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Production of V_3 Centers in KCl by X Rays*

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The growth of the V_3 band has been studied in x-ray-irradiated KCl at room temperature, by measuring the optical absorption as a function of x-ray dose. In the region in which the F band grows linearly with time (after the initial "fast coloration"), the V_3 band height increases approximately as the square root of the time. The V_3 band growth rate varies with x-ray intensity and depth in the crystal in the same way as that of the F band, however. Although the F band can be optically bleached without affecting the V_3 band, if the F band is optically bleached *during* the x-ray irradiation, the V_3 band likewise fails to grow. These facts are thought to be consistent with a model of the V_3 center in which a Cl_3^- molecular ion is located at a cation vacancy. The center could be formed by the x-ray production of an anion vacancy-interstitial pair and the diffusion of a cation vacancy to the interstitial.

I. INTRODUCTION

An F center is formed in an irradiated alkali halide crystal when an electron-hole pair is created and the electron is trapped at an anion vacancy in the lattice. The hole is presumably trapped elsewhere in the lattice, and is supposed to give rise to the optical absorption in the V bands at shorter wavelengths than the F band. Seitz proposed,[1] by analogy with the electron traps, that the holes were trapped at cation vacancies or vacancy aggregates. Känzig and others have since discovered, by identification of the electron spin paramagnetic resonance spectra of some of the V centers,[2–5] that what was overlooked in the proposed structures was the strong tendency for the halogens, unlike the alkali metals, to form a molecular bond. Thus, although distorted versions of some of Seitz's structures have been confirmed, it proves to be more appropriate to regard the V centers as halogen molecules or molecular ions, which are incorporated into the lattice in various ways, perhaps in association with vacancies.

The approximate wavelengths of V bands which are observed[3,6–8] in pure KCl are listed in Table I. The only V band which is produced at 5°K is H. The only ones which are stable at 300°K are V_3 and V_2, and V_3 can be produced *only* near room temperature. At intermediate temperatures the other bands are produced and bleached. The simplest absorption spectra therefore are found either at very low temperatures or at high temperatures.

It is seen that the absorption bands fall into two groups with respect to wavelength: H, V_1, and V_K are close together; and V_3, V_2, and V_4 are somewhat more spread out. An important clue to the structure of the centers was given by Hersh's observation[9] that halogen molecules and molecular ions in solution show corresponding absorption bands, at wavelengths which do not depend strongly on the environment of the molecule. For example, the Cl_2 absorption is at 335 mμ, and the Cl_3^- at 230 mμ. Thus the longer wavelength group of absorption bands in the KCl crystal could be expected to result from Cl_2, possibly ionized or associated with vacancies, and the other group from Cl_3^-, again possibly further ionized or associated with vacancies.

The structures which have so far been determined with some assurance confirm this expectation. The H center[4] is a Cl_2^- molecular ion which occupies an anion vacancy. It has no analog in Seitz's models, but would have been described as a hole trapped at an interstitial Cl^- to form an interstitial Cl atom. The V_K center[2,3] could be formed from an H center with the addition of another anion vacancy. Chemically it is the "self-trapped hole," but the trapping occurs by the formation of a molecular bond instead of by polarization of the lattice. The V_1 center is not paramagnetic, but it is probably an H center which has trapped another hole, to form a Cl_2 molecule occupying an anion vacancy. (Another center, similar to the "antimorph of the F center," has been found[10] in LiF. It is like an H center next to an anion-cation vacancy pair, but its optical absorption band has not been identified.)

A Cl_3^- molecular ion would not be paramagnetic, but a Cl_3^{--} center has been found[5] and tentatively identified with the V_4. It is a hole trapped on three Cl^- ions next to a complex of two cation and one anion vacancies, and is similar to Seitz's original model. On the other

TABLE I. Peak wavelengths (in mμ) of V bands formed by x rays in pure KCl.

V_3	V_2	V_4	H	V_1	V_K
215	230	255	345	355	365

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* Supported by the National Science Foundation.

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[2] T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957); T. O. Woodruff and W. Känzig, *ibid.* **5**, 268 (1958).

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[5] M. H. Cohen, W. Känzig, and T. O. Woodruff, J. Phys. Chem. Solids **11**, 120 (1959).

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[10] W. Känzig, Phys. Rev. Letters **4**, 117 (1960).

hand, the V_3 center may be a Cl_3^- center. This point will be discussed more fully in Sec. IV.

