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First-principles simulations of H centers in CaF₂

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ABSTRACT

H center, a hole trapped at an interstitial anion site, placed in the bulk and the (111) surface of calcium fluoride CaF₂, has been studied by using density functional theory (DFT) with hybrid exchange potentials, namely DFT-B3PW. The H center orients the (111) direction for the bulk case and the (100) direction for the surface case, and the hole is mainly localized on the interstitial fluorine. The surface H center leads to a remarkable XY-translation of the surface atoms. Spin and hyperfine coupling calculations show a considerable interaction between the unpaired spin and the spin of neighboring nuclei, and the surface effect strengthens the spin polarization and hyperfine structure. The hole induces an empty level in the β -spin band gap, located 2.88 eV above the valence band (VB) top, corresponding to the first optical absorption band, and the surface effect heightens the hole level considerably. Density of states (DOS) calculations reveal that the hole band mainly consists of the H-center p-orbitals, and the interstitial fluorine does the major contribution. Further study regarding the electron-hole pair, named FH pair in this paper, shows that the geometrical structure is similar to an F center and an H center paired together, whereas the hole localized on the H center in the isolated H-center case, moves to the fluorine vacancy (V_F) site. The electron-hole pair induces seven defect levels in the VB-CB (conduction band) gap, three of them located near the Fermi energy, being occupied, and four of them located above the Fermi level, forming the hole bands. The *p*-orbitals of the interstitial fluorine form the three electron bands and the four hole bands are composed of the *s*- and *p*-orbitals of the V_F .

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1. Introduction

Alkaline-earth fluorides such as CaF_2 and BaF_2 , whose band gaps are larger than 10 eV, are very important for many optical applications. Because of the large band gaps, 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. Additionally, CaF_2 can be chosen as an optical material also due to its cubic crystal structure with perfect optical isotropy, due to its chemical durability and its mechanical properties which make it applicable for lens fabrication [1–3]. Also, CaF_2 can be used as a material for radiation detection [4]. Considering the high technological importance of alkaline-fluorides, it is not surprising that during the last years, they have been the subject of many experimental and theoretical studies [5–28].

It is well known that optical and mechanical properties of crystals are strongly affected by defects and impurities unavoidably present in any real material. Contemporary knowledge of defects

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http://dx.doi.org/10.1016/j.commatsci.2014.03.058 0927-0256/© 2014 Elsevier B.V. All rights reserved. in solids has helped to create a field of technology, namely *defect engineering*, which is aimed at manipulating the nature and concentration of defects in a material so as to tune its properties in a desired manner or to generate different behaviors. CaF₂ could become important optical materials if one could avoid or, at least, control the photoinduced defect formation, which so far in applications degrades its optical quality. Therefore, it is significative to understand the nature of defects in CaF₂.

A kind of important point defect, *H* center (a hole trapped at an interstitial anion site), which is relevant and similar to the V_k center, a self-trapped hole, is readily formed in crystals doped with the heavier trivalent rare-earth ions (such as Re^{3+}). *H* centers produced by X-irradiation of rare-earth doped crystals have been identified in CaF₂ by Hall et al. [29] and in CaF₂, SrF₂ and BaF₂ by Beaumont et al. [30]. In suitably grown crystals these ions introduce charge-compensating fluorine interstitials (F_i^-) and a fraction of these are not closely associated with the rare-earth ions. When such crystals are X-irradiated at 77 K large concentrations of V_k centers are produced and a relatively small concentration of *H* centers. However, when the crystals are heated to induce migration of V_k centers a fraction of the moving holes are retrapped at (F_i^-) sites producing







additional H centers. The hole is located on the interstitial fluorine and a nearest substitutional fluorine giving a (111) oriented molecular ion (X_2^{-}) . H centers may also be produced in undoped alkaline-earth fluorides by heavy irradiation with 1 MeV electrons at 77 K. In some orientations of the external magnetic field the EPR lines of *H* centers produced by electron irradiation show partly resolved structure suggesting perturbation by another defect produced by the radiation [31]. For the optical absorption, Beaumont et al. found evidence for the existence of an absorption band of the *H* center peaking at about 4.03 eV in CaF_2 and 3.76 eV in BaF_2 [30]. Additionally, a two-photon process will separate charges and will create an electron-hole pair [32,33]. The charges of the electron and the hole have further the possibility to lower their energy by distorting the surrounding lattice. This means that a localization of the electron-hole pair takes place together with a lattice distortion. The resulting state is called an *FH* pair [34,35] or a self-trapped exciton (STE) [36].

According to our knowledge, few theoretical investigations on H centers in CaF₂ were addressed in the literature. As a subsequent research of our previous work regarding defects in CaF₂, such as F centers [22], hydrogen impurities [24] and oxygen-vacancy dipoles [25], we performed calculations for H centers in CaF₂ crystal and surface. As an extension, we also reported the calculated results regarding *FH* pairs in CaF₂ in this paper.

