JOURNAL OF SOLID STATE CHEMISTRY 4, 243–249 (1972)

New Electron-Excess Color Centers in KCl: Effect of O^{2-} and SO_4^{2-} Ions*

G. LEHMANN, E. H. COKER, AND ALLEN B. SCOTT

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received April 26, 1971

Two new absorption bands, along with the *T* bands previously reported by Ring and Grossweiner, have been observed in additively colored KCl. The bands are developed by bleaching *F* centers at high temperature in relatively pure KCl, but may be produced rapidly at room temperature in colored KCl crystals containing O^{2-}, or in sulfate-doped KCl which has been additively colored. It is proposed that the development of these bands is accelerated by the presence of negative ion vacancies introduced as charge compensation for the divalent anions, and that the new centers are aggregates containing one or more *F* centers with a vacancy pair.

The segregation coefficient of K_2SO_4 in KCl, between crystal and melt, was found to be 1.0×10^{-3}.

Introduction

A number of electron-excess centers in colored alkali halide crystals have been identified by means of their optical properties, and the structures of a substantial proportion of these are now known. The simplest of these is the *F* center; the others may, in the main, be described as aggregates of *F* centers which may be neutral, positively charged, or negatively charged.

In the process of examining the effects of long periods of illumination upon KCl, two previously unreported absorption bands were observed, along with three bands which appear to be those designated by T_1, T_2, and T_3. The nature of the bleaching products was studied as a function of bleaching temperature, hydroxyl ion content, and sulfate ion content of the original uncolored crystal.

Experimental

The single crystals of KCl were from several sources. The KCl with a moderate concentration of OH^- ion (less than 10^{16} cm^{-3}) was supplied by the Harshaw Chemical Company; KCl of higher OH^- concentration (1.3×10^{16} cm^{-3}) was supplied by the Vinor Laboratories; and KCl with a low OH^- concentration (less than 10^{14} cm^{-3}) was grown from the melt in this laboratory from Merck reagent grade salt, purified by both cation and anion exchange, which was then treated during and after melting with dry HCl.

Single crystals of KCl were grown from melts containing K_2SO_4, in a nitrogen atmosphere.

The crystals were additively colored, the concentration of *F* centers being about 10^{16} cm^{-3}. The absorbance was measured, by means of a Beckman Model DK-1 spectrophotometer, in a cryostat at 78°K and room temperature. The samples could be heated while in the cryostat up to 150°C, with or without simultaneous illumination. For heating at higher temperatures, they were removed from the cryostat and wrapped in aluminum foil; handling before and after the heat treatment was done under low intensity red light.

The concentration of O^{2-} ions, n_O, in colored KCl crystals was found from the absorbance per cm at the peak of the 283 nm band, A_{283}, using the relation (*1*), valid at 80°K,

$$n_O = 1.7 \times 10^{16} A_{283}.$$

Results and Discussion

KCl with High Oxygen Content

Upon additive coloration of KCl crystals having a prominent absorption band at 204 nm, due to OH^-, new bands with maxima at 214, 283, and 435 nm appeared. Fischer, Gründig, and Hilsch (*1*) show that these bands and a fourth at 194 nm, outside the range of the spectrophotometer used here, arise from O^{2-} ion. Accompanying the O^{2-} bands, Fischer et

---

* Supported by the National Science Foundation and by ONR.

al. observed a band at 177 nm, that is, at the peak position of the α-band. This band is known to be due to negative ion vacancies.

It is to be expected that negative ion vacancies (denoted as α-centers) will be present with O^{2-} ions, in order to compensate the extra charge of the latter; the α-centers and O^{2-} ions are essentially all present in the form of complexes (*2*). Evidently, the presence of O^{2-} as a neighbor does not perturb the location of α-center absorption appreciably.

Whether in the present instance OH^- was reduced quantitatively during additive coloration is not certain, but the O^{2-} concentration after additive coloration usually was in the same range as the OH^- concentration before coloration. Fischer and Gründig (*3*) state that electrolytic coloration of KCl does not reduce OH^-; on the other hand, SH^- is reduced by this means, and OH^- is reduced in NaCl by heating the crystal in alkali metal vapor.

