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Optical Transitions of Chalcogen-Vacancy Centers in Ionic Crystals

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The chalcogen-vacancy centers (chalcogen- O^{2-} , S^{2-} , Se^{2-} , Te^{2-}) have been studied extensively since 1965, when Fischer et al. opened a new type of impurity centers in KCl /1, 2/. Recently, the oxygen-vacancy centers were studied by optical methods in CaF_2 /3, 4/. The centers have four absorption bands. Three bands are related with "inside" transitions and the highest energy band with exciton transitions disturbed by anion vacancies of the centers /1/. The model of electron transitions of chalcogen-vacancy centers was first postulated by Gümmer for the oxygen vacancy in KCl and KBr /5/. According to the model the electron from the oxygen ion levels is transferred by absorption to the levels of the anion vacancy (i. e. levels of the F-center without electron). The first absorption band is related to the electron transfer into the ground state F-level. The second band is related to the transfer into the first excited F-center level. Later, the third absorption band was explained as an electron transfer into level L_1 of the F-center /6/.

In this note we improve the model of Gümmer by the assumption that the chalcogen-vacancy centers and the hydrogen halide molecules have - in first approximation - the same scheme of electron levels.

The emission of the oxygen-vacancy centers in KCl, KBr takes place under irradiation with light into the second or third absorption band at temperatures lower than 77 K /5/. The electrons have two ways to return to the ground state. The first one is the transfer from the second excited level to the ground level directly (with the emission of a visible photon). The second one is the transfer from the second excited to the first excited level (with a perturbed F-emission) /5/. Photodissociation of the chalcogen-vacancy centers takes place also under irradiation with light into the second or third absorption bands. The reaction products are F-centers and Ch^- ions, which are only

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stable when irradiation was done at temperatures above 200 K /7/. At liquid helium temperatures photodissociation takes place also but the formed F-centers are now perturbed by the neighbouring Ch^- ions. The absorption band of this perturbed F-center is shifted to low energies (by 0.05 eV) and is broadened (by 0.1 to 0.2 eV) in comparison to "normal" F-absorption /8/. This type of F aggregate centers was called " F_H -centers". The perturbation from the anion impurities on the F-center is too weak to lead to a sizable splitting of the 2p excited state (like in the F_A case). Several F_H -centers were discovered and studied recently (with H^- , OH^- , CN^- , F^- impurities) /9 to 12/. At liquid helium temperatures the $\text{F}_\text{H}(\text{Ch}^-)$ centers are stable. Above 77 K they are converted back into chalcogen-vacancy centers /8/. The emission and photochemistry results lead to the conclusion that the electrons of the chalcogen-vacancy centers in the ground state are localized on the chalcogen ions while the excited states originate from levels of F-centers.

We can see some analogies between the hydrogen halide molecules and chalcogen-vacancy centers. The Ch^- ion and halides have a p^5 outer shell. The F-center and H atom both have one 1s electron so that the F-center in alkali halides can in first approximation be described as an H atom. The ground state electron is in the 1s level, the first (F-band) and second (K-band) absorption is related with the transfer to 2p and 3p levels, respectively. Let us take the Ch^- ion and F-center and put them into the nearest anion sites of the lattice. What will occur to the F-center electron? The experiments show that the electron will be moved to the ground chalcogen-vacancy state (at high enough temperatures), i. e. the chalcogen-vacancy configuration is more stable than the $\text{F}_\text{H}(\text{Ch}^-)$ one /8/. If the z-axis is along the Ch-F direction, the p_x , p_y electrons are not taking part in the chemical bond, because of a small intersection between 1s(F) and p_x , $p_y(\text{Ch}^-)$ orbitals. From $p_z(\text{Ch}^-)$ and 1s(F) orbitals, however, originate two σ orbitals. The lower energy orbital is commonly a p_z orbital with small addition of 1s (Fig. 1). The molecule has four electrons in the π antibonding orbitals (which are from the p_x , p_y orbitals of chalcogen) and two electrons on the σ bonding orbital. The ground state is $^1\Sigma^+$.

The first absorption band of the chalcogen-vacancy centers is related to the transition from the p chalcogen levels to the 1s level of F-center. For our scheme we can write the two following lowest excited terms: $(\sigma^2, \pi^3, \sigma^1)^1, ^3\Pi$

