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$F_H(O^{2-})$ Centers in Calcium Fluoride Crystals

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The spatial structure of $F_H(O^{2-})$ centers in CaF_2 is studied by optical dichroism and ESR methods. The dichroism of absorption is induced by light in both F_H bands in additively and X-ray colored samples. The results are correlated with the C_2 crystal axes of F_H defects. The ESR spectrum of F_H centers is rather similar to that of pure F centers. Both dichroism and ESR results prove that an oxygen ion occupies a (110) anion site around the F center.

Пространственная структура $F_H(O^{2-})$ центров в кристаллах CaF_2 изучена с помощью оптического дихроизма и ЭПР. Дихроизм поглощения наводился светом из обоих F_H полос как в аддитивно окрашенных так и в кристаллах окрашенных рентгеновским излучением. Результаты находятся в соответствии с ориентациями осей F_H центров по C_2 кристаллическим осям. Спектр ЭПР F_H центров подобен спектру невозмущенных F центров. Результаты по дихроизму и ЭПР доказывают, что ион кислорода занимает (110) анионный узел около F центра.

1. Introduction

F_H centers in alkali halide crystals are formed by association of F centers with anionic impurities like OH^- , CN^- , H^- , F^- , etc. [1]. The other possible anionic impurities which may trap the F centers are chalcogens. The $F_H(O^{2-})$ centers were found in LiF, NaCl, CaF_2 [2], and BaFBr [3] crystals recently. The F_H centers have pronounced different properties in host crystals with different structures [4]:

(i) In cesium halides and alkali earth fluorides the F_H centers are characterized by a strong (≈ 0.7 eV) splitting of the electronic absorption. The large splitting of the F_H absorption band is due to an anionic impurity on a next-nearest neighbor lattice site with respect to the F center in the cesium halide lattice. In a previous paper, on the basis of the rather large (≈ 0.35 eV) splitting of the $F_H(O^{2-})$ absorption band in CaF_2 , we assumed that the oxygen ion occupies a nearest lattice anion site [2]. In the fluorite lattice the first shell around the F center consists of metal ions and the second, third, and fourth ones of fluorine ions.

(ii) In contrast to this F center–anionic impurity association in crystals of NaCl structure and in BaFBr the normal F center absorption only broadens and shifts without splitting. It is usually assumed that the impurity anion is in the second shell, i.e. in a (110) position. The ENDOR measurement shows that the F^- , H^- , OH^- impurity ions occupy a (200) position, i.e. a fourth shell position in contrast to expectation and the CN^- impurity ion occupies a (110) position [1].

The absorption and dichroism of absorption of F_H centers disturbed by O^{2-} ions in CaF_2 crystals was studied for the first time by Rauch and Schwotzer [5]. They assumed the existence of two types of F_H centers with $\langle 100 \rangle$ and $\langle 111 \rangle$ symmetry axes.

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In this paper we study the $F_H(O^{2-})$ spatial structure in CaF_2 crystals by ESR and optical dichroism methods and conclude that the oxygen ion occupies a third shell (110) position.

2. Experimental

The crystals were grown by the Stöber method in a graphite crucible in vacuum. No efforts were made to remove the oxygen impurity from the CaF_2 powder and the prepared samples contain about 10^{18} to 10^{19} cm^{-3} oxygen–vacancy centers. The concentration was estimated measuring the absorption band at 6.45 eV and using the relation between this absorption and the oxygen concentration published in [6].

The F_H centers in oxygen-doped crystals can be created through X-irradiation or additive coloration procedures. The optical properties of both F_H centers are the same. The X-irradiated crystals contain a large amount of some hole centers which obscured the observation of the weaker ESR spectra of electron excess centers. Therefore we used the additively colored samples for the ESR measurements.

The crystals were additively colored by the van Doorn method [7]. Samples were heated at 750 °C in a calcium vapour inside the evacuated nickel tube. After 1 to 2 h the crystals were slowly cooled to room temperature. Then the samples were cut out or sawed in the desired orientation and size and polished if necessary. Just before the measuring procedure the samples were annealed at 600 °C in an Al foil and rapidly quenched.

