Quantum-Chemical Simulation of Paramagnetic F-Center in CaF_2, SrF_2 and BaF_2

A.Yu. Kuznetsov, A.B. Sobolev, A.S. Makarov

Ural State Technical University – UPI, 19 Mira St., Ekaterinburg, 620002, Russia, E-mail: kay@dpt.ustu.ru

Abstract – The electronic structure and some magnetic properties of F-centers in CaF_2, SrF_2 and BaF_2 crystals were calculated. Band structures of ideal and defect-containing crystals and Mulliken charge distributions were analyzed. Optical properties of a defect-containing crystal were calculated. The calculations were made using the CRYSTAL98 code in terms of the supercell model describing a point defect.

Isotropic superfine interaction constants, which describe the interaction between an unpaired electron and nuclear spins of the nearest neighbors of a defect up to the 4th coordination sphere inclusive, were calculated using two different schemes with the exchange-correlation potential. The obtained theoretical results were in satisfactory agreement with known data of electron paramagnetic resonance experiments. The change of the defect formation energy was analyzed for some supercells of different shapes and dimensions (24, 81 and 192 atoms).

1. Introduction

Alkaline-earth fluorides occupy a special place among wide-gap dielectrics. Crystals of these compounds having the fluorite space group are widely used currently as ionizing radiation detectors, perspective elements of power optics, in scintillation equipment, etc. The use of this class of materials is impossible if their electronic structure and the formation of chemical bonds are not known in detail. A special interest presents the study of imperfect crystals, because defects in crystals may be either a positive or negative factor for their practical applications.

The present study deals with specific features of the electronic structure, optical and paramagnetic properties in the homologous series of CaF_2, SrF_2 and BaF_2 alkaline-earth fluorides. Crystals of the fluorite group with F-centers were taken as defective crystals. These defects are model ones and have been adequately explored. With respect to theoretical methods, the interest to the study of F-centers stems from the need to describe both the defect wave function and displacements of ions surrounding a vacancy. An F-center presents interest for this class of research, because it allows analyzing the relationship between electron and nuclear spins for a sufficiently large set of adjacent nuclei. In this study the calculated superfine interaction constants were compared with constants, which were determined experimentally for four nearest neighbors.

Today such problems are solved using first-principle or *ab initio* methods for calculation of the electronic structure [1–5]. Calculations were made by the method of linear combinations of atomic orbitals in the Hartree-Fock approximation using the supercell model. The method was realized in the CRYSTAL98 program package. Two different calculation schemes were used, namely the Hartree-Fock approximation and the B3PW hybrid method.

2. Models, methods and calculation parameters

The present paper describes results of analysis of the electronic structure, optical and paramagnetic properties of CaF_2, SrF_2 and BaF_2 crystals containing *F*-centers. All the three crystals had the cubic structure of the fluorite (the space group *Fm3m*). Calculations were made using the program package CRYSTAL98 [6, 7] that realizes *ab initio* methods. For the purpose of simulating the periodicity, the crystal orbitals were expanded to linear combinations of Bloch functions and were estimated by a regular three-dimensional net in the reciprocal space. Each Bloch function was formed by localized atomic orbitals, which represented contractions (linear combinations with constant coefficients) of Gaussian type functions (GTF).

Simulation was performed both in the Hartree-Fock (HF) approximation and in terms of the density functional theory (DFT). A hybrid method, which included Becke's gradient correction of the exchange functional [8] for the HF exchange and Perdew and Wang's gradient correction of the correlation functional (B3PW) [9], was used. Identical basis sets (BS) and other calculation parameters were used.

Ions were described using BS, which were earlier adopted in the CRYSTAL package for other compounds. Exponents of outer sp- and d-shells were optimized in the BS for the crystals at hand using a program code for minimization of the total energy on the basis of the gradient method. So, the full BS with 12 functions (7, 3, 1 and 1 GTF for 1s, 2sp, 3sp and 4sp shells) and 24 functions (8, 6, 5, 1, 1 and 3 GTF for 1s, 2sp, 3sp, 4sp, 5sp and 3d shells) were obtained for fluorine and calcium respectively. These BS were tested earlier in calculations for CaF_2 [1]. Effective core potentials (ECP) [10] were used for heavy *Sr* and *Ba* ions. In this case, effective potentials replaced the exact description of wave functions of core electrons. As a result, the computing time was reduced. Valence BS were described by 8 functions for *Sr* (3, 1, 1 and 3 GTF for 4sp, 5sp, 6sp and 4d shells) and 6 functions for *Ba* (3, 1, 1 and 1 GTF for 5sp, 6sp, 7sp and 5d shells). In the case of DFT calculations, the exchange and correlation potentials were expanded in terms of the auxiliary Gaussian BS (AUX) [7].

