

## Formation of $F$ Centers at Low and Room Temperatures\*

HERBERT RABIN AND CLIFFORD C. KLINK

*United States Naval Research Laboratory, Washington, D. C.*

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It has been found that the x-ray production of  $F$  centers at liquid helium temperature is primarily dependent on the type of alkali halide and not on the defect structure of the particular specimen in contrast to observations at room temperature. This result indicates that the low-temperature production of  $F$  centers is a bulk property of the alkali halide and occurs as a result of the creation of halide ion vacancies by the ejection of halide ions from their normal lattice sites. The formation of  $F$  and  $H$  centers in pairs at liquid helium temperature is in accord with this model and is supported by the fact that the energy required to produce an  $F$  center at liquid helium temperature in a variety of alkali halides depends on the interstitial space available for accepting the halide atom. A comparison of the energy required to form  $F$  centers under various conditions at low temperature and at room temperature gives additional evidence for a two stage coloration process at room temperature.

### INTRODUCTION

IT is well known that the character of the optical absorption spectrum of an alkali halide crystal exposed to ionizing radiation is very much dependent on the temperature. Absorption bands appearing after low-temperature irradiation in many cases do not appear if the irradiation is performed at room temperature, while the reverse is also observed.<sup>1</sup> Of the large number of optical absorption bands which have been studied, none appears over the entire range from room temperature to liquid helium temperature as prominently as the  $F$  band. Thus the  $F$  center occupies a key position with respect to color center phenomena at all temperatures. It is the purpose of this paper to report on a number of optical absorption measurements of the  $F$  band in a variety of x-ray irradiated alkali halide crystals at low and room temperatures and to interpret these measurements in terms of the mechanisms of  $F$ -center formation.

### EXPERIMENTAL PROCEDURE

The x-ray irradiations and optical absorption measurements performed in this study at room, liquid nitrogen, and liquid helium temperatures<sup>2</sup> were made in a low-temperature apparatus that has been described in an earlier publication.<sup>3</sup> This apparatus was provided with a beryllium window (approximately 0.75 mm thick) for crystal irradiation, and quartz windows which could be rotated into position to measure the resulting absorption spectrum. The procedure that was adopted was periodically to interrupt the x-ray exposure to perform the optical measurement. Thus optical measurements were made at the same temperature as the irradiation temperature. These measurements were

made with a Bausch and Lomb grating monochromator used with either a 1P21 or 1P28 photomultiplier with appropriate dc amplifier and recorder. All crystals were exposed to the same incident x-ray flux from a Machlett OEG-50 tungsten-target tube operated at 43 kvp and 20 ma.  $F$ -center concentrations were computed from Smakula's formula using an oscillator strength of 0.8 for all alkali halides. Since the absorption of x rays through the body of the irradiated crystal was not uniform, the  $F$ -center concentrations are averages over the crystal thickness of approximately 0.4 mm. All alkali halides used in this work were single crystals cleaved from larger blocks. A list of crystals studied and the peak positions of the  $F$  bands at helium temperature are given in Table I.

The energy to form an  $F$  center at liquid helium temperature was determined for all the alkali halide crystals

TABLE I. Coloration of the crystals studied

Crystals investigated <sup>a</sup>	Peak position of $F$ band at liquid He temperature (m $\mu$ )	Average energy to produce an $F$ center at liquid He temperature (ev/ $F$ center)
Optovac NaCl	450	$1.4 \times 10^4$
NRL NaCl:0.5M% CaCl <sub>2</sub>		
Harshaw NaCl		
Natural NaCl <sup>b</sup>		
Natural NaCl, heated and quenched <sup>c</sup>	539	$1.3 \times 10^3$
NRL KCl:0.01M% SrCl <sub>2</sub>		
NRL KCl		
NRL KCl:0.14M% KOH		
Harshaw KBr	602	$1.4 \times 10^3$
Harshaw KBr:KH <sup>d</sup>		
Optovac NaF		
Harshaw LiF		
Harshaw KI	666	$5.2 \times 10^4$
NRL NaBr	526	$8.3 \times 10^5$

<sup>a</sup> Impurity concentrations added to various crystals are specified in terms of mole percent (M%) added to the melt. All NRL crystals were grown by the Kyropoulos technique.

