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# *Ab initio* calculations of the *F* centers in MgF<sub>2</sub> bulk and on the (001) surface

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## Abstract

We present and discuss the results of atomic and electronic structure calculations of the *F* centers in MgF<sub>2</sub> bulk and on the (001) surface. The calculations are based on the B3PW Hartree–Fock and density functional theory hybrid exchange–correlation functional. Most of the electronic density of a missing fluorine ion is localized in the bulk vacancy and a little bit less—in a surface vacancy. It is shown that the electronic *F* center is a deep donor. The lattice distortion and defect formation energy on the neutral (001) surface and in the bulk are also compared.

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(Some figures may appear in color only in the online journal)

## 1. Introduction

Lenses and optical windows made of magnesium fluoride (MgF<sub>2</sub>) are transparent over an extremely wide range of photon energies, from vacuum ultraviolet to infrared. It is also a radiation-resistant material, the energy required to form a stable primary radiation defect known as the *F* center (fluorine vacancy with trapped electron) between 5 K and room temperature is much higher than in other alkali halides [1]. These two factors make MgF<sub>2</sub> an important material for space telescopes and similar applications. However, it is essential for materials scientists to understand at the atomistic level the reasons behind MgF<sub>2</sub>'s high radiation stability. Despite several *ab initio* calculations of basic MgF<sub>2</sub> properties (both bulk [2, 3] and surfaces [4, 5]), we are not familiar with defect studies in this material at the *ab initio* level (unlike other fluorites—CaF<sub>2</sub> and BaF<sub>2</sub> [6–8]). In this paper, we present results of the *ab initio* calculations of the *F* centers in the bulk and on the (001) surface of MgF<sub>2</sub>.

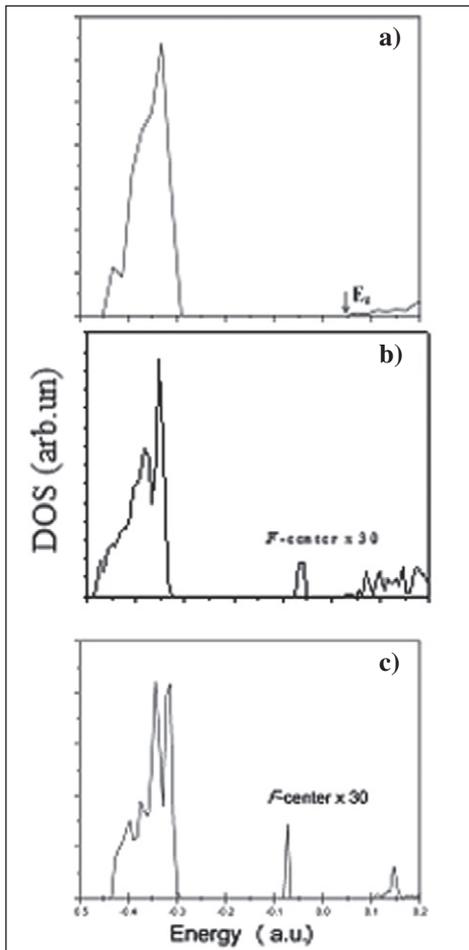
## 2. Computational method and surface models

MgF<sub>2</sub> (rutile) has a tetragonal P4<sub>2</sub>/mnm structure with two formula units in the unit cell. As in previous calculations on the MgF<sub>2</sub> bulk and (001) surface [4, 5], we used here the CRYSTAL computer code [9] using localized, Gaussian-type

basis sets. An advantage of this code is the treatment of *isolated* two-dimensional slabs, without an artificial periodicity in the *z* direction perpendicular to the surface, as commonly employed in most previous surface-band structure plane-wave calculations. Our spin-polarized calculations were performed using the density functional theory–Hartree–Fock (HF) hybrid exchange–correlation B3PW functional [10] which gives better agreement of the calculated and experimental MgF<sub>2</sub> optical gap than other functionals (9.5 eV (B3PW) versus 19.65 eV (HF), 6.9 eV (generalized gradient approximation by Perdew, Burke and Ernzerhof (GGA-PBE)), compared with the experimental value of 12.5 eV—see [4] and figure 1(a)).