Absorption spectra were taken with “Specord M40” spectrophotometer and the ESR spectra with a RE1306 ESR spectrometer. Light irradiation was carried out using a 500 W high pressure mercury lamp through appropriate filters. The X-irradiations were performed with a Pd tube operating at 40 kV and 50 mA.

3. Results and Discussion

3.1 X-ray coloration and pre-annealing

In a previous paper [2] we found that under X-irradiation the $F_H(O^{2-})$ and V_k centers were created simultaneously and we assumed that the $F_H(O^{2-})$ center was created when a mobile electron was captured by an oxygen–vacancy complex. We have found new data which prove our assumption.

As in other crystals the oxygen–vacancy dipoles in CaF_2 above 100 °C can aggregate. This leads to a decrease of the thermal depolarization peak at 151 K and the decreasing curve corresponds to a dimerization process. When a quenched sample was previously annealed above 100 °C the coloration effectiveness decreased also. After annealing the sample was X-irradiated in liquid nitrogen, heated to room temperature, and the absorption spectrum was measured. When a CaF_2 sample doped with oxygen was X-irradiated at 80 K the $F_H(O^{2-})$ and V_k bands appeared. After heating to room temperature the V_k center disappeared and $F_H(O^{2-})$ centers transformed into F_{2H}^+ ones. In the F_{2H}^+ center the electron is bound to a pair of anion vacancies. The perturbation of the F_{2H}^+ center by anionic impurities usually is designated as F_{2H}^+ . Therefore, the heights of the F_{2H}^+ bands are directly proportional to the $F_H(O^{2-})$ ones before heating. The decreasing curves of the F_{2H}^+ absorption bands and of the 151 K thermal depolarization peak due to pre-annealing, are rather similar (Fig. 1). When the annealing temperature was increased, the dipole concentration and the X-ray colorability decrease faster. These results prove that the creation of F_H -oxygen centers is related to dipoles, not to dimers or other oxygen dipole complexes.

