where

$$\epsilon=-\tfrac{1}{3}\Xi_u(S_{11}-S_{12})T;\quad S_{11}\text{ and }S_{12},$$

are the elastic compliance constants, T is the applied stress and Ξ_u is the shear-deformation-potential constant of the conduction-band minima. Also, $6\Delta_c$ = chemical splitting of the ground state. The $1s(E)$ and $1s(T_1)$ states are assumed to be degenerate. The solutions to the secular equation are

$$\epsilon-\Delta_c\ (3\text{ roots}),\ -2\epsilon-\Delta_c,\text{ and}$$

$$\tfrac{1}{2}[(4\Delta_c-\epsilon)\pm(9\epsilon^2+12\epsilon\Delta_c+36\Delta_c^2)^{1/2}].$$

The variation of the ground states with strain is shown in Fig. 15. It is seen that the two states described by the first two types of roots vary with strain in a manner which is identical to that of the p states.

The following linear combinations of the effective-mass wave functions permit the selection rules of Fig. 12 to be deduced

$$\begin{array}{lll}
\alpha_j^{(1)}: & 2^{-1/2}(1,-1,0,0,0,0) & (B_2),\\
\alpha_j^{(2)}: & (a,a,b,b,b,b) & (A_1),\\
\alpha_j^{(3)}: & \tfrac{1}{2}(0,0,1,1,-1,-1) & (B_1),\\
\alpha_j^{(4)}: & 2^{-1/2}(0,0,1,-1,0,0) & \multirow{2}{*}{(E),}\\
\alpha_j^{(5)}: & 2^{-1/2}(0,0,0,0,1,-1) & \\
\alpha_j^{(6)}: & (c,c,d,d,d,d) & (A_1),
\end{array}$$

where, for $\chi_j=F_j\varphi_j$ (see Ref. 6), the corresponding wave functions are

$$\psi^{(i)}=\sum_{j=1}^{6}\alpha_j^{(i)}\chi_j,$$

and the valleys labeled $j=1,\cdots,6$, have their major axes along [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$], respectively;

$$a^2=\tfrac{1}{4}(1+\beta),\ b^2=\tfrac{1}{8}(1-\beta),\ c^2=\tfrac{1}{4}(1-\beta)\text{ and }d^2=\tfrac{1}{8}(1+\beta)$$

and

$$\beta=(3\epsilon+2\Delta_c)(9\epsilon^2+12\epsilon\Delta_c+36\Delta_c^2)^{-1/2}.$$

The letters in parentheses refer to the irreducible representations of D_{2d}, the point group symmetry of the impurity for $\mathbf{F}\|[100]$.

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Color Centers Produced in KCl and KBr by Prolonged X Irradiations at Low Temperatures

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The principal purposes of this study were to observe the effect of an x irradiation of extended duration on the production of color centers in KCl and KBr at low temperatures and to examine the implications with regard to possible color-center models. Growth curves were determined at 5°K for the F, K, M, and H bands in KCl and KBr and for a new band at 245 mμ in KCl and at 278 mμ in KBr, called the H' band. Growth curves were determined at 80°K for the F, K, and M bands in KCl and KBr. The growth of the V_4 band in KBr and of a band having its absorption maximum at 240 mμ in KCl, designated as the $V(240)$ band, was also followed at 80°K. The ratio of the absorptions at the peak of the F and K bands was found to remain constant indicating that both of these bands arise from transitions in the same center. The concentration of M centers was found to depend quadratically on the F-center concentration. This result gives conclusive support to the model proposed by van Doorn and Haven that the M center consists of a pair of associated F centers. The F-to-H ratio was observed to be constant for short x-ray exposures, supporting the viewpoint that the two centers are produced as complementary defects; however, for prolonged exposures, this ratio is no longer constant. The number of F centers is in constant ratio to the combined concentrations of H and H' centers provided that the oscillator strength of the H' band is suitably chosen. The linear dependence of the generation of both V_4 centers in KBr and $V(240)$ centers in KCl on F-center concentration suggests that the V_4 and $V(240)$ centers, rather than V_1 centers, are fundamentally related to the mechanism of formation of F centers near liquid-nitrogen temperature for a prolonged irradiation.

I. INTRODUCTION

IT is well known that the types of color centers produced by ionizing radiation and the concentrations of each are very much dependent on the temperature of irradiation. Accordingly, a considerable effort has been expended in studying the role of temperature in the formation of radiation-induced defects in the alkali halides. The major part of this research has been confined to three principal temperature regions, conveniently defined, as follows: the liquid-helium temperature range (at 5°K), the liquid-nitrogen range (at 80°K) and room temperature (295° to 300°K). The principal

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features of color-center generation characteristic of each region are presented in the following summary.

It is for the first temperature region that the defect models are best understood. Here the basic effect of x rays is to create an interstitial halogen atom (an H center) leaving a vacancy in the lattice.[1,2] The latter is then free to trap an electron to form an F center. The H center serves as the complement of the F center in that the perfect lattice would be restored by a recombination of the two centers. It is also known that F-center coloration near 4°K is independent of the initial concentration of negative ion vacancies, the concentration of chemical impurities and the degree of strain of a crystal.[3] For x irradiation in the liquid-nitrogen temperature range, a comparable level of knowledge has not been attained. In this case, the prominent growth of the F band is accompanied by a progressive coloration due to the generation of a variety of trapped-hole or V-type centers.[4,5] The prominence of the V_1 band during the initial stages of irradiation has led to the suggestion that the V_1 center is the dominant defect induced at this temperature.[6] More recently, x-ray exposures of KBr for longer durations have shown that the V_1 band saturates whereas absorptions associated with the V_4 and V_7 continue to grow. On this basis, it has been suggested that the latter are the most important hole defects formed in KBr near 80°K.[7] Likewise, an extended x irradiation of KCl at 80°K has revealed the growth of a prominent band with maximum at 240 mμ that is proportional to the intensity of the F band.[8] At room temperature, the process of coloration by x rays is known to depend strongly on the purity of the crystal, its dislocation density, and even on the x-ray intensity.[9,10] Furthermore, unambiguous defect models have not as yet been assigned to many of the centers generated at this temperature.

This investigation presents the results of prolonged x irradiation (about 60 h) on the production of color centers. The procedure consisted in observing the relation between F centers and other types of color centers that are generated by x rays at liquid-helium and at liquid-nitrogen temperatures. The experiment was restricted to these temperatures in view of the strong structure sensitivity of coloration processes at room temperature indicated in the above summary. The observation that M centers are generated by x rays at these low temperatures has already been reported.[11]

II. EXPERIMENTAL PROCEDURE

A. Crystals

The crystals employed in the low-temperature x-ray studies were constituted as follows: two specimens each of pure KCl and KBr, one of KCl doped with strontium[12] and one of KBr doped with calcium.[13] The pure crystals were grown by the Harshaw Chemical Company. The strontium-impurity concentration in the KCl:Sr crystal was 0.1 mole% as determined by emission spectroscopy. The results of an analysis based on a specific colorimetric technique[14] and a measurement of the ionic conductivity of the KBr:Ca crystal were provided by Rolfe.[15] The excess-calcium concentration was observed to be 3.2×10^{-4} mole%; there was also present about 1.4×10^{-4} mole% of an unidentified divalent negative impurity.

The single crystals were cleaved into plates approximately 1-cm square and ranging in thickness from 0.09 to 0.20 mm. The pure crystals were mounted in the low-temperature apparatus immediately after being cleaved. The cleaved divalent-doped crystals were annealed at 500°C for several minutes and rapidly quenched to room temperature in an attempt to break up possible divalent complexes. Pure KCl and KBr crystals were employed in connection with the M-band half-width measurements. Some of these specimens were additively colored at 600°C in potassium vapor,[16] annealed at 500°C, and rapidly quenched to room temperature in the dark in order to disperse any aggregate centers that might be present. Some of the pure crystals were x irradiated briefly at room temperature to form F centers. F centers were converted to M centers by illumination with light absorbed by the F centers. Data shown for the long x-ray exposures were generally taken on a single sample but were found to be consistent with data taken for exposures of several hours on similar samples.

B. Apparatus

X-ray irradiations and optical-absorption measurements were performed in a stainless-steel low-temperature Dewar of conventional design.[17] Each crystal sample was positioned so as to cover a circular aperture in the copper cold finger. Since the thinness of most of the crystals in this study precluded a direct measurement of the sample temperature, only the temperature of the holder was determined. With liquid helium in the inner Dewar vessel and liquid nitrogen in the outer one, the equilibrium temperature of the holder, as measured with

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a calibrated germanium thermometer, was 5°K; with liquid nitrogen in both vessels, the corresponding temperature was determined to be 80°K by means of a copper-constantan thermocouple. The Dewar was provided with a beryllium x-ray entrance window (0.75 mm thick) as well as a pair of quartz windows for optical observations. These windows were mounted in a rotatable head so that optical measurements could be carried out on a sample without any intervening warmup. Irradiations were performed in the dark and periodically interrupted for optical-absorption measurements.

All of the crystals were exposed in the dark to the same incident x-ray flux from a Machlett OEG-60 tungsten-target tube operated at a constant potential of 50 kV and a filament current of 37.5 mA. The flux was measured to be 5.6×10^{19} eV/cm²-h at the sample position within the Dewar by means of silver-activated metaphosphate glass dosimetry.[18] A comparison of the absorbed x-ray energy with previous workers is difficult. If the maximum concentration of *F* centers is used as an index, the prolonged irradiations (about 60 h) described here generated *F* centers in concentrations three to ten times greater than reported in the earlier experiments.[3,7,19] Optical measurements were performed with a Cary Model 14 double-beam recording spectrophotometer. The optical density of the samples was determined relative to an aperture before and after exposure of the crystals to x rays. It was assumed that the samples were sufficiently thin that they were uniformly colored and hence the absorption constant, α, was directly proportional to the optical density. No change in the absorption spectrum was produced by the measuring light, since two consecutive absorption measurements gave the same results. The usual range of optical-density values measured by the Cary instrument from 0 to 2 (in two scales: 0–1 and 1–2) was extended to an upper limit of 6 by inserting screens of known optical density in the reference beam of the instrument. Accuracy was severely limited by scattered light within the instrument for optical density values greater than 6. The measurement of the extremely weak absorption of the *M* band in the early phases of growth was facilitated by the use of an auxiliary slide wire which increased the sensitivity of the instrument by converting the 0–1 and 1–2 optical-density scales to 0–0.1 and 0.1–0.2, respectively.

III. RESULTS AND DISCUSSION

A. Absorption Spectra

Prior to a detailed discussion of the growth of individual color-center bands resulting from x-ray irradiation at low temperatures, some representative optical-absorption spectra will be presented. In all of these spectra, the peak positions of the various bands were located by inspection. No account was taken of the shift in the peaks arising from overlapping structures. In most instances, a band which did not possess an accepted letter designation was specified by the wavelength at which its peak position was observed at the conclusion of the irradiation.

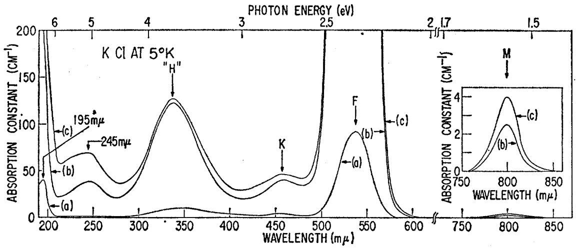

FIG. 1. The optical-absorption spectra of a KCl crystal measured at 5°K after x-ray exposures of (a) 15 min, (b) 14.4 h, and (c) 59.6 h at the same temperature. The corresponding numbers of *F* centers/cm³ are (a) 2.1×10^{17}, (b) 2.6×10^{18}, and (c) 3.2×10^{18}, respectively. The inset shows the spectral details of the *M* band.

