

Ab Initio Calculation of Charge-Transfer Absorption in CaF_2 and SrF_2 Crystals With Eu^{3+} and Yb^{3+} Impurities

Alexandra Myasnikova, Evgeny Radzhabov, and Andrey Mysovsky

Abstract—In this paper we present the results of *ab initio* calculations of charge-transfer absorption bands in Eu^{3+} and Yb^{3+} -doped CaF_2 and SrF_2 crystals, which are due to transitions from the top of valence band to 4f state of trivalent rare-earth ion. The density-functional theory calculations have been performed in embedded-cluster approach. It was shown that low-energy absorption band is caused by charge-transfer transitions between 2p-states of interstitial fluorine and 4f state of the impurity ion.

Index Terms—Alkali-earth fluoride, charge transfer, embedded cluster approach, Eu^{3+} -doping, Yb^{3+} -doping.

I. INTRODUCTION

THE ABSORPTION band in the VUV region of alkali-earth fluorides doped with some lanthanide impurities is well known to consist of $4\text{f}^n \rightarrow 4\text{f}^{n-1}\text{5d}$ intense band [1], [2] and low-energy part, which is related to charge-transfer transitions from valence band ($\text{F}, 2\text{p}$) to 4f state of rare-earth impurity ion (CT₁ transitions) [3]–[6]. One of the important effects of the rare-earth (RE^{3+}) impurity introduction is the appearance of fluorine interstitial ions (F_i^-), which enter the crystal as compensators of excess charge of trivalent impurities; and nearest neighbor (NN) defects (C_{4v} symmetry) are created mainly for CaF_2 and SrF_2 crystals [7]. The interstitial fluorine ions are due to the appearance of levels in the band gap. When the concentration of impurity is increased to a few mol. percent, this interstitial ion levels create a subband in the band gap of the crystal. Appearance of an interstitial fluorine subband can influence the mechanism of charge-transfer transitions. In absorption spectra of Eu^{3+} and Yb^{3+} -doped CaF_2 and SrF_2 crystals weak absorption bands in the 6–7 eV region was observed [6]. It was supposed that this band is due to electron transition between interstitial fluorine and 4f impurity levels (CT₂ transitions) (see Fig. 1).

In this paper we present the results of *ab initio* cluster calculations of charge-transfer transitions in Eu^{3+} and Yb^{3+} -doped CaF_2 and SrF_2 crystals, with lattice distortion in the presence of interstitial fluorine ions taken into account.

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The authors are with the A. P. Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Science, 664033 Irkutsk, Russia (e-mail: sasham@igc.irk.ru).

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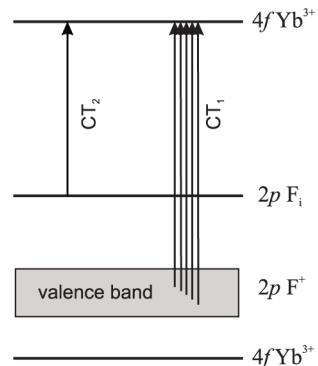


Fig. 1. Charge-transfer transitions scheme for alkali-earth fluorides with Eu^{3+} and Yb^{3+} impurities.

II. CALCULATION DETAILS

The *ab initio* density functional theory (DFT) calculations of charge-transfer transitions have been performed in the embedded-cluster approach implemented in the GUESS computer code [8]. In this approach a quantum-mechanical (QM) cluster with the defect and its NNs is surrounded by several hundreds of ions, which are treated classically in the shell model. Between QM and classical regions one needs to place an interface area in order to avoid the distortion of geometric and electronic structure at the edge of QM cluster. In the case of purely ionic crystals like CaF_2 or SrF_2 a quite simple interface is sufficient. All quantum-mechanical, interface, and classical ions are allowed to relax during the geometry optimization run. This region is surrounded by several thousands of fixed atoms, which are represented as point charges and provide accurate electrostatic potential inside classical and QM regions. GUESS does not itself calculate electronic structure of QM cluster, but calls another quantum-chemical program (Gaussian 03 [9]) for this purpose and then adds classical terms to the obtained total energy.