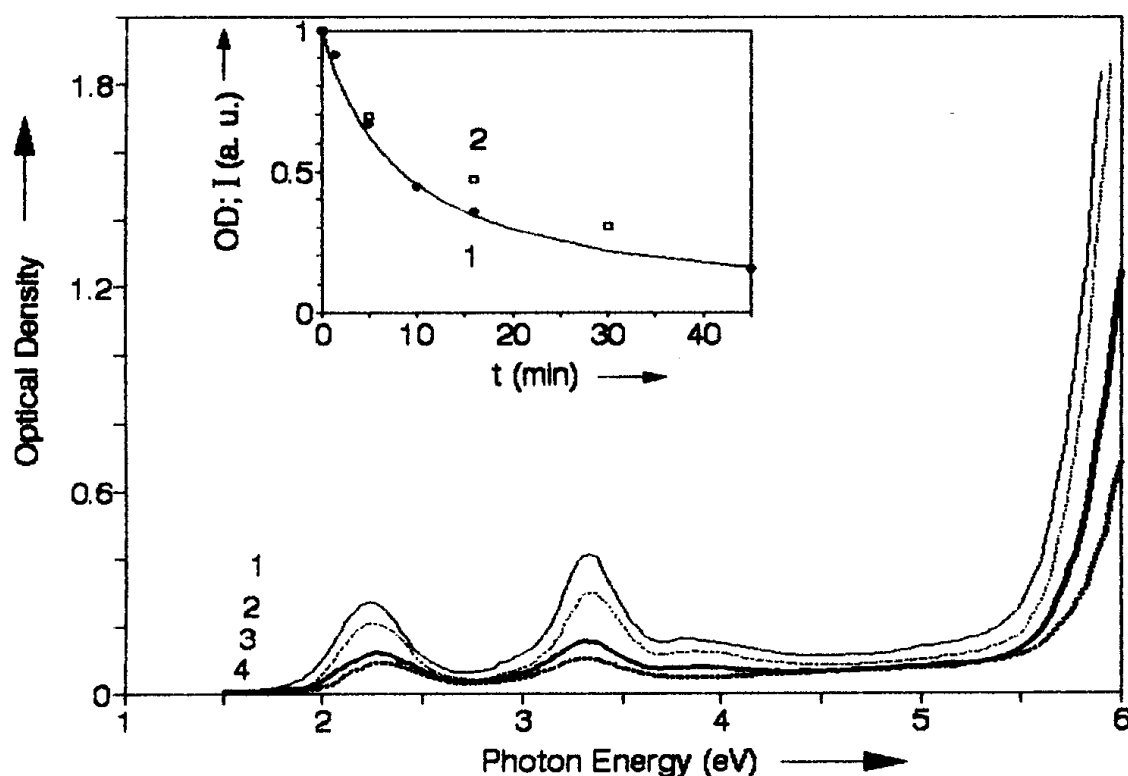


Fig. 1. Decrease of X-ray coloration of the CaF₂ crystal due to pre-annealing at 150 °C for 3 min (2), 10 min (3), 35 min (4). Curve (1) without pre-annealing. Inset: dependence of the 3.35 eV absorption band (1) and 151 K thermal depolarization peak (2) on pre-annealing time at (2) 137 and (1) 140 °C

The X-ray coloration at room temperature decreases due to pre-annealing also. The coloration intensity at room temperature is several times higher than at 77 K due to thermally activated dissociation of excited oxygen–vacancy centers [8]. The coloration process at room temperature is more complicated than at 77 K but also directly related to the initial concentration of oxygen–vacancy dipoles.

When CaF₂ samples were annealed above 700 °C, the maximum aggregation stage, estimated by X-ray colorability and shift of the absorption edge near 6 eV, was several times lower than at 600 °C annealing. The reason for this behavior is unknown.

3.2 Conversion of centers

After quenching, the additively colored sample has an absorption spectrum which belongs mostly to F₄ centers (four F centers arranged on adjacent sites) [9] and has no measurable ESR spectrum. When the sample was irradiated with 313 nm light near room temperature, the primary absorption spectrum completely changed to that of F_{2H}⁺ (F₂⁺ disturbed by oxygen) (Fig. 2). The resulting ESR spectrum was rather smooth (Fig. 3). Then with 313 nm irradiation at 77 K the F_{2H}⁺ centers converted to F_H(O²⁻) ones with a double absorption band at 2.85 and 3.2 eV (Fig. 2). The ESR spectrum becomes more resolved (Fig. 3). As much as 2/3 of the initial F_{2H}⁺ centers can be optically transformed to F_H(O²⁻) ones. When the crystal is heated, the F_H(O²⁻) centers exhibit a back reaction to F_{2H}⁺, as seen from the optical and ESR spectra. Such thermal conversion was studied earlier in CaF₂ crystals doped with oxygen X-irradiated at 77 K [5] and more extensively in additively or X-ray

