Hall, conductivity and thermoelectric power data.[25] Other published estimates[6,26] of the hole mass ratio in gray tin range from 0.2 to 3.0.

The electron mass ratio could not be deduced directly from the parameters of sample N1 because of the small value of $\Delta N$. While heavily doped $n$-type crystals have been grown, they do not show the high quality optical surfaces required for reflectance measurements. Attempts to extract the electron mass ratio using the tabulated electrical and optical parameters of several samples simultaneously were not successful due to the similarity of three of the samples.

It was found that the imaginary part $2nk$ of the complex dielectric constant did not show a simple $\lambda^3$ dependence. Spitzer and Fan[20] have pointed out that the expression for the wavelength dependence of the conductivity involves the relaxation time $\tau$ when $(\omega\tau)^2 \gg 1$, which is not the case for the susceptibility. Therefore, if $\tau$ is energy-dependent, $2nk$ can have a complicated $\lambda$ dependence even when $n^2-k^2$ is linearly dependent on $\lambda^2$. An extreme example of this type of behavior is shown by the results of Spitzer and Fan[20] for $p$-type indium antimonide where the absorption coefficient $\alpha$ is almost independent of wavelength, but nevertheless the free-carrier susceptibility shows a good $\lambda^2$ dependence.

## ACKNOWLEDGMENTS

The authors wish to thank S. Groves for informative correspondence and L. Liu for several clarifying discussions.

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[25] A. N. Goland and A. W. Ewald, Phys. Rev. **104**, 948 (1956).

[26] See Ref. 18, p. 40.

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# Optical Bleaching of $V_3$ Centers in KCl†*

T. P. Zaleskiewicz and R. W. Christy
*Dartmouth College, Hanover, New Hampshire*

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Bleaching of $V_3$ centers by uv light absorbed in the $V_3$ band was studied in Harshaw KCl crystals which had been x-ray irradiated at room temperature. The bleaching measurements were made in the temperature range from 75 to 110°C, where the uv bleaching rate was appreciable but purely thermal bleaching (in the dark) was not significant. The $V_3$ band decay was approximately exponential in time. Furthermore, the decay constant was approximately an exponential function of inverse temperature, with an activation energy of 0.6 eV. The calculated quantum efficiency for the bleaching was small throughout this temperature range, being given by $\eta \approx 10^6 \exp(-0.6\ \mathrm{eV}/kT)$. Some interaction between $V_3$ centers and $F$ centers was observed, since bleaching of either band by light absorbed in the band led to partial bleaching of the other band. The results are interpreted in terms of a model for the $V_3$ center consisting of a $Cl_3^-$ molecular ion at a cation vacancy. The $V_3$-band bleaching differs from $U$-band bleaching in its strong temperature dependence and the lack of any accompanying $F$-band production.

## I. INTRODUCTION

RADIATION damage in the alkali halides produces, in addition to the $F$ band in the visible, various optical absorption bands in the uv region.[1] Electron-spin resonance measurements have conclusively established that some of the uv bands formed by irradiation at low temperature are electron-deficit halogen-molecule centers, which complement the $F$ center (an electron trapped at an anion vacancy) in one way or another. The radiation damage mechanism at higher temperature is less clear, however, since the $V_3$ center, the principal uv companion of the $F$ center in "pure" crystals irradiated at room temperature, has a structure which is not yet definitely understood. Beside the molecular halogen centers, various impurities also give rise to absorption bands in the uv, and some of these may be modified by irradiation. In particular, the absorption due to $H^-$ ($U$ band) and $OH^-$ ions located on an anion site should be noted. In KCl, these absorption bands peak at 215 and 204 nm, respectively.

The $V_3$ band in KCl, which also peaks at 215 nm, has been attributed to a $Cl_3^-$ center that contains a cation vacancy, on the basis of its production by x rays[2] and its effect on electrical conductivity.[3] The $Cl_3^-$ ion is observed in solution to have a linear, symmetrical configuration, with the charge concentrated at the ends,[4] and its optical absorption peaks at roughly the same

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* Work supported by the National Science Foundation.

† Based on a thesis submitted by T. P. Zaleskiewicz in partial fulfillment of the requirements for the M.A. degree.

[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), Chaps. IV, V.