We used 6–31G* basis set of Petersson *et al.* [10] on fluorine and calcium ions and CEP-4G (Stevens–Basch–Krauss ECP minimal basis [11]) on strontium, europium, and ytterbium ions. We replaced all cations in the radius of 6 Å around the QM cluster with interface ions, which had LANL1 ECP (Hay–Wadt large core pseudopotential) and no basis functions.

In this work the electronic structure of QM cluster has been calculated in the DFT method with the use of a modified B3LYP functional. Original B3LYP is hybrid functional, which contain 20% of Hartree–Fock exchange and 80% of DFT exchange. This functional can be well used for defect calculations in solid state with some modification. Namely, we change the ratio of Hartree–Fock and DFT exchanges (40% of former and 60%

TABLE I
PARAMETERS OF PAIR POTENTIALS FOR CaF_2

	A (eV)	ρ (Å)	C (eV·Å ⁶)
Classical region			
Ca-F	1326	0.3	0.1
F-F	1323	0.27	18
Interface region			
$\text{Ca}_{\text{face}}\text{-F}_{QM}$	500	0.3	0.1
Shell parameters	Y (e)	k (eV·Å ⁻²)	
F	-2.38	67	

A, ρ, C — parameters of Buckingham potential

$$U(r) = A \exp(-r/\rho) - C/r^6,$$

Y — shell charge, k — spring constant

TABLE II
PARAMETERS OF PAIR POTENTIALS FOR SrF_2

	A (eV)	ρ (Å)	C (eV·Å ⁶)
Classical region			
Sr-Sr	13013	0.35	0.38
Sr-F	1055	0.32	0.46
F-F	2131	0.26	68
Interface region			
$\text{Sr}_{\text{face}}\text{-Sr}_{QM}$	3012	0.35	0
$\text{Sr}_{\text{face}}\text{-F}_{QM}$	235	0.32	0
Shell parameters	Y (e)	k (eV·Å ⁻²)	
F	-2.10	38	

A, ρ, C — parameters of Buckingham potential

$$U(r) = A \exp(-r/\rho) - C/r^6,$$

Y — shell charge, k — spring constant

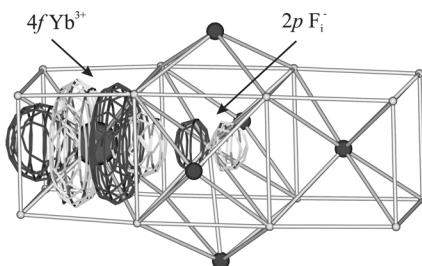


Fig. 2. Cluster $[\text{Me}_5\text{F}_{17}\text{RE}^{3+}]^{-4}$. States with orbital moment projection $l_z = 0$ is shown.

of latter). The modified functional showed most adequate electron state localization and was successfully used for DFT calculations of oxygen centers and excitons in CaF_2 [12], [13]. Time-dependent DFT (TD DFT) [14] methods were applied for calculation of transition energies.

For a classical region GUESS requires parameters of pair potentials. We took parameters in buckingham form from [15] and slightly adjust them for our purposes so that the pair potentials reproduce well lattice constant, elastic, and dielectric constants of CaF_2 or SrF_2 . The parameters obtained are shown in Tables I and II.

We performed calculations for a $[\text{Me}_5\text{F}_{17}\text{RE}^{3+}]^{-4}$ cluster, which consists of five cations (Ca^{2+} or Sr^{2+}), 17 anions (F^-), and one rare-earth ion (Eu^{3+} or Yb^{3+}); the interstitial fluorine ion F_i^- creates the C_{4v} -defect (Fig. 2).

