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Radiation Effects in Alkali Halides at Low Temperatures

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When KBr and KCl are x-rayed at liquid helium temperatures two large bands, the α- and γ-bands, are formed. These bands are much larger than F and H bands. It is suggested that the α- and γ-bands arise from an interstitial halide ion and halide ion vacancy which have not separated far and that the F and H bands arise from the same defects separated by 10 lattice spacings or more. Coloration efficiencies for various alkali halides have been measured under 2 Mev electron radiation and with x-rays of differing quality. A significant variation of efficiency with type of radiation is found. Analysis of this variation suggests that F-centers do not arise primarily from single ionizations nor from Auger processes in the kinds of radiation employed here.

It has been fairly well established that on x-raying alkali halides at low temperatures Frenkel defects are formed[1),2)]. The forms in which these have been studied are the F-center, a halide ion vacancy with an electron, and the H-center, an interstitial halogen atom. In a variety of easy to color alkali halides the efficiency for production of F-centers by x-rays has been found to be about 2000 ev/F-center[3)].

An investigation has been made of the absorption spectra of both KCl and KBr near the fundamental absorption edge after x-raying at 4°K. The spectrum for KBr is shown in Fig. 1. It consists of a small F-band and a small H-band at low energies and three bands of increasing size toward high energies. The first of these ultra-violet bands has roughly the area of the F-band and is broad. It occurs in the region where V_3, U, and OH bands have been observed. The second band is the α-band, associated with negative ion vacancies, which has an area 8 times that of the F-band. The third band has not previously been seen and will be called here the γ-band. It has an area about 20 times that of the F-band. The ultra-violet β-band at 6.46 ev associated with F-centers, is not seen because of the relatively few F-centers present. Similar results are found in KCl. The first band is again a broad band with a peak at 6.4 ev and an area about that of the F-band; the second band is the α-band at 6.96 ev with an area 6 times that of the F-band; the third band peaks at 7.56 ev and has an area about 16 times that of the F-band. In KCl the β-band is at 7.36 ev[4)].

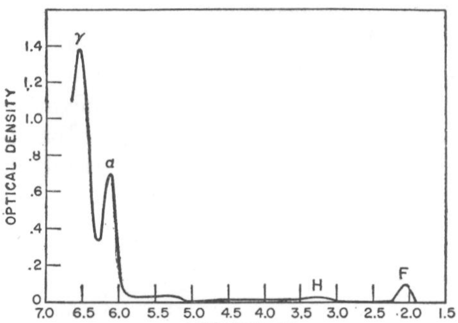

Fig. 1. Absorption spectrum of KBr at 4°K after x-raying at 4°K.

The large α-band observed under these conditions is identical in peak position and width to the α-band made by bleaching F-centers. It shows one very important difference, however. If F-centers are bleached with light to make isolated negative ion vacancies and then the crystal is lightly x-rayed, F-centers are quickly formed[5)]. In the present work vacancies, seen as the α-band appear unable to trap electrons to form F-centers.

It is proposed that the primary effect of x-ray radiation is to produce a Frenkel defect. In about 10 percent of the cases these defects separate about 10 lattice distances or more[6)] and become F- and H-centers. The remainder of the halogen interstitials and vacancies remain relatively close together. If the interstitial is charged, it may produce an electric field at the nearby vacancy sufficiently large to prevent it from trapping an electron, thus leading to the large observed α-band[7)]. If this model is correct, about 10 times as many Frenkel defects are produced in KBr as are seen in F-center production. This would lead to an efficiency of 200 ev/Frenkel defect for ordinary x-rays and would appear to result from an extraordinarily efficient process.

Because of the low energy of the photo-electrons produced in x-raying with the usual machine, direct displacements by "knock-ons" appear impossible. Several other possibilities have been suggested. One class of possibilities is that the Frenkel defects arise from a singly ionized isolated halide ion[8),12)]. This possibility has not been developed in detail, but arises from the fact that irradiation with light in bands due to H^- and OH^- impurities are known to result in interstitial ions. The other class of possibilities is that some more complex ionization is responsible. Mechanisms have been proposed involving doubly ionized halide ions[9),10)] and pairs of singly ionized halide ions[11),12)].

