using the values d = 0.06 mm, n' = 1.52, $W_{78^{\circ}K}$ = 0.188 ev and f = 0.9.

[2]The white light actually does the bleaching, for the F-centers will bleach extremely slowly in the dark, apparently remaining for years in KCl.

[3]The presence of a sizable V_n-band in KCl at the onset of x-raying a crystal which has been bleached with white light at room temperature has no effect on the growth rates of the F-, F'-, V_o- and V_1-bands, i.e., their growth is independent of the number of V_2-centers present at any time.

(a) Under the given conditions the number of $F-$, $F'-$, V_1- and V_o- centers present at any given time of x-ray exposure has two fixed values, dependent only on whether the crystal is in the dark or under F'-light. It is independent of the previous F'-bleaching conditions.

(b) The growth rate of the V_2- centers in KCl and V_4- centers in KBr is not only independent of the F'-bleaching conditions but is quite independent of the number of $F-$, $F'-$, V_o- and V_1- centers present.

(c) The capture cross section for electrons of the V_2 - centers in KCl and V_4- centers in KBr at $78^{\circ}K$ is extremely small. This is concluded from the fact that the sudden release of a large burst of electrons by bleaching of the F'-band does not measurably change the number of V_2 or V_4-centers (see Figs. 37 and 38).

(d) Warming to room temperature and bleaching with white light is apparently sufficient to restore the imperfections responsible for the $F-$, $F'-$, V_o-, and V_1- centers to their original states.[1]

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[1] The band at 290 mμ occurring on warming KCl to room temperature under white light bleaches at higher temperatures, but its presence has no measurable effect on the growth rate of the other bands at $78^{\circ}K$. Similarly the V_2-band in KBr does not fully bleach but its presence has no measurable effect on the future growth rates of the other bands at $78^{\circ}K$.

D. Speculations

To synthesize the experimental results given in this chapter and those of the previous workers discussed in Chapter I into an extensive model for the color centers occurring during x-raying is not possible. Many more experiments and theoretical studies will be necessary before this can be done. The experimental results presented do permit, however, a further insight into certain of these processes and suggest experiments which may continue toward a synthesis. Hence, several interpretations or speculations on these results will be given.

Several major assumptions are required here, the evidence for which has been discussed in Chapter I. Briefly these assumptions are:

(1) An F-center consists of an electron trapped at a negative-ion vacancy.

(2) An F'-center consists of two electrons trapped at a negative-ion vacancy, i.e. an F-center plus an electron.

(3) The diffusion of ions and vacancies for more than several lattice sites at temperatures below $78^{\circ}K$ is highly improbable except possibly during x-raying.

(4) Holes and electrons may diffuse through the lattice below $78^{\circ}K$, the holes in the normally "filled" band and the electrons in the conduction band.[1]

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[1] It is not meant here to exclude excitons and phonons in this assumption. These particles are omitted because they will not be explicitly used in the following discussions.

(5) Holes and electrons can interact with color centers with the effect of transmuting or destroying the center.

(6) The stability of a color center is dependent on temperature.

On the basis of these assumptions the results presented in this chapter in conjunction with the published data discussed in Chapter I suggest the following possibilities:

(1) The H_1-band appearing in KCl and KBr at $5^{\circ}K$ (see Figs. 30 and 31) is a trapped-hole center. Similarly the 330 mμ band appearing at $5^{\circ}K$ in NaCl (see Fig. 29) may be a trapped-hole center, although it cannot be certain that it is the H_1-band. This conclusion is based on the bleaching of the F-band when the H_1-centers become unstable between $5^{\circ}K$ and $78^{\circ}K$. It is fortunate that they decay in a matter of minutes in KBr at $78^{\circ}K$ permitting a more controlled observation on the bleaching effect of the F-band.