2. Calculation Method

To study H centers in CaF₂, we applied the first-principles hybrid density functional theory (DFT-B3PW) method, according to our previous studies dealing with CaF2, BaF2 and SrF2 perfect crystals, which gave the best agreement with experiments for the lattice constant, bulk modulus and optical band gap. The hybrid exchange-correlation B3PW functional involves a hybrid of nonlocal Fock exact exchange, local density approximation (LDA) exchange, and Becke's gradient-corrected exchange functional [37] combined with the nonlocal gradient-corrected correlation potential by Perdew and Wang [38–40]. Because of the presence of an unpaired electron in the H center, the spin-unrestricted approximation approach has been used in our calculations. All numerical calculations of H centers in CaF₂ were performed by the CRYSTAL-2009 computer code [41]. The CRYSTAL-2009 code employs Gaussian-type functions (GTF) localized at atoms as the basis for an expansion of the crystalline orbitals. In order to employ the LCAO-GTF (linear combination of atomic orbitals) method, it is desirable to have optimized basis sets (BS). In our calculations, we applied the all electron basis sets developed by Catti et al. [7]. The basis sets are believed to be transferable, so that, once determined for some chemical constituents, they may be applied successfully in calculations for a variety of chemical substances where the latter participates. To characterize the the chemical bonding, covalency effects and charge redistribution after the creation of H center, we used a standard Mulliken population analysis for the effective static atomic charges and other local properties of the electronic structure as described, for example, in Refs. [42,43].

The reciprocal space integrations were performed by sampling the three-dimensional (3D) and two-dimensional (2D) Brillouin zones of the 96- and 108-atom supercells with $4 \times 4 \times 4$ and 6×6 Pack–Monkhorst nets [44], respectively. The thresholds *N* (i.e., the calculation of integrals with an accuracy of 10^{-N}) in our calculations were chosen as a compromise between the accuracy of calculations and the large computational time for large supercells. They are 7, 7, 7, 7 and 14 for the Coulomb overlap, Coulomb penetration, exchange overlap, the first-exchange pseudo-overlap and the second-exchange pseudo-overlap, respectively [45]. For the lattice constant (a_0) of CaF₂ bulk, we use the theoretical optimized value of 5.50 Å from our former work [22].

To simulate *H* centers in CaF₂, we created a 96-atom supercell and a 108-atom (111) slab for the bulk and surface *H*-center calculations, respectively. After an interstitial fluorine atom is added, the atomic configuration of surrounding atoms is re-optimized via a search for the total energy minimum as a function of the atomic displacements from the regular lattice sites. The *H* center has the same charge as the substituted F^- in the ideal ionic case, so the supercell is neutral in our calculations and the electrostatic potential interactions between the neighboring defect supercells are eliminable.

3. Results and discussions

3.1. H centers in the CaF_2 bulk

Firstly, we performed calculations of different configurations for the *H* center in CaF₂ bulk. Considering the symmetry $(Fm\bar{3}m)$ of alkaline-earth fluorides, we calculated two simple configurations in which the *H* center orients along the (100) or (111) direction. The (100)- and (111)-oriented H centers are labeled $H_{(100)}$ and $H_{(111)}$ respectively in this paper. According to our calculations, we found that the energetically more favorable configuration of the *H* center is Config $H_{(111)}$, and the total energy of Config $H_{(100)}$ is larger than that of Config $H_{(111)}$ by around 0.83 eV. We also simulated some other configurations with the orientation slightly diverging the (111) axis and the results show that those configurations converge to Config $H_{(111)}$ after geometrical relaxations via a search of the minimum total energy. Therefore, Config $H_{(111)}$ should be the most stable configuration of the H center in CaF₂ and we mainly focus our current discussion on Config $H_{(111)}$ in this paper.

Next, we present the geometrical relaxation of the atoms surrounding the H center in the CaF_2 bulk (see Fig. 1). The calculated atomic displacements of the H center and surrounding atoms are listed in Table 1. The three Ca1 atoms and one Ca2 atom are repulsed from the H center by 1.06% and 0.82% of the lattice constant (a_0) , respectively. F2, F3 and F4 atoms also shift backward the *H* center and their displacements are 2.43%, 0.35% and 1.13% of a_0 , respectively. Oppositely, F1 atoms are attracted to the H center by 0.93% of a_0 . And finally, the fluorine atom of H1 moves from the regular anion site towards the H2 atom by 0.81% of a_0 . The distance between the *H*1 and *H*2 (or named the length of the *H* center) is 1.98 Å and much shorter than the F–F distance (2.75 Å). The analysis of the relaxation of the *H* center and surrounding atoms in CaF₂ shows that the relaxation is slightly stronger than for the F-center and Hydroxyl-impurity cases in CaF₂ and F2 atoms have considerable movements.

Table 1 also presents the effective charges of the *H* center and surrounding atoms for Config $H_{(111)}$. The total charge of the H center, i.e., the sum of the H1 and H2 charges, is -0.947 e, being larger than the substituted fluorine atom (-0.902 e) by 0.045 e. Around 0.066 e, localized on first- and second-nearest fluorine atoms, transfer inward to the H center and the four nearest Ca atoms. The H1 charge is -0.658 e and larger than the H2 charge (-0.289 e) by an approximate factor of two. Therefore, the total charge of the H center in CaF₂ is not distributed equally between the two F atoms. Hall et al. [29] and Beaumont et al. [30] demonstrated that the hole is located on the interstitial fluorine. Our calculations of effective charges are in qualitative agreement with their measurements. The Mulliken population analysis shows that there is practically no chemical bonding between H1 and H2 in the H center, since the relevant bond population (-68 me for Config) H_{111}) is even negative, which indicates a repulsion.



Fig. 1. A view of the (111)-oriented *H* center for Config $H_{(111)}$. The arrows show the directions of the atomic displacements surrounding the *H* center. According to the symmetries of the atoms, different labels are defined in spheres.