In Fig. 1 is shown the result of illumination and heat treatment of a KCl crystal containing $7 \times 10^{15}/\text{cm}^3$ O^{2-} ions and $25 \times 10^{15}/\text{cm}^3$ *F* centers after additive coloration. Moderate bleaching of the *F* band with 560 nm light (so-called "*F* light") at room temperature resulted in the usual aggregate-center bands, but extended bleaching (e.g., the absorption of 10^{19} photons/cm³ as in curve 3) gave rise to additional absorption bands in the region of the *T* bands of Ring and Grossweiner (*4*), and decreased the N_2 band markedly. The most prominent peak lay at 930 nm; we have designated it the T_{2A} band.

Heat treatment for 5 min in the dark at 120°C, followed by the absorption of 8×10^{18} photons/cm³ at room temperature resulted in further decrease of the N_2 band and some change in the relative intensities of other bands. Finally, the crystal was heated 5 min in the dark at 200°C; the *F* band was largely regenerated and a broad band (in older papers referred to as the *R′* band) (*5*) remained on the long wavelength side of the *F* band.

It should be noted that the height of the O^{2-} band at 435 nm was practically unaffected by these treatments. Since this band overlaps the *K* band, it is seen that the apparent ratio of the heights of the *F* and *K* bands will, unless the *K* band is corrected for the absorption of O^{2-}, vary widely not only during bleaching but also from sample to sample of varying *F* center and O^{2-} concentrations. This undoubtedly accounts for the variable ratio reported by Etzel and Geiger (*6*), who also used Harshaw crystals.

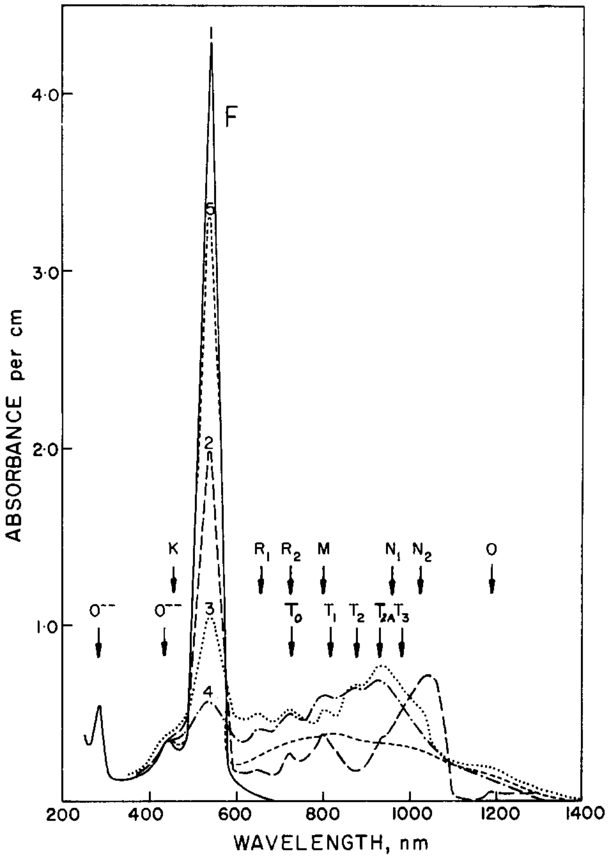

FIG. 1. Bleaching of colored KCl (Harshaw Company) containing O^{2-} ions. Spectra at 80°K. Curve 1: original spectrum. 2: After short bleaching with *F* light, 25°C. 3: After absorption of 10^{19} photons/cm³. 4: After 5 min at 120°C, and further bleaching. 5: After 5 min at 200°C.