<sup>b</sup> Natural NaCl, originally from near Baden-Baden, Germany, was obtained from the Smithsonian Institution through the courtesy of Dr. S. Switzer.

<sup>c</sup> Heated for 15 hours at 700°C and quenched in air at room temperature.

<sup>d</sup> Prepared by heating in a hydrogen atmosphere a Harshaw KBr crystal that had been additively colored with potassium.

\* A preliminary report of this work was given at the March 1959 meeting of the American Physical Society at Cambridge, Massachusetts, Bull. Am. Phys. Soc. Ser. II, 4, 147 (1959). The title of this report erroneously refers to  $\gamma$  rays rather than x rays.

<sup>1</sup> See F. Seitz, Revs. Modern Phys. 26, 7 (1954), for a comprehensive review of this subject.

<sup>2</sup> The liquid nitrogen and helium temperatures are nominal since a precise temperature measurement was not made.

<sup>3</sup> G. A. Russell and C. C. Klick, Phys. Rev. 101, 1473 (1956).

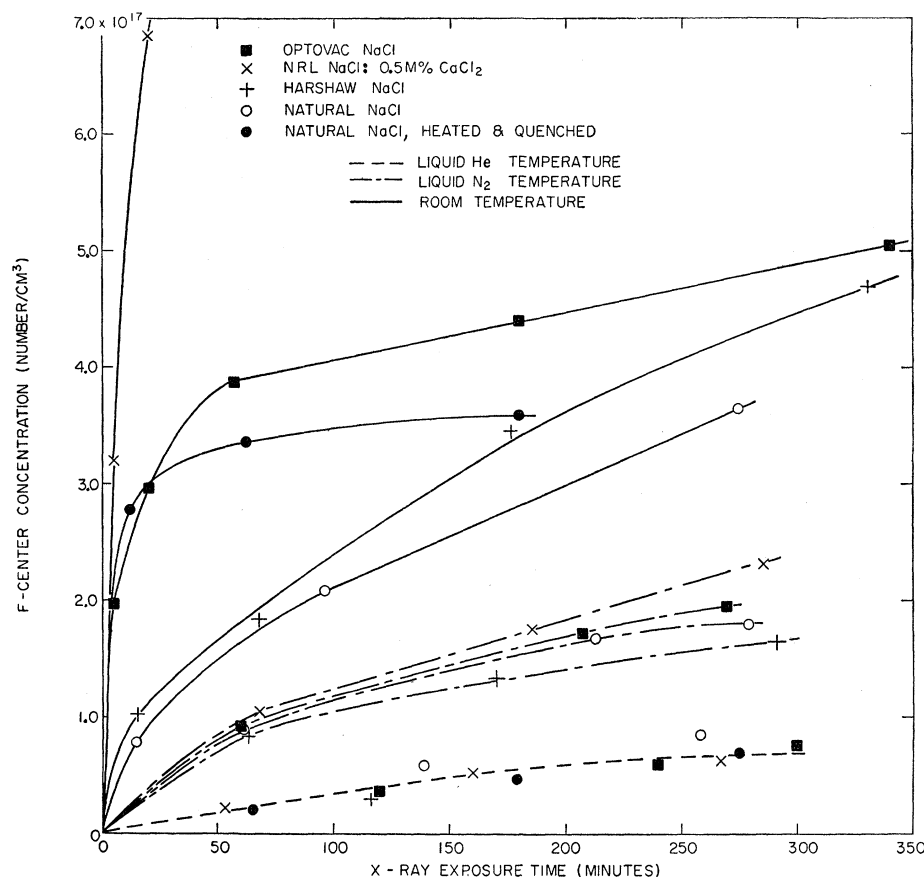


FIG. 1. Growth of the  $F$  band in various NaCl crystals exposed to x-ray radiation at room, liquid nitrogen, and liquid helium temperatures.