The reciprocal space integration was performed by sampling the Brillouin zone with 5 × 5 × 5 Pack–Monkhorst mesh [11]. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7 and 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap and second exchange pseudo-overlap, respectively [8]. In calculations we applied the basis set developed by Catti *et al* [12] for the F atom and by McCarthy and Harrison [13] for the Mg atom. The effective atomic charges were calculated using the Mulliken population analysis [14].

To simulate the *F* centers, we started with a six-atom (bulk) unit cell with one missing fluorine atom. After the fluorine atom is removed, the atomic configuration of the



**Figure 1.** DOS of defect-free  $\text{MgF}_2$  (a), the  $F$  center in bulk calculated using a  $2 \times 2 \times 2$  extended supercell (b) and the surface  $2 \times 2$  supercell (c). The peak below  $-0.3$  a.u. is the  $F(2p)$  valence band. The arrow in (a) indicates the position of the conduction band bottom (the experimental value is  $12.5$  eV). The Fermi energy coincides with the top of the defect band.

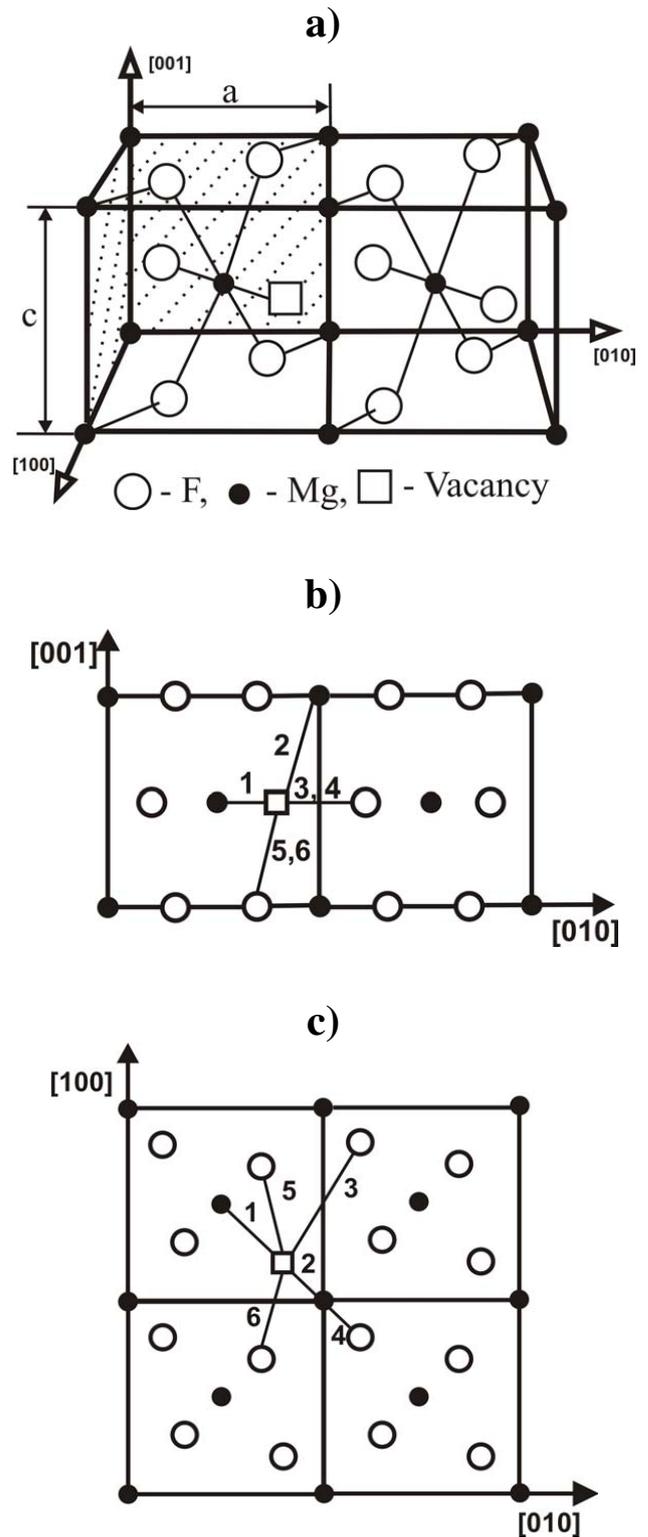
surrounding atoms is reoptimized via a search of the total energy minimum as a function of the atomic displacements from the regular lattice sites. This corresponds to a high defect concentration of 25%. Then we repeated these calculations for a  $2 \times 2 \times 2$  times expanded supercell (3% defect concentration) in the bulk and a  $2 \times 2 \times 1$  supercell for the surface (a slab model consisting of nine neutral  $\text{MgF}_2$  crystalline layers—12.5% of surface defects). As a result of these calculations, we obtained the relaxed lattice geometry, effective atomic charges and bond populations, the band structure, density of states (DOS) and defect formation energies.

