

phys. stat. sol. (b) **149**, 441 (1988)

Subject classification: 61.70 and 71.55; 78.50; S9.11

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## Reaction of OH<sup>-</sup> and F Centers in Sodium Halides

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The influence of an additive coloration procedure on the absorption spectra of sodium halides doped with hydroxide is studied. The reaction of OH<sup>-</sup> and F centers leads to the creation of H<sub>a</sub><sup>-</sup> and O<sup>2-</sup>-vacancy centers in NaF, NaCl, NaBr crystals. The reaction yields H<sub>a</sub><sup>-</sup> and O<sup>-</sup> centers in NaF doped with LiOH. Photodissociation of H<sub>a</sub><sup>-</sup> and O<sup>-</sup> vacancy is studied, too. The possibility of the reaction of F and OH<sup>-</sup> centers in alkali halides is estimated on the base of the effectiveness of the reaction of free alkali metals with metal hydroxides. The reaction in alkali halides doped with LiOH is observed, too.

Изучено влияние аддитивного окрашивания на спектры поглощения галоидов натрия с примесью гидроксила. Реакция между F и OH<sup>-</sup> центрами приводит к образованию центров H<sub>a</sub><sup>-</sup> и O<sup>2-</sup>-вакансия в кристаллах NaF, NaCl, NaBr. Реакция приводит к образованию H<sub>a</sub><sup>-</sup> и O<sup>-</sup> центров в кристаллах NaF с примесью LiOH. Исследована также фотодиссоциация центров H<sub>a</sub><sup>-</sup> и O<sup>-</sup>-вакансия. Возможность реакции между F и OH<sup>-</sup> центрами в щелочногалоидных кристаллах оценена на основе эффективности реакции между свободными щелочными металлами и гидроксидами металлов. Рассматривалась также реакция в щелочногалоидных кристаллах с примесью LiOH.

### 1. Introduction

The reaction between OH<sup>-</sup> and F centers during additive coloration of NaCl was first studied by Etzel and Patterson [1] and Etzel [2]. The H<sub>a</sub><sup>-</sup>(U) band and two oxygen bands (O<sub>I</sub> — 5.4 eV and O<sub>II</sub> — 4.2 eV after Etzel's notation [2]) have appeared in colored crystals [2]. The concentration of H<sub>a</sub><sup>-</sup> in colored crystals was proportional to the OH<sup>-</sup> concentration before coloration [1]. The reaction between free sodium and sodium hydroxide is operative above 300 °C,



Etzel [2] assumed that the same reaction is operative in NaCl crystals, too. Later, the O<sub>I</sub> band was ascribed to O<sup>-</sup>-vacancy (or O<sup>-</sup>v<sub>a</sub><sup>+</sup>) centers on the base of dielectric relaxation results [3]. The O<sub>II</sub> band was ascribed to O<sup>-</sup>-vacancy centers also [4, 5]. Recently we found the high-energy band of the O<sup>-</sup>-vacancy center at 7.4 eV and studied the photochemical reaction of H<sub>a</sub><sup>-</sup> and O<sup>-</sup>-vacancy centers in NaCl [6].

Apart from NaCl, the reaction of OH<sup>-</sup> and F centers in KCl, KBr, and KI is absent or very ineffective [5, 7 to 9]. The SH<sup>-</sup>, SeH<sup>-</sup>, TeH<sup>-</sup> centers reacted with F centers in KCl and yielded H<sub>a</sub><sup>-</sup> and chalcogen-vacancy centers [7, 10].

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We found that the reaction of  $\text{OH}^-$  and F centers, besides NaCl, is effective in NaF and NaBr also and do some speculations about the effectiveness of the reaction in alkali halides.

## 2. Experimental

Crystals were grown by Kyropoulos method on air (NaCl, NaBr) and the Stockbarger method in graphite or platinum crucible in helium gas (NaCl, NaF). Crystals were colored in a nickel container under helium atmosphere. Absorption spectra in the vacuum ultraviolet region were measured with a VMR2 monochromator controlled by an SM1 computer. Before measurement crystals were annealed at 500 to 700 °C and cooled on a copper plate.

## 3. Results

### 3.1 Sodium chlorides

Before coloration the NaCl crystals had the distinct  $\text{OH}^-$  band (at 6.7 eV at room temperature [11]). After additive coloration the  $\text{H}_a^-$  band (at 6.5 eV at 77 K [12]) and  $\text{O}^{--}$ -vacancy bands (at 4.2, 5.5, 7.4 eV at 80 K) appeared (Fig. 1).