(2) The H_1-band may be the true "hole captured at a positive-ion vacancy" band rather than the V_1-band proposed by Seitz.[1] This is proposed because the H_1-band appears to have about the same qualifications for fitting this model as the V_1-band in that both destroy F-centers when they bleach.

The effect, or rather lack of effect that the bleaching of the H_1-band has on the V_1-band in KCl and KBr places further doubt on the true nature of the V_1-band in these crystals. This question is based on the

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

assumption that there will be positive-ion vacancies present[1] after x-raying at $5^{\circ}K$.

Therefore, when holes are released from the H_1-centers they should build up further V_1-centers, *if* the V_1-center is as suggested. This build up does not occur, however, as can be deduced from the special KBr experiment, described at the end of Section B of this chapter, in the following manner.

The growth rate of the V_1-band with and without the F'-band present in KBr at $78^{\circ}K$ can be accurately obtained from Fig. 44. In this special KBr experiment the V_1-band built up for 41 minutes x-raying at $78^{\circ}K$ with an F'-band present. Then the crystal was lowered to $5^{\circ}K$, the F'-band bleached and the crystal x-rayed 21 minutes more. When the crystal was raised back to $78^{\circ}K$ the height of the V_1-band **after** the H_1-band had completely bleached had not changed from its value after 41 minutes x-raying at $78^{\circ}K$ (see Fig. 33); but this is exactly what would have occurred if at the end of 41 minutes x-rays at $78^{\circ}K$ the F'-band had been bleached and the crystal x-rayed for 21 minutes more at $78^{\circ}K$ while the F'-band was bleached.[2] For in this case the V_1-band would have dropped at 41

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[1] Electrons can destroy hole centers just as holes can destroy electron centers, e.g., F-centers. This is evidenced by the data of Section C of this chapter, where the release of electrons from the F'-centers destroys part of the V_1-centers. Similarly during x-raying the electrons present should combine with holes captured at positive-ion vacancies, thus freeing these vacancies.

[2] The F'-band was not actually bleached with F'-light at $5^{\circ}K$. It merely does not form to any extent and hence may be considered as being bleached.

minutes from the growth curve with an F'-band present to the one

without an F'-band present (see Fig. 44), and continued along the lower

curve of this figure 21 minutes more out to 62 minutes. As can be noted,

the value of the V_1-band at 41 minutes before bleaching the F'-band is

approximately the same as that for the V_1-band at 62 minutes with the F'-

band bleached. Hence, the bleaching of the H_1-band did not build up any

V_1-centers beyond those built during the x-raying.

It should be pointed out that this expected effect of the H_1-center

bleaching on the V_1-centers does occur in NaCl (see Fig. 28). When the

broad 330 mμ band formed at 5°K bleaches on warming to 78°K, the V_1-band

is created. Also, the F-band is reduced when this 330 mμ band bleaches.

Thus, it would appear that the 330 mμ band is also produced by a hole-

center as with the H_1-center. The holes released on the bleaching of the

330 mμ centers would destroy F-centers as well as being captured to form

the V_1-centers. These holes are again released at 78°K when the V_1-

centers decay and apparently diffuse through the lattice until they com-

bine with and so destroy further F-centers.

(3) The growth rate of the F-band in KBr (and possibly KCl) is

higher at 5°K than at 78°K. This occurs because holes which otherwise

would destroy F-centers are captured by other sites to form H_1-centers

which are stable at 5°K.[1] On warming back to 78°K, these holes are again

[1] This creation and destruction of centers seems more plausible than the direct recombination of holes and electrons. Their recombination cross section in germanium has been estimated as less than 1/400 the area of a germanium atom from experiments by H. Suhl and W. Schockley, Phys. Rev. 75, 1617 (1949); 76, 180 (1949). This subject is further discussed by W. Schockley, Electrons and Holes in Semi-conductors, pp. 66-75, 318-328 D. Van Nostrand, New York: 1950.

released and combine with F-centers to bleach part of the F-band.