[2] R. W. Christy and D. H. Phelps, Phys. Rev. **124**, 1053 (1961). References to previous work are given here.

[3] R. W. Christy and E. Fukushima, Phys. Rev. **118**, 1222 (1960).

[4] E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, Advan. Inorg. Chem. Radiochem. **3**, 133 (1961).

wavelength as the $V_3$ band.[5] On the other hand, it has also been suggested[6] that the coincidence between the $V_3$-band and $U$-band peaks is not accidental, and they are the same center. This suggestion rests on the fact that $U$ centers can be produced by irradiation of $OH^-$ centers[6–8] (accidentally present in the crystal), and the observation that the production of $V_3$ centers is dependent on the OH content of the sample.

The purpose of the present investigation is to observe the photochemical behavior of the $V_3$ band, with the hope that further data may cast light on the structure of the center responsible for this absorption. The $V_3$ band is known to be very resistant to bleaching at room temperature,[9] but in the vicinity of 100°C we have obtained appreciable bleaching rates. In the following, we describe these as a function of the temperature of the crystal.

## II. EXPERIMENTAL

The KCl specimens were cleaved from Harshaw single crystals. A number of specimens was cleaved from the same block, and stored in a dessicator until used. Typical sample dimensions were $0.15\times0.75\times2$ cm. The x-ray irradiation was done at room temperature, using a Norelco FA-60 tungsten target tube operated at 50 kV and 40 mA. The sample was irradiated through the broad face, about 3 cm from the tube window, and was covered by a KCl filter 0.22 cm thick, in order to screen the soft x-ray component and promote uniform coloration. Typical irradiation time was 6 h.

Optical absorption measurements were made with a Unicam SP 700 recording spectrophotometer, in the wave number range 53 000 to 4200 $cm^{-1}$ (6.5 to 0.5 eV). The optical path through the sample was the same as that of the x-ray beam, and the measurements were made at room temperature. The spectrophotometer reference compartment was usually left empty, and the curve taken before the x-ray irradiation was subtracted from subsequent absorption measurements.

In order to do the optical bleaching of the samples with reasonably monochromatic light (and in particular to avoid the $L$-band region), the bleaching light was dispersed with a Bausch and Lomb 250-mm grating monochromator. This instrument has a constant dispersion of 6.6 nm/mm. Our usual settings were 220 nm with the entrance and exit slits opened to 3.18 mm. The pass band of the monochromator is triangular. Therefore our bleaching light contains wavelengths in the range from about 200 to 240 nm, peaking at 220 nm.

Because our monochromator was not very efficient in this wavelength region, a high intensity uv source was necessary. The source used was a high pressure mercury arc, the General Electric UA-2. This combination gave adequate intensity at 220 nm, but it had the disadvantage that the stray visible light was appreciable, because of the intense visible-light content of the source. The stray-light problem is significant, because the $F$ band is much more sensitive to bleaching than the $V_3$ band.

The output of the monochromator was measured as a function of wavelength using an RCA 935 phototube in conjunction with a Keithley 610A electrometer. Three different phototubes were used, and their average response was assumed to be given by the manufacturer's calibration curve. This procedure probably gives the light intensity to within about 20%. The result was an exit beam intensity, at the position of the sample, of about 10 $\mu W/cm^2$ at 220 nm and about 50 $\mu W/cm^2$ in the $F$-band absorption region near 560 nm. The stray visible light was measured by setting the monochromator at 220 nm and measuring the exit beam intensity through a green filter; the result was less than 0.2 $\mu W/cm^2$.

The samples were bleached at a position about 6.5 cm from the exit lens of the monochromator, where the exit beam was sufficiently large to cover the x-rayed area of the sample. During bleaching the sample was clipped to a copper plate which could be electrically heated for bleaching runs above room temperature. The temperature was measured with a Chromel-Alumel thermocouple soldered to the copper plate about 1 cm from the sample.

During bleaching the sample was enclosed in a light-tight box; about 1-min exposure to subdued light was necessary for alignment, but this exposure caused negligible accidental bleaching. In order to have uniform uv bleaching through the sample thickness, the absorption must be negligible. This condition was not satisfied initially, since the initial optical density at the $V_3$-band peak was usually about 0.3 (50% absorption). Thus, the initial light intensity at the back of the crystal was only about $\frac{1}{2}$ that at the front, but the orientation (front or back) was random after each absorption measurement. This effect accounts for some of the scatter of the bleaching data, and limited the range over which bleaching could be measured.