Table 1

Atomic relaxations (D (% a_0): as a percentage of the lattice constant of 5.50 Å) and effective charges (Q (e)) of the H center and surrounding atoms in the CaF₂ 96-atom supercell for Config $H_{(111)}$. ΔQ (e) is the charge difference between the defective and perfect crystals $Q_{Ca} = +1.803$ e, $Q_F = -0.902$ e in perfect CaF₂). Spin is the result of the spin difference between electrons with different spin directions ($n_{\alpha} - n_{\beta}$) also in unit (e). The shell labels have been defined in Fig. 1.

Atoms (shell)	No.	$D(\% a_{0})$	Q (e)	$\Delta Q(e)$	Spin (e)
H1	1	0.81	-0.658	+0.244	+0.305
H2	1	-	-0.289	+0.613	+0.660
Ca1	3	1.06	+1.799	-0.004	-0.001
Ca2	1	0.82	+1.792	-0.011	+0.002
F1	3	0.93	-0.900	+0.002	+0.002
F2	3	2.43	-0.895	+0.007	0.000
F3	6	0.35	-0.900	+0.002	0.000
F4	3	1.13	-0.894	+0.008	+0.005
F8	3	0.15	-0.901	+0.001	0.000

The localization of an unpaired electron at the *H* center is clearly shown in the spin density map (see Fig. 2). From Fig. 2, we can see that the spin density around the F5 atom is remarkable, the spin density around the F1 and F4 atoms is much weaker and the spin polarization of other neighbor atoms almost disappears. According to our calculations, the F5 spin charge $(n_{\alpha} - n_{\beta})$ is +0.014 e, the F1 and F4 spin charges are +0.002 e and +0.005 e, respectively. The spin charges for *H*1 (+0.305 e) and *H*2 (+0.660 e) are also in accordance with the spin density map, in which the spin density around the *H*2 is higher than the *H*1, and with the fact that the hole is primarily located on the interstitial fluorine. Additionally, the spin density of the *H* center looks like a spindle-shaped pattern, which suggests the unpaired electron mainly consisting of *p*-orbitals.

Next, we researched the hyperfine structure of the H center in CaF₂. Due to the presence of an unpaired electron and the interaction between the unpaired spin and the spin of neighboring nuclei, a hyperfine structure of the electron paramagnetic resonance (EPR) spectra can be detected. The isotropic hyperfine interaction is caused by the non-zero probability of an electron being in the

position of a given nucleus. The anisotropic contribution is due to the presence of higher order poles, and it is indicative of the deformation of the electronic density with respect to the spherical distribution. Usually, the experimental hyperfine coupling data are reported in terms of the isotropic *a* and anisotropic *b* hyperfine coupling constants. For each nucleus *N*, they are expressed (in MHz) as [46]

$$a = \frac{2\mu_0}{3h} g\beta_e g_N \beta_n \rho^{\alpha-\beta}(0) \tag{1}$$

$$b = \frac{\mu_0}{4\pi\hbar} g \beta_e g_N \beta_n \left[T_{11} - \frac{1}{2} (T_{22} + T_{33}) \right]$$
(2)

where the spin density $\rho^{\alpha-\beta}$ at *N*, the elements of the hyperfine coupling tensor T, and the electron g factor are the only terms that depend on the electronic structure of the system. All other multiplicative factors in Eq. (1) and (b) are tabulated constants [46,47] (h is the Planck constant, β_e and β_n the electronic and nuclear magnetons, μ_0 the permeability of the vacuum, and g_N the nuclear g factor). T is a tensor of rank 2, which is obtained as the field gradient of the spin density at N. Our calculated hole and neighbor fluorine hyperfine parameters are collected in Table 2. Because the hole is mainly located on the H2 and very close to the H1, the hyperfine couplings between the unpair electron and the fluorine nuclei of H1 and H2 are much stronger than other neighbor fluorine nuclei. Additionally, compared with the F-center case, the hyperfine coupling effect is more remarkable in the H-center system. Our calculated results are also in qualitative agreement with the spin density map, and the spin polarization is remarkable near H1, H2 and F5, as we can see in Fig. 2. Unfortunately, we did not find any experimental data regarding the hyperfine structure of *H* center in CaF₂ in the literature.

Alkaline-earth fluorides with defects degrade their optical quality and exhibit optical absorption. CaF_2 with H centers exhibit optical absorption, centered around 4.03 eV [30]. Our calculations on the defect levels induced between the valence bands (VBs) and conduction bands (CBs) suggest a possible mechanism for the optical absorption. Due to the presence of an unpaired electron, the



Fig. 2. Electron spin density contours in CaF₂ with the *H* center of Config $H_{(111)}$ from the (110) side view, being from -0.02 to 0.1 e/bohr^3 with a linear increment of 0.004 e/bohr^3 .

Table 2

Calculated isotropic (a) and anisotropic (b) hyperfine constants (in MHz) for the nearest fluorine atoms. The shell labels have been defined in Fig. 1.

