

## *Ab initio* calculations of MgF<sub>2</sub> (001) and (011) surface structure

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### ABSTRACT

We present the results of calculations of surface relaxations, rumplings, and charge distribution for the MgF<sub>2</sub> (001) and (011) surfaces using *ab initio* code Crystal-2003 and the hybrid exchange–correlation B3PW functional. These two neutral and polar surfaces show very small relaxation and negligible increase of covalent contribution to the chemical bonding thus remaining considerably ionic. The calculated bulk optical band gap is in a good agreement with the experimental value, whereas optical band gap for the polar (011) surface is reduced by 0.6 eV compared with the calculated bulk value, in contrast to the (001) surface gap which remains very close to the bulk.

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## 1. Introduction

The MgF<sub>2</sub> crystal has several technological applications, including use in the electrolysis of aluminium ore and anti-reflective coatings [1,2], for which the surface structure and quality are of primary importance. Magnesium fluoride is transparent over an extremely wide range of wavelengths. Windows, lenses, and prisms made of this material can be used over the entire wavelength range, from 0.120 μm (vacuum ultraviolet) up to 8.0 μm (infrared). Along with lithium fluoride, it is one of the two materials that transmit in the vacuum ultraviolet range at 121 nm and this is where it finds its main applications. Lower grade MgF<sub>2</sub> is sometimes used in the infrared but here it is inferior to calcium fluoride.

Considering high technological importance of MgF<sub>2</sub>, it is surprising that during the last few years there have been no theoretical studies dealing with the MgF<sub>2</sub> (001) and (011) surfaces. MgF<sub>2</sub> (sellaite) is tetragonal P4<sub>2</sub>/mnm with two formula units in the unit cell [3]. The experimental lattice constants for MgF<sub>2</sub> are 4.615 Å (*a=b*) and 3.043 Å (*c*) [3]. In this paper, we performed first *ab initio* calculations of the atomic and electronic structure of these surfaces.

## 2. Computational method and surface models

We used the CRYSTAL-2003 computer code [4]. Unlike the plane-wave codes employed in most surface calculations, the localized, Gaussian-type basis set is used in this code. An additional advantage of the CRYSTAL-2003 code is treatment of *isolated* 2D slabs, without an artificial periodicity along the *z* direction perpendicular to the surface, as commonly employed in most previous surface-band structure plane-wave calculations. Our calculations were performed using the hybrid exchange–correlation B3PW functional involving a hybrid of nonlocal Fock exact exchange, LDA exchange, and Becke's gradient-corrected exchange functional combined with the nonlocal gradient-corrected correlation potential as suggested by Perdew and Wang [5]. We have chosen the hybrid B3PW functional in our current study because it yields excellent results for the bulk lattice constant and bulk modulus of many fluorites and oxides, e.g. SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, CaTiO<sub>3</sub>, CaF<sub>2</sub>, and BaF<sub>2</sub> [6–13].

The reciprocal space integration was performed by sampling the Brillouin zone with a 5 × 5 × 5 Pack–Monkhorst mesh [14]. To achieve high accuracy, large 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 [4]. The total energy was calculated with the high accuracy of 10<sup>−6</sup> a.u. In our calculations for MgF<sub>2</sub>, we applied the basis set developed by Catti et al. [15] for the F ion and by McCarthy and Harrison [16] for the Mg ion.

The non-polar MgF<sub>2</sub> (001) surfaces were modelled using symmetric (with respect to the mirror plane) slabs consisting of

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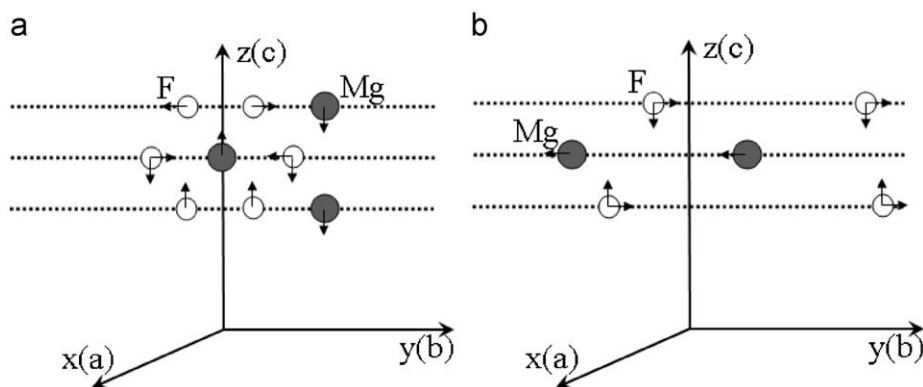


Fig. 1. Schematic side-view of the neutral (001) (a) and (011) (b) surfaces.