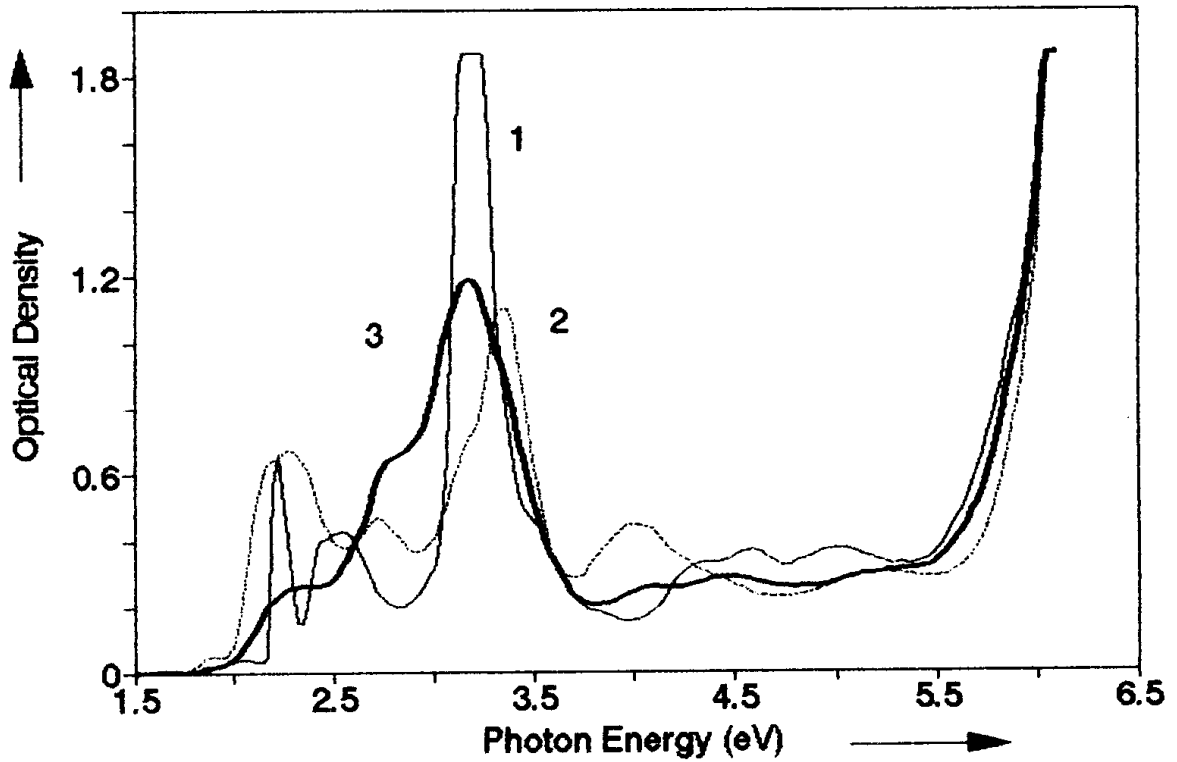


Fig. 2. Absorption spectra at 80 K of an additively colored CaF₂ crystal, (1) quenched from 600 °C, (2) irradiated with 313 nm light at room temperature, and (3) subsequently at 80 K