Figure 1 shows absorption spectra corresponding to three stages in the x irradiation of a pure KCl crystal at 5°K. Curve (a), obtained after 15 min of irradiation, gives results comparable to those observed by Duerig and Markham[19] at 5°K. After 14.4 and 59.6 h of x irradiation, the optical absorption is as shown in curves (b) and (c), respectively. The spectral properties as well as detailed growth of the prominent bands observed at this temperature, viz., the *F*, *K*, "*H*" and the 245-mμ band, will be discussed later. A similar treatment will be carried out for the extremely weak band having its peak position at 799 mμ and identified as the *M* band. Although a short irradiation revealed the presence of a band with a maximum at 195 mμ, in agreement with Duerig and Markham, details of its growth were masked by the rapid deepening of coloration in the spectral region below 200 mμ. The band has been studied by Klick and Patterson[20] by means of vacuum uv spectrophotometry and its presence has been ascribed to a Frenkel defect in which an interstitial negative ion is located extremely close to a negative-ion vacancy.

The absorption spectra of a pure KBr crystal subjected to a prolonged x-ray exposure at 5°K may be seen in Fig. 2. The result of 15 min of irradiation shown in curve (a) is similar to data presented by Duerig and Markham[19] for KBr x irradiated at the same temperature. The absorption resulting from a 10.0-h and 64.0-h irradiation are shown by curves (b) and (c), respectively. As for KCl, the discussion of the spectral properties and growth data of the bands designated as the *F*, *K*, *M*, *H*, as well as the 278-mμ band will be postponed until later.

Several comments are in order regarding the other bands which appear in Fig. 2 since they are not to be treated in detail. A very prominent α band peaking at 202 mμ is known to form at liquid-helium temperature.[21]

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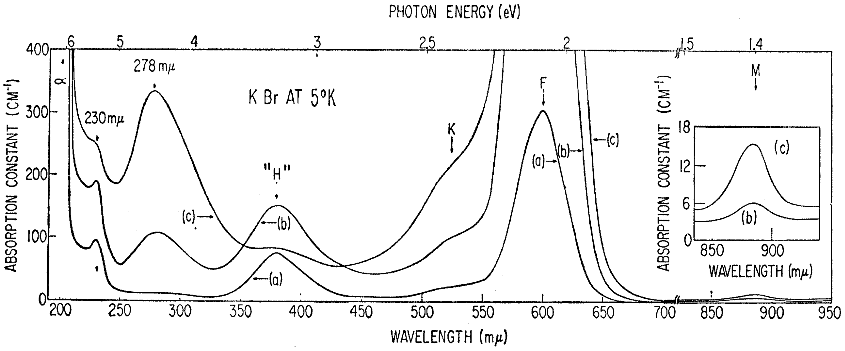

FIG. 2. The optical-absorption spectra of a KBr crystal measured at 5°K after x-ray exposures of (a) 15 min, (b) 10.0 h, and (c) 64.0 h at the same temperature. The corresponding numbers of F centers/cm^3 are (a) 6.7×10^{17}, (b) 2.7×10^{18}, and (c) 5.2×10^{18}, respectively. The inset shows the spectral details of the M band.

However, the induced absorption is so large in this spectral region after the 15-min irradiation that the peak of the band is beyond the ordinary optical range of the spectrophotometer. As a result, only the long-wavelength side of the band is observed. The band at 230 mμ, observed as a shoulder of the α band, has been investigated by Klick and Patterson. These authors suggest that the defect center responsible for this band is the same as for the 195-mμ band in KCl.[20] There is evidence of an extremely weak F' band at the tail of the F band in agreement with the observations of Duerig and Markham[19] and this is seen to lie beneath the resolved M band. It is interesting that the formation of the F' band was not observed in KCl at 5°K.

The effect of elevating the irradiation temperature from 5 to 80°K may be seen by comparing the absorption spectra in Figs. 3 and 4 with those of Figs. 1 and 2, respectively. Figure 3 shows three stages of coloration observed during a prolonged x irradiation of a KCl crystal at 80°K. In curve (a) are shown the absorptions produced by a brief irradiation of 30 min. The results are in agreement with previous reports by Casler, Pringsheim, and Yuster,[4] Dorendorf,[5] and Duerig and Markham.[19] The absorption spectra corresponding to 9.5 and 52.0 h of x-ray exposure are shown in curves (b) and (c), respectively. A detailed presentation and discussion of the properties and growth of the F, K, and M bands as well as some of the aspects of L_1-band growth will be given below. A similar treatment will be provided for the band first observed as a composite of the V_2 and V_4 bands and later seen to develop into a prominent absorption peaking at 240 mμ. This band is designated for the present as the $V(240)$ and is presumed to be the same band recently studied by Pretzel.[8] Although the formation of V_1, and to a lesser extent V_K centers, is of considerable interest in brief x-ray exposures at liquid-nitrogen temperature, the early saturation of the V_1 and V_K bands suggests that neither center contributes significantly in defect formation in a prolonged irradiation.

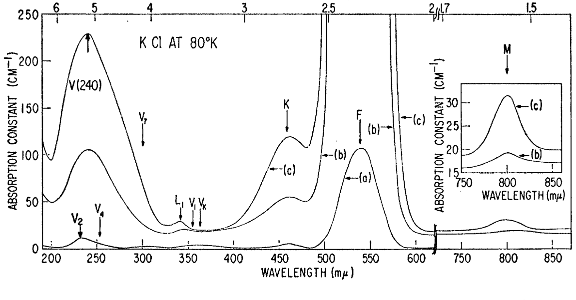

FIG. 3. The optical-absorption spectra of a KCl crystal measured at 80°K after x-ray exposures of (a) 30 min, (b) 9.5 h, and (c) 52.0 h at the same temperature. The corresponding numbers of F centers/cm^3 are (a) 2.4×10^{17} (b) 2.5×10^{18}, and (c) 6.6×10^{18}, respectively. The inset shows the spectral details of the M band.

In addition to the above color-center bands, several other absorbing regions in Fig. 3 are worthy of brief comment. The progressive coloration noted at wavelengths shorter than 200 mμ is possibly associated with the α band known to have its maximum near 177 mμ.[22] Next, there appears to be an appreciable unresolved contribution to the long-wavelength side of the $V(240)$ absorption band which is assumed to be due to the presence of the V_7 band.[5] Finally, the continued growth of the broad absorption on the long-wavelength side of the F band which extends beneath the M band is identified as the well-known F' band.

The final series of absorption spectra shown in Fig. 4 illustrate the growth of absorption induced in a KBr crystal during the course of an extended x irradiation at 80°K. The result of an exposure of 30 min is represented by curve (a) and corresponds to data reported previously.[5,19] Curves (b) and (c) exhibit the state of coloration attained at 9.9 h and at the conclusion of the 54.5 h irradiation, respectively. As in the case of the KCl crystal studied at 80°K, a discussion of the growth and characteristics of the F, K, M, L_1, V_1, and V_K bands will be presented later. The prominent band peaking at a wavelength of 275 mμ is identified as the V_4 in accordance with Kingsley's investigation.[7] The band appears to be a counterpart of the $V(240)$ band observed in KCl and will be treated in detail below. No attempt was made to resolve and follow the growth of the α band in view of the extremely strong absorption band known

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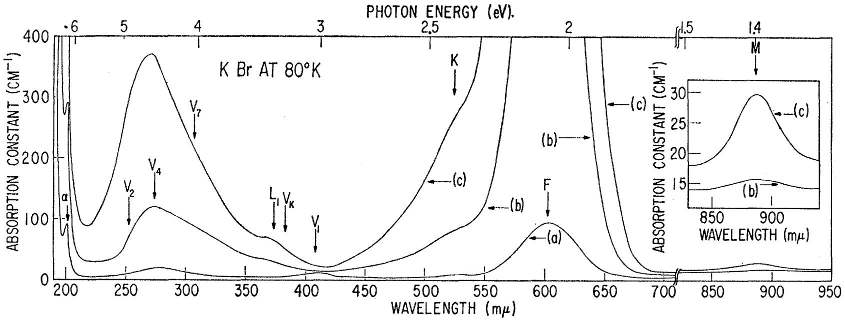

Fig. 4. The optical-absorption spectra of a KBr crystal measured at 80°K after x-ray exposures of (a) 30 min, (b) 9.9 h, (c) 54.4 h at the same temperature. The corresponding numbers of F centers/cm^3 are (a) 2.5×10^{17}, (b) 2.3×10^{18}, and (c) 7.2×10^{18}, respectively. The inset shows the spectral details of the M band.

to peak at 193 mμ, the β band.[23] Comments similar to those made in connection with absorbing regions due to the V_7 and F' bands in KCl at 80°K are also applicable to KBr at the same temperature.

B. The *F* Band

1. Spectral Properties (5 and 80°K)

In the subsequent treatment of the data of F-band growth resulting from x-ray irradiation performed on KCl and KBr crystals at 5°K and 80°K ,the assumption was made that there was no shift in the wavelength at which the maximum absorption of the F band occurred and furthermore that there was no change in the shape of the F band throughout the course of the irradiation. No significant change in either the peak position or band shape was observed for optical densities as great as 6 at the peak of the F band. Whenever the optical density at the maximum of the band exceeded a value of 6, the optical density at the half-width or third-width wavelengths provided a means for determining the magnitude of the peak absorption. The half-width and third-width wavelengths are here defined as the wavelengths for which the optical density or absorption constant is a half and a third, respectively, of the maximum value and were very carefully determined during the earlier stages of coloration. The validity of the above assumption appeared to be supported by the general consistency of the data when the relation of F-band growth with respect to the generation of other absorbing bands was considered.

The procedure for determining the absorption at the peak of the F band was modified for irradiations carried out at 80°K in both KCl and KBr. The spectra presented in Figs. 3 and 4 above showed a broad F' band contributing significantly to the F-band absorption constant during the early stages of irradiation. Accordingly, the F' component was estimated and subtracted from the total measured absorption constant at the appropriate wavelengths in accordance with the spectral shape of the F' band near 77°K as given by Kingsley[24] for KCl and by Pick[25] for KBr. In view of the fact that in the later stages of irradiation this contribution constituted approximately 2% of the absorption observed at the wavelength corresponding to the F-band peak, the above procedure was only necessary during the early observations.

The quantities utilized for the calculation of the F-center concentration by means of Smakula's formula as recast by Dexter[26] and the peak positions of the F band are presented in Table I. All of the quantities have been determined by direct optical measurements carried out in connection with the present investigation except for the values of the oscillator strength f_F. The latter represent average values based on data taken from the literature for a Gaussian F band in KCl[27–30] and in KBr.[28,30] Values of n, the index of refraction of the crystal at the peak position of the F band, required for the calculation of the F-center concentration were drawn from several sources.[31]

2. Growth in KCl (5°K)

A typical growth curve of the F band produced in pure KCl by x irradiation at 5°K is shown in Fig. 5.

Table I. Peak positions and half-widths of the F band produced at low temperatures in KCl and KBr. Average values of the oscillator strengths of a Gaussian F band are taken from the literature.