In Fig. 2 are shown the results of a similar experiment using a crystal supplied by the Vinor Company, in which, after additive coloration, the O^{2-} ion concentration actually exceeded the *F*-center concentration. As seen in curve 4, the *F* band could be suppressed relative to the O^{2-} band and the long-wavelength bands, which at these concentrations strongly overlap.

Because of this overlap, the identification of individual absorption bands other than the *R*, *M*, and *N* bands cannot be made solely on the basis of curves such as those of Figs. 1 and 2. Rather, one must make use of additional information.

The T_{2A} band was developed more fully in a crystal containing an equal concentration (2.1×10^{16} cm^{-3}) of *F* centers and O^{2-} ions. After the absorption of 3×10^{16} photons of *F* light, the spectrum was that shown by curve 1 of Fig. 3. Illumination with N_2 light then markedly enhanced the T_{2A} band (curve 3) with a simultaneous growth of the *F* band. After standing in the dark, the intensity of the T_{2A} band relaxed somewhat (curve 2).

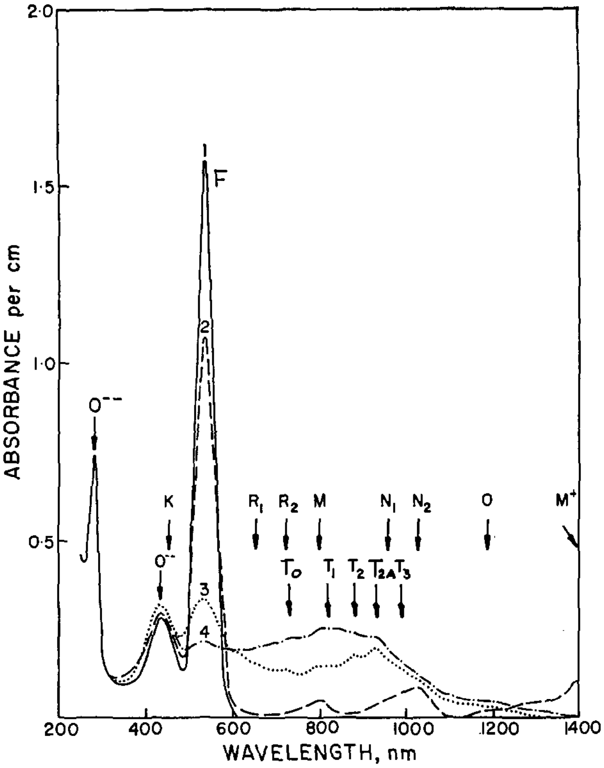

FIG. 2. Bleaching of colored KCl (Vinor Company). Spectra at 80°K. Curve 1: original spectrum. 2, 3, and 4: Successive stages in bleaching with F light at 25°C.

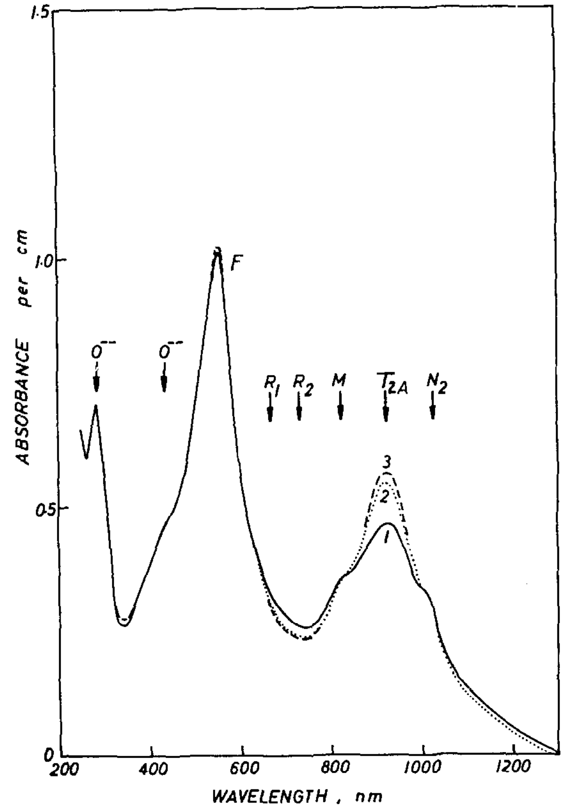

FIG. 3. Curve 1: The T_{2A} band in KCl. Curve 3: After N-light illumination. Curve 2: After several hours in darkness.