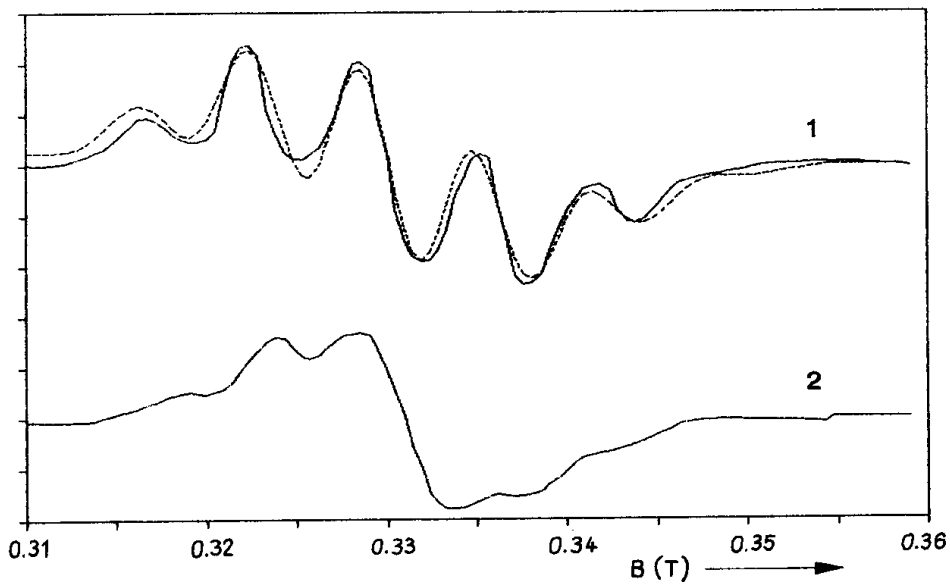


Fig. 3. ESR spectra of CaF₂ irradiated with 313 nm light, (1) at room temperature and then at 77 K and (2) after heating up to 290 K, measured at 77 K with $B \parallel \langle 111 \rangle$. The dashed curve shows the spectrum which was calculated with the following parameters: seven Gaussian peaks with intensity ratio 1:6:15:20:15:6:1, peak to peak distance 5.9 mT, individual linewidth 3.5 mT

colored CaF₂ doped with Na⁺ [10]. We found that this process in CaF₂ can be initiated by optical excitation into the F_H(O²⁻) bands at 77 K also. The back conversion was detected by optical and ESR absorption. The thermal and optical conversion processes at 77 K — F_{2H}⁺ to F_H(O²⁻) and vice versa — is fully reversible and can be repeated many times. It seems that the forward and backward reactions occur through electron transfer only. In CaF₂:Na⁺ crystals photoconductivity was found under irradiation at high energy bands of F_{2A}⁺ and at both bands of F_A(Na⁺) centers [10]. The photoconductivity at both F_H(O²⁻) bands in CaF₂:O²⁻ was found also [5]. The creation of F_H(O²⁻) centers under X-irradiation occurred when a mobile conduction band electron is trapped by an oxygen–vacancy center [2]. Probably, when a CaF₂ crystal is irradiated with 313 nm light the electron of the F_{2H}⁺ center transfers through the conduction band to the oxygen–vacancy center. It leads to the conversion of F_{2H}⁺ to F_H(O²⁻) centers. The back process under light irradiation seems to be an electronic transfer also.

When a sample with F_{2H}⁺ is kept for a long time at room temperature or is briefly heated to 100 °C, a new absorption band appears in the F-band region together with a drop of the F_{2H}⁺ bands. The ESR spectrum of the new centers is very similar to that of the F centers. In the <100> direction the spectrum is a little bit less resolved than in other ones. Above 150 °C both this new absorption band and the ESR spectrum completely decrease and other absorption bands together with a single ESR line near $g = 2.00$ appear. Possibly, in this case the initial stage of the thermal destruction of the F_{2H}⁺ centers has occurred and we observe the almost “pure” ESR and optical spectra of the released F centers. Above 150 °C the liberated F centers are trapped by some defects and disappear from the optical or ESR absorption spectra.

3.3 Dichroism of absorption

For studying the dichroism of absorption we use samples sawed out parallel to (100) crystal planes. For studying the <100> dichroism the sample was first bleached optically by light polarized along a <001> axis and then two absorption spectra were measured: one with light polarized along to the <001> axis and the other along the <010> one. The difference between the spectra taken perpendicular and parallel to the polarization of bleaching light characterized the value and sign of the dichroism of the absorption bands.

Both the <110> and <100> dichroism were induced by the irradiation in the low or high energy bands of F_H(O²⁻) centers in the additively colored samples (Fig. 4). While the <110> dichroism shows the usual behavior, the spectra of the <100> dichroism are rather unusual.

To exclude the influence of the F_{2H}⁺ absorption on the F_H(O²⁻) one we measured the dichroism of absorption of X-ray colored samples. When samples were photobleached in either of both F_H(O²⁻) bands, all bands (F_H(O²⁻) and V_k) decreased. This process can be prolonged until full disappearance of the color of the sample. The following X-irradiation leads to the creation of the same F_H(O²⁻) and V_k bands as before. The F_H(O²⁻) bands in X-rayed samples were bleached optically extremely easy, about 100 times faster than in the additively colored ones.

The attained X-ray colorability of the samples is about four times lower than in the additively colored samples. Nevertheless the relative value of the dichroism of F_H(O²⁻) bands in X-rayed samples was higher than in additively colored ones.

