First-Principles Calculations for the H Center in SrF$_2$ Crystals

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The ground state of H-center systems for the SrF$_2$ crystal is simulated with two different arrangements, which are oriented along either [100] or [111] axes. The calculations are based on hybrid Hartree–Fock and density functional theory exchange functionals by using Becke's three-parameter method combined with the nonlocal correlation functionals of Perdew and Wang. The energy difference between H centers with different orientations shows that the H center oriented in the [111] direction in alkaline earth fluorides is the most stable configuration. The geometric relaxations of the neighboring atoms surrounding the H centers are presented. The combination energy of an H center and the formation energy of the related F–H pair in both alkaline earth fluorides are discussed. We report also the electronic structure of the H center systems. The effective charges and spins of the substitutional and interstitial fluorine atoms show that the hole is located at the interstitial fluorine in the system with the [111] orientation of the H center. The band structures are illustrated. With the help of studying the total and partial density of states, the constituents of the defect bands are clarified.

I. Introduction

Because of large band gaps (all above 10 eV), the alkaline earth fluorides are transparent in a very large frequency region. As a member of the alkaline earth fluorides, the perfect SrF$_2$ crystal has a large band gap about 11.24 eV in experiment.[1] Therefore it is commonly used as window materials for both infrared and ultraviolet wavelengths. Because of its high technological potential, the alkaline earth fluorides have been studied during the last years by many experimental and theoretical groups.[2–13] The alkaline earth fluorides are ionic large-gap insulators with $Fm\bar{3}m$ structure. The metallic cation M^{2+} (in this work Sr^{2+}) locates at the origin point in a face-centered cubic (fcc) unit cell and the anion F$^-$ at the diagonal point $((1)/(4), (1)/(4), (1)/(4))a$, where a is the lattice constant ($a = 5.799$ Å for SrF$_2$ in experiments[14,15]). The direct band gaps at the Γ point between the conduction band (CB) and valence band (VB) obtained with B3PW simulations (10.96 eV for SrF$_2$) is discussed in ref 16.

Here we focus our work on the H center (a hole trapped at an interstitial anion) in SrF$_2$ crystal using ab initio calculations with the B3PW method. A hole here means an electron deficiency at the metallic atom. The H center is a two (fluorine) atomic defect center in the SrF$_2$ crystal. One of them is called a substitutional fluorine, which substitutes a fluorine atom at the lattice point, and the other one is called an interstitial fluorine because it is located at the interstitial site. H centers can be readily formed by irradiating with 50-kV X-rays at 4 K in alkaline earth fluoride crystals doped with heavier trivalent rare-earth ions (Re^{3+}).[17] In undoped alkaline earth fluorides one needs heavy irradiation with about 1 MeV electrons to produce H

centers at 77 K.[18] In addition, experiments have shown that the hole is located on the interstitial fluorine (H2 atom) and a nearest substitutional fluorine (H1) giving a [111]-oriented molecular ion.[18,19] We simulated all three conceivable arrangements of the H center (i.e., [100]-, [110]-, and [111]-oriented arrangements). According to our simulations, the [110] case is unstable and relaxes into the [100] arrangement. The two fluorine atoms (H1 and H2) with [100] arrangements are moved to both sides of the lattice point during the atomic relaxation but are oriented still in direction [100]. Namely, one can not distinguish the interstitial and substitutional fluorine in this situation, because the H1 and H2 atoms lie at the symmetric points with each other. The lowest total energy and hence the most stable configuration belongs to the [111] arrangement of the H center, in accordance with the experimental result. Even though in this work we also show the results of the calculation for the [100] case, just as a reference configuration for the [111] case. By studying the effective charge and spin of the H center and its neighbors, we demonstrate that the hole is located at the H2 atom in the [111] case. Such calculations can also interpret the geometrical relaxations of the H center and its neighboring atoms. The negative overlap population between the H1 and H2 atoms implies that there is no covalent bond between them. The ground-state band structures and the density of states (DOS) sketches of the single H center system in the SrF$_2$ crystal are also reported in this work. Note that abbreviation is adopted for the H centers oriented along [100] and [111] axes as H⟨100⟩ and H⟨111⟩ in the following text, respectively.

