

The Refinement of Self-Trapped Excitons Structure in CaF_2 and SrF_2 Crystals: An Ab Initio Study

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Abstract—We present the results of ab initio calculations of self-trapped excitons (STE) in CaF_2 and SrF_2 crystals performed with BHHLYP density functional in embedded cluster approach. As a motivation for this theoretical study, we also report some previously unpublished experimental results on STE luminescence. They concern new luminescence bands of STE approximately 1 eV higher than the main band. The new bands have much lower intensities in pure crystals, however they remain almost unaffected by impurity doping while the main band is quenched by impurities. As possible candidates for excitonic configuration responsible for these high-energy bands, four possible configurations of the off-center STE are considered and rejected. For the on-center STE, i.e., $V_K + e$, stable configuration has been found. The calculated luminescence energy of on-center STE is 6.57 eV in CaF_2 and 6.31 eV in SrF_2 crystal. On the basis of these energies (much higher than energies of new excitonic luminescence bands) and low stability of on-center STE, it is also rejected as a candidate for new bands. Finally, the hypothesis of electron self-trapping is considered. We have found electron self-trapping in CaF_2 and SrF_2 crystals to be energetically favorable, however the value of energy gain lies within the possible calculation error. It was also found that there is a barrier about 0.3 eV for electron self-trapping. Self-trapped electron is a center with trigonal symmetry and can be considered as perturbed F-center. Calculated isotropic hyperfine couplings of self-trapped electron are given. On the basis of these results, we tentatively suggest that self-trapped electrons are the precursors of yet unknown excitonic configuration responsible for the new luminescence bands.

Index Terms— CaF_2 , density functional theory, self-trapped excitons, SrF_2 .

I. INTRODUCTION

THE history of the investigation of self-trapped excitons (STE) in alkaline-earth fluorides counts already almost 40 years. Since the first observation of excitonic luminescence by Beaumont *et al.* in 1970 [1], extensive spectroscopic and magnetic resonance studies had been performed (see [2] for review). Despite that, the mechanism of STE creation and transformation and even its structure cannot be considered as completely clear at the present moment. Several important and, in fact, basic questions remain unanswered. Among them, the most intriguing are the following, pointed by Catlow [3].

- Why are the pure alkaline earth fluorides much more resistant to coloration at room temperature than the pure alkali halides?

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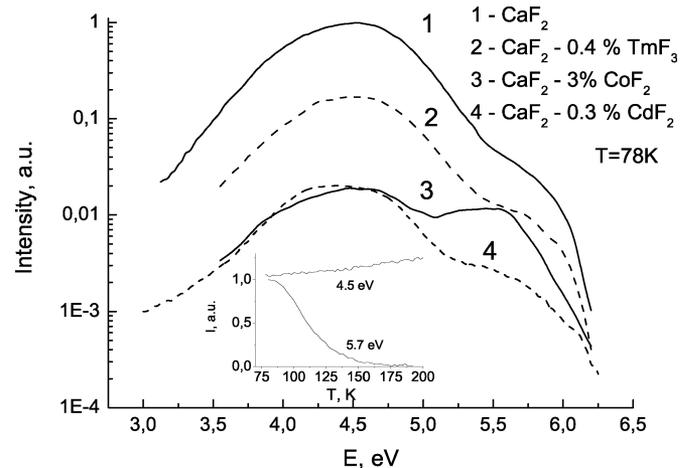


Fig. 1. Emission spectra of pure and doped CaF_2 crystals at 78 K. The spectra were recorded under the X-ray excitation. The inset shows the temperature dependence of the emission bands intensity in CaF_2 -3% CoF_2 crystal.

- Why are V_K centers produced in the alkaline earth fluorides in the initial radiolysis step in contrast to the H center observed in irradiated alkali halides?

We will show in the experimental section that optical properties of STE in alkaline-earth fluorides also cannot be considered as fully known. In this work, we attempted to clarify these issues by means of ab initio calculations.