Таблица 1. Calculated and experimental values of lattice constant a (Å), bulk modulus B (GPa), valence band width (E_v) and first (E_{g1}) and second (E_{g2}) band gaps (eV)

	CaF_2			SrF_2			BaF_2		
	exp. [12,13]	HF	B3PW	exp. [12,13]	HF	B3PW	exp. [12,13]	HF	B3PW
a	5.46	5.533	5.510	5.80	5.900	5.849	6.20	6.369	6.288
B	84.7	85.4	86.8	76.2	68.4	71.4	63.5	51.1	57.5
E_{g1}	12.3	20.11	10.48	11.6	19.85	10.02	11.0	19.94	10.56
E_v	4.8	2.00	1.89	4.4	1.71	1.65	3.4	1.45	1.44
E_{g2}	12.8	16.44	15.36	7.9	9.92	10.18	3.8/5.8	5.08	6.20

3. The electronic structure of the perfect crystals

All calculations of the electronic structure, optical and paramagnetic properties of the crystals were made at the minimum point of the total energy. For this purpose, the lattice constant of each crystal was minimized. Using these data, it was possible to determine the bulk modulus B, which is calculated from curves that describe the change of the total energy depending on the relative deformation of a unit cell. The calculated values correlated fairly well with the corresponding experimental data. This fact pointed to the correctness of the basis sets used (rows 1 and 2 in Table 1).

The next stage of the study included calculations of the electronic structures of defect-free CaF_2, SrF_2 and BaF_2 crystals. According to the calculation results, the valence band in all the three crystals was formed mainly by 2*p* states of *F*, while the lower levels of the conduction band were due to *s* and *d* states of cations (with the impurity *s* of fluorine), that is 3*d* and 4*s* *Ca*, 4*d* and 5*s* *Sr*, and 5*d* and 6*s* *Ba*. The valence band narrowed in the series CaF_2 – BaF_2 (see Table 1). This narrowing was probably due to the growth of the lattice constant and, consequently, the decrease in the overlap of 2*p* shells of *F*. The second energy gap E_{g2} also decreased in this series. The decrease was predetermined by the position of *p*-levels of cations whose energy considerably lowered in the series Ca^{2+}-Sr^{2+}-Ba^{2+} relative to vacuum [11]. This tendency led to the double-fold difference between E_{g1} and E_{g2} in BaF_2, making it possible to observe the cross luminescence.

All what has been said above is characteristic of both research methods, but each of them has its individual features in different parts of the energy spectrum. In the region of occupied states ($E < 0$) the HF approximation is more reliable. The hybrid methods provide much better results for the energy gap, while HF calculations overestimate the band nearly two times. This conclusion is confirmed by the calculation results given in Table 1, which demonstrate a good agreement between B3PW results and experimental data for E_{g1}.

The effective charges, which were determined from the Mulliken charge density distribution, suggested the purely ionic character of chemical bonds in these compounds: the charge was nearly +2 for cations and –1 for F^- anions. Generally, the data obtained for the energy gaps were in satisfactory agreement with known experimental and calculation results [13].

4. F-Centers in CaF_2, SrF_2 and BaF_2 Crystals Specific features of simulation of defect-containing systems. The case of a point defect

From the physical viewpoint, an F-center is an electron, which is localized by the Coulomb field of the crystal lattice at an anion vacancy site. Simulation of this defect in a crystal has some specific features. Since the system under study contains an odd number of electrons, it is necessary to use the unrestricted Hartree-Fock method. For the exact description of an unpaired electron in a vacancy, the BS corresponding to the "ghost" atom (it suffices to take one diffuse *sp*-shell as this atom) is added [2]. In this case, it follows from the analysis of the Mulliken charge density distribution that the quantity of the electron charge, which may be assigned to the vacancy, approaches very closely to 1.

