F' and K Centers in Additively Colored KCl Crystals

FELIX E. GEIGER, JR.
United States Naval Research Laboratory, Washington, D. C.
(Received April 11, 1955)

Measurements are reported on the $F-F'$ process, and the K band in additively colored KCl. The crystals are colored with distilled potassium, and subjected to repeated cycles of optical bleach with F light (5450 A) at 170°K and thermal bleach of the F' centers at room temperature. It is found that the optical quantum efficiency of conversion of F to F' centers varies in two ways: (a) The quantum efficiency varies significantly for different specimens of colored KCl all cleaved from the same one-inch cube of KCl grown by the Harshaw Company. (b) The optical quantum efficiency drops significantly after each cycle of F-center bleach and subsequent thermal bleach of the F' centers. Ultimately, the quantum efficiency appears to decrease to a point where the crystal is essentially unaffected by F light at 170°K. K centers are influenced to a lesser degree, if at all, than F centers by optical bleaching in the F band at 170°K. All absorption measurements are made in the visible part of the spectrum.

INTRODUCTION

THE formation of F' centers was thoroughly investigated by Pick[1] in additively colored crystals of KCl, KBr, and NaCl. Pick established that the optical quantum efficiency[2] for the conversion of F centers into F' centers in KCl is a maximum at approximately 190°K with a value of 2.0. For NaCl and KBr crystals, the quantum efficiency obtained by him is considerably less.

This report grew out of an investigation of F-band bleaching at low temperatures in additively colored KCl. We noticed in the course of these experiments that the F'-center formation at temperatures of approximate maximum quantum efficiency, i.e., 170°K, was accompanied by several effects not found by Pick. A systematic investigation of F'-center formation and attendant effects in the presence of R and presumably M and N centers was therefore undertaken. In addition, this work yielded new data on the relative behavior of F and K bands at low temperatures.

EXPERIMENTAL PROCEDURE

Figure 1 is a schematic diagram of the apparatus used in the additive coloring process. The glass vial, containing half a dozen pieces of KCl, was outgassed at

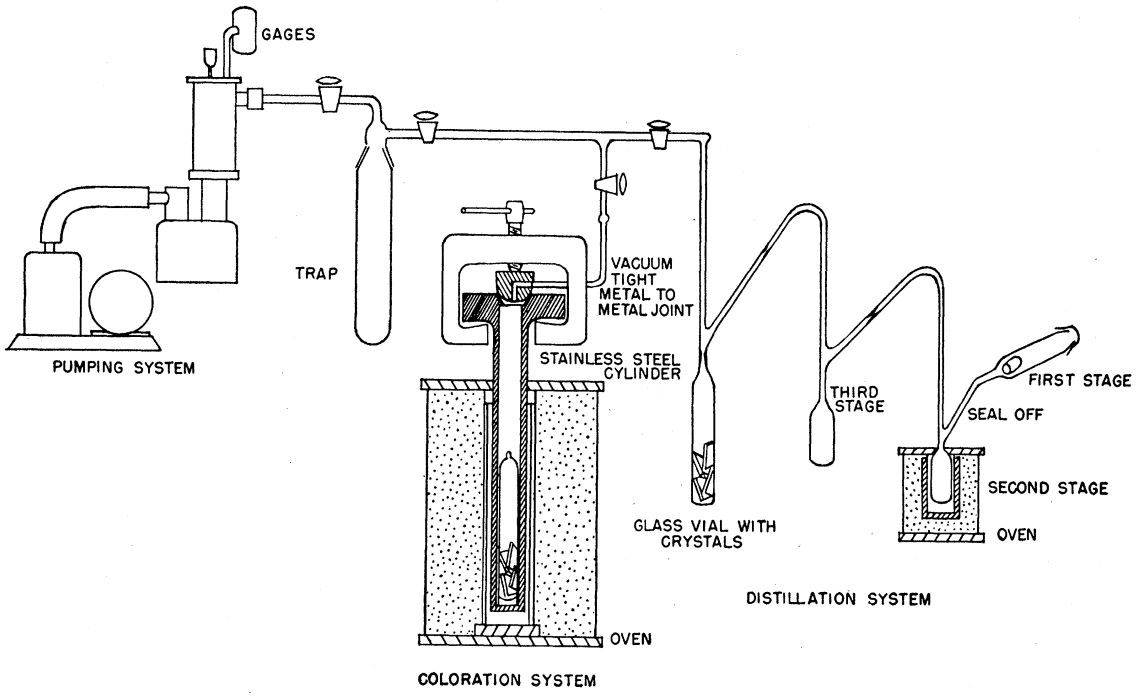

FIG. 1. Schematic diagram of the apparatus used in the distillation of potassium and the additive coloring of KCl crystals.