In order to get an accurate description of the  $F$  center, an extra basis set has been centered in the fluorine vacancy, corresponding to the *ghost* atom. For the *ghost* atom, we used the same basis set as that used for the  $F^-$  ions of the bulk  $\text{MgF}_2$ .

The defect formation energy was calculated as usual:

$$E^{\text{form}}(F) = E(\text{Fluorine}) + E(F) - E(\text{perfect}), \quad (1)$$

where  $E(\text{Fluorine})$  is the energy for the isolated fluorine atom,  $E(F)$  and  $E(\text{perfect})$  the energies of the defective crystal containing the  $F$  center and the perfect crystal, respectively.



**Figure 2.** (a) A schematic view of the  $\text{MgF}_2$  lattice with shaded (100) and (001) planes, (b)  $F$  center nearest-neighbor geometry (unit cell extension  $2 \times 2 \times 2$ ) projected onto the (100) plane and (c) onto the (001) plane. Full circles are Mg ions, empty circles F ions.

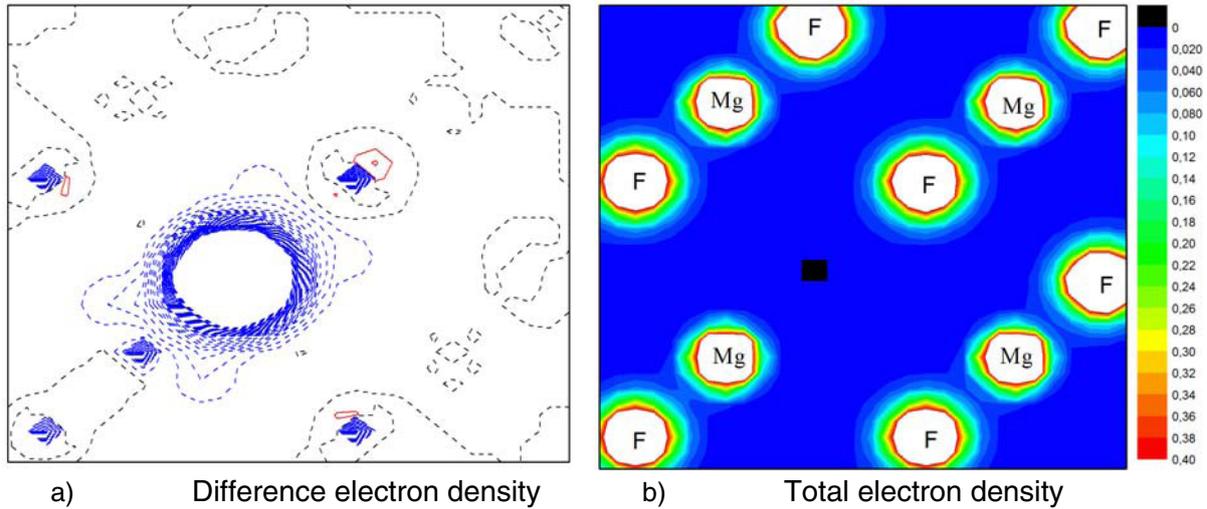
### 3. Main results

#### 3.1. Bulk defect

The fluorine vacancy formation energy, calculated for the small supercell of six atoms is 9 eV, which is a typical value

**Table 1.** Displacements of the defect nearest neighbors (see atomic labeling in figure 2(b)), values are both in Å and in fractions (%) with respect to the tetragonal lattice parameters.

