

# Radiation defects in $\text{CaF}_2$ and $\text{SrF}_2$ crystals doped with cadmium or zinc

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## Abstract

The formation of radiation defects in calcium and strontium fluoride single crystals doped with cadmium or zinc has been investigated by luminescence and absorption spectroscopy, as well as by electron spin resonance spectroscopy. It was found that x-irradiation could convert divalent impurity ions located at essentially cubic sites into the univalent state. Three types of  $\text{Cd}^+$  or  $\text{Zn}^+$  centers differing by local environment with point symmetries  $O_h$ ,  $C_{3v}$  and  $C_{2v}$  are identified in the crystals. The formation of the last two results from the interaction between reduced impurities in the cubic environment and anion vacancies. The latter are intrinsic radiation defects and are not created by x-irradiation in undoped crystals. We also discuss the possible implications of the electric field of the charge impurity defects on separation of the intrinsic radiation defects in these crystals.

## 1. Introduction

Radiation damage studies have contributed significantly to our understanding of defect creation and interaction. Under ionizing radiation such as x-rays and  $\gamma$ -rays, the appearance of a variety of lattice defects in solid crystals has attracted the interest of many researchers in the fields of solid-state physics and scintillation materials research.

It is now well established that, in alkali halides, F centers (electrons trapped at anion vacancies) are produced by a radiationless transition from excitons  $e^0$ . H centers, i.e. neutral interstitial species (which in the alkali halides bind to a lattice anion to give an  $X_2^-$  molecule occupying an anion site), are produced as the complementary defect [1–4]. Besides the F–H pairs, the pairs comprising an  $\alpha$ -center (or  $V_a^+$ , anion vacancy) and I center (or  $F_i^-$ , interstitial anion) are also generated in alkali halides. It appears that  $\alpha$ –I pairs are not primary radiation defects. It has been suggested that the tunneling transition of the electron localized on the F center to the H center converts an F–H pair to an  $\alpha$ –I pair [5]. The formation of stable radiation defects includes two stages: the creation of close F–H pairs and subsequent separation of these defects to a stable position by thermal stimulation processes.

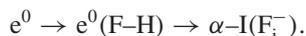
The defect reactions which occur in irradiated alkaline earth fluorides are less well understood than those in alkali

halide crystals [6, 7]. As in alkali halides, the formation of the radiation defects in these crystals is due to the radiationless decay of self-trapped excitons. However, it has been shown that the configuration of the self-trapped exciton in alkaline earth fluorides is different from that of the  $V_k$ -e configuration [8, 9] which is observed for alkali halides. A self-trapped exciton in alkaline earth fluorides has been considered to be the closest F–H pair [10, 11].

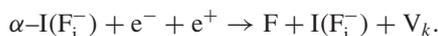
It has been found that alkaline earth fluoride crystals which have not been deliberately doped with impurities are much less susceptible to coloration at room temperature by x-irradiation than most alkali halides. Undoped  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals may be colored by x-rays much more readily at 4 or at 77 K than at room temperature, but the coloration efficiency, especially in the case of  $\text{CaF}_2$  is still much slower than in most alkali halides [6, 7]. The extremely slow coloration rate of undoped alkaline earth fluorides by x-irradiation is due to inefficient separation of close F–H pairs. It has also been found [12] that the holes complementary to the F centers produced by x-irradiation at both 77 and 4 K are  $V_k$  centers. In alkali halides, by contrast, the irradiation in the helium temperature range generally produces H centers rather than  $V_k$  centers [13].

The exception to this is with crystals of pure  $\text{BaF}_2$ . It has been found [14] that x-irradiation at 77 K of undoped  $\text{BaF}_2$

efficiently produces  $V_k$  and F centers having absorption bands at 3.4 and 2.3 eV, respectively. It has been concluded [14] that interstitial anion vacancy pairs with sufficient separation to trap electrons may be created by x-irradiation at 77 K in pure  $BaF_2$ :



The anion vacancy can then trap an electron to become an F center:



The low colorability of the  $BaF_2$  at room temperature may be attributed to the high mobility of  $V_k$  centers at these temperatures ( $V_k$  centers become mobile above 100 K).

Therefore, at some point in the evolution of the primary defects in alkaline earth fluorides, the close F–H pairs that are to become stable defects must convert to F–I pairs plus  $V_k$  centers, because this is the observed charge state of the stable defect pair at low temperature. The I center is found as a perturbing influence on F centers formed by ionizing radiation at low temperature [4, 2].

So the main intrinsic stable defects in alkaline earth fluorides are charged defects, in contrast to alkali halides in which neutral stable defects (F and H centers) are dominant. The probability of the separation of the charged defects in alkali earth fluorides may be enhanced by the assistance of an electric field. An applied electric field lowers the original barrier over which the charged defect of the close  $\alpha$ –I pair has to be thermally hopped in order to reach the stable position according to the Poole–Frenkel mechanism [15–17]. The dominant sources of electric microfields vary from material to material and may be optical phonons, impurities, dangling bonds or other potential fluctuations associated with disorder. The significant electric fields are associated with the longitudinal optical phonons in ionic solids. Various estimates give values for the effective phonon fields of between  $10^5$  and  $10^7$  V cm<sup>-1</sup> [18, 19]. The root-mean-square electric fields in ionic materials having a typical concentration of charged impurities are  $10^4$ – $10^5$  V cm<sup>-1</sup> [19, 20]. Close values for the electric field have been obtained from charge induced infrared absorption in  $\gamma$ -irradiated para- $H_2$  crystals [21].