[1] H. Pick, Ann. Physik **31**, 365 (1938); **37**, 421 (1940).
[2] The optical quantum efficiency is defined as the ratio of the number of destroyed (or bleached) F centers to the number of absorbed light quanta.

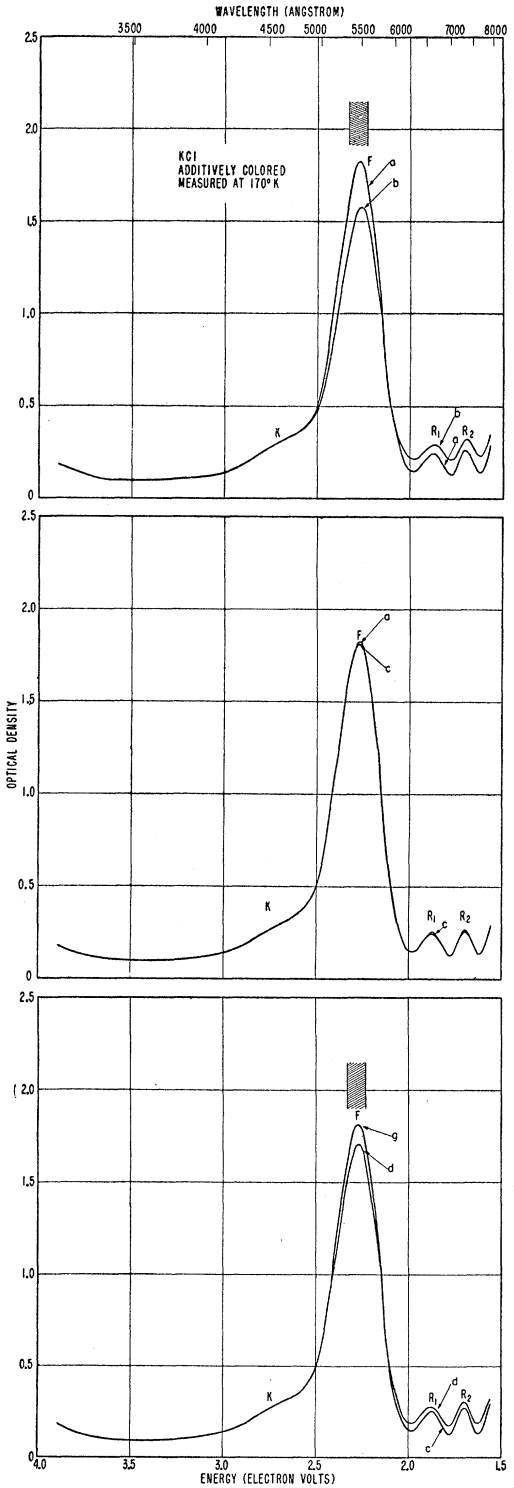

FIG. 2. A sequence of absorption measurements on additively colored KCl 0.017-inch thick, crystal specimen No. 4, subject to repeated cycles of optical bleach at 170°K with F-band light and thermal bleach at room temperature in the dark. The absorption measurements were made at 170°K. Curves (a), (b), (c), and (d) correspond to successive stages of optical and thermal bleaching. Curve (a), no optical or thermal bleach; Curve (b), after two hour optical bleach with F light (5450 A) at 170°K; Curve (c), after 12-hour thermal bleach of F' centers at room temperature. Curves (a) and (c) are shown together to illustrate the degree of recovery of the F band after the thermal bleach; Curve (d), after two-hour optical bleach in the F band. Curves (c) and (d) are plotted together so that the F bands may be easily compared before and after the optical bleach. The shaded area represents the wavelength region covered by the F light during bleaching.