listed in Table I. This efficiency for  $F$ -center production was obtained by dividing the total x-ray energy absorbed in the crystal by the total number of  $F$  centers produced after about thirty minutes of irradiation.<sup>4</sup> The x-ray energy absorbed in the crystal was determined by silver-activated phosphate glass dosimetry<sup>5</sup> which employs the optical absorption change of the glass as an index of the energy flux of the radiation beam. This flux corresponded to  $2.25 \times 10^{19}$  ev/cm<sup>2</sup>-hour for the irradiation conditions in this study. The fraction of incident x-ray radiation absorbed by various alkali halides was determined by exposing the glass dosimeter to the x-ray beam with and without an intervening crystal.

## RESULTS AND DISCUSSION

### Growth of the $F$ Band

Figures 1–3 give the rate of  $F$ -center formation in various specimens of NaCl, KCl, and KBr, respectively.

<sup>4</sup> This efficiency corresponds essentially to the value during the initial growth of the  $F$  band since the coloration rate at liquid helium temperature does not change rapidly during its initial stages, as will be seen later in the text. Owing to the exceptionally poor colorizability of KI and NaBr at liquid helium temperatures, only one measurement of the  $F$ -band growth was obtained for these crystals after irradiations of 90 and 180 minutes, respec-

Data is plotted at room temperature and liquid helium temperature for all crystals and also at liquid nitrogen temperature in the case of NaCl. It is clear that the wide range of coloration rates that appears in various crystal specimens of the same alkali halide at room temperature disappears at low temperature. Particularly noticeable is the absence at low temperature of the large enhancement of coloration in calcium-doped NaCl over undoped NaCl which is observed at room temperature; a similar effect is noted in the case of hydrided KBr and untreated KBr. Also the change in coloration rate that is produced at room temperature by heating and quenching the natural NaCl crystal is largely suppressed when the coloration is measured at liquid helium temperature. The behavior of KCl and KBr differs from that of NaCl in that the low-temperature production of  $F$  centers exceeds that at room temperature in several cases; for NaCl the magnitude of the coloration is observed to diminish at successively lower temperatures in all cases.

The fact that all specimens of a particular alkali halide color at almost identical rates at liquid helium

tively; the energy required to produce an  $F$  center is based on these measurements.

<sup>5</sup> J. H. Schulman, C. C. Klick, and H. Rabin, *Nucleonics* **13**, No. 2, 30 (1955).