The mechanism proposed here for this change in F-center growth rate is analogous to that proposed by Seitz[1] to explain the increase of F-centers when divalent impurity ions are present in the lattice. He suggests that the divalent ions capture holes which would ordinarily destroy a part of the F-centers. Similarly at $5^{\circ}K$ the H_1-centers capture holes which would have destroyed F-centers if they had remained free.

(4) That there are free negative-ion vacancies present after x-raying KBr at $78^{\circ}K$[2/] is further supported by this work. This is proposed because more F-centers occur at $5^{\circ}K$ than at $78^{\circ}K$. Hence, there will be at least those negative-ion vacancies present at $78^{\circ}K$ which have been formed from the destruction of F-centers by the extra holes present at $78^{\circ}K$ as suggested in the above proposal (3).

(5) The band which has been labeled V_4 in KBr is the same as that labeled V_2 in KCl (see Fig. 12). This conclusion is based on two experimental observations. First, the growth rates of these two bands are similar in both their constancy of slope (see Figs. 42 and 45) and lack of effect of the presence of the F'-band. Second, both bands

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[1]See Chapter II-F(3).

[2]This proposal has already been made by Delbecq, Pringsheim and Yuster (see Chapter II-C(5) and J. Chem. Phys. 9, 574 (1951)) as an explanation of the α-band appearing in KI after x-raying at low temperatures. A similar band appears in KBr when it is x-rayed at low temperatures (see Martienssen, Naturwiss 38, 482 (1951) and Fig. 14 in Chapter II-C(5)).

appear under the same conditions when a crystal x-rayed at 5°K is raised to 78°K (see Figs. 30 and 31).

(6) The V_4-center in KBr is converted to another center at 5°K by the capture of another particle, i.e., either a hole or an electron. This new center becomes unstable between 5°K and 78°K and releases the additional particle, converting it back to a V_4-center again. This speculation is based on the disappearance of the V_4-band established at 78°K when KBr is further x-rayed at 5°K and its subsequent reappearance when the crystal is raised back to 78°K (see curves 1, 3 and 4 of Fig. 33). Since the V_2-band of KCl appears on raising to 78°K the same model should apply to this center in KCl (see curves 1 and 2 of Fig. 30).

(7) None of these experiments give an indication of the nature of the 230 mμ band appearing in KBr at 5°K (see curve 1 of Fig. 31). It bleaches completely somewhere below 78°K. It might occur in KI x-rayed at 5°K. In this case, it should appear further to the red, making its structure more obtainable on the Beckman Spectrophotometer.

(8) The difference in width of the F-band (see Section B of this chapter) produced at low temperatures by x-rays with that produced at room or high temperatures by x-rays or additive coloration may be due to a perturbation effect.[1] On the basis of this difference in half width

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[1]The possibility of the F-center being perturbed by a vacancy cluster or dislocation near the center has been suggested by J. J. Markham in a letter to appear in the May 1, 1952 Phys. Rev.

and also the restoration properties of a crystal,[1] the following

mechanism for this perturbation is suggested.

When a crystal is x-rayed, F-centers may be created by electrons

trapped at incipient vacancies at the jog of a Taylor dislocation, as

suggested by Seitz.[2] However, at low temperatures the F-center may

diffuse away only the distance of about the lattice constant from the

jog. The thermal energy required for this diffusion would be pro-

vided by the x-ray photons and would occur as a transient local heating

of the lattice.

Thus, at low temperatures the F-centers could be formed in the

vicinity of these perturbations which in turn may affect the half-

width of the F-band. At room temperature the F-centers may be removed

from the perturbations by diffusion and this lack of any perturbations

might result in a different half-width of the F-band. It would be

this diffusion at room temperature which could account for the

restoration property of the crystal.

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[1]In Section C of this chapter it was shown experimentally that the
imperfections responsible for the growth of the $F-$, $F'-$, V_o- and V_1-
bands at $78°K$ are restored to their initial states merely by warm-
ing the crystal to room temperature and irradiating it with white light.