	Temperature of measurement (°K)	λ_F(mμ)	W_F(eV)	f_F
KCl	5	537	0.169	0.53
	80	540	0.194	
KBr	5	599	0.158	0.48
	80	603	0.190	

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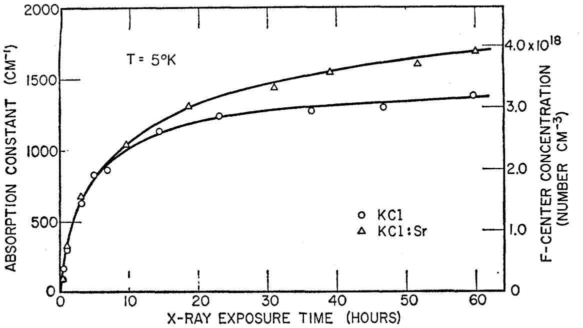

FIG. 5. The growth of the F band in KCl and in KCl:Sr as a function of x-ray irradiation time at 5°K. The scale on the left gives the absorption constant determined at the peak position of the F band whereas that on the right gives the F-center concentration calculated by Smakula's formula for a Gaussian F band with oscillator strength $f_F=0.53$.

The data are very similar in appearance to room temperature growth curves for KCl reported by Mitchell, Wiegand, and Smoluchowski[32] and by Gordon and Nowick[33] for NaCl. First, there is a region of rapid coloration which is nearly linear from the origin to an F-center concentration of approximately 2×10^{18} centers/cm^3. This is followed by a region of progressively slower coloration up to a concentration of roughly 3×10^{18} centers/cm^3. The extremely small value of the slope of the growth at the time that the irradiation was discontinued gives a strong indication that saturation was being approached. It should be emphasized that it is only the similarity in shape between the growth curves for liquid-helium temperature and room temperature that is being cited. The work of Känzig and Woodruff[1] and of Rabin and Klick[3] has indicated the essential difference in the mechanism of F-center production in the two temperature regions.

The growth curve for the KCl:Sr crystal is also included in Fig. 5. A comparison of the data for the pure and the divalent-doped KCl shows that in the region of rapid coloration, identical results are obtained. This observation completely corroborates the conclusion of Rabin and Klick[3] that the concentration of F centers produced by x-ray irradiation at liquid-helium temperature is independent of impurity content. This result has particular significance since the strontium concentration in the present instance is at least an order of magnitude larger than that of the KCl:Sr crystal used by Rabin and Klick. However, in the region of slower coloration, i.e., beyond an F-center concentration of 2×10^{18}/cm^3, there is a gradual divergence between the two growth curves and this becomes more pronounced with increasing irradiation time. As a result, the doped crystal is more intensely colored at the conclusion of the irradiation and attains a concentration of 4×10^{18} F centers/cm^3. Just as was the case in the pure specimen, it appears as though F-center saturation has begun to set in although it is clear that a longer x-ray exposure would be required for full saturation in the divalent-doped crystal than in the pure specimen.

It is evident that neither the slight difference in thickness between the two crystals nor the probable experimental error (estimated at less than 10% for optical-absorption measurements involving large optical densities) can account for all of the observed difference in F-center concentration between the pure and strontium-doped crystal. First, the relative difference in thickness was measured as 3% with the doped crystal having the greater thickness. Second, the observed difference in F-center concentration had reached a value approximately 17% of the total concentration after nearly 60 h of irradiation. Finally, in the region of slow coloration, it was the doped crystal which consistently yielded the larger absorption constant. No satisfactory explanation for this effect is suggested at this time.

3. Growth in KBr(5°K)

The growth curve of the F band induced in a pure KBr crystal by x-ray irradiation at 5°K is presented in Fig. 6. The data exhibit the same general type of behavior shown by KCl for an irradiation conducted at the same temperature. There is a region of relatively fast coloration which is approximately linear, from the origin to an F-center density of 2×10^{18} centers/cm^3; this is followed by a second region of slower coloration which is also nearly linear, up to the termination of the irradiation at a concentration of well over 5×10^{18} F centers/cm^3. In contrast to KCl, there is much less tendency for saturation in the coloration of KBr.

A plot of the F-band growth for a calcium-doped crystal is also given in Fig. 6. The data for both the pure KBr and the KBr:Ca are seen to fall on the same curve in the initial stage of coloration in agreement with the observation by Rabin and Klick.[3] In the region of

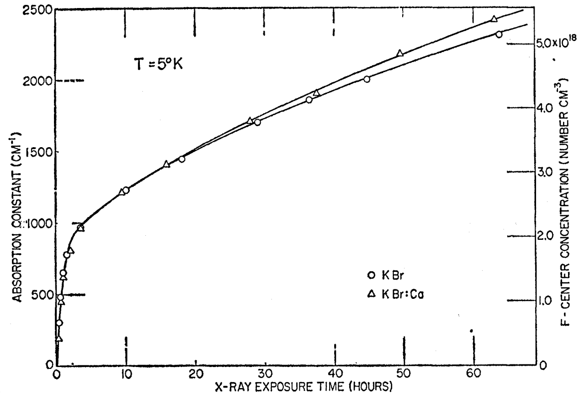

FIG. 6. Growth curves of the F band in KBr and in KBr:Ca following x-ray exposure at 5°K. The absorption constant measured at the peak position of the F band is shown by the scale on the left and the corresponding number of F centers/cm^3 is given on the right. The latter is computed by means of Smakula's formula with the oscillator strength for a Gaussian F band $f_F=0.48$.

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[32] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **117**, 442 (1960) and **121**, 484 (1961).

[33] R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 997 (1956).

slow coloration, a larger F-center concentration was produced in the doped KBr crystal. The presence of divalent impurities appears to enhance the coloration of both KCl and KBr for high coloration levels. Although the effect is more marked in the crystals with the heavier doping, as might be expected, the exact dependence of the excess coloration upon a particular divalent impurity concentration is not yet clear. Previously, it was pointed out that the excess absorption represented 17% of the total F absorption after 60 h of irradiation of the KCl:Sr crystal; a similar x-ray exposure of the KBr:Ca crystal yielded a value of 5%. While this variation is within the experimental error related to the optical absorption measurements (for large values of the optical density), it is felt that this may be a true effect. The measured values of the optical absorption constant were consistently larger for the divalent-doped KBr in the region of slower coloration even though the pure KBr crystal was only 40% as thick as the KBr:Ca specimen. A dependence upon crystal thickness, as would occur for a nonuniform coloration, would result in a larger absorption constant for the thinner sample —just opposite to that observed.

4. Growth in KCl and KBr (80°K)

The principal features of F-band growth resulting from the x-ray irradiation of KCl and KBr samples at 80°K are quite similar as many be concluded from the data shown in Figs. 7 and 8, respectively. Accordingly, the growth curves may be discussed together leaving individual differences to be singled out as they occur. All of the plotted data represent values of the F-band absorption constant following the subtraction of the F' component from the total observed absorption.

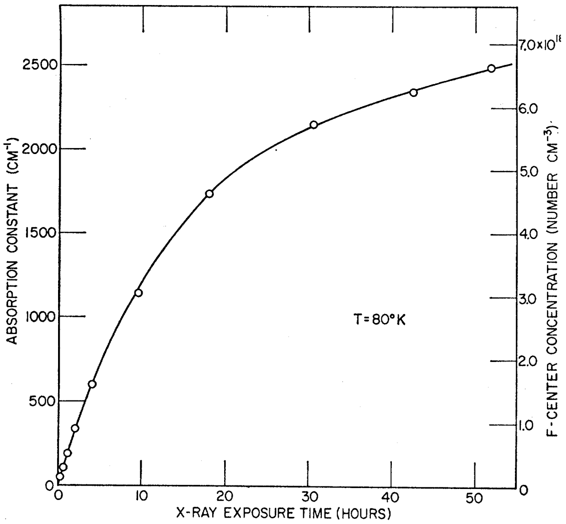

FIG. 7. The growth curve of the F band for a KCl crystal as a function of x-ray exposure time at 80°K. The scale on the left shows the absorption constant determined at the peak position of the F band while the right-hand scale shows the corresponding F-center concentration calculated with Smakula's formula and a value of oscillator strength $f_F=0.53$.

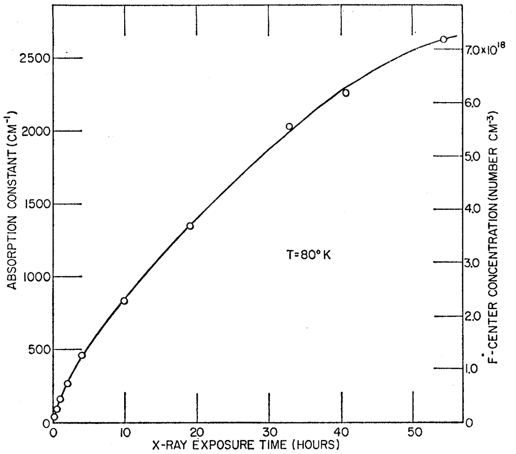

FIG. 8. The growth of the F band in a KBr crystal resulting from an x-ray irradiation at 80°K. The absorption constant determined at the peak position of the F band is presented by the scale on the left; the F-center concentration calculated for a Gaussian F band with oscillator strength $f_F=0.48$ is shown by the scale on the right.

The initial growth of the F band is relatively rapid in both crystals, but there is little evidence of linear growth as was observed for irradiations carried out in the liquid-helium temperature range. This is in agreement with data presented by Duerig[34] which show that the nonlinear behavior of the F-band growth curves of x-irradiated KCl and KBr at 78°K extends to extremely brief exposures. In fact, the rate of F-band growth observed in x-irradiated KCl and KBr at 80°K may be described as one which continuously decreases for the entire irradiation. Thus the typical radiation-induced growth behavior exhibited at 5°K which was characterized by two rather well-defined regions of coloration does not extend to coloration produced at 80°K. The gradual decrease in the growth rate indicates that a state of saturation of the F band is being approached in both cases although a much earlier saturation is indicated for the KCl crystal. It should be noted that the concentration of color centers attained at 80°K is significantly greater than at 5°K where a pronounced saturation has occurred. The role of impurities in the production of F centers at 80°K has not been investigated although impurity concentration is known to have an effect at this temperature.[3]

C. The *K* and L_1 Bands

1. The K-to-F Ratio in KCl (5 and 80°K)

A shoulder on the short-wavelength side of the F band, designated as the K band, was first observed in additively colored KCl by Kleinschrod.[27] Mott and

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[34] W. H. Duerig, thesis, University of Maryland, 1952 (unpublished).

Gurney[35] have suggested that this band results from the transition of an F-center electron to a higher excited state. More recently, Lüty[30] conducted an exhaustive study of the absorption spectra of additively colored specimens of the face-centered cubic alkali halides. Evidence of the presence of the K band was found in many alkali halides in which it had not been previously resolved. Lüty also measured the K-to-F ratio, i.e., the ratio of the absorption coefficients measured at the peak position of the K and F bands or the value of (α_K/α_F). He found that this ratio is independent of the F-center concentration for a given alkali halide, as would be expected from the Mott-Gurney model.

The present investigation extends the results of Lüty's experiments performed with additively colored crystals to crystals colored by x irradiation at low temperatures. Consequently, the data pertaining to K-band growth is presented in its relation to the growth of the F band.

The absorption spectra of KCl specimens x irradiated at 5 and at 80°K which were pictured in Figs. 1 and 3 above show various stages in the growth of the K band. The peak positions of the band are observed at wavelengths of 458 and 460 mμ for irradiations carried out at 5 and 80°K, respectively. It is apparent that there is considerable overlapping between the F and K bands with the F band contributing significantly to the K-band absorption and the latter making a somewhat smaller contribution to the absorption of the F band. In the subsequent presentation, the absorption coefficient measured at the peak position of the K band is called α_K despite the fact that a certain fraction of it represents a component of the F band. It is the ratio of this value to that of α_F which is designated as the K-to-F ratio, in accord with Lüty's presentation. Since the shapes of the F and K bands appear to be unchanged during irradiation, a constant value of the K-to-F ratio throughout the course of the irradiation indicates that the ratio of the corrected values of the K- and F-band absorption constants at the proper peak positions also remains constant.