Additionally we would like to point out that while the alkali halides are ‘normal’ ionic solids with low cation conductivity, the alkaline earth fluorides are known to be superionic conductors, the charge carriers being mainly anti-Frenkel defects, involving equal concentrations of anion vacancies and  $F^-$  interstitials [22]. This means that, in contrast to the neutral defects (F and H centers), the separation of charged defects ( $\alpha$  and I centers) occurs in alkaline earth fluorides.

The role of cation impurities in defect formation in alkali halides has been mainly investigated in terms of the secondary reaction of halogen interstitials or their interaction with the impurity. The behavior of x-irradiated alkaline earth fluorides doped with cation impurities differs markedly from that of the pure crystals. The photochromic centers are produced either by x-irradiation or by additive coloration of  $CaF_2$  and  $SrF_2$  crystals doped with certain rare earths ions (La, Ce, Gd, Tb

and Lu) or yttrium. On the basis of optical and electron paramagnetic resonance (EPR) work, it has been suggested that the ionized and thermally stable photochromic centers in  $CaF_2$  and  $SrF_2$  crystals consist of one and two electrons bound at an anion vacancy adjacent to a trivalent impurity cation [6, 23]. It has been found that photochromic centers can be formed by the weaker trivalent traps, e.g. by Y, La, Ce, Gd and Tb, where low third ionization potentials are expected; the stronger traps with the higher ionization potentials will form divalent ions. Therefore anion vacancies are created during x-irradiation in those crystals doped with trivalent impurities which do not change their effective positive charge.

This paper contains the results of an investigation of radiation induced impurities and intrinsic defects in  $SrF_2$  and  $CaF_2$  crystals doped with cadmium or zinc. In these crystals x-irradiation at room temperature leads, as in the case of crystals doped with certain rare earths ions (La, Ce, Gd, Tb and Lu) or yttrium, to the formation of defects consisting of reduced impurities adjacent to the anion vacancies, which are not essentially created by x-irradiation in the undoped crystals. We discuss a possible mechanism for the creation of such intrinsic defects in these crystals by x-irradiation.

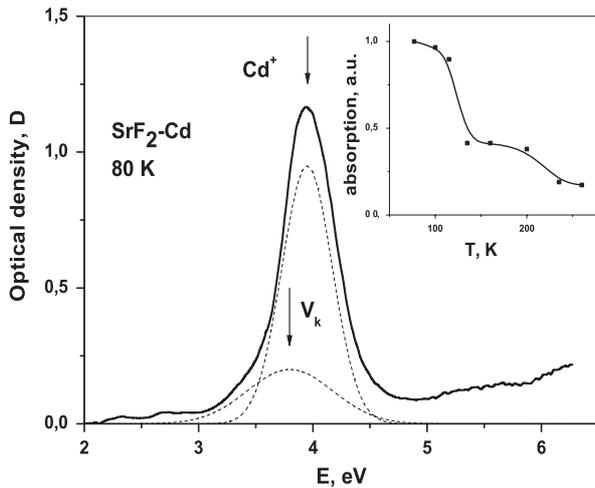
## 2. Experimental technique

Crystals of  $CaF_2$  and  $SrF_2$  doped with cadmium or zinc (with a concentration up to 1 mol%) were grown from the melt by the Bridgman–Stockbarger method. In the growth of alkaline earth fluoride single crystals a small amount of  $CdF_2$  (or  $PbF_2$ ) is generally used as a scavenger in order to remove oxides and oxyfluorides contained in the raw materials by the reaction  $CdF_2 + CaO(SrO) \rightarrow CdO + CaF_2(SrF_2)$ .  $CdO$  and excess  $CdF_2$  evaporate completely from the melt before crystallization begins. Because of the appreciable vapor pressure of  $CdF_2$  or  $ZnF_2$  at the melting point of  $CaF_2$  or  $SrF_2$  it was necessary to confine the impurity-doped melt in the crucible by means of a floating graphite plug, which reduced the open surface area of the melt and thus decreased impurity evaporation. The samples were of high optical quality with no indication of oxygen contamination. Atomic emission spectrometry analyses were carried out on several samples in order to determine the concentrations of Cd and Zn in the grown crystals. Optical absorption measurements were made with a Specord UV/vis spectrophotometer. The crystals were irradiated at 77 or 295 K by x-rays from a Pd tube operating at 50 kV and 50 mA for no more than 1 h. After such treatment no intrinsic defects can be detected by optical and EPR measurements in pure calcium and strontium fluoride crystals. The EPR experiments were done on an X-band spectrometer (RE-1306) in connection with a cryostat suitable for temperatures of 77 and 295 K.

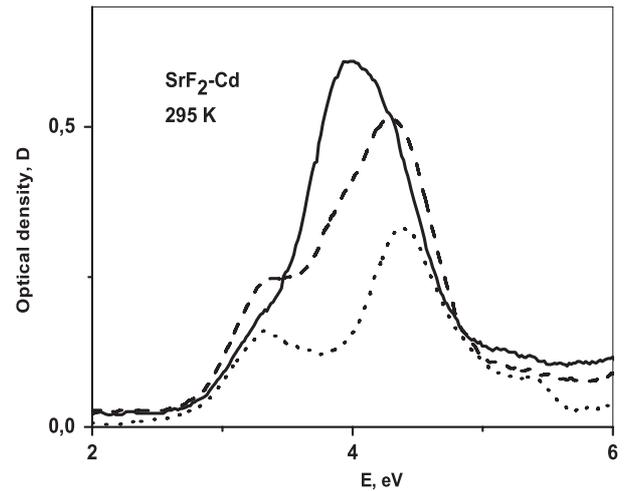
## 3. Experimental result

### 3.1. $SrF_2$ –Cd

Divalent metal ions, such as  $Cd^{++}$  or  $Zn^{++}$ , simply enter into the lattice of alkaline earth fluoride crystals by replacing an alkaline earth ion, forming a defect with cubic symmetry.