## III. RESULTS

X-ray irradiation of Harshaw KCl crystals at room temperature produces the $F$ band and the $V_3$ band, accompanied by much smaller $M$ and $V_2$ bands. In the present experiments, the concentration of $F$ and $V_3$ centers produced was of the order of $10^{17}$ $cm^{-3}$, well beyond the initial (and very structure sensitive) region of "fast coloration."[2] The unirradiated crystals contained an OH band at 204 nm whose height was of the order of 1 $cm^{-1}$; it was subtracted from all the data reported. No correlation between the OH-band height and the rate of $V_3$-center production was observed for

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[7] J. Rolfe, Phys. Rev. Letters **1**, 56 (1958).

[8] H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

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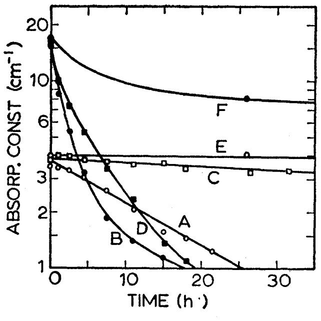

FIG. 1. Bleaching of the $V_3$ band (curves A, C, E) and $F$ band (curves B, D, F) at 100°C. Curves A and B: uv plus stray visible light. Curves C and D: stray visible light only. Curves E and F: no light (purely thermal bleaching).

these samples. Because of the possibility that the $V_3$ band is produced photochemically from the OH band, it is important to note that very much larger $V_3$ bands could be produced—up to 150 times the OH-band height, with no sign of saturation in the $V_3$-band growth rate. Even if the oscillator strength of the OH band is small,[10] this number of $V_3$ centers is much larger than the original number of OH$^-$ centers. Hydroxide could also be present as Ca(OH)$_2$, for example, in which state it does not contribute to the 204-nm band.[8] It still contributes to the infrared OH absorption at 2.8 $\mu$, however, and in our Harshaw crystals the absorption at 2.8 $\mu$ was less than 0.02 cm$^{-1}$. Furthermore, activation analysis[11] of Harshaw crystals indicates only a few parts per million of impurities. It therefore seems unlikely that sufficient hydrogen can be present in Harshaw crystals to account for the $V_3$ band. In our bleaching experiments, small $V_3$ concentrations were used, in order to promote uniform light absorption.

At room temperature, the $V_3$-center bleaching rate (quantum efficiency) for uv light absorbed in the $V_3$ band is extremely small. The effect of visible light is even less, and the $F$ band can be completely bleached with no perceptible effect on the $V_3$ band. The $V_3$-band bleaching rate increases with increasing temperature, however; our source gave reasonable bleaching rates above about 75°C. At elevated temperatures, three effects must be distinguished in the bleaching of the $V_3$ band: bleaching by uv light absorbed in the band, bleaching which accompanies $F$-center bleaching by visible light (if any), and purely thermal bleaching (in the dark).

These three effects are all in evidence in Fig. 1, which shows the decay of the $V_3$ and $F$ bands (absorption constant at the band maximum) at 100°C. Curves A and B show the decay of the $V_3$ and $F$ bands under uv illumination, i.e., with the monochromator set at 220 nm. It will be seen below that this $V_3$ bleaching rate is primarily due to the uv light absorbed in the band, and the $F$ bleaching rate is primarily due to stray visible light (unavoidably present in the monochromator output) absorbed in the $F$ band. The $V_3$ band bleaches approximately exponentially with time. A small $V_2$ band on the shoulder of the $V_3$ band disappeared during the first hour, and a conversion of $V_2$ to $V_3$ centers can account for the initial deviation from the straight line. This exponential decay of the $V_3$ band due to light absorbed in the band, and its dependence on temperature, is the effect which is the primary subject of this paper, but it is important to consider perturbations caused by stray visible light and thermal decay in the dark.