The data for the KCl samples x irradiated at 5 and at 80°K are shown in Fig. 9. In this instance, the values of the absorption constants measured at the peak position of the K band are plotted as ordinate against the corresponding F-band absorption values as abscissa. Observations of the F-band absorption at 80°K have been corrected by the subtraction of contributions due to the F' band. Although the F' band is known[24] to have an extremely small component in the spectral region of the K band, it is ignored in the present instance without a significant loss of accuracy.

The straight lines shown in Fig. 9 are drawn on the basis of a least-squares fit of all the data recorded at the two temperatures of interest. In each case, the line appears to accommodate all of the observations made at the appropriate temperature. Furthermore, the presence of a heavy concentration of divalent impurities, as in the KCl:0.1 M% Sr sample, does not appear to have a measurable effect on the K-to-F ratio despite the appreciable enhancement of the formation of F centers for long irradiation times. The slopes of the two lines yield the values of the K-to-F ratio at 5° and at 80°K. The value of the ratio for the 80°K data is 0.048 and a value of 0.035 is obtained from the irradiation at 5°K. The former figure is in good agreement with Lüty's determination of a value of 0.046 for a wide range of additive coloration in KCl crystals measured at liquid-nitrogen temperature. There is also good agreement with the value of 0.047 cited by Duerig and Markham[36] for KCl crystals x irradiated and measured at 78°K. The value obtained at 5°K is in fair agreement with the K-to-F ratio of 0.037 which is obtained from Lüty's data for an additively colored crystal cooled to 23°K. The apparent variation of the K-to-F ratio with temperature results from measuring the absorption constant at a given wavelength instead of the area under the resolved absorption curves.

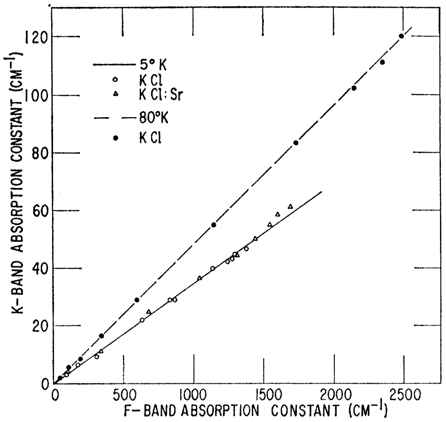

FIG. 9. The linear relationship between the peak intensity of the K band and F band in KCl and KCl:Sr crystals x-rayed and measured at 5 and 80°K.

2. K-to-F Ratio in KBr (5 and 80°K)

An examination of the absorption spectra of KBr crystals at different stages of prolonged x irradiation (Figs. 2 and 4) shows that the shoulder located on the short-wavelength side of the F band, i.e., the K band, is less well resolved in KBr than in KCl. Thus, the two bands overlap to a greater degree and there is a larger contribution from the F-band absorption to that observed at the peak position of the K band. The wavelength assigned to the peak position of the K band by Lüty is 525 mμ and the absorption constant measured at this wavelength is designated as α_K. The K-to-F

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

[36] W. H. Duerig and J. J. Markham (private communication to F. Seitz, Ref. 6).

ratio in KBr is investigated by plotting each value of α_K as ordinate against the corresponding α_F value as abscissa. The F-band measurements at 80°K are corrected by subtraction of the F' component. The KBr results are presented in Fig. 10 where the two straight lines constitute a least-squares fit for the data at 5 and 80°K, respectively. The value of the ratio is determined to be 0.097 at 80°K and 0.084 at 5°K. Each of these values is more than twice as large as the corresponding values in KCl. The apparent variation of the K-to-F ratio with temperature results from taking the absorption constant at a given wavelength instead of the area under the resolved absorption curves.

The results of the present experiments on KBr and KCl are in good agreement with the results obtained by Lüty on additively colored crystals. It seems quite reasonable to conclude that the K and F bands are intimately related and arise from transitions of the same defect, in support of the Mott and Gurney model of the K center. It should also be noted that the constancy of the K-to-F ratio provides a means of determining the absorption coefficient at the peak of the F band in crystals having a very high absorption.

3. *The L_1 Band in KCl and KBr (80°K)*

In the course of his experiments on the K band in various additively colored alkali halides, Lüty[30] observed three weaker absorption bands at wavelengths shorter than that of the K band. They were designated as the L_1, L_2, and L_3 bands in order of increasing photon energy and were attributed to additional transitions of an F-center electron. On the basis of the spectral properties determined by Lüty, it is possible to make a quantitative estimate of the degree of induced absorption to be expected from each of the L bands relative to a given F-band absorption in a particular alkali halide. Since the various L bands are located in a spectral region sufficiently removed from the F band to preclude any overlap with it, a straightforward application of Smakula's formula[26] yields values of the F-to-L ratio, i.e., the ratio of the absorption constant at the peak position of the F band to the corresponding peak value for each of the L bands. Klick and Kabler[37] have argued on this basis to show that L bands are formed in KCl and KBr by x rays. In particular, they were able to resolve the L_1 band after x irradiation at room temperature and the L_3 band following irradiation at liquid-helium temperature. In each instance, resolution of the remaining L bands was prevented by the presence of prominent absorption bands associated with other defects.

In the present experiment, prolonged exposure of KCl and KBr crystals to x rays at liquid-nitrogen temperature resulted in the formation of very weak absorption bands having maxima at wavelengths assigned by Lüty as peak positions of the L_1 band, viz., 344 mμ in KCl and 375 mμ in KBr. The F-to-L_1 ratio in KCl at 80°K is calculated to be 230 on the basis of Lüty's figures for the half-width and oscillator strength of the K band and the corresponding F-band values given in Table I. If the F-band absorption data shown in Fig. 5 are utilized, the absorption constants measured at the L_1 peak position after 9.5 and 52.0 h of irradiation should be 5 and 11 cm^{-1}, respectively.

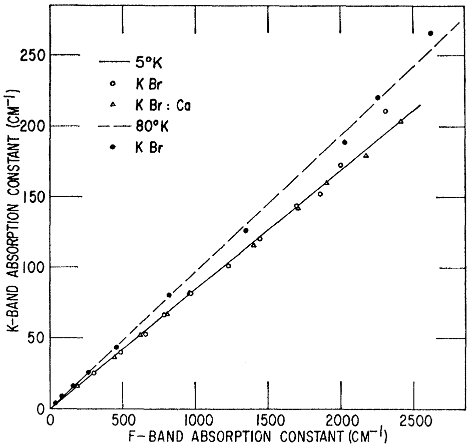

FIG. 10. The linear relationship between the absorption coefficient at the peak position of the K band and that of the F band in KBr and KBr:Ca crystals exposed to x rays and measured at 5 and 80°K. The peak position of the K band was taken as 525 mμ as suggested by Lüty Ref. 30.

Reference to curves (b) and (c) of Fig. 3 shows that the observed data are in good agreement with the computed values. If the results of an analogous calculation carried out for the L_1 band in KBr at 80°K are compared with the data exhibited in Fig. 4, there is also close agreement between the observed and computed values of the absorption constant at 375 mμ. It may be assumed that the L_2 and L_3 bands are formed at 5°K and at 80°K and are present with roughly the same intensities as the L_1 band but due to their unfavorable spectral location are incapable of resolution in the present experiment.

D. The *M* Band

1. *Spectral Properties (5 and 80°K)*

The absorption spectra, shown in Figs. 1–4, indicate that x irradiation of KCl and KBr crystals at low temperatures generates an extremely weak band on the long-wavelength side of the F band. Resolution of the band and the determination of its spectral properties led to its identification as the M band. Unequivocal identification of this band was made by comparing its spectral properties with those of M bands produced by the well-known techniques of heating and rapid quenching of additively colored KCl and KBr, as well as the bleaching of crystals containing F centers with light of the F-band wavelength. Measurements of the peak position and the half-width of the resulting M band in

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[37] C. C. Klick and M. N. Kabler, Phys. Rev. 131, 1075 (1963).

TABLE II. Peak positions and half-widths of the M band produced by different methods in KCl and KBr and measured at various temperatures. Method of production: I. X ray at RT, bleach in F band. II. Additively color, heat to 600°C, quench to RT. III. X ray at 5°K. IV. X ray at 80°K.

		KCl		KBr	
Method	Temperature of measurement	λ_M(mμ)	W_M(eV)	λ_M(mμ)	W_M(eV)
I	5°K	799	0.055	884	0.051
	80°K	802	0.065	887	0.063
	RT	825	0.12	918	0.12
II	5°K	798	0.054	883	0.053
	80°K	801	0.064	887	0.065
	RT	823	0.12	918	0.13
III	5°K	799	0.057	884	0.051
	80°K	802	0.067	887	0.062
	RT	824	0.12	918	0.13
IV	5°K	798	0.056	884	0.051
	80°K	801	0.065	887	0.062
	RT	822	0.12	917	0.12

each instance were made at room temperature, at 80 and at 5°K. The same spectral properties were also determined at these three temperatures for KCl and KBr crystals x irradiated for prolonged periods at 5°K and at 80°K. A comparison of the results of the preceding measurements showed complete agreement whatever the method of M-band production, as may be seen by reference to Table II.

2. *Growth in KCl and KBr* (*5°K*)

The growth of the M band in pure and in strontium-doped KCl crystals which had been exposed to x rays at 5°K is shown by the growth curves presented in Fig. 11. The growth of the band is the most rapid during the first few hours of irradiation; thereafter, it proceeds at a continually decreasing rate for the balance of the x-ray exposure time. The band appears to be approaching a state of saturation at the time that the irradiation is discontinued. The early growth of the band is characterized by the fact that M-center coloration induced in KCl at 5°K is insensitive to the presence of strontium impurity. However, after approximately 10 h of irradiation time, the KCl: Sr sample shows a larger absorption than the pure crystal and this excess absorption continues to increase until it represents approximately 25% of the total M-band peak absorption observed at the conclusion of the irradiation.

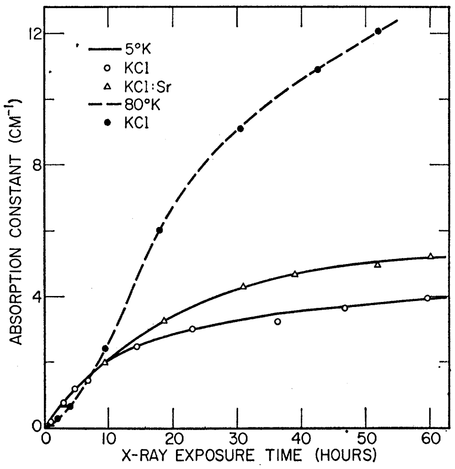

FIG. 11. The growth of the M band in KCl and KCl: Sr crystals x irradiated and measured at 5°K (full curves) and in KCl exposed to x rays and observed at 80°K (dashed curve).

The M-band growth curve resulting from the extended x irradiation of pure and calcium-doped KBr at 5°K is given in Fig. 12. The growth of the band is seen to be most rapid at the outset of the irradiation and continues at a progressively slower rate for approximately the first five hours of x-ray exposure. Finally, the observed absorption constant at the band maximum appears to increase at almost a uniform rate for the balance of the irradiation. Unlike the results presented for the KCl: Sr crystal, there is no measurable excess absorption observed in the calcium-doped sample over that recorded for the pure KBr. Accordingly, a single curve is suitable for a satisfactory fit of the data for both crystals.