The paper is organized as follows. Section two introduces the calculational method and reports all required parameters. Section three presents the orientations of the H center in the SrF$_2$ crystal and the geometrical relaxations. The electronic properties, e.g., effective charge and spin of the H center and its neighbors, are discussed in section four. The electron density map and spin map are also illustrated there to help understanding

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TABLE 1: Distances between H1 and H2 Atoms of H⟨100⟩ and H⟨111⟩ Centers in CaF$_2$, SrF$_2$, and BaF$_2$ Calculated in 24-, 48-, 81-, and 96-Atom Supercells in Units of Ångstroms

size of supercell	H⟨100⟩			H⟨111⟩		
	CaF$_2$	SrF$_2$	BaF$_2$	CaF$_2$	SrF$_2$	BaF$_2$
24	1.85	1.87	1.90	1.98	1.97	1.98
48	1.85	1.88	1.91	1.98	1.97	1.98
81	1.86	1.88	1.91	1.98	1.98	1.98
96	1.86	1.88	1.91	1.98	1.98	1.98

the electronic properties of the H center systems. Band structures and DOS sketches are illustrated in section five.

II. Methodology and Parameters of Calculations

It is well-known that the Hartree−Fock (HF) method considerably overestimates the optical band gap, while density functional theory (DFT) underestimates the gap.[20] And the hybrid B3PW functional method has been testified to achieve remarkably accurate electronic and geometrical structures for alkaline earth fluorides[16,20−23] as well as for ABO$_3$ perovskites.[24−27] In the former work dealing with F and M centers, oxygen-vacancy dipoles and hydrogen impurities,[16,20−23] reliable band gaps have been obtained for them by using the B3PW method. Therefore the calculations in this work are also performed with this method. The hybrid exchange-correlation B3PW functional involves a hybrid of exact nonlocal Fock exchange, LDA exchange, and Becke's gradient-corrected exchange functional[28] combined with the nonlocal gradient-corrected correlation potential introduced by Perdew and Wang.[29−31] To perform the first-principles DFT-B3PW calculations we used the 2006 version of the CRYSTAL computer code, i.e., CRYSTAL06,[32] which can calculate periodic systems by using Gaussian-type functions (GTFs) localized at atoms as the basis for an expansion of the crystalline orbitals. The importance for this study is that CRYSTAL06 calculates the electronic structure of materials within both HF and Kohn−Sham (KS) Hamiltonians.

To employ the linear combination of atomic orbitals (LCAO)-GTF method, it is desirable to have the optimized basis sets (BS). In this paper, the Hay−Wadt small-core effective core pseudopotential (ECP) was adopted for the Sr atom.[25,33] Fluorine atoms were treated with the all-electron BS developed in a previous work.[34] It is shown in refs 16, 20, and 21 that these sets lead to better agreement of the calculated lattice constant and bulk modulus with experimental data.

The reciprocal space integration was performed by sampling in the Brillouin zone of the three atoms unit cell with a 6 × 6 × 6 Pack−Monkhorst net.[35] For the lattice constant of SrF$_2$, the values (5.845 Å) from former works[16,23] was used, because the energy minimum of a perfect SrF$_2$ bulk was found with this values in the simulations. The calculations for H centers were done with 96-atom supercells, which is sufficient to guarantee converged results. The distances of H centers oriented along the [111] and [100] axes, varying from the 24-atom supercell to the 96-atom supercell, converges for 81-atom supercells as shown in Table 1. It proves again that the 96-atom supercell is large enough for the calculations for H center systems not only for SrF$_2$ but also for CaF$_2$ and BaF$_2$. The effective charges of the atoms and overlap populations between nearest neighbors are obtained by using the standard Mulliken analysis.

III. Atomic Structures

There are two possible arrangements in our simulation for an H center in the SrF$_2$ crystal. The interstitial and substitutional