In the next section, a method for developing the T_0 band more fully is described.

The band at 1180 nm in Fig. 1 is probably the O band (7), thought to be an aggregate band, while the absorption at 1400 nm formed in the early stages of bleaching (Fig. 2) may be the M^+ band of Schneider and Rabin (8). While these authors did not produce the M^+ band in this manner, and in fact it did not persist at room temperature, in the present case its formation was likely favored by the presence of α-centers provided by the dissociation of O^{2-} vacancy complexes.

KCl with Low Oxygen Content

No O^{2-} bands could be detected after additive coloration of a crystal with an OH^- concentration $<10^{14}$ cm^{-3}. Bleaching with F light at room temperature did not produce any of the new centers. Bleaching at higher temperatures produced new centers rapidly, as seen in Fig. 4. A bleaching temperature of 80°C resulted in the formation of bands at 820, 880, and 985 nm which we believe to be the T_1, T_2, and T_3 bands, respectively, of Ring and Grossweiner (4). In fact, except for minor changes in wavelength, our curve 1 of Fig. 4 virtually duplicates the spectrum reported by Ring and Grossweiner for a crystal bleached with white light at 25°C and then irradiated with "$F+N$ light" at 100°C. Similar results were obtained by them with "$F+M$ light." Evidently, sufficiently long bleaching with F light at 80°C develops the T bands to the same extent as does the treatment of Ring and Grossweiner; this is to be expected since M centers and probably also N-centers have excited transitions underlying the F band, so that, after some bleaching, F light also excites the aggregate centers.

In addition to the T bands, the M and N bands were evident after bleaching with F light at 80°C, as well as a band in the location of the R_2 band, i.e., at about 725 nm. No indication of an R_1 band appeared. Since the R_1 and R_2 bands arise from transitions of the same center, and since in any case R centers are destroyed at temperatures above 50°C, the 725 nm band produced in this way must arise from a new center, which we designate T_0.

Bleaching at 140°C enhanced the formation of the T_0 band markedly. When, after bleaching at 140°C,

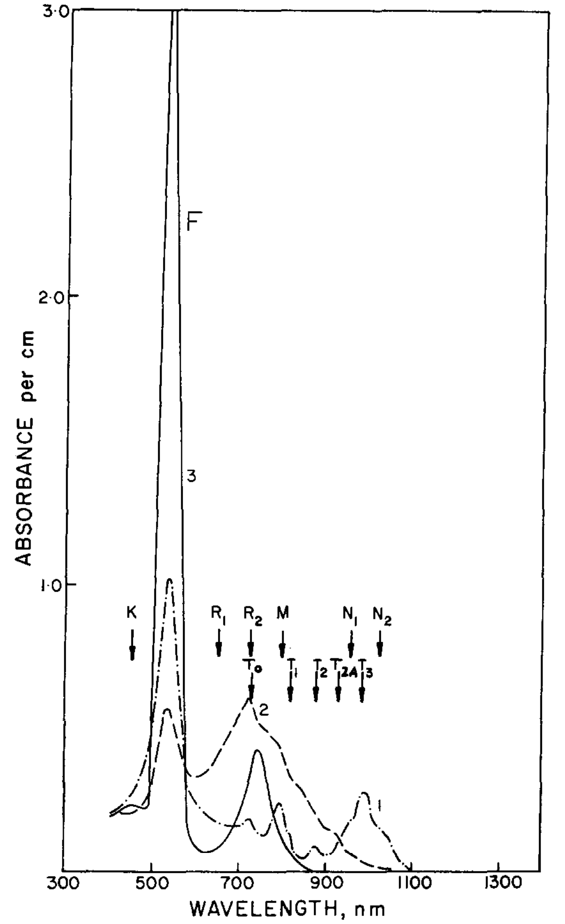

FIG. 4. Bleaching of colored oxygen-free KCl. Spectra at 80°K. Curve 1: Bleached with F light at 80°C. 2: Bleached at 140°K. 3: After 17 hr in darkness at 200°C.