415°C for about twelve hours. The potassium was heated in each stage of the distillation process for twenty-four hours at 360°C and 10^{-4} mm Hg, and transferred to the glass vial, which was sealed off and put into the stainless steel container. The steel cylinder was evacuated to prevent collapse of the glass tube at high temperatures. All crystals used in this experiment were heated for twenty-eight hours at 477°C, and quenched by quickly submerging the cylinder in ice water. Absorption measurements were made on crystal sections approximately $\frac{3}{8}$ by $\frac{3}{8}$ by 0.017 inch, which were cleaved from $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{8}$ inch pieces of colored KCl. The crystals were obtained in one-inch cubes from the Harshaw Company. Optical measurements and F-band irradiations were made with a Cary automatic recording spectrophotometer in the wavelength range 3000–8000 A. The apparatus and techniques used in the low-temperature absorption measurements are described in detail elsewhere.[3]

The experimental procedure was as follows: The crystal was illuminated in the F band (5450 A) at 170°K for two hours at a slitwidth of 1.5 mm (250 A). The area of irradiation was limited by a $\frac{5}{16}$-inch aperture. Absorption curves were of course taken at 170°K before and immediately after the optical bleach. The F-band bleach was followed by a thermal bleach of the F' centers at room temperature and in the dark. The length of the thermal bleach was varied, with a minimum of twelve hours. This should have been sufficient to destroy all F' centers, since the half-life of F' centers at room temperature is but a few hours.[4] After this thermal bleaching period the crystal was again subjected to the same optical bleach, and subsequent thermal bleach. This cycle of optical and thermal bleach was repeated a number of times. Absorption measurements were made on approximately a dozen crystals, which had been cleaved from different $\frac{1}{8}$-inch thick colored pieces of KCl. All optical density determinations were made against a clear comparison crystal of KCl. The light source used in the optical bleaching of the crystals was voltage-controlled.

RESULTS

The results can best be discussed with reference to two typical examples shown in Fig. 2 and Fig. 3. Curve (a), Fig. 2, shows the absorption spectrum of an additively colored crystal of KCl (specimen No. 4) clearly exhibiting F and R centers and to a lesser extent

[3] F. E. Geiger, Jr., Rev. Sci. Instr. **26**, 383 (1955).
[4] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 130.

TABLE I. Optical densities of F and R bands in additively colored KCl, crystal specimen No. 4, after repeated optical bleach in the F band, and subsequent thermal bleach of F' centers at room temperature. Irradiation in the F band was carried out at 5450 A, at 170°K with a 1.5 mm (250 A) slit for two hours. The thermal bleach was in the dark at room temperature and of varying length. All absorption measurements were made at 170°K. Thickness of crystal 0.017 inch. See Fig. 2, Curves (a), (b), (c), and (d).

F-band density	% reduction of F centers after optical bleach	R_1-band[a] density	R_2-band[a] density	Remarks
1.82		0.24	0.27	Initial absorption measurement
1.58	13.2	0.29	0.32	Absorption after optical bleach
1.81		0.25	0.27	Absorption after thermal bleach of 12 hours
1.71	5.5	0.27	0.30	After optical bleach
1.77		0.25	0.27	After 12-hour thermal bleach
1.70	3.9	0.27	0.29	After optical bleach
1.78		0.23	0.25	After 84-hour thermal bleach
1.71	3.9	0.25	0.28	After optical bleach
1.77		0.23	0.24	After 36-hour thermal bleach
1.71	3.4	0.25	0.27	After optical bleach
1.76		0.21[b]	0.22[b]	After 300-hour thermal bleach
1.67	5.1	0.23	0.24	After optical bleach

[a] The R bands are superimposed on the F' band, and the apparent growth of the R bands is of course due to F'-center formation.
[b] The decrease in R centers is almost certainly attributable to thermal bleaching.

K centers. Curve (b) is the absorption curve immediately after the two-hour F-light (5450 A) bleach at 170°K. It shows a 13.2 percent reduction in the number of F centers, and a fairly uniform increase of absorption on the low-frequency side of the F band due to the very broad F' band. Curve (c), obtained after a twelve-hour thermal bleach of the F' centers at room temperature, is compared with Curve (a) on the same graph. It shows complete recovery of the F centers within the accuracy of the instrument. The crystal is now subjected to another F-light bleach at 170°K, the result is shown in Curve (d). We now find that an equal number of absorbed light quanta effects only a 5.5 percent reduction in F centers. This means the quantum efficiency has dropped by 58 percent. Table I is a complete record of F- and R-band optical densities for six optical and five thermal bleaches.