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

(9) From the growth-rate curves at 78°K presented in Section C

of this chapter, it may be concluded that under certain conditions a

fixed equilibrium occurs between the production of holes, electrons and

vacancies and the creation and destruction of certain of the color

centers with these particles. Further, the number of F-, F'-, V_o- and

V_1-centers is a constant for any given x-ray exposure time with the

crystal in the dark and a different constant with the crystal in F'-

light. This conclusion is in part an extension of Harten's work[1], (see

Fig. 21). He showed that the limiting number of F-centers in KCl at

room temperature was independent of the initial number of F-centers.

(10) The imperfections responsible for the F-, F'-, V_o-, and V_1-

centers are restored to the states they were in originally before x-ray-

ing at 78°K by warming the crystals to room temperature under white

light.[2] In order to make this result consistent with the density de-

crease experiment of Estermann, Leivo and Stern[3], it again appears

reasonable that the centers produced at low temperatures do not result

from extensive diffusion of vacancies or ions but rather from effects

localized in the vicinity of the color centers. Warming to room

temperature permits these local perturbations to be restored by the

thermal action of the lattice.

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[1] H. Harten, Z. Physik 126, 619 (1949).

[2] Actually the light is used to bleach the F- and V_o-bands while the V_1- and F'-bands bleach entirely by the action of warming to room temperature (see Fig. 12).

[3] I. Estermann, W. Leivo, and O. Stern, Phys. Rev. 75, 627 (1949).

APPENDIX I

IMPURITY BIBLIOGRAPHY

Addink, N. "The Degree of Imperfection of Crystals". Effect of impurities on the apparent value of Avogardo's number determined from the crystals. Rec. Trav. Chem. Pays-Bas 70, 202 (1951).

Akpinar, S. "Introduction of Chemically Defined Additions to Alkali Halides". Bands produced by addition of S to alkali halides. Ann. Physik 37, 429 (1940).

Arsenjawa, A. "Influence of x-Rays on Absorption of Alkali Halides". Sharp absorption bands occur in phosphors containing Pb and Tl. Z. Physik 57, 163 (1929).

Arzybysev, S. and Parfianovic, U. "Electrolysis of Cu into Rocksalt". Cu produces similar bands as Na vapor. Comptes Rendus de l'Acad. des Sciences, USSR 4, 25 (1934).

Arzybysev, S. and Toporec, A. "Nature of the Red 'Hood' at the Boundary of the Colored Zone in Alkali Halides". Penetration of Cu into crystals. J. de Physique et le Radium 5, 619 (1934).

Blau, M. "Effects of Impurities on Colored Crystals". Effect of impurities on absorption bands in alkali halides produced by electrolysis. Got. Nach., Math. Phys., 401 (1933).

Bogomolowa, M. "Gold and Copper in Rocksalt and Synthetic Sylvine". Mobility of Au and Cu ions versus temperature and field strength. Acta Physiocochimica 5, 161, 173 (1936).

Bose, H. and Sharma, J. "Luminescence Spectra of Alkali Halides". Effect on luminescent spectra of KI when Tl is added. Proc. Nat. Inst. Sci. India 16, 47 (1950).

Breckenridge, R. "Low Frequency Dispersion in Ionic Crystals Containing Foreign Ions". J. Chem. Phys. 18, 913 (1950).

Burstein, E., Oberly, J., Henvis, B., and Davisson, J. "A Note on the Distribution of Impurities in the Alkali Halides". NaCl containing Pb^{++} is optically studied. Phys. Rev. 81, 459 (1951).

Chatterjee, A. "On the x-Ray Luminescence Spectra of Thallium-Activated Alkali Halide Crystals". Indian J. Phys. 24, 331 (1950).