II. EXPERIMENTAL RESULTS

Recently, we have observed new excitonic luminescence bands in CaF_2 , SrF_2 , and BaF_2 crystals under X-ray irradiation. From the luminescence spectra shown in Figs. 1 and 2, it can be seen that new bands are situated approximately 1 eV higher than well-known main excitonic emission bands. In pure crystals, these new bands are almost indistinguishable due to much lower intensity than that of main bands. However, doping with impurities efficiently suppresses the main STE band. The origin of this suppression is the recombination of electrons and holes on the impurity sites preventing them from forming STE, as it has been shown in [4]. When the intensity of the main excitonic band decreases, the presence of high-energy band becomes clear. It should be stressed that the intensity of the latter does not increase with larger impurity concentration; it just remains unaffected by impurities in wide range of concentrations, while the intensity of the main band drops very fast. It should be also noted that different dopants (Cd, Co, Tm, and others) have a very similar effect on the intensity of the main excitonic band, and the difference between the spectra presented on Fig. 1 is mainly due to a concentration effect.

The inset on Fig. 1 shows temperature dependence of new high-energy luminescence bands. They disappear in the range

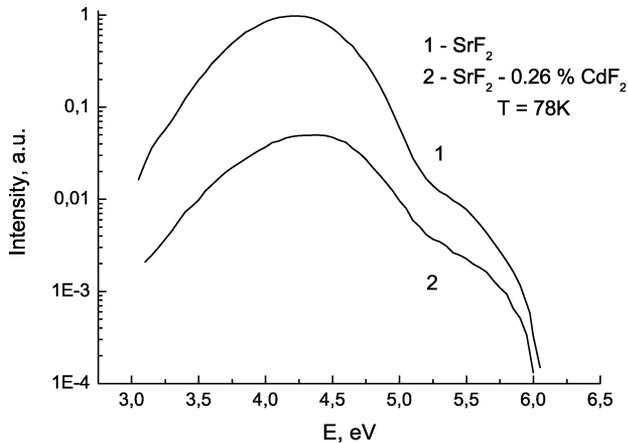


Fig. 2. Emission spectra of pure and doped SrF_2 crystals at 78 K under the X-ray excitation.

TABLE I
PEAK POSITIONS OF EXCITONIC LUMINESCENCE BANDS IN ALKALINE-EARTH FLUORIDE CRYSTALS

Crystal	Main band (eV)	New band (eV)
CaF_2	4.5	5.66
SrF_2	4.4	5.33
BaF_2	4.25	5.05

between 90 and 150 K. Table I summarizes the peak position energies for the new and old bands of STE emission.

There should exist some configuration of exciton responsible for the new band. What could it be? To answer this question, extensive theoretical investigation is necessary (and had been started by us), but one thing can be established in the very beginning. This unknown excitonic specie *must differ from usual STE by formation mechanism*, otherwise it is impossible to explain why impurities efficiently suppress the formation of usual STEs and does not affect the new bands.

III. CALCULATION RESULTS

Calculations in the present work have been performed with BHHLYP [5] density functional in an embedded cluster approach. BHHLYP stands for “B half and half LYP” and differs from the famous B3LYP functional by a different proportion of Hartree–Fock and DFT exchange terms. Namely, BHHLYP energy contains 50% of the former and 50% of the latter. On Ca and F ions, a 6–31 G basis set was used. We also placed two additional d-type shells on Ca ions. For Sr ion, a suitable all-electron basis set of DZP quality (double zeta + polarization) has been taken from [6] and [7].

The embedded cluster approach we use allows to treat a quantum cluster (usually of several tens of atoms) with accurate quantum-chemical method, while the larger surrounding region is treated classically by means of pair potentials. This classical region consists of several hundreds of atoms, and coordinates of these atoms are included in the geometry optimization procedure together with those of the quantum cluster. The described method allows to model defects in polarizable and deformable crystal lattice. In the present work, Buckingham pair potentials were used for the classical region. Their parameters were fitted to reproduce experimental dielectric and elastic constants of CaF_2 and SrF_2 crystals and are presented in Table II. The

