

Ab initio calculations for SrF₂ with *F*- and *M*-centers

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Abstract

In an *ab initio* study of vacancies in the alkaline earth fluoride SrF₂ we calculated the electronic bulk properties of perfect SrF₂ crystals and with *F*- and *M*-centers. By means of the hybrid B3PW method, in which Hartree–Fock exchange is mixed with density functional theory exchange functionals, using Becke’s three-parameter method, combined with the non-local correlation functionals by Perdew and Wang, our result for the band gap of SrF₂ (11.31 eV) agrees with experimental data (11.25 eV) very well. Different kinds of vacancy basis sets for the *F*- and *M*-center in SrF₂ are tested to find the best description for simulating structural and electronic properties of such defects in SrF₂. The resulting set is found to work also best for vacancies in CaF₂ and BaF₂.

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1. Introduction

Similar to CaF₂ and BaF₂, SrF₂ is a large-gap fluoride with *Fm*3*m* structure. There are three atoms in the unit cell, the cation Sr²⁺ locates at the origin point, and two anions F[−] on the diagonal points ($\frac{1}{4}a, \frac{1}{4}a, \frac{1}{4}a$) and ($\frac{3}{4}a, \frac{3}{4}a, \frac{3}{4}a$), where *a* is the lattice constant, *a* = 5.799 Å in experiment [1]. The experimental value [2] of the direct band gap of perfect SrF₂ is 11.25 eV. In recent years several experimental and theoretical investigations [3–6] of SrF₂ have been performed.

In a SrF₂ crystal *F*-centers and more complicated vacancies, which consist of combinations of *F*-centers, can exist permanently. Here we will theoretically investigate the electronic properties of *F*-centers and the simplest combination of two *F*-centers, the *M*-center. Many electronic structure calculations for such cases use the basis sets of the absent atoms as those of the corresponding vacancies. However, the results obtained by such approach often deviate significantly from experiments, e.g. those obtained in electron

paramagnetic resonance (EPR) [7]. To shed some light on this point we have checked first the formation energies of *F*- and *M*-centers with the standard basis set 7_311 of the fluorine atom. The basis set from [8] describes the fluorine electronic configuration as an s shell with seven exponents and three sp hybrid shells with three, one, one exponents, respectively. Therefore we abbreviate this standard basis set as 7_311. The results then showed that the vacancies in SrF₂ prefer not combining together, since two times of the formation energy of the *F*-center is found smaller than the formation energy of the *M*-center. In order to simulate the properties of vacancies in SrF₂ more properly, we repeated these calculations using five other vacancy basis sets (see Table 1), which were firstly proposed in [9]. We abbreviate also these five other vacancy basis sets. As shown in Table 1 the first set has two sp hybrid shells each with only one exponent. We name this set 11_sp_sp. The other four basis sets have only one s or sp shell with one exponent. For this reason we called them 1_s and 1_sp and give the corresponding exponent in parentheses. The results show that the set 1_s(0.073) produces the best description for vacancies in SrF₂. Not only binding and the hyperfine

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Table 1
Five possible simple basis sets for F -centers in SrF_2

Basis set [9]	Index	Shell	Exponent	Coefficients	
				s	p
1l_sp_sp		sp	0.437	1.0	1.0
		sp	0.137	1.0	1.0
l_sp	1	sp	0.093	1.0	1.0
	2	sp	0.073	1.0	1.0
l_s	1	s	0.093	1.0	1.0
	2	s	0.073	1.0	1.0

parameters of the F -center are now considerably improved, but also the band position of the M -center agrees with experimental data (2.08 eV) in good accuracy. For a more comprehensive study, we investigated also the electronic properties in two other alkaline earth fluorides, CaF_2 with lattice constant 5.5 Å and BaF_2 with lattice constant 6.26 Å. With the new vacancy set 1_s(0.073) we got clearly better results than those found in [10,11], which used the standard set 7_311. This shows that the choice of an appropriate vacancy basis set is a quite critical point in such defect calculations and that the simple 1_s(0.073) basis in alkaline earth fluoride systems does not only save computational costs, but also gives a more accurate physical description.