Etzel, H. and Maurer, R. "The Concentration and Mobility of Vacancies in Sodium Chloride". The electrical conductivity of NaCl with CdCl added was determined. Impurity table included. J. Chem. Phys. 18, 1003 (1950).

Glaser, G. "Electrical Observations Relating to Optical Formation of Color Centers in KBr and KCl". Effect of U-centers and other impurity centers on Photocurrent. Ann. Physik 27, 217 (1936).

Grosev, L. "Spectral Distribution of Photocurrent in KCl and NaCl Colloidally Colored with Cu by Electrolysis". Comptes Rendus de L'Acad. des Sciences, USSR 4, 378 (1934).

Harten, H. "x-Ray Produced Electron Currents in KCl". Effect of impurities as electron traps on magnitude of electron currents produced by x-rays. Nach. Wiss. Got. IIa, 15 (1950).

Heiland, G. and Kelting, H. "Absorption of KCl Containing Excess K with $CaCl_2$ Additive and of KBr containing Excess K with $CaBr_2$ Additive". Z. Physik 126, 689 (1949).

Hilsch, R. "Spectra of Some Alkali Halides to which Tl and Pb have been Added". Z. Physik 44, 860 (1927).

Hilsch, R. "Alkali Halide Phosphors Containing Heavy Metals". Phys. Soc. Proc. 49, 40 (Special Section) (1937) and Phys. Zeit. 38 1031 (1937).

Hilsch, R. "Absorption of KCl at He Temperatures". Colloidal Pb and Tl in KCl exhibit no change in absorption spectra at liquid He temperatures. Phys. Zeit. 40, 592 (1939).

von Hippel, A. "Electrical Breakdown of 12 Alkali Halides". Effects of foreign salts added to pure crystals. Z. Physik 88, 358 (1934).

Käding, H. "Effect of Inclusion of Small Amounts of Pb in Alkali Halides Crystallized from Solution". Z. Physik Chem. 162, 174 (1932).

Kahanowicz, M. "Lateral Radiation and Nature of Coloring Substance in Natural Blue NaCl". Z. Physik 57, 163 (1929).

Kelting, H. and Witt, H. "KCl Crystals with Added Alkaline Earth Chlorides". Contribution of impurities to conductivity. Z. Physik 126, 697 (1949).

Koch, W. "Ionic Impurity Content in Alkali Halides". Tl and Pb added and absorption measured in several alkali halides. Z. Physik 57, 638 (1929).

Kondo, K. and Suita, T. "Absorption Spectra of KCl Containing Several Kinds of Impurities". J. Phys. Soc. Japan 5, 200 (1950).

Lehfeldt, W. "Electrical Conductivity of Alkali Halides". Effect of impurities on conductivity. Z. Physik 85, 717 (1933).

Lüpke, A. "Sensitisation of Photochemical Effect in Alkali Halides". Effect of foreign substances on absorption spectra. Ann. Physik 21, 1 (1934).

MacMahon, A. "Alkali Halide Phosphors in the Presence of Copper". Absorption bands produced by adding Cu to melt. Z. Physik 52, 336 (1928).

Martienssen, W. "Photo-Chemical Processes in Alkali Halides". The influence of hydrogen on bands in KBr. Naturwiss 38, 482 (1951).

Meyeren, W. "Thallium-Containing Alkali Halides". Absorption spectrum measured down to -180°C. Z. Physik 61, 321 (1930).

Mollwo, E. "Absorption Spectrum of Na and K in the Melts of their Halogen Salts". Normal color centers replaced by wide-band centers. Got. Nach., Fachgruppe 2, 203 (1935).

Mott, W. "Theory of Photoconductivity". Impurities in solids may prevent photo-currents from approaching zero as the temperature decreases. Phys. Soc., Proc. 50, 196 (1938).

Ottmer, R. "Absorption Spectra of Photoelectric Conducting Alkali Halides". Considerable attention paid to purity of crystals. Z. Physik 46, 798 (1928).

