

Optical Absorption and Electron Spin Resonance after Optical and Thermal Bleaching of F Centers

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A correlation is observed between changes in the half-width and peak position of the F band and the presence of M and R centers in x-irradiated KCl crystals. The changes in the shape of the F band caused by optical bleaching are attributed to absorption bands of M and R centers located in the spectral region of the F band. The narrowing of the electron spin resonance line which occurs during optical bleaching of x-irradiated KCl crystals is removed by thermal treatment at 140°C . The narrowing is tentatively attributed to the presence of a second, narrow resonance line, due to either R_2 or N centers, which is superimposed on the line attributed to F centers. The results also suggest that M , R , and V_2 centers are not paramagnetic. Both the optical absorption and the electron spin resonance measurements indicate that F centers are present even after prolonged optical bleaching and that the character of the F center is not changed during bleaching.

I. INTRODUCTION

It has generally been observed, during bleaching of F centers with F light near room temperature, that the half-width of the F band increases.¹⁻³ In a previous paper⁴ the author had suggested two interpretations of this effect. The first is an extension of an interpretation first proposed by Oberly⁵ in which F centers are thought to be present throughout the bleaching process. The broadening of the F band is considered to arise through a difference in the character of those F centers observed after short bleaching times (first stage) and those observed after prolonged bleaching (second stage). According to this interpretation, the absorption of F centers during the second stage is perturbed due to interactions with near lying M , N , and R centers and possibly with dislocations. Alternatively, it was considered that all F centers are removed during the first stage of bleaching and that the absorption observed in the vicinity of the F band during the second stage arises from one or more excited states of another center. This second hypothesis has recently been used by Noble and Markham⁶ to explain the narrowing of the electron spin resonance line which is observed during optical bleaching.

The present experiments were designed to determine if either of the proposed interpretations accounts for the observed effects. Accordingly, detailed low-temperature optical absorption measurements and room temperature electron spin resonance (ESR) measurements were made on KCl crystals which had been subjected to varying amounts of x-ray irradiation and varying periods of optical and thermal bleachings.

II. EXPERIMENTAL PROCEDURE

Samples of approximate dimensions $7\text{ mm} \times 7\text{ mm} \times 1\text{ mm}$ were obtained by cleaving from a large block of

Harshaw KCl. All samples were irradiated at room temperature with x rays from a Cu target operated at 40 kv and 20 ma. The soft component of the x-ray beam was filtered out by placing a 2-mm thick crystal of KCl in front of the sample. Optical absorption measurements were made on a Cary model 14R spectrophotometer with a resolution in the F -band region of the spectrum of better than 0.3 Å. The reflectivity of all samples was determined prior to x irradiation and subtracted from the absorption after irradiation. Optical bleaching was performed at room temperature with a 100-watt tungsten lamp and various filters. The bandwidth of F light ($\lambda = 560\text{ m}\mu$) was $9\text{ m}\mu$. Thermal bleaching was accomplished at a number of temperatures between 30° and 200°C by wrapping the sample in aluminum foil and placing it, in air, in a controlled resistance furnace. All optical absorption measurements were performed at 80°K , unless otherwise specified, in a low-temperature optical Dewar which has been described previously.⁷ The vacuum system of the optical Dewar was modified in order to eliminate pump oil deposition on the cooled samples. This was simply accomplished by placing between a forepump and the

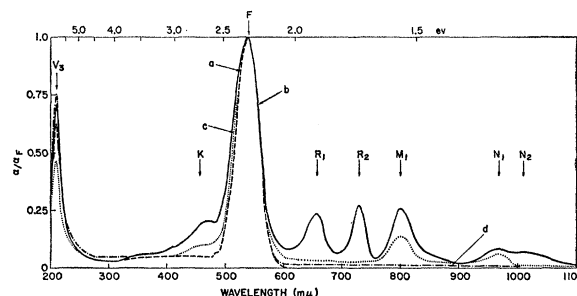


FIG. 1. Optical absorption spectra of x-irradiated KCl. Curve a—after 1, 2, and 190 hr of x irradiation at room temperature. Curve b—after 5000-sec illumination with F light. Curve c—after subsequent heating at 100°C for one hour. Curve d—after prolonged heating at 140°C . All absorption spectra are taken at 80°K . Note that the peak height of the F band does not actually remain constant during x irradiation and bleaching. All curves are normalized to the peak absorption of the F band.