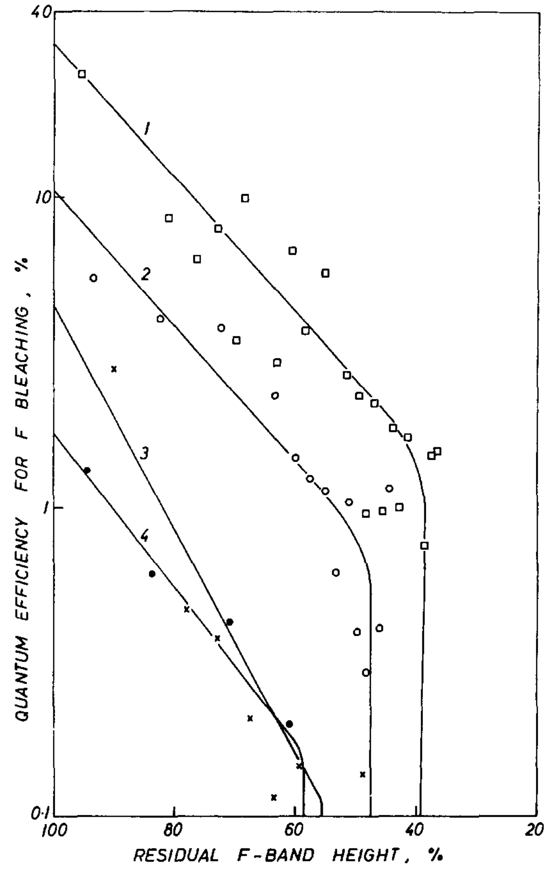

FIG. 5. Quantum efficiency for F-center bleaching. Concn. O^{2-}; Curve 1: 2×10^{16} cm^{-3}. 2: 7×10^{15} cm^{-3}. 3: 1×10^{15} cm^{-3}. 4: $<1 \times 10^{15}$ cm^{-3}.

the sample was held in the dark 17 hr at 200°C, the F band was regenerated and all the longer wavelength bands except the T_0 band were destroyed. A shift of the maximum of this band to about 740 nm was observed.

Quantum Efficiency for Bleaching

The connection between O^{2-} content and quantum efficiency for bleaching F centers was examined in four crystals, having a wide range of O^{2-} concentrations. The quantum efficiency is given by the ratio of the number of F centers destroyed during a short bleaching period to the number of photons absorbed; we express it here in percent. In Fig. 5 the variation of the logarithm of the quantum efficiency with degree of bleaching is given. These data were collected in the course of a large number of experiments conducted for other specific purposes, so that the duration of the bleaching period used to find the quantum efficiency, the light intensity, and the previous light- or heat-treatment all varied considerably, resulting in a scatter of the data points. Nonetheless, it is clear that not only was the initial quantum efficiency markedly increased by increasing O^{2-} concentration but also the maximum extent to which the F band could be bleached was noticeably enhanced. This is attributed to the effect of increased α-center concentration upon the rate of combination of α and F' centers to yield M centers.

KCl Containing Sulfate Ions

To test the uniformity of SO_4^{2-} concentration in sulfate-doped crystals, $K_2^{35}SO_4$ was added to give a melt activity of about 50 mCi/g; following crystal growth, radioautograms were taken of crystal sections. Densitometer traces of the radioautograms showed only random fluctuations of sulfate concentration, within about 1%, along directions normal to the crystal-pulling axis, provided the growing crystal was rotated at a speed greater than 90 rpm. A regular variation in sulfate concentration was observed parallel to the growth axis, caused by an increase in K_2SO_4 concentration in the melt during growth of the crystal.

