

Mr. E. P. Warekois for orienting all the samples by means of x-ray techniques, Mr. B. Feldman for his assistance with the experiments and Dr. J. W. Meyer for the use of and aid with his x-band paramagnetic spectrometer.

*Note added in proof.*—Evidence of an additional resonance occurring above  $H_c$  given by  $H_0 = [(\omega/\gamma)^2 + 2H_B H_A]^{\frac{1}{2}}$  at  $T=0$  has

recently been observed at 35 kMc/sec in  $MnF_2$ . This resonance appears to be extremely sensitive to orientation of the  $c$  axis with respect to  $H_0$  at this frequency.

*Note added in proof.*—Similar antiferromagnetic resonance observations have been made on a single crystal of  $Cr_2O_3$  kindly furnished by Dr. E. J. Scott of the Naval Ordnance Laboratory. Resonance data at 35 kMc/sec have been obtained from 77°K up to 325°K ( $T \cong 307^\circ K$ ) to date. The results of these experiments will be presented in the near future.

Effect of Bleaching on the Optical Band Width of the  $F$  Center in KCl

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Measurements have been made of the absorption in the  $F$  region in KCl at 78°K. It has been found that the structure in this region is dependent on the presence of the  $M$ ,  $N$ ,  $R$ , and  $K$  bands. The broadening in the presence of small amounts of  $M$  absorption indicates that it is not simply due to the overlapping of  $R$ ,  $M$ , and  $N$  bands but is caused by an additional structure. These measurements support the present interpretation of the work of Van Doorn and Haven; they can explain the difference in the measurements of Pick and Geiger as well as the difference in the half-width observed by Mollwo and more recent data.

VAN DOORN and Haven<sup>1</sup> investigated the dichroism of the  $F$  and  $M$  bands in additively colored KCl, and suggest that there is a band under the  $F$  band which arises from the same center which causes the  $M$  band. Petroff,<sup>2</sup> working with additively colored KCl, indirectly deduced the presence of a band under the  $F$  band (the  $B$  band). We assume that bleaching should affect the optical absorption structure of the  $F$  band, and therefore carried out the following experiments.

Absorption measurements were made on additively colored KCl containing varying concentrations of  $F$  and  $M$  bands.<sup>3</sup> All colorations and quenches were performed in the absence of light. The quenches in oil were made as rapidly as possible (15 sec) from coloration temperature ( $\sim 730^\circ C$ ) to room temperature in order to obtain only  $F$  centers. All measurements were made at 78°K with a Beckman Model DU spectrophotometer between 1.0 ev and 3.5 ev.<sup>4</sup>  $M$  and  $R$  centers were induced by bleaching at room temperature with a tungsten lamp.

The  $F$  band may be characterized by four wavelengths: the peak,  $\epsilon_M$ ; the half-height to the red,  $\epsilon_r$ ; the half-height to the violet,  $\epsilon_v$ ; and the half-width,  $\Delta\epsilon$ , the difference between  $\epsilon_v$  and  $\epsilon_r$ . The ratios of the  $M$  band and the  $K$  band to the  $F$  band ( $M/F$  and  $K/F$ , respectively) are reported in terms of the maximum absorption at the peaks.

An element of uncertainty occurs due to selection of a base line. When only  $F$  bands are present, the flatness

to the red of the  $F$  band determines the line and the peak absorption with little doubt. When  $M$ ,  $R$ , and  $N$  bands are present, we selected for the base a straight line from the absorption value at 1.1 ev to the lowest value on the violet side of the  $F$  band. If there is some true absorption at either or both of these points, the half-widths reported here are too small. Our selection, therefore, indicates the minimum  $\Delta\epsilon$  to be expected.

The facts are as follows: when a crystal exhibiting mainly an  $F$  band is bleached, the  $\Delta\epsilon$  increases and  $M$  band arises. Upon further bleaching the  $N$ ,  $R_1$ , and  $R_2$  bands appear, the  $M$  band increases, while the  $F$  band drops, its peak shifts to the violet, and  $\Delta\epsilon$  further increases. From Fig. 1 we see that the increase in  $\Delta\epsilon$  is not due to overlap on the red side. Subtraction of the  $K$  band still leaves a half-width wider than the value for

TABLE I. Summary of data on the  $F$  center in KCl.