The stray visible light contribution to the bleaching is shown in curves C and D in Fig. 1. In this case a second sample cleaved from the same crystal was irradiated and bleached under identical conditions, except that a glass plate was interposed in the monochromator beam, in order to cut out the uv (below 300 nm) and pass only the stray visible light. The $V_3$-band decay is now very much slower, indicating that the decay in curve A is mainly due to light absorbed in the band itself. The $F$-band decay is slower than before but still faster than the response of the $V_3$ band to the uv light. This fact expresses the greater stability of the $V_3$ band to bleaching, since the intensity of the stray $F$ light is only about 1% of the $V_3$ light. The effect of purely thermal bleaching in the dark is shown in curves E and F, which show the decay in a third sample, treated identically except that the bleaching source was not turned on. The thermal bleaching of the F band is relatively small and that of the $V_3$ band is unmeasurable. (More points on these two curves were measured at longer times.)

Some interaction between the $V_3$ centers and the $F$ centers is indicated by the curves in Fig. 1. There is some bleaching of the $V_3$ band even though no light is absorbed in the band (curve C), presumably because F centers are being destroyed (curve D). Conversely, the bleaching rate of the F band is enhanced (curve B, compared with curve D) during the destruction of $V_3$ centers by uv light (curve A). The first effect was displayed explicitly (Fig. 2) by bleaching another sample with a tungsten lamp (30 cm from a 75-W bulb) at 123°C. The $V_3$ band is rather rapidly destroyed as a result of the visible illumination, in marked contrast to the behavior at room temperature, where little change in the $V_3$ band accompanies bleaching of the $F$ band. (The purely thermal decay of the $V_3$ band at 123° was

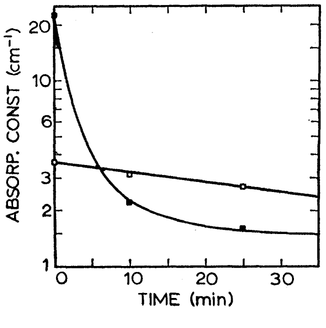

FIG. 2. Bleaching of the $F$ band (solid squares) and $V_3$ band (open squares) with visible light at 123°C.

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[10] B. Fritz, F. Lüty, and J. Anger, Z. Physik 174, 240 (1963).

[11] S. Anderson, J. S. Wiley, and L. J. Hendricks, J. Chem. Phys. 32, 949 (1960).

6 times slower than the rate in Fig. 2.) This effect becomes more significant as the temperature increases. These interactions, while important for an interpretation of the $V_3$-center structure, nevertheless are a small fraction of the main effects, which are bleaching of the bands by light absorbed in the band, at least below about 110°C.

Further evidence that the $V_3$-center bleaching rate is determined primarily by the uv light absorbed in the band itself, rather than by interactions occurring during bleaching of the $F$ centers by $F$-band light, is obtained by looking at the high temperature uv bleaching rate of the $V_3$ band in samples where the $F$ band is absent. As already remarked, the $F$ band can be removed by bleaching with visible light at room temperature, without appreciably affecting the $V_3$ band. In Fig. 3 is shown the bleaching rate under uv illumination at 95°C of a sample whose $F$ band had previously been bleached at room temperature with a tungsten lamp. The curves A and B of Fig. 1, for a sample under similar conditions but with the $F$ band present, are redrawn here for comparison. It is seen that the $V_3$-band bleaching rate is sensibly the same in the two cases (curves A and G). The initial flat portion of curve A is absent in curve G, probably because the $V_2$ centers were in the latter case already converted to $V_3$ centers during the preliminary $F$-band bleaching at room temperature. The initial rise in absorption at the $F$-band maximum in the crystal with previously bleached $F$ band (curve H) can be accounted for by the reconversion of electron aggregate centers and colloids to $F$ centers. After room temperature bleaching of the $F$ band, a broad aggregate band remained on the long-wave side of the $F$ band. During the initial stage of the high-temperature bleaching, the $F$-band absorption increased at the expense of these aggregate bands, but the total area under these combined bands did not increase. Thus the uv bleaching rate of the $V_3$ band is practically independent of the state of the $F$ band, and there is no formation of $F$ centers as a result of the destruction of $V_3$ centers.

It is interesting to note that the sample is apparently restored to its virgin state as a result of the high-temperature uv bleaching. When a bleached sample was re-irradiated with x rays, the regrowth of the $F$ and $V_3$ bands approximated the original growth rates in the virgin crystal. This behavior is in marked contrast to the regrowth of the $F$ band after visible light bleaching at room temperature; in that case, the growth curve essentially takes up where it left off.