The <110> dichroism of 3.2 and 2.85 eV bands in the X-rayed samples was rather large when the sample was bleached in 2.85 or 3.2 eV bands (Fig. 5). The <100> dichroism shows

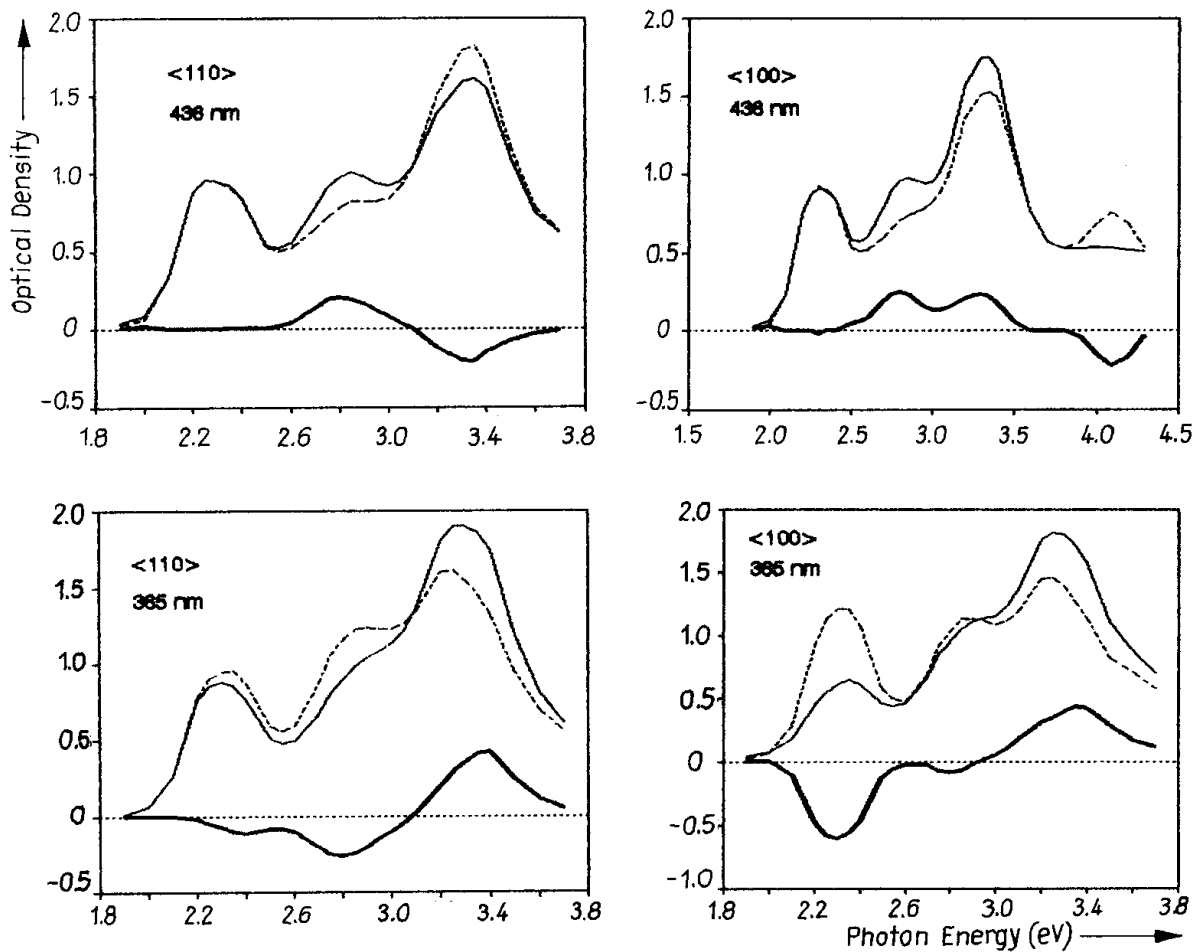


Fig. 4. Dichroism of additively colored CaF_2 samples induced with $\langle 110 \rangle$ or $\langle 100 \rangle$ light. --- measured parallel to the bleaching light, ——— measured perpendicular to the bleaching light, ——— difference spectrum

the same behavior as the $\langle 110 \rangle$ one but the degree of $\langle 100 \rangle$ dichroism was about two or three times lower (see Fig. 5).