**Figure 1.** Optical absorption spectrum of SrF<sub>2</sub>-0.016 wt% Cd crystal after x-irradiation at 80 K. Dashed curves are Gaussian bands to simulate the measured spectrum. Inset: temperature dependence of the Cd<sup>+</sup> center absorption.



**Figure 2.** Optical absorption spectrum at 295 K of SrF<sub>2</sub>-Cd crystal after x-irradiation at 295 K for 1 min (solid) and subsequent thermal annealing at this temperature: after 2 min (dash) and after 30 min (dot).

The crystals of SrF<sub>2</sub> doped with cadmium, as-grown, were transparent in a wide spectral region. It was only found that the fundamental absorption edge shifts to lower energies with increasing cadmium concentration in the crystal [24].

X-irradiation at 77 K of SrF<sub>2</sub> crystals doped with cadmium results in the creation of absorption bands at 3.95 eV of Cd<sup>+</sup> centers [25] and 3.8 eV of V<sub>k</sub> centers [26] (figure 1). In this case the absorption band of the V<sub>k</sub> center cannot be clearly distinguished from the absorption of the Cd<sup>+</sup> ions. Electron spin resonance of SrF<sub>2</sub> crystals doped with cadmium after x-irradiation at 77 K was also studied. The simplest structure is observed for  $B \parallel \langle 100 \rangle$ : two distinct paramagnetic centers were observed by the EPR method in the crystals. The self-trapped hole, or V<sub>k</sub> center, is readily produced by x-irradiation of cadmium-doped crystals at 77 K. In addition to the V<sub>k</sub> centers we observe electrons trapped by Cd<sup>2+</sup> ions and the formation of paramagnetic Cd<sup>+</sup> ions. The spectrum of Cd<sup>+</sup> ions with even nuclear spin measured with  $B \parallel \langle 100 \rangle$  exhibits a well-resolved structure consisting of nine equally spaced lines with a separation of about 11.2 mT. This indicates a superhyperfine interaction with eight equivalent fluorine nuclei, and the Cd<sup>+</sup> ions occupy a cubic lattice and possess cubic point symmetry O<sub>h</sub>. The results are in agreement with those obtained previously [27]. In this case the optical absorption arises from a transition of the Cd<sup>+</sup> electron from the s-like ground state transforming as  $a_{1g}$  to the p-like excited state transforming as  $t_{1u}$ .

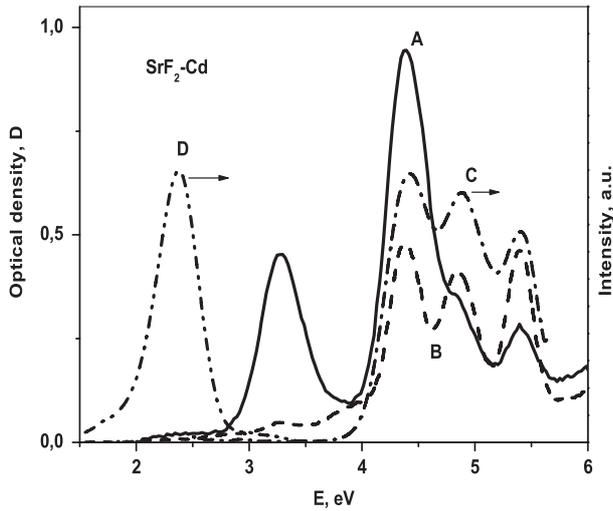
So it would seem that there is a simple case. The exposure of SrF<sub>2</sub>-Cd crystals at 77 K to x-irradiation results in the trapping of holes as F<sub>2</sub><sup>-</sup>, V<sub>k</sub> centers and electron as Cd<sup>+</sup>. At temperatures above the onset of V<sub>k</sub> center mobility ((V<sub>k</sub> centers become mobile above 100 K) one would expect that the mobile holes will thus annihilate the Cd<sup>+</sup> centers. However, thermal annealing at about 130 K leads to the destruction of some portion of the Cd<sup>+</sup> centers (figure 1). The remaining Cd<sup>+</sup> centers are destroyed above 200 K. A small fraction of Cd<sup>+</sup> ions created by irradiation at 77 K survive to room temperature.

Some remarks about the reasons for such hole behavior can be found in our previous work [28]. Similar results have also been obtained in Mn-doped SrF<sub>2</sub> crystals [29].

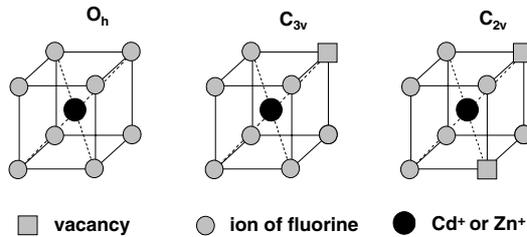
The Cd<sup>+</sup> centers with cubic symmetry (hereafter Cd<sup>+</sup>(O<sub>h</sub>) etc) created by x-irradiation at 77 K are converted on thermal annealing at room temperature to Cd<sup>+</sup> centers with lower symmetry. The absorption band of the former is split into two absorption bands with peaks at 3.3 and 4.39 eV with an intensity ratio of 1:2 (figure 2). If it is assumed that the reduction of symmetry of the latter Cd<sup>+</sup> center is due to the attachment of additional, unexpected defects at nearest neighbor sites, so the symmetry of the center reduces to C<sub>3v</sub> and the p-like excited state of the Cd<sup>+</sup> ion will be split into two sets of levels transforming as  $a_2$  and  $e$ . X-irradiation at room temperature of SrF<sub>2</sub>-Cd crystals leads to the same results.