Neighbors of <i>F</i> center (vacancy)	Atomic displacements					
	$\Delta x(\text{Å})$	$\Delta x/a$	$\Delta y(\text{Å})$	$\Delta y/b$	$\Delta z(\text{Å})$	$\Delta z/c$
Mg (1)	0.0065	0.14	0.0065	0.14	0	0
Mg (2)	-0.0094	-0.20	-0.0094	-0.20	0.0029	0.10
F (3)	0.0034	0.07	0.0064	0.14	0	0
F (4)	-0.0057	-0.12	-0.0057	-0.12	0	0
F (5)	0.0003	0.01	0.009	0.20	0.0027	0.07
F (6)	-0.0118	-0.25	-0.0027	-0.06	0.0024	0.08

**Figure 3.** The difference (a) and total electron density (b) distributions around the bulk *F* center (marked by a black square in (b)). The effect of a small electron density delocalization from a vacancy over nearest neighbors is seen in (a).**Table 2.** The effective charges  $Q(e)$  of the *F* center and nearest neighbors in the  $\text{MgF}_2$  bulk calculated for a supercell containing 48 atoms and their deviations from a perfect crystal. Atomic labels as in table 3.

Atom	$Q(e)$	$\Delta Q(e)$
Mg (1)	1.75	0.006
Mg (2)	1.745	0.011
F (3)	-0.88	0.002
F (4)	-0.883	0.005
F (5)	-0.883	0.005
F (6)	-0.887	0.009

for the *F* centers in alkali halides and ionic solids. An analysis of the effective charges of atoms surrounding the *F* center shows that the electron associated with the removed fluorine atom is well localized inside the fluorine vacancy ( $-0.769e$ ). Note that the effective charges in the defect-free crystal are  $1.755e$  (Mg) and  $-0.878e$  (F) [4]. The relevant Mg–F bond population in a perfect crystal is 42 me (milli electrons), quite low, which is typical for ionic solids. That is, most of the electron density of a missing fluorine ion is localized in the vacancy even at such high defect concentrations, only  $\approx 10\%$  is delocalized over the nearest ions.

An incorporation of a vacancy produces anisotropy in the bond populations: some Mg–F bonds became less populated (14 me) than those in the perfect crystal whereas others show larger populations (60 me). These is also a very weak overlap

of the electronic density in a vacancy and one of nearest Mg ions (14 me).

The calculated DOS shows that due to the small size of the unit cell and thus a short distance between periodically repeated defects, they strongly interact which results in a very broad defect band ( $\approx 3$  eV) which overlaps with the bottom of the conduction band.

Next, calculations were performed for a more realistic defect concentration of 3% (one F ion removed from a 48 atom supercell with 32 F ions) shown schematically in figure 2.

The DOS (figure 1(b)) clearly indicates that at this concentration periodic defects interact only moderately, which result in a narrow *F* center band (width  $\approx 0.5$  eV). The defect band lies deep below the conduction band bottom. Its formation energy is 7.8 eV, smaller than for the high defect concentration discussed above, and surprisingly close to that in fluorite crystals— $\text{CaF}_2$  and  $\text{BaF}_2$  (7.9 and 7.8 eV, respectively [6, 7]).

Notice that we calculated the formation energies of a single *F* center. This energy typically is much smaller than the irradiation energy necessary to produce one *stable F* center [1], since most of the *F* centers recombine in the secondary reactions, e.g. with mobile complementary defects—*H* centers (interstitial F ions). For instance, the efficiency of the *F* center accumulation in  $\text{MgF}_2$  is by an order of magnitude smaller than in LiF crystals [15]. To understand this effect, after the present calculations of the defect static properties, defect mobilities and aggregation should be simulated.