The mechanism by which the *F* and *V* centers are produced by the radiation is less well understood. The growth rate of the *F* band has been studied as a function of the amount of x-ray irradiation,[11–14] and it is concluded that the irradiation produces new anion vacancies, in addition to those present in the crystal before the irradiation, so that the attainable concentration of *F* centers is not limited to the initial concentration of vacancies. At room temperature this vacancy production is structure-sensitive,[11,13,14] but at 4°K it is not.[12,13] It should be noted that an *F* center and an *H* center could combine to give the perfect crystal. This fact is therefore additional evidence that at low temperature the basic reaction is the production of an *F* center—*H* center pair from the perfect lattice, and mechanisms for the production have been discussed.[15–17] At high temperatures, however, another reaction may predominate. Mechanisms for the production of anion vacancies at dislocations have also been considered[14,18,19]; these involve the creation of cation vacancies as well as anion vacancies.

The growth rates of the *V* bands have not previously been studied. Our purpose is to determine how one of these bands, the V_3, grows as a function of the x-ray irradiation at room temperature. In KCl, *F* and V_3 are essentially the only bands below 6.5 ev which are produced at room temperature. (After heavy irradiation *M* and V_2 are also observed, but these centers are present in smaller numbers.) We have concentrated on the region of heavier coloration (not the initial "fast" coloration), where new vacancies are being produced by the x-rays. Therefore the results should throw new light on the production mechanism, as well as on the structure of the V_3 center.

II. EXPERIMENTAL

The KCl samples were cleaved from Harshaw single crystals, usually to a thickness of about 1 mm. They were x-ray irradiated using a Norelco FA-60 tungsten target tube. The samples were placed about 3 cm from the tube window, with their thin dimension parallel to the x-ray beam. Unless otherwise stated, the x rays were filtered only by the tube window. Generally the tube current and voltage were held constant at 40 ma and 50 kv, and the optical absorption of the samples was measured after different durations of irradiation. The x-ray intensity at the window is stated to be about 5 000 000 r/hr.

The optical absorption was measured with a Unicam SP 700 recording spectrophotometer. The wave-number range of this instrument is from 54 000 cm^{-1} to 2800 cm^{-1}, i.e., from about 0.35 to 6.7 ev. The sample absorption was usually compared with that of a reference crystal, and differences between the two were corrected by making a run on the uncolored sample before the irradiations. (The OH band absorption was occasionally measured, however, by comparing the uncolored sample with an empty reference compartment.) The optical path through the sample was in the same direction as that of the x-ray beam. All the optical absorption measurements were made at room temperature.

Occasionally, when the optical density was off scale, we estimated the *F*-band height by measuring the optical density where the band had the known half-width. This procedure is dangerous, however, because we found that the half-width of the band decreased as the height increased. Therefore, we never carried this extrapolation very far.

III. RESULTS

1. Growth of Absorption Bands with Time

The growth of the absorption bands which are produced by x-ray irradiation at room temperature was followed up to irradiations of 15-hr duration. The bands observed in KCl in the wavelength range 190–2500 mμ

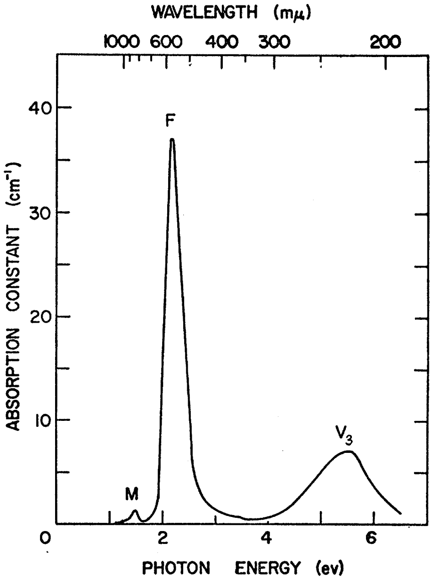

FIG. 1. Absorption spectrum of KCl crystal irradiated for 2 hr. The sample was 0.110 cm thick and was covered by a KCl filter 0.045 cm thick.

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were V_3, F, R_1, R_2, M, and N. The R and N bands appeared only after heavy irradiations. A typical absorption spectrum is shown in Fig. 1, and peak wavelengths, energies, and widths at half-maximum observed for the V_3, F, and M bands are listed in Table II. The measured V_3- and F-band absorptions corresponded to concentrations up to about 10^{18} centers/cm^3; the M-center concentration produced was about 1% of the F-center concentration. The R- and N-center absorptions were even less than the M-center, and these were not analyzed in detail.

