It is a pleasure to thank P. C. Michaelis for the careful susceptibility measurements, which are shown in Fig. 2, and H. J. Williams for additional magnetization measurements on gallium iron oxide.

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IONIZED F-AGGREGATE COLOR CENTERS IN KCl

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The existence of ionized F-aggregate color centers in alkali-halide crystals has never been established.[1] This note reports new evidence for the existence of such ionized centers in KCl, specifically the F_2^+ and F_3^+ centers, which are ionized M and R centers, respectively.[2] A new absorption band occurring at 1.4 μ is believed to be due to a transition of the F_2^+ center,[3] and it appears very likely that a band at about 960 mμ arises from a transition of the F_3^+ center.

The technique employed for the production of ionized centers was the following. KCl crystals, additively colored in potassium vapor by the van Doorn method,[4] were exposed to light in the high-energy tail of the F band at room temperature to produce relatively large concentrations of F-aggregate centers. These crystals were subsequently cooled to liquid-helium temperature and exposed to x rays in order to introduce trapped-hole defects which could lead to the ionization of F aggregates. Without warming the crystal, bleaching of trapped-hole centers was then induced with 335-mμ light corresponding to the spectral region of the V_K and H bands; this light also produced bleaching of the F-aggregate centers.

The formation of the 1.4-μ band is most easily observed in a crystal which contains F and M centers predominantly. After the liquid-helium-temperature x irradiation, the 1.4-μ band grows in constant proportion to the decrease of the M band during the exposure of the crystal to 335-mμ light. The ratio of the change of absorption coefficients at the peak of the respective bands, $|\Delta\alpha_M/\Delta\alpha_{1.4\,\mu}|$, is 4.2. It is found that this ratio is also maintained during the reverse process, 1.4 $\mu \rightarrow M$ band, which is stimulated by F-light excitation near the F-band maximum. This reverse conversion is interpreted as resulting from the capture of F electrons by F_2^+ centers.

Since the M center has a $\langle 110\rangle$ axis of symmetry, it is expected that the F_2^+ center should be characterized by this same axis. Figure 1 shows that the 1.4-μ band exhibits $\langle 110\rangle$ dichroism when produced from an M band with the same dichroism. Similar data have shown that $\langle 100\rangle$ dichroism is induced in the 1.4-μ band, if the M band is initially oriented at room temperature with $\langle 100\rangle$ M light. These data are consistent with the expected $\langle 110\rangle$ symmetry axis for the F_2^+ center; they further indicate that the $F_2 \rightarrow F_2^+$ conversion under 335-mμ light occurs largely without a reorientation of the axes of the centers. However, as seen in Fig. 1, the reverse process $F_2^+ \rightarrow F_2$ under F light occurs with some loss of orientation of both the F_2^+ and F_2 centers. A further interesting observation regarding the 1.4-μ band is that it can result from x-ray exposure alone (cf. curves 2a and 2b, Fig. 1). This would be expected, for example, if a free hole is captured by a M center, or if the M center is directly photoionized by the x ray itself.

We believe the foregoing results are most easily interpreted by assuming that the 1.4-μ band is due to a transition of the F_2^+ center. The possible centers which might form from M-center bleaching are severely limited. At the low temperatures employed, ionic processes are improbable. Considering the other

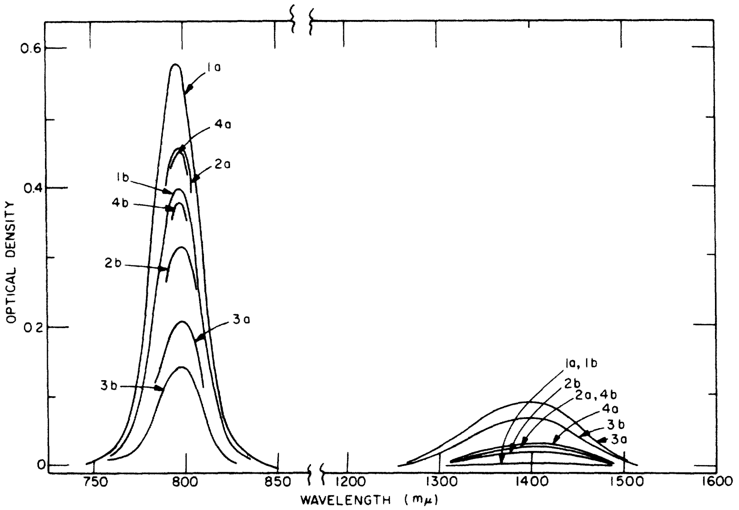

FIG. 1. Absorption spectra of the M and 1.4-μ bands in an additively colored KCl crystal at liquid-helium temperature. The M band was initially polarized with [011] M light at room temperature, and measured with polarized light prior to x-ray exposure (curves 1a, 1b); after x-ray exposure (curves 2a, 2b); after unpolarized 335-mμ illumination (curves 3a, 3b); and after unpolarized F-light illumination (curves 4a, 4b). (a) indicates measurements made with $[0\bar{1}1]$ polarized light, and (b), [011] polarized light. (Zero-phonon lines are omitted.)