**Table 3.** The same as table 1 for the surface F center (see atomic labeling in figure 4).

Neighbors of <i>F</i> center	Atomic displacements					
	$\Delta x(\text{\AA})$	$\Delta x/a$	$\Delta y(\text{\AA})$	$\Delta y/b$	$\Delta z(\text{\AA})$	$\Delta z/c$
Mg (1)	0.0581	1.25	-0.0581	-1.25	-0.1838	-5.86
Mg (2)	0.0046	0.10	-0.0046	-0.10	0.0267	0.85
F (3)	0.0861	1.84	-0.0858	-1.84	0.0327	1.04
F (4)	0.0399	0.86	-0.1209	-2.60	0.0327	1.04
F (5)	-0.0399	-0.86	-0.0399	-0.86	0.0057	0.18
F (6)	-0.0002	-0.01	-0.0466	-1.00	-0.0664	-2.12
F (7)	-0.0357	-0.77	-0.0143	-0.31	-0.048	-1.53
F (8)	0.0466	1.00	0.0002	0.01	-0.0664	-2.12
F (9)	0.0143	0.31	0.0357	0.77	-0.048	-1.53

**Table 4.** The effective charges  $Q(e)$  of atoms surrounding the *F* center on the (001) surface. Atomic symbols as in figure 4.

Atom	$Q(e)$	$\Delta Q(e)$
Mg (1)	1.668	0.088
Mg (2)	1.741	0.015
F (3)	-0.874	-0.004
F (4)	-0.874	-0.004
F (5)	-0.880	0.002
F (6)	-0.911	0.033
F (7)	-0.897	0.019
F (8)	-0.911	0.033
F (9)	-0.897	0.019

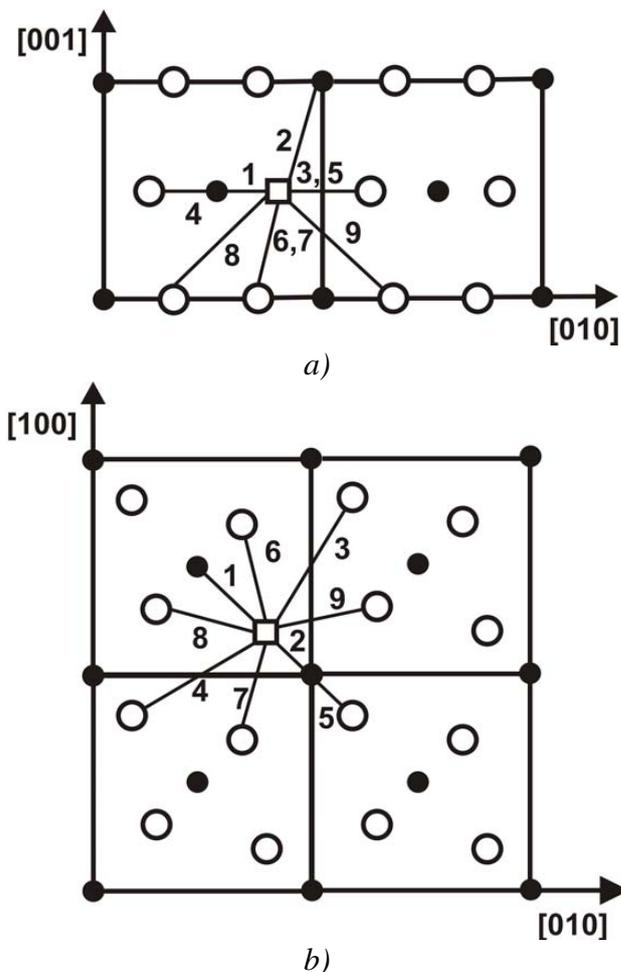
The defect formation energy could be also determined with respect to the thermodynamic reference energy—the *F* atom in a free  $F_2$  molecule. For this estimate half the binding energy of the  $F_2$  molecule (1.6 eV) should be subtracted from the energy calculated with respect to a free atom, which gives 7.0 eV.

Table 1 presents the calculated lattice relaxation around the defect, in absolute values and as fractions of the tetragonal lattice parameters (the optimized values in a perfect  $MgF_2$  are:  $a = b = 4.654 \text{\AA}$ ,  $c = 3.139 \text{\AA}$  [4] which is close to experimental data).

As one can see here, ionic relaxation around the defect is small, displacements are less than 2%. This is accompanied by small changes in the relevant atomic charges (table 2), whereas the charge of a vacancy itself is increased to  $\geq 0.1e$ , due to the density delocalization over the nearest ions. This is confirmed by the electron density maps in figure 3.