⁷ W. E. Bron and A. S. Nowick, Phys. Rev. **119**, 114 (1960).

¹ St. Petroff, Z. Physik **127**, 443 (1950).
² J. D. Konitzer and J. J. Markham, Phys. Rev. **107**, 685 (1957).
³ N. G. Politov, Optics and Spectroscopy **10**, 87 (1961).
⁴ W. E. Bron, Phys. Rev. **119**, 1853 (1960).
⁵ J. J. Oberly, Phys. Rev. **84**, 1257 (1951).
⁶ G. A. Noble and J. J. Markham, Bull. Am. Phys. Soc. **5**, 419 (1960).

TABLE I. Changes in the half-width and peak position of the F band as a function of x irradiation and optical and thermal bleaching. Measurements are made at 80°K.

x irradiation (hours)	F light (seconds)	Thermal bleaching		α_M/α_F	$\alpha(R_2)/\alpha_F$	H (ev)	e_m (ev)
		Temp (°C)	Time (hr)				
1	0	0	0.196	2.300
2	0	0	0.196	2.300
190	0	0	0.196	2.300
190	100	0.11	0.02	0.205	2.293
190	5000	0.26	0.27	0.223	2.307
190	5000	100	1.0	0.15	0	0.201	2.295
190	5000	140	2.0	0	0	0.196	2.300

Dewar a liquid nitrogen, cooper foil trap and an activated alumina baffle (Biondi trap). Indium O-rings were used at the optical windows of the Dewar in order to eliminate the butane contamination of the sample obtained from rubber O-rings.

The electron paramagnetic resonance was measured in a standard Varian V-4500 EPR spectrometer. The sample was thermally bleached in the microwave cavity, by placing a controlled heater around the cavity. All resonance measurements were performed at room temperature. Various scanning speeds from 10 to 40 gauss/min were used over a scan of g values from about 1.93 to 2.07. Power levels at the sample were varied from 40 to 75 mw. The time constant of the detecting equipment was 3 seconds.

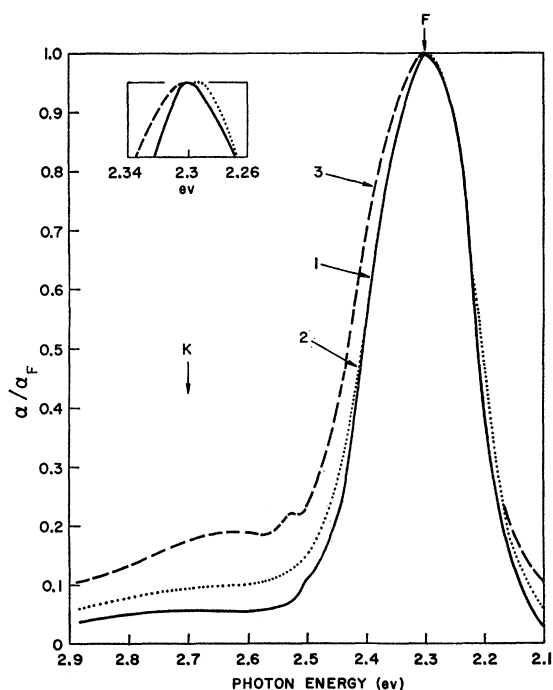


FIG. 2. Optical absorption spectra in the F - and K -band region. Curve 1—after 1, 2, and 190 hours of x irradiation at room temperature. Curve 2—after 100 sec of illumination with F light. Curve 3—after 5000 sec of illumination with F light. Absorption spectra are taken at 80°K. Note that the peak height of the F band does not actually remain constant during x irradiation and bleaching. All curves are normalized to the peak absorption of the F band.