possible centers that might be produced by purely electronic transfers, the doubly ionized defect F_2^{++} would occur with lower probability than F_2^{+}, and it would not be expected to give rise to an optical transition in the near-infrared region. Negatively charged centers such as the M' center seem to be excluded because (1) the M' band at[5] 1.94 μ is not produced in these experiments, and (2) 335-mμ irradiation of crystals without prior x-ray exposure does not result in the 1.4-μ band.

When R centers are present in a KCl crystal it would be expected that similar experiments should produce ionized R centers. When additively colored crystals containing R centers were x rayed and exposed to 335-mμ light at liquid-helium temperature, the R bands bleached during the light exposure and the 960-mμ band grew in a fixed ratio, $|\Delta\alpha_{R_2}/\Delta\alpha_{960\ \mathrm{m}\mu}| = 1.0$. Furthermore, the reverse conversion 960 mμ $\rightarrow R$ was induced by subsequent F-light excitation. The essential features of the conversion $R \rightarrow 960$ mμ are depicted in Fig. 2. It is observed that this conversion always occurs more rapidly than the conversion of the M band to the 1.4-μ band. As in the M-center case, x-ray exposure itself results in R-center bleaching and 960-mμ formation. The increase in M-center concentration following x-ray irradiation is consistent with x-ray conversion of R and perhaps

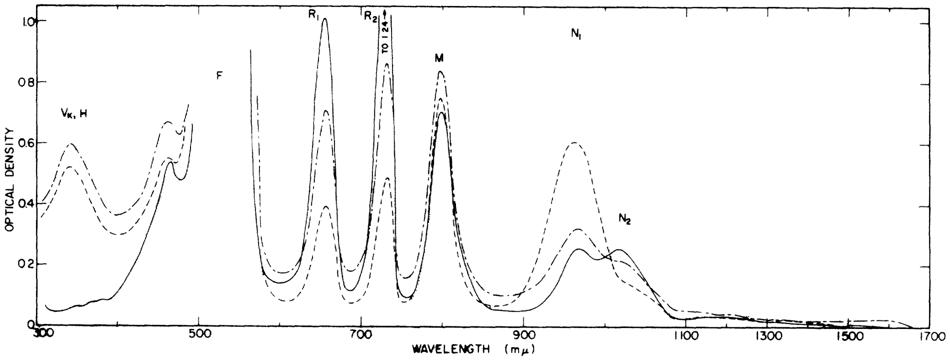

FIG. 2. Absorption spectra of an additively colored KCl crystal at liquid-helium temperature: solid curve, prior to x-ray exposure; dash-dot curve, after x-ray exposure; dashed curve, after 1 min of 335-mμ illumination; and dotted curve, after 21 min. of 335-mμ illumination. (Zero-phonon lines are omitted.)

N centers into M centers. We have also investigated the changes in anisotropy of the 960-mμ band during $R \rightarrow 960$ mμ conversion in crystals initially containing dichroic R bands. A detailed account of these studies will follow later.

We interpret the process $R \rightarrow 960$ mμ analogously to our interpretation of the earlier described conversion $F_2 \rightarrow F_2^+$. Assuming the F_3 model of the R center, we believe that the simplest interpretation of the experimental findings is to attribute the 960-mμ band to an optical transition of the F_3^+ center. Although in KCl the 960-mμ band and the previously known N_1 band are spectrally similar, we believe that they are overlapping transitions of different centers. This point of view is supported by measurements in KBr which show that the band produced by R-center ionization is located at about 1.02 μ, whereas the N_1 band is located at ~1.07 μ. Moreover, in both KCl and KBr, the bands ascribed to F_3^+ centers are convertible to the R bands under F light at low temperature. Also the reverse conversion $R \rightarrow N_1$ can be stimulated with R light. This behavior is noted in both KCl and KBr in normal, additively colored crystals which have been illuminated with F light at room temperature or crystals x rayed in the dark at room temperature.

If one assumes that the N centers consist of an F_4 structure,[6] it can be anticipated that an ionized product of these centers, such as the F_4^+, should be seen in optical-absorption studies. Measurements carried out to wavelengths of 2.5 μ have revealed weak absorption occurring near 1.6 μ, as seen in Fig. 2. This absorption has not as yet been identified with any specific center.

As a final point we note that the F_2^+ and F_3^+ centers are interesting centers for electron paramagnetic-resonance studies. The double-electron center, F_3^+, might be observable in a triplet-state experiment such as has been performed on the M center by Seidel.[1]

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