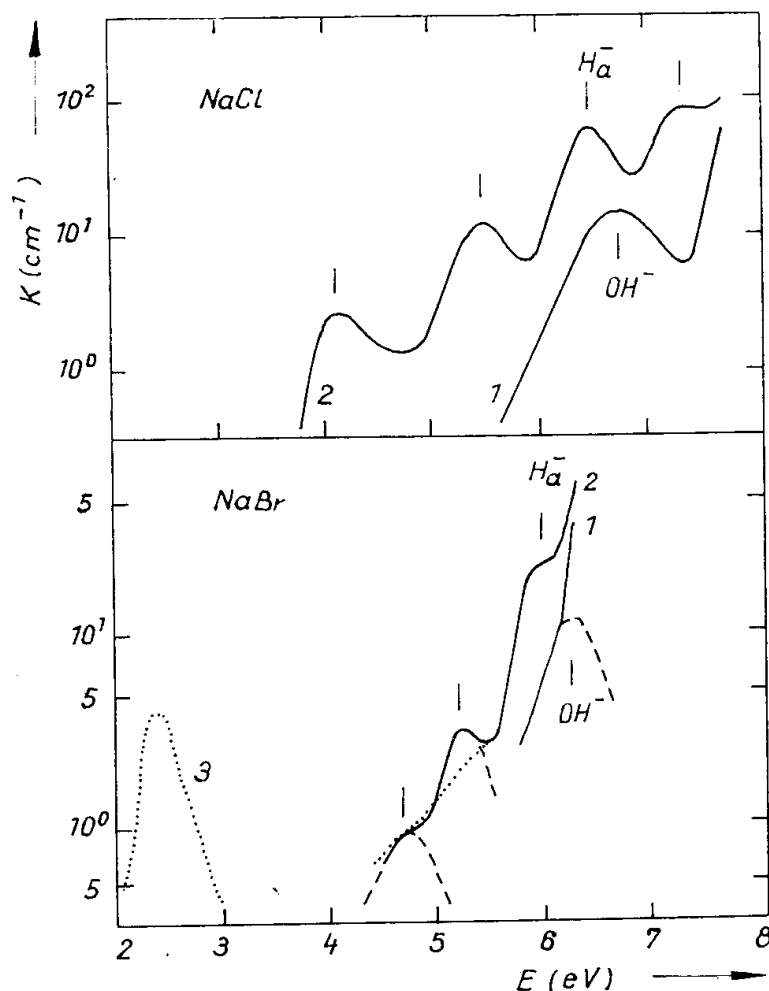


Fig. 1. Absorption spectra at 80 K of (1) uncolored and (2), (3) additively colored NaCl and NaBr crystals with hydroxide impurity; (3) was measured after irradiation at 270 K by light of a DDS30 deuterium lamp through UFS5 filter (5.3 to 4.5 eV region). The marks show the  $\text{O}^{--}$ -vacancy bands

The photodissociation of O<sup>2-</sup>-vacancy centers is possible above 200 K and yields F and O<sup>-</sup> centers. The O<sup>-</sup> band is situated at 7.27 eV at 77 K [12] and was not measured in our crystals due to the decrease of the high energy band of O<sup>2-</sup>-vacancy centers.

The photodissociation of H<sub>a</sub><sup>-</sup> at 80 K by light of a deuterium lamp leads to the appearance of H<sub>i</sub><sup>-</sup>, v<sub>a</sub><sup>+</sup> and then H<sub>i</sub><sup>0</sup>, F centers. The O<sup>2-</sup>-vacancy bands changed, too. Possibly the hydrogen interstitials were trapped by the O<sup>2-</sup>-vacancy centers.

### 3.2 Sodium bromide

The OH<sup>-</sup> absorption band is rather close to the exciton absorption [11]. We have crystals with a rather low OH<sup>-</sup> concentration ( $<10^{17}$  cm<sup>-3</sup>) and the OH<sup>-</sup> absorption band cannot be seen clearly (Fig. 1). The new bands at 4.7, 5.27, 6.0 eV appeared after additive coloration (see Fig. 1). The 6.0 eV band belongs to H<sub>a</sub><sup>-</sup> centers (band at 5.9 eV [13]) and two other bands to O<sup>2-</sup>-vacancy centers. The 4.25 eV band was seen in colored crystals, too. The centers giving rise to this band had an own photochemical behavior, not related to H<sub>a</sub><sup>-</sup> or O<sup>2-</sup>-vacancy centers but to unknown impurities.