2. Methodology of calculations

In this work we use the latest 2006 version of the CRYSTAL computer code [20] to calculate structural and electronic properties of the perfect SrF_2 crystal and that with vacancies. For the perfect SrF_2 crystal, in addition to the Hartree–Fock method and the local density approximation (LDA) method, we implemented in our calculations two other hybrid methods: Becke’s exchange functionals using Becke’s three-parameter method [14] combined with the nonlocal correlation functional of Perdew and Wang [15–17] (B3PW), as well as that with the nonlocal correlation functional of Lee et al. [14,18,19] (B3LYP). In what follows we discuss the F - and M -center in SrF_2 crystals only on the basis of the hybrid B3PW method, since it turns out to be more appropriate for simulating the perfect crystal.

CRYSTAL06 can calculate periodic systems by using the approximation of linear combination of atomic orbitals (LCAO) [20,21]. The basis set of Sr , we used in our work, is from Habas et al. [22] and optimized by the Hay-Wadt small-core effective core pseudopotential (ECP). The F -basis set is from Nada [8]. The reciprocal space integration is performed by sampling the Brillouin zone with a $8 \times 8 \times 8$ Pack-Monkhorst net [23]. The F - and M -center calculations are mainly done with 96-atom supercells which is sufficiently large to guarantee converged results.

3. SrF_2 bulk structure

First we investigated the lattice constant and bulk modulus with different methods, since they can be easily verified

Table 2
Lattice constant, bulk modulus and direct band gap $\Gamma \rightarrow \Gamma$ of the perfect SrF_2 crystal

Method	LDA	B3PW	B3LYP	HF	Experiment
a (Å)	5.685	5.845	5.880	5.895	5.799 [1]
B (GPa)	117.54	77.11	79.52	77.35	74.53 [13]
$\Gamma \rightarrow \Gamma$ (eV)	8.806	11.306	11.185	20.941	11.25 [2]

in experiments. Our results and experimental data are shown in Table 2. The relative error of the lattice constant a_0 and bulk modulus B are 1.7% and 3.8% in the HF method without correlation correction, 2.0% and 57.7% in the LDA method, 1.4% and 6.7% in the hybrid B3LYP method, and 0.8% and 3.5% in the hybrid B3PW method. The hybrid B3PW method gives clearly the best results, a finding which is consistent with similar results for other fluorides.

Next, we used the so-called Mulliken population analysis to investigate the effective charges. The effective charges of Sr and F are $+1.897e$ and $-0.948e$ in LDA, $+1.944e$ and $-0.972e$ in HF and $+1.909e$ and $-0.954e$ in B3PW, all of them only have a very small deviation from the ideal ionic values ($+2e$ and $-1e$). This is the inevitable result of that SrF_2 is a highly ionic bound crystal.

In an ionic crystal, the overlap populations between nearest neighbors should be close to zero, i.e. there would be no covalent coupling between Sr and F , as well as between F and F . In our calculations the overlap populations of the charge clouds turn out to be even slightly negative, $-42me$ for $\text{Sr}-F$ and $-8me$ for $F-F$, which is in accordance with the highly ionic character of the material.

The analysis of band gaps is an important aspect for insulating materials. According to Rubloff [2] the experimental result for the direct band gap ($\Gamma \rightarrow \Gamma$) in SrF_2 is 11.25 eV. In Table 2 we present our theoretical results for four different methods. The result from LDA is 8.806 eV, which coincides with the well-known fact that DFT-LDA calculations underestimate the band gap by a factor up to two. The HF method overestimates the band gap almost two times larger than the experimental value, while the results of hybrid B3PW and B3LYP methods are considerably better. The best result (from B3PW), 11.306 eV, only deviates from the experimental value by 0.50%. In Fig. 1 the electronic band structures obtained from the HF and B3PW method are shown.

4. F -center in SrF_2

In most of our simulations of F -centers we used 96-atom supercells. The first EPR-spectrum study of the F -center in SrF_2 was carried out by Hartog and Arends in 1967 [12], and the first ENDOR-spectrum study by Stoneham et al. in 1968 [7]. As shown in Fig. 2, the fluorine vacancy is in the middle of the supercell with an extra electron remnant. In order to simulate the properties of the F -center more accurately, we have implemented calculations with six

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