Bleaching <sup>a</sup>	Concentration of $F^b$	$\epsilon_{max}$ (ev)	$\epsilon_v$ (ev)	$\epsilon_r$ (ev)	$\Delta\epsilon$ (ev)	% $M/F$	% $K/F$
None	$3.67 \times 10^{16}$	2.303	2.409	2.216	0.193	1.2	4.0
None	$4.41 \times 10^{16}$	2.304	2.410	2.215	0.195	1.7	3.2
None	$4.62 \times 10^{16}$	2.300	2.410	2.215	0.195	0.7	3.8
None	$4.18 \times 10^{16}$	2.304	2.411	2.215	0.196	1.4	3.6
None	$3.92 \times 10^{16}$	2.304	2.411	2.215	0.196	1.6	4.1
None	$4.16 \times 10^{16}$	2.308	2.410	2.214	0.196	5.8	4.8
None	$4.57 \times 10^{16}$	2.308	2.415	2.218	0.197	1.1	3.8
10 min	$4.15 \times 10^{16}$	2.308	2.413	2.214	0.199	7.8	4.9
5 min	$2.78 \times 10^{16}$	2.300	2.415	2.210	0.205	29.4	8.1
5 min	$3.18 \times 10^{16}$	2.304	2.431	2.213	0.218	20.4	8.8
15 min	$2.08 \times 10^{16}$	2.308	2.439	2.206	0.233	29.2	15.1
30 min	$1.87 \times 10^{16}$	2.302	2.445	2.210	0.235	23.0	18.4
30 min	$2.20 \times 10^{16}$	2.310	2.442	2.206	0.236	21.6	16.5
1 hr	$1.80 \times 10^{16}$	2.310	2.453	2.210	0.243	25.3	20.4
30 min	$1.96 \times 10^{16}$	2.310	2.454	2.210	0.244	24.3	16.3
3 hr	$1.50 \times 10^{16}$	2.312	2.457	2.205	0.252	38.6	25.1
X-300°K 3 hr	$4.30 \times 10^{16}$ <sup>d</sup>	2.304	2.410	2.218	0.192	2.2	4.7
X-78°K 3 hr	$3.35 \times 10^{16}$ <sup>d</sup>	2.304	2.409	2.214	0.195	0	4.6

<sup>a</sup> Optical bleaching (tungsten lamp) at room temperature.

<sup>b</sup> Calculated using Smakula's formula ( $f=0.81$ ).

<sup>c</sup> Measured to  $\pm 0.001$  ev.

<sup>d</sup> Average value. Filtered x-ray (140 kvp).

<sup>1</sup> C. Z. Van Doorn and Y. Haven, *Phys. Rev.* **100**, 753 (1955).

<sup>2</sup> St. Petroff, *Z. Physik* **127**, 443 (1950).

<sup>3</sup> G. A. Noble and L. Bronstein, *Bull. Am. Phys. Soc. Ser. II*, **1**, 33 (1956).

<sup>4</sup> H. N. Hersh, *Phys. Rev.* **105**, 1158 (1957).