The photodissociation of H<sub>a</sub><sup>-</sup> at 80 K led to the appearance of H<sub>i</sub><sup>-</sup> (with absorption band at 5.3 eV) and v<sub>a</sub><sup>+</sup> (with absorption at  $\approx 6.2$  eV). Thermal annealing of H<sub>i</sub><sup>-</sup> and v<sub>a</sub><sup>+</sup> (after 300 K pulse anneal) restored the H<sub>a</sub><sup>-</sup> band. Photodissociation of H<sub>i</sub><sup>-</sup> centers at 80 K led to the creation of the H<sub>i</sub><sup>0</sup> band at 4.75 eV and the F band at 2.4 eV. H<sub>i</sub><sup>0</sup> centers disappeared after pulse annealing to 100 K.

Photodissociation of O<sup>2-</sup>-vacancy centers took place at 270 K and higher temperatures and did not occur at 80 K. The 5.27 eV band decreased and an F band was created (see Fig. 1). Photodissociation can be done with 4.5 to 5.5 eV light. The relation  $\Delta D(\text{F})/\Delta D(5.27 \text{ eV})$  was equal to 3.7. These properties of O<sup>2-</sup>-vacancy centers in NaBr are close to those in other alkali halides.

### 3.3 Sodium fluoride

The NaF–NaOH crystals had a distinct OH<sup>-</sup> band (at 8.15 eV [14]). The band at 7.95 eV (H<sub>a</sub><sup>-</sup> [14]) and others at  $\approx 9.0, 6.3, 5.6, 4.0$  eV appeared after coloration (Fig. 2). The value of the new bands in colored crystals was directly proportional to that of the OH<sup>-</sup> band before coloration (see Fig. 2). Consequently, the bands besides the H<sub>a</sub><sup>-</sup> band may be related to O<sup>2-</sup>-vacancy centers.

Photodissociation of H<sub>a</sub><sup>-</sup> at 295 K leads to the appearance of F and  $\beta$  bands (Fig. 2). The bands at 6.3 and  $\approx 9.0$  eV decreased together with the H<sub>a</sub><sup>-</sup> band. The relation between the created F centers and decreased H<sub>a</sub><sup>-</sup> centers was  $\approx 2$  times higher in additively colored NaF–NaOH than in NaF–NaH. This means that an “additional” F center is created due to the decrease of centers with 6.3, 9.0 eV bands. The results show that the O<sup>2-</sup>-vacancy centers in NaF can be photodissociated at room temperature by light with photon energy above 7.7 eV. Photoluminescence, aggregation, and other properties of O<sup>2-</sup>-vacancy centers in sodium fluoride will be reported elsewhere.

The NaF–LiOH crystals had the same OH<sup>-</sup> absorption band as NaF–NaOH. The H<sub>a</sub><sup>-</sup> band and bands at higher energy near 8.8 eV were measured in additively colored NaF–LiOH crystals. The low energy bands (O<sup>2-</sup>-vacancy center) were not measured. Only the H<sub>a</sub><sup>-</sup> band decreased after irradiation by light of a hydrogen discharge lamp. The band at 8.8 eV in colored NaF–LiOH can be related to O<sup>-</sup> centers (band at 8.8 eV [15]).

The results show that in NaF–NaOH the products of the reaction of F and OH<sup>-</sup> centers are H<sub>a</sub><sup>-</sup>, O<sup>2-</sup>-vacancy centers and in NaF–LiOH H<sub>a</sub><sup>-</sup>, O<sup>-</sup> centers.