Atoms (shell)	H1	H2	F2	F4	F5
a	605.9	707.9	8.8	8.5	31.4
b	531.4	1063.6	3.3	12.7	32.1

band structure for the *H*-center system is polarized into α - and β -spin band structures (see Fig. 3). Unlike unpolarized band structure curves whose states can be occupied by two electrons with up- and down-spin states, only one electron occupies one state. In the one-electron approximation scheme, the experimentally observed optical absorption could be due to an electron transfer from the *H*-center ground state, to the empty band at β -spin induced by a hole localized on the *H* center (see Fig. 3). The corresponding calculated value is 2.88 eV, which is reasonable, however, is underestimated with respect to the experimental result. The presence of an unpaired electron is also revealed by the band structure of the defective system given Fig. 3. Unlike the F-center case, the bound unpaired electron level labeled α band lies in the gap, but very closes to the top of VB, as we can see in the α -spin band structure in Fig. 3. The empty level induced by a hole localized on the H center appears in the β -spin band 2.88 eV above the VB top. Because of the selection rules, the electron transition from the α occupied band to the β unoccupied band is forbidden. Therefore, optical absorption mentioned before could be due to an electron transfer from the β -VB top to the empty level, induced by the hole localized on the H center. The VB-CB band gaps for CaF_2 crystal containing H centers at Γ point are both 10.69 eV for the α - and β -spin states, which are slightly reduced with respect to the band gap of perfect CaF₂ crystal (10.96 eV).

The total and partial density of states (DOS) of the *H* center in CaF₂ bulk is displayed in Fig. 4. The results of our calculations show that the *H*1 and *H*2 *p*-orbitals form the β -hole band and the *H*2 does the major contribution, which is consistent with our previous discussion regarding the spin density. There are also some contributions from the *H*-center *p*-orbitals to the top of VB, as we can see in Fig. 4. In comparison with other defects, such as *F* centers and OH⁻ impurities investigated in our previous works, the defect levels induced by *H* centers in the α -band structure is extremely close to the VB top. We suggest that it is due to this α defect level also consisting mainly of F *p*-orbitals. However, the defect bands of *F*-center and OH⁻-impurity systems, unlike the *H*-center case, are induced by other impurity species, such as *ghost* electron, hydrogen and oxygen atoms.

3.2. H centers in the CaF₂ surface

As an extension of the previous study on H centers in CaF₂ bulk, we performed calculations for surface H centers. For a (111) slab of CaF₂, there are three sublayers in each F–Ca–F layer from the side view and H centers could be only located at the upper and lower fluorine sublayers. We calculated four different configurations of the surface H centers, named Config H_{11}, H_{12}, H_{21} and H_{22} , corresponding to the substitutional fluorine atom labeled H1 locating at No. 1, 3, 4 and 6 fluorine sublayer, respectively, as we can see in Fig. 5. As discussed before, H centers orient the (111) direction in CaF₂ bulk. However, we could not confirm whether the H centers orient also the (111) direction for surface H-center systems. Therefore, we additionally simulated the four configurations mentioned above, but whose initial guessed orientations are not along the (111) axis accurately, in which some configurations do not



Fig. 3. Calculated B3PW band structure of a 96-atom supercell modeling the H center in CaF₂ for Config $H_{(111)}$.



Fig. 4. Total and partial density of states (DOS) for the *H* center of Config $H_{(111)}$ in CaF₂ crystal.

converge to the (111) direction after geometrical relaxations via a search of the minimum total energy, indicating that the (111)oriented *H* center is not the most stable configuration for surface *H*-center systems. We add the superscript (|) or (\) to express the (111)-oriented and (111)-unoriented *H* centers respectively, such as Configs $H_{11}^{(i)}$ and $H_{11}^{(i)}$. Our calculated results show that the energetically most favorable configuration for the surface *H* center is Config $H_{11}^{(i)}$, in which the angle between the *H*-center axis and the (111) direction is around 47.7°. Table 3 lists the relative energies of Config $H_{11}^{(i)}$ for other configurations. The total energies of other configurations are all larger than that of Config $H_{11}^{(i)}$, implicating a trend of *H* centers locating near the surface. Additionally, we also investigated the F-atom adsorption on the (111) surface. We



Fig. 5. Schematic sketch of the (111) slab containing *H* centers. The solid and hollow circles denote substitutional (*H*1) and interstitial (*H*2) fluorine atoms, respectively.

Table 3

Total energies (eV) of all the surface *H*-center configurations with respect to Config $H_{(1)}^{(1)}$. (|) and (\) express the (111)-oriented and (111)-unoriented *H* centers, respectively. Sublayer labels have been defined in Fig. 5.

Sublayer	11	12	21	22
(\)	0.00	+0.71	+1.04	+1.03
()	+0.26	+0.80	+1.21	+1.12

evaluated the adsorption energy computed by subtracting the energies of the optimized 108-atom (111) perfect slab and an isolated fluorine atom from the energy of the optimized 109-atom (111) slab containing the surface *H* center, i.e., the total energy of Config $H_{11}^{(v)}$, as shown in the following formula:

$$E_{ad} = E_H^{(n+1)} - E_F^{(1)} - E_{perfect}^{(n)}$$
(3)

Table 4

Geometrical properties of the surface *H* centers (*H*-center length (Å) and deviation angle shown in brackets) for all Configs. (|) and (\) express the (111)-oriented and (111)-unoriented *H* centers, respectively. Sublayer labels have been defined in Fig. 5.