fluorine atoms could be aligned in either the [100] or [111] directions. We also attempted to obtain the other arrangement of the H center, in the [110] direction. But this H-center system in SrF$_2$ relaxed unprompted into the arrangement in the [100] direction. In 1970, Beaumont, Hayes, Kirk, and Summers[17] detected that the H centers in alkaline earth fluorides are all located in the [111] direction. Therefore we discuss the H center in the SrF$_2$ crystal only with arrangements in the [100] and [111] directions, which are the stable configurations in our simulation systems. The arrangement in the the [110] direction is invalid in our study. The sketches for both [100] and [111] arrangements are shown in Figure 1. Panel a, the left part of Figure 1, shows that the interstitial and substitutional fluorine atoms lie on the edge of a cell, i.e., along the [100] axis, and the lattice point is located exactly in the middle of the two fluorine atoms. Because of the crystal symmetries, both fluorine atoms, which constitute an H center in the SrF$_2$ crystal, are identical with each other. Therefore we can not make certain which one is the interstitial fluorine atom and which one is the substitutional in the [100] arrangement of an H center in the SrF$_2$ crystal. In this case we label the fluorine atoms of the H center just interchangeably as H1 and H2 (H1 ⇋ H2). The investigations of the geometric relaxation and other electronic properties in the next section prove this again, that the H1 and H2 atoms are equivalent and can not be named just the interstitial or substitutional fluorine atom. The [111] arrangement of an H center in the SrF$_2$ crystal is shown in the right panel of Figure 1. Different from the left one, the interstitial and substitutional fluorine atoms can be easily distinguished. The substitutional fluorine, labeled as H1 in the sketch, is moved a little bit from the lattice point along the [111] axis toward the interstitial fluorine which is located on the body diagonal of a cube constituted with fluorine atoms on the lattice points. In the sketch we label the interstitial fluorine as H2 atom in the [111] arrangement. In this situation, the (substitutional) H1 and (interstitial) H2 atoms are no longer equivalent.

It is a constraint that a more stable state or configuration should have a lower total energy. By eq 1, we define and calculate the combination energies of the H centers in the arrangements [100] and [111]

$$E_c(H) = E_d^{n+1} - E_F - E_p^n \qquad (1)$$

where E_F denotes the total energy of an isolated fluorine atom, E_d^{n+1} denotes the total energy of the system with an H center, and E_p^n denotes the total energy of the perfect n-atom supercell system, respectively. In other former works, the authors used similar formulas to calculate the formation energies of several other defects in crystals, such as vacancies and impurities in the alkali halides and alkaline-earth fluorides. The values of the energy differences appear to be negative with the equation in our case. The combination energies of H⟨100⟩ and H⟨111⟩ in the SrF$_2$ crystal are −7.75 and −8.66 eV, respectively. But that does not mean the H center system was more stable than the perfect system together with an isolated fluorine atom. In fact, the H center in alkaline-earth fluorides is always accompanied with an F center (the fluorine vacancy), which is the vacancy created by removing a fluorine atom from the perfect bulk system. Now we can modify eq 1 as follows (eq 2) to calculate the so-called formation energy for a F−H pair in the SrF$_2$ crystal.

$$E_f(FH) = E_d^{n-1} + E_d^{n+1} - 2E_p^n \qquad (2)$$
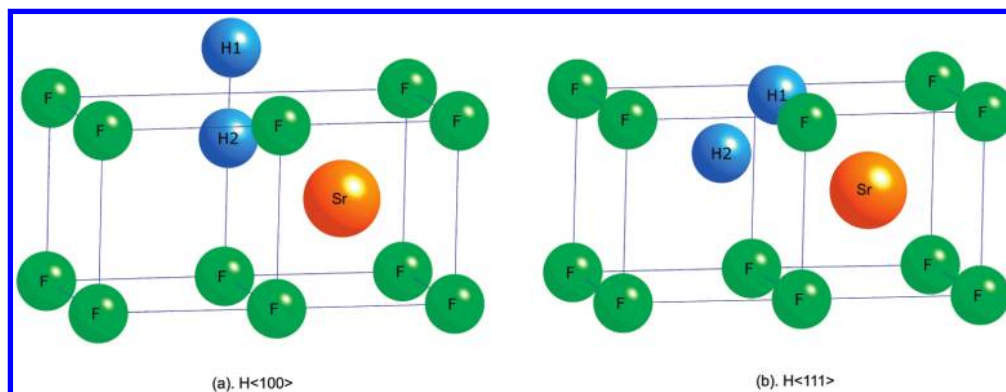
Figure 1. The sketches of the arrangements of the H center in SrF_2 crystal oriented along (a) the [100] axis and (b) the [111] the axis. (a) The two fluorine atoms of the H center are equivalent with each other, labeled exchangeably as H1 and H2 (H1 $\rightleftharpoons$ H2). (b) The substitutional and interstitial fluorine atoms of the H center are labeled as H1 and H2, respectively. The metal atoms (strontium) are labeled as Sr in the sketches.