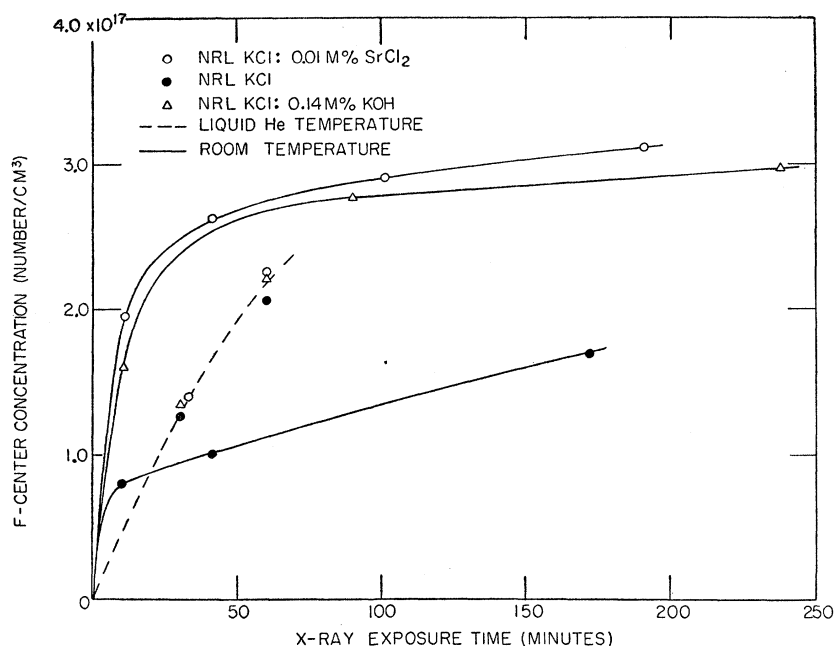


FIG. 2. Growth of the *F* band in several KCl crystals exposed to x-ray radiation at room and liquid helium temperatures.

temperature, while wide differences are observed at room temperature may be examined in light of the defect structure of these crystals. In a recent investigation of x-ray induced expansion of NaCl crystals<sup>6</sup> estimates were obtained of the initial halide ion vacancy concentrations of the crystals of Fig. 1 and were found to vary over a considerable range. The Harshaw NaCl had a concentration prior to irradiation of about  $1 \times 10^{16}/\text{cm}^3$ , the Optovac NaCl about  $2 \times 10^{17}/\text{cm}^3$ , and the calcium-doped NaCl at least  $6 \times 10^{17}/\text{cm}^3$ . Although an estimate was not obtained for the natural NaCl, indirect evidence indicated that a value less than  $1 \times 10^{16}/\text{cm}^3$  was appropriate for the specimen that was not heat treated. Not only is there a variation in the halide ion vacancy concentration in these crystals, but a considerable range in dislocation density and impurity content is also represented. The natural crystal was highly strained as evidenced by observation with polarized light, and under etching this crystal showed a dislocation density many times larger than the Optovac crystal. Although only one NaCl crystal was purposely doped with impurity (the calcium-doped crystal), undoubtedly a variety of trace impurities were present considering the different crystal origins.<sup>7</sup> Thus from the point of view of vacancies, dislocations and impurities, the NaCl crystals of Fig. 1 have appreciable diversity. The relative defect structure of the various KCl and KBr crystals was not known to the extent that it was known for NaCl (aside from impurities purposely added), but it is reasonable to assume that a fair range in defects were represented in these alkali halides if for no other reason than the variations observed in

room temperature coloration of specimens of the same alkali halide. With the rate of *F*-band growth at liquid helium temperature independent of the defect structure, one is led to conclude that the production of *F* centers in NaCl, KCl, and KBr at liquid helium temperature is strictly a bulk property of the particular lattice. In this case the x-ray formation of *F* centers at liquid helium temperature is most simply pictured as resulting from Frenkel defects consisting of halide ion vacancies generated by the ejection of halide ions from their normal lattice sites into the interstices of the lattice. By contrast most of the previous speculations concern-

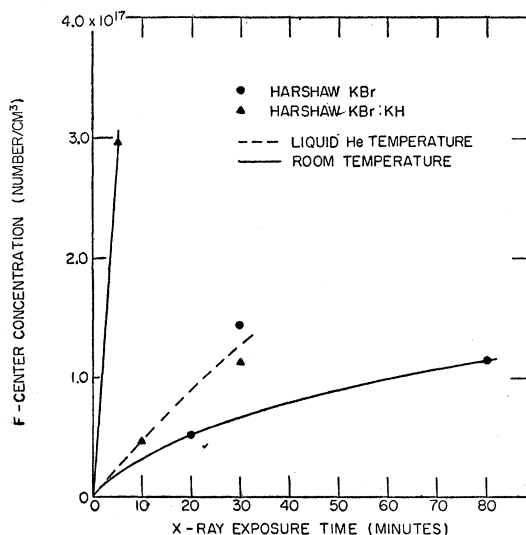


FIG. 3. Growth of the *F* band in undoped and hydrided KBr crystals exposed to x-ray radiation at room and liquid helium temperatures.