The NaF crystals have a rather large resistance to the coloration procedure. When crystals contain OH<sup>-</sup> ions the time of coloration should increase. One can see that

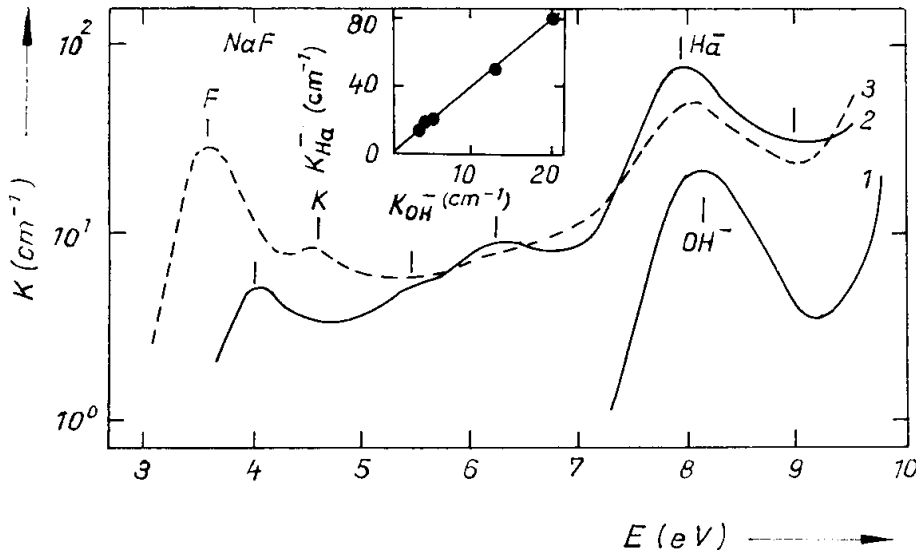


Fig. 2. Absorption spectra at 295 K of (1) uncolored and (2, 3) additively colored NaF-NaOH crystals; (3) was measured after irradiation at 295 K by unfiltered light of a VMF25 hydrogen lamp with MgF<sub>2</sub> window. The marks show the O<sup>2-</sup>-vacancy bands. The inset shows the dependence of the value of the H<sub>a</sub><sup>-</sup> band in a colored crystal versus that of the OH<sup>-</sup> band before coloration

the depth of the colored layer in NaF-LiOH is larger than in NaF-NaOH with nearly equal OH<sup>-</sup> absorption bands. On the basis of the diffusion process [9] we can write

$$x^2/t = 2D(C(\text{OH})/C(\text{F})), \quad (2)$$

where  $x$  is the depth of the colored layer,  $t$  the time,  $D$  the diffusion constant,  $C(\text{OH})$  the concentration of OH,  $C(\text{F})$  the saturated F-center concentration. Then we can write

$$(x(\text{NaOH})/x(\text{LiOH}))^2 = (N_1 C(\text{LiOH})) / (N_2 C(\text{NaOH})), \quad (3)$$

where  $N_1$ ,  $N_2$  are the numbers of F centers which are needed for reaction with one OH<sup>-</sup> center in NaF-LiOH and NaF-NaOH, respectively. The results show that the  $N_1/N_2$  ratio is equal to 2 to 3. This means that for the reaction with equal numbers of OH<sup>-</sup> in NaF-NaOH two to three times more F centers were needed than in NaF-LiOH.

#### 4. Discussion

The experimental results show that hydroxide ions interact with F centers in sodium halide crystals doped with NaOH by the reaction



The other reaction was found in NaCl [18] and NaF doped with LiOH,



One can think that reaction (5) is the first stage of reaction (4). The second stage is



The second stage can be stopped by lithium ions in crystals with LiOH impurity.

The experimental results show that the reaction of OH<sup>-</sup> and F centers is effective in sodium halides and is ineffective in potassium halides. One may think that the

reason of the reaction is energy gain (i.e. the total energy of the reaction products is lower than the energy OH<sup>-</sup> + F). The common form of reaction (1) is



where Me means alkali metal. The crystal analog of this reaction is (4). We can estimate the effectiveness of reaction (4) on the basis of reaction (7). The energies of incoming and outgoing products of reaction (7) were calculated by the Gibbs potential taken from [16]. The results show that in the alkali metals the reaction (7) is effective with Li, Na and ineffective with K, Rb, Cs (Fig. 3). Therefore, we may think that the reaction (4) is effective in Li, Na halides and ineffective in K, Rb, Cs halides. For the Na and K halides this was experimentally proved. For lithium metal the energy gain is eight times higher than for sodium metal (see Fig. 3) and we can expect that the reaction (4) will be effective also. For the Rb and Cs metals the energy loss is 1.5 to 2 times higher than for K metal and we can expect that in Rb, Cs halides (as in potassium halides) the reaction (4) will be ineffective.