TABLE 2: Atomic Displacements and Effective Charges of H Centers Oriented along the [100] and [111] Axis Calculated in a 96-Atom Supercell of the SrF_2 Crystal (in Percentage of the Lattice Constant $a_0 = 5.845$ Å)[a]

Shells		H⟨100⟩					H⟨111⟩			
	no. atoms	D $(a_0\%)$	Q	ΔQ	spin	no. atoms	D $(a_0\%)$	Q	ΔQ	spin
H1	1	+16.12%	−0.506	+0.448	0.444	1	+0.63%	−0.666	+0.288	0.337
H2	1	+16.12%	−0.506	+0.448	0.444	1		−0.319	+0.635	0.644
Sr1	2	+3.17%	+1.896	−0.013	−0.001	3	+1.04%	+1.908	−0.001	−0.001
Sr2	2	+3.17%	+1.896	−0.013	−0.001	1	+0.92%	+1.905	−0.004	0.002
F1	1	+4.00%	−0.893	+0.061	0.057	3	−0.93%	−0.954	0	0.001
F2	4	+0.11%	−0.954	0	0	3	+1.47%	−0.951	+0.003	0
F3	4	+0.78%	−0.954	0	0	6	+0.23%	−0.954	0	0

[a] Positive signs in the D columns indicate the outward movements relative to origin where the H1 atom of the H center should be located in a perfect crystal bulk. The effective charges are listed in Q columns in unit [e]. "+" indicates cations and "−" indicates anions. ΔQ labels the change in the effective charge compared to a perfect SrF_2 crystal ($Q_{Sr} = +1.909$ e, $Q_F = −0.954$ e[16]). Spin is the result of the spin difference of electrons with different spin directions ($n_\alpha − n_\beta$) also in unit [e].

where E_d^{n-1} denotes the total energy of the system with an F center. There are two isolated subsystems which are taken into account in this formula. The first subsystem is the SrF_2 crystal with a single H center. The other one is the SrF_2 crystal that contains an accompanying F center and lies far away from the first subsystem to ensure that there is no interaction between the F and H centers at all. By use of the formation energy of the F center (10.00 eV) with a quite simple basis set 1_s (0.073) from the conclusion in ref 16, these combination energies of H⟨100⟩ and H⟨111⟩ now allow to calculate the formation energies of the F−H pairs in SrF_2 from eq 2. The calculated formation energies are 2.25 and 1.34 eV for F−H⟨100⟩ and F−H⟨111⟩ pairs, respectively. The energy difference between the two arrangements of the H center in the SrF_2 crystal (0.91 eV) implies that the arrangement of an H center along the [111] axis is more stable than that along the [100] axis. This theoretical conclusion is in agreement with experiment.[19] The large difference of the relaxation energies, i.e., the difference between the total energies for the relaxed and unrelaxed atomic configurations, (1.47 eV) between the H⟨100⟩ and H⟨111⟩ arrangements, shows also that the H⟨100⟩ configuration in SrF_2 crystal is very difficult to exist in nature. On the contrary, the H⟨111⟩ configuration just needs 0.29 eV relaxation energy in the SrF_2 crystal.

The distance between H1 and H2 (or named the length of the H center) of the H⟨111⟩ arragement in the SrF_2 is 1.98 Å, which is much shorter than the F−F distance (2.92 Å). It is essentially the same as the length of the H⟨111⟩ in CaF_2 and BaF_2 crystals (see Table 1). The length of the H⟨100⟩ in SrF_2 is 1.88 Å and different from the values in CaF_2 and BaF_2 because of the instability of the H⟨100⟩ configuration in alkali-earth fluorides.