A defect breaks the translation symmetry of an ideal crystal. The standard technique, which allows the use of the periodic model for calculations of defect-containing crystals, is the supercell (SC) scheme. In this case, the primary unit cell is multiplied by SC translation vectors. The defect is located at the center. For simulation of properties of a point defect, SC should be sufficiently large and should satisfy the following conditions:

(a) The interaction between defects in adjacent cells should be insignificant.

(b) All atoms, which undergo relaxation in the presence of a defect, should belong to the SC and the effect of adjacent defects on these atoms should be a minimum.

The SC should be symmetric relative to the defect as much as possible. By varying factors of m translation vectors of the unit cell (m = 2, 3, 4), we used SC with 24, 81 and 192 ions, which are labeled further in the text as SC24, SC81 and SC192.

Relaxation of the nearest environment of an F-center

Distortions, which arise in the vicinity of a defect during calculations by band methods, are difficult to take into account, because in this case not only the local symmetry, but also the space symmetry of the problem changes. The analysis is often limited to

symmetric distortions of one-two coordination spheres of a defect since the electronic structure is already well defined in this case. If spheres of higher ranks are considered, only the defect formation energy decreases insignificantly [14].

The SC with 24 atoms was chosen for calculation of the relaxation of the nearest environment of an F-center for reasons of time saving and the condition (b). It contained, in addition to all atoms of two nearest coordination spheres of the defect (4 cations and 6 fluorine ions), the important anion in the [111] position and its equivalent anions in the ion sublattice of fluorine, some of which were assigned a considerable spin density according to the paramagnetic resonance analysis.

The relaxation was calculated by minimizing the total energy of the SC24 with the symmetrical shift of ions in the 1st and 2nd coordination spheres of the defect. The relaxation direction corresponded to the tetrahedral symmetry of the defect. In this case, the cations repelled one another and shifted from the position of the F-center cornerwise of the fluorine cube, while the anions approached the F-center along the edges of the same cube. The other coordination spheres were not considered. According to results of the minimization, the relaxation of cations increased from 0.25 to 0.35%*a* (*a* being the lattice constant) in moving from CaF_2 to BaF_2. The relaxation of fluorine ions in the coordination sphere of the F-center was much smaller and was within 0.02%*a*.

For calculation of the defect formation energy (E_{Fc}) in terms of the CRYSTAL98 simulation, we used the following values of the energy of an isolated *F* atom: –99.69827 Hartree in the B3PW hybrid scheme and –99.37689 Hartree in the HF calculations. In this case, $E_{Fc} = E_{def} - E_{perf} + E_F$ where E_{def} and E_F denote the energies of the defective SC and an isolated fluorine atom, and E_{perf} is the energy of the ideal SC.

The electronic structure of crystals with a defect

In the energy band diagram, which was plotted by high-symmetry points in the first Brillouin zone (Fig.), the level of the bound unpaired electron was in the energy gap (α-electrons). The corresponding electron-hole level appeared in the band structure of β-electrons in the same band, but in the region of positive energies (the dashed line). Both methods gave this result, but the energy difference was smaller in the hybrid scheme than in the HF calculations.

The data on the band structure and the corresponding experimental results are given in Table 2. The experimental absorption energy of the F-center is compared with the energy difference between the conduction band bottom and the F-center level ΔE_{Fc}. (This is acceptable since excitation levels of the F-center are located near the conduction band bottom.) It follows from the analysis of these results that good conversion at large was achieved for the SC192. The hybrid method described more precisely the excitation parameters of the defect.

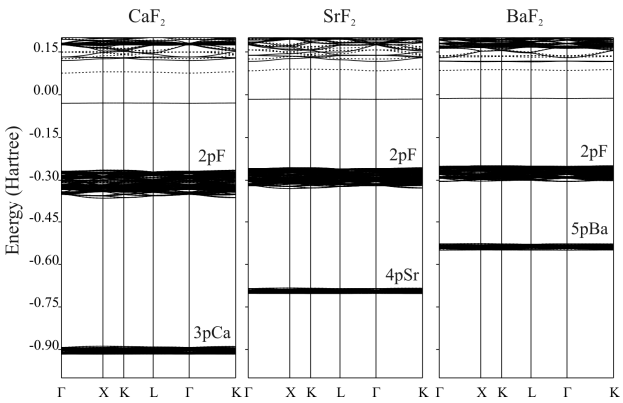

Fig. Bottom conduction (positive energies) and valence with core (negative energies) bands of an *F* – center in CaF_2, SrF_2 and BaF_2 (B3PW – method, SC81)