Figure 3 illustrates the behavior of the colored crystal specimen No. 5, subjected as before to alternate optical and thermal bleaches. This time, however, the F' centers were bleached thermally for 60 hours after the first F-band bleach. The F band has recovered now only 95 percent of its original number of centers [Curves (e) and (g)], and we note again a reduction of 44.6 percent in the quantum efficiency for the second optical bleach.

Figure 2, Curve (b) and Fig. 3, Curve (f), show another curious behavior of the optical quantum efficiency. The number of F centers destroyed after the first F-light bleach varies considerably for different crystal specimens although the number of quanta absorbed by each crystal is essentially the same. Results on a few crystal specimens are summarized in Table II. K centers appear on all absorption curves, though un-

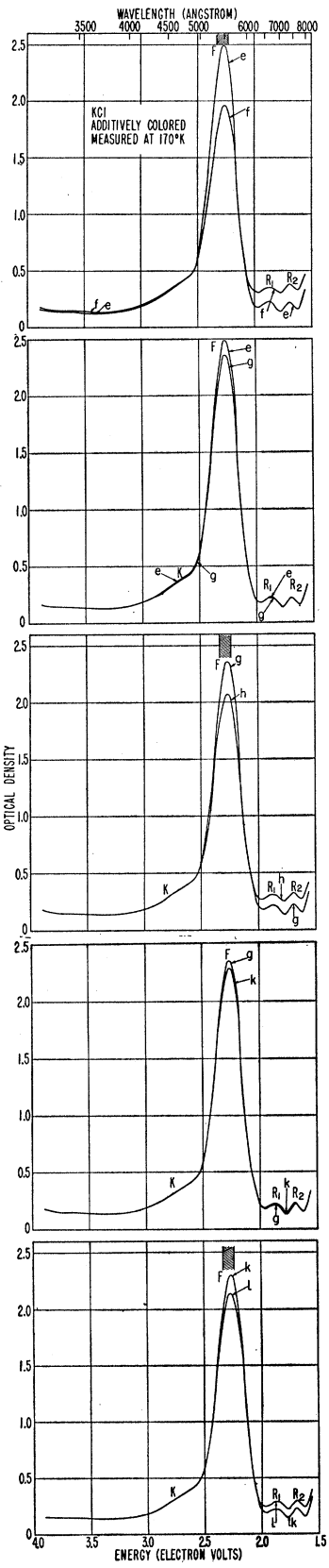

FIG. 3. A sequence of absorption measurements on additively colored KCl 0.017 inch thick, crystal specimen No. 5, subject to repeated cycles of optical bleach at 170°K with F-band light and thermal bleach at room temperature in the dark. The absorption measurements were made at 170°K. Curves (e), (f), (g), (h), (k), and (l) represent successive stages of optical and thermal bleaching. Curve (e), no optical or thermal bleach; Curve (f), after two-hour optical bleach with F-band light (5450 A) at 170°K; Curve (g), after 60-hour thermal bleach of F' centers at room temperature. Curves (e) and (g) are shown together to show the degree of recovery of the F band after the thermal bleach. Curve (h), after two-hour optical bleach with F light (5450 A) at 170°K. Curves (g) and (h) are plotted together to show the decrease in the number of F centers due to the F light bleach. Curve (k), after 36-hour thermal bleach at room temperature. Curves (g) and (k) are shown together for comparison; Curve (l), after two-hour optical bleach in the F band at 170°K. Curves (k) and (l) should be compared with Curves (e) and (f). They show clearly the decrease in the number of bleached F centers after three optical bleaches and two thermal bleaches, even though the number of quanta absorbed in each optical bleach is the same. The shaded area represents the wavelength region covered by the F light during bleaching.

TABLE II. Destruction of F centers in additively colored KCl in various crystal specimens after irradiation in the F band (5450 A) at 170°K and a slit width of 1.5 mm (250 A).