<sup>6</sup> H. Rabin, Phys. Rev. **116**, 1381 (1959).

<sup>7</sup> W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

ing low-temperature coloration assumed the production of  $F$  centers from Schottky defects.<sup>1</sup>

Owing to the difficulty of accounting for the production of equal numbers of  $F$  centers in specimens of the same alkali halide with grossly different halide ion vacancy concentrations, it must be assumed that the halide ion vacancies originally in the crystal play a negligible role at liquid helium temperature. One might argue that these vacancies are in some configuration (perhaps aggregated with alkali ion vacancies) which does not allow for their efficient conversion to  $F$  centers at liquid helium temperature. This argument is supported by experimental evidence which indicates that halide ion vacancies are easily converted to  $F$  centers at liquid helium temperature if they exist as isolated vacancies. The following experiment carried out at liquid helium temperature is a case in point. A NaCl crystal was first x-ray irradiated for about three hours to produce a sizable  $F$  band and then optically bleached with white light removing a large fraction of this  $F$  band. The crystal was then re-irradiated with x-rays for a short time (five minutes) and its  $F$  band was again measured. It was found that approximately the same  $F$ -center concentration appeared after the second x-ray irradiation as existed prior to bleaching.<sup>8</sup> It is concluded that the production of  $F$  centers at liquid helium temperature can be accomplished with comparative ease during a short irradiation if halide ion vacancies are initially isolated.

### Efficiency of $F$ -Center Production

Duerig and Markham<sup>7</sup> have demonstrated that x-ray irradiation of alkali halide crystals (NaCl, KCl, and KBr) at liquid helium temperature results in two prominent optical absorption bands, the  $F$  band and the  $H$  band. In a recent investigation Känzig and Woodruff,<sup>9</sup> using the techniques of electron spin resonance, have associated this optical  $H$  band with a center which may be roughly visualized as three halide ions plus a halide atom that have been squeezed into the position normally occupied by three halide ions along a face diagonal; thus the  $H$  center is the exact chemical equivalent of an interstitial halide atom. This identification appears more certain in KCl than in KBr.

Känzig and Woodruff have taken note of the fact that the usual model of the  $F$  center and their model of the  $H$  center are complements of one another, i.e., the perfect lattice would be restored if these centers were combined, and they suggest the possibility that under ionizing radiation at low temperature these centers are created as pairs. The work reported here emphasizes that  $F$  centers are formed in the perfect lattice and that this can most simply be understood as

the production of a pair of defects consisting of an interstitial halide atom and a halide ion vacancy with an electron. Thus the conclusions of Känzig and Woodruff on the nature of the  $H$  center and those reported here on the creation of the  $F$  center support each other.

It does not yet seem possible to ascertain in detail the mechanism of production of the defects. Varley<sup>10</sup> has proposed that double ionization of the halide ion would produce free electrons and would lead to a reversal of the normal ionic charge; the ion would then be ejected into an interstitial position by Coulomb forces. Capture of a free electron by the interstitial positive halide ion would produce a halide atom which corresponds to the Känzig-Woodruff  $H$  center, and capture of a free electron by the halide ion vacancy would produce the  $F$  center. It is, however, also conceivable that thermal spikes produced by energetic photoelectrons might be responsible for the production of the same centers.