The widths of the F and V_3 bands were actually somewhat variable. The F band narrowed slightly when it was very high. The V_3 band was wider near the front surface of the crystal (i.e., with less filtration), although at a given depth the width remained approximately constant as the band grew. Most of the widening was on the low-energy side of the band, and probably came from another unresolved band on the shoulder. This is thought to be the V_2 band, for reasons which will be described in Sec. 5.

The growth of the V_3, F, and M bands as a function of time is shown in Fig. 2. Here the absorption constant at the peak of the absorption band is plotted versus the time of irradiation with a tungsten target x-ray tube operated at 50 kv, 40 ma. This KCl sample was 0.092 cm thick, and it was covered by a KCl filter 0.075 cm thick.

TABLE II. Energy, wavelength, and width at half-maximum for the bands studied in KCl. The widening of the V_3 band is probably due to an unresolved V_2 contribution.

	$h\nu$ (ev)	λ (mμ)	W (ev)
M	1.49	830	0.12
F	2.20	560	0.36−0.44
V_3	5.7	217	0.9(−1.2)

As has been previously observed,[11,14] the F band grows linearly with time in the region roughly from 20 to 200 cm^{-1} (concentration $10^{17}-10^{18}$ cm^{-3}). At lower F-center concentrations the curve shows some initial curvature, in the region of "fast coloration," which has been analyzed previously.[14] In the following discussion, when we refer to the rate of F-center production, we mean the slope of this linear portion of the growth curve.

The M-band peak also grows more or less linearly, with the F band, although at a rate which is some 20 times slower than the F band. Since in addition the M band is only about $\frac{1}{3}$ as wide as the F band, the M centers form an insignificant fraction of the electron centers produced by the x irradiation.

By contrast, the V_3 band does not grow proportionally to time t, but approximately as $t^{\frac{1}{2}}$: The curve drawn in Fig. 2 is a parabola. The points plotted are actually three times the V_3-band height, but since the V_3 band is roughly three times wider than the F band, the two curves are representative of the relative numbers of color centers of the two kinds (assuming that the oscillator strengths are about 1). In the early stages of coloration, the V_3-band height is greater than the F-band height, but later the F centers outstrip the V_3 centers.

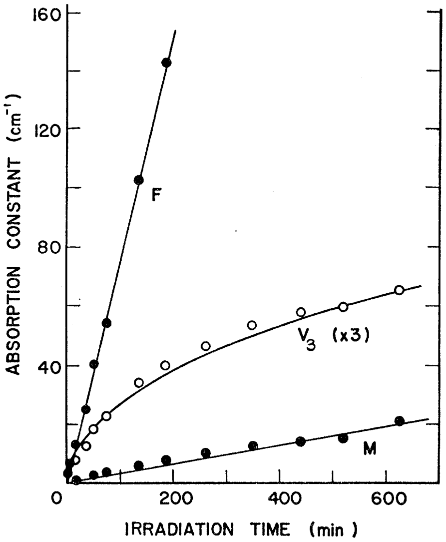

FIG. 2. Absorption constant at the band peak for the V_3, F, and M bands, after successive periods of x-ray irradiation. The values for V_3 are multiplied by 3 for better visibility.

The growth was reproducible to within 10% among samples cleaved from the same crystal, but varied by as much as a factor of 2 or 3 among different crystals. The V_3-band growth rate was proportionately greater in crystals where the F-band growth rate was large.

Appreciable thermal bleaching, of the order of 5%, occurred in the F band when the irradiation was suspended and the crystal was kept at room temperature overnight. A concomitant increase in M-band height was observed, since F centers are transformed to M centers. These changes were fully reversed by a further irradiation, however; that is, after the next irradiation the point lay on the original F- and M-center growth curves. Similar thermal bleaching was seldom observed in the V_3 band. In fact, sometimes the height of the band *increased* on standing, by as much as 10%. These increases were unfortunately not very reproducible, and we have not studied them more thoroughly. (See Sec.5, however.)