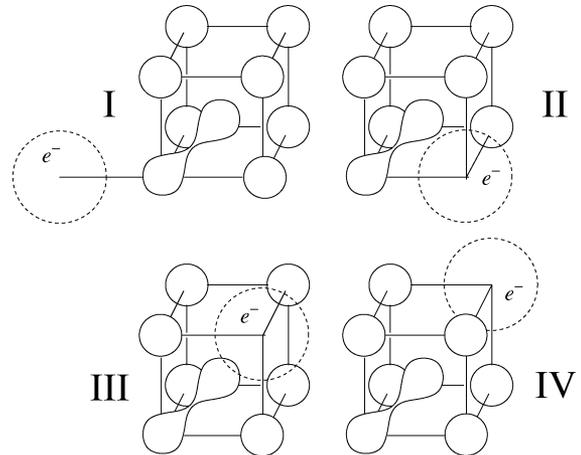


Fig. 3. Configurations of the off-center STE in CaF_2 and SrF_2 crystals.

TABLE II
PARAMETERS OF PAIR POTENTIALS FOR THE CLASSICAL REGION

Crystal	Interaction	A, eV	$\rho, \text{\AA}$	$C, \text{eV} \cdot \text{\AA}^6$
CaF_2	F-F	2877.72	0.2573	56.76
	Ca-F	752.44	0.3235	0.0
	Ca-Ca	2814.61	0.3711	0.28
SrF_2	F-F	1047.60	0.2705	48.01
	Sr-F	971.78	0.3241	6.46
	Sr-Sr	1516.95	0.4500	0.37

A, ρ, C - parameters of Buckingham potential $U(r) = A \exp(-r/\rho) - C/r^6$

classical region, in its turn, is surrounded by point charges necessary to provide correct Madelung potential inside the classical and quantum regions.

To implement this approach, we have modified PC GAMESS 7.1.2 quantum chemistry code. Namely, we have added the possibility to calculate classical region with simple pair potentials. PC GAMESS [8] is a very efficient modification of the GAMESS-US package [9].

A. Off-Center STE

Four possible configurations of the off-center STE are shown on Fig. 3. These configurations were first suggested and enumerated by Williams *et al.* [10]. Early theoretical studies were performed in mid-1980s by semiempirical extended ion method (for example, [11]; see [2] for the review). Despite the lack of computational power in that time, the predictions were made very accurately, and it is difficult to add something to those results.

We have found that configuration III does not exist, i.e., does not correspond to the local minimum of total energy. This is not crucial for the off-center STE model since the most important is configuration II. The calculated parameters of configurations I, II, and IV are listed in Table III. From total energies E_{tot} , it follows that conf. I is slightly more energetically favorable than conf. II, however this cannot be considered as the evidence of conf. I domination. Low efficiency of the formation channel for conf. I can be the simplest reason for the domination of conf. II.

The equilibrium bond length of F_2^- molecular ion, isotropic hyperfine couplings on the fluorine atom displaced in the interstitial position (A_{iso}) and of that it is bonded to (B_{iso}) are also given in Table III.

TABLE III
CALCULATED PARAMETERS OF DIFFERENT CONFIGURATIONS OF THE OFF-CENTER STE

Crystal	Conf.	Calculated						Experimental		
		E_{tot}, eV	$R(F_2^-), \text{\AA}$	A_{iso}, G	B_{iso}, G	Δ_{SCF}, eV	$TDDFT, eV$	A_{iso}, G	B_{iso}, G	E_{lum}, eV
CaF ₂	I	0.00	1.96	319	272	2.34	2.14	386.7	314.3	4.5
	II	0.23	1.95	404	291	3.62	3.73			
	III	Does not exist		–	–	–	–			
	IV	0.40	1.95	376	282	2.88	3.20			
SrF ₂	I	0.00	2.02	330	271	1.88	1.75	409.7	318.3	4.4
	II	0.28	1.96	385	298	3.24	3.44			
	III	Does not exist		–	–	–	–			
	IV	0.36	1.96	347	261	2.42	2.72			

