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Vacuum Ultraviolet Absorption and Dissociation

of H_a^- and OH^- Centers in NaF

By

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The infrared absorption of H_a^- or U centers in sodium fluoride was studied by Dötsch et al. /1/. They produced centers by two methods: X-irradiation of NaF:NaOH at room temperature, or heating of NaF with sodium metal in a hydrogen atmosphere. Meistrich found a new small absorption band at 7.9 eV in X-irradiated NaF:NaOH and assumed it to be due to the H_a^- centers /2/. The OH^- band in NaF was assumed by Freytag as a band at 8.3 eV /3/. Meistrich corrected the OH^- band to 8.2 eV /2/.

We measured the H_a^- and OH^- absorption more reliably and studied the dissociation of both centers.

The "pure" NaF crystals were grown by the Stockbarger method in a graphite crucible. The NaF:NaOH crystals were regrown from "pure" NaF crystals in a platinum crucible with an addition of NaOH. The H_a^- centers in NaF were produced by two methods: 1) the pieces of NaF were heated with Na metal in a hydrogen atmosphere /1/. The depth of centers was about 2 mm, when the crystal was heated at 900 °C for some days; 2) the NaF:NaOH crystals were colored in sodium vapour. One of the products of the reaction between the OH^- and F centers at high temperatures are H_a^- centers (for NaCl see /4, 5/). The full picture of this reaction will be published elsewhere.

The NaF:H crystals show a strong absorption band at 7.95 eV with a half-width of 0.65 eV and a weak band at about 8.9 eV at room temperature (Fig. 1). At 80 K the main absorption band shifts to 8.1 eV. Both bands can be photo-bleached at room temperature by light with an energy of about 8 eV and more effectively by light from the 9 to 10 eV region. The disturbed F (3.6 eV) and (9.7 eV) bands are appearing (see Fig. 1). The photo-dissociation of H_a^- centers in alkali halides occurs by the following reactions:

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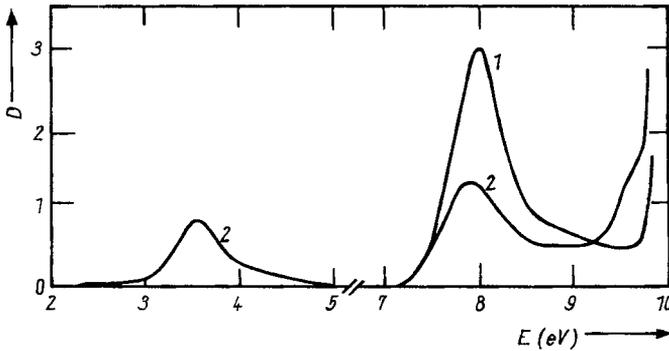
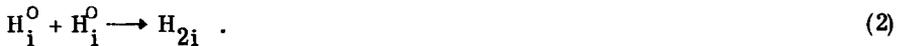


Fig. 1. Absorption spectra of NaF:H crystal before (1) and after (2) irradiation with unfiltered light from a hydrogen discharge lamp with MgF₂ window at 295 K. Crystal thickness 0.3 mm



The H_{2i} absorption cannot be seen in IR, UV, or ESR spectra in KCl /6/. According to this we see a decrease of the 7.95 and 8.9 eV and an increase of the F bands in NaF:H. Therefore, both bands belong to H_a⁻ centers in sodium fluoride. Goto et al. found two additional H_a⁻ bands in the KCl, KBr, NaCl crystals /7/. They named these new bands as U_a and U_b. The U_a band was shifted by about 0.5 eV to higher energy from the U band, and the U_b band was under the exciton band. It is reasonable that the 8.9 eV band has the same nature as the U_a band in other alkali halides. The relative oscillator strength was estimated from the H_a⁻ → F conversion (see Fig. 1) with $f(\text{H}_a^-)/f(\text{F}) = 1.73$. This value is higher than in other alkali halides /8/.