In view of the evidence that  $F$  and  $H$  centers are formed in pairs and that the process involves the production of an interstitial halide atom, it seemed likely that the total energy used in creating a pair of centers would be dependent on the interstitial space available to accept the halide atom and the size of the halide atom. Table I lists the number of electron volts required to produce an  $F$  center at liquid helium temperature for the various alkali halides, and Fig. 4 shows a plot of these values as a function of the ratio of the quantities  $S$  to  $D$ , where  $S$  is the space between adjacent halide ions along a  $\langle 110 \rangle$  direction in the normal lattice<sup>11</sup> and  $D$  is the diameter of the halogen atom.<sup>12</sup> The quantity  $S/D$  obviously is a measure of the space available to a halogen atom for insertion between two halide ions along a face diagonal. Accordingly, it would be expected that as  $S/D$  decreases it becomes successively more difficult to produce an  $F$  center- $H$  center pair, and the total energy required to create an  $F$  center increases. As indicated in Fig. 4 this is precisely the behavior noted for KBr, NaCl, KI, and NaBr; the energy per  $F$  center for these crystals increases consecutively over a range of about 600 while  $S/D$  decreases by a factor of approximately two.<sup>13</sup> An interesting result of the data of Fig. 4 concerns the fact that for KBr, KCl, and NaF the energy required to produce an  $F$  center is approximately the same, about 1300 to 1400 eV/ $F$  center, as  $S/D$  increases from

<sup>10</sup> J. H. O. Varley, *J. Nuclear Energy* **1**, 130 (1954).

<sup>11</sup>  $S$  was computed from recently revised values of ionic radii given by B. S. Gourary and F. J. Adrian, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959), Vol. 9.

<sup>12</sup> Atomic diameters were taken from G. H. Dieke, *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Sec. 7.

<sup>13</sup> It is expected that  $F$ -center production in NaI at low temperature is particularly difficult since  $S/D$  is only 0.17 for this crystal. H. Rüchardt, *Phys. Rev.* **103**, 873 (1956), notes that NaI, NaBr, and KI all color quite poorly; it would be interesting to confirm that NaI is the poorest of the three.

<sup>8</sup> W. D. Compton and C. C. Klick, *Phys. Rev.* **110**, 349 (1958), have obtained similar results for KCl and KBr.

<sup>9</sup> W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1959).

0.46 to 0.70; thus for a value of  $S/D$  larger than roughly 0.5 it does not become any easier to create an *F* center-*H* center pair. This result may be significant. If it is assumed that the central ion in the array of three normal halide ions in the drawing of Fig. 4 is moved along the face diagonal a distance  $S$  to meet one of its neighbors, a total space  $2S$  is available for insertion of a halide atom. It may be that alkali halides with values of  $S/D$  larger than roughly 0.5 have the requisite interstitial space available to form the *H* center with a minimum amount of ionic readjustment thus leading to stable *H* centers.

If the Varley mechanism for formation of the color centers at low temperature is correct, the limiting process in coloration may be the diffusion of the positive halide ion. The diameter of such an ion ( $D^+$ ) does not appear to be known so that a comparison of it with  $S$  is not possible. It is likely that the halogen atoms with the largest values of  $D$  would also have the largest values of  $D^+$  so that the general order of alkali halides in Fig. 4 would probably be maintained if it were possible to plot  $S/D^+$  on the abscissa. While it is not certain which one of several possible factors limits the ability of an alkali halide to color at low temperature, it does appear that this factor is related to the amount of interstitial space in the particular alkali halide and the size of the halogen atom or the positive halide ion.

The fact that LiF does not fit the general scheme of the data of Fig. 4 is not particularly surprising in that the behavior of LiF has previously been found to be different from that of other alkali halides. Aside from the fact that the electron distributions of LiF overlap to a far greater degree than the more typical alkali halides such as NaCl,<sup>14</sup> an additional absorption band in LiF to the long wavelength side of the *F* band (peaking at about 360 m $\mu$ ) was observed at liquid helium temperature contrary to observations on other alkali halides.

The mechanisms of low-temperature coloration and the efficiencies of production of *F* centers can be used in understanding the coloration processes at room temperature. Gordon and Nowick<sup>15</sup> have proposed a two stage x-ray coloration process at room temperature in which the first stage consists merely of placing electrons in halide ion vacancies already existing in the crystal. In the second stage, vacancies are created by the radiation, and the efficiency of production is much lower. Recent measurements<sup>6</sup> on the expansion of NaCl under x rays support this two stage model.

