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Optical Properties of Oxygen-Vacancy Centers in Fluorite

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The chalcogen-vacancy centers (chalcogen- $O^{2-}$ ,  $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$ ) were extensively studied in alkali halides commonly by optical and relaxation methods /1, 2/. Another type of hosts where the centers can exist are the alkaline-earth fluorides. These crystals have a rather large forbidden energy gap and the absorption of the centers has to lie in the vacuum ultraviolet (VUV) region. There is one paper on the oxygen impurity absorption of fluorite in the VUV region only /3/ and no one on other hosts. The presence of dissolved oxygen ions in fluorite leads to the appearance of some absorption bands in the VUV region /3/ and to the thermostimulated depolarisation (TSD) peak at 151 K /4, 5/. The existence of the TSD peak shows that the oxygen ion in  $CaF_2$  is connected with the anion vacancy. This note deals with the absorption, emission, and photo-dissociation of oxygen-vacancy centers in fluorite. There are two ways for the notation of the centers:  $O^{2-}v_a^+$  and  $O^{2-}F_v$ . We will use the first one and numerate the absorption bands of the centers from low to high energy.

The crystals were grown by the modified Stockbarger method /6/ in a graphite crucible in vacuum. The oxygen is removed from the melt by adding some quantity of  $CdF_2$ . At high  $CdF_2$  doping the grown crystals contain cadmium impurities and the 7.8 eV absorption band can be seen in such crystals. At "normal"  $CdF_2$  doping (usually 1 to 2 wt%) the grown crystals have no absorption bands in the VUV and are transparent up to 10 eV (Fig. 1). At low doping the grown crystals contain oxygen. The oxygen incorporates into the crystals by regrowing the "pure" crystals in poor vacuum, too. The concentration of oxygen in crystals is estimated on the basis of data published in /3/. The experimental VUV technique is described elsewhere /7/.

Absorption The spectra of  $CaF_2:O^{2-}$  crystals have two distinct bands with peaks at 6.7 and 8.5 eV at 295 K (see Fig. 1). At 80 K these peaks are

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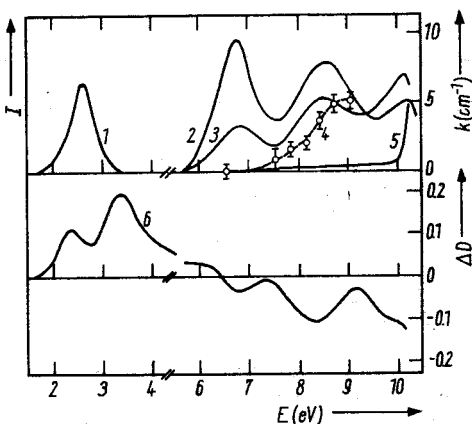


Fig. 1. The emission (1), excitation (2), absorption (3), (5), creation (4), and photodissociation (6) spectra of "pure" (5) and oxygen doped  $\text{CaF}_2$ . The emission was measured at 80 K, other curves at 295 K; in (3) the absorption of the "pure" crystal was subtracted. The creation spectrum was measured by the  $\text{F}_{2A}$  photoluminescence. The centers  $\text{O}^{2-}_v^+$  were photodissociated by unfiltered light of a DDS30 deuterium lamp

situated at 6.9 and 8.7 eV. The absorption of "pure" fluorite crystals is slowly rising from 7 to 10 eV due to unknown impurities. The absorption of unknown impurities was about  $0.5 \text{ cm}^{-1}$  in the 8 to 9 eV region and much lower at energies up to 7.5 eV. The absorption above 10 eV evidently is due to a low energy wing of the exciton band. If we subtract the absorption of "pure" crystals from the oxygen doped ones, we see a knee on the absorption curve at about 9.8 eV and the absorption band near 10.1 eV (see Fig. 1). Both absorptions appear in the photodissociation spectrum, too (see below). The results indicate the existence of four absorption bands at 6.7, 8.4, 9.8, and possibly 10.1 eV related to oxygen-vacancy centers in fluorite.

**Photochemistry** The oxygen-vacancy centers in alkali halides are photodissociated when the crystal is irradiated in the second or third absorption band /8/. The photodissociation leads to the creation of  $\text{F}$  and  $\text{O}^-$  centers:



The photodissociation of oxygen-vacancy centers in fluorite takes also place when the crystal is irradiated in the second absorption band (see below). The bands at 6.7, 8.4, 9.8, and 10.1 eV decrease and new bands at 2.3 to 2.4, 3.4 eV originate (see Fig. 1). These centers possess a fluorescence polarization, the sign of the polarization is changed from minus in the 3.4 eV band to plus in the 2.3 eV one. This property of  $\text{F}_{2A}(\text{O}^{2-})$  centers in fluorite was discovered by Feofilov /9/. The efficiency of photodissociation of  $\text{O}^{2-}_v^+$  in alkali halides dropped to zero when the temperature of crystals decreased to

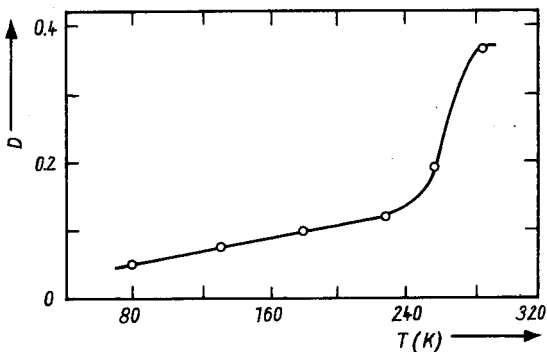


Fig. 2. Temperature dependence of the 3.4 eV absorption band of  $F_{2A}$  centers created by  $O^{2-} v_a^+$  photodissociation ( $O^{2-}$  concentration  $2 \times 10^{18} \text{ cm}^{-3}$ )