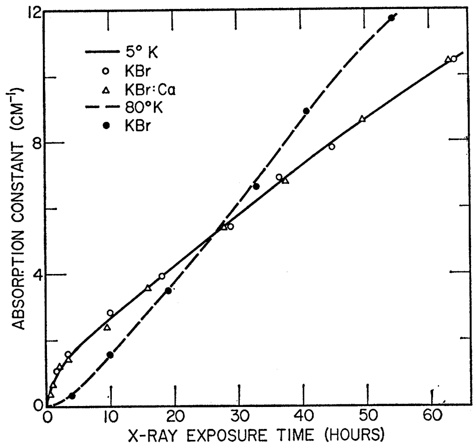

FIG. 12. Growth curves of the M band in KBr samples following x irradiation and measurement at the same temperature. Results are shown for KBr and KBr:Ca at 5°K (full curve) and for KBr at 80°K (dashed curve).

3. *Growth in KCl and KBr* (*80°K*)

The absorption spectra observed in pure KCl and KBr crystals resulting from x irradiation at 80°K showed a weak M band superimposed on a broad F' band, as exhibited above in Figs. 3 and 4. Each value of the M-band absorption constant was determined by subtracting the component ascribed to the F' band from the total absorption observed at the wavelength corresponding to the peak position of the M band. It is on the basis of these data that the growth curves of the M band in KCl and in KBr are presented in Figs. 11 and 12, respectively. The growth behavior is sufficiently similar in each type of crystal so that only a single discussion is required.

The initial growth is seen to be comparatively slow and is followed by a region of more rapid M-band coloration. The latter region is characterized by a nearly uniform rate of growth during the course of which the values of the M-band absorption constant observed at 80°K overtake the values corresponding to equal x-ray exposure times for the same type of crystal at 5°K. These growth curves differ from all of the other curves observed in this investigation in that they each possess a point of inflection. This is to be expected if the quadratic relation between M- and F-band absorption (to be discussed later) is valid. In fact, the validity of this relation requires that the M-band growth curves at 5°K also have points of inflection. It is suggested that they may simply be hidden for short irradiation times. As has been recently shown by Wallis and Faraday,[38] this behavior of the growth curves is important in understanding the kinetics of the growth of the F and M centers.

4. The F^2 versus M Relation

A comparison of the data relating the growth of the M band (exhibited in Figs. 11 and 12) with the results of F-band growth (presented in Figs. 5-8) shows that the concentration of M centers produced by these low-temperature irradiations is a quadratic function of the F-center concentration. This is seen quite clearly in Fig. 13 where the absorption constant at the peak position of the M band is plotted against the square of the corresponding F-band absorption constant for KCl. A similar quadratic relation between the M- and F-band absorption has been previously reported for KBr.[11] The conclusion supported by both sets of observations is that each M center is composed of two F centers. Furthermore, the data demonstrate that the relative concentration of F and M centers is not altered by the presence of divalent impurities and the accompanying positive-ion vacancies. This suggests that the M center does not involve a positive-ion vacancy as is proposed by the Seitz[39] model and its modification.[40]

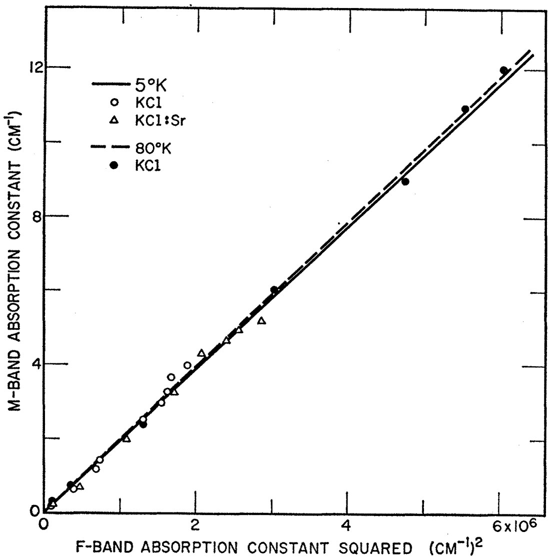

FIG. 13. Absorption constant of the M band versus absorption constant of the F band squared for KCl crystals exposed to x rays at 5 and 80°K and measured at the irradiation temperature.

The quadratic dependence of the M-center concentration upon the F-center concentration agrees with the results obtained by van Doorn[41] on the thermal equilibrium of F and M centers in additively colored crystals. Thus, the present observations together with those of van Doorn support the proposal of van Doorn and Haven[42] and of Pick[43] that the model of the M center is a pair of associated F centers (F_2 model). The trapping of two electrons by the two adjacent negative-ion sites yields a model which is in accord with the requirements of inversion symmetry,[44] the absence of dielectric loss,[45] magnetic susceptibility,[46] and electron spin resonance[47] of the M center. In addition, the present work shows that the presence of a large concentration of divalent impurities (as in KCl:0.1M% Sr) and the accompanying positive-ion vacancies do not alter the relative concentration of F and M centers formed by irradiation at low temperatures. This implies that the positive-ion vacancy does not enter into the formation of M centers. The observed dependence of the M-center concentration upon divalent impurities is just a reflection of the F-center dependence and has no real significance for the M-center model.

E. The H Band

1. Growth in KCl (5°K)

Before the growth data for the H band in KCl are presented, some prior experimental work pertaining to the spectral characteristics of this band will be reviewed. The peak position of the H band in KCl was reported as 345 mμ by Duerig and Markham.[19] Compton and Klick[48] confirmed this observation and suggested the possibility of the band being a composite of other bands on the basis of optical measurements; furthermore, the fact that both H and V_K centers were present in KCl crystals exposed to x rays near liquid-helium temperature was evident from electron-spin-resonance results[1]

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[38] R. F. Wallis and B. J. Faraday, Phys. Rev. **133**, A1360 (1964).
[39] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).
[40] R. S. Knox, Phys. Rev. Letters **2**, 87 (1959).
[41] C. Z. van Doorn, Phys. Rev. Letters **4**, 236 (1960).
[42] C. Z. van Doorn and Y. Haven, Philips Res. Rept. **11**, 479 (1956); C. Z. van Doorn, Philips Res. Rept. **12**, 309 (1957).
[43] H. Pick, Z. Physik **159**, 69 (1960).
[44] A. W. Overhauser and H. Rüchardt, Phys. Rev. **112**, 722 (1958).
[45] G. Jacobs, J. Chem. Phys. **27**, 217 (1957).
[46] E. Sonder, Bull. Am. Phys. Soc. **6**, 114 (1961).
[47] W. C. Holton, H. Blum, and C. P. Slichter, Phys. Rev. Letters **5**, 197 (1960); H. Gross and H. C. Wolff, Naturwiss. **48**, 299 (1961); H. Blum, Phys. Rev. **128**, 627 (1962).
[48] W. D. Compton and C. C. Klick, Phys. Rev. **110**, 349 (1958).

and from recent optical-absorption measurements.[49] Cape and Jacobs[50] investigated the thermal bleaching of the two centers and were able to show that the 345 mμ band resulted from the superposition of two or more bands—the *H* band peaking at 335 mμ,[51] the V_K band peaking at 365 mμ,[52] and, possibly, the V_1 band with its maximum located at a wavelength of 356 mμ.[5] The experiment did not establish whether the V_1 absorption observed when the temperature of the KCl crystal was raised above 56°K (the bleaching temperature of the *H* center) was an original component of the 345 mμ band or whether it was formed as a product of the thermal bleaching of the *H* center. The latter alternative had been shown to be a possibility as a result of the bleaching experiments of Känzig and Woodruff[1] and of Teegarden and Maurer.[53]

In the present investigation, the peak position of the most prominent band in the near ultraviolet in KCl after 15 min of x-ray exposure at 5°K was observed to be at 345 mμ, in agreement with the Duerig and Markham[19] data. This band is designated as the "*H*" band in order to differentiate it from the simple *H* band which peaks at 335 mμ. The spectral shape of the band in the initial stage of growth was shown previously, viz., in curve (a) of Fig. 1. As the irradiation progressed, the peak position of the band shifted rapidly toward shorter wavelengths. Thus, after an hour's exposure of the crystal to x rays, the peak position was observed to be at 338 mμ. The wavelength of the peak shifted very little for longer irradiations. The final value of 337 mμ was attained when saturation of the band was observed after approximately 20 h. There was no significant variation in the shift of the peak position for the KCl:Sr crystal from that observed for the pure KCl. The shift in the wavelength at which the maximum optical absorption of the "*H*" band occurred was accepted as an indication of the composite nature of the band. From the ultimate peak position at 337 mμ, it was inferred that the principal component of the band was the *H* band (335 mμ) with a smaller contribution from one or more bands which peaked at longer wavelengths, presumably the V_K, and possibly, the V_1. It is also clear from the above data that any contributions due to the V_K and V_1 centers were significant only in the early stages of growth of the "*H*" band and represented a small fraction of the observed absorption. It was estimated that this contribution was less than 5% of the total absorption at saturation on the basis of a more detailed study of the first half-hour of x-ray irradiation to be described below. Accordingly, the distinction which has been made between the composite "*H*" band and the simple *H* band peaking at 335 mμ will be discontinued for KCl and the data will be presented in terms of the *H*-band growth without any attempt being made to subtract off components due to bands peaking at longer wavelengths.

The curves tracing the growth of the *H* band in KCl and in KCl:Sr at 5°K are shown in Fig. 14. The curves are quite similar to those which have been presented to describe the growth of the *F* band in KCl, in Fig. 5, particularly during the early stages of coloration. Such correlation is to be anticipated if *F* and *H* centers are formed simultaneously in conformity with the earlier summary of the coloration process near liquid-helium temperature. Thus, the early growth of the *H* band is relatively rapid, nearly linear, and appears to develop independently of the divalent impurity content. The present data indicate that the assertion of Rabin and Klick[3] concerning the insensitivity of *F*-center coloration to the presence of impurities in this temperature range is also applicable to at least the initial stage of *H*-center coloration. The termination of the region of fast coloration is marked by a rapid diverging of the two growth curves until saturation takes place. At this time, the absorption constant at the *H*-band maximum measured for the KCl:Sr sample is observed to be approximately 10% larger than that of the pure crystal. Thereafter, the curves remain reasonably parallel for the duration of the irradiation.

In a supplementary experiment, the extremely early growth of the "*H*" band was examined by exposing a pure KCl crystal to x rays for 30 min with observations being made at approximately 2-min intervals. During the first 10 min of irradiation, the rate of generation of the "*H*" band was observed to be continuously variable and measureably higher (between 5 and 10%) than the constant rate assumed during the last 20 min of the exposure. It is suggested that the excess "*H*"-band coloration responsible for the nonlinear early growth was due to the formation of V_K, and possibly, V_1 centers in accordance with the discussion carried out above.

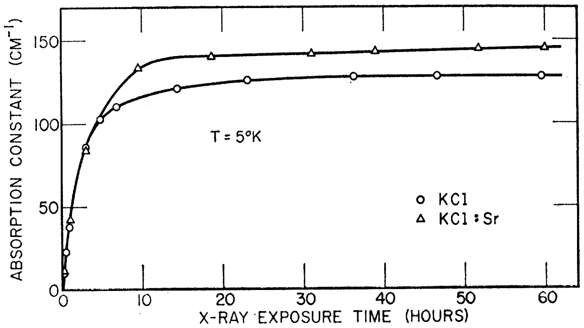

FIG. 14. Growth curves of the H band in KCl and KCl:Sr as a function of the x irradiation time at 5°K. Observations were made at the same temperature.

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[49] T. M. Srinivasan and W. D. Compton, Phys. Rev. **137**, A264 (1965).

[50] J. Cape and G. Jacobs, Phys. Rev. **118**, 946 (1960).

[51] J. D. Kingsley, Air Force Office of Scientific Research, Tech. Notes Nos. 1 and 2, AFOSR-TN 60-634 and 60-635, University of Illinois, May and June 1960 (unpublished).

[52] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

[53] K. J. Teegarden and R. J. Maurer, Z. Physik **138**, 284 (1954).