Apart from these absorption bands, two weaker bands at 4.82 and 5.4 eV (recorded at 77 K for better resolution (figure 3)) are observed after thermal annealing at room temperature. Optical bleaching of Cd<sup>+</sup>(C<sub>3v</sub>) centers by white light at room temperature destroys most of them and increases the former bands. The spectrum of new centers consists of three bands with close intensities (figure 3, curve B).

Photoexcitation at room temperature in these bands leads to the appearance of green emission with a peak at 2.35 eV (527 nm), which shifts to 2.1 eV (590 nm) at 77 K. The emission spectrum is asymmetric; there is a long-wave tail. The excitation spectrum of the emission at 77 K exhibits three well separated bands (figure 3) with nearly equal intensities and correlates with the absorption spectrum. If it is granted that the three separated bands in the excitation and absorption spectra are due to the splitting of the p-state of the Cd<sup>+</sup> ion into three levels, so there is another Cd<sup>+</sup> center with lower symmetry. The attachment of two additional defects at the nearest neighbor site of the cubic Cd<sup>+</sup> center reduces the symmetry to C<sub>2v</sub>. For such symmetry a p-state should be split into three levels and transform as  $a_1$ ,  $b_1$  and  $b_2$ .



**Figure 3.** Spectra of optical absorption at 80 K (A, B), excitation (C) and emission (D) at 295 K of SrF<sub>2</sub>-Cd crystals after x-irradiation at 295 K (A) and subsequent optical bleaching by white light at 295 K (B–D)



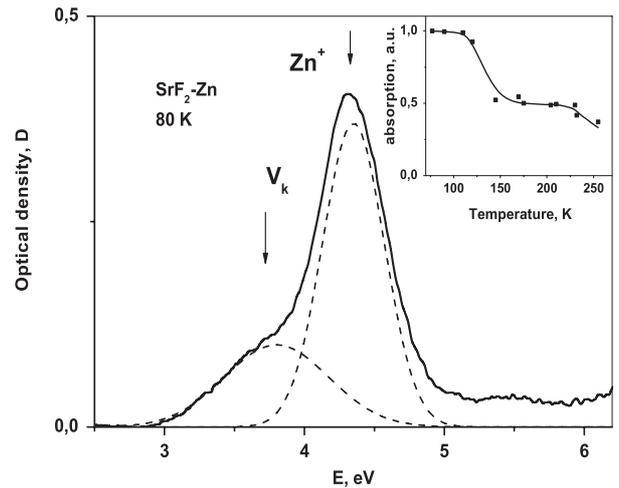
**Figure 4.** Models for the reduced impurity centers.

The nature of the perturbing defect has not yet been established, but as we shall show below it is reasonable to assume that it may be an intrinsic defect, such as an anion vacancy, arising from radiationless decay of self-trapped excitons. The models for the reduced impurity centers, consistent with the experimental results, are pictured in figure 4.

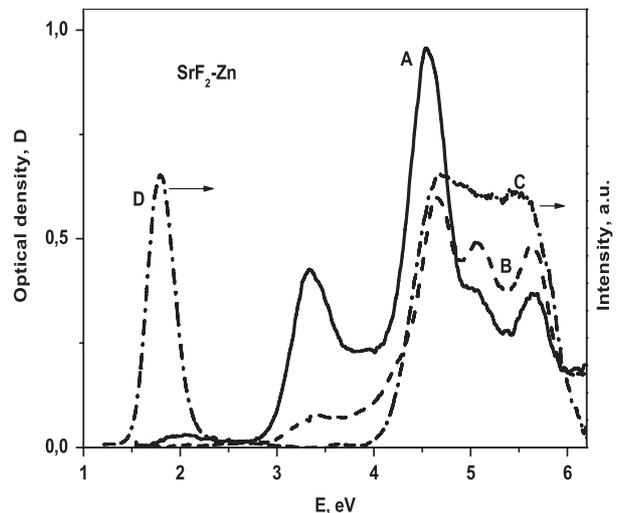
The measured luminescence decay time increases significantly with decreasing temperature down to the temperature of liquid helium. The decay kinetics retain a single-exponential character with decrease in temperature, and at 14 K the decay constant is 2380 μs. This value is appreciably larger than that for the free ion.