NaF:NaOH crystals show a 8.15 eV absorption band with 0.85 eV halfwidth in the VUV (Fig. 2), and a 3728 cm⁻¹ band in the IR region. The strengths of the VUV and IR absorptions relate as 10³:1. The broad 3728 cm⁻¹ band was assigned to free OH⁻ ions and the narrow lines between 3500 and 3650 cm⁻¹ to various complexes of the OH⁻ ion with impurities /2/. Therefore, the 8.15 eV absorption band can be assigned to free OH⁻ ions in sodium fluoride. Freytag saw the

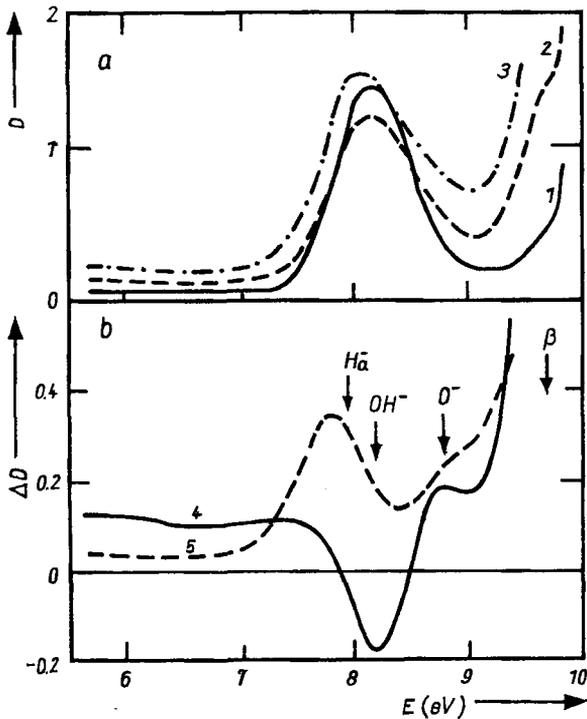


Fig. 2. a) Absorption spectra of NaF:NaOH crystals before (1) and after X-ray irradiation (40 kV, 50 mA) at 295 K during 0.5 (2) and 3 (3) h; b) change of absorption due to first (4) and second (5) irradiation. Crystal thickness 0.5 mm

8.3 eV band with halfwidth 1.1 eV and the 3600 cm^{-1} band in NaF /3/. The broad 8.3 eV band together with a narrow 3570 cm^{-1} band was seen in our NaF:Na₂O₂ crystals. The VUV and IR bands are related in strength as $10^2:1$. It is reasonable to assign the 8.3 eV band to complexes of the OH impurity. Meistrich /2/ had crystals with an 8.2 eV absorption band and with IR absorption related to the OH⁻ and OH⁻ impurity complexes. We think that this 8.2 eV band consists of 8.15 eV and 8.3 eV bands.

The radiation damage of the OH⁻ ion in NaF consists of two stages. At the first stage the hydroxile ions dissociate by the reaction



The interstitial hydrogen atoms aggregate into molecular form. The primary OH^- photo-dissociation rate in KCl is temperature independent over the whole range from 0 to 300 K /9/. The X-ray dissociation of OH^- ions in NaF was seen above 170 K. This means that the dissociative energy was supplied to OH^- ions by relaxed excitons or self-trapped holes (V_k centers). At the second stage H_a^- centers were also created (see Fig. 2). It seems that the H_a^- center is created when an H_i^0 interstitial is trapped by an F center. Such a reaction was studied in KCl /10/. In the first stage the F center concentration is too low and we see the OH^- dissociation only. When the concentration of F centers is high enough the H_i^0 are trapped by F centers. The reaction of thermally mobile H_i^0 interstitials with F centers in KCl leads always first to the electron transfer reaction



At temperatures above 200 K the H_i^- centers in KCl become mobile and will be trapped by anion vacancies /10/. Centers with absorption band near 200 cm^{-1} grow together with H_a^- centers at the second stage of X-irradiation of NaF:NaOH. These centers were tentatively attributed to complexes of H_i^- defects /11/. The growth of H_i^- defect complexes in X-irradiated NaF:NaOH crystals points out that the trapping process $\text{H}_i^0 + \text{F}$ in NaF takes place through the reaction (4), too. Then one part of the H_i^- centers will be trapped by vacancies and the other one by some defects. The resulting free anion vacancies together with F centers may build up F_2^+ centers, producing in NaF:OH with high efficiency /11/.

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