**Table 1**  
The bulk band gap calculated using different exchange–correlation functionals.

Method	Band gap (eV)
Experiment	13.0 [19]
B3PW	9.48
B3LYP	9.42
HF	19.65
PWGGA	6.94
PBE	6.91

nine neutral  $\text{MgF}_2$  layers (Fig. 1a) whereas the polar (110) surface (Fig. 1b) contains a sequence of oppositely charged  $\text{F}_2/\text{Mg}/\text{F}_2/\text{Mg}/\dots$  planes. All atoms in slabs were allowed to relax to the minimum of total energy.

### 3. Results

As the starting point for our calculations, we optimized the  $\text{MgF}_2$  lattice constants ( $a=b=4.654 \text{ \AA}$  and  $c=3.139 \text{ \AA}$ ), i.e. deviation from the experimental values are 0.85% and 3.48%, respectively. To characterize the chemical bonding and possible covalency effects, we used the standard Mulliken population analysis for the effective atomic charges  $Q$  and bond populations [17,18]. The calculated effective charges are 1.756e for the Mg ion and  $-0.878e$  for the F ion. The bond population between Mg and F ions is negligibly small, 0.042e. The F–F bond population is negative  $-0.024e$ , which indicates repulsion between F ions. That is,  $\text{MgF}_2$  is essentially ionic solid. The calculated forbidden gap depends considerably on the choice of the exchange–correlation functional (Table 1). As usual, the Hartree–Fock gap is overestimated whereas GGA underestimated. The best results are obtained for the hybrid B3PW method used later on in this paper.

The calculated density of states (DOS) (Fig. 2) demonstrates the 5 eV-wide valence band consisting from F2p atomic orbitals well separated from the conduction band consisting from Mg3s orbitals.

From the results of Table 2, one can see that displacements of atoms from regular lattice sites are quite small and do not exceed 6% in the surface plane. In deeper layers, the displacements of atoms from their crystalline positions are quickly decreasing. Mg atom moves only down along the z-axis whereas F atoms are displaced along the surface in the upper layer. As a result, the F ions at the surface sit above surface Mg ions with the 6% rumpling.

The effective charges of ions on the (001) surface (Table 3) are similar to those in the bulk. Deviation does not exceed 0.05e and

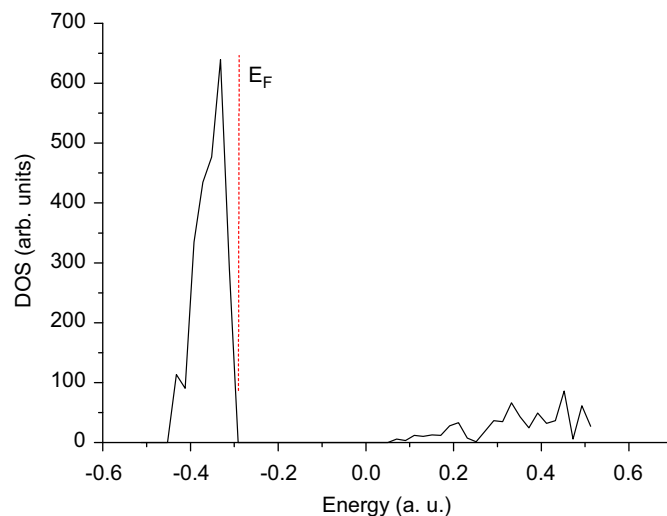


Fig. 2. The B3PW calculated DOS for the  $\text{MgF}_2$  bulk.  $E_F$  denoted the last occupied energy.

**Table 2**  
Atomic displacements in upper three layers on the (001) surface along different axes (see directions in Fig. 1), values are both in  $\text{\AA}$  and with respect to the lattice parameters.