2. *Growth in KBr (5°K)*

Prior to a consideration of the growth behavior of the *H* band in KBr, the foregoing discussion pertinent to the spectral shape of the "*H*" band in KCl can be extended to include some earlier observations reported for KBr. Duerig and Markham[19] first observed the "*H*" band in KBr at a wavelength of 380 mμ following x irradiation carried out at liquid-helium temperature. Somewhat later, the results of the thermal bleaching experiments of Cape and Jacobs[50] suggested the possibility that the band also possessed a composite nature in KBr, although differently constituted than the corresponding band in KCl. In KBr, for example, no V_K component of the "*H*"-band absorption was observed by Cape and Jacobs to be a product of x irradiation at liquid-helium temperature as had been the case for KCl. On the other hand, only the optical absorption associated with the V_1 band at 410 mμ was observed when the temperature of the irradiated KBr crystal was raised above the bleaching temperature of the *H* center (30°K). In this respect, the KBr results were comparable to those obtained from the KCl experiment to the extent that the production of the V_1 absorption could not be unequivocally assigned to either direct V_1-center generation by exposure of the crystal to x rays at liquid-helium temperature or to the thermal conversion of *H* centers to V_1 centers in accordance with the observations of Teegarden and Maurer[53] and Känzig.[54] More recently, Srinivasan and Compton[49] have employed optical-absorption measurements to show that V_K as well as *H* centers are formed in KBr by x rays near liquid-helium temperature. Thus, the "*H*" band is also composite in KBr.

In the current work, the observation of the wavelengths corresponding to the peak position of the "*H*" band in KBr as a function of the x-ray exposure time was again utilized to provide some indication of the relative growth of components of the band, viz., the *H* band, the V_K, and, perhaps, the V_1 band. The initial peak position of the band after 15 min of x irradiation was observed to be 381 mμ, in satisfactory agreement with previous observations.[19,48,55] However, in contrast with KCl results, no evidence of any measurable change in the wavelength of the peak position of the "*H*" band was noted throughout the entire irradiation. Essentially the same results were obtained from the observations of the wavelengths at which the "*H*" band peaked in the KBr:Ca specimens following x irradiation at 5°K.

The observation of the "*H*"-band absorption maximum at the same wavelength that Kingsley[51] had shown to be the peak position of the simple *H* band, as well as the absence of any measurable shift in this wavelength throughout the course of the irradiation, supports the viewpoint that the simple *H* band is generated by prolonged x irradiation at 5°K with only a small admixture of other absorbing bands in the immediate spectral vicinity. It is, of course, difficult to rule out completely any contribution from the V_K or V_1 absorption bands, peaking at 385 and 410 mμ, respectively, due to the proximity of each to the peak of the "*H*" or *H* band at 381 mμ. However, the discussion pertaining to the data presented above indicates that any contribution of this type is rather insignificant and accordingly, the distinction between the composite "*H*" and simple *H* bands can be dropped for the balance of the KBr remarks.

The growth of the *H* band resulting from the exposure of pure and calcium-doped KBr to x rays at 5°K is shown by the solid curve in Fig. 15. The early growth of the band is quite similar to that observed for KCl at the outset and can be described in the same general terms. Furthermore, the shape of the above curve during its early growth stage is similar to that of the *F*-band growth in the region of rapid *F* coloration (shown earlier in Fig. 6). The *H*-band growth curve levels off and attains its maximum value at saturation within the first four hours of x-ray exposure. Continued irradiation for 45 h results in a gradual decrease in the absorption constant to approximately 55% of that observed at its maximum value. Thereafter, no further significant in the absorption constant is noted. The same growth curve accommodates the results for both the pure and calcium-doped KBr for the complete irradiation. Although the values of the *H*-band absorption constant for the KBr:Ca specimen are consistently larger than the corresponding values for the pure KBr after saturation is reached, the differences are so small, i.e., less than 5% of the total observed absorption, that there is no particular advantage for the plotting of two separate curves. The fact that an increase in the *F*-center concentration is accompanied by a decrease of the *H* band during the extended irradiation indicates that the formation of defects does not simply involve the production of stable *F* and *H* centers. This question will be reconsidered on a more quantitative basis below.

While the previous discussion has been based almost

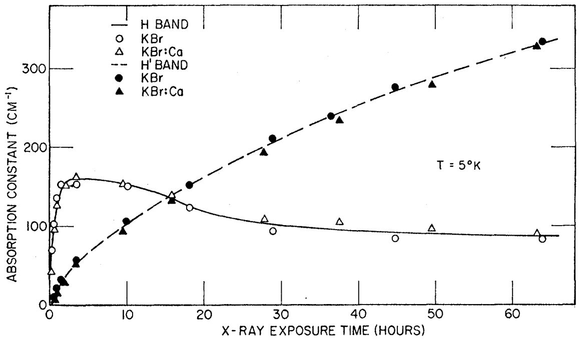

FIG. 15. The growth of the *H* and *H'* bands in KBr and KBr:Ca following x-ray exposure at 5°K. Measurements carried out at the irradiation temperature are shown for the *H* band (full curve) and for the *H'* band at 278 mμ (dashed curve).

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[54] W. Känzig, Phys. Rev. **99**, 1890 (1955).

[55] J. A. Cape, Phys. Rev. **122**, 18 (1961).

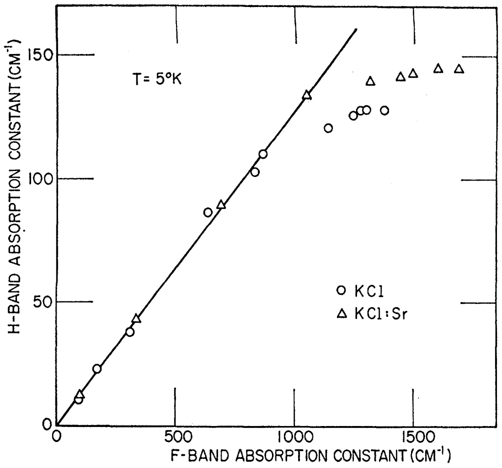

FIG. 16. The H-band absorption constant versus the F-band absorption constant produced by x rays at 5°K in KCl and KCl:Sr and measured at the same temperature. The straight line is plotted in accord with a least-squares fit of the data accumulated during the first 10 h of irradiation.

entirely on an examination of the behavior of the absorption constant observed at the peak position of the H band as a function of the x-ray exposure time, a more complete description is afforded by reference to the spectra of a KBr crystal x irradiated at 5°K. Curves (a), (b), and (c) of Fig. 2 are the spectra of a KBr crystal after 0.25, 10.0, and 64.0 h of x-ray exposure, respectively. The selective character of the H-band bleaching resulting from the extended irradiation is aptly illustrated by a comparison of the latter two curves. The bleaching is seen to be restricted to the spectral region lying roughly between 360 and 430 mμ, while the absorption bands on either side, i.e., the K band at longer wavelengths and the 278 mμ band at shorter wavelengths continue to grow as the irradiation progresses.

3. *H-to-F Ratio; the H′ Band*

In the earlier discussion of the H-band growth curves for KCl and KBr, it was emphasized that during the initial rapid stage of H coloration induced by x rays at 5°K, the similarity in shape between the H- and F-band growth curves supports the viewpoint that F and H centers are produced simultaneously by the ionizing radiation. The same data may be re-examined on a more quantitative basis by plotting the values of the absorption constant at the peak position of the H band against the corresponding values for the F-band absorption. Accordingly, the data for the pure and strontium-doped KCl crystals may be taken from Figs. 5 and 14 and replotted as illustrated in Fig. 16. It is seen that the points pertaining to the initial rapid F- and H-band growth fall on a single straight line passing through the origin. In the case of observations made for x-ray exposures in excess of 10 h, there is a significant deviation from a straight-line relationship as the rate of H-center generation falls behind the rate at which F centers are formed. The straight line which is shown represents a least-squares fit of the data accumulated within the first 10 h of irradiation. The slope of this line will be called the H-to-F ratio. For KCl. then, the fact that the H-to-F ratio is found to be reasonably constant for irradiations up to approximately 10 h constitutes a quantitative verification of the viewpoint that F and H centers are formed by a single event. The gradual decrease in the H-to-F ratio for longer irradiation times suggests that some other mechanism becomes operative in the heavily irradiated crystal.

A similar representation of the KBr data may be carried out but is not shown since it is quite clear that any linear relationship which may hold between the F- and H-absorption constants is seriously impaired by the bleaching of the H band resulting from an extended x-ray exposure. An examination of the data included in Figs. 6 and 15 shows that the H-to-F ratio in the pure and calcium-doped KBr remains constant up to 4 h of irradiation but decreases rapidly thereafter. Since the deviation from constancy is more pronounced and occurs earlier in KBr than in KCl, first consideration will be given to a modification of the coloration mechanism in KBr in the liquid-helium temperature region.

Reference to the absorption spectrum of a KBr crystal x irradiated for 15 min at 5°K given by curve (a) of Fig. 2 shows a weak band on the short-wavelength side of the H band. The band has a poorly resolved peak at approximately 281 mμ and is probably the same one reported by Duerig and Markham[19] at a wavelength of 285 mμ. Some indication of the manner in which the band develops may be obtained from curves (b) and (c), the absorption spectra for an x-ray exposure of 10.0 and 64.0 h, respectively. The small shift in the wavelength of the peak position of the band from 281 to 278 mμ observed during the first few hours of irradiation provides evidence that the band is of composite structure resulting from the superposition of two or more simple bands. However, the spectral position of the absorption maximum of the band remains unchanged at 278 mμ for the balance of the irradiation. Although contributions from components peaking at wavelengths longer than 278 mμ are significant in the early stages of the growth, it is estimated that these represent less than 5% of the total observed absorption of the band and may be ignored in the subsequent discussion. The progressive development of the 278 mμ band in KBr and KBr:Ca is provided by the broken-line curve in Fig. 15. The 278-mμ band will be called the H' band for the remainder of this discussion for reasons to be presented below. Several comments pertaining to the growth behavior of the band are in order. First, the early rapid growth of the H' band should be discounted somewhat insofar as the components of the band which peak at longer wavelengths appear to make a significant contribution during the first few hours of irradiation. Second, no significant dependence on calcium impurity content was observed for the growth of the H' band in KBr at 5°K. Finally, after about 15 h of x-ray irradiation, the absorption constant values of the H' band exceed the corresponding values of the H band. Unlike most of the other absorption bands whose growth is the subject of this investigation, the H' band shows no evidence of saturation after an extended irradiation.

A consideration of the growth curves of the F, H, and H' bands in KBr suggests the possibility that the decrease in the H-center concentration is a result of the formation of H' centers from the H centers. If this is correct, a linear combination of the H- and H'-absorption constants should exist which is directly proportional to the corresponding F-band value at any time during the irradiation. Alternatively stated, the problem resolves itself into searching for a constant k_1 for which the ratio of $(\alpha_H+k_1\alpha_{H'})$ to α_F is equal to another constant k_2. For a value of k_1 equal to 1.4, a satisfactory least-squares fit of the data of Figs. 6 and 15 is obtained by means of the straight line shown in Fig. 17. The data for both the pure and calcium-doped KBr appear to be satisfactorily fitted by the same line. The value of the slope of the line is equal to the constant k_2 and is estimated to be 0.23.

