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Abstract
Using the B3PW method we simulate the ground state of H center systems for CaF$_2$ and BaF$_2$ crystals. 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. We present the geometric relaxations of the neighboring atoms surrounding the H center. 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 also report 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. The band structures are presented. By studying the DOS sketches the constituents of the defect bands are clarified.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Because of the large band gaps (all above 10 eV) the alkaline earth fluorides are transparent in a very large frequency region. Therefore they are commonly used as window materials for both infrared and ultraviolet wavelengths. CaF$_2$ is particularly important as an ultraviolet optical material for integrated circuit lithography. Due to such high technological potential the alkaline earth fluorides have been studied during recent years by many experimental and theoretical groups [1–18]. The alkaline earth fluorides are ionic large-gap insulators with a $Fm\bar{3}m$ structure. The metallic cation M^{2+} (in this work: Ca^{2+} and Ba^{2+}) locates at the origin point in a three-atom face-centered-cubic (fcc) unit cell and two anions F$^-$ at the diagonal points $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})a$, where a is the lattice constant ($a = 5.4630$ Å for CaF$_2$ and $a = 6.20$ Å for BaF$_2$ in experiments [19, 20]). We have already presented the direct band gaps at the Γ point between the CB (conduction band) and VB (valence band) obtained with B3PW simulations (10.96 eV for CaF$_2$ and 11.30 eV for BaF$_2$) in [14] and [15].

Here we present our work on the H center (a hole trapped at an interstitial anion) in CaF$_2$ and BaF$_2$ crystals using *ab initio* calculations with the B3PW method. H centers can be readily formed by irradiation using 50 kV x-rays at 4 K in alkaline earth fluoride crystals doped with heavier trivalent rare earth ions (Re^{3+}) [21]. In undoped alkaline earth fluorides one needs heavy irradiation, with about 1 MeV electrons, to produce H centers at 77 K [22]. 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 [22, 23]. 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 lowest total energy and hence the most stable configuration belongs to the [111] arrangement of H centers, in accordance with the experimental result. In the work we also show some 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
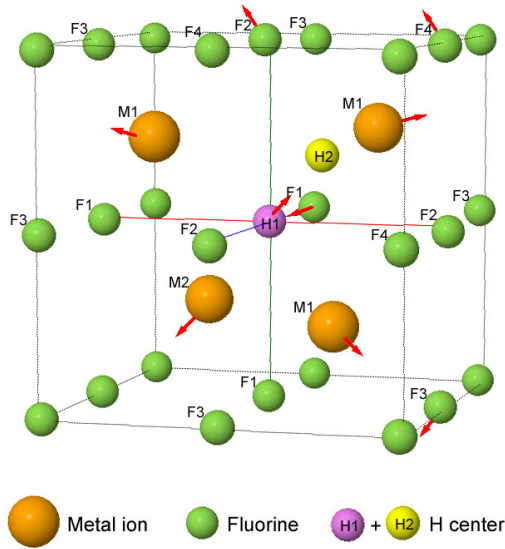
Figure 1. H center oriented along the [111] axis. The arrows show the directions of the atomic displacements surrounding the H center. Different labels are defined according to the symmetries of the various atoms.

Table 1. Distances between H1 and H2 atoms of H centers in CaF_2 and BaF_2 crystals calculated in 24-, 48-, 81- and 96-atom supercells in units of (Å).

Size of supercell	H⟨100⟩		H⟨111⟩	
	CaF_2	BaF_2	CaF_2	BaF_2
24	1.85	1.90	1.98	1.98
48	1.85	1.91	1.98	1.98
81	1.86	1.91	1.98	1.98
96	1.86	1.91	1.98	1.98

neighbors we determine that the hole is located at the H2 atom. Such calculations can also interpret the geometrical relaxations of the H center and its neighboring atoms. The even negative overlap population between the H1 and H2 atoms shows that there is no valence bond between them. The ground state band structures and the DOS sketches of an H center system in CaF_2 and BaF_2 crystals are also reported in this work.