The concentration in horizontal sections taken from four different crystals was determined by isotopic dilution analysis. Allowing for the growth-axis gradient in concentration, the segregation coefficient, that is, the ratio of sulfate concentration in the crystal to that in the melt, was found to be $(1.04 \pm 0.03) \times 10^{-3}$.

The segregation coefficient was sensitive to the presence of divalent cations. Relative sulfate ion concentrations may be obtained by comparison of the intensities of the ir absorption due to the sulfate ion. The transmission of a crystal grown from a melt containing 1.0 mg K_2SO_4 and 4.0 mg $CaCl_2$ per g KCl was compared to that for a crystal grown from a melt containing 2.5 mg K_2SO_4 and 0.2 mg $CaCl_2$ per g KCl. The segregation coefficient in the former case was found to be approximately twice that in the latter; an increased concentration of divalent cations in the melt enhances the solubility of sulfate ion in the crystal. This enhancement is to be expected, as the incorporation of a divalent anion along with a divalent cation does not require the expenditure of the energy of formation of vacancies.

Figure 6 shows the ir absorption spectrum of KCl containing K_2SO_4 before and after additive coloration. Before coloration a set of prominent, overlapping bands in the 1100–1200 cm^{-1} region known to be due (*9*) to SO_4^{2-} was observed. After coloration these bands totally disappeared, while a new band at 875 cm^{-1} appeared. A normal *F* band was produced. Evidently SO_4^{2-} is quantitatively reduced during additive coloration.

To confirm this conclusion, a crystal containing $K_2^{35}SO_4$ was additively colored, following which ^{35}S was recovered by precipitation with $AgNO_3$ as Ag_2S. The reduction product was thus shown to be sulfide, thioperoxide (SO^{2-}), or sulfoxylate (SO_2^{2-}) ion, or a combination of these ions, all of which yield Ag_2S upon treatment with $AgNO_3$.

The band at 875 cm^{-1} may arise from either SO^{2-} or SO_2^{2-}. The vibrational frequency of $^{35}Cl^{19}F$, isoelectronic with SO^{2-}, is 793 cm^{-1}. Assuming no change in force constant, $^{32}S^{16}O^{2-}$ should absorb at 850 cm^{-1}. The asymmetric stretch of $^{35}Cl^{16}O_2^-$, isoelectronic with SO_2^{2-}, has a frequency of 844 cm^{-1}; $^{32}S^{16}O_2^{2-}$ should absorb at 858 cm^{-1}.

Two peaks were also found in the ultraviolet, at 284 and 364 nm (measured at 80°K), in the additively colored crystal. We believe these are due to electronic transitions in SO^{2-} or SO_2^{2-}. Similar bands, at 265, 325, and 393 nm, due to S^{2-} have been reported (*3*).

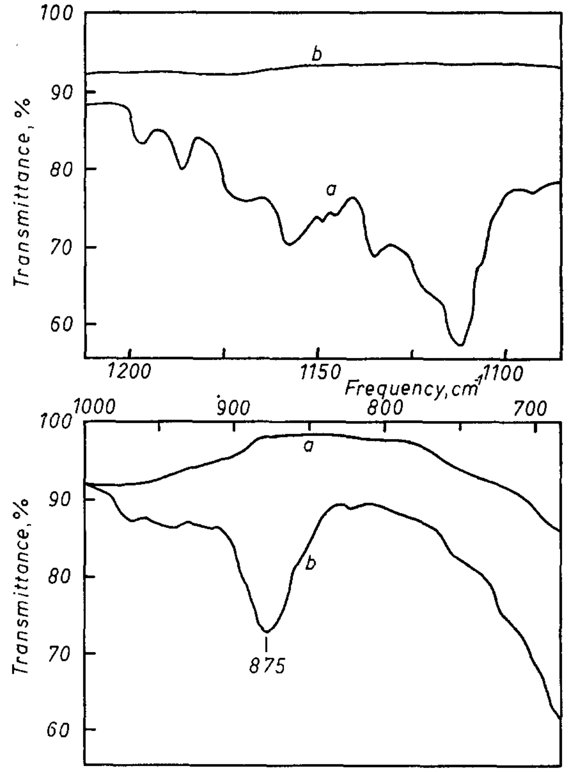

FIG. 6. Infrared absorption spectrum of KCl containing K_2SO_4 (a) before, (b) after additive coloration.