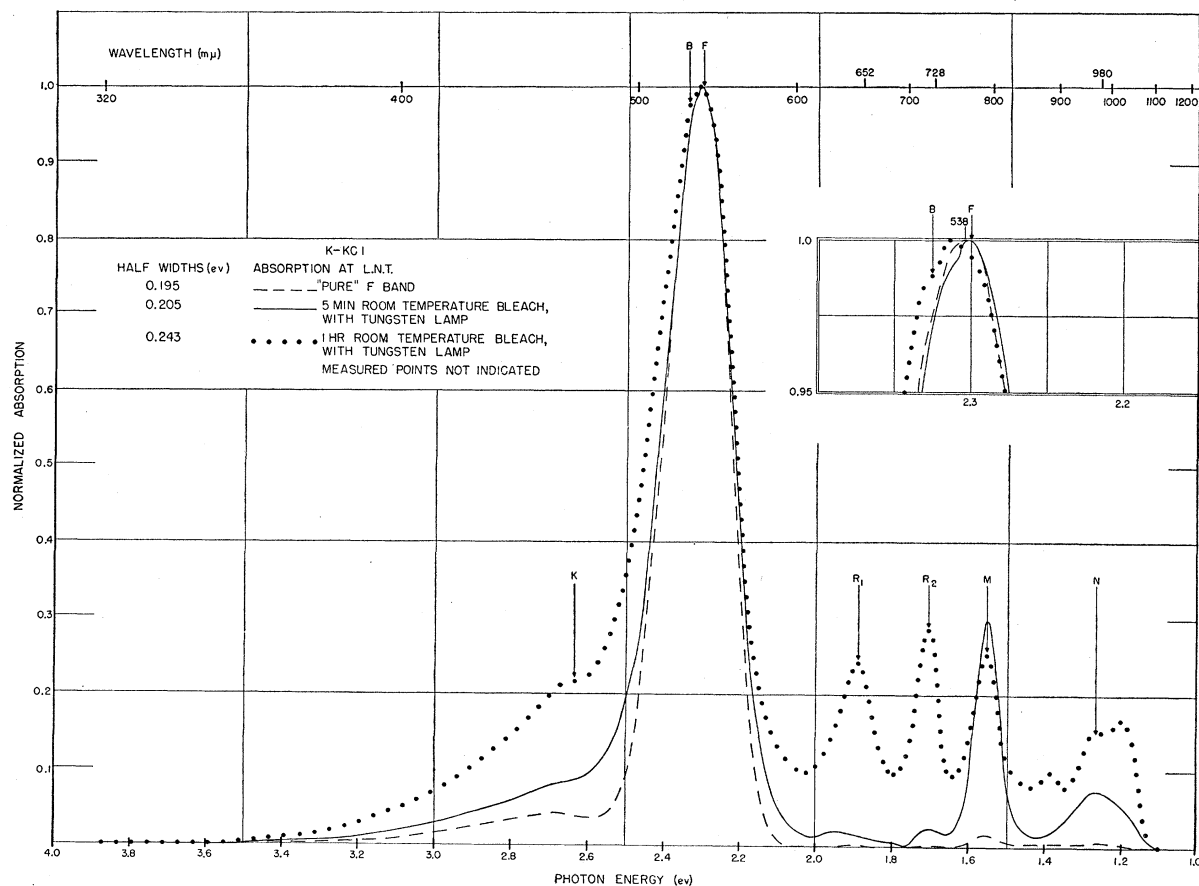


FIG. 1. Effect of bleaching on the absorption of the *F* structure. Absorption measurements at liquid nitrogen temperature.

the "pure" *F* band. In the small drawing of Fig. 1, note that the peak of the *F* band shifts and the *B* band appears to be somewhat resolved.

Table I shows that  $\Delta\epsilon$  and the *M/F* and *K/F* ratios increase with increasing bleaching. Notice that a quantitative relationship does not exist between the *F* band and the *M/F* and *K/F* ratios. The table indicates that the concentration of *M* centers alone does not determine  $\Delta\epsilon$ . It seems to increase monotonically while *M* rises and then falls. The x-ray data show that it is not affected greatly for an *M/F* ratio of 2.2%.

Similar effects are now being studied in KBr.

Undoubtedly there has been confusion in the past, for no one has been careful to distinguish between the pure *F* and the *F* composite bands. The distinction resolves some of the contradictory behavior of the *F* band. For example, a comparison of our data with those of Mollwo<sup>5</sup> indicates that his values for KCl and KBr refer to the composite rather than the "pure" *F* band. Table I disagrees with values given by Russell and Klick,<sup>6</sup> whose data reflect a theoretical interpretation

rather than actual experimental values. The distinction also resolves at least some of the differences between the work of Pick<sup>7</sup> and Geiger.<sup>8</sup> Geiger studies the quantum yield for the composite band while Pick's work refers to the true *F* center.

To summarize, as the *F* band is bleached, its half-width increases. This increase is due in part to some overlap of the *F* band with its side bands, but mainly due to the formation of another band or bands under the *F* which arise under the same conditions that cause the *M* band, namely, bleaching the *F*. This band, Petroff's *B* band, is probably the same one which gives rise to the dichroism noticed by Van Doorn and Haven.

In future work concerning the *F* band, we believe a careful distinction must be made as to whether one is treating the *F* band itself or the *F* composite bands. We would like to stress that at present there is no reliable information on the temperature variation of the peak and half-width or the shape of the *F* band.

We would like to thank Dr. H. N. Hersh and Dr. G. A. Noble for their assistance.

<sup>5</sup> E. Mollwo, Z. Physik 85, 56 (1933).

<sup>6</sup> G. Russell and C. Klick, Phys. Rev. 101, 1473 (1956).

<sup>7</sup> H. Pick, Ann. Physik 37, 421 (1940).

<sup>8</sup> F. E. Geiger, Phys. Rev. 99, 1075 (1955).