The paper is organized as follows. Section 2 introduces the calculational method and reports all the required parameters. Section 3 presents the stable orientation of H centers in CaF_2 and BaF_2 crystals, and the geometrical relaxations. The electronic properties, e.g. effective charge and spin of the H center and its neighbors, are presented in section 4. The electron density map and spin map are also illustrated there to help the reader to understand the electronic properties of the H center system. Band structures and DOS sketches are illustrated in section 5.

2. Methodology and parameters of calculation

It is well known that the Hartree–Fock (HF) method considerably overestimates the optical band gap and density functional theory (DFT) underestimates it. But the hybrid B3PW functional has been shown to achieve remarkably accurate electronic and geometrical structures for alkaline earth fluorides [14–18], as well as for ABO_3 perovskites [24–27]. In our former work dealing with F and M centers, oxygen-vacancy dipoles and hydrogen impurities [14–18], reliable band gaps for these defect systems have been obtained by using the B3PW method. Therefore, our 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 by

Perdew and Wang [29–31]. To perform the first-principles DFT-B3PW calculations we used the latest 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. It is most important for this study that CRYSTAL06 calculates the electronic structure of materials within both HF and Kohn–Sham (KS) Hamiltonians.

However, in order to employ the linear combination of atomic orbitals (LCAO)-GTF method, it is desirable to have optimized basis sets (BS). In the present paper, we used the same BS for Ca atoms as in [14]. The Hay–Wadt small-core effective core pseudopotential (ECP) was adopted for the Ba atom [25, 33]. Fluorine atoms were treated with the all-electron BS developed in [34]. It was shown in [14, 15] and [17] 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 the Brillouin zone of the three atoms unit cell with a $6 \times 6 \times 6$ Pack–Monkhorst net [35]. For the lattice constant of CaF_2 and BaF_2 we use the values (5.50 and 6.26 Å) from our former work [14, 15]. The present calculations for H centers are done with 96-atom supercells, which is sufficient to guarantee converged results. The distances of H centers, oriented not merely along the [111] axis, but also along the [100] axis, going from the 24-atom supercell to the 96-atom supercell, have converged 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 in CaF_2 and BaF_2. The effective charges of the atoms and overlap populations between nearest neighbors are obtained using the standard Mulliken analysis.

3. Mechanical properties

The hole in the H center in alkali earth fluorides is located primarily on an interstitial fluorine and another nearby fluorine substituting a lattice fluorine [23], i.e. an H center in these systems consists of two fluorine atoms. Experiments [22] have shown that the two fluorines of the H center in alkaline earth fluorides form a [111] oriented molecular ion, as shown in figure 1. The interstitial and substitutional fluorine are labeled H1 and H2, respectively. Even though no H center oriented in the [100] direction exists, we also report some calculations for this orientation. H centers in the [110] direction were also tested. But during the relaxation of various atoms the interstitial fluorine, which was located at the center of a face of

Table 2. Atomic displacements and effective charges of H center oriented along the [111] axis calculated in a 96-atom supercell of CaF$_2$ and BaF$_2$ crystals (in per cent of the lattice constant: $a_0 = 5.50$ Å for CaF$_2$; $a_0 = 6.26$ Å for BaF$_2$). Positive signs in the D columns indicate 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 the Q columns in units of e. '+' indicates cations and '−' indicates anions. ΔQ labels the change in the effective charge compared to perfect CaF$_2$ and BaF$_2$ crystals ($Q_{Ca} = +1.803$ e, $Q_F = -0.902$ e in CaF$_2$ [14] and $Q_{Ba} = +1.845$ e, $Q_F = -0.923$ e in BaF$_2$ [15]). Spin is the result of the spin difference of electrons with different spin directions ($n_\alpha - n_\beta$) also in units of e. M indicates the metal atoms (calcium and barium) in CaF$_2$ and BaF$_2$, respectively.