The behavior of the dichroism in X-rayed samples is fully consistent with the orientation of the defect axis along the C_2 crystal axes. The dichroic behavior will be similar to the azimuthal dependence of the polarization of luminescence, which was considered in detail by Feofilov [11]. For a (100) cut crystal plate the existence of $\langle 100 \rangle$ and twice larger $\langle 110 \rangle$ dichroism means that the defects are oriented along the C_2 crystal axes. Both these features were measured in our case. Obviously the 'abnormal' behavior of the $\langle 100 \rangle$ dichroism of $F_H(O^{2-})$ centers in additively colored samples is caused by the presence of the 3.4 eV band of the F_{2H}^+ centers. It is not so clear how the 436 nm light irradiation can orient the F_{2H}^+ centers (see Fig. 4). The comparison of Fig. 4 and 5 allows us to conclude that the dichroism of additively colored samples is formed not only by $F_H(O^{2-})$ centers but by F_{2H}^+ also. The full picture of dichroism curves in additively colored samples is rather complicated. But it is clear that the $F_H(O^{2-})$ centers in additively and X-ray colored samples are the same.

When the F center is disturbed by a nearby defect the degenerate p-like excited state is split in two ones and the F absorption band will be split in two bands. In one band the

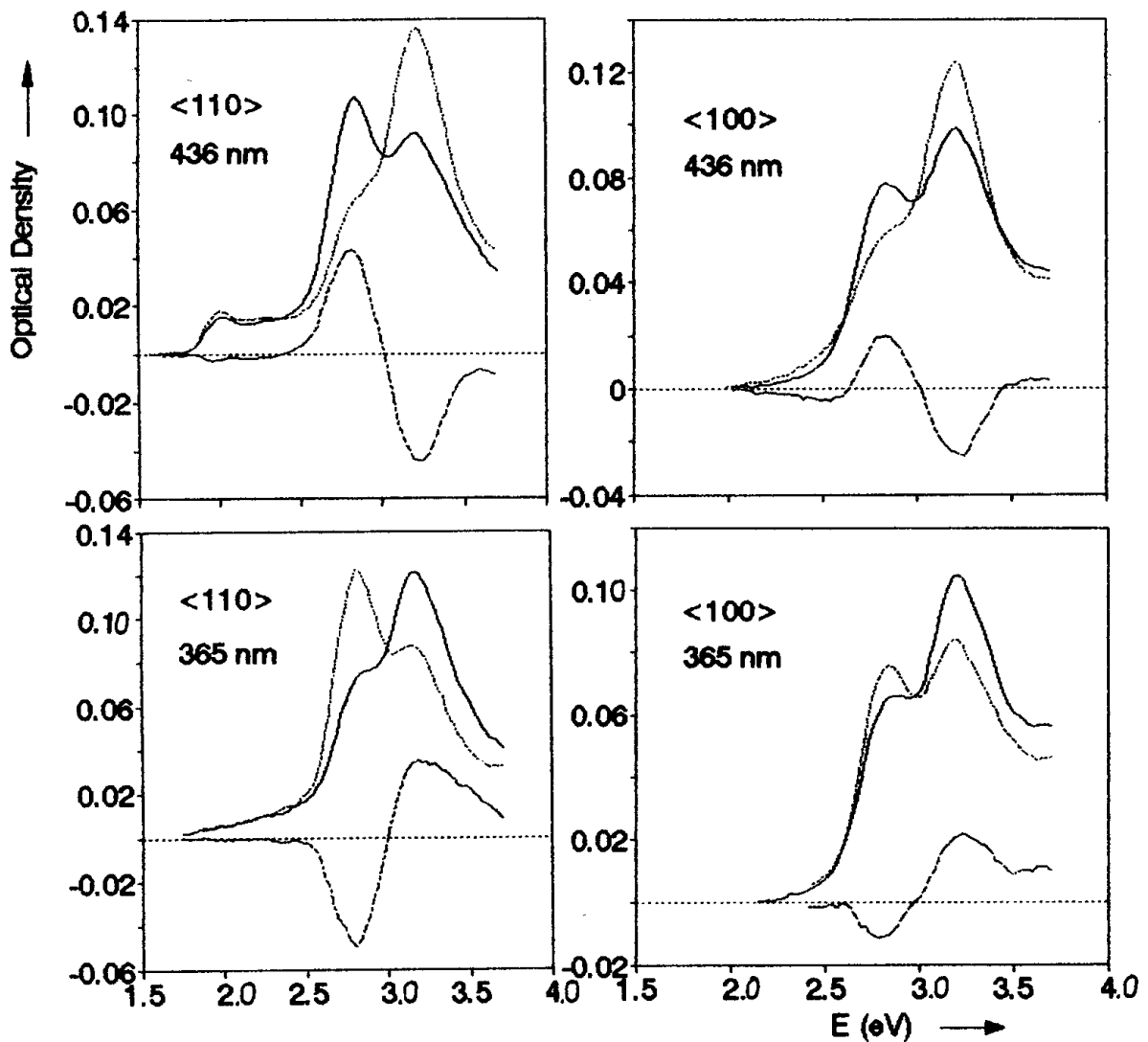


Fig. 5. Dichroism of X-ray colored samples. measured parallel to the bleaching light, ——— measured perpendicular to the bleaching light, - - - difference spectrum

transitions will be oriented along the axis between F center and defect and in the other band the transition will be oriented in the plane perpendicular to that axis. From the dichroism of absorption one can conclude that the O^{2-} ion is in a position along a $\langle 110 \rangle$ direction from the F center. In contrast to the assumption of Rauch and Schwotzer [5] on the existence of two types of $F_H(O^{2-})$ centers with C_4 and C_3 axes, our results point to a single type of center with a C_2 axis.