The geometry relaxations of the H1 fluorine and the neighboring atoms surrounding the H⟨100⟩ and H⟨111⟩ centers are reported in columns D of Table 2 expressed in percentage of the lattice constant of perfect SrF_2 crystal. The labels of the atoms in Table 2 are defined according to the symmetries of the atoms in the fcc lattice to distinguish the various atoms. The numbers by the letters indicate the orders of the neighboring atoms of the H center. All of the neighboring atoms are moved outward relative to origin where the fluorine atom of the H⟨100⟩ center should be located in a perfect crystal bulk. The movements of the H1(H2) atom and the neighboring metal atoms in the H⟨100⟩ system are much larger than those in the H⟨111⟩ system. The H1 (substitutional) atom of the H⟨111⟩ center is also moved about 0.63% outward the lattice point, toward the H2 (interstitial) atom along the [111] axis. The first neighboring fluorine atoms (F1) of the H⟨111⟩ center are relaxed about 0.93% toward the origin. The influence on the second neighboring fluorine atoms (F2) from the H⟨111⟩ center is much bigger than that from the H⟨100⟩ center. The difference of the geometry relaxations of the both configurations can be explained through the study of their electronic structures, which will be analyzed in the next section.

IV. Electronic Properties

By use of the Mulliken population analysis, we can estimate partial atomic charges from calculations based on the LCAO method which we used through the whole work. The atomic charges will be changed after the defect formation from the perfect crystal bulk. The redistribution of the electrons are illustrated in Figures 2 and 3 for the H⟨100⟩ system and the H⟨111⟩ system, respectively. The inserted fluorine atom leads

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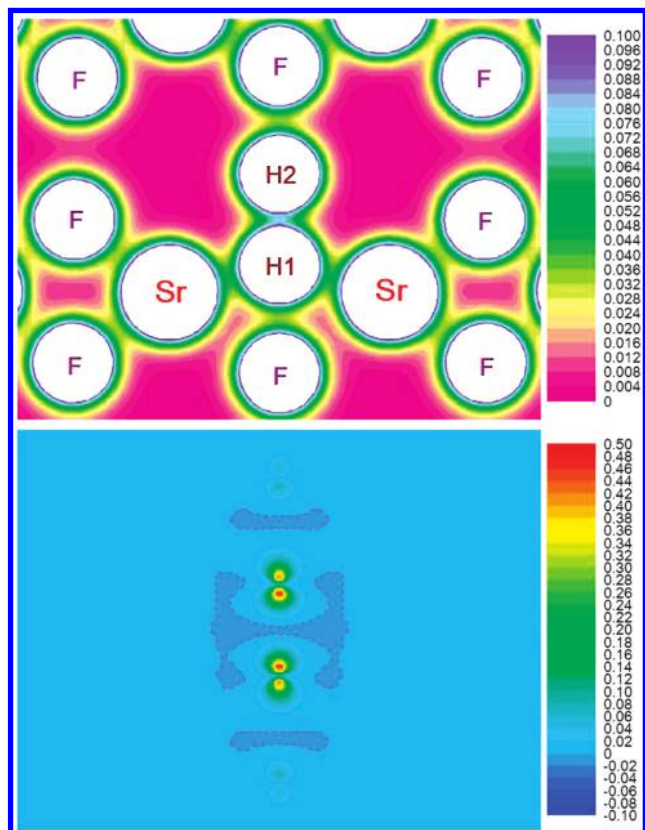
Figure 2. Electron denstity (upper) and spin density (down) contour plot in the (1$\bar{1}$0) plane of a SrF$_2$ crystal with an H center oriented along the [100] axis, from 0 to 0.1 e/bohr^3 with a linear contour spacing of 0.004 e/bohr^3 and from −0.1 to 0.5 e/bohr^3 with a linear spacing of 0.02 e/bohr^3, respectively. The short dotted lines in the panel indicate null isodensity lines.

to an unpaired electron in our defect systems. To account for the unpaired electron, the spin density diagrams are displayed in Figure 2 and 3. The spin densities of H⟨100⟩ and H⟨111⟩ centers present two ellipsoids with a point of tangency at the nucleus (or referred to as a dumbbell), which suggests the unpaired electron mainly consists of a p orbital. Comparing the two spin density diagrams, the H⟨111⟩ center possesses more polarization than the other one.

