

**IMPURITY CENTERS OF Eu^{3+} IN EPITAXIAL HETEROSTRUCTURES
 $\text{CdF}_2/\text{CaF}_2/\text{Si}$**

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Abstract.

Stark energy levels of $\text{Eu}^{3+}(4f^6)$ ions in $\text{CdF}_2\text{-CaF}_2\text{:Eu}$ epitaxial superlattices on Si have been calculated in exchange charge model. Two types of centers have been considered in CaF_2 layer: “interface center”, close to the $\text{CdF}_2/\text{CaF}_2$ interface, and “remote center” located in the core of a layer. The influence of distortion, created by silicon substrate, has been taken into consideration. The calculations confirmed earlier suggested “electron” model of the interface center.

1. Introduction

It is known that cubic CaF_2 and CdF_2 crystals are wide band gap materials, $E_g(\text{CaF}_2) = 12.1$ eV, $E_g(\text{CdF}_2) = 8.0$ eV. Their lattice parameters (5.46 and 5.39 Å correspondingly) are quite close to that of Si (5.43Å). This enables growing high structural quality pseudomorphic (coherent with the substrate) superlattices on Si(111) [1]. In these SLs strain lowers crystal symmetry of the fluorite layers from cubic to the rhombohedral one.

It was revealed that in such SLs with Eu doped CaF_2 layers ultraviolet photoexcitation is accompanied by efficient tunneling from excited state of Eu^{2+} ions into CdF_2 conduction band [2]. This results in conversion of Eu^{2+} into Eu^{3+} , which is the most efficient near $\text{CdF}_2/\text{CaF}_2\text{:Eu}$ interfaces. By means of laser spectroscopy it has been recently found that positions of Eu^{3+} energy levels for the Interface (I) center having 9 Ca and 3 Cd cation neighbors and Remote (R) center with 12 Ca cation neighbors are noticeably different. Taking into account temperature and addition illumination dependences of the Interface center photoluminescence (PL) intensity, it was suggested that in this center extra electron charge

compensation is provided by an electron trapped by a Cd ion neighboring to the Eu^{3+} ion [3, 4]. The heterostructures $\text{CdF}_2/\text{CaF}_2:\text{Eu}/\text{Si}$ were grown at the Ioffe Institute using a conventional MBE process. Layers of CaF_2 and CdF_2 are sequentially deposited on (111) oriented Si substrates. The spectroscopic measurements of the ${}^5\text{D}_1$ and ${}^7\text{F}_1$ triplet splitting were carried at the Ioffe Institute too.

In this work, we present results of calculations high of the ${}^5\text{D}_1$ and ${}^7\text{F}_1$ triplet splitting for the Interface and Remote centers in the exchange charge model [5].

2. Calculations of the crystal structures

The sequence of calculations for impurity centers is as follows: calculation of local crystal structure of impurity center and then energy levels calculations. For crystal structure calculations we have used the shell model and pair potential approximation. Then the lattice energy can be written as:

$$U_{lat} = \frac{1}{2} \sum_i \sum_{k(\neq i)} V_{ik} + \frac{1}{2} \sum_i k_i \bar{\delta}_i^2 \quad (1)$$

where $k_i \bar{\delta}_i^2$ – the energy of core-shell interaction of i -th ion and V_{ik} – the interaction energy between i -th and k -th ions, which can be expressed as:

$$V_{ik} = \frac{X_i X_k}{|\vec{r}_i - \vec{r}_k|} + \frac{Y_i X_k}{|\vec{r}_i - \vec{r}_k + \vec{\delta}_i|} + \frac{X_i Y_k}{|\vec{r}_i - \vec{r}_k - \vec{\delta}_k|} + \frac{Y_i Y_k}{|\vec{r}_i - \vec{r}_k + \vec{\delta}_i - \vec{\delta}_k|} + f_{ik}(|\vec{r}_i - \vec{r}_k|) + g_{ik}(|\vec{r}_i - \vec{r}_k + \vec{\delta}_i - \vec{\delta}_k|) \quad (2)$$

where the function

$$f_{ik}(r) = -A_{ik} \exp(-B_{ik} r) / r \quad (3)$$

describes the short-range screening of electrostatic interaction between ion cores, the function