TABLE III
CALCULATION RESULTS OF CHARGE-TRANSFER ABSORBTION FROM 2P INTERSTITIAL FLUORINE TO 4F RARE-EARTH IMPURITY STATES. DISTANCES BETWEEN INTERSTITIAL FLUORINE AND RARE-EARTH IONS ARE GIVEN BOTH IN ANGSTROMS AND IN THE PERCENT OF NONOPTIMIZED $\text{RE}^{3+} - \text{F}_i^-$ -DISTANCE

Crystal	$\text{RE}^{3+} - \text{F}_i^-$ distance, Å	$\text{RE}^{3+} - \text{F}_i^-$ distance, %	Oscill. strength	E, eV, calc. CT_2
CaF_2	Eu^{3+}	2.49	91	0.0037
	Yb^{3+}	2.56	94	0.0031
SrF_2	Eu^{3+}	2.55	88	0.0073
	Yb^{3+}	2.83	98	0.0021

TABLE IV
CHARGE-TRANSFER ABSORBTION ENERGY IN COMPARISON
WITH THE EXPERIMENTAL ONE [6]

Crystal	E (eV) exp. Eu^{3+}	E (eV) exp. Yb^{3+}	E (eV) calc. Eu^{3+}	E (eV) calc. Yb^{3+}
CaF_2	8.3	8.7	6.3	8.4
	6.8	7.2	4.7	7.2
SrF_2	7.9	8.5	6.1	7.8
	6.6	6.9	4.9	6.5

III. RESULTS AND DISCUSSION

The Yb^{3+} ion has thirteen 4f electrons with multiplicity equaling two. The Eu^{3+} ion has six 4f electrons with multiplicity equaling seven. Therefore the calculation of ground and excited states for an Eu^{3+} ion is more difficult than for a Yb^{3+} ion.

As a first step, we calculated the equilibrium geometry of the cluster $[\text{Me}_5\text{F}_{17}\text{RE}^{3+}]^{-4}$, which contains interstitial fluorine and rare-earth ions. The results of geometry optimization are presented in Table III. The maximum displacement of the interstitial fluorine ion takes place for Eu^{3+} -doped crystals. The least distance between interstitial fluorine and europium ions (in absolute value) is observed for CaF_2 : Eu^{3+} (2.49 Å). However maximum displacement in the percent of nonoptimized $\text{RE}^{3+} - \text{F}_i^-$ -distances occur in SrF_2 : Eu^{3+} (distance between interstitial fluorine and europium ions decreased by 12%).

After lattice relaxation three states of interstitial fluorine ion were splitted from the valence band: the upper 2p state directed along fourfold symmetry axis of the cluster and two other are degenerate states. The transitions from 4f rare-earth ion state with orbital moment projection $l_z = 0$ to upper 2p interstitial fluorine state is allowed; the other transitions are symmetry forbidden. The states with allowed transitions are shown in Fig. 2. Calculated energies and oscillator strengths for the charge-transfer transitions between 2p interstitial fluorine and 4f impurity levels are presented in Table III.

Besides the transitions from interstitial fluorine state we have made calculations of absorbtion bands which are related to charge-transfer transitions from valence band to 4f state of rare-earth impurity ion. The results of these calculations are presented in Table IV. The calculation results of charge-transfer

absorbtion for Yb^{3+} -doped crystals agree well with the experimental data of [6]. In the case of Eu^{3+} -dopping one can see that energies of both CT_1 and CT_2 transitions are in satisfactory agreement with experimental data, being all underestimated by approximately the average value of 2 eV. We assume that this underestimation is connected with height multiplicity of Eu^{3+} ion. Despite this fact we can conclude that low-energy CT_2 absorbtion band is due to electron transitions between interstitial fluorine and 4f impurity levels, with the fluorine ion creating the NN defect.

IV. CONCLUSION

In this paper we have studied charge-transfer absorbtion of Eu^{3+} and Yb^{3+} -doped CaF_2 and SrF_2 crystals using *ab initio* DFT calculations in an embedded-cluster approach. According to the data obtained, we can conclude that the CT_2 band in absorbtion spectra is caused by transitions between 2p interstitial fluorine and 4f impurity levels.

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