According to the former work,[16] the effective charges of the fluorine and strontium atoms are −0.954 and +1.909 e in the perfect SrF$_2$ crystal bulk, respectively. In the H⟨111⟩ system, the total effective charge of the H1 and H2 atoms is −0.985 e, close to the charge of a single fluorine anion in the SrF$_2$ perfect crystal. The H1 charge is −0.666 e and is larger than the H2 charge (−0.319 e) by a factor of around two. The effective charges of the neighboring atoms have almost not been changed in this situation. The nonzero spin charge of electrons is also centered on the H1 and H2 atoms. In this case, the spin charge on the H2 atom (0.664 e) is just 2-fold larger than that on the H1 atom (0.337 e). The calculations of the effective charges and spin charges for the H⟨111⟩ system are in qualitative agreement with the measurements in refs 17 and 36 showing that the hole is located on the interstitial fluorine. However, the effective charges of H1 and H2 atoms in the H⟨100⟩ system are identical, and the corresponding value is −0.506 e. The effective charges of the surrounding atoms of the H⟨100⟩ center are also changed, but the change of the first neighboring fluorine atom is particularly big (+0.061 e). The spin charges of both H1 and H2 atoms are 0.444 e. The first neighboring fluorine

atom shows also some spin difference (0.057 e). All the data can be found in Table 2.

The overlap populations of H centers and their neighbors are obtained as well. In H⟨100⟩ and H⟨111⟩ systems, the overlap populations between H1 and H2 atoms are −192 me and −68 me, respectively. The negative values prove that there is no covalent bond between the H1 and H2 atoms and even show a repulsion force between them following the Pauli principle. The overlap population between the H2 atom and its first neighbor F2 atom in the H⟨111⟩ system is −64 me. However, the overlap population between H1 (or H2) atom and its first neighboring fluorine atom F1 is −130 me in the H⟨100⟩ system, even two times bigger than the previous. Between the H1 (or H2) atom and its first neighboring strontium atom Sr1 (or Sr2), there exists also an overlap population of −94 me. The more negative overlap population in the H⟨100⟩ system is responsible for the more instability of the H⟨100⟩ center.

V. Band Structure of H Centers on the Surfaces

Evidence for the existence of a broad absorption band of the H center peaking at about 308 nm in CaF$_2$ and SrF$_2$ and at about 330 nm in BaF$_2$ has been found by Beaumont et al. in ref 17. In other words, CaF$_2$, SrF$_2$, and BaF$_2$ with H⟨111⟩ centers exhibit optical absorption centered around 4.03, 4.03, and 3.76 eV, respectively. There is no such experimental result for the alkaline earth fluorides with H⟨100⟩ center because of its instability in nature. The calculated results for defect levels (see Figure 4) are in good agreement with the experimentally observed optical absorption. In the one-electron approximation scheme, the experimentally observed optical absorption could be due to an electron transfer from the ground state, to the empty β-spin band induced by a hole localized on the H center (see Figure 4). The corresponding calculated transition energies are 3.01 eV for SrF$_2$ with an H⟨111⟩ center and 3.36 eV with the H center oriented along the [100] axis. This looks reasonable considering the fact that we work here within a ground-state theory only. This theoretical underestimation of excitation energies with respect to the experimental results was presented already in our former work.[16] More recent schemes based on the Bethe−Salpeter equation in many body perturbation theory can give a better description of such excited-state properties.[37] If one investigates the right panel of the band sketch for the H⟨100⟩ system in Figure 4 carefully, it would be found that the minimum of the energy difference between the VB top and the empty β-spin band does not locate at the Γ point any more. Only the value (3.36 eV) at the M point for the H⟨100⟩ system is presented, because the VB top between X and R and the total empty β-spin band are very straight. The calculated band gaps (distance between VB and CB) in SrF$_2$ containing H⟨111⟩ centers at the Γ point are 11.19 eV for both α- and β-spin states. However, for the defective H⟨100⟩ system we find the band gaps to be 10.74 and 10.12 eV at the Γ point for the α - and β-spin states, respectively, which are smaller than those with the other orientation. The primary cause of this band gap reduction is the transformation of the VB top during the formation of the H⟨100⟩ center in SrF$_2$ crystal. There is almost no difference between the CBs of the H⟨100⟩ and H⟨111⟩ systems. The α-spin bands lie very close to the VBs under the Fermi level in both cases. But in the case of H⟨100⟩ orientation, a single band is explicitly separated from the VB.