2. Dependence of Growth Rate on X-Ray Intensity

Growth curves similar to those in Fig. 2 were measured at three different x-ray tube currents, with a fixed voltage of 50 kv. If the law of growth of absorption constant α is expressed as

$$\begin{aligned} \alpha_F &= k_F{}^2 t, \\ \alpha_V &= k_V t^{\frac{1}{2}}, \end{aligned} \qquad (1)$$

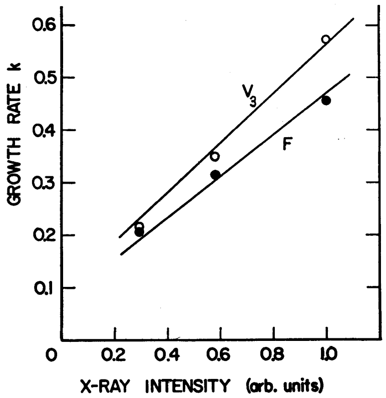

FIG. 3. Growth rate of V_3- and F-band heights as a function of relative x-ray intensity. The growth rate constants k are defined by Eq. (1) in the text; the units are cm$^{-\frac{1}{2}}$ min$^{-\frac{1}{2}}$ for the F band and cm^{-1} min$^{-\frac{1}{2}}$ for the V_3 band. (Sample 0.11 cm thick, KCl filter 0.04 cm thick.)

for the F and V_3 bands, respectively, the values found for k are plotted in Fig. 3. The values of k_V and k_F are approximately proportional to each other. (Since the units are not the same, the near equality of k_V and k_F is accidental.)

The value of k_F has previously been reported to be proportional to x-ray intensity.[14] At the higher dose rates used in our experiments, the proportionality does not hold strictly, but from Fig. 3 it can be inferred that k_V depends on intensity in the same way as k_F. That is, the F-band height increased with the square of x-ray intensity, and the V_3 band increases with the first power of x-ray intensity.

3. Dependence of Growth Rate on Depth in the Crystal

Since the rate of production of color centers depends on the x-ray intensity, the rate of coloration decreases with depth in the crystal, as the x-ray beam is absorbed by upper layers. The x-ray absorption constant depends on x-ray energy. In addition, the density of color centers produced by an absorbed x-ray photon also depends on x-ray energy, since soft x rays produce higher ionization densities. Thus, if the x rays are not monochromatic, the rate of coloration may be expected to depend in a complicated way on depth in the crystal.

The dependence for the V_3, F, and M bands in KCl is shown in Fig. 4. A stack of crystal slabs was exposed to x rays from the tungsten-target tube for successive periods of time, and growth curves similar to those of Fig. 2 were obtained for each slab in the stack. The "depth" is taken as the total thickness of the slabs above the slab in question, plus one-half the thickness of that slab itself, so that the absorption is averaged over the slab, of thickness approximately 1 mm. Figure 4 shows that the growth rate constants k defined in Eq. (1) for the V_3 and F bands depend on depth in the crystal, and therefore also on x-ray photon energy, in approximately the same way (since it has been shown above that k_V and k_F depend on intensity in the same way). Probably the M-band growth rate has a similar dependence, although the experimental uncertainty is too large to be unequivocal.

It has, of course, always been realized that coloration is much heavier on the surface because of the strong absorption of soft x rays, and it is common practice to filter the radiation to eliminate the softest component, in order to have a more uniform coloration of the sample. The flattening out of the curves in Fig. 4 shows the value of such filtration. It seemed possible to us that, in addition to this depth effect, there could be a true surface effect. The rate of coloration is known to depend on oxygen and water vapor contamination, and ozone is produced by the x-ray beam. We tested the possibility that coloration was actually enhanced near a free surface of the crystal in two different ways. First, the rate of coloration of each of an irradiated stack of slabs was compared with that of slabs of equal thickness cleaved after irradiation from a solid crystal. In the former case all the slabs had two free surfaces during irradiation, but not in the latter case. Secondly, the coloration of identical crystals was compared when the irradiation occurred in air or in dry nitrogen atmosphere. In both experiments the result was negative: The results were the same whether or not the sample had a free surface in contact with air.

4. Simultaneous Irradiation with X Rays and Visible Light

When the F band is bleached with white light in a crystal containing both F and V_3 bands, the F band can

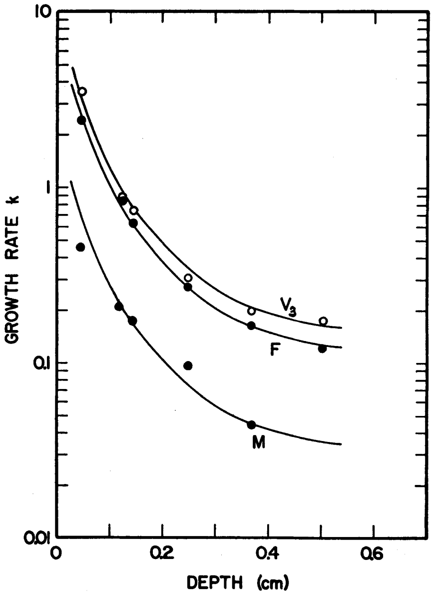

FIG. 4. Variation of growth rate with depth in the crystal for the V_3, F, and M bands. The units of k are as in Fig. 3.