$$g_{ik}(r) = C_{ik} \exp(-D_{ik} r) - \lambda_{ik} / r^6 \quad (4)$$

describes short-range repulsion between ion shells (which is written in the form of the Born-Mayer potential) and the Van-der-Waals interaction; X_i and Y_i are the core and shell charges of the i -th ion, \vec{r}_i is the vector, defining position of ion core. $\vec{\delta}$ is the vector, defining position of ion shell relative to ion core. We have used the following values for the core charges: $X_F = +5$, $X_{Ca, Cd} = +8$, $X_{Eu} = +11$. The shell charges have been determined from condition: $Z_i = X_i + Y_i$, where Z_i - ion charge in the compound. The parameters of the $F-F$ interaction have been obtained non-empirically by using the

Hartree-Fock and the configuration interaction method [6]. The parameters of the Me^{2+} - F short-range repulsive and parameter k_i of core-shell interaction for Me^{2+} have been obtained by fitting the calculated crystal properties to the experimental data for the crystals MeF_2 ($Me=Ca, Cd$): the lattice constants, the dielectric constants ϵ_0 and ϵ_∞ , the elastic constants C_{11} , C_{12} and C_{44} , the frequencies of the fundamental vibrations ω_{TO} and ω_R . Thus, eight experimental values have been used for fitting three parameters. The parameters of the short range electrostatic screening have been calculated by numeric integration of the interaction of the free ions electron densities. The short-range interaction between the metal ions could not be taken into consideration because they are too far from each other. The values of the parameters are given in table 1.

Table 1. The short-range interaction potential parameters (at. un.)

Pair	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	λ
F ⁻ - F ⁻	36.456	1.3778	157.083	1.8927	69.5469
Ca ²⁺ - F ⁻	31.720	1.5490	249.468	2.0421	-
Cd ²⁺ - F ⁻	68.207	1.5453	254.516	2.0574	-
Eu ³⁺ -F ⁻	-	-	196.857	1.9002	-
$k_F = 4.1797, k_{Ca} = 11.1692, k_{Cd} = 10.6329, k_{Eu} = 25.1710$					

Calculated with these parameters lattice constants are 544.7 (CaF₂) and 538.6 (CdF₂) pm. Lattice constants taken from experiment [7] are 544.3 and 535.6 pm accordingly. The agreement with experiments is very good. The parameters of Eu-F were fitted to the EuF₃ structure (tables 2,3). Three parameters were fitted to twelve experimental values. The agreement with experiments is quite good.

Table 2. Lattice constants of EuF₃, A (experiment - [8])

	Experiment	Calculation
A	6.620(1)	6.663
B	7.016(1)	7.586
C	4.392(2)	4.768

Table 3. The position of ions in the cell of EuF₃ (experiment - [8])

atom	site		x	y	z
Eu	4c	exp.	0.365(1)	0.25	0.063(1)
		calc.	0.371	0.25	0.056
F(1)	4c	exp.	0.522(2)	0.25	0.576(6)
		calc.	0.524	0.25	0.574
F(2)	8f	exp.	0.171(2)	0.065(2)	0.393(4)
		calc.	0.177	0.072	0.406

The silicon substrate distorts the CaF₂ and CdF₂ layers. The symmetry is reduced from a cubic to a rhombohedral. There is a decrease in the angle (from 90° to 89.760°) and also the lattice constant (from 544.3 to 543.5 pm) of cubic cell as a result of this distortion. The values of the distorted angle and lattice constant were determined from X-ray data. Positions of the ions in the cell are unknown. We used the elementary cell in H-system, which contained 3 layers of Cd and 3 layers of Ca in order to reproduce the sequence of calcium and cadmium layers.

To take the distortion into account we fixed the elementary cell sidebar according to measured values. The ions inside the cell could relax to minimal energy.

For the calculations of the structure of impurity centers, we used the Mott-Littleton method. In the calculations, the internal region around impurity ion consists of about 1300 ions. And 40-85 thousands of ions, depending on complication of defects, in the adjoining region to the internal region could relax restrictedly. We used the GULP 3.0 program for the calculations.