The total and partial DOS of the H⟨100⟩ center in SrF$_2$ are displayed in Figure 5. The p orbitals of the H⟨100⟩ center form the β band, and H1 and H2 act in the same role. The total and partial DOS of the H⟨111⟩ center in SrF$_2$ are displayed in Figure
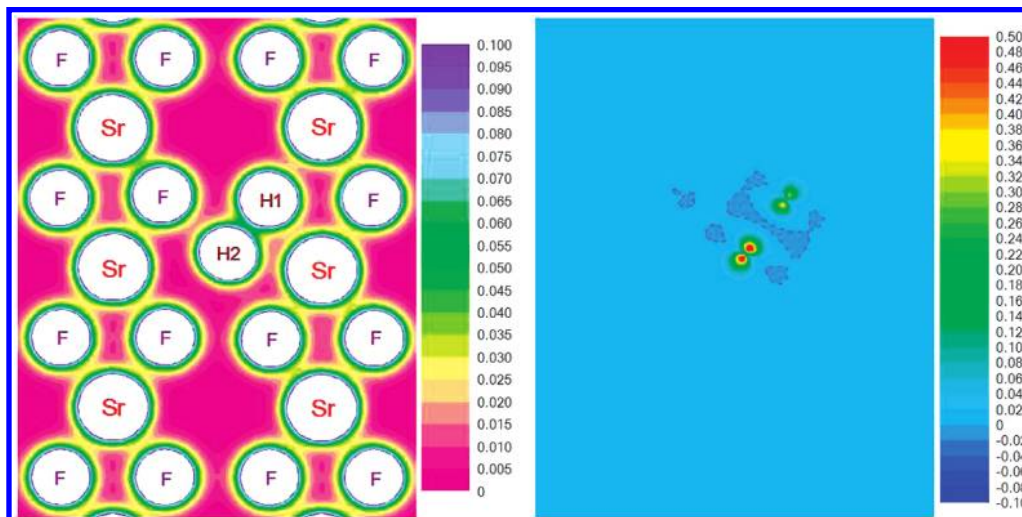
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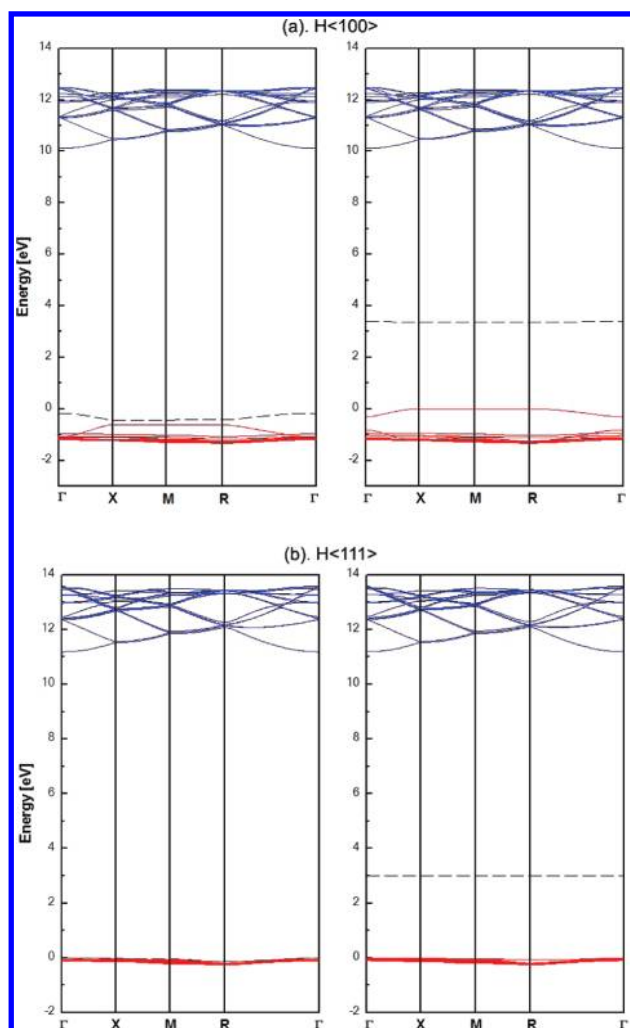
Figure 4. B3PW band structure simulations of H center in the (a) [100] and (b) [111] directions in a 96-atom supercell of SrF_2. The dashed lines in the left figures of both horizontal panels show the α (spin-up)-defect bands. However they both lie very close to the top of the valence band. In the right figures of both panels, the dashed lines indicate the β (spin-down)-defect band well separated within the band gap. The (horizontal) k axis goes through the path: (000) → (00(1)/(2)) → ((1)/(2)0(1)/(2)) → ((1)/(2)(1)/(2)(1)/(2)) → (000).
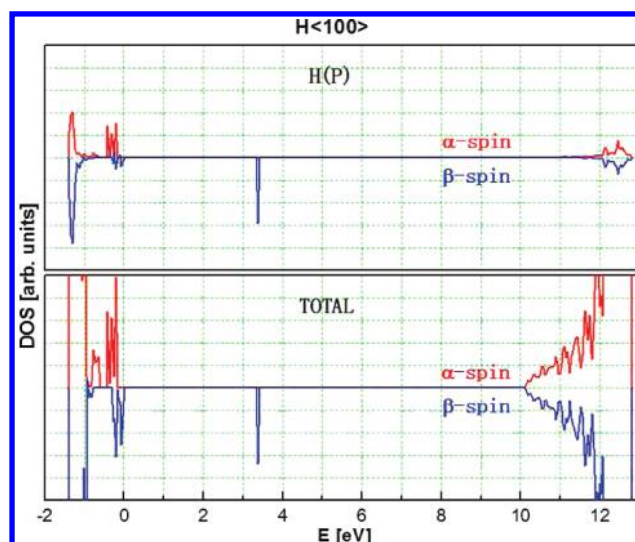
Figure 5. Total and projected DOS for the H⟨100⟩ center in SrF_2. The Fermi level lies at 0 eV.