Initial optical density of F band	Decrease in F-band density ΔD	Decrease in F-band density %	Length of F-band bleach (hours)	Thickness of crystal (inch)	Colored crystal specimen No.
2.04	0.04	2.0	$2\frac{1}{4}$[a]	0.014	1[b]
1.28	0.04	3.1	$2\frac{3}{4}$[a]	0.014	2[b]
2.53	0.16	6.3	2	0.018	3
1.82	0.25	13.7	2	0.017	4 See Fig. 2, Curves (a), (b)
2.48	0.56	22.6	2	0.017	5 See Fig. 3, Curves (e), (f)
1.86	0.27	14.5	2	0.016	6
3.01	0.34	11.3	2	0.019	7

[a] Light source not voltage-stabilized.
[b] Specimens No. 1 and No. 2 were obtained from the same, crystals No. 3 to No. 7 from a different one-inch cube grown by the Harshaw Company.

resolved because of the relatively high crystal temperature.

CONCLUSIONS

The initial variation of the optical quantum efficiency when the additively colored KCl is bleached in the F band is perhaps not quite so unexpected considering the results on KBr and NaCl by Pick.[1] More astonishing is the extent of the variation of the quantum efficiency, which is an order of magnitude.[5] These variations follow no predictable pattern and do not appear to be a consequence of the type of coloring procedure used, although definitive data on this point are lacking. In fact, control experiments were carried out with crystals colored with undistilled potassium, but the program was not extensive enough to reach any clear-cut conclusions.

The decrease of the optical quantum efficiency after each bleaching cycle, i.e., one optical bleach and one thermal bleach, is surprising. Here again we note a considerable variation in the amount of decrease in the quantum efficiency from one crystal to the other. But despite the quantitative individuality of the specimens, there is no doubt about their qualitative behavior after successive F'-center formation and thermal destruction.

To determine whether the growth of the bands on the low-frequency side is due predominantly to F' centers and not R centers, the crystal was irradiated with F light at 230°K for two hours. The optical bleach resulted in a definite enhancement of the R centers which remained undiminished after a twelve-hour thermal bleach at room temperature. Therefore, no R centers are formed at 170°K, but at 230°K the R center formation predominates and few F' centers are stable enough to be measured.

It is not clear whether the partial recovery of the F band after optical bleaching is connected with the successive decrease of the quantum efficiency. Apparently, it is not [see Fig. 2, Curves (a) and (c)]. However, the electrons freed by the partial F-band recovery ought to coagulate with vacancy clusters evidenced in the absorption spectrum by increased absorption of existing bands or new bands. Neither could be observed in the wavelength range considered.

The behavior of the ratio of F to K centers is of considerable theoretical interest.[4,6,7] Figure 3, Curves (e) and (f) show a reduction in the number of F centers of 22.6 percent after the usual optical bleach. A proportionate reduction of K centers expected on the basis of Mott and Gurney's theory[4] would reduce the K-band density to 0.30. If we assume that the growth of the F' band contributes roughly 0.06 density units to the K band, then the K band after bleaching should have a density of approximately 0.36. Figure 3, Curve (f) shows that the actual reduction of K centers was much less than 22.6 percent.

Pick[1] obtained the shape of the F' band by subtracting the absorption curves before and after the F-light bleach. Subtracting curve (e) from (f) of Fig. 3 one obtains instead of a broad band with a maximum at 1.80 ev (F' band), three broad bands with peaks at 1.97 ev, 1.79 ev, and 1.64 ev. It appears as if the F' band has superposed on it three weak bands. The control experiments at 230°K, which gave an increase in R centers after F-light exposure did not show these three bands.

ACKNOWLEDGMENTS

I am indebted to Dr. H. Friedman for having suggested a reinvestigation of additively colored alkali halides, and to Dr. D. Dexter, Dr. H. Etzel, and Dr. C. Klick for various helpful discussions on F centers. I am grateful to Dr. R. Tousey and Mr. L. Dunkelman for generously allowing me to use their Cary spectrophotometer almost uninterruptedly for more than a year. I am happy to acknowledge Dr. M. A. Garsten's help in discussing my manuscript, and Dr. Jordan Markham's discussion on new F'-center results.

[5] Dr. James H. Schulman has kindly called my attention to a paper by A. Smakula [Z. Physik **59**, 603 (1930)] in which considerable variations in the quantum efficiency of x-rayed NaCl was found.

[6] H. W. Etzel and F. E. Geiger, Jr., Phys. Rev. **96**, 225 (1954).
[7] F. E. Geiger, Jr., Phys. Rev. **97**, 560 (1955).