3. Calculations of the energy levels

We calculated the energy levels of Eu³⁺(4f⁶) in Remote and Interface centers. We used standard for lanthanide ions ‘effective Hamiltonian’ for 4f electrons that acts only within the 4f configuration [9]. The free ion Hamiltonian parameters were taken from work [10]. For the calculations we used programs of Dr. Michael F. Reid (University of Canterbury), given to us by the author.

Crystal-field parameters were calculated in the exchange charge model [5]. It takes into account the electrostatic fields generated by point charges and dipoles of the neighboring ions, as well as the exchange interaction of the 4f shell of the rare-earth ion with ligand electrons. The B_p^q parameters are the sum of the electrostatic and exchange terms:

$$B_p^q = B_{p\ el}^q + B_{p\ s}^q \quad (5)$$

The electrostatic term is

$$B_{p\ el}^q = K_p^q (1 - \sigma_p) e^2 \langle r^p \rangle \sum_{\alpha} (-z_{\alpha}) P_p^q(x_{\alpha}, y_{\alpha}, z_{\alpha}, r_{\alpha}) r_{\alpha}^{-(2p+1)} \quad (6)$$

where the summation is taken over all the cores and shells of the neighboring ions having coordinates x_{α} , y_{α} , z_{α} in a fixed Cartesian coordinate system with the center at the 4f core of the rare-earth ion, r_{α} is the distance from the lanthanide ion to the core or the shell of the

ion of crystal matrix, $P_q^p(x_\alpha, y_\alpha, z_\alpha, r_\alpha)$ are homogeneous polynomials of degree p listed in [11], $\langle r^p \rangle$ is the mean value of r^p for $4f$ electrons [12], σ_p is the shielding factor which allows for polarization of the closed $5s^25p^6$ shells within the rare-earth ion and its effect on the crystal field at the $4f$ core, e is the electron charge, Z_α is the effective charge number which takes on the value of X_α for the core and Y_α for the shell of the corresponding ions, and K_q^p are the numerical coefficients arising from the replacement of spherical harmonics by polynomials. Its values are given in [5, 13]. The exchange term is

$$B_{q\ s}^p = \frac{2(2p+1)}{7} K_p^q e^2 \sum_{\alpha} S_p(r_\alpha) P_p^q(x_\alpha, y_\alpha, z_\alpha, r_\alpha) r_\alpha^{-(p+1)}, \quad (7)$$

where the summation over α is carried out over the cores of the nearest fluorine ions only. Here S_p is combination of squares of overlap integrals of the $4f$ wave functions of the rare-earth ion with $2s$ and $2p$ functions of the fluorine ions:

$$S_p(r) = G_s S_s(r)^2 + G_\sigma S_\sigma(r)^2 + K_p G_\pi S_\pi(r)^2 \quad (8)$$

The dependences of S_s, S_σ, S_π on the Rare-earth – F distance can be fitted by the exponential

$$S_k(r_\alpha) = S_k^0 \exp(-\delta_k r_\alpha^{n_k}).$$

The values

$$S_s^0 = 0.299, \delta_s = 0.805, n_s = 1.607, \quad S_\sigma^0 = 0.120, \delta_\sigma = 0.431, n_\sigma = 1.776, \\ S_\pi^0 = 1.534, \delta_\pi = 2.167, n_\pi = 0.965,$$

where r_α is given in Angstroms.

These values as well as the shielding constants $\sigma_2 = 0.60, \sigma_4 = \sigma_6 = 0$ were calculated and kindly given to us by professor B.Z. Malkin. There are three empirical parameters G_s, G_σ and G_π in term (8), which are named “exchange charges”. The parameters are fitted to experimental Stark energy levels. We fitted the parameters to energy levels of cubic center $\text{CaF}_2:\text{Eu}^{3+}$ (table 4). Good results were obtained with equal parameters, $G_s = G_\sigma = G_\pi = 9.6$. Thus, only one empirical parameter was used in the model: $G = 9.6$. Crystal field parameters for cubic center $\text{CaF}_2:\text{Eu}^{3+}$ are shown in table 5.