Although the present evidence is insufficient for the formulation of a physical model to explain the interaction among the F, H, and H' centers, the experimental results suggest that the concentration of F centers, n_F, present in KBr at any time during the irradiation is equal to the sum of the concentrations of H centers, n_H, and of H' centers, $n_{H'}$, or

$$n_F=n_H+n_{H'}. \tag{1}$$

Assuming that the H and H' bands are Gaussian in shape and that the concentrations of H and H' centers can be correctly calculated by means of Smakula's formula,[26] it may be shown that

$$(\alpha_H+k_1\alpha_{H'})/\alpha_F=k_2, \tag{2}$$

where

$$k_1=(C_{H'}/C_H)(f_H/f_{H'})(W_{H'}/W_H)$$

and

$$k_2=(C_F/C_H)(f_H/f_F)(W_F/W_H).$$

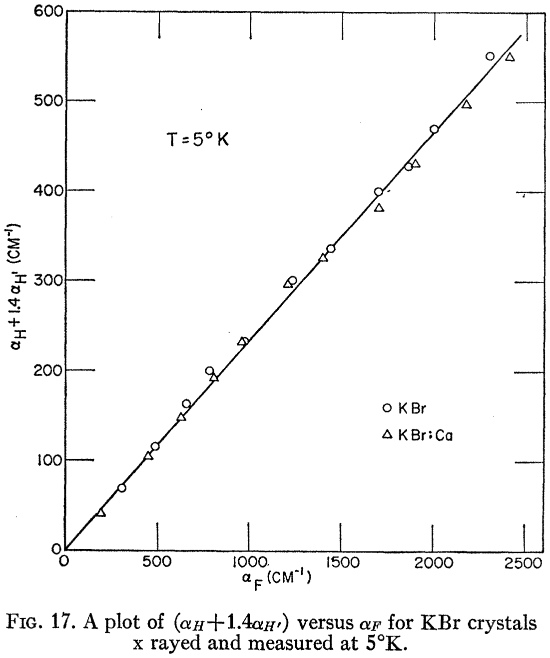

FIG. 17. A plot of $(\alpha_H+1.4\alpha_{H'})$ versus α_F for KBr crystals x rayed and measured at 5°K.

TABLE III. Half-widths and oscillator strengths of H and H' bands produced at 5°K in KCl and KBr. The bands are assumed to be Gaussian in shape.

	W_H(eV)	f_F/f_H	f_H	$W_{H'}$(eV)	$f_F/f_{H'}$	$f_{H'}$
KBr	0.48	1.5	0.32	0.9	1.2	0.40
KCl	0.65	1.8	0.29	1.0	1.4	0.38

Here the symbols, α, W, and f have the same meaning as defined previously and $C=n/(n^2+2)^2$, n being the index of refraction of the crystal. The indices F, H, and H' refer to the F, H, and H' bands, respectively. The quantities k_1 and k_2 assume constant values for a particular crystalline substance and for the temperature at which the irradiation and measurements are carried out. Table III includes a tabulation of the measured half-widths of the H and H' bands in KBr as well as the values of the oscillator strength ratios (f_F/f_H) and $(f_F/f_{H'})$. Values of the oscillator strengths f_H and $f_{H'}$ were calculated on the basis of average values of f_F for a Gaussian F band as given in Table I. The values relating to the H band in KBr are in fair agreement with those reported by Compton and Klick[48] on the basis of a polarized bleaching experiment performed with crystals which had been x irradiated near liquid-helium temperature. They measured W_H to be 0.45 eV in KBr and determined the (f_H/f_F) ratio to be ≥ 0.5, i.e., the ratio $(f_F/f_H)\leq 2.0$.

A similar point of view may be adopted in order to account for the coloration in KCl in the liquid-helium temperature range. Accordingly, the 245-mμ band in KCl whose spectrum was included in Fig. 1 is assumed to correspond to the 278-mμ band in KBr and will also be designated as the H' band. While there was an observable shift in the wavelength at the peak position of the band from 250 to 245 mμ during the first two hours of irradiation, signifying the presence of a composite band structure, the constancy of the peak position for the balance of the x-ray exposure time was taken as evidence that the contribution from components peaking on the long-wavelength side of 245 mμ could be neglected. The growth curves of the H' band in pure and strontium-doped KCl are presented in Fig. 18. These curves show that the production of H' centers is most rapid at the beginning of the irradiation and that the initial formation of H' centers appears to proceed independently of the divalent-impurity content. After about 5 h of x-ray exposure, the growth in the

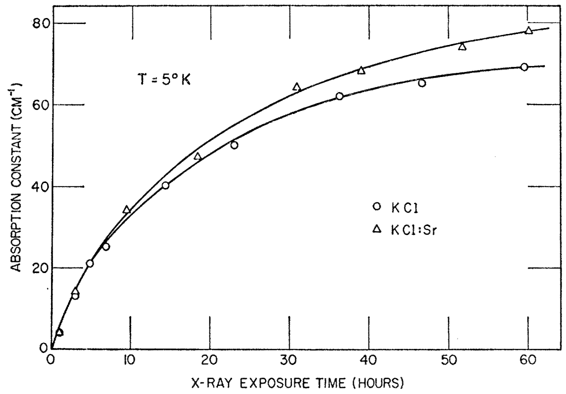

FIG. 18. Growth of the H' band in KCl and KCl:Sr as a function of the time of x irradiation at 5°K. Measurement were made at the peak position of the band (245 mμ) and at the irradiation temperature.

strontium-doped sample begins to proceed at a greater rate than in the pure crystal. However, both crystals show a progressively decreasing growth rate as the irradiation continues so that a state of saturation is being approached at the conclusion of irradiation. The divergence between the two growth curves is observed to increase gradually until the excess H' coloration in the KCl:Sr sample measures about 10% of the total observed absorption at 245 mμ when the irradiation is discontinued.

The data for the H' band contained in Fig. 18 are combined with the H-band observations of Fig. 14 and the F-band results of Fig. 5 in a manner analogous to that utilized for KBr. Accordingly, the value of $(\alpha_H+1.1\alpha_{H'})$ is plotted against α_F and a fairly good least-squares fit of the above data is obtained by the straight line shown in Fig. 19, which has a slope of 0.15. However, for values of α_F in excess of 1500 cm^{-1}, the corresponding data for the divalent-doped sample falls off significantly. No explanation for this behavior is offered at the present time. The values of k_1 and k_2 which are equal to 1.1 and 0.15, respectively, are utilized in the calculation of the oscillator strength ratios (f_F/f_H) and $(f_F/f_{H'})$. The values corresponding to these quantities as well as the values of the oscillator strengths f_H and $f_{H'}$ calculated on the assumption that all of the bands are Gaussian in shape are listed in Table III. Also included in the tabulation are the half-width values of the H and H' bands. The latter values are estimated from the absorption spectra of each band, but the composite nature of the "H" band discussed above precludes a satisfactory direct measurement and so the value of 0.65 eV is taken from Cape's determination[55] for the pure H band in KCl at 15°K. A comparison of the (f_F/f_H) value of 1.8 determined in the present work with that measured by Compton and Klick[48] in the polarized bleaching experiment shows reasonable agreement. On the basis of a value of 0.75 eV for W_H, they determined the (f_H/f_F) ratio to be ≥ 0.3, or, the (f_F/f_H) ratio ≤ 3.3.

It will be seen later that a prolonged x irradiation at 80°K produces prominent bands in the vicinity of the spectral region occupied by the respective H' bands at 5°K. In KBr, for example, the V_4 band with a peak position at approximately 275 mμ is observed and in KCl a band designated as the $V(240)$ results from a similar irradiation. A comparison of some of the other spectral properties, i.e., the half-width and oscillator strength, provides good evidence for the viewpoint that the H' band cannot be identified with the V_4 band in KBr or with the $V(240)$ band in KCl. If a Gaussian band shape is assumed, the oscillator strength of the $V(240)$ is found to be 0.14 and can be compared with Kingsley's[7] value of 0.17 for the V_4. These values are significantly smaller than the corresponding values of $f_{H'}$, viz., 0.40 in KBr and 0.38 in KCl. Furthermore, the half-width of both the V_4 and $V(240)$ bands at 80°K is determined to be 0.6 eV; this value is much smaller than the 0.9 and 1.0 eV half-widths observed for the H' band in KBr and KCl, respectively, at 5°K. From the above discussion, it appears that the H' band is not to be identified with the V_4 band in KBr or the $V(240)$ band in KCl. However, Duerig and Markham[19] showed that warming their x-irradiated KBr sample from 5 to 78°K resulted in the bleaching of the 285-mμ band (presumably the H' band) and the reappearance of another band (possibly the V_4 band) at 277 mμ. Similarly, the 255 mμ band produced in KCl at 5°K (probably the H' band) bleached on warming to 78°K and another band [possibly the $V(240)$ band] appeared at 238 mμ. These observations suggest that warmup of the crystal samples from liquid-helium temperature to liquid-nitrogen temperature results in a thermal conver-

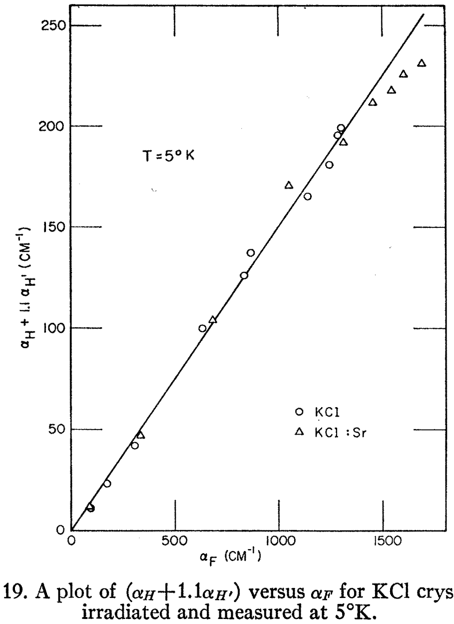

FIG. 19. A plot of $(\alpha_H+1.1\alpha_{H'})$ versus α_F for KCl crystals x irradiated and measured at 5°K.

sion of H' centers to V_4 centers in KBr and a similar transformation of H' centers to $V(240)$ centers in KCl in analogy with the well-known conversion of H centers to V_1 centers produced by a warmup of x-irradiated KCl and KBr crystals. A further investigation of H' centers by thermal bleaching techniques would be helpful.

One final observation that ought to be made is that Duerig,[34] in an unpublished work, designated each of the absorption bands at 380 and 345 mμ in KBr and KCl, respectively, as the H_1 band. Subsequent investigation showed these bands owed their origin to the H center. In addition, each of the bands which were observed to peak at 285 and 255 mμ in KBr and KCl, respectively, was called the H_2 band. In the published account of this work, neither the H_1 nor the H_2 designation was employed by Duerig and Markham.[19]

F. Growth of the V_1 Band in KCl and KBr (80°K)

Reference to the absorption spectra presented in Figs. 3 and 4 above show that a 30 min x irradiation at 80°K results in a broad poorly resolved absorption near 360 mμ and at approximately 400 mμ in KBr. No attempt is made to separate these absorptions into their components which are known to include a V_1 band peaking at 356 mμ and a V_K band with a maximum at 365 mμ in KCl and a similar superposition of a V_1 band at 410 mμ and a V_K band which peaks at 385 mμ in KBr. The growth of the V_1 band is followed by measuring the value of the absorption constant at 356 mμ in KCl and at 410 mμ in KBr as a function of the x-ray exposure time. Observations made after 4 h of irradiation show that no further growth in absorption due to either the V_1 or V_K bands is seen. These results are in agreement with Kingsley[7] who concluded that both the V_1 and V_K bands saturate following a prolonged irradiation (8 h). It appears evident that the V_1 center does not play a decisive role in defect formation for extended x irradiations carried out in KCl and KBr at liquid-nitrogen temperature.