Experiments have been conducted to attempt to decide between these two classes. LiF, NaCl, KCl, and KBr have been irradiated with different kinds of ionizing radiation at 4°K ranging from 10 kv x-rays to 2 Mev electrons and the efficiency of F-center production has been measured. The results for LiF are shown in Fig. 2. If singly ionized isolated halide ions were responsible for F-centers, the 2 Mev curve would lie highest since the stopping power for this radiation is small and single isolated ionization predominates. The low energy x-rays have a densely ionized track which would lead to a larger fraction of multiple ionizations. In all the alkali halides which have been measured, the 2 Mev curve lies below that for 50 kv x-rays indicating that some multiple process is responsible for coloration. For 10 kv x-rays the curve again is low. This may mean that for very dense tracks wasteful processes or annealing due to local heating becomes important. Detailed comparison of this data with theory[13)] argues that Auger processes are not primarily responsible for the production of F-centers.

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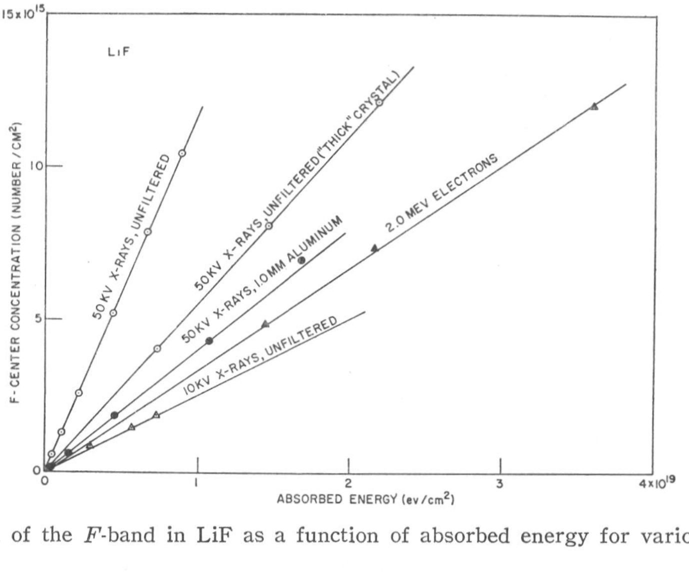

Fig. 2. Growth of the F-band in LiF as a function of absorbed energy for various radiations.

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DISCUSSION

Crawford, J. H.: Was an attempt made to ascertain the effect of ionization intensity in the case of 2 Mev electron bombardment of your crystals?

Klick, C. C.: I believe that Mr. Ritz did vary the beam intensity by a factor of five to investigate this point. There did not appear to be a dependence of coloration on beam intensity.

Smoluchowski, R.: What are the effects at the same voltages for chloride and fluoride?

Klick, C. C.: The energies of formation of F-centers in ev/F-center are given in the table below.

	3 Mev electrons	50 kv x-rays 1 mm Al filter	50 kv x-rays unfiltered	15 kv x-rays unfiltered	10 kv x-rays unfiltered
KBr	4700 ev	2740 ev	1700 ev	3300 ev	4600 ev
KCl	3750	2900	2400		4000
LiF	3000	2500	800 (thin crystal) 1800 (thick crystal)		3800
NaCl			10100		34000

Pick, H.: Do you think there is a γ-band as you show in Fig. 1? May this be produced by scattered light, if one measures in the range of the long wavelength side of the fundamental absorption?

Klick, C. C.: In KBr at 4°K the optical density at the short wavelength limit of the Cary Model 14M spectrophotometer was about 0.7 and the scattered light in this double monochromator is still less than 1/100 of the measuring light. The γ-band was measured for a variety of optical densities so that scattered light would vary in importance. The same band was found in each case.

In KCl the γ-band is better separated from the fundamental edge and the energy in the vacuum ultra-violet monochromator is not rapidly varying in the γ-band region so that this measurement also appears to be quite reliable.

Howard, R.: I estimate that most Auger ejection in alkali chlorides irradiated at kilovolt energies follow from single ionizations in the L shell and that the efficiency of such L ionization is roughly independent of radiation energy. Aren't your results on the chlorides consistent with this?

Klick, C. C.: Yes, but Varley's estimate of the number of doubly ionized halide ions formed by simple ionization and Ritz's calculations of the numbers of pairs in LiF are also in reasonable agreement with observation. Therefore it seems necessary to examine other experiments to decide which mechanisms are predominant.