3.4 ESR spectra

The ESR spectrum of the $F_H(O^{2-})$ centers (see Fig. 3) is rather similar to that of F centers. The calculated spectrum correlates well with the observed one if the parameters of individual lines are close to those of the F center (see Fig. 3). The spectrum is weakly anisotropic. With the magnetic field along a $\langle 111 \rangle$ direction the spectrum is best resolved. The seven-line structure with intensity ratios 1:6:15:20:15:6:1 points to the fact that the second shell

around the F center consists of six equivalent fluorines (with spin 1/2). The peak to peak distance between the lines is 5.9 mT which is rather close to the 6.1 mT observed for F centers [12]. The individual linewidth was 3.5 mT which is about 50% higher than for F centers (2.3 mT [12]). One can conclude that the enlarged individual linewidth is caused by the presence of some defects in the third shell around the F center.

3.5 Spatial structure

Why is the oxygen ion located in the third shell around the F center and not in the nearest anion site? The reason is unclear. In most of the known F_H centers the impurity ion occupies a fourth shell (200) position, while the CN^- ion occupies a second shell (110) position in the KCl crystal [1].

The other question is why the splitting of the $F_H(O^{2-})$ band in CaF_2 is so large. The other known F_H centers with impurity ion in (110) or (200) sites only slightly disturb the excited states of the F centers. Possibly the excess charge on the oxygen ion is the reason for the splitting. The theoretical estimations show that both a positive and negative charge leads to a rather large splitting of the excited states of F centers in alkali halide lattices [13, 14]. In this case the F center is disturbed by long-range Coulomb forces.

4. Conclusion

Our experimental results show that the $F_H(O^{2-})$ center in CaF_2 consists of an F center disturbed by an oxygen ion in the third shell around the F center.

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