Shells	No. of atoms	CaF$_2$				BaF$_2$			
		D (a_0%)	Q	ΔQ	Spin	D (a_0%)	Q	ΔQ	Spin
H1	1	+0.77%	−0.659	+0.243	0.303	+0.24%	−0.621	+0.302	0.363
H2	1	—	−0.287	+0.615	0.662	—	−0.339	+0.584	0.626
M1	3	+0.99%	+1.799	−0.004	−0.001	+0.99%	+1.843	−0.002	−0.001
M2	1	+0.82%	+1.792	−0.011	0.003	+0.81%	+1.842	−0.003	0.005
F1	3	−0.92%	−0.900	+0.002	0.002	−0.66%	−0.924	−0.001	0
F2	3	+1.70%	−0.895	+0.007	0	+1.20%	−0.915	+0.008	0
F3	6	+0.24%	−0.901	+0.001	0	+0.21%	−0.922	+0.001	0
F4	3	+0.91%	−0.894	+0.008	0.005	+0.61%	−0.916	+0.007	0.002

the fluorine cube at the outset, moves to one side of the cube. This means the [110] orientation is unstable and turns to a metastable [100] orientation. The H center along the [111] axis is referred to as the H⟨111⟩ center and the other one oriented in the [100] direction is called the H⟨100⟩ center in the following text.

The calculated distances between the H1 and H2 are listed in table 1. For H⟨111⟩ they are essentially the same in both CaF$_2$ and BaF$_2$. The H⟨111⟩ center in SrF$_2$ was also tested and the corresponding distance is also 1.98 Å. This value is much shorter than the corresponding F–F-atoms distance in the perfect bulk material. The fact that the distances between H1 and H2 are essentially the same for all three systems shows the high stability of the H⟨111⟩ compared to the metastable H⟨100⟩. For the metastable H⟨100⟩ the distances are clearly different for all three crystals. The distance of the H⟨100⟩ center in SrF$_2$ is 1.88 Å, just in-between the values of 1.86 Å and 1.91 Å for CaF$_2$ and BaF$_2$, respectively. Comparing the total energies of the H⟨100⟩ and H⟨111⟩ systems, the total energies of H⟨111⟩ systems are reduced by 0.83 eV and 0.90 eV for CaF$_2$ and BaF$_2$, respectively. The energetically most favorable configuration of the H center in an alkaline earth fluoride crystal is thus the H⟨111⟩ configuration, in full agreement with experiment.

The relaxation energies, i.e., the difference between the total energies for the relaxed and unrelaxed atomic configurations, in both configurations (H⟨100⟩ and H⟨111⟩) and both crystals (CaF$_2$ and BaF$_2$ 2) are also calculated. The values for H⟨100⟩ in CaF$_2$ and BaF$_2$ (2.36 eV and 3.80 eV, respectively) are much larger than those of the H⟨111⟩ configuration (CaF$_2$: 0.36 eV; BaF$_2$: 0.18 eV). In [14–18, 36, 37] and [38], the various authors used similar formulae such as the following equation (1) to obtain then the so-called formation energies of their defect systems:

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

where E_F denotes the total energy of a single fluorine atom, and E_d^{n+1} and E_p^n the total energies of the system with and without an H center, respectively. Using this equation, we obtain negative energy values for each H center

system. This is distinct from the cases of other charge centers [14–18]. Because an H center is always accompanied by an F center, we cannot really call the energy from the equation (1) a formation energy of an H center anymore, but prefer the designation *combination* energy of the interstitial and substitutional fluorine in the H center. The combination energies of H⟨111⟩ in CaF$_2$ and BaF$_2$ crystals are −8.53 eV and −8.96 eV, respectively. The corresponding values in H⟨100⟩ systems are −7.69 and −8.03 eV. Using in addition the calculated formation energy of the F center in [14] and [15] for CaF$_2$ (16.14 eV) and BaF$_2$ (16.23 eV), these combination energies of H centers now allow one to calculate the so-called formation energies of F–H center pairs in CaF$_2$ and BaF$_2$ from the following equation (2):