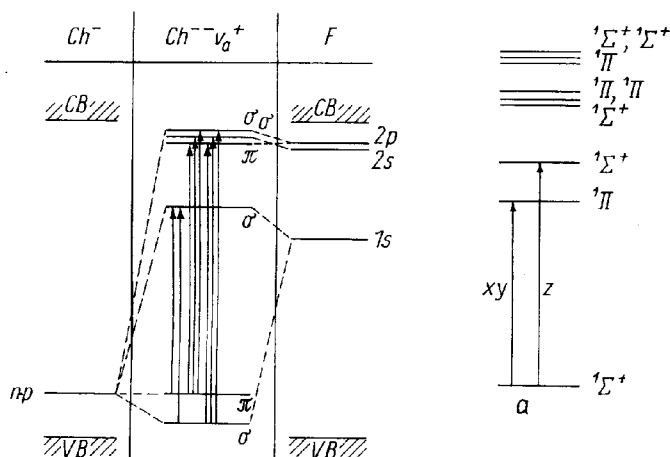


Fig. 1. Energy level-schemes of one-electron orbitals of Ch^- , $\text{Ch}^{2-}v_a^+$, and F-centers in ionic crystals. The valence and conduction bands are schematically plotted for the Ch^- and F centers (VB and CB); a) energy terms of the first and second absorption bands of the chalcogen-vacancy centers

and $(\sigma^1, \pi^4, \sigma^1)^1, 3\Sigma^+$. The allowed transitions are $1\Sigma^+ \rightarrow 1\Sigma^+$ and $1\Sigma^+ \rightarrow 1\Pi$. Both transitions are oriented. $1\Sigma^+ \rightarrow 1\Pi$ is oriented perpendicularly to the molecular axis and $1\Sigma^+ \rightarrow 1\Sigma^+$ along the axis (see Fig. 1a). Consequently, the first absorption band must be split into two components and the sign of polarization of the emission must be changed within the absorption band (if the emission transition is $1\Pi \rightarrow 1\Sigma^+$). The splitting value depends on the intersection between the p_z and $1s$ orbitals. The splitting of the first absorption band cannot be observed in crystals with oxygen- or sulfur-vacancy centers. But the selenium and tellur-vacancy centers show a splitting of the first absorption band (about 0.25 and 0.6 eV) /13/. The size of chalcogen ions increases in the sequence of O, S, Se, Te and it is reasonable that for the largest ions the splitting of the absorption band is large enough to be seen in the spectra. The polarization of emission was measured for oxygen-vacancy centers in LiF /14/ and CaF_2 (Fig. 2). The polarization sign is changing when exciting it across the first absorption band in LiF . The polarization of emission in CaF_2 is more pronounced. The polarization changes sign from plus when exciting at the low energy side of absorption band to minus at high energy excitation (see Fig. 2). The splitting of the oxygen-vacancy first absorption band is less than 0.2 eV in both crystals and cannot be seen in the absorption or excitation spectra.

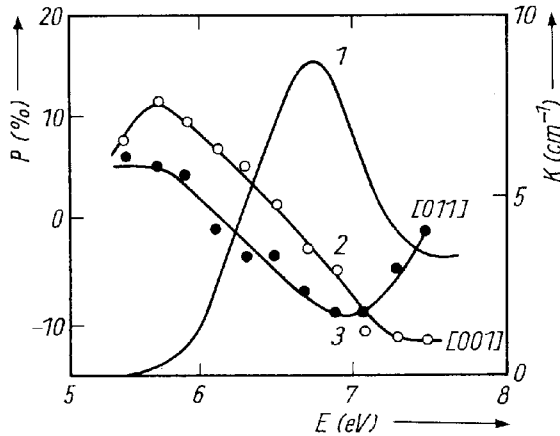


Fig. 2. Absorption (1) and polarization (2), (3) spectra of oxygen doped crystal of CaF_2 . Polarization of the 2.6 eV emission was measured with a pile of fused silica plates. The spectra were taken at room temperature. The oxygen concentration was 10^{18} cm^{-3}

The energy of the 2s level of an F-center in alkali halides is rather close to the energy of the 2p level /15/. Therefore, the second absorption band of chalcogen-vacancy centers is related with the transfer of electrons to the 2s and 2p F-center levels. The 2s level transforms into the σ orbital, and the 2p one into σ , π orbitals. The addition of p chalcogen orbitals is much smaller than in the case of the first excited state. In total six transitions are allowed (see Fig. 1a), so that the structure of the second absorption band is more complicated than the first one. All transitions can be singled out into two groups. In the first group the transitions started from π orbitals, in the second group from σ orbitals. When the σ - π separation is high enough (in the case of Se, Te ions) the splitting of the band can be seen /13/.

The nature of the third absorption band is not so clear as that of the two lower energy bands. This absorption can be related with highly excited states of F-centers (K- or L-states).

What is the range of validity of this model? We think the molecular-like model will be valid for impurities whose levels are rather far from band states. If the impurity levels have a well defined atomic or ionic character, the crystal environment cannot drastically change the molecular picture of levels. The levels of an F-center originate approximately from s levels of the host metal.

Nevertheless the ground and first excited levels of the F-center have a rather "atomic" character. We think the molecular description of the chalcogen-vacancy transitions is a good approximation for the first and second absorption bands, but it is less correct for the third one.

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