Two different approaches were used to estimate luminescence energies of STE. The first (Δ_{SCF}) was to optimize the geometry of triplet exciton, and then to calculate the difference between total energies of triplet and singlet states. The second was to perform TD DFT (time-dependent DFT) calculation in the geometry of relaxed triplet exciton. Both energies are listed in the same table. It can be seen that calculated energies for conf. II are underestimated with respect to experimental excitonic luminescence bands by about 1 eV. Underestimation of transition energies is a common feature of DFT methods, although it is less common for hybrid functionals as that used in the present work. The reason for such a large discrepancy is yet to be understood. The luminescence energies of other configurations are lower by more than 1 eV. It is possible that conf. I and IV are present in irradiated crystals in small concentrations and contribute to the low-energy wing of excitonic luminescence. None of the considered configurations can be responsible for new high-energy bands.

B. On-Center STE

On-center STE in alkaline-earth fluorides (i.e., V_K center with an electron in bound state in certain vicinity) had never been observed experimentally. However, the possibility of an on-center STE appearance as a very short-living intermediate stage in an electron-hole pair relaxation on its way to the formation of the off-center STE had been discussed, for example, by Tanimura [12].

According to our calculations, on-center STE configuration is stable in the sense that it corresponds to the local minimum of total energy. However, the minimum is very shallow, and small fluctuations can make on-center STE unstable. The geometry of this defect is shown in Fig. 4. The separation between fluorine ions in the F_2^- molecular ion is 1.9 Å in CaF₂ and 1.92 Å in SrF₂ crystal. The lattice deformation in SrF₂ is qualitatively and quantitatively very similar to that in CaF₂ shown on Fig. 4.

In Table IV, calculated isotropic hyperfine parameters together with the formation and luminescence energies are listed. Constants A_{iso} , B_{iso} , and C_{iso} correspond to the fluorine ions having A, B, and C labels on Fig. 4, respectively. The luminescence energies calculated as the total energy difference between triplet and singlet states are larger than the new excitonic band energies by more than 1 eV. The overestimation of transition energies by DFT methods should not normally happen. On this ground, we can exclude on-center STE from the candidates for new bands. Besides, its low (if any) stability also allows to exclude it.

TABLE IV
CALCULATED ON-CENTER STE PARAMETERS

Crystal	A_{iso}, G	B_{iso}, G	C_{iso}, G	Formation energy, eV	Lumin. energy, eV
CaF ₂	480	117	104	9.5	6.57
SrF ₂	490	95	94	7.1	6.31

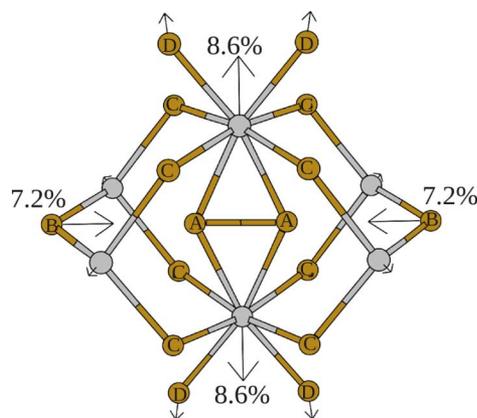


Fig. 4. On-center STE in CaF₂ crystal. All fluorine ions are labeled. Symmetry-equivalent ions have the same labels. Two bonded fluorine ions labeled "A" form F_2^- ion. Arrows show the direction of displacements, while their values are given in % of lattice fluorine-fluorine separation $a = 2.76 \text{ \AA}$.

C. Electron Self-Trapping Hypothesis

The suggestion that conductive band electron self-trapping might occur in CaF₂ and SrF₂ crystals has been first discussed by Catlow [3]. It has not been proven nor refuted—it has been forgotten. We have calculated the configuration of the self-trapped electron in both crystals and found it to be energetically favorable.

Hypothetical electron self-trapping occurs when the lattice fluorine is displaced into the nearest interstitial position, and the fluorine vacancy that is formed traps the electron, thus becoming the F-center. In other words, the self-trapped electron is an F-center and interstitial F^- ion in the nearest neighborhood. This defect possesses trigonal symmetry (C_{3V} group) with a threefold axis directed from the vacancy site to the interstitial fluorine, i.e., $\langle 111 \rangle$ axis. The configuration of this center is shown in Fig. 5 together with the largest displacements of the nearest ions.