$$E_f(FH) = E_f(F) + E_c(H), \qquad (2)$$

where the $E_f(F)$ denotes the formation energy of the F center, and $E_c(H)$ is the combination energy from equation (1). We obtain 7.61 eV and 7.27 eV as the formation energies of a F–H center with the H center oriented along the [111] direction in CaF$_2$ and BaF$_2$ crystals, respectively. To calculate the formation energies of the F centers in a 96-atom supercell of CaF$_2$ and BaF$_2$ crystals, we use the same setting as in the calculations of the H centers in the present work. The F center is the vacancy created by removing a fluorine atom from the perfect bulk system. From the result of [17] we know that the simple BS 1_s(0.073) is more suitable to simulate the F center in alkaline earth fluorides than other more complicated BS. Thus we use here also the BS 1_s(0.073).

The geometry relaxation of the H1 fluorine and the neighboring atoms surrounding the H⟨111⟩ center is also shown in figure 1. According to the symmetries of the atoms in the fcc lattice, we define different labels to distinguish the various atoms. The arrows at the atoms show the direction of their relaxation due to the forming of the H center. The calculated atomic displacements of the important atoms are listed in columns D of table 2 as percentage of the lattice constant arranged according to the labels in figure 1. For the CaF$_2$ H⟨111⟩ case, firstly, the three Ca1 atoms and one Ca2 atom are repelled from the origin by 0.99% and 0.82% of
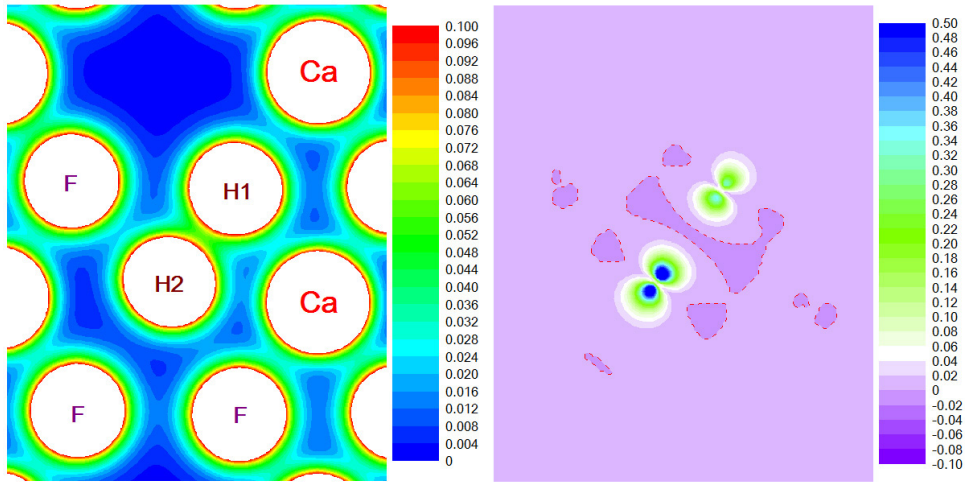
Figure 2. Electron density (left) and spin density (right) contour plot in the $(1\bar{1}0)$ plane of a CaF_2 crystal with an H center along the [111] direction, from 0 e/bohr^3 to 0.1 e/bohr^3 with a linear contour spacing of 0.004 e/bohr^3 and from -0.1 e/bohr^3 to 0.5 e/bohr^3 with a linear spacing of 0.02 e/bohr^3, respectively. The short dotted lines in the right panel indicate null isodensity lines.