Sublayer	11	12	21	22
(\)	1.96 (47.7°)	2.08 (0.6°)	1.97 (2.1°)	2.00 (1.8°)
()	2.02	2.08	1.96	2.01

where $E_F^{(1)}$ denotes the total energy of an isolated fluorine atom, and $E_H^{(n+1)}$ and $E_{perfect}^{(m)}$ the total energies of the slab with and without an H center, respectively. Our calculated adsorption energy equals to -0.60 eV, and with the definition of Eq. (3), the negative E_{ad} corresponds to stable adsorption. We also calculated some other adsorption cases in which a fluorine atom is located at other positions above the (111) surface, and the results show that those cases converge to Config $H_{11}^{(i)}$ or some metastable configurations with higher total energies. So, we can conclude that the F-atom adsorption on the (111) surface has a trend of forming Config $H_{11}^{(i)}$. Although the total energy of Config $H_{12}^{(i)}$ is larger than the absolute value of adsorption energy, implying a tendency to separation, we can consider it a metastable state since the relaxation-optimized procedure via a search for the total energy minimum as a function of the





atomic displacements from the regular lattice sites could be successful in an appropriate initial geometrical guess. Config $H_{11}^{(\setminus)}$ is more stable than other deeper-layer *H*-center systems, therefore, we mainly focus our current discussion on Config $H_{11}^{(\setminus)}$.

The geometrical structures of surface H centers for all the configurations, are calculated and depicted in Table 4. According to our studies on bulk *H*-center systems, the length of *H* center in CaF₂, BaF_2 and SrF_2 are all 1.98 Å, indicating that the H center as an (F_2^-) -style molecular has a steady geometrical structure in alkaline-earth fluorides. Our calculated CaF₂ surface *H*-center lengths for Configs $H_{11}^{(1)}, H_{12}^{(1)}, H_{21}^{(1)}$ and $H_{22}^{(1)}$ are 1.96 Å, 2.08 Å, 1.97 Å and 2.00 Å, respectively. The surface effect on the length of H center is very remarkable for Config $H_{12}^{(1)}$, and the H1–H2 distance is stretched by around 5.1%, with respect to the bulk *H*-center length. On the other hand, from Table 4, we found that Config $H_{11}^{(1)}$ has a very big deviation angle of 47.7°, and the orientations of other Configs. i.e., deeper surface *H* centers, approach to the (111) direction. In an ideal cubic CaF_2 bulk, the angle between the (111) and (100)axes is 54.7°, being close to the big obliquity of Config $H_{11}^{(i)}$ (47.7°). Therefore, we can consider this Config with big deviation angle as Config $H_{(100)}$, namely the (100)-oriented configuration in the bulk case, locating on the top of the (111) surface. It is implied that despite the (111)-oriented H center is energetically more favorable in CaF₂ bulk, *H* centers located at the first fluorine sublayer prefer to the (100) orientation.

The relaxation of atoms surrounding the surface *H* center is shown in Fig. 6 and Table 5. For Config $H_{11}^{(i)}$, all the atoms near the surface shift towards the positive *Y* axis from the top view, as we can see in Fig. 6. The *H*1 has a big shift around 6% of a_0 . The four nearest fluorine atoms, i.e., F1 and F2, have considerable *XY*-shifts over 2% of a_0 , the *XY*-displacements of fluorine atoms located at the lower sublayer of the first layer and the upper sublayer of the second layer are around 1–2% of a_0 , and the *XY*-translations of the fluorine atoms on the lower sublayer of the second layer are less than 1% of a_0 . Here, we can conclude that the first atomic layer containing surface *H* centers has an remarkable *XY*translation. Because of the surface shrinking effect, the atomic coordinates (in the *Z* direction) of most of the surface atoms

Table 5

Atomic relaxations (as a percentage of the lattice constant: 5.50 Å) and effective charges (*Q* (e)) of the (111) CaF₂ surface containing an *H* center, for Configs $H_{11}^{(1)}$. Positive signs in *Z* column correspond to outward atomic displacements (toward the vacuum). The directions of atomic displacements in the *XY*-plane are indicated in Fig. 6. ΔQ (e) labels the change in the effective charge compared to perfect CaF₂ crystal (Q_{Ca} = +1.803 e, Q_F = -0.902 e). The symbols in Atom column are defined in Fig. 6.

Layer	Sublayer	Atoms	XY	Ζ	Q (e)	$\Delta Q(e)$
No. 1	1	H1	5.93	+0.46	-0.636	+0.266
		H2	-	-	-0.264	+0.638
		F1 (2)	2.32	-0.93	-0.888	+0.014
		F2 (2)	2.70	-1.07	-0.887	+0.015
		F3 (2)	1.24	-0.75	-0.883	+0.019
	2	Ca1 (1)	0.26	+0.75	+1.786	-0.017
		Ca2 (2)	2.79	-0.77	+1.788	-0.015
	3	F4(1)	1.20	-0.88	-0.899	+0.003
		F5 (2)	2.07	+0.34	-0.908	-0.006
		F6(1)	1.32	-0.87	-0.906	-0.004
		F7 (2)	1.78	-1.15	-0.905	-0.003
No. 2	1	F1 (1)	1.27	+0.22	-0.900	+0.002
		F2 (2)	1.83	-0.23	-0.900	+0.002
		F3 (1)	1.48	-0.29	-0.900	+0.002
		F4 (2)	1.80	+0.36	-0.901	+0.001
	2	Ca1 (1)	1.22	-0.45	+1.802	-0.001
		Ca2 (2)	1.11	+0.20	+1.803	0
	3	F5 (1)	0.64	-0.03	-0.902	0
		F6 (2)	0.78	-0.54	-0.901	+0.001
		F7 (2)	0.55	-0.20	-0.901	+0.001
		F8 (2)	0.88	-0.42	-0.901	+0.001

 Table 6

 Effective charges (e) and spins (e) of surface H centers for all the (111)-unoriented configurations.