III. RESULTS

Figure 1 illustrates the observed changes in the optical absorption spectrum of a typical KCl sample which was first x irradiated at room temperature, then optically bleached with F light followed by thermal bleaching. Figure 2 gives the results in greater detail for the F - and K -band region. Table I is a listing of the observed changes in half-width and peak position of the F band as measured at 80°K. The results for other samples irradiated to a greater or lesser extent were qualitatively the same as those shown in Figs. 1 and 2. Only the F and V_3 bands are observed after a 1-hr x irradiation (curve a, Fig. 1 and curve 1, Fig. 2). When measured at 80°K, the photon energy at the peak of the F band (e_m) is 2.300 ± 0.002 ev, and the half-width (H) is 0.196 ± 0.004 ev in agreement with the results of Konitzer and Markham.⁸ After 1 hr of irradiation, the absorption coefficient at the peak of the F band (α_F) is 2.1 cm^{-1} for all samples. An additional hour of x irradiation increases α_F to 3.1 cm^{-1} , but causes no change in e_m or H . In fact, the entire F band, including the K -band region, can be superimposed on the band obtained after 1 hr of irradiation if the two bands are normalized to the peak absorption. Such superposition of the normalized F band is observed even after prolonged irradiation into the second stage of coloration⁴ (190 hr for the sample shown in Figs. 1 and 2). This can be done providing extreme care is taken not to expose the sample to F light. In this way only a very small amount of R or M centers are formed. (The growth of a large number of M and R centers during x irradiation, as reported previously by the author,⁴ apparently arose through inadvertent exposure of the samples to light when the samples were transferred from an x -ray unit to a spectrophotometer.)

The x -irradiated samples were then exposed at room temperature to F light. As is generally observed, the F band decreases continuously, while the M , R , and N bands grow (see, for example, reference 4). During the early stage of bleaching the M band grows and then decreases after reaching a maximum. The R and N_1 bands grow at an initially slower rate than the M band and reach a saturation value after the M band has

⁸ J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

passed its maximum. During the early stage, when only the growth of the *M* band is significant, an increase in *H* is observed, and e_m is shifted slightly to lower energies (curve 2 in Fig. 2). An increase in the relative absorption in the *K*-band region to that at the peak of the *F* band is also observed. Further shifts in e_m to lower energies occur until the maximum in the *M*-band absorption is reached. Thereafter, the ratio of the *R*₁-band or the *R*₂-band absorption to that at the *M* band tends rapidly to unity. Simultaneously e_m , which during the growth of the *M* band has decreased to values less than 0.196 ev, begins to increase with the growth of the *R* bands to values eventually greater than 0.196 ev. *H* continues to increase, and the absorption in the *K*-band region increases markedly (see curve b, Fig. 1, and curve 3, Fig. 2). The final values of *H* and e_m after prolonged bleaching with *F* light depend on the relative absorptions at the *F*, *R*, and *M* bands. (The largest observed value for *H* was 0.235 ev and that for e_m was 2.312 ev in a particular sample which had been x irradiated for 250 hr followed by 5000 sec of *F* light.) At this point, the *F*, *R*₁, *R*₂, *M*, *N*₁, *N*₂, and *V*₃ absorption bands are observed (curve b, Fig. 1). No structure was observed in the vicinity of the peak of the *F* band to indicate the presence of the *B* band reported by Konitzer and Markham.² As noted in Table I, after prolonged optical bleaching the ratio of absorption at the *M* band to that of the *F* band is about 0.26, and the ratio of that at the *R*₂ band to that at the *F* band is also about 0.26. Similar ratios were obtained after prolonged bleaching for all samples tested. (This result is equivalent to the room temperature ratio of about 0.4 reported previously.)⁴

That *H* depends strongly on the relative absorption at the *F*, *R*, and *M* bands is illustrated in Fig. 3. A sample was bleached with *F* light to just past the maximum in the *M*-band absorption (curve a), and then exposed for 200 sec to white light from a 100-w tungsten