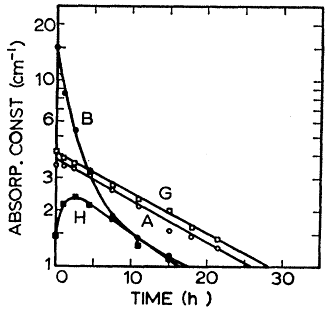

FIG. 3. Bleaching of the $V_3$ band (curves A and G) and the $F$ band (curves B and H) with uv (plus stray visible) light near 100°C. Curves G and H: F band previously bleached with visible light at 25°C. Curves A and B: from Fig. 1.

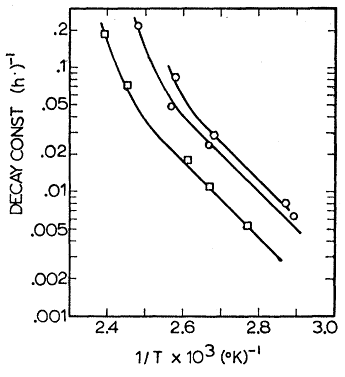

FIG. 4. Decay constant for optical bleaching of the $V_3$ band, as a function of inverse temperature. The three sets of points are for different Harshaw KCl crystals.

The temperature dependence of the uv bleaching rate was determined by measuring the rate of the $V_3$-band decay at several different temperatures, on a series of samples cleaved from the same large block, under the same conditions of illumination. In order to ascertain the degree of uniformity among different crystals, this series of measurements was repeated for groups of samples cleaved from two more large blocks. The results of these measurements are shown in Fig. 4. Each individual sample exhibited an approximately exponential decay of the optical absorption at the $V_3$-band maximum as a function of time (Fig. 1, curve A):

$$\alpha=\alpha_0 e^{-\lambda t}. \tag{1}$$

In Fig. 4 are plotted the values of $\lambda$ as a function of inverse temperature, for the three different crystals. The fact that the points lie approximately on straight lines over a certain region indicates a relation of the form

$$\lambda=\lambda_0 e^{-E/kT}. \tag{2}$$

The lines drawn in the figure have the same slope in the lower temperature range, with

$$E\cong 0.6 \text{ eV},$$

suggesting a unique activation energy for the bleaching process. The pre-exponential factor varies from crystal to crystal, but its order of magnitude is

$$\lambda_0\approx 10^6 \text{ h}^{-1}\approx 3\times 10^2 \text{ sec}^{-1}.$$

Above a decay constant of about 0.03 $\text{h}^{-1}$, this relation breaks down, because purely thermal bleaching becomes significant and $F$-center bleaching by stray visible light has a greater effect on the $V_3$ band.

## IV. DISCUSSION

In order to discuss the physical significance of the bleaching data, it is necessary to convert the bleaching rates to a quantum efficiency for destruction of the $V_3$

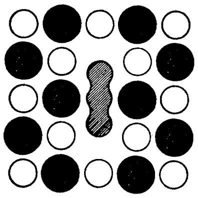

FIG. 5. Proposed model for the $V_3$ center. The solid circles represent $\mathrm{Cl}^-$ ions, the open circles $\mathrm{K}^+$ ions, and the shaded area a $\mathrm{Cl}_3^-$ molecular ion.

center. Let the optical absorption constant at the band maximum $\alpha$ be related to the density of centers $n$ by

$$\alpha = \sigma n; \tag{3}$$

and let the rate of bleaching the centers be related to number of photons absorbed per unit volume per unit time $P$ by

$$dn/dt = -\eta P, \tag{4}$$

where $\eta$ is the quantum efficiency. Then

$$d\alpha/dt = -\eta\sigma P.$$

If the absorption is small compared to unity, the rate of absorption per unit volume is proportional to $\alpha$,

$$P = K\alpha. \tag{5}$$

Thus

$$d\alpha/dt = -(\eta\sigma K)\alpha,$$

and comparison with Eq. (1) shows that

$$\eta = \lambda/\sigma K. \tag{6}$$

If $\lambda$ is given by Eq. (2), then

$$\eta = \eta_0 e^{-E/kT}, \tag{7}$$

with

$$\eta_0 = \lambda_0/\sigma K. \tag{8}$$

In order to get a numerical value for $\eta_0$, we must first calculate $K$ from the measured monochromator output, $V_3$-band absorption, and sample thickness, using Eq. (5). The result is

$$K \approx 3\ \mu\mathrm{W/cm^2} \approx 3\times 10^{12}\ \text{photons cm}^{-2}\ \text{sec}^{-1}.$$