Layer	Atom	Displacements					
		$\Delta x$ ( $\text{\AA}$ )	$\Delta x/a$	$\Delta y$ ( $\text{\AA}$ )	$\Delta y/b$	$\Delta z$ ( $\text{\AA}$ )	$\Delta z/c$
I	Mg	0	0	0	0	-0.2	-0.06
	F	-0.09	-0.02	-0.09	-0.02	0	0
	F	0.09	0.02	0.09	0.02	0	0
II	Mg	0	0	0	0	0.1	0.03
	F	-0.02	-0.004	-0.02	-0.004	-0.05	-0.02
	F	0.02	0.004	0.02	0.004	0.05	0.02
III	Mg	0	0	0	0	-0.04	-0.013
	F	0	0	0	0	0.02	0.01
	F	0	0	0	0	0.02	0.01

again confirms ionic nature of the chemical bonding. In fact, no increase of bond covalency on the surface takes place which is often observed on surfaces of nonmetallic crystals.

As follows from Table 4, on the polar (011) surface F ions are displaced in the upper plane towards the slab center, by 1% of the lattice constant. Mg ions in the second layer – unlike the (001) surface – are not displaced along the z-axis and only by 2% in the x and y planes. Displacements of ions in the third plane are negligibly small.

**Table 3**

The effective charges  $Q$  of ions near the (001) surface and their deviation from the bulk charges,  $\Delta Q$ .

Plane	Atom	Effective charge $Q$ (e)	$\Delta Q$ (e)
I	Mg	1.705	0.051
	F	−0.853	−0.025
	F	−0.853	−0.025
II	Mg	1.766	−0.01
	F	−0.884	0.006
	F	−0.884	0.006
III	Mg	1.752	0.004
	F	−0.874	−0.004
	F	−0.874	−0.004

**Table 4**

The same as Table 2 for the polar (011) surface.

Layer	Atom	Displacements					
		$\Delta x$ (Å)	$\Delta x/a$	$\Delta y$ (Å)	$\Delta y/b$	$\Delta z$ (Å)	$\Delta z/c$
I	F	0.04	0.01	0.05	0.01	−0.04	−0.01
	F	−0.04	−0.01	0.05	0.01	−0.04	−0.01
II	Mg	−0.11	−0.02	−0.02	−0.004	0	0
	Mg	0.11	0.02	−0.03	−0.006	0	0
III	F	−0.01	−0.002	0.01	0.002	0	0
	F	0	0	0.005	0.001	0	0

**Table 5**

The same as Table 3 for the (011) surface.

Plane	Atom	Effective charge, $Q$ (e)	$\Delta Q$ (e)
I	F	−0.848	−0.03
	F	−0.848	−0.03
II	Mg	1.737	0.019
	Mg	1.737	0.019
III	F	−0.883	0.005
	F	−0.883	0.005

The effective ionic charges on this (011) surface (Table 5) are very close to those in the bulk, similarly to those calculation for the (001) surface: Maximum deviation from the bulk value is 0.03e. Thus, even the polar (011) surface demonstrates its ionic nature.

From the calculations of the band structure for the above-discussed 2D slabs with neutral (001) and polar (011) surfaces, we calculated the relevant forbidden gaps which could be checked experimentally by means of optical measurements for similarly-terminated thin films. Thus, using the B3PW method the calculated forbidden gaps for the thin films terminated with the (001) and (011) surfaces are 9.51 and 8.89 eV, respectively; that

is the optical band gap corresponding to the (011) surface is considerably reduced regarding the calculated  $\text{MgF}_2$  bulk gap (9.48 eV) whereas the (001) surface gap (9.51 eV) practically coincides with the calculated bulk value.

#### 4. Conclusions

Using *ab initio* hybrid B3PW approach, we have demonstrated that both neutral (001) and polar  $\text{MgF}_2$  (011) surfaces are as much ionic and the bulk, revealing neither considerable surface relaxation nor near-surface chemical bond covalency.

The forbidden optical gap for the thin films terminated with the polar (011) surface is considerably (0.6 eV) reduced with respect to the calculated bulk and neutral (001) surface gaps. Similar trend, the reduction of surface band gaps of other ionic fluorites,  $\text{CaF}_2$  and  $\text{BaF}_2$ , was calculated earlier by Shi et al. [12,13].

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