### 3.2. SrF<sub>2</sub>-Zn

Strikingly similar results are obtained for strontium fluoride doped with zinc. X-irradiation of the SrF<sub>2</sub> crystals doped with zinc at 77 K results in the creation of absorption bands at 4.35 eV of Zn<sup>+</sup> centers with cubic symmetry (hereafter Zn<sup>+</sup>(O<sub>h</sub>)) and 3.8 eV of V<sub>k</sub> centers (figure 5). The absorption band of the cubic Zn<sup>+</sup>(O<sub>h</sub>) centers shifts to higher energy as compared with the absorption of the Cd<sup>+</sup>(O<sub>h</sub>) center (figure 1): so the absorption bands of hole and electron centers are better separated. The EPR spectrum of Zn<sup>+</sup>(O<sub>h</sub>) centers for B ||



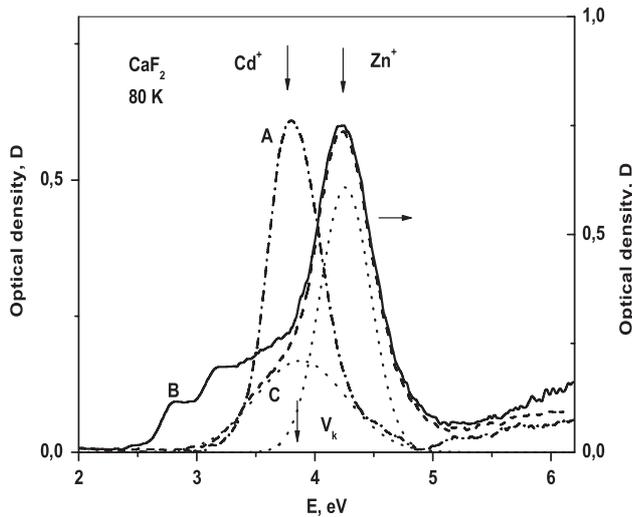
**Figure 5.** Optical absorption spectrum of SrF<sub>2</sub>-Zn crystal after x-irradiation at 80 K. Dashed curves are Gaussian bands to simulate the measured spectrum. Inset: temperature dependence of the Zn<sup>+</sup> center absorption.



**Figure 6.** Spectra of optical absorption at 80 K (A, B), excitation (C) and emission (D) at 295 K of SrF<sub>2</sub>-Zn crystals after x-irradiation at 295 K (A) and subsequent optical bleaching by white light at 295 K (B–D).

⟨100⟩ consists of nine equally spaced lines with a separation of about 9.6 mT. This corresponds to hyperfine structure from eight equivalent fluorine nuclei with nuclear spin  $I = 1/2$ . The splitting between lines for Cd<sup>+</sup>(O<sub>h</sub>) centers is larger than that for Zn<sup>+</sup>(O<sub>h</sub>) centers according to decreasing of ionic radius from Cd<sup>+</sup> to Zn<sup>+</sup>.

The Zn<sup>+</sup> centers with cubic symmetry created by x-irradiation at 77 K are converted on thermal annealing at room temperature to Zn<sup>+</sup> centers with lower C<sub>3v</sub> point symmetry and having two absorption bands with peaks at 3.35 and 4.55 eV with an intensity ratio of 1:2 (figure 6, curve A). X-irradiation at room temperature of SrF<sub>2</sub>-Zn crystals produces Zn<sup>+</sup> centers with C<sub>3v</sub> symmetry without cubic Zn<sup>+</sup> centers, contrary to the cadmium-doped crystals. After optical bleaching with white light at room temperature, the Zn<sup>+</sup>(C<sub>3v</sub>) centers are almost



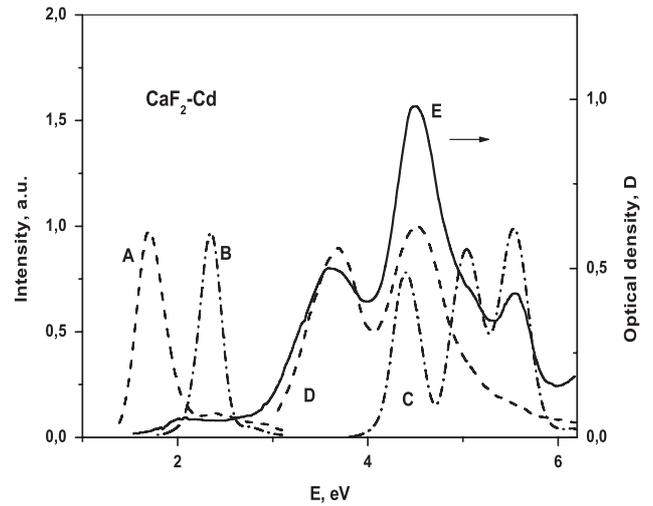
**Figure 7.** Optical absorption spectra of  $\text{CaF}_2\text{-Cd}$  (A) and  $\text{CaF}_2\text{-Zn}$  crystals (B, C) after x-irradiation at 80 K (A, B) and subsequent optical bleaching by white light at 80 K (C).

fully destroyed and some  $\text{Zn}^+(\text{C}_{2v})$  centers having three well separated absorption bands are formed (figure 6, curve B).

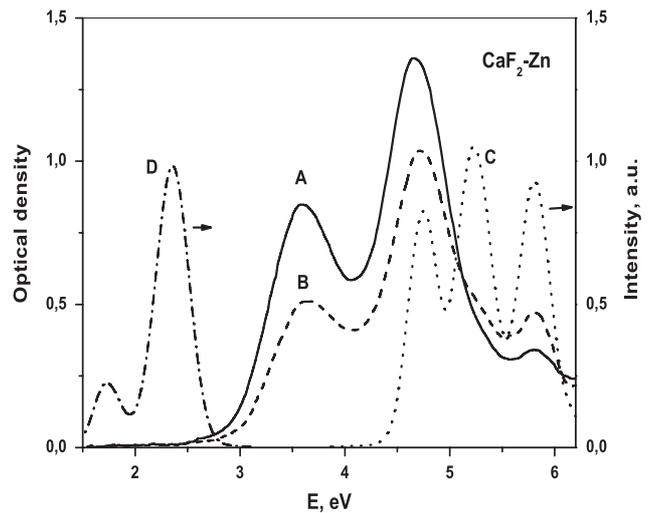
Photoexcitation at room temperature in these bands leads to the appearance of red emission with a peak at 1.8 eV (690 nm). The excitation spectrum of the emission at 300 K exhibits three poorly (as compared with the excitation spectrum of cadmium) separated bands (figure 6, curve C) with nearly equal intensities and correlates with the absorption spectrum. The emission of  $\text{Zn}^+$  with  $\text{C}_{2v}$  symmetry at 77 K is strongly suppressed and becomes more complicated, in contrast to the  $\text{Cd}^+$  emission.