The first stage coloration at room temperature would have its counterpart at low temperature when a crystal is x-rayed, optically bleached, and then x-rayed a second time. As previously mentioned, the second

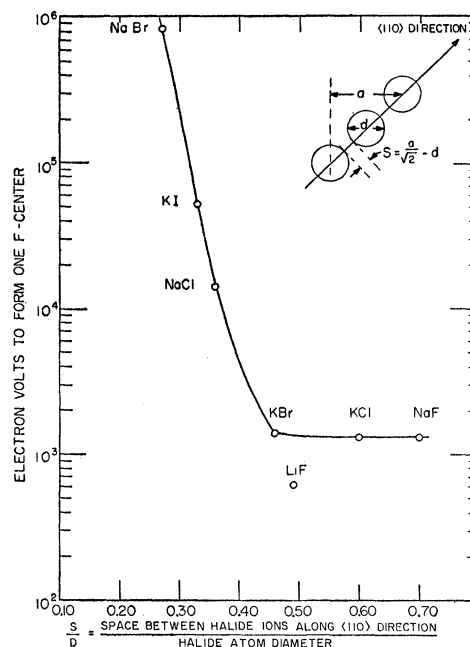


FIG. 4. Total x-ray energy required to form one *F* center at liquid helium temperature for various alkali halides as a function of the ratio  $S/D$ , where  $S$  is the space between adjacent halides in a (110) direction of the normal lattice and  $D$  is the diameter of the halogen atom.  $S$  is given by  $[(a/\sqrt{2}) - d]$  where  $a$  is the lattice constant and  $d$  is the halide ion diameter.

x-ray exposure colors the crystal very much faster than does the first exposure and is believed to correspond to the simple filling of isolated halide ion vacancies with electrons. This low-temperature coloration was found to occur for KCl with an expenditure of as little as 28 ev per *F* center which may be compared with values from 18 ev to 120 ev per *F* center<sup>16</sup> found for the first stage coloration of KCl at room temperature. This range may reflect the varying concentrations of negative ion vacancies in different crystals.

The second stage coloration at room temperature should be comparable to the initial x-ray coloration at low temperature since vacancies would need to be created in both cases. For Optovac NaCl the second stage coloration at room temperature requires  $11 \times 10^8$  ev per *F* center; undoped KCl requires  $7.1 \times 10^8$  ev per *F* center. At low temperatures the corresponding initial coloration for the same materials was  $14 \times 10^8$  and  $1.3 \times 10^8$  ev per *F* center, respectively.

This order of magnitude agreement between the energies required for corresponding processes at the two temperatures lends further support to the two stage mechanism of coloration at room temperature. It is not clear, however, that the creation of vacancies at room temperature is by a Frenkel defect process, as seems to be the case at low temperatures; one of several

<sup>14</sup> H. Witte and E. Wölfel, Z. physik. Chem. **3**, 296 (1955) and J. Krug, H. Witte, and E. Wölfel, Z. physik. Chem. **4**, 36 (1955).

<sup>15</sup> R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956) and A. S. Nowick, Phys. Rev. **111**, 16 (1958).

<sup>16</sup> H. U. Harten, Z. Physik **126**, 619 (1949) and E. E. Schneider, *Photographic Sensitivity* (Butterworth Scientific Publications, London, 1951).

proposed mechanisms for the production of Schottky defects may equally well predominate.

### CONCLUSIONS

The two principal experimental observations reported in this paper suggest that the formation of  $F$  centers at liquid helium temperature occurs as the result of the ejection of a halide ion (or atom) into the interstices of the lattice, leaving a vacancy which subsequently traps an electron and becomes an  $F$  center. These observations are as follows: first,  $F$  center formation at liquid helium temperature appears to be essentially a bulk property of the alkali halide, independent of both the defect structure and the

coloration at room temperature; and second, the energy required to form an  $F$  center at liquid helium temperature for various alkali halides is in agreement with the interstitial space available to accept the ejected halide ion (or atom). The suggestion of Känzig and Woodruff that the formation of  $F$  centers and  $H$  centers at liquid helium temperature is a paired process is in accord with these observations.