the lattice constant a_0, respectively. F2 and F4 atoms also shift backward from the origin and their displacements are 1.70% and 0.91% of a_0, respectively. In contrast, F1 atoms are attracted to the origin by 0.92% of a_0. And finally, the substitutional fluorine H1 moves slightly from the anion site towards the interstitial fluorine H2 by 0.77% of a_0. The analysis of the relaxation of the H$\langle 111 \rangle$ center and surrounding atoms in CaF_2 shows that the relaxation is slightly stronger than for the F center in CaF_2 and F2 atoms exhibit considerable shifts [14]. This phenomenon can be explained by the effective charges, see below. For BaF_2, the relaxation pattern of the H$\langle 111 \rangle$ center and the surrounding atoms is similar to the CaF_2 case. The H1 and H2 atoms in the H$\langle 100 \rangle$ system are equivalent. H1 and H2 atoms of the H$\langle 100 \rangle$ center are positioned on both sides of origin at half the distance of the H$\langle 100 \rangle$ center. The first neighboring atom of the H$\langle 100 \rangle$ center, which is a fluorine atom labeled as F1, are repelled from the origin by 5.44% and 2.62% of a_0 in CaF_2 and BaF_2 crystals, respectively. The second neighboring atoms of the H$\langle 100 \rangle$ center (two metal atoms) shift backwards from the origin by 3.15% and 2.97% of a_0 in CaF_2 and BaF_2 crystals, respectively; also much larger than the case of the H$\langle 111 \rangle$ systems.

4. Electronic properties

The charge density map for the H$\langle 111 \rangle$ center in CaF_2 is shown in the left panel of figure 2. The H$\langle 111 \rangle$ center for the BaF_2 crystal has a similar charge density map. Table 2 presents also the effective charges of the H$\langle 111 \rangle$ center and surrounding atoms for CaF_2 and BaF_2 in column Q. The analysis of the effective charges shows that the total effective charge of the H1 and H2 atoms in CaF_2 or BaF_2 is close to the charge of a single fluorine anion in the CaF_2 or BaF_2 perfect crystal. These calculated results can explain the weak relaxations of the atoms surrounding the H$\langle 111 \rangle$ center in CaF_2 and BaF_2. For the CaF_2 case, the total charge of the H$\langle 111 \rangle$ center is

-0.946 e and larger than the fluorine charge in perfect CaF_2 bulk (-0.902 e) by 0.044 e. The H1 charge is -0.659 e and is larger than the H2 charge (-0.287 e) by a factor of around two. For the BaF_2 crystal, the calculated H$\langle 111 \rangle$ center charge equals -0.960 e and is also more than the fluorine charge in perfect BaF_2 bulk (-0.923 e) by 0.037 e. The absolute value of the H1 charge is also larger than the corresponding value of H2 by an approximate factor of two. Therefore, for the CaF_2 and BaF_2 systems, the total charge of the H$\langle 111 \rangle$ center is not distributed equally between the two F atoms, like in the H$\langle 100 \rangle$ case. The calculations of effective charges are in qualitative agreement with the measurements in [39] and [21] showing that the hole is located on the interstitial fluorine. Opposite, the effective charges of H1 and H2 atoms in an H$\langle 100 \rangle$ system are identical and the corresponding values are -0.472 e and -0.468 e in CaF_2 and BaF_2, respectively.

Using Mulliken population analysis we obtain the overlap populations of H centers and their neighbors. In the H$\langle 111 \rangle$ system, the overlap populations between H1 and H2 atoms are -68 me and -66 me for CaF_2 and BaF_2, respectively. The negative values prove that there is no covalent bond between the H1 and H2 atoms in the H$\langle 111 \rangle$ system and even show a repulsion force between them. The overlap populations between the H2 atom and its first neighbor F2 atom are also negative, -86 me and -34 me, respectively. In the H$\langle 100 \rangle$ system, the overlap populations of the H center are -216 me and -140 me for CaF_2 and BaF_2, respectively, almost three times larger than in the H$\langle 111 \rangle$ system. They are -176 me and -76 me between H1 (or H2) and its first neighboring fluorine atom F1.