Atoms	Charges (e)	$H_{11}^{(\setminus)}$	$H_{12}^{(igvee)}$	$H_{21}^{(\backslash)}$	$H_{22}^{(\setminus)}$
H1	Q	-0.636	-0.707	-0.629	-0.667
	∆Q	+0.266	+0.195	+0.273	+0.235
	Spin	+0.313	+0.251	+0.331	+0.291
H2	Q	-0.264	-0.217	-0.314	-0.303
	ΔQ	+0.638	+0.685	+0.588	+0.599
	Spin	+0.682	+0.745	+0.638	+0.651

reduce, whereas atoms Ca1 and F5 on the first layer, and Ca2, F1 and F4 on the second layer, shift outward the surface. We found that it is mainly due to the attraction from *H*2 on those neighbor atoms.

Table 6 presents the effective surface *H*-center charges for all the (111)-unoriented configurations. The H-center charges of Configs $H_{11}^{(i)}$ (-0.900 e) and $H_{12}^{(i)}$ (-0.924 e) are smaller than the *H*-center charge in CaF₂ bulk (-0.947 e). Especially for Config $H_{11}^{(i)}$, the decrement reaches to around 0.047 e. As a whole, the surface effect induces that electrons localized on the surface fluorine atoms transfer inward the surface, therefore the H-center charges of Configs $H_{11}^{(1)}$ and $H_{12}^{(1)}$, in which the *H* center is located on the first surface layer, decrease considerably. For Config $H_{21}^{(n)}$, namely an H center located on the upper sublayer of the second layer, because the charges from the first-layer fluorine atoms move downward, compensating the charge outward transfer from the H center, the effective charge of the H center (-0.943 e) closes to the value of the *H*-center bulk case. For Config $H_{22}^{(\setminus)}$, the *H*-center charge equals to -0.970 e and is larger by around 0.023 e than that in the bulk case. It is also due to the electron downward transfer from upper fluorine atoms, whereas the electrons localized on the H center transfer outward slightly. We also calculated the H center located at deeper layers and found that the *H*-center charges converge to the value of the bulk case. As mentioned before, we consider Config $H_{11}^{(1)}$ as the bulk H center Config H_{100} located on the (111) surface. However, according to our calculation for Config H_{100} of the bulk case, the effective charges distribute on both fluorine atoms of the *H* center equally, unlike Config H_{111} , in which the hole is mainly localized on the interstitial fluorine atom. So, for the electronic property regarding effective charges, we can not consider Config $H_{11}^{(n)}$ as the bulk H center Config H_{100} located on the (111) surface. Table 5 also shows the effective charges of the surface H center and surrounding atoms for Config $H_{11}^{(1)}$. Because of the surface effect, -0.022 e and -0.025 e localized on the H1 and H2, respectively, transfer inward the surface. The charge differences of deeper fluorine and calcium atoms are negligible, whereas the electron transfer regarding the first-layer atoms is considerable.

As mentioned before, the surface H-center charge is smaller than that in the bulk case. However, the total surface H-center spin defined as the sum of H1 and H2 spins (+0.995 e and +0.996 e for Configs $H_{11}^{(n)}$ and $H_{12}^{(n)}$, respectively) is much larger than the bulk H-center spin (+0.965 e), implicating a stronger spin polarization of the surface H center and a more localized unpaired electron. Our hyperfine coupling calculations for the surface case demonstrated that the interaction between the unpaired spin and the spin of neighboring nuclei is stronger than that in the bulk case, being in accordance with the spin polarization calculations. The isotropic hyperfine constants (a) of H1 and H2 for Config $H_{11}^{(i)}$ equal to 802.6 and 819.8 MHz, respectively, and are larger than the corresponding values in the bulk H-center case. Table 6 also lists the H-center spins of other Configs. We can see that their spins are close to the spin of bulk H center and there is no remarkable surface effect on other Configs.

Table 7

Direct optical band gaps (eV) $(\Gamma \rightarrow \Gamma)$ of the surface *H* centers for the four (111)unoriented configurations and the bulk case (Config H_{111}).

Gaps	$VB \rightarrow H$		$VB \to CB$		
	α	β	α	β	
$H_{11}^{(\setminus)}$	-	4.12	10.77	10.77	
$H_{12}^{(\backslash)}$	_	2.76	10.58	10.54	
$H_{21}^{(\backslash)}$	-	2.75	10.69	10.70	
$H_{22}^{(\backslash)}$	-	2.75	10.69	10.69	
H111	-	2.88	10.69	10.69	