200 K /8/. We studied the photodissociation efficiency at low temperatures not directly in the VUV absorption but through the creation of  $F_{2A}$  bands. The oxygen-vacancy efficiency in fluorite is dropped at 295 to 240 K and slowly decreased at 240 to 80 K (Fig. 2). This dependence is rather unusual. The two stages indicate two different energy barriers for the dissociation of oxygen-vacancy centers in fluorite. Another feature of the low temperature photochemistry is the creation of new centers absorbed between the  $F_{2A}$  absorption bands. The centers originate at a temperature of 230 K and lower (Fig. 3). A part of the new centers is converted into  $F_{2A}$  centers when the crystal was warmed up to 295 K. The difference curve shows the two absorption bands of the centers at 3.2 and 2.8 eV (see Fig. 3). The  $F_A$  centers in oxygen doped fluorite, created by X-irradiation at 80 K, have two absorption bands at 3.2 and 2.8 eV /10/. The aggregation of  $F_A$  to  $F_{2A}$  in  $\text{CaF}_2:O^{2-}$  was coming about at 150 K /10/. Therefore we think that the F centers in  $\text{CaF}_2$  as in alkali halides are the primary products of the oxygen-vacancy photodissociation. The creating F centers then transform to  $F_A$  and  $F_{2A}$  centers.

The photodissociation at different photon energies was studied by measuring the photoluminescence of  $F_{2A}$  centers created by monochromatic VUV

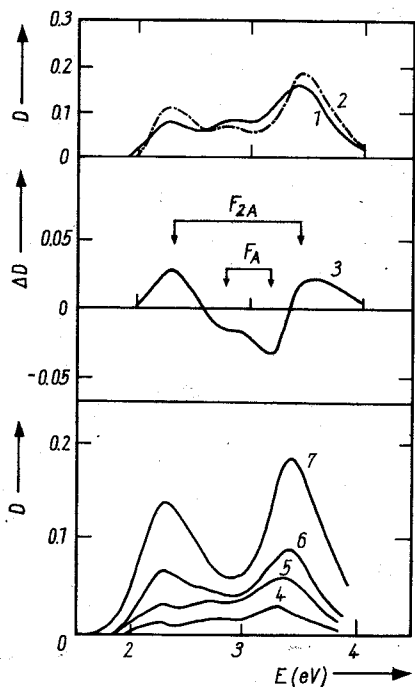


Fig. 3. Absorption spectra at 80 K of oxygen doped fluorite ( $2.5 \times 10^{18} \text{ cm}^{-3}$ ) irradiated by a DDS30 lamp at 130 (4), 230 (1), (5), 260 (6), 295 K (7). The crystal was heated then to 295 K (2); (3) is the subtracted curve between (1) and (2). The crystal was irradiated for 2 h

irradiation (see Fig. 1). The photodissociation was beginning at 7 eV, the maximum of the creation curve was at 9 eV. The results show that the photodissociation of oxygen-vacancy centers in fluorite takes place when the crystal is irradiated in the second and third bands of the centers.

It is not clear where the absorption of  $\text{O}^-$  ions in fluorite is. Absorption of  $\text{O}^-$  in alkali halides is between the third of the  $\text{O}^{2-}\text{v}_a^+$  bands and the exciton band. That is not the case with fluorite. There is no ad-

ditional band near the exciton absorption which appeared after the photodissociation of the oxygen-vacancy centers (see Fig. 1). The  $\text{O}^-$  ions cannot diffuse and aggregate to another form in fluorite at room temperature. The thermal stability of  $\text{O}^-$  at room temperature was proved by ESR /11/. Probably, the  $\text{O}^-$  absorption band in fluorite is rather close to the exciton band and cannot be seen in our spectra.

**Aggregation** The oxygen-vacancy centers in alkali halides at temperatures above room temperature diffuse and aggregate to dimers and more complex centers /8/. The centers in LiF are more stable, they diffuse above 200  $^\circ\text{C}$  /13/. We tried to find this process in fluorite. The temperature 800  $^\circ\text{C}$  is sufficient for CaO dissolution in fluorite /4, 12/. First, we annealed the crystals at 800  $^\circ\text{C}$  and then at temperatures between 50 and 500  $^\circ\text{C}$  for 1 to 20 h. There was no detectable change of the VUV absorption.

**Photoluminescence** The spectrum consists of one emission band with a maximum at 2.6 eV and a halfwidth 0.5 eV at 80 K, which exists in all ab-

sorption bands (see Fig. 1). The emission intensity increases by about 30% from 295 to 80 K. The photoluminescence in  $\text{CaF}_2$  and LiF is close to each other and sufficiently differs from that in KCl and KBr. The two radiative transitions from the second excited level to the first excited and ground levels were seen in KCl and KBr at temperatures lower than 77 K /8/. In LiF /13/ and  $\text{CaF}_2$  there is one radiative transition from the first excited to the ground level.

The optical properties of oxygen-vacancy centers in  $\text{CaF}_2$  are commonly close to those in alkali halides (absorption, emission, photochemistry).

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