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α and β Bands in Sodium Chloride

J. D. RIGDEN*
Radio and Electrical Engineering Division, National Research Council, Ottawa, Canada
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The peak energy of the α and β bands in sodium chloride crystals have been measured at 77° with a vacuum ultraviolet monochromator. The β band was well defined, and occurred at 7.40 ev with a half-width of 0.4 ev. The oscillator strength of the β band was calculated to be 0.55. No resolved α band could be produced, but subtraction of absorption curves indicated that it occurred near 7.20 ev.

THE α and β bands were first discovered in additively colored KI,[1] and have since been reported in several other alkali halides.[2,3] These two bands have been attributed to modified exciton absorption near negative-ion vacancies and F centers, respectively.

Most of the measurements that have been made of the optical absorption of alkali halides have been confined to the region above 1900 A. With the advent of small commercial vacuum ultraviolet monochromators the situation is beginning to change and crystals which are transparent below 1900 A are receiving more attention.

The present measurements were made on NaCl crystals grown in this laboratory from the melt, using recrystallized reagent-grade material. These crystals showed an absorption edge occurring at a higher energy than in crystals grown directly from reagent material. Absorption measurements were made manually using a Jarrel-Ash half-meter vacuum monochromator with a Seya-Namioka mounted grating. A molecular hydrogen discharge was used as a source and a photomultiplier coated with sodium salicylate was the detector.

Specimens containing F centers produced by any means showed an absorption band at 7.4_0 ev measured at liquid nitrogen temperature (LNT) (Fig. 1). The growth curve of this band with gamma irradiation was found to be proportional to the growth curve of the F band in a similar specimen. It is suggested, therefore, that this is the β band.

Efforts to produce the α band proved much more difficult than in KI. Delbecq *et al.* reported that in additively colored KI, a 35-minute bleach with F light at LNT produced a large easily resolved α band. Bleaching gamma-irradiated NaCl with F light for 4 hours at LNT produced a small band at 7.1_8 ev which was unresolved and could be observed only by subtracting the two absorption curves. At the same time the β band decreased by a small amount. Similar treatment of additively colored NaCl failed to produce a more substantial α band.

X-irradiation at dry ice temperature produced a wide band with an absorption peak at 7.3_5 ev, when measured at LNT (Fig. 2). Upon warming the crystal to room temperature and recooling to LNT, the normal β band was seen at 7.4_0 ev. The difference between these two curves shows a peak at 7.2_4 ev. It is thought probable that this band and the one produced by bleaching are α bands, and that the difference in peak photon energy is introduced by the subtraction necessary to resolve these wide overlapping bands. Further experiments are necessary to confirm this suggestion.

As the numbers of F and β centers are the same, we obtain from Smakula's equation:

$$f_F/(K_F\Delta E_F)=f_\beta/(K_\beta\Delta E_\beta),$$

where K and ΔE are the peak absorption and half-width of the two bands in the same specimen. Assuming a value of 0.86 for f_F,[4] and measuring the F and β bands

* National Research Council Post-doctorate Fellow. From November, 1960, at Bell Telephone Laboratories, Murray Hill, New Jersey.

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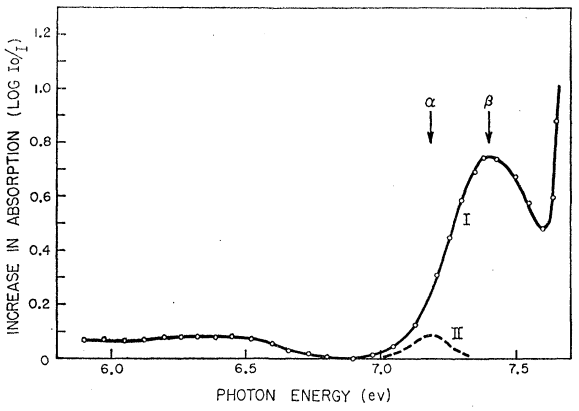

FIG. 1. (I) Increased absorbance in NaCl after an 8×10^6-roentgen, 1-Mev gamma dose. (II) Typical extra absorbance induced by 4 hours irradiation with F light at LNT.

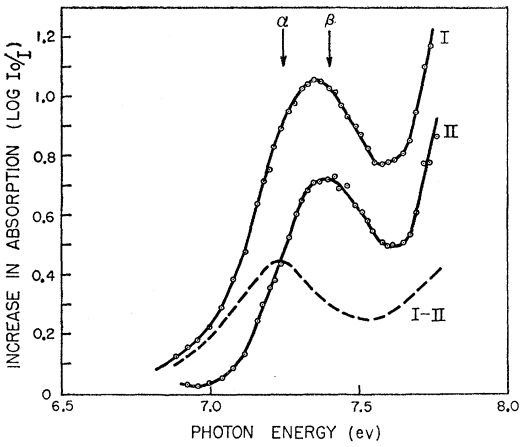

FIG. 2. (I) Increase in absorbance in NaCl after 1000 ma min irradiation with 50-kv x rays at dry ice temperature. (II) After warming to room temperature. Both measurements made at liquid nitrogen temperature.

in similar specimens with identical gamma doses, we get

$$f_\beta = 0.5_5 \pm 0.1.$$

This is in agreement with Dexter's[5] value for the oscillator strength of the β band of 0.6. A similar estimate cannot be made for f_α as the number of negative-ion vacancies is not known.

Fuchs[6] extended Dexter's theory and obtained six transitions for the β center. He suggested that the two lowest energy transitions should be visible below the absorption edge and that the β band in NaCl might show this doublet structure. No definite structure has been observed even at liquid helium temperature. However, the width of the β band in NaCl ($\approx$0.4 ev) is about twice that observed in other alkali halides, and it is possible that it is composed of two unresolved bands. The sum of the oscillator strengths calculated by Fuchs for his two bands is much less than the observed value.

From the results obtained during this work it seems that compared to other alkali halides, already measured, the F center in NaCl is more stable and resists bleaching at low temperatures. This same effect is shown by the difficulty of producing the α band by bleaching with F light at LNT, and the fact that the β band produced by x raying at dry ice temperature does not decrease when warmed to room temperature (Fig. 2).

To sum up, the β band in NaCl occurs at 7.4_0 ev and is about 0.4 ev wide. The α band which is also wide and not resolved from β occurs near 7.2_0 ev, the exact position being difficult to establish.

Recently, Onaka and Fujita[7] have reported the α and β bands in several alkali halides including NaCl. They report the peak energies as 7.1_6 ev for α and 7.3_8 ev for β in fair agreement with the present measurements. Unpublished results of J. Sharma, made while he was at this laboratory, indicated that the α and β bands in NaCl were at 7.2_4 ev and 7.5_1 ev, respectively. These values were obtained from measurements of photographic plates.

ACKNOWLEDGMENTS

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