DEFECT INTERACTIONS IN IRRADIATED CALCIUM-DOPED POTASSIUM CHLORIDE

J. H. Crawford, Jr., and C. M. Nelson

Solid-State Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee

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The marked enhancement of the rate of formation of F centers in alkali halides containing alkaline earth impurity has long been recognized.[1,2] Recent studies of Etzel and Allard[3] have shown that the energy required for this structure-sensitive process is quite small in calcium-doped NaCl colored at room temperature. Rabin[4] has observed little expansion in NaCl crystals containing Ca^{++} during x irradiation until the structure-sensitive stage is exhausted. In view of the law of mass action:

$$N_V^+ N_V^- = A e^{-E_s/kT}, \qquad (1)$$

where N_V^+ and N_V^- are, respectively, the concentration of cation and anion vacancies and E_s is the energy of formation of a pair of isolated vacancies, and the fact that Ca^{++} introduction enhances the concentration of cation vacancies, one would expect N_V^- to be drastically suppressed. Consequently, on this basis a decrease rather than an increase in the rate of F-center production would be expected in crystals doped with divalent cations. One must therefore conclude that the presence of divalent alkaline earth impurity and the accompanying cation vacancies assist in some manner the creation of anion vacancies by the ionizing radiation.

Perhaps the simplest reasonable mechanism employs the isolated cation vacancy.[5] One may visualize the capture of a hole by a halide neighbor of the cation vacancy, the resulting halogen atom relaxing into the cation vacancy and the energy released in the hole capture process assisting the anion vacancy so created to escape from the site of the event. This center can be described as a Cl_2^- molecule-ion oriented in the $\langle 100 \rangle$ direction. Further ionization of the center by loss of an electron would lead to a Cl_2 molecule localized at the site of the original cation vacancy.[6] The mechanism satisfies the experimental requirements of small energy absorption[3] and small volume change[4] per F center.

By electron spin resonance techniques, Hayes and Nichols[7] have identified a center in Ca^{++}-doped KCl x-irradiated at 195°K which absorbs at 323 mμ with a Cl_2^- molecule-ion oriented in the $\langle 100 \rangle$ direction. They attribute the center to hole capture at an associated Ca^{++}-vacancy complex. Very similar centers were also observed in Sr^{++}- and Ba^{++}-doped KCl and their counterparts in KBr containing alkaline earth impurity were observed as well. This type of center has the characteristics required by the mechanism described above, and, although Hayes and Nichols suggest that minor differences in peak position and thermal stability for the different alkaline earth ions indicate an intimate connection with the impurity ion in question, we submit that, since these differences are near the limit of experimental precision, the peak near 325 mμ in KCl may equally well be ascribed to an isolated cation-vacancy which has been converted to Cl_2^- and an anion-vacancy by hole capture.[8]

The 325-mμ band in KCl:Ca begins to disappear relatively rapidly on warming to the vicinity of -40°C. The purpose of this note is to describe the decomposition products of the center. As mentioned above, further decomposition of the Cl_2^- center may occur by the process

$$Cl_2^- \rightarrow Cl_2^0 + e^-. \qquad (2)$$

This reaction would not appreciably affect the F band, since it occurs above the temperature at which the F' band is stable ($\sim 200°K$). Crystals of KCl containing 2.6×10^{-4} mole fraction of Ca^{++} were x irradiated (40 kv, 15 ma, 5 cm from target) at 195°K. The optical absorption in the near uv region before [Curve (a)] and after warming to $\sim -10°C$ [Curve (b)] is shown in Fig. 1. The 325-mμ band markedly decreases in intensity and there is a marked growth in the V_2-V_3 region (2200 Å). The difference in absorption between Curves (a) and (b) is plotted as Curve (a) in Fig. 2. During this process the F band decreased only $\sim 10\%$ in intensity.