### 3.3. $\text{CaF}_2\text{-Cd}$ , $\text{CaF}_2\text{-Zn}$

Similar results are obtained for  $\text{CaF}_2\text{-Cd}$ ,  $\text{CaF}_2\text{-Zn}$  crystals. X-irradiation at 77 K also produced cubic reduced impurity centers in the crystals (figure 7). As in the doped  $\text{SrF}_2$  crystals, after subsequent heating to room temperature and further optical bleaching at this temperature reduced impurity centers with  $\text{C}_{3v}$  and  $\text{C}_{2v}$  are successively formed. However, there are some special features. The reduced impurity centers with  $\text{C}_{3v}$  symmetry are not destroyed by optical bleaching in the low energy absorption band, but only in the high energy band. Thus in  $\text{CaF}_2\text{-Cd}$  crystals we have observed emission from  $\text{Cd}^+(\text{C}_{2v})$  ions upon photoexcitation not only in absorption band of  $\text{Cd}^+(\text{C}_{2v})$  centers (as in  $\text{SrF}_2\text{-Cd}$ ,  $\text{SrF}_2\text{-Zn}$ ), but also in absorption bands of  $\text{Cd}^+(\text{C}_{3v})$  centers (figure 8). The emission at 1.7 eV at 295 K of  $\text{Cd}^+(\text{C}_{3v})$  is also observed upon excitation in second absorption band at 4.53 eV, while this photobleaching leads to the destruction of the centers. However, the efficiency of such photobleaching is low compared with the doped strontium fluoride crystals, and complete destruction of the centers is not obtained. In  $\text{CaF}_2\text{-Zn}$  crystals we also observed two emission bands, but upon photoexcitation in the absorption bands of  $\text{Zn}^+(\text{C}_{2v})$  centers (figure 9). The excitation of the green emission at 2.26 eV at 16 K as well as the red emission at 1.75 eV is well correlated with absorption of  $\text{Zn}^+(\text{C}_{2v})$  centers.



**Figure 8.** Spectra of emission (A, B), excitation (C, D) and absorption (E) of  $\text{CaF}_2\text{-Cd}$  crystals after x-irradiation and subsequent optical bleaching by light with  $E = 4.5$  eV at 295 K. Emission spectra are measured with excitation light of  $E = 3.5$  eV at 295 K (A) and  $E = 5.4$  eV at 77 K (B). Spectra of excitation are measured for light with  $E = 1.6$  eV at 295 K (D) and  $E = 2.4$  eV at 80 K (C).



**Figure 9.** Spectra of absorption (A, B), excitation (C) and emission (D) of  $\text{CaF}_2\text{-Zn}$  crystals after x-irradiation at 295 K (A) and subsequent optical bleaching by light with  $E = 4.4$  eV (B). Spectrum of emission is measured by excitation light with  $E = 5.7$  eV at 17 K (D). Spectrum of excitation is measured for light with  $E = 2.4$  eV at 17 K (C).

### 3.4. Summary

Three different types of  $\text{Cd}^+$  or  $\text{Zn}^+$  centers are identified in strontium and calcium fluoride crystals doped with cadmium or zinc which have one, two or three absorption bands. The experimental results are summarized in tables 1–3. It is reasonable to suggest that the reduced impurity ion sees a different environment leading to different point symmetry and, therefore, to splitting of the p-state of the impurity center. Thermal annealing and optical bleaching of the x-irradiated crystals shows the consequent change in the symmetry of

**Table 1.** Peak positions  $E$  and half-width  $\Delta H$  of optical absorption bands of the  $\text{Cd}^+(\text{O}_h)$  and  $\text{Zn}^+(\text{O}_h)$  centers.

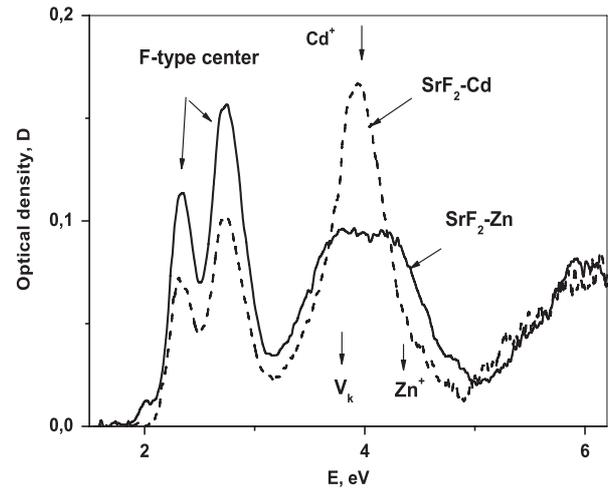
Crystal	Impurity center	Absorption (eV)		
		$E$	$\Delta H$	$T$ (K)
$\text{CaF}_2$	$\text{Cd}^+(\text{O}_h)$	3.8	0.6	295
		3.82	0.5	80
$\text{SrF}_2$		3.95	0.6	295
		3.95	0.52	80
$\text{BaF}_2$ [25, 30]		4.08	0.64	295
		4.1	0.54	80
$\text{CaF}_2$	$\text{Zn}^+(\text{O}_h)$	4.26	0.5	80
$\text{SrF}_2$		4.3	0.8	295
$\text{SrF}_2$		4.35	0.52	80