To investigate the surface effect on the optical band gaps, we studied the band structures of surface *H*-center systems. The theoretical optical band gaps for all the (111)-unoriented configurations are collected in Table 7 and the band structure of Config $H_{11}^{(1)}$ is shown in Fig. 7. For these four surface Configs, all the band gaps between VB and CB are close to those of the bulk H-center system (10.69 eV for α - and β -spin band structures), and the surface effect slightly widens and narrows the VB-CB gaps for Configs $H_{11}^{(\backslash)}$ and $H_{12}^{(\backslash)}$, respectively. For Configs $H_{12}^{(\backslash)}$, $H_{21}^{(\backslash)}$ and $H_{22}^{(\backslash)}$, the β defective level induced by the hole on the H center lies around 2.75-2.76 eV above the VB top, being smaller than the corresponding value in the bulk H-center system by around 0.13 eV. We also calculated the band gaps of other deeper H-center configurations and their values are comparable to the gap of Config $H_{12}^{(i)}$, and with a deeper H-center location, the defect level becomes more and more close to the β -hole band for the bulk *H*-center case. On the other hand, the defect level for Config $H_{11}^{(i)}$ is quite different from other deeper H-center configurations, and located 4.12 eV above the VB top, magnified 1.24 eV, increasing by around 43%, with respect to the gap of bulk H-center system. Whereas the VB-CB gap of Config $H_{11}^{(i)}$ changes slightly, suggesting a marked hole-level movement toward CB. It has been known that the hole is on the interstitial fluorine and for Config $H_{11}^{(n)}$, this fluorine atom is significantly outside of the slab, so the surface effect on this hole is more pronounced than on the hole in other configurations.

To further study the electronic structure and electron transitions in a surface H-center system, we calculated DOS of surface *H*-center systems. The total and projected DOS of Config $H_{11}^{(i)}$ is displayed in Fig. 8. Our previous bulk H-center study demonstrated that H1 and H2 *p*-orbitals form the β -hole band, and H2 does the major contribution. Because of the isotropic symmetry of projected *p*-orbitals in CaF₂ bulk, p_r -, p_{ν} - and p_r -orbitals of the H center are equivalent in contribution to the formation of β -hole band. Nevertheless, this symmetry is broken by the (111)-terminated surface, and the *p*-state electrons are not equivalent in the three directions. According to our DOS calculations, we found that for Config $H_{11}^{(n)}$, the β -hole band mainly consists of p_{y} - and p_{z} -orbitals of the surface H center, as we can see in Fig. 8, whereas for other deeper H-center configurations, only p_z -orbitals form the β -hole band. As geometrical structure and spin density discussed before, the surface *H*-center orientation of Config $H_{11}^{(i)}$ has a big deviation from the Z axis and is in the YZ-plane (see Fig. 6), therefore the spin pattern of the H center in the spin density map looking like a spindle, being a typical *p*-shape electron cloud, has the *Y* and *Z* projections. It leads to a mixture of p_{v} - and p_{z} -orbitals, forming the β -hole band. However, for the deeper surface H-center configurations, the orientations are very close to the (111) direction, so the contribution from p_v -orbitals could be negligible. From Fig. 8, the H1 peak is much smaller than the H2 peak, being in agreement with previous view that the hole mainly locates on H2. Because of the surface effect, the p_y - and p_z -orbitals of the *H* center move upward, toward the CB, with respect to the H-center p-orbitals in the bulk case, and this leads to widening of the VB \rightarrow H gap.



Fig. 7. Calculated B3PW band structure for Config $H_{11}^{(i)}$.



Fig. 8. Total and projected DOS for Config $H_{11}^{(i)}$.

3.3. FH pairs in CaF₂

Finally, we studied the combination of F and H centers in CaF₂. We calculated nine *FH*-pair configurations, named Configs *FH*1, *FH*2, ..., *FH*8 and *FH*9, in which the *F* center is located at F1, F2, ..., F8 and F9 sites, respectively (see Fig. 1). According to our calculations, we found that Configs *FH*2, *FH*4 and *FH*5 are not stable structures, in which the interstitial fluorine labeled *H*2 approaches to the neighbor *F*-center site, converging to the perfect crystal. From Fig. 1, we can see that F2, F4 and F5 are the nearest sites to the hole and there is no calcium atom in the *F*-*H* intervals, so the attraction between the *F* and *H* centers leads *H*2 to move to the *F* center, forming the perfect crystal. The energetically most favorable configurations are Configs *FH*1, *FH*3 and *FH*6, and the total

energies of other configurations are higher with respect to Configs *FH*1, *FH*3 and *FH*6 by 0.33, 0.33 and 0.45 eV for Configs *FH*7, *FH*8 and *FH*9, respectively. Here, we can define the creation energy of an *FH* pair as the energy difference between the supercell with and without an *FH* pair, and the corresponding value for Configs *FH*1 equals to around 2.35 eV.

The analysis of effective charges for the FH pair shows that the charge of the F center reduces to around -0.129 e for Configs FH1, FH3 and FH6, and the trapped electron in the V_F is much more delocalized than that in the isolated F-center case (-0.752 e). Compared with the isolated *H* center in bulk, the *H*1 and *H*2 charges equal to around -0.893 e and -0.790 e, being close to the charge of fluorine atom in perfect CaF₂ crystal (-0.902 e), and increase by 0.235 e and 0.501 e, respectively. Here, we can conclude that the H2 fluorine atom, on which the hole localized for the isolated H-center case, is not a hole properly anymore for FH-pair cases, and the hole moves to the V_F . For Configs FH7, FH8 and FH9, the charge of V_F decreases even further to around -0.052 e, almost delocalizing completely. F center denotes an electron trapped in a fluorine vacancy, and H center denotes a hole trapped at an interstitial fluorine site, therefore we can also consider a combination of an F and an H centers as an electron-hole pair. However, the FH pair discussed here is not a true pair of an F and an H centers, since the hole is not located at the interstitial fluorine site and the electron is not located at the V_F primarily, but it is still an electron-hole pair. So, the exact object studied here should be electron-hole pairs.

