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Photodissociation of $O^{--}V_a^+$ Centers in Lithium Fluoride

By

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The photochemical reactions of chalcogen-vacancy centers (chalcogens: O^{--}, S^{--}, Se^{--}, Te^{--}) have been studied in some papers /1 to 7/. The centers cause three absorption bands in alkali halides /7/. Photochemical reaction takes place when a crystal is irradiated in the second or third absorption band at temperatures above 200 K. Part of chalcogen-vacancy centers converts to Ch^- ions and F centers:

$$Ch^{--}V_a^+ \rightarrow Ch^- + F \ . \tag{1}$$

When a crystal is irradiated at liquid helium temperatures the new F centers are disturbed by the Ch^- anion in the nearest neighbourhood /6/.

The optical properties of oxygen-vacancy centers in lithium fluoride have been studied in previous papers /8, 9/. In this note we report some results on photodissociation of $O^{--}V_a^+$ centers in lithium fluoride.

Crystals doped with 0.08 wt% of Li_2O in the melt were studied /9/. The absorption spectra were taken with a VMR-2 1m vacuum grating monochromator. The light source used was a duoplasmatron with a discharge in hydrogen atmosphere /10/. The light detector was a solar blind photomultiplier FEU142 with MgF_2 window. It can be used up to 10.9 eV. At higher energies light was detected by a VEU-6 channeltron, or a usual photomultiplier covered with sodium salitsilate. All detectors have been used in photon counting regime. The experimental devices were driven by a SM1 minicomputer. Absorption spectra have been measured at room temperature. The photodissociation of $O^{--}V_a^+$ centers was accomplished by the unfiltered light of a VMF 25 hydrogen lamp with MgF_2 window.

The $O^{--}V_a^+$ centers in lithium fluoride have two absorption bands at 6.5 and near 11 eV /9/. There was no photochemical reaction when a crystal was irradiated in the first absorption band at 6.5 eV. Irradiation with VMF 25 light

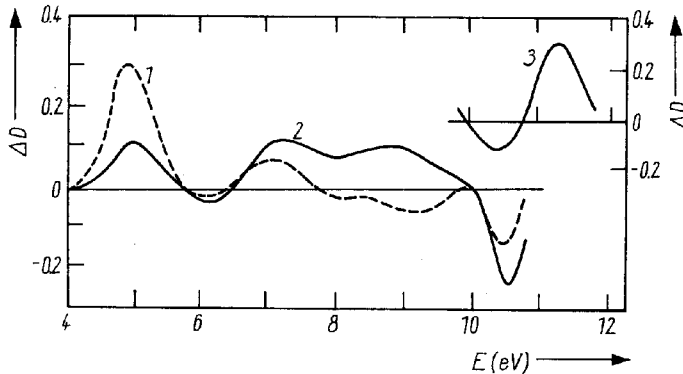---

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Fig. 1. Change of optical absorption due to irradiation of $LiF:Li_2O$ by un-filtered light of a VMF 25 hydrogen lamp at (1) 80 K, (2), (3) 295 K. The thickness of crystals was 0.68 mm (1), (2) and 0.33 mm (3)

at 295 K converted the $O^{--}V_a^+$ centers to centers at 4.95 eV (F center) and 11.3 eV and centers at 7.3 and 8.8 eV (Fig. 1). The 11.3 eV centers are probably O^- ions. Therefore the photochemical reaction is

$$O^{--}V_a^+(6.5, \ 10.5 \ eV) \rightarrow O^-(11.3 \ eV) + F(4.95 \ eV) \ .$$
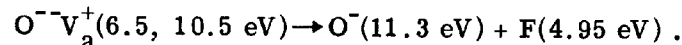
Possibly, the two other centers at 7.3 and 8.8 eV are originated when part of F centers $(e^- + V_a^+)$ is connected with some unknown impurities. The new F centers created by photochemical reaction decay at 200 to 300 °C and the initial quantity of $O^{--}V_a^+$ centers is recovered. The efficiency of photodisso-ciation of $O^{--}V_a^+$ centers at 80 K was about three times smaller than at room temperature. The part of F centers at 80 K was created by the decomposition of 9.3 eV centers (see Fig. 1).

The O^- ions in alkali halides are also produced by photodecomposition of OH^- ions /11/. The photodissociation process is

$$OH^- \rightarrow O^- + H_i^o$$
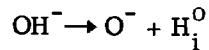
in which neutral interstitial hydrogen atoms (U_2 centers) and substitutional O^- centers are formed. The presence of O^- ions was detected by magnetic res-onance only in RbCl /12/. The absorption bands of O^- ions were found in KCl, KBr, NaCl crystals by Kerkhoff et al. /13/. The photodissociation of OH^- ions in NaF was studied by Freytag /14/. He found a new band at 8.8 eV, which he related to O_2 molecules. His conclusion was based on the fact that the

Table   1

Experimental and calculated values of O^- absorption in alkali halides (in eV). Absorption bands measured at 20 K (NaCl, KCl, KBr) and at 295 K (LiF, NaF)

	LiF	NaF	NaCl	KCl	KBr
$E(O^-)_{exp.}$	11.3	8.8	7.27	6.77	6.37
$E(O^-)_{calc.}$	10.4	9.1	7.3	7.1	6.7

O^- ions at room temperatures aggregated to molecules in KCl, KBr /13/. In alkali fluoride the diffusion of O^- ions is more difficult than in chloride and bromide, because of the smaller radius of F^- ions. We think the 8.8 eV band in NaF is more probably related with O^- ions.

The O^- ion in alkali halides may be regarded as impurity with smaller electron affinity than a halogen ion. Therefore, the energy level of O^- ions has to be placed somewhat higher than the top of the valence band (p-band of halogens). Exciton absorption related to O^- ions (when electron transfer from the p-level of O^- to the s-level of alkali metal occurs), has to lie on the low energy side of the first exciton band of the pure crystal. The simplest expression for the energy required in such a charge transfer process is

$$E = E_A - E_I + E_M \ ,$$

where E_A electron affinity, E_I first ionization potential of alkali metals, E_M Madelung energy. Kapphan and Lüty had success in calculating the OH^- absorption bands in alkali halides on the base of such a relation /14/. One can hope that such a simple relation is applicable to the O^- absorption and the Mollwo-Ivey type relation can be used. The calculated energies of O^- absorption rather well agree with experimental data (Table 1), if we take a value of $E_A = 3.5$ eV. This value is much greater than the experimental value of the free O^- ions (1.47 eV). The used value of E_A can be regarded as an "effective" one, which includes all of the neglected polarisation effects. The Mollwo-Ivey type relation between absorption energies and lattice constant is valid, too (Fig. 2). It is interesting that the slope of the line for O^- ions is equal to that for OH^- ions. It means that the charge transfer process is
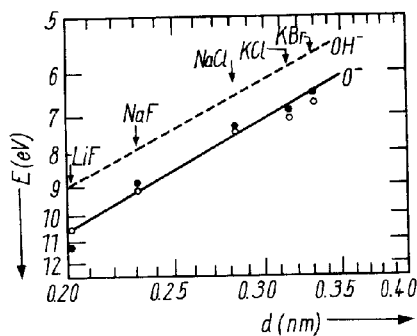
Fig. 2. Mollwo-Ivey type relation for O^- and OH^- centers in alkali halides. Open circles are calculated and full ones are experimental data

operative for both absorptions.

The experimental results led us to the following conclusion: the $O^{--}V_a^+$ centers in lithium fluoride are converted to O^- ions and F centers when the crystal is irradiated in the second absorption band, like in other alkali halides.

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