Previously, Duerig[34] showed that the growth curves of the F and V_1 bands resulting from very brief x irradiations of KCl and KBr at 78°K were of similar shape. A plot of his data shows that a reasonably linear relation appears to exist between F- and V_1-center formation at this temperature. Since the present work was primarily concerned with the results for a prolonged irradiation and not a verification of Duerig's data, it suffices to state that no such linear relation between F- and V_1-center generation was observed for long x-ray exposures.

G. Growth of the V_4 Band in KBr (80°K)

The absorption spectra of Fig. 4 show the prominent role assumed by the V_4 band during the course of a prolonged x irradiation of KBr at 80°K. This observation supports the viewpoint of Kingsley[7] who characterized the V_4 center as one of the most important hole defects formed at 80°K since the V_4 band exhibits continuing growth while the V_1 and V_K bands are observed to saturate. Kingsley established that the V_4 center has ⟨100⟩ symmetry on the basis of polarized bleaching studies and suggested that it could be a hole trapped at a positive-ion vacancy. Before the growth behavior of the V_4 band is described, some consideration is given to the spectral properties of the band as revealed during the course of the irradiation.

The early growth of the V_4 band is known to be accompanied by an appreciable V_2 band, peaking at roughly 254 mμ, and poorly resolved from the V_4 maximum at 275 mμ. The peak position which was first observed for the V_2-V_4 composite was seen to be approximately at 272 mμ. Intermediate observations made between the times that the spectra in curves (a) and (b) were recorded indicate that the V_2 band saturates within several hours of x-ray exposure and apparently makes no further contribution to the growth of the V_4 band. The peak position of the latter band is noted to be 274 mμ after 9.9 h of irradiation and remains at this wavelength until the irradiation is discontinued. Reference to curve (c) of Fig. 4 shows that there is some overlapping between the long-wavelength side of the V_4 band and the absorption identified by Kingsley[7] as the V_7 band with its peak position at approximately 310 mμ.[5] In addition, extremely weak x-ray induced absorptions associated with the L_1, L_2, and L_3 bands extend throughout the same spectral region covered by the V_4 band. Despite the complicated situation, it is assumed that the absorption constant measured at the peak position of the V_4 band is due primarily to the presence of the V_4 center and absorptions resulting from other defects are considered as negligible.

The growth curve of the V_4 band at 80°K shown in Fig. 20 bears a strong resemblance to the shape of the F-band growth curve in KBr at 80°K, as shown in Fig.

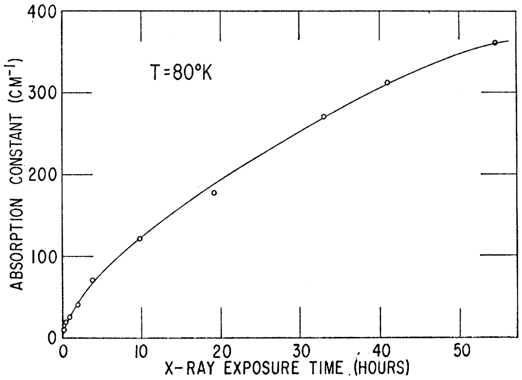

FIG. 20. The growth of the V_4 band in KBr following x ray irradiation at 80°K. Observations of the absorption constant were made at the peak position of the band (274 mμ) and at the irradiation temperature.

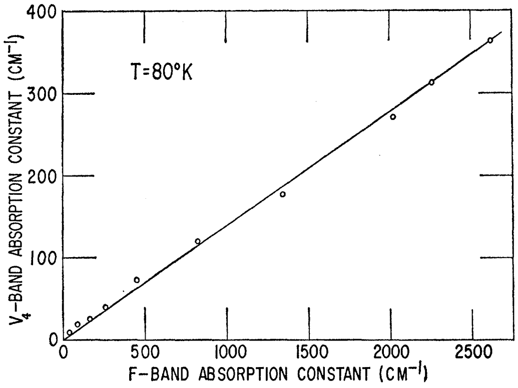

FIG. 21. The linear relation between the V_4-band absorption constant and the F-band absorption constant in KBr x rayed and measured at 80°K.

8. Accordingly, the growth rate may be characterized as being most rapid at the outset of the irradiation and diminishing gradually and continuously for the remainder of the time that the crystal is exposed to x rays. The V_4 absorption constants are plotted against the corresponding F-band absorption values in Fig. 21. The resulting straight line represents a least-squares fit to the data. It is seen that the early observations lie consistently above the plotted line and are presumed to contain contributions from the V_2 band which is known to saturate after a short irradiation.

The linear relation between the growth of the F and V_4 bands suggests that the defect centers responsible for these bands are generated in equal concentrations, i.e., $n_F = n_{V_4}$. The concentration of each center at any time during the x irradiation of KBr at 80°K may be determined by means of Smakula's formula.[26] The quantities required for the calculation are provided by the absorption data shown in Figs. 8 and 21, the spectral properties of the F band in KBr at 80°K given in Table I, and the corresponding properties of the V_4 band reported by Kingsley.[7] He measured the half-width of the V_4 band to be 0.6 eV (verified in the present experment) and the oscillator strength ratio (f_F/f_{V_4}) as 2.8. The calculation shows that for an x-ray exposure in excess of 4 h, the concentration of F centers is very nearly that of V_4 centers (within 10%). For shorter irradiation times, the computed values of n_{V_4} exceed the corresponding n_F values by as much as 35%. This is ascribed to the presence of contributions from V_2 centers which were not subtracted off from the principal absorption.

H. Growth of the $V(240)$ Band in KCl (80°K)

The absorption spectra of a KCl sample x irradiated at 80°K (Fig. 3) showed the development of a broad weak band having a poorly resolved peak at about 235 mμ into a strong well-resolved band after 52.0 h of x-ray exposure. The spectral behavior of this band is somewhat similar to that described for the V_4 band in the preceding section. In the early phase of the growth, the absorbing region located approximately between 220 and 270 mμ appears to be composite in nature and is constituted principally of absorptions peaking at 230 and 254 mμ which have been designated in KCl as the V_2 and V_4 bands, respectively. After four hours of x irradiation, the peak position of the band shifts to 240 mμ and remains unchanged for the remainder of the exposure. The shape of the prominent $V(240)$ band pictured in curves (b) and (c) of Fig. 3 suggests that there are present within its envelope components due to the V_2, V_4, and V_7 bands. The constancy of the peak position after four hours implies that the absorptions associated with the first two bands saturate rapidly. Furthermore, the separation between the peak positions of the $V(240)$ band and the V_7 band (300 mμ)[5] appears to rule out a sizable contribution of the latter to the absorption observed at 240 mμ. Finally, in accord with the earlier discussion of the various L bands, it is likely that there is also present a very small contribution from the L_3 band known to peak at 250 mμ in KCl. In view of the above considerations, it is assumed that the absorption observed at 250 mμ is predominantly due to the $V(240)$ absorption band.

The growth of the $V(240)$ band as a function of the x-irradiation time at 80°K is pictured in Fig. 22. Its growth behavior closely resembles that exhibited by the V_4 band in KBr. Thus the growth is most rapid at the beginning of the irradiation and proceeds at a progressively slower rate thereafter. The similarity in shape between the growth curves of the $V(240)$ and the F bands at 80°K suggests that each absorption constant value at 240 mμ be plotted against the corresponding F-band absorption observations taken from Fig. 7. The straight line shown in Fig. 23 represents a least-squares fit for these data.

The linear relation between the F and $V(240)$ bands suggests that F centers and the centers responsible for the latter band are formed in equal concentrations. Accordingly, Smakula's formula[26] may be utilized to

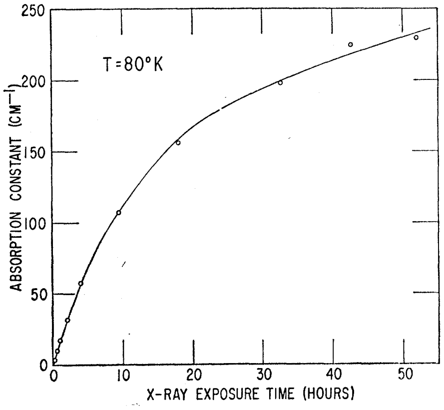

FIG. 22. Growth curve of the $V(240)$ band in KCl resulting from x raying at 80 °K. Measurements at the irradiation temperature were made at the peak position of the band.

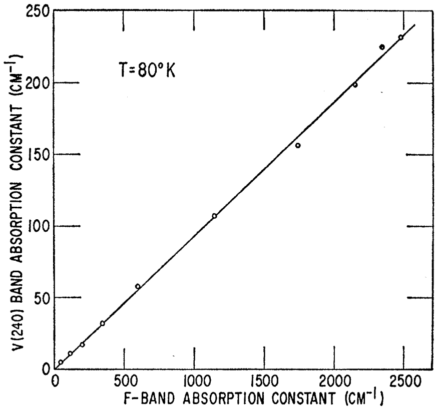

FIG. 23. The linear relation between the absorption constant of the $V(240)$ band and the F band in KCl x irradiated and measured at 80°K.

specify the value of the oscillator strength of the $V(240)$ band, $f_{V(240)}$. Since the slope of the straight line in Fig. 23 is 0.093 and the estimated value of the $V(240)$ band at 80°K is 0.6 eV, the oscillator strength ratio $(f_F/f_{V(240)})$ is 3.8. The value of $f_{V(240)}$ is, therefore, 0.14 on the basis of $f_F=0.53$.

Pretzel[8] has also observed a band in KCl at 240 mμ following x irradiation at 80°K, annealing at 270°K and further x irradiation at 80°K. Although the technique of formation is somewhat different than used in the present experiment, the band is probably the same. Pretzel has suggested that the defect responsible for this band is a Cl_3^- complex situated on individual lattice sites.

The results of observations made during the course of the prolonged x irradiation at 80°K support the viewpoint of this investigation that the $V(240)$ and V_4 centers are related to the fundamental mechanism of coloration at 80°K. While the present experiment sheds little light on the question of the true nature of the defects which are involved, it does appear that the defect centers which give rise to the V_4 band in KBr and to the $V(240)$ band in KCl are probably of the same type.

IV. SUMMARY

Growth curves of various absorption bands resulting from the prolonged x irradiation of thin samples of KCl and KBr at 5°K and at 80°K were determined and studied in relation to the growth behavior of the F band. The principal results of this investigation are summarized as follows:

(1) The initial growth stage of each of the absorption bands studied at 5°K, viz., F, K, M, H, and H', was observed to be insensitive to the presence of divalent impurities. This constituted an extension of the Rabin-Klick[3] statement which applied only to F-band formation near liquid-helium temperature.

(2) The F-to-K ratio of each material was found to be independent of impurities, or F-center concentration, thereby supporting the view that both bands arise from transitions in the same center.

(3) The concentration of M centers was found to depend quadratically on the F-center concentration in support of the van Doorn-Haven model that the M center consists of a pair of associated F centers.

(4) The constancy of the H-to-F ratio for irradiations of several hours implied that H and F centers are generated in equal concentrations. For prolonged irradiations, the rapid decrease of the H-to-F ratio was accompanied by the prominent growth of a band designated as the H' band (at wavelengths shorter than those of the H band in the two materials). It is suggested that the H' band has a close relationship to the H center since a suitable choice of the H' oscillator strength indicates that the number of F centers is in a constant ratio to the sum of the H and H' centers.

(5) The early saturation of the V_1 band at 80°K suggested that the V_1 center does not play a dominant role as the hole-trapping defect for prolonged x irradiations at liquid-nitrogen temperature.

(6) The linear relation observed between the growth of the F band and the growth of the V_4 and $V(240)$ bands in KBr and KCl, respectively, suggested that the V_4 center as well as the center responsible for the $V(240)$ band are involved with the fundamental mechanism of coloration at 80°K. Furthermore, it is suggested that that it is the same defect which gives rise to each band in the two materials.

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