be completely removed without affecting the V_3 band.[20] Since the F band can be bleached indepently of the V_3 band, we expected that if the F band were prevented from growing by illuminating the sample with white light during the x-ray irradiation, the growth rate of the V_3 band would be unaffected. On the contrary, we found that the V_3 band was not produced at all when the F band was prevented from growing.

The previous experiments were repeated, with the KCl crystals illuminated during the irradiation with the light from a 500-w lantern-slide projector, about 25 cm away. Under these conditions, for example, in a 1-mm thick specimen covered by a 1-mm thick crystal, the V_3- and F-band heights were both of the order of 1 cm^{-1} after a 10-hr irradiation. The illumination caused the specimen temperature to rise to about 45°C, but it was established that this result was not a thermal effect. (See Sec. 6.)

5. Alternate Irradiation with X Rays and Visible Light

Because the V_3 band failed to grow when the F band was prevented from growing by simultaneous bleaching during the x-ray irradiation, it was also of interest to observe the rate of production in a crystal which had been irradiated and then bleached.

These effects are shown in Fig. 5. Curve 1 is the OH band at 204 mμ in the uncolored crystal. This band is given only to indicate the purity of the sample, and is subtracted from all the other curves. Curve 2 shows the V, F, and M bands after 170 min x-ray irradiation. The dose rate was comparatively high, and a relatively wide V band was produced. Curve 3 shows the same sample, after 12 hr bleaching (about 9 in. from a 300-w tungsten lamp, behind a water filter). The F band is almost completely removed, although the sample had a light blue color due to colloid and aggregate bands. These were absent when the specimen was less heavily colored initially. The V_3 height is very little changed, but the long-wavelength shoulder is removed. The difference between curves 2 and 3 is plotted as curve 4, whose peak at 232 mμ corresponds to the V_2 band. This is less prominent at smaller x-ray intensities.

The changes in area under these curves as a result of the bleaching were compared by arbitrarily assuming a boundary between electron and hole absorption at 3.4 ev. Some of the F centers of curve 2 remain as the aggregated electron centers of curve 3 below 3.4 ev. It is also assumed that other F-center electrons might annihilate the V_2 centers of curve 4. After these areas are subtracted from the area under curve 2 below 3.4 ev, about 70% of the original F-band area is still unaccounted for. That is, there is an integrated electron absorption of 14.3 ev cm^{-1} which has disappeared without a corresponding decrease of absorption in the uv within the range of the spectrophotometer. This missing area corresponds to 1.4×10^{17} F centers cm^{-3} using Doyle's experimental figure[21] of 1.0×10^{16} $\text{cm}^{-3}/\text{ev cm}^{-1}$. Presumably there are compensating absorption changes beyond the range of our instrument, above 6.5 ev.

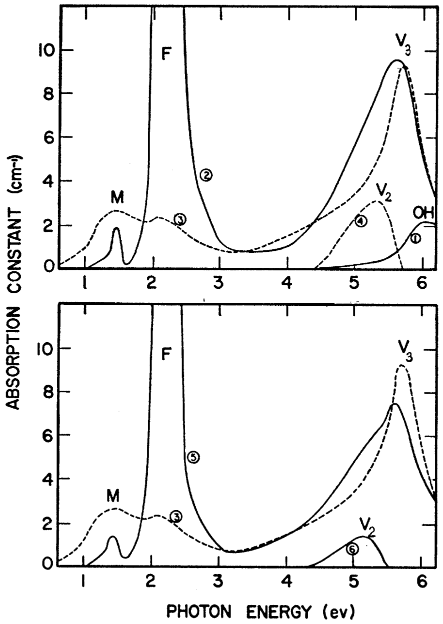

FIG. 5. Absorption spectrum of KCl sample 0.122 cm thick irradiated through Al filter 0.106 cm thick. Curve (1): Sample as received from Harshaw, showing the OH band (which is subtracted from the other curves). (2): After 170-min x-ray irradiation; F-band peak is at 55 cm^{-1}. (3): After bleaching with white light for 12 hr. (4): Curve (2) minus curve (3), showing the V_2 band which was destroyed by the bleaching. (5): Irradiated with x-rays for 5 min more; F-band peak 29 cm^{-1}. (6): Curve (5) minus curve (3), showing the V_2 band which is created by the x rays.