the reduced impurity centers from cubic  $\text{O}_h$  to  $\text{C}_{3v}$  and further to  $\text{C}_{2v}$ . The cubic reduced impurity ion occupies the body center position of the cubic interstitial site with eight equivalents nearest fluorine ions on the corners of a cube. We assume that the reduction in the symmetry is due to the attachment of one or two additional defects to the nearest neighbor site. Let us also assume that the additional defect is an anion vacancy which is not essentially created by x-irradiation in the undoped crystals. In the next paragraph we try to show how an anion vacancy is created in the doped crystals. The reduced impurity ion adjacent to an anion vacancy which is neutral and has  $\text{C}_{3v}$  point symmetry is similar in some ways to the model of photochromic centers in calcium fluoride doped with rare earth ions [23]. However, there are appreciable differences. Photochromic centers are formed by the weaker trivalent traps, e.g. by Y, La, Ce, Gd, Tb and Lu, where low third ionization potentials are expected; the stronger traps with higher third ionization potentials form divalent ions [31]. The divalent cadmium or zinc ions act as efficient deep traps for free electrons. Therefore an additional electron is bound at the reduced impurity but not at the anion vacancy in contrast to photochromic centers.

All the obtained defects are paramagnetic. Strong paramagnetic resonance is observed for reduced impurities in a cubic environment. The EPR spectrum of the centers with lower symmetries is also observed but its intensity is considerably weaker compared with that of the reduced impurities of cubic symmetry and the spectrum is more complicated. The results of the EPR investigations of centers with lower symmetries will be discussed in a further publication.

### 3.5. Formation of intrinsic defects by radiation

In the  $\text{SrF}_2$  or  $\text{CaF}_2$  crystals doped with a low concentration of impurities (cadmium or zinc) in the range from 0.001 to 0.01 wt%, x-irradiation at 77 K produces, in addition to the reduced impurity ions, F-perturbed centers, which are not essentially created by x-irradiation in the undoped crystals, and additional  $V_k$ -centers (figure 10). The F-perturbed centers are also observed after x-irradiation at room temperature. The perturbed F-band is the same in both  $\text{SrF}_2\text{-Zn}$  and  $\text{SrF}_2\text{-Cd}$  crystals. The position of the F-perturbed band is close to

**Figure 10.** Optical absorption spectra of  $\text{SrF}_2\text{-0.008 wt% Cd}$  (dashed line) and  $\text{SrF}_2\text{-0.003 wt% Zn}$  (solid line) crystals after x-irradiation at 80 K.

that of the F-band in undoped  $\text{SrF}_2$  [12] but the splitting is considerably larger than that in the latter case. The nature of the perturbing defect has not yet been established, but the fact that the same F absorption is found for both  $\text{SrF}_2\text{-Cd}$  and  $\text{SrF}_2$  suggests that it may be an intrinsic defect, such as an interstitial fluorine ion, arising from F-center formation. This is not a surprise because in alkaline earth crystals all F centers produced by x-irradiation are perturbed, probably by  $F^-$ -interstitials [2, 31]. The large splitting indicates that the perturbing defect may be located at a nearest neighbor position.

The F-perturbed centers are easily destroyed by optical bleaching into the absorption bands at 77 K. Simultaneously, some of the  $V_k$ -centers are also destroyed by the bleaching. The bleaching of the irradiated crystals at room temperature produces a small number of reduced impurity centers.

The formation of F and  $V_k$  centers in the doped crystals indicates that in contrast to the extremely slow coloration rate of undoped strontium and calcium fluorides by x-irradiation, which is due to inefficient production of separated interstitial anion vacancy pairs, in the doped crystals this process can take place.

As in the case of pure  $\text{BaF}_2$  [14], in the doped  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals interstitial anion-anion vacancy pairs with sufficient separation to trap electrons may be created by x-irradiation:  $e^0 \rightarrow e^0(\text{F-H}) \rightarrow \alpha\text{-I}(\text{F}_1^-)$ . The anion vacancy ( $\alpha$ -center) can then trap an electron to become an F center. We consider that the defect electric field stimulates the detachment of charged intrinsic defects from close interstitial anion-anion vacancy pairs by the lowering of the Coulomb barrier or/and by the prevention of recombination between them. At higher impurity concentrations (above approximately 0.01 wt%) the reduced impurity centers are observed without F-perturbed centers. Presumably, these are competing processes with characteristic different probabilities of trapping electrons by anion vacancies or by impurities.

**Table 2.** Peak positions  $E$  and half-width  $\Delta H$  of optical absorption and emission bands of the  $\text{Cd}^+(\text{C}_{3v})$  and  $\text{Zn}^+(\text{C}_{3v})$  centers.

Crystal	Impurity center	Absorption, Excitation (eV)				Emission (eV)		
		$E_1$	$\Delta H_1$	$E_2$	$\Delta H_2$	$E$	$\Delta H$	$T$ (K)
CaF <sub>2</sub>	Cd <sup>+</sup> (C <sub>3v</sub> )	3.65	0.64	4.53	0.62	1.7	0.34	295
SrF <sub>2</sub>		3.3	0.64	4.39	0.6			295
		3.28	0.4	4.39	0.4			80
CaF <sub>2</sub>	Zn <sup>+</sup> (C <sub>3v</sub> )	3.6	0.7	4.67	0.7			295
SrF <sub>2</sub>		3.5	0.76	4.56	0.76			295
		3.35	0.48	4.55	0.48			80

**Table 3.** Peak positions  $E$  and half-width  $\Delta H$  of optical absorption (excitation) and emission bands of the  $\text{Cd}^+(\text{C}_{2v})$  and  $\text{Zn}^+(\text{C}_{2v})$  centers.