To infer the value of $\sigma$ requires a knowledge of the oscillator strength of the $V_3$ band. Assuming the oscillator strength is about 1, Smakula's formula gives

$$\sigma \approx 10^{-16}\ \mathrm{cm}^2.$$

Combining these estimates with the experimental value of $\lambda_0$ yields by Eq. (8)

$$\eta_0 \approx 10^6.$$

The interpretation of the expression for $\eta$ depends on examining the model for the bleaching process. Suppose that after excitation by absorption of a photon, the $V_3$ center returns to its ground state with a probability $1/\tau_r$, in competition with a bleaching process which has the probability $1/\tau_b$. The quantum efficiency for bleaching is

$$\eta = 1/\tau_b/(1/\tau_r + 1/\tau_b). \tag{9}$$

For $\eta \ll 1$, as is the case in our experiment ($\eta \approx 1\%$ at 100°C),

$$\eta \cong \tau_r/\tau_b.$$

Inserting $\eta$ from Eq. (7),

$$1/\tau_b = (1/\tau_0)e^{-E/kT}, \tag{10}$$

with

$$1/\tau_0 = \eta_0/\tau_r.$$

If we guess that the lifetime of the excited state should be in the range

$$\tau_r \approx 10^{-8} - 10^{-6}\ \text{sec},$$

and use the value estimated above for $\eta_0$, we find the exponential bleaching probability given by Eq. (10), with the values

$$1/\tau_0 \approx 10^{12} - 10^{14}\ \text{sec}^{-1}, \quad E \cong 0.6\ \text{eV}.$$

A mechanism for the bleaching process can be suggested which is consistent with the previously considered model of the $V_3$ center.[2] This model, illustrated in Fig. 5, is a $\mathrm{Cl}_3^-$ molecular ion located on two anion and one cation sites. It is similar to Varley's model[12] in that it contains a cation vacancy. A possible bleaching mechanism would be the thermally activated loss of the cation vacancy while the center is in an excited state after absorption of the uv photon. The frequency $1/\tau_0 \approx 10^{13}\ \text{sec}^{-1}$ is what one would expect for an atomic jump. The activation energy $E = 0.6$ eV is not unreasonable, compared with the value of 0.75 eV for a cation vacancy,[13] in view of the severe distortion of the normal arrangement of the surrounding ions. The probability for the separation of the negatively charged cation vacancy might be greater in the excited state than in the ground state of the center, since the larger hole orbit in the excited state would leave the center negatively charged. The configuration after this step is shown in Fig. 6. The $\mathrm{Cl}_2$ molecule located at an anion site is like an $H$ center with one additional hole, and is probably the $V_1$ center.[1] It is unstable even at room temperature, and so it will rapidly recombine with two nearby $F$ centers to form one anion vacancy. (The $V_1$ center could combine with one $F$ center to form a $V_k$ center, followed by an electron capture.) These two steps can be represented by

$$V_3 \to V_1 + K\square^+, \quad 2F + V_1 \to \mathrm{Cl}\square^-,$$

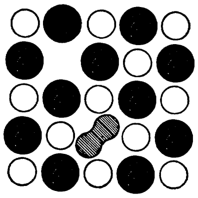

FIG. 6. Configuration resulting after the separation of a cation vacancy from the center of Fig. 5.

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[12] J. H. O. Varley, J. Nucl. Energy **1**, 130 (1954).

[13] A. R. Allnatt and P. W. M. Jacobs, Trans. Faraday Soc. **58**, 116 (1962).

of which the first step is rate controlling. The over-all reaction is

$$2F+V_3\rightarrow \mathrm{Cl}\square^{-}+K\square^{+},$$

so that the perfect crystal is restored (except for the excess vacancy pairs), in agreement with the experimental observation.