Curve 5 shows the effect of a further 5 min of x-ray irradiation. The F band is largely (61%) recovered. The V_3 peak goes down somewhat, on the other hand, and the V_2 band reappears. The total area under the combined V bands remains constant, so that some of the V_3 centers have apparently been converted to V_2 centers.

These changes are summarized for several cycles of x-ray irradiation and optical bleaching in Fig. 6. The F band makes a rapid recovery after having been bleached, the over-all growth rate being as great as if the bleaching had not intervened. The V-band growth is similar, except for the initial destruction of the V_3 band immediately after bleaching.

6. Temperature Dependence of Growth Rate

In KCl irradiated at liquid nitrogen temperature, the V_3 band is not produced. Instead, absorption in the *uv* occurs principally in the V_1 and V_2 bands.[6,7] The V_1 band is unstable above −100°C. Above −40°C, the V_3 band begins to appear significantly, and the V_2 band

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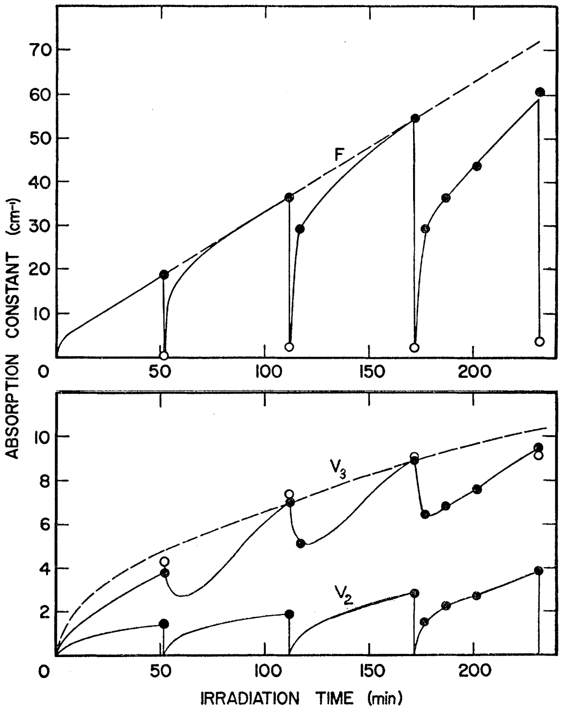

FIG. 6. Peak heights for V_3, V_2, and F bands, after successive cycles of x-ray irradiation and white-light bleaching. The open circles represent the bleached sample. The points at 170 min and 175 min show the heights of the bands in Fig. 5.

becomes less prominent.[7] The F band, on the other hand, forms at all temperatures down to the liquid helium range.

Since the V_3 band production seems to be favored by higher temperatures, we measured the growth rate of the V_3 and F bands when the crystals were x rayed at temperatures of about 50°C. The growth rate of the F band at 50°C was about half the rate at room temperature. The rate of V_3-band production was also smaller at the elevated temperature, but the decrease was not so great as for the F band. The formation of the V_3 band, therefore, seems to be favored at the elevated temperature, but since the interpretation of higher temperature measurements is complicated by simultaneous thermal bleaching, these experiments were not pursued. The measurement shows, however, that the almost total repression of the V_3 band when the F band is optically bleached during the x-ray irradiation, as described in Sec. 4, cannot be a thermal effect.

IV. DISCUSSION

In the foregoing, we have sought relations between the production of V_3 centers and F centers. It has been shown that the rates of production by x rays for the two kinds of centers are closely linked, so that both kinds are probably formed in the same elementary process. On the other hand, it is by no means true that the numbers of the two kinds of centers are always *equal*, so that their concentrations do not reflect the fact that electrons and holes must be created in pairs (assuming that the V_3 center is a hole center). That is, in trying to interpret the formation process in terms of a mechanism, it must be assumed that other undetected absorption changes are also occurring outside our range of observation from about 0.5 to 6.5 ev.