We conclude that additive coloration reduces SO_4^{2-} to either SO^{2-} or SO_2^{2-}, according to

$$SO_4^{2-} + 6K = SO^{2-} + 3O^{2-} + 6K^+ \quad (+3\alpha),$$

$$SO_4^{2-} + 4K = SO_2^{2-} + 2O^{2-} + 4K^+ \quad (+2\alpha).$$

Assuming that the divalent anions all occupy a halide ion site, these processes result in the formation of additional α centers as indicated in parentheses. Consequently, the concentration of α centers, either free or complexed with divalent anions may be 3 or 4 times higher than in the sulfate-doped crystal prior to coloration.

Figure 7 shows the effect of room-temperature bleaching and heat treatment of a KCl crystal originally containing 1.5×10^{16} SO_4^{2-} ions per cm^3 after additively coloring to an *F* center concentration of 7.5×10^{17} cm^{-3}. The *F* band was bleached about 4 times more rapidly than in ordinary KCl. The formation of *R* bands was suppressed. The most prominent absorption bands produced by bleaching had maxima near 820 and 875 nm, respectively. Because of overlap with the *M* band the peaks

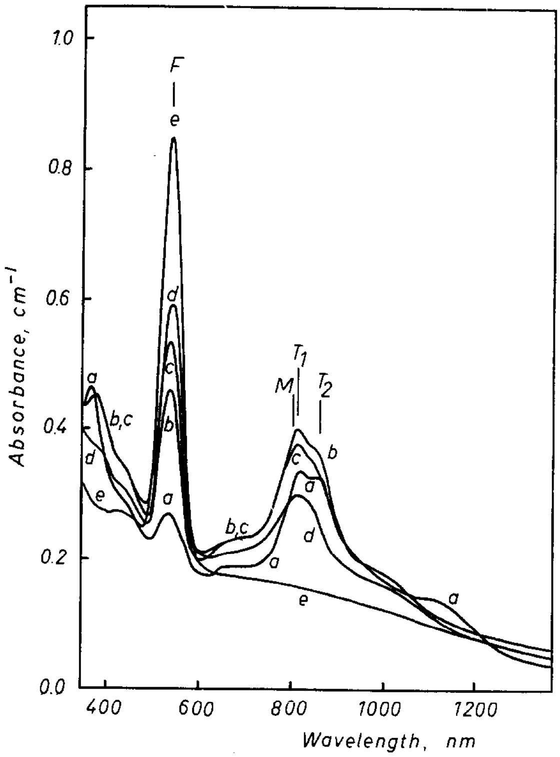

FIG. 7. Bleaching and heat treatment of additively colored KCl(K_2SO_4). Spectra at 80°K. Curve *a*: After 2-hr *F*-light bleaching at 25°C. *b*: After 20 min at 105°C. *c*: After 10 min at 120°C. *d*: After 30 min at 126°C. *e*: After 40 min at 150°C.

cannot be located with accuracy, but again appear to be the T_1 and T_2 bands of Ring and Grossweiner. Heating at 126° practically destroyed the T_2 band but not the T_1 band. After 40 min at 150°, all of the aggregate bands were destroyed and the *F* band was regenerated.

The T_0, T_{2A}, and T_3 bands are weakly developed under these conditions.

On the Structure of the New Centers

The evidence at hand does not permit a decision to be made concerning the composition or structure of any of the centers responsible for the new bands. However, guided by the observation that their formation is accelerated by a ~~high α-center~~ concentration but even in crystals of low α-center concentration long bleaching at somewhat elevated temperatures still leads to their formation, we propose that the new centers are aggregates composed of one or more *F* centers with a vacancy pair. The simplest of these, with one *F* center, corresponds to the model proposed for the *M* center many years ago by Seitz (*10*).