An alternative bleaching mechanism would involve an electronic rather than an ionic rearrangement as the rate-controlling step. A $V_3$-center hole, optically excited to a higher bound state, could be thermally ionized to an unbound state, in analogy with the known thermal activation of $F$-center bleaching.[14] An ionization energy of 0.6 eV from the excited state—about 10% of the excitation energy—is not unreasonable, nor is the pre-exponential factor of $10^{13}$ $\mathrm{sec}^{-1}$, although the latter value is perhaps somewhat too large. Nevertheless, two other considerations make this mechanism seem unlikely. First, if ionization of a hole leads to the destruction of the $V_3$ center, then capture of an electron should do likewise, and in the latter case there should be no thermal activation required. Large numbers of free electrons are produced during visible-light bleaching of the $F$ band, and yet the accompanying $V_3$-band bleaching has a temperature dependence even greater than that for the uv bleaching of the $V_3$ band. Secondly, the loss of a hole (or capture of an electron) by the $V_3$ center would result in a $\mathrm{Cl}_2^-$ molecular ion at an anion site, next to a cation vacancy, according to our model of the $V_3$ center. Such a paramagnetic center has been observed,[15] but it is stable only at low temperatures,[16] spontaneously reverting to what is probably the $V_3$ center above $-40$°C. Thus the transition in the opposite direction is unlikely. The direct experimental way to distinguish a mechanism involving ionization of the center is to observe photoconductivity, but the small quantum efficiency for the $V_3$-band bleaching makes this measurement out of the question in the present case. Indirectly, however, experimental evidence does not favor this bleaching mechanism.

The $V_3$-center bleaching which accompanies $F$-center bleaching with visible light at elevated temperatures might be accounted for by the migration of the ionized anion vacancy to the $V_3$ center. This mechanism would explain a larger temperature dependence for this process, since the anion vacancy has a higher activation energy for motion than the cation vacancy. An $F$ center is presumably less mobile than the anion vacancy, because the presence of the $F$-center electron would discourage a neighboring $\mathrm{Cl}^-$ ion from jumping onto the site. When the $F$ band is bleached with visible light before the high-temperature uv bleaching, the uv bleaching rate of the $V_3$ center may be slightly enhanced. This situation is difficult to interpret, however, because the configuration which results from optical bleaching of the $F$ band at room temperature is unknown. No other large changes in absorption have been detected after the $F$ band is bleached, and one cannot say what has happened to the $F$-center electron.

It does not seem to be possible to interpret the $V_3$-band bleaching process in a way that is consistent with the hydrogen-ion model of the $V_3$ center, in which the $V_3$ center is assumed to be identical with the $U$ center. A $U$ center is an $\mathrm{H}^-$ ion which replaces a $\mathrm{Cl}^-$ ion in the lattice. When the center absorbs uv light at higher temperatures, an H atom leaves the site, with the electron remaining behind in the vacant anion site to form an $F$ center. Thus the result of bleaching in the $U$ band is the conversion of $U$ centers to $F$ centers, in contrast to our observation that the $V_3$ band and the $F$ band bleach together, leaving the perfect crystal. (To reiterate, the initial $F$-band increase seen in Fig. 3 is accounted for by the reconversion of aggregate and colloid centers to $F$ centers.) A second difficulty with the hydrogen-ion model is in the quantum efficiency of bleaching. For the $U$ center, the quantum efficiency has a very small temperature dependence,[17] but our results indicate a relatively strong temperature dependence for the $V_3$ band. Thus both the temperature dependence of the bleaching rate and the relation to $F$-band bleaching seem to rule out this model.

In summary, the $V_3$ band in KCl can be bleached by light absorbed in the band, with a small but rather strongly temperature-dependent quantum efficiency. The result of the bleaching is to restore the crystal to its virgin state. Interactions between the $V_3$ centers and $F$ centers lead to partial bleaching of the other band when either type of center is optically bleached. These results are in agreement with a model of the $V_3$ center consisting of a $\mathrm{Cl}_3^-$ molecular ion and a cation vacancy, but do not support the assumption that the $V_3$ center is identical to the $U$ center. It is suggested that the rate-controlling step in the $V_3$-center bleaching event is the loss of the cation vacancy by the electronically excited $V_3$ center.

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