First, the V_3 centers cannot be identified with impurities. (The fact that the band peak is at about the same wavelength as that of the U band, due to hydrogen, makes this point especially worth noting.) The V_3 centers have been produced in numbers approaching 10^{18} cm^{-3}, whereas impurities would not be expected[22] to be present in numbers greatly exceeding 10^{16} cm^{-3}. In particular, the observed OH band corresponds to about this number. In addition, the number of lattice sites in the immediate vicinity of dislocation lines should normally be of about the same order of magnitude or less. Thus the number of V_3 centers can be far greater than the number of impurities or the number of atoms along dislocations. This fact does not mean, however, that the production of V_3 centers is not somehow catalyzed by impurities or dislocations. In fact, that is probably the case, since the growth rate of this band, as well as that of the F band, has been found to be a structure-sensitive property, varying from one crystal to another.

Secondly, the growth rate constant for the V_3 band depends in the same way as that of the F band on all the parameters which have been investigated. They depend in the same way on x-ray intensity, and also on depth in the crystal (and therefore on x-ray energy). Crystals which color more rapidly in the F band also show a more rapid growth of the V_3 band. These facts suggest that V_3 centers are produced by the same events which produce the F centers, although the possibility that the V_3 centers are produced by a similar mechanism but at independent locations cannot be excluded.

Another indication of the close connection between F center and V_3 center production is the observation that the x rays do not produce V_3 centers if the F centers are destroyed by simultaneous optical bleaching. The V_3 centers are probably formed in the vicinity of the F centers, since the release of F center electrons is able to prevent the formation of V_3 centers.

In spite of these close connections, however, there is certainly not a one-one correspondence between F centers and V_3 centers. During the x-ray irradiation, the integrated absorption in the F band becomes much larger than the V_3 band absorption, so that F centers are formed without the corresponding formation of a V_3 center. That is, some of the holes are trapped elsewhere than at a V_3 center, and these give an absorption which is outside our range of observation. Not only can the number of F centers be greater than the number of V_3 centers, but also the opposite preponderance can occur.

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The F band can be completely removed by optical bleaching with visible light, and yet practically no V_3 centers are destroyed. Thus at least some of the F-center electrons must become trapped elsewhere in the lattice after bleaching, again giving an absorption outside the range of observation.

The numbers of F and V_3 centers cannot, of course, be equal if the F band grows linearly with time while the V_3 band growth is nonlinear. If the V_3 band growth is proportional to the square root of irradiation time, but the proportionality constant is always related to the slope of the F-band growth curve, an inference can be made with regard to the growth rates. Letting n_F and n_V be the numbers of the two kinds of centers per unit volume,

$$n_F = c_F{}^2 t, \quad n_V = c_V t^{\frac{1}{2}},$$

where c_F and c_V are constants which have been found to be proportional to each other under all circumstances (at a given temperature). Then, since $dn_F/dt = c_F{}^2$ and $dn_V/dt = c_V/2t^{\frac{1}{2}} = c_V{}^2/2n_V$, we have

$$\frac{dn_V}{dt} = k\frac{1}{n_V}\frac{dn_F}{dt},$$

where k is a proportionality constant. That is, the V_3-center growth rate is proportional to that of the F centers, but also inversely proportional to the existing density of V_3 centers. This interpretation suggests that the V_3 centers are formed along with the F centers, but that their formation depends on another component, for which they are competing with each other, so that as they are formed this component becomes more scarce.

Another property of the V_3 center which is brought out by its growth rate is its stability. Apparently in its embryonic stages it is easily destroyed by electrons released from F centers by optical bleaching, but once it has been stabilized, it is very resistant to bleaching (thermal as well as optical). This enhanced stability could be merely a matter of distance from the F center, but it seems more likely that it is due to the acquisition of the additional component posited in the preceding paragraph.

In any case, the V_3 center very likely gains its stability by the mechanism of diffusion, since higher temperatures favor the formation of this center. It is not formed at all below −40°C, and becomes increasingly prominent as the temperature is raised. The diffusion involved could be simply in the separation of the V_3 center from the F center. Because of the all-or-none character of the stabilization against optical bleaching, however, it probably depends on the diffusion of something else to the proto-V_3 center, namely the additional component suggested above.

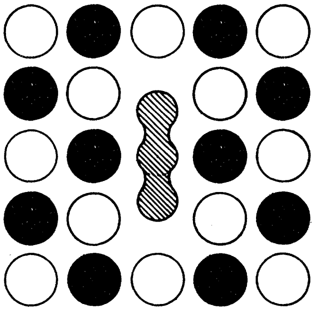

FIG. 7. Proposed Cl_3^- molecular ion model for the V_3 center. The white circles are K^+ ions, the black circles are Cl^- ions, and the three gray Cl^- ions share two trapped holes. One of the gray ions is at a K^+-ion site.