Table 4. Experimental and calculated energy levels of the cubic center in bulk CaF₂:Eu³⁺

Term	Irrep	Experiment [14], cm ⁻¹	Calculation, this work , cm ⁻¹
⁷ F ₁	T _{1g}	339	352
⁷ F ₂	T _{2g}	812	797
	E _g	1339	1356
⁷ F ₃	T _{1g}	1855.5	1882
	T _{2g}	1968	2018
	A _{2g}	–	2210
⁷ F ₄	A _{1g}	–	2398
	T _{1g}	2884	2899
	T _{2g}	–	3178
	E _g	–	3183
⁷ F ₅	T _{2g}	–	3829
	T _{1g}	–	4027
	E _g	–	4255.4
	T _{1g}	–	4256.0
⁷ F ₆	A _{1g}	–	5047
	T _{1g}	–	5112
	T _{2g}	–	5158
	A _{2g}	–	5351
	T _{2g}	–	5358
	E _g	–	5361
⁵ D ₀	A _{1g}	17275.5	17345
⁵ D ₁	T _{1g}	19030	19099
⁵ D ₂	E _g	21538	21524
	T _{2g}	21428	21613

Table 5. Crystal field parameters in cubic and tetragonal centers CaF₂:Eu³⁺ (cm⁻¹)

	Cubic center		Tetragonal center	
	Stevens normalization	Wybourne normalization	Stevens normalization	Wybourne normalization
B_0^2	-	-	280	561
B_0^4	-274	-2193	-97	-775
B_4^4	-1370	-1310	-1260	-1205
B_0^6	47	747	61	982
B_4^6	-980	-1397	-688	-981

We calculated energy levels of tetragonal center CaF₂:Eu³⁺ with the same parameter G in order to verify it. Good results have been received (see table 6). Crystal field parameters for tetragonal center CaF₂:Eu³⁺ are presented in table 5.

Table 6. Experimental and calculated energy levels of the tetragonal A-center in bulk CaF₂:Eu³⁺ in [cm⁻¹].

Term	Irrep	Exp. [15] (in air cm ⁻¹)	Calc., this work
⁷ F ₁	E	309	330
	A ₂	457	472
⁷ F ₂	B ₂	852	848
	E	973	971
	B ₁	1123	1176
	A ₁	1263	1233
⁷ F ₃	E	1815	1840
	B ₂	1835	1860
	E	1955	1965
	A ₂	1976	1986
	B ₁	2130	2125
	A ₁	2512	2540
⁷ F ₄	E	2799	2793
	A ₂	2945	2960
	E	3006	3037
	B ₁	3089	3049
	B ₂	3114	3126
	A ₁	3156	3153

We calculated the energy levels of the Remote and Interface centers in CdF₂-CaF₂:Eu SLs with mentioned above value of parameter G .

As fluorides have rhombohedral symmetry in the superlattices, B_{20} parameter is not equal to zero. It is necessary to take into account the contributions of large number of ions for correct parameter calculation. Therefore we summarized the contributions of ions up to distance 65 angstroms for the calculations of crystal field parameters B_{kq} , which corresponds the contributions from 60000 ions. Such summation allows us to calculate B_{20} with accuracy 2 cm⁻¹. The calculations have shown that starting from 40 angstroms for radius of the summation the oscillations of B_{20} do not exceed 2 cm⁻¹. The increase of the radius up to 80 angstroms does not change results of the calculations.

The calculated values of splitting in ⁵D₁ and ⁷F₁ multiplets for Remote centers are 1.5 and 3.5cm⁻¹. Determined in experiments values are 0.8 and 6.0cm accordingly. It is clear that the calculated values of splitting are in reasonable agreement with the experimental data. The lower level in the ⁵D₁ and ⁷F₁ multiplets is singlet in accordance with experimental data. For ⁵D₁ multiplet we have a discrepancy with experiment: the lower level is doublet according to our calculations. The discrepancy can be explained by small values of splitting in the ⁵D₁ multiplet.