If Process (2) is responsible for the variation in absorption, we must ascribe the 220-mμ band to Cl_2^0 localized near the original vacant cation site. Since Cl_2^- is unstable above -40°C, the Cl_2^0 center would be resistant to optical bleaching near room temperature, such as has been observed for the V_3 center. (This does not necessarily mean that the 220-mμ band is identical with the V_3 band.) However, at 195°K where the Cl_2^- center is stable, release of electrons in the
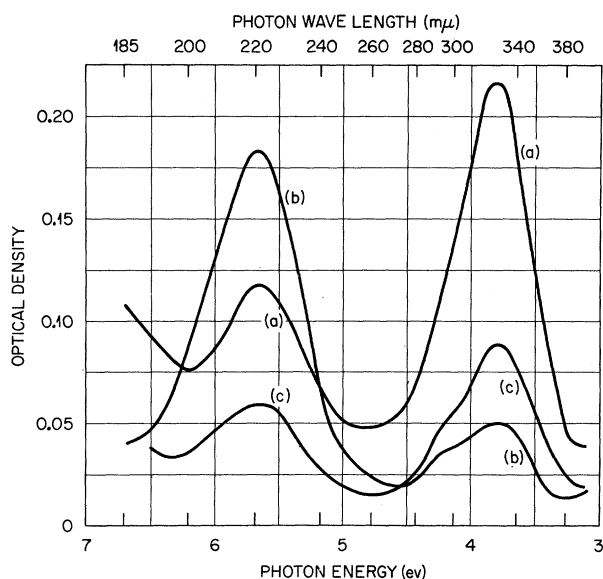
FIG. 1. Optical density of x-irradiated KCl:Ca crystal after various treatments: Curve (a), after the exposure to x rays at 195°K; Curve (b), after warming to 263°K; Curve (c), after 5-min illumination with F light at 195°K.

FIG. 2. Change in optical density after various treatments: Curve (a), difference between Curves (a) and (b) of Fig. 1; Curve (b), difference between Curves (b) and (c) of Fig. 1.

crystal by F-band illumination should cause the reverse of Process (2) to occur. The results of F-band illumination at ~195°K with light in the range 540 to 550 mμ are shown in Fig. 1, Curve (c), and the difference between Curve (b) and Curve (c) is plotted in Fig. 2 as Curve (b). The process is indeed reversed.

These results suggest that the mechanism proposed above for the enhancement of F-center production in alkali halides is indeed reasonable. The primary step is hole capture at a cation vacancy. The subsequent rearrangement creates an anion vacancy and a halogen atom in the cation site. Several questions remain, namely (1) what happens to the excess electrons released by the thermal ionization of the Cl_2^- center, and (2) is the 220-mμ center to be identified with either the V_2 or the V_3 band? The first may find an explanation in the fact that an absorption below 190 mμ disappears with the thermal bleaching of the 325-mμ band.

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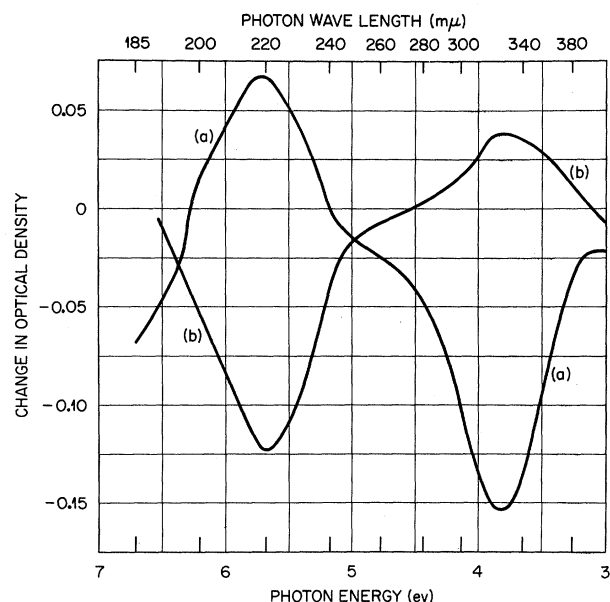
[1]H. Hummel, quoted by F. Seitz, Revs. Modern Phys. 26, 7 (1954).

[2]H. W. Etzel, Phys. Rev. 87, 906 (1952).

[3]H. W. Etzel and J. G. Allard, Phys. Rev. Letters 2, 452 (1959).

[4]H. Rabin (to be published).

[5]Evidence exists that Ca^{++}-vacancy complexes are appreciably dissociated at room temperature. C. Bean [quoted by F. Seitz, Revs. Modern Phys. 26, 7 (1954)] finds that the association energy in NaCl is less than 0.08 ev. Hence the viewpoint that isolated vacancies are involved is not unreasonable.

[6]The term Cl_2 molecule is simply descriptive. The actual center may be the linear Cl_3^- molecule-ion of the type described by H. N. Hersch [Phys. Rev. 105, 1410 (1957)]. Alternatively, it may be a true Cl_2 molecule with one component in the cation site and the other in a nearest neighbor anion site.

[7]W. Hayes and G. M. Nichols, Phys. Rev. 117, 993 (1960).

[8]The Ba^{++}-doped crystals indeed seem to respond differently since x irradiation introduces two bands: one close to the position of the center considered here and one at longer wavelength. See reference 7.