The localization of the unpaired electron at the H$\langle 111 \rangle$ center is clearly shown in the spin density map of CaF_2 (see the right panel of figure 2). From this map we can see that the spin polarization of the neighbor atoms almost disappears. According to our calculations, the F4 and F2 spin charge ($n_\alpha - n_\beta$) are 0.005 e, 0.002 e in CaF_2 and 0.002 e, 0 e in BaF_2, respectively. The spin charges for H1 (CaF_2: 0.303 e;
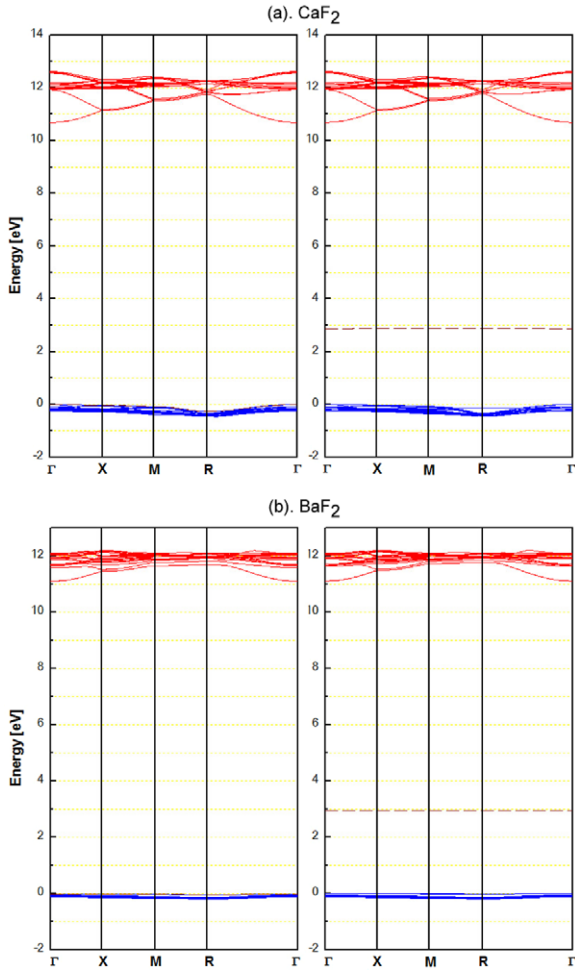
Figure 3. B3PW band structure simulations of H centers in the [111] direction in a 96-atom supercell of (a) CaF_2 and (b) BaF_2. The short lines in the left figures of both horizontal panels show the α (spin–up)-defect bands. However they both lie very close to the top of the valence band and are thus essentially indistinguishable from the bulk bands. 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: $(000) \rightarrow (00\frac{1}{2}) \rightarrow (\frac{1}{2}0\frac{1}{2}) \rightarrow (\frac{1}{2}\frac{1}{2}\frac{1}{2}) \rightarrow (000)$.

Figure 4. Total and projected density of states (DOS) for the H center in CaF_2 and BaF_2. The Fermi level lies at 0 eV.

BaF_2:.363 e) and H2 (CaF_2: 0.662 e; BaF_2:0.626 e) are also in accordance with the fact that the hole is primarily located on the interstitial fluorine.