### 3.2. Surface *F* centers

For a comparison, we calculated the *F* center on the neutral  $MgF_2$  (001) surface. The defect formation energy is 8.4 eV, larger than in the bulk. Such effects were observed also in other materials, e.g. on the LaO (100) surface of  $LaMnO_3$  [16]. The calculated atomic displacements are summarized in table 3, with a schematic configuration shown in figure 4. First of all, ions at the surface show large vertical displacements, up to  $\approx 6\%$  of the lattice constant. Second, surface cations are displaced inwards whereas anions are displaced off the surface, qualitatively similar to the defect-free surface [6]. This leads to the surface rumpling. Relaxation in the surface plane along the  $x, y$  axes is also larger than in the bulk, up to  $\approx 2\%$ . This results from additional delocalization of the electronic density from the surface

**Figure 4.** The same as figure 2, for the surface *F* center.

vacancy which contains only  $-0.622e$ , i.e. increased by  $0.12e$  compared with the bulk defect. This could be one of reasons for the increased defect formation energy. The width of the defect band in the DOS (figure 1(c)) is 0.4 eV, slightly smaller than for the bulk *F* center whereas the electronic density map remains qualitatively similar to that in the bulk (table 4).

## 4. Conclusions

Our *ab initio* calculations show that use of  $2 \times 2 \times 2$  supercell (48 atoms) with 3% defect concentration gives reasonable results and could be employed in further  $MgF_2$  studies. The relevant *F* center formation energy is similar to that

calculated for  $\text{CaF}_2$  with a fluorite structure. Most of the electronic density of a missing fluorine ion is localized in the bulk vacancy and, a little bit less, in a surface vacancy. The electronic  $F$  center is a deep donor. The defect formation energy on the neutral (001) surface is larger than in the bulk, thus, this surface is expected to have a low defect concentration. This is important for the material space applications in a radiation environment. In a forthcoming study we will discuss  $F$  center diffusion which is expected to differ considerably in rutile ( $\text{MgF}_2$ ) and fluorite ( $\text{CaF}_2$ ,  $\text{BaF}_2$ ) crystals.

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### References

- [1] Blunt R F and Cohen M I 1967 *Phys. Rev.* **153** 1031  
Buckton M R and Pooley D 1972 *J. Phys. C: Solid State Phys.* **5** 1553
- [2] Catti M, Pavese A, Dovesi R, Roetti C and Causa M 1991 *Phys. Rev. B* **44** 3509
- [3] Babu K R, Lingam Ch B, Auluck S, Tewari S P and Vaitheeswaran G 2011 *J. Solid State Chem.* **184** 343
- [4] Vassilyeva A F, Eglitis R I, Kotomin E A and Dauletbekova A K 2010 *Physica B* **405** 2125
- [5] Vassilyeva A F, Eglitis R I, Kotomin E A and Dauletbekova A K 2011 *Cent. Eur. J. Phys.* **9** 515
- [6] Shi H, Eglitis R I and Borstel G 2005 *Phys. Rev. B* **72** 045109
- [7] Shi H, Eglitis R I and Borstel G 2006 *J. Phys.: Condens. Matter* **18** 8367
- [8] Shi H, Jia R and Eglitis R I 2011 *Solid State Ion.* **187** 1
- [9] Saunders V R, Dovesi R, Roetti C, Causa M, Harrison N M, Orlando R and Zicovich-Wilson C M 2006 *CRYSTAL User Manual* (Torino, Italy: University of Torino)
- [10] Becke A D 1993 *J. Chem. Phys.* **98** 5648
- [11] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [12] Catti M, Dovesi R, Pavese A and Saunders V R 1991 *J. Phys.: Condens. Matter* **3** 4151
- [13] McCarthy M I and Harrison N M 1994 *Phys. Rev. B* **49** 8574
- [14] Catlow C R A and Stoneham A M 1983 *J. Phys. C: Solid State Phys.* **16** 4321
- [15] Lisitsyna L A, Lisitsyn V M, Korepanov V I and Grechkina T V 2004 *Opt. Spectrosc.* **96** 230
- [16] Mastrikov Yu, Merkle R, Heifets E, Kotomin E A and Maier J 2010 *J. Phys. Chem. C* **114** 3017