Next, based on the calculations for the band structures of *FH*-pair systems, we investigated the electron transitions regarding the optical absorptions. Because the supercell containing an *FH* pair has an even number of electrons and there is no unpaired electron, the band structure is unpolarized, unlike the isolated *H*-center case mentioned before. Fig. 9 shows the band structure of the *FH*-pair system for Config *FH*1 and Table 8 lists the optical band gaps regarding the electron transitions. According to our calculations and Fig. 9, there are seven defect bands between the VB–CB gap, and three of them (labeled e_1 , e_2 and e_3), being occupied, locates near the fermi level, and four of them (labeled h_1 , h_2 , h_3 and h_4), being unoccupied, locates in the gap of the fermi



Fig. 9. Calculated B3PW band structure for Config FH1.

Table 8 Direct optical band gaps (eV) ($\Gamma \rightarrow \Gamma$) of the *FH* pair for Config *FH*1.

Gaps		Gaps	
$e_1 \rightarrow h_1$	2.37	$e_2 \rightarrow h_1$	2.38
$e_1 \rightarrow h_2$	5.67	$e_3 ightarrow h_1$	2.42
$e_1 \rightarrow h_3$	5.76	$VB \rightarrow h_1$	5.70
$e_1 \rightarrow h_4$	5.77	$VB \to CB$	9.70



Fig. 10. Total and projected DOS for Config FH1.

energy and VB bottom, named electron- and hole-band here, respectively. An optical absorption should be due to an electron transition from an occupied band to an unoccupied band. So, for the *FH*-pair system of Config *FH*1, we can summarize that the electron transitions have the following possibilities: $e_{1,2,3} \rightarrow h_{1,2,3,4}$ and $e_{1,2,3} \rightarrow \text{CB}$. The corresponding values are shown in Table 8. The gap of $e_1 \rightarrow h_1$ equals to 2.37 eV and is smaller than the relevant gap in the isolated *H*-center system (2.88 eV), whereas the gaps of $e \rightarrow h_{2,3,4}$ are around 5.7 eV, being

much larger than the *H*-center case. Additionally, the VB–CB gap (9.70 eV) is narrowed considerably by around 1.26 eV with respect to the perfect CaF₂ case (10.96 eV).

DOS calculations reveal the compositions of defect levels, as we can see in Fig. 10. The *p*-orbitals of *H*2 form the three occupied bands $(e_1, e_2 \text{ and } e_3)$ located near the Fermi energy. Broken symmetry leads a non-equivalence of the p_{x^-} , p_{y^-} and p_z -orbitals, so the *e*-band is split into three bands, and according to our calculations, the p_z level is slightly higher. The first unoccupied hole-band labeled h_1 consists of *s*-orbitals of the V_F , and the *p*-orbitals of the V_F do the most contributions to the upper three hole-bands of h_2, h_3 and h_4 . The DOS results also indicate that the hole is not located on the *H* center anymore for the electron–hole pair cases, and transfers to the neighbor V_F site, being in accordance with previous discussion regarding effective charges. We also found that the fluorine atom of *H*1, unlike the isolated *H*-center case, plays a role of regular fluorine atom, and there is almost no contribution to the defect levels from it, similar to other fluorine atoms.

4. Conclusions

We applied the first-principles approach within the hybrid DFT-B3PW scheme to calculations on *H* centers in CaF₂. Two bulk configurations including Configs $H_{(100)}$ and $H_{(111)}$, and eight surface configurations including four (111)-oriented and four (111)-unoriented *H* centers were studied. For the bulk case, Config $H_{(111)}$, in which the *H* center orients the (111) axis, is the energetically most favorable configuration, and the hole is mainly localized on the interstitial fluorine, in agreement with the experimental observations. Spin and hyperfine coupling calculations show a remarkable interaction between the unpaired spin and the spin of neighboring nuclei. The hole induces an empty level in the β -spin band gap of the CaF₂ crystal, located 2.88 eV above the VB top. Using the DOS investigation, we found that the unoccupied hole band is composed of *H*-center *p*-orbitals, and the *H*2 does the major contribution.

For the surface case, we found that Config $H_{11}^{(1)}$, in which the H center located at the upper fluorine sublayer of the first surface layer and the obliquity is around 47.7°, is the most stable configuration for the surface H-center systems, implicating a preference for H centers to locate near the surface, and geometrically, this configuration corresponds to a (100)-oriented H center located at the (111) surface. The calculations of the relaxations of atoms surrounding the surface H center demonstrated that the atomic layers containing surface H centers have a remarkable XY-translation. The surface effect decreases the effective charge of the surface H center of Config $H_{11}^{(n)}$, whereas enhances the spin polarization and hyperfine coupling with the neighboring nuclei. The studies on band structures of the surface H-center systems demonstrate that the surface effect widens considerably the β -spin VB-hole gap, which corresponds to the first optical absorption, for Config $H_{11}^{(n)}$, and narrows it sightly for other configurations, with respect to the bulk H-center case.

Finally, as an extension study regarding H centers, we investigated electron-hole pairs, i.e. FH pairs in this paper. The creation energy of an FH pair equals to around 2.35 eV. We found that the geometrical structure of the FH pair is similar to an F center and an H center paired together, however, the hole localized on the Hcenter in the isolated H-center case, moves to the V_F site. The electron-hole pair induces seven defect levels in the VB–CB gap, three of them located near the Fermi energy, being occupied, and four of them located above the Fermi level, forming the hole bands. DOS calculations show that the p-orbitals of H2 form the three electron bands and the four hole bands consist of the s- and p-orbitals of the V_F .

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