A possible model for the V_3 center, which is apparently consistent with what is known about the center, is shown in Fig. 7. It is a Cl_3^- molecular ion, oriented in the [001] direction, occupying two anion and one cation sites. Chemically it is equivalent to an H center plus a cation vacancy plus another trapped hole. The diffusion of the cation vacancy could be the thermal process involved, assuming that production of anion vacancy-interstitial pairs is the fundamental reaction in the F-center formation. The assumption that the center contains a cation vacancy is supported by the observation[20,23] that ionic conductivity, due to migration of cation vacancies, is very much smaller in crystals containing V_3 centers. The center is assumed to contain two holes because it is unlikely that it is paramagnetic. A search[24] revealed no resonance in a sample containing over 10^{16} centers, either before of after bleaching the F band.

The possibility that V_3 has the structure shown has been raised previously.[25] Hayes and Nichols[26] discovered a Cl_2^- center which gives an absorption at 325 mμ in KCl doped with Ca^{++}. It differs from the other Cl_2^- centers (H and V_K), however, in that it is aligned in the [100] direction instead of the [110]. They suggest that it is a Cl_2^- occupying an anion-cation vacancy pair, which composition is chemically equivalent to an H center plus a cation vacancy. Crawford and Nelson[25] found that this center, which is produced at 195°K, disappears above 235°K, and that when it is thermally bleached the absorption at 220 mμ is enhanced. It therefore seems that the 325-mμ center[27] has the structure shown in Fig. 8. When it loses another electron at high temperature, it converts into the Cl_3^- center of Fig. 7, the two holes now being shared by three chlorine ions. (We favor this configuration, rather than a neutral Cl_2, because of the large difference in wavelength absorbed by the center with one hole and that with two holes.[9]) A Cl_3^{--} center corresponding to Fig. 7 is apparently not formed when the Cl_3^- gains an electron

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[23] R. W. Christy and W. E. Harte, Phys. Rev. **109**, 710 (1958).

[24] W. T. Doyle (unpublished).

[25] J. H. Crawford, Jr., and C. M. Nelson, Phys. Rev. Letters **5**, 314 (1960).

[26] W. Hayes and G. M. Nichols, Phys. Rev. **117**, 993 (1960).

[27] Hayes and Nichols believe that the center is next to the impurity, whereas Crawford and Nelson disagree. Without committing ourselves on this point with regard to the doped crystal at low temperatures, we suggest that in the pure crystal at room temperature the V_3 has the structure shown in Fig. 7.

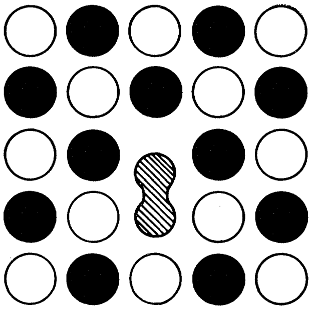

FIG. 8. Possible Cl_2^- configuration resulting from the addition of an electron to the center of Fig. 7. One trapped hole is shared by the two gray Cl^- ions. The other Cl^- ion has reverted to its normal state. (This center may be stable only when it is next to a divalent cation impurity.)

because the chemically equivalent Cl_2^- of Fig. 8 is more stable (at least at 195°K or in the vicinity of an impurity).

The V_2 center seems to be somehow related to the V_3, since it is apparently transformed into V_3 on warming from low temperatures[7] and transformed from V_3 on re-irradiation of an optically bleached sample. It is probably not worthwhile to speculate on the structure of V_2, however, until more is known about it, although it is tempting to identify it with the Cl_3^{--} just discussed.

V. CONCLUSIONS

The V_3 center is probably formed in the same event with some of the F centers and its stabilization involves diffusion of ions. Its structure may be a Cl_3^- oriented in the [100] direction, i.e., an H center plus a cation vacancy (plus another hole). This structure would conform to the absorption band groupings suggested by Hersh, and would require the diffusion of a cation vacancy to the center. It also suggests that the fundamental process in the formation of (at least some of) the F centers at room temperature is the production by the x-rays of anion vacancy-interstitial pairs. The rate of this production is structure sensitive, but the total number of pairs produced is not limited to the number of imperfections in the crystal. The formation of other F centers by a mechanism involving production of anion-cation vacancy pairs is not excluded, and in fact this mechanism could provide the cation vacancies required for the assumed model of the V_3 center. In any event, the numbers of F centers and V_3 centers are not equal, so that some other optical absorption must occur outside our range of observation, probably on the edge on the fundamental absorption band.