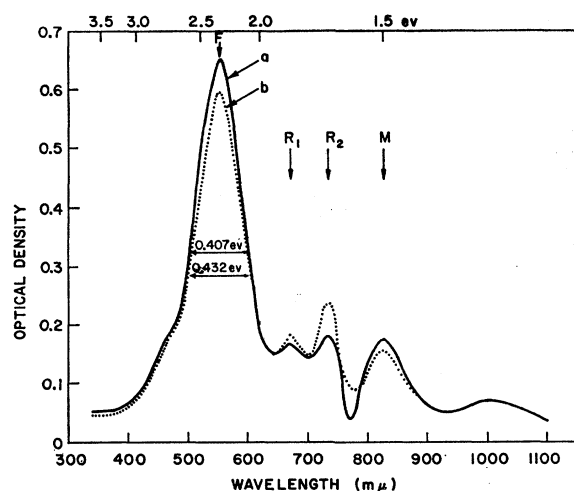


FIG. 3. Room temperature absorption spectra after 250 sec of *F* light (curve a) followed by 200 sec of illumination with white light (curve b).

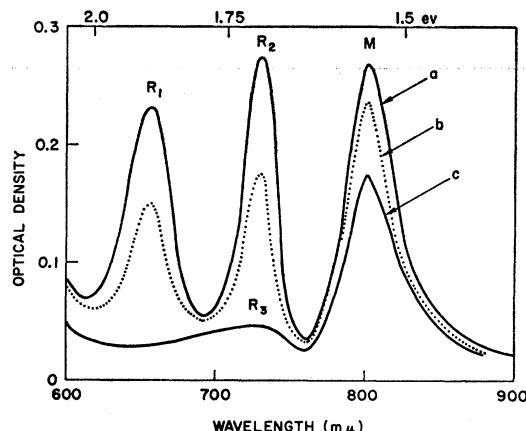
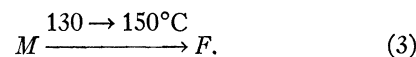
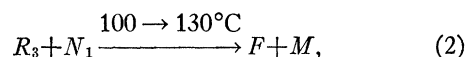
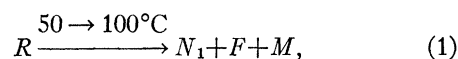


FIG. 4. Absorption in the *R*- and *M*-band region before (curve a) and after 15 min (curve b) and 1 hr (curve c) of heating to 100°C. Measurements are made at 80°K.

lamp. This treatment produces a change in the relative absorptions at the *M* and *R* bands to that at the *F* band by increasing the concentration of *R* centers at the expense of *M* and *F* centers (curve b). Simultaneously, *H* increases from 0.407 ev to 0.432 ev, as measured in this case at room temperature, and e_m shifts from 2.241 ev to 2.246 ev. (The room temperature values for *H* and e_m when only *F* and *V*₃ bands are present are *H*=0.350 ev and e_m =2.227 ev.)

Tomiki⁹ has recently shown for additively colored KCl that the relative magnitudes of the *F*, *R*, *M*, and *N* bands can also be changed by heating the samples to various temperatures from room temperature to about 150°C. Tomiki's results may be summarized as follows:



In the stated temperature ranges reactions 1, 2, and 3 are observed to go to completion. (The *R*₃ band is discussed in detail in a following section.) Similar results were obtained in the present experiment for x-irradiated KCl with the exception that the temperature range of reaction 3 was observed to extend down to 100°C. Heating to 100°C for a period of one hour suffices to remove the *R*₁, *R*₂, and *N*₂ absorptions, and simultaneously causes a small decrease in the *M* band and an increase in the *F* and *N*₁ bands (curve c, Fig. 1). Removal of the *R*₁, *R*₂, and *N*₂ bands thermally results in a reversal in the values of *H* and e_m to those observed during the early stage of bleaching when only *F* and *M* bands are present. That is, *H* decreases to values near 0.201 ev and e_m shifts to about 2.295 ev. A decrease in

⁹ T. Tomiki, J. Phys. Soc. Japan 15, 488 (1960).

TABLE II. Width of ESR line as a function of optical and thermal bleaching.

Centers present	Width at maximum slope of resonance line (gauss)
F, V_3	45
$F, R_1, R_2, R_3, M, N_1, N_2, V_3$	34
F, R_3, M, N_1, V_3	34
F, M, V_3	45

the absorption in the K -band region is also observed. The N_2 absorption band always varies in magnitude in direct proportion to variations in the R_1 and R_2 absorptions, and disappears simultaneously with the disappearance of the R bands. This strongly suggests that the N_2 band arises from an absorption of the R center.