Crystal	Impurity center	Absorption, Excitation (eV)						Emission (eV)			
		$E_1$	$\Delta H_1$	$E_2$	$\Delta H_2$	$E_3$	$\Delta H_3$	$E$	$\Delta H$	$\tau$ ( $\mu\text{s}$ )	$T$ (K)
CaF <sub>2</sub>	Cd <sup>+</sup> (C <sub>2v</sub> )	4.4	0.32	5.04	0.32	5.53	0.32	2.42	0.26	195	295
SrF <sub>2</sub>		4.39	0.48	4.86	0.48	5.39	0.46	2.35	0.26	235	80
		4.38	0.32	4.85	0.36	5.4	0.34	2.1	0.26	570	295
									1650	80	
									2380	14	
CaF <sub>2</sub>	Zn <sup>+</sup> (C <sub>2v</sub> )	4.75	0.32	5.24	0.34	5.79	0.32	2.36	0.32		17
SrF <sub>2</sub>								1.75	0.26		17
								1.8			295
		4.65	0.42	5.11	0.44	6.63	0.44				80

#### 4. Conclusion

Most ionic materials are pervaded by an electric field of considerable strength [20, 19]. The effects of these fields can be significant, but up to now a little attention has been given to the radiation effects which may be caused by naturally occurring electric fields that are known to arise at charged defects in ionic solids. X-irradiation at 77 K of SrF<sub>2</sub> and CaF<sub>2</sub> crystals doped with cadmium or zinc produces single charged defects with charges of both signs (reduced impurity ions-Cd<sup>+</sup> or Zn<sup>+</sup> and V<sub>k</sub>-centers) which are randomly placed in the crystals. On the basis of the present experimental data, there is reason to believe that the electric field of the impurity charge defect (Cd<sup>+</sup> or Zn<sup>+</sup>) stimulates the separation of charged intrinsic  $\alpha$ -I(F<sub>i</sub><sup>-</sup>) defects. At room temperature one or two anion vacancies may then be trapped by the reduced impurity ion. As a result, three types of Cd<sup>+</sup> or Zn<sup>+</sup> centers differing by their environment are formed.

The formation of intrinsic defects (such as anion vacancies) in both alkaline earth fluorides doped with certain rare earth ions (La, Ce, Gd, Tb, and Lu) or yttrium and in the crystals doped with Cd or Zn strongly suggests that the underlying physics is the same in both cases. The third ionization potentials are lowest for Y<sup>3+</sup> and for the lanthanides, both at the beginning of the series, i.e. for La and Ce, and for the elements half-way along the lanthanide series, i.e. Gd and Tb and for Lu at the end of the series. Photochromic centers will be formed by the weaker trivalent traps, e.g. by Y, La, Ce, Gd, Tb and Lu where low third ionization potentials are expected; the stronger traps with the higher ionization potentials will form divalent ions. These ions have charge relative to the lattice and their charge is not changed by x-irradiation.

The significant electric fields are associated with longitudinal optical phonons in ionic solids [19], and it is believed that this is enough for separation of the intrinsic defects ( $\alpha$ -I pair) in pure barium fluoride crystals but not in pure calcium and strontium fluorides. In the latter case an additional electric field is needed from charge defects for stimulation of separation of the intrinsic defects.

It is believed that a charge induced electric field can be invoked to explain some radiation effects in the doped alkaline earth fluorides. In Na-doped CaF<sub>2</sub> crystals, the F<sub>A</sub> charge centers are formed by electron or x-irradiation at low temperature as a result of simple capture of electrons by anion vacancies of Na<sup>+</sup>-V<sub>a</sub><sup>+</sup> complexes. However, on warming the crystals to room temperature the F<sub>A</sub> centers are fully converted to (F<sub>2</sub><sup>+</sup>)<sub>A</sub> centers according to the thermal conversion process F<sub>A</sub> +  $\alpha$  → (F<sub>2</sub><sup>+</sup>)<sub>A</sub> [32]. This may indicate that x-irradiation at low temperature produces, in addition to F<sub>A</sub> centers,  $\alpha$  centers (free anion vacancies). The latter are unexpected radiation defects. It is believed that in this case also the electric field of the charge defects (F<sub>A</sub> centers) aids separation of the intrinsic charge defects from the complexes ( $\alpha$ -I(F<sub>i</sub><sup>-</sup>) pairs).

We emphasize that in the Cd-doped barium fluoride crystals x-irradiation at 77 K as well as at 295 K generally results in the formation of reduced impurity centers with cubic symmetry. It is difficult to obtain Cd<sup>+</sup> centers with lower symmetry in BaF<sub>2</sub> as well as photochromic centers. However, two species of Cd<sup>+</sup> centers have been observed; photoexcitation of one of them leads to red emission [30]. It is believed that in the doped BaF<sub>2</sub> crystals the radiation processes of the formation of intrinsic defects and the reduction of impurities are spatially separated from each other, in contrast to the behavior discussed above for doped CaF<sub>2</sub> and SrF<sub>2</sub> crystals. As result we have only observed the result of competition between these processes.

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