Using a pseudochemical notation for convenience, in which α^+ and π^- are written for the negative ion and positive ion vacancies, respectively, with $F_2 \equiv M$, $F_3 \equiv R$, and so on, we write the processes leading to the *F*-plus–vacancy-pair complex as

$$M + \alpha^+ = F_2^+ + F, \tag{1}$$

$$F_2^+ + \pi^- = F\alpha\pi. \tag{2}$$

The first process may take place by ionization of the *M* center or by the migration of α centers. The rate will depend on the concentration of α centers in either case and will be increased by increasing temperature at least in the second case.

Equilibrium concentrations are governed by the same processes and corresponding equilibrium constants:

$$K_1 = (n_F \cdot n_{F_2^+})/(n_M \cdot n_{\alpha^+}), \quad \text{and}$$

$$K_2 = n_{F\alpha\pi}/(n_{F_2^+} \cdot n_{\pi^-})$$

The equilibrium concentrations of α^+ and π^- are given by the Schottky product:

$$K_s = n_{\alpha^+} \cdot n_{\pi^-}.$$

Combining the equilibrium constant equations above, it is apparent that

$$n_{F\alpha\pi} = K_1 K_2 K_s (n_M/n_F).$$

The above demonstrates that the rate of formation of the complex $F\alpha\pi$ should be increased by increasing α-center concentration, but that the equilibrium concentration will be independent of α-center concentration, and depend only on the ratio n_M/n_F.

Similar arguments may be applied to complexes such as $M\alpha\pi$ and $R\alpha\pi$, in the former case, for example, the equilibrium concentration being proportional to n_R/n_F.

Thus, if bleaching is continued until the ratio of the aggregate centers *M*, *R*, etc., compared to *F* centers is sufficiently high, the vacancy pair complexes should appear even in crystals in which the individual vacancy concentrations are established intrinsically. The rapid attainment of a high ratio such as n_M/n_F is favored both by the quantum efficiency of bleaching and the high attainable degree of bleaching in crystals containing, for example, O^{2-} ions.

According to this scheme, the enhancement of the T_{2A} band upon N_2-light illumination (Fig. 3) may be accounted for in the following way. It is thought that N_2 centers consist of four *F* centers (*11*). Ionization of an N_2 center would yield the N_2^+ center; on trapping a cation vacancy the product would be $R\alpha\pi$. This may be tentatively assigned as the center responsible for the T_{2A} band.

All of the results so far in hand are consistent with the proposal that the new centers are a series, such as $F\alpha\pi$, $M\alpha\pi$, and so on.

Acknowledgment

The hospitality afforded one of us (A.B.S.) by the Hebrew University, Jerusalem, during a portion of this work, is gratefully acknowledged.

References

1. F. Fischer, H. Gründig, and R. Hilsch, *Z. Phys.* **189**, 79 (1966).
2. G. Gummer, *Z. Phys.* **215**, 256 (1968).
3. F. Fischer and H. Gründig, *Z. Phys.* **184**, 299 (1965).
4. J. G. Ring and L. I. Grossweiner, *J. Appl. Phys.* **35**, 2257 (1964).
5. A. B. Scott and L. P. Bupp, *Phys. Rev.* **79**, 341 (1950).
6. H. W. Etzel and F. E. Geiger, *Phys. Rev.* **96**, 225 (1954).
7. J. Schulman and W. D. Compton, "Color Centers in Solids," p. 113. Macmillan, NY (1962).
8. I. Schneider and H. Rabin, *Phys. Rev. Lett.* **13**, 690 (1964).
9. J. C. Decius, E. H. Coker, and G. L. Brenna, *Spectrochim. Acta* **19**, 1281 (1963).
10. F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1946).
11. S. Schnatterly and W. D. Compton, *Phys. Rev.* **135**, A227 (1964).