5. The band structure of H centers

CaF_2 and BaF_2 with H$\langle 111\rangle$ centers exhibit optical absorption, centered around 4.03 eV and 3.76 eV, respectively [21]. Our calculated results for defect levels (see figure 3) allow us to explain this experimentally observed optical absorption. In the one-electron approximation scheme, the experimentally observed optical absorption could be due to an electron transfer from the H$\langle 111\rangle$ center ground state, to the empty β-spin band induced by a hole localized on the H$\langle 111\rangle$ center (see figure 3). The corresponding calculated transition energies are 2.88 eV for CaF_2 and 2.95 eV for BaF_2, which looks reasonable in
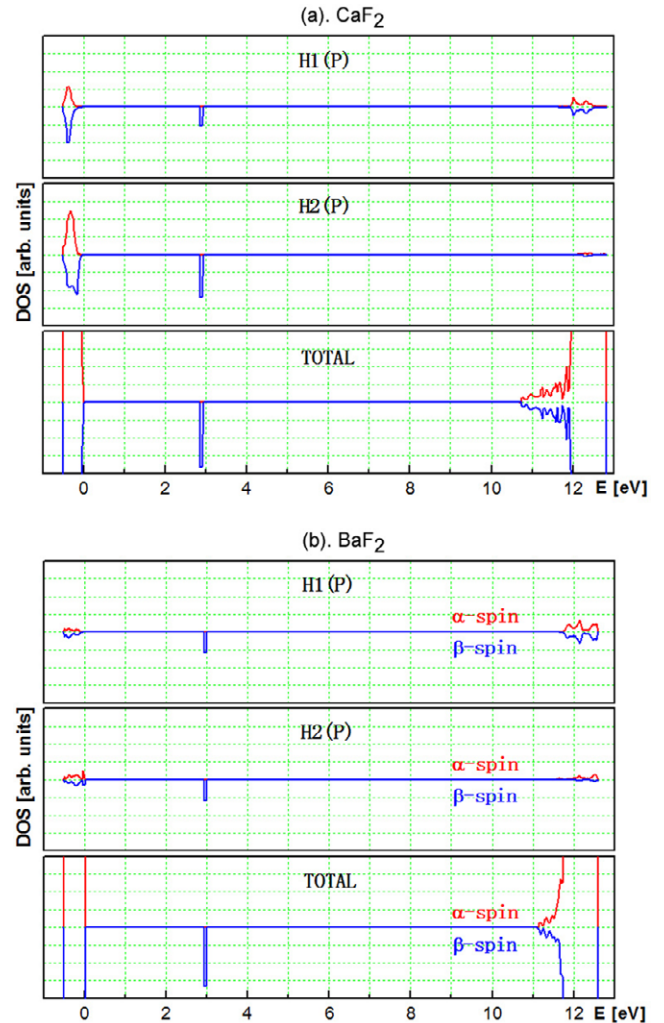
view of the fact that we work here within a ground state theory only. This theoretical underestimation of excitation energies with respect to the experimental results was found already in our former work [17]. More recent schemes based on the Bethe–Salpeter equation in many body perturbation theory can give a better description of such excited state properties. Our calculated band gaps (distance between VB and CB) for CaF_2 containing H$\langle 111\rangle$ centers at the Γ point are 10.69 eV for both α- and β-spin states. For the defective BaF_2 system we find 11.11 eV for both α- and β-spin states.

The total and partial density of states (DOS) of the H$\langle 111\rangle$ center in CaF_2 and BaF_2 are displayed in figure 4. The results of our calculations show that the H1 and H2 p-orbitals form the β band, and the H2 makes the major contribution. There is also some contribution from the H$\langle 111\rangle$ center p-orbitals to the top of VB, as we can see from figure 4. According to our previous work [14, 15] 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$\langle 111\rangle$ center p-orbitals, whereas the CB bottom consists mainly of metal ion d-orbitals.

6. Conclusion

The present results show, that the H center orientation in the [111] direction in CaF_2 and BaF_2 crystals is the energetically more favorable one, in agreement with experiment, and by 0.84 and 0.93 eV more favorable as an 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 agreement with the experimental observations, and induces an empty level in the β-spin band gap of the CaF_2 and BaF_2 crystals, located 2.88 eV and 2.95 eV above the VB top, respectively. Using the DOS investigation, we found that the β-spin defect band is mainly composed of H⟨111⟩ center p-orbitals.

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