Table 2. Values of the energies of formation (E_{Fc}) and optical absorption (ΔE_{Fc}) of the defect (eV) for SC192

		exp. [15]	HF	B3PW
CaF_2	E_{Fc}	-	6.49	7.36
	ΔE_{Fc}	3.3	10.06	4.02
SrF_2	E_{Fc}	-	6.29	7.46
	ΔE_{Fc}	2.85	9.80	3.48
BaF_2	E_{Fc}	-	6.01	7.29
	ΔE_{Fc}	2.03	8.79	3.52

Paramagnetic properties of an F-center

Electron resonance methods can provide the experimental demonstration of the presence of an unpaired electron. These experiments produce useful information about the spin density distribution and the configuration of defects. The direct comparison of calculated and experimental data is possible in the case of the superfine interaction constant *a*, which determines the superfine structure of spectra.

Calculated and experimental [15] values of the isotropic constant *a* for fluorine ions are given in Table 3. The HF approximation provided satisfactory results, demonstrating convergence to the SC81. It should be noted however that this method generally underestimates experimental values [2]. The results obtained by the B3PW hybrid scheme were closer to the experimental values for fluorine ions that were nearest to the F-center. Other "fluorine" spheres were difficult to

analyze because of the negative spin density of these spheres. This negative spin density is not correct from the physical viewpoint.

Table 3. Calculated and experimental values of the superfine interaction constant a (MHz) for the nearest neighbors of the defect

	Atom	exp. [15]	HF	B3PW
CaF_2	F_{100}	182.51	123.77	181.99
	F_{110}	10.85	3.84	7.07
	F_{111}	21.33	9.87	8.74
	$F_{\overline{111}}$	3.72	1.03	-1.14
	F_{200}	3.26	1.09	-6.61
SrF_2	F_{100}	121.6	74.01	107.96
	F_{110}	9.7	2.66	-15.49
	F_{111}	29.6	15.93	2.74
	$F_{\overline{111}}$	3.49	0.78	0.87
	F_{200}	1.94	0.48	11.30
BaF_2	F_{100}	53.8	30.88	66.97
	F_{110}	5.1	0.75	-9.31
	F_{111}	42.6	22.35	14.05
	$F_{\overline{111}}$	2.2	0.35	-14.07
	F_{200}	0.86	0.14	0.55

The coordination sphere of fluorine ions in [111] positions were divided into two spheres (F_{111} и $F_{\overline{111}}$), which differed one from the other by the presence or absence of the cation between these fluorine ions and the F-center. In this case, the fluorine on the far side of the cation had a larger a value. Early calculations of superfine interaction constants [15, 16] did not reveal differences between the anions in this coordination sphere. Our calculations demonstrated these differences.

5. Conclusion

A systematic study was given to the electronic structure of CaF_2, SrF_2 and BaF_2 crystals. The electronic and magnetic properties of F-centers in these crystals were analyzed too. Calculations were made using the CRYSTAL98 program package and the method of linear combinations of atomic orbitals in the Hartree-Fock approximation and in terms of the B3PW hybrid functional. Advantages and drawbacks of each of the methods in the analysis of various properties of the crystals were shown.

The study provided data on the relaxation of the nearest environment of F-centers, the Mulliken charge density distribution, and band structure diagrams. These data are useful for interpretation of a wide set of experimental data.

The effect of the supercell on the convergence of properties of the defect was analyzed. The convergence at large was obtained in the supercell of 192 atoms.

The calculated isotropic constants were in satisfactory agreement with values determined in electron paramagnetic resonance experiments. The best agreement was provided by the hybrid method for F_{100} fluorine and its equivalents. The HF approximation was more stable as a research method and provided a correct determination, from the physical viewpoint, of superfine interaction constants for several coordination spheres.

It was shown that the excitation parameters of both the crystal and an F-center (E_{g1}, the optical absorption energy of the defect) agreed much better with the corresponding experimental values when they were calculated by the hybrid method than just by the HF approximation.

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