Concurrently with the removal of the R_1 , R_2 , and N_2 bands, the existence of a broad band of low magnitude becomes apparent in the spectral region of the R_1 and R_2 bands. This band is illustrated in curve c of Fig. 4 and termed the R_3 band in accordance with Tomiki who has observed it in additively colored KCl. It seems likely that the R_3 band is present even before thermal treatment. This is indicated by the relative stability of the background absorption between the R_1 and R_2 bands, and between the R_2 and M bands during thermal bleaching (curves a and b, Fig. 4). The R_3 band is only weakly sensitive to temperature changes between 80° and 300°K, and could not be polarized with 700-m μ and 725-m μ light at 80°K or at 273°K.

Further heating for ten minutes at 140°C removes the R_3 and N_1 bands and decreases the M band. No significant change in H and e_m is observed. Prolonged heating at 140°C completely removes the M band, as H returns to 0.196 eV and e_m to 2.30 eV. The normalized F band, including the K -band region, can now again be superimposed on the F -band absorption which was obtained prior to the formation of the secondary bands (curve d, Fig. 1).

The magnitude of the V_3 band remains essentially constant throughout optical and thermal bleaching. (The ratio of the V_3 - to F -band absorption does, of course, change. This is seen in Fig. 1.)

The results of the concurrent electron paramagnetic resonance experiments are given in Table II. Prior to optical bleaching, when only F and V_3 bands are present, the width at the maximum slope of the ESR line is 45 gauss as measured at room temperature. This value is in agreement with that reported by Kip *et al.*¹⁰ and Noble and Markham⁶ for additively colored samples. Prolonged bleaching with F light to form R , M , and N centers, results in a narrowing of the resonance line to 34 gauss. Variations of the scanning speed or of the microwave power level at the sample over the range of values mentioned earlier, did not result in any observable change in the narrow line. Removal of about half

the R_1 and the R_2 bands, and the partial removal of the N_2 band by thermal treatment of 100°C does not cause a change in the narrow resonance. The ESR line does, however, return to its original width of 45 gauss during the ten minute treatment at 140°C which removes the R_3 and N_1 absorption. It could not however be determined with certainty, with the present equipment, that a one to one relationship exists between changes in the resonance line and the removal of the R_3 and N_1 bands. Subsequent removal of the M band after prolonged heating at 140°C causes no further change in the ESR line.

IV. DISCUSSION

The experimental results show that there exists a direct relationship between the presence of M and R centers in a crystal and the shape of the F -band absorption. In view of these results the broadening of the F band and the extra absorption in the K -band region are most easily interpreted in terms of the presence of absorption bands, belonging to M and R centers, which are located in the spectral region of the F band. This interpretation is in accord with the recent results of Tomiki⁹ and Okamoto.¹¹ The latter has shown, by selective polarization of M and R centers at 0°C, that there exist four M -center absorptions and two R -center absorptions in the spectral region of the F and K absorptions. Both authors show that the combined absorption due to M and R centers, directly under the peak of the normal F band, does not exceed the magnitude of the absorption observed at the normal M and R bands. Since the absorption at the F band after prolonged optical bleaching is always observed at 80°K to be about four times greater than that of the R and M bands, one is led to conclude that some F centers are present even after prolonged optical bleaching. Furthermore, it is shown in the present experiment to within the accuracy of the measurements, that a normal F -band absorption is observed when M and R centers are removed thermally from optically bleached samples.

The accuracy of the measurements is dependent on the smallest concentration of centers detectable by spectrophotometric means. This has been shown by Fisher¹² to be 10^{16} to 10^{17} per cc in samples of about 1 mm thickness. The effect of R and M centers in concentrations less than this amount could not, therefore, be detected optically.

In view of the models of R and M centers proposed by Seitz,¹³ van Doorn and Haven,¹⁴ Pick,¹⁵ and Knox,¹⁶ it had been thought that either or both of these centers would be paramagnetic. Measurements of electron spin resonance during bleaching would, therefore, be ex-

¹¹ F. Okamoto, Phys. Rev. **124**, 1090 (1961).