According to calculation results, there is a barrier about 0.3 eV for electron self-trapping in the CaF₂ crystal. As it was

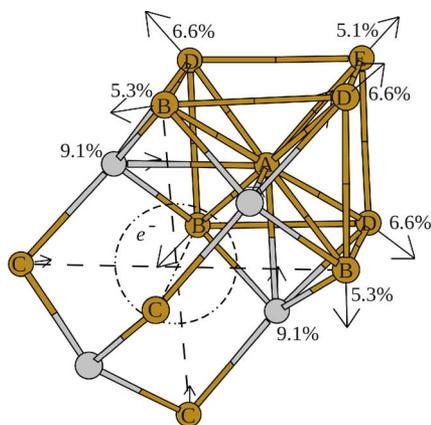


Fig. 5. Self-trapped electron in CaF_2 crystal. All fluorine ions are labeled; symmetry equivalent ions have the same label. The crossing point of dashed lines shows the position of the vacancy, dashed circles schematically represent the electron trapped in the vacancy, and the fluorine ion labeled "A" is the ion that moved from the site of that vacancy into interstitial position.

TABLE V
"HYPERFINE PORTRAIT" OF SELF TRAPPED ELECTRON

Crystal	A_{iso}, G	B_{iso}, G	C_{iso}, G
CaF_2	61.5	36.7	112.0
SrF_2	52.9	16.8	96.4

mentioned, the self-trapped electron configuration is slightly energetically favorable, but the value of energy gain lies within possible calculation error. Thus, at the present moment, the existence of a self-trapped electron in CaF_2 and SrF_2 crystals cannot be unambiguously established.

Table V contains a "hyperfine portrait" of this defect. From isotropic hyperfine couplings, this defect can be considered as a strongly distorted F-center. One question is very obvious when the hypothesis of electron self-trapping is discussed: If it is possible, then why has such a defect not been observed experimentally? The possible answer is the following: In irradiated crystals, perturbed F-centers of various symmetries and configurations are observed. It is possible that a self-trapped electron was observed among them, but has never been identified.

Another question is also obvious: If electron self-trapping is favorable, then why are not all the electrons excited during the irradiation of crystal relax into this configuration? At least some of them are trapped by V_K centers and form usual off-center STEs, the luminescence of which is well known. The possible clue is the existence of an energy barrier for self-trapping. To be self-trapped, a conductive band electron must have kinetic energy at least higher than the barrier value. It means that there exists an energy range where self-trapping is possible. The electron excited during crystal irradiation, after thermalization, continues to lose its energy, getting scattered on lattice defect and thermal phonons. If it passes the energy range of self-trapping, i.e., its energy becomes lower than the barrier value, then it will be trapped either by impurities or by V_K centers. Trapping by V_K centers leads to excitonic luminescence; trapping by impurities leads to the quenching of this luminescence.

However, if there is certain probability that an electron can be self-trapped before these two channels become operational, then the creation rate of self-trapped electrons will not depend on impurities in a wide concentration range. Self-trapped elec-

trons can be precursors of a yet unknown exciton configuration responsible for the new excitonic luminescence bands.

IV. CONCLUSION

There is a new excitonic band in CaF_2 , SrF_2 , and BaF_2 crystals about 1 eV higher the main band of STE luminescence.

Its intensity does not depend on impurities in a wide range of impurity concentration, in contrast to the quenching of main bands.

The defect specie responsible for this band must differ from usual off-center STE by the formation mechanism.

On-center STE ($V_K + e$) should have the luminescence sufficiently higher than the energy of new band. Besides, on-center STE is unstable and relaxes into off-center configuration after overcoming very a small energy barrier.

It follows from calculation results that self-trapping of electron is possible in CaF_2 and SrF_2 crystals. Self-trapped electron is a center with trigonal symmetry and can be considered as a perturbed F-center. There is a barrier for self-trapping about 0.3 eV.

It can be tentatively suggested that self-trapped electrons are the precursors of a yet unknown excitonic configuration responsible for the new luminescence bands.

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