The energy balance was estimated for the reaction with MeSH, too. The Gibbs potential is available for sodium metal only. The results show that such reactions have  $\approx 1.5$  eV energy gain compared with MeOH and we expect that the reaction (7) will be effective with K, too. This is consistent with the observed effectiveness of the reaction of F and SH<sup>-</sup> centers in KCl [7].

Another consequence of reaction (7) is that the reaction OH<sup>-</sup> + F is also possible at room temperature. We studied this possibility in NaF-NaOH. The crystal was X-irradiated at room temperature. Some part of OH<sup>-</sup> ions was transformed to H<sub>a</sub><sup>-</sup> centers and a large concentration of F centers was created. Then we irradiated the crystals with F light at room temperature. After that the F centers drastically decreased and H<sub>a</sub><sup>-</sup> and O<sup>-</sup> centers were created. We believe that the new centers were created by reaction (5), which is the first stage of reaction (4). It should be noted that the F-light photoaggregation in additively colored KCl-KOH crystals united the F centers with OH ions in the form of F<sub>H</sub>(OH) centers [17].

The hydroxyde ions have to be near the lithium ions in sodium halides doped with LiOH, because LiOH has a more negative Gibbs potential than NaOH. Evidently, after additive coloration the Li ion has to be near the O<sup>-</sup> ion, because in another situation the formation of O<sup>-</sup>-vacancy centers cannot be stopped. Then we can write for the process of additive coloration

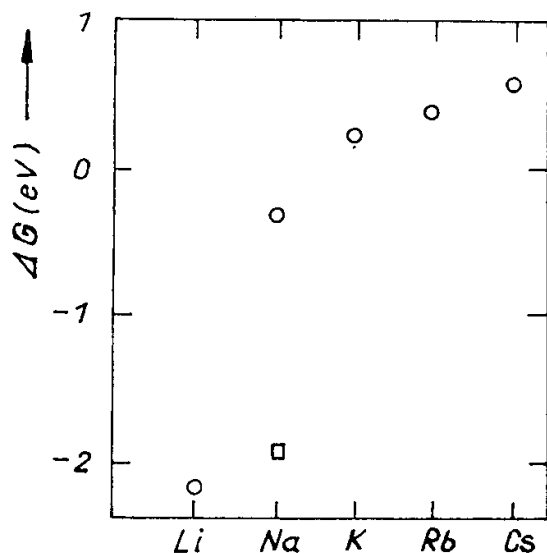


Fig. 3. The Gibbs energies of the reaction of alkali metal with metal hydroxide (○) and Na with NaSH (□) on the standard state

LiO does not exist in free state. Such a type of substance in free state exists in the form of Me<sub>2</sub>O<sub>2</sub>. The results show that the oxygen ion is more stable in the form of LiO (O<sup>-</sup> with nearest Li<sup>+</sup>) than of Na<sub>2</sub>O or possibly NaLiO (O<sup>-</sup> vacancy with nearest Li<sup>+</sup>) in the sodium halides doped with LiOH. This means that LiO has such a "crystal" Gibbs potential that reaction (8) is more effective than reaction (4) in NaCl-LiOH. With such a Gibbs potential reaction (8) will be effective in K, Rb, Cs halides, too. The H<sub>a</sub><sup>-</sup> and O<sup>-</sup> absorption bands were measured in additively colored KCl and RbCl doped with LiOH [18].

### 5. Conclusion

The reaction of OH<sup>-</sup> and F centers, which yields H<sub>a</sub><sup>-</sup> and O<sup>-</sup>-vacancy centers, is effective in NaCl, NaBr, and NaF doped with NaOH. The reaction yields H<sub>a</sub><sup>-</sup> and O<sup>-</sup> (possibly with the nearest Li<sup>+</sup> ions) centers in NaF (and NaCl [18]) doped with LiOH impurity.

The estimation of the effectiveness of the reaction of free alkali metal and metal hydroxide coincides with experimental results on the reaction of OH<sup>-</sup> and F centers in Na, K halides doped with NaOH. The estimation predicts that the reaction will be effective in Li halides and ineffective in Rb, Cs halides. The reaction which yields H<sub>a</sub><sup>-</sup> and O<sup>-</sup> centers seems to be effective in Na, K, Rb, Cs halides doped with LiOH.

### Acknowledgements

The author would like to thank V. Motorov for the preparation of NaF crystals and V. Brukvin for the NaBr crystals.

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(Received March 7, 1988)