¹² F. Fischer, Z. Physik **154**, 534 (1959).

¹³ F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

¹⁴ C. Z. van Doorn and Y. Haven, Philips Research Repts. **11**, 479 (1956); C. Z. van Doorn, *ibid.* **12**, 309 (1957).

¹⁵ H. Pick, Z. Physik **159**, 69 (1960).

¹⁶ R. S. Knox, Phys. Rev. Letters **2**, 87 (1959).

¹⁰ A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. **91**, 1066 (1953).

pected to yield added information on the interactions between these centers. No resonance absorptions due to R , M , or V_3 centers were, however, observed at room temperature and over a range of g values of 1.93 to 2.07. Also, the presence of these centers did not noticeably affect the F -center resonance line. In view of the proposed models for R and M centers it seems unlikely that their ESR would have g values outside of the experimental range. The results, therefore, suggest that R and M centers, and possibly V_3 centers, are not paramagnetic.

Two interpretations may be advanced for the observed narrowing of the ESR line during bleaching. Narrowing can be caused by a strong spin interaction between F centers and some other paramagnetic center.¹⁷ Kip *et al.*¹⁰ have found no narrowing of the F -center line in samples where the distance between centers was approximately 30 Å. The concentration of centers in the present experiment being about 10^{16} to 10^{17} cm⁻³, the distance between centers, assuming a random distribution, is of the order of 100 Å. If the proposed interpretation is correct then one is forced to conclude that F centers and the other paramagnetic centers are not randomly distributed, but are located in the vicinity of each other.

Alternatively, the narrowing of the ESR line can be accounted for even if the spin systems of F centers and that of another paramagnetic center do not interact. Narrowing of a composite ESR line can occur if the g value associated with the second center is very close to that of the F center, and if the half-width of the line of this center is much smaller than that of the F center. This interpretation is supported by the recent results of Holton and Blum¹⁸ who have investigated room temperature, optically bleached KCl crystals by a fast passage technique. They found that the resonance line obtained at 1.3°K was asymmetric and could be decomposed into two resonance lines. One is due to a broader, slower relaxing center with a linewidth of 49.5 ± 3.1 gauss and a g value of 1.9955 ± 0.0014 , and the other due to a faster relaxing center with a linewidth of 34.5 ± 2.7 gauss and a g value of 1.9973 ± 0.0006 . The broader line corresponds well to the F -center line. The second line did not correlate with the concentration

of M centers in the crystal. Correlations with other absorption centers were, however, not attempted. The resonance line observed during a second pass of a pair of fast passages was always asymmetric which makes it unlikely that the narrowing of the ESR line is due to spin interactions with another center.

In Table II, it is shown that the narrowing of resonance line can be removed by thermal treatment. The shape of the resonance so obtained, and that of the slower relaxing center obtained by Holton and Blum, is not different from the normal F -center line.

The fact that the narrowing of the ESR line disappears when R_3 and N_1 centers are removed suggests that one of these centers is the second paramagnetic center. Moran *et al.*¹⁹ have recently found that the saturation behavior of the narrow ESR line does not have a one to one correlation with the concentration of either the R_3 or N center as determined by optical means. In view of the complex nature of the resonance line, as indicated by Holton and Blum, it is not certain, however, that a simple correlation can be made between the saturation properties of the composite resonance line and small changes in the optical absorption. It is hoped that this unresolved point will stimulate a more detailed examination of this problem by the fast passage technique.

In conclusion, optical absorption and ESR measurements indicate that F centers are present in x-irradiated KCl crystals throughout subsequent optical bleaching. The observed changes during optical bleaching in the optical and ESR absorptions of F centers can be attributed to the superposition of other absorption bands over that of the F center. No change in the character of F centers is indicated.

ACKNOWLEDGMENTS

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¹⁷ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹⁸ W. C. Holton and H. Blum (to be published).

¹⁹ P. R. Moran, S. H. Christensen, and R. H. Silsbee, Phys. Rev. **124**, 442 (1961).