6. The results of our calculations illustrate that H1 and H2 p orbitals form the β band, and H2 does the major contribution. There is also some contribution from the H⟨111⟩ center p orbitals to the top of VB, as shown in Figure 6. According to our previous work [20,21] we can conclude that the p orbitals of the F atoms form the upper VB and the β-spin defect level is mainly composed of H⟨111⟩ center *p*-orbitals, whereas the CB bottom consists mainly of metal ion *d*-orbitals.

VI. Conclusions

The results show that the H center orientation in the [111] direction in SrF_2 crystal is the energetically more favorable one, in agreement with experiment. It is 0.91 eV lower than the H center orientated in the [100] direction. The H1 atom of the H⟨111⟩ center relaxes to the interstitial H2 atom due to an increase of the potential energy at the substitutional point. According to our calculations, the hole is mainly localized on the interstitial fluorine in the H⟨111⟩ system, in agreement with the experimental observations, and induces an empty level in the β-spin band gap of the SrF_2 crystal, located 3.01 eV above the VB top. But for the metastable H⟨100⟩ system, we can only

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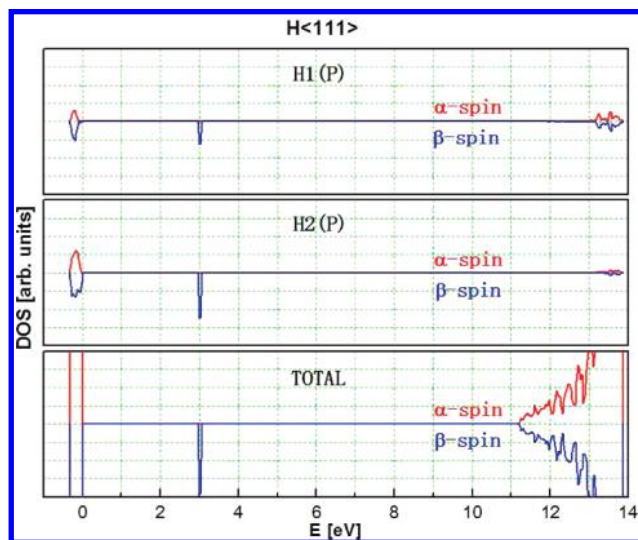
Figure 6. Total and projected DOS for the H⟨111⟩ center in SrF₂. The Fermi level lies at zero eV.

be sure that the hole is localized between the H1 and H2 atoms, because the H1 and H2 atoms are identical in this case. The β-spin band is located 3.36 eV above the VB top. By use of the DOS investigation, we found that the β-spin defect band is composed of H center p orbitals and H2 does the major contribution to the β-spin defect band in the H⟨111⟩ system.

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