Parfianovich, I. "Migration of Palladium Ions into Sodium Chloride". Optical properties of crystals with Pb in ionic and colloidal state discussed. J. Exp. Theor. Phys., USSR 18, 790 (1948).

Parfianovich, I. "Luminescence of NaCl-Ni, NaCl-Cu and NaCl-Ag Phosphors". J. Exp. Theor. Phys., USSR 19, 605 (1949).

Pick, H. "Color Centers in KCl Crystals Containing Traces of Alkaline Earth Ions". A number of absorption bands produced by adding impurities in vapor. Ann. Physik 35, 73 (1939), and Z. Physik 114, 127 (1939)

Poser, E. "Color Centers and Plastic Deformation of Synthetic NaCl". Effects on crystals containing foreign atoms $(SrCl_2)$. Z. Physik 91, 593 (1934).

Rexer, E. "Heat Treatment and Diffusion in NaCl and KBr". Interior of crystals heated in vapor exhibit different properties than surface. Presumed to be caused by foreign atom penetration. Z. Physik 106, 93 (1937).

Seitz, F. "Alkali Halide-Thallium Phosphors". The theory is presented that long wavelength absorption peaks not contained in pure alkali halides may be attributed to excitation of Tl ions. J. Chem. Phys. 6, 150 (1938).

Seitz, F. "Color Centers in Additively Colored Alkali Halide Crystals Containing Alkaline Earth Ions". Models are given for the absorption centers of certain impurities. Phys. Rev. 83, 134 (1951).

Smakula, A. "Absorption Spectra of Alkali Halides". Bands produced by addition of Ag and Cu to NaCl, KCl, NaBr and KBr reported. Z. Physik 45, 1 (1927).

Smakula, A. "Excitation and Bleaching of Photochemically Conducting Alkali Halides". Effect of Tl in NaCl on the build-up rate of the F-band by x-rays. Z. Physik 59, 603 (1930).

Smakula, A. "On Mechanical and Optical Excitation of Color Centers in Alkali Halides". Review and discussion of color center phenomena with and without impurities. Z. Physik 116, 525 (1940).

Stasiw, O. "Binding of Excess K in Potassium Halide Crystals". Bands occur when excess K is introduced into alkali halides containing Tl which can be thermally and optically bleached. Göt. Nach. Fachgrouppe 2, 1 (1936).

Toporec, A. "Formation of Atomic and Colloidal Centers of Silver in Alkali Halides". Alkali halides heated in Ag vapor. Comptes Rendu de L'Acad. des Sciences, USSR 15, 245 (1937).

Wolff, H. "Nature of Excited Centers in Alkali Halides". Centers are produced in crystals of varying degrees of purity. Comparison of displacement of absorption bands by impurity content with similar shifts by plastic deformation. Z. Physik 101, 234 (1936); 110, 512 (1938).

VITA

Name in full	William Henry Duerig
Permanent address	10428 Julep Avenue, Silver Spring, Maryland
Degree to be conferred; date	Ph.D.; 7 June 1952
Date of birth	10 September 1921
Place of birth	New York City, New York
Secondary education	Dobbs Ferry High School, Dobbs Ferry, New York

Collegiate Institutions Attended	Dates	Degree	Date of Degree
New York University	39-43	BS	June 1943
New York University	43-44	-	-
University of Maryland	47-52	Ph.D.	June 1952

Publications

W. H. Duerig, Bull. Am. Phys. Soc. 27, No. 2, U3 (1952)
W. H. Duerig, Phys. Rev., Letter to appear in May 15, 1952 issue.

Positions Held

Graduate Assistant in Physics, New York University, New York,
    June 1943 - April 1944.
Junior Physicist, University of California Radiation Laboratory,
    Berkeley, California, April 1944 - July 1945.
Associate Physicist to Principal Staff Member, The Johns Hopkins
    University Applied Physics Laboratory, Silver Spring, Maryland,
    July 1945 - present.