A comparison of the energy necessary to produce  $F$  centers at room temperature and low temperature lends additional support to the view that room temperature coloration occurs in two stages: the first consists of filling existing vacancies with electrons; in the second stage vacancies must be created.

## Pressure Effects of Helium and Argon on the First Sharp Series Doublet of Indium\*

SHANG-YI CH'EN, ALLEN SMITH, AND MAKOTO TAKEO  
University of Oregon, Eugene, Oregon

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The shift, half-width, and asymmetry of the  $\text{In}\lambda 4101$  and  $\lambda 4511$  lines produced by various pressures of helium and argon up to 120 atmospheres and the appearance of satellite bands near these lines are described. The entire absorption line contours and the wings of the pressure-broadened lines were studied. The experimental observations were compared with the Anderson-Talman theory at general pressures.

### I. INTRODUCTION

IN contrast to the much studied pressure broadening and shift of alkali doublets<sup>1</sup> with  $^2S$  as ground state, the corresponding study of the first sharp series doublet ( $5^2P_{1/2}-6^2S_{1/2}$ ,  $5^2P_{3/2}-6^2S_{1/2}$ ) of In ( $\lambda 4101$  and  $\lambda 4511$ ) facilitates the investigation of the perturbation of energy levels whose fine structure separation is due to the ground states  $^2P$ . The line contours, the shifts, and the satellites of these lines were observed for pressures up to 120 atmospheres of He and Ar by means of a 35-foot grating in Wadsworth mounting. For helium, the temperature of the absorption tube ranged from 800°C–1000°C for both lines, and for argon the temperature was constantly 800°C for  $\lambda 4101$  and 900°C for  $\lambda 4511$ .

### II. RESULTS

The speed of the grating spectrograph was  $f/35$ , and the plate constants for the  $\lambda 4101$  and  $\lambda 4511$  regions were 1.55 and 1.53 Å/mm, respectively. The slit width was 30  $\mu$ . Two different lengths of absorption column were used, 4.4 and 4.95 cm. Kodak type 103-0 plates were calibrated by means of step filters, and the line contours were analyzed with a recording microphotometer. During the course of this research great care was taken in designing the absorption tube to keep the

temperature of the absorption column uniform and constant. The accuracy of relative density values of foreign gases should be within 2%.

#### 1. The Shift

Figure 1 is a plot of the observed values of shift  $\Delta\nu_m$ , in  $\text{cm}^{-1}$ , vs the relative density (r.d.) of argon or helium. For argon the *red* shift of the  $\lambda 4101$  ( $^2P_{1/2}$ ) component is practically the same as that of the  $\lambda 4511$  ( $^2P_{3/2}$ ) component. For He the *violet* shift of the  $\lambda 4101$  component is slightly smaller than that of the  $\lambda 4511$  component. The magnitude of the red shift produced by argon is about three times greater than the violet shift produced by helium. Empirical equations which describe the present data are:

For In 4101/argon:

$$-\Delta\nu_m = 0.408(\text{r.d.}) + 0.012(\text{r.d.})^2 \text{ cm}^{-1}. \quad (1)$$

For In 4511/argon:

$$-\Delta\nu_m = 0.454(\text{r.d.}) + 0.0095(\text{r.d.})^2 \text{ cm}^{-1}.$$

For helium as a perturber we can obtain a relation similar to Eq. (1), but the error appearing in the second term would be very large. A theoretical equation for the line shift is given in Part III.

\* Sponsored by the Office of Ordnance Research, U. S. Army.  
<sup>1</sup> S. Y. Ch'en and M. Takeo, Revs. Modern Phys. **29**, 20 (1957).