Three variants of charge compensation have been considered in Interface center: (i)- charge compensating electron was removed from CdF₂/CaF₂ interface, (ii)- the electron was localized on six nearest cadmium in CdF₂ layer, and (iii) the electron was localized on the three nearest cadmium in CdF₂. Local crystal structure calculations for the impurity center were carried out before energy levels calculations in all three cases. We added $-1/6$ (or $-1/3$) to shell charges of six (or three) nearest cadmium in crystal structure calculations to take into account the additional electron charge in the last two cases.

It follows from the calculations that in the case when the electron is moved away from CdF₂/CaF₂ interface, the energy structure of ⁵D₁ and ⁷F₁ multiplets is opposite to experimental data: the doublet is higher than the singlet (see figure 1). When the charge compensating electron is localized at six or three nearest cadmium, the doublet is lower than singlet as in the experiment. These results confirm the presence of charge compensating electron on the closest to europium cadmium ions.

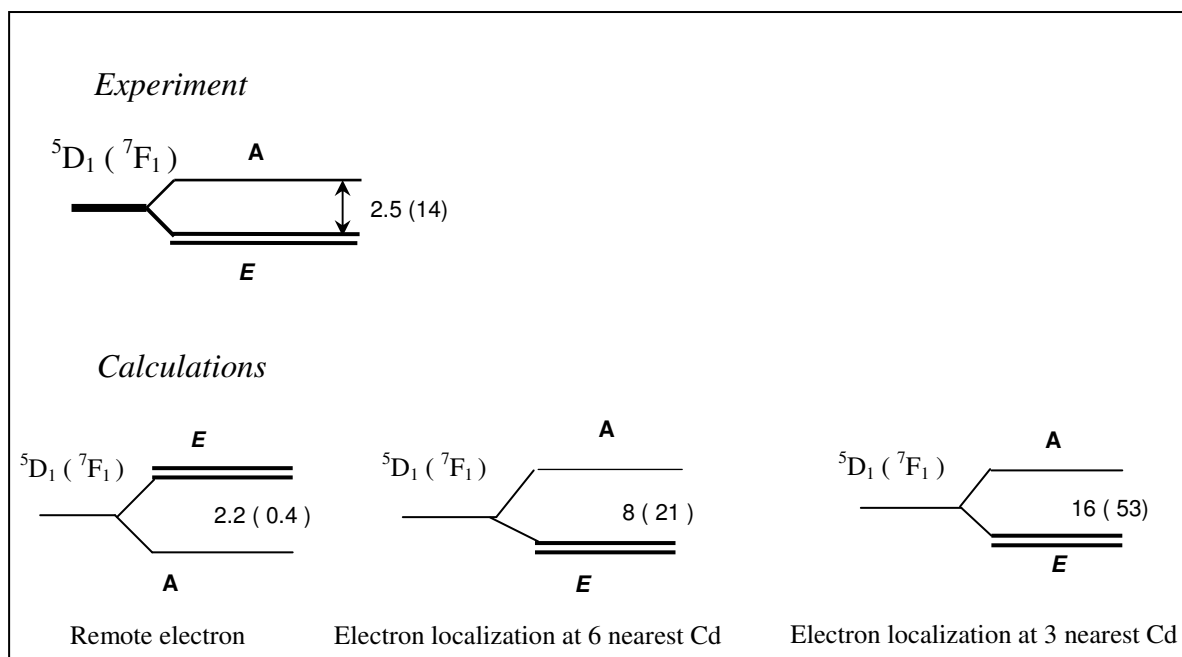


Figure 1. Comparison of the experimental and calculated in different models splitting of ⁵D₁ and ⁷F₁ multiplets in the Interface center.

4. Conclusion

As it was demonstrated by the calculations, the splitting of the Interface centre Eu³⁺ levels is in the good agreement with the experiment in assumption that extra charge compensating electron is localized at nearest Cd ions. The results confirm the conclusion that main reason of the optical spectrum transformation of Eu³⁺ in Interface center is electron in the neighboring CdF₂ layer. The calculations showed that experimentally observed splitting of

5D_1 and 7F_1 manifolds in the Remote centers is caused by the elastic strains existing in the fluoride layers of the pseudomorphic CdF_2 - CaF_2 superlattices on silicon.

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