

Ab initio calculations of the atomic and electronic structure of MgF_2 (011) and (111) surfaces*

Research Article

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Abstract: The results of *ab initio* slab calculations of surface relaxations, rumplings and charge distribution for the different terminations of the MgF_2 (011) and (111) polar surfaces are presented and discussed. We have employed the computer code CRYSTAL with the Gaussian basis set and the hybrid B3PW exchange-correlation functional. Despite the ionic nature of the chemical bonding at both surfaces, a considerable decrease of the optical band gap is predicted (1.3 eV or 10%) for the (111) surface as compared to the bulk.

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1. Introduction

Magnesium fluoride (MgF_2) is a unique optical material which remains transparent over an extremely wide range of photon energies [1]. Along with lithium fluoride, it is one of the two materials that transmits in the vacuum ultraviolet range and this is where it finds its applications (optical windows, lenses, prisms). The MgF_2 crystal has also several other technological applications, including use in the electrolysis of aluminium ore and anti-reflective coatings [2], for which the surface structure and quality are of primary importance.

Considering the high technological importance of MgF_2 , it is surprising that during the last years only a single theoretical study [3] has been published dealing with the optical properties of the MgF_2 surfaces. In this paper, we performed the first *ab initio* calculations of the atomic and electronic structure of the MgF_2 (011) and (111) polar surfaces. The method and model used are discussed in Section 2, main results in Section 3, and Conclusions are summarized in Section 4.

2. Computational method and surface models

MgF_2 crystal has the tetragonal $P4_2/mnm$ symmetry with two formula units in the unit cell [4]. The experimen-

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tal lattice constants for MgF_2 are 4.615 Å ($a = b$) and 3.043 Å (c). We used here the CRYSTAL-2003 computer code¹. Unlike the plane-wave codes employed in most surface calculations, this code uses localized Gaussian-type basis sets. An additional advantage of the CRYSTAL-2003 code in modelling surfaces is its treatment of *isolated* 2D 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 calculations were performed using the hybrid exchange-correlation B3PW functional which is a hybrid of nonlocal Fock exact exchange, LDA exchange, and Becke's gradient-corrected exchange functional combined with the nonlocal gradient-corrected correlation potential by Perdew and Wang [5-7]. We have chosen the hybrid B3PW functional because it yields excellent results for the properties of many relevant fluorides, e.g. CaF_2 , BaF_2 , SrF_2 [8-11], and it was successfully used also in our previous MgF_2 surface study [3].

The reciprocal space integration was performed by sampling the Brillouin zone with a $5 \times 5 \times 5$ Pack-Monkhorst mesh [12]. To achieve high accuracy, large tolerances of 7, 8, 7, 7, and 14 were chosen in calculations of the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap, and second exchange pseudo-overlap integrals, respectively¹. We used the basis sets for F [13] and Mg atoms [14].

The neutral MgF_2 (001) surface consists of a sequence of MgF_2 planes, the polar (011) surface contains the sequence of oppositely charged planes $\text{F}_2/\text{Mg}_2/\text{F}_2/$ whereas the polar (111) surface contains $\text{MgF}_2/\text{F}/\text{Mg}/\text{F}/\dots$ planes. In a recent paper [3] we modelled the (001) surface and the (011) surface with the $\text{F}_2/\text{Mg}_2/\text{F}_2$ termination. We found that both surfaces remain ionic (as well as the bulk) but the polar (011) surface with $\text{F}_2/\text{Mg}_2/\text{F}_2$ termination reveals a reduced (by 0.6 eV) band gap compared to the bulk one. In this paper, we study another possible termination of the (011) surface containing two surface planes of fluorine ($\text{F}_2/\text{F}_2/\text{Mg}_2/\text{F}_2/\text{F}_2/\text{Mg}_2/\text{F}_2/\text{F}_2$) and the (111) surface terminated with MgF_2 .

Both surfaces were modelled using stoichiometric 2D slabs consisting of nine planes (Figs. 1 and 2). All atoms in the slabs we allowed to relax to the minimum of total energy.

As the starting point for our calculations, we optimized the MgF_2 bulk lattice constants ($a = b = 4.654$ Å and $c = 3.139$ Å), i.e. deviation from the experimental values are 0.85 and 3.48%, respectively. To characterize the

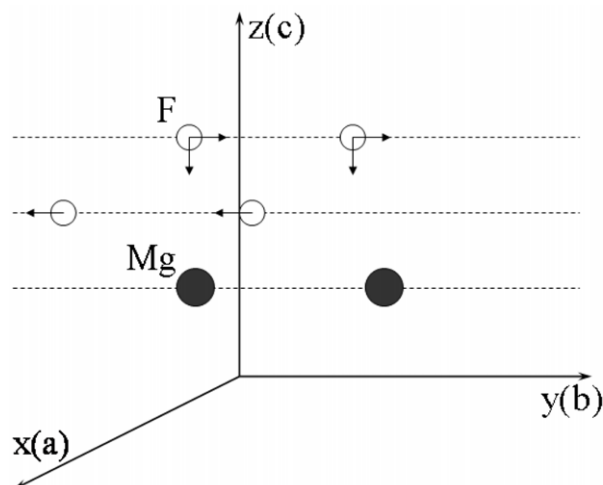


Figure 1. Schematic side-view of the $\text{F}_2/\text{F}_2/\text{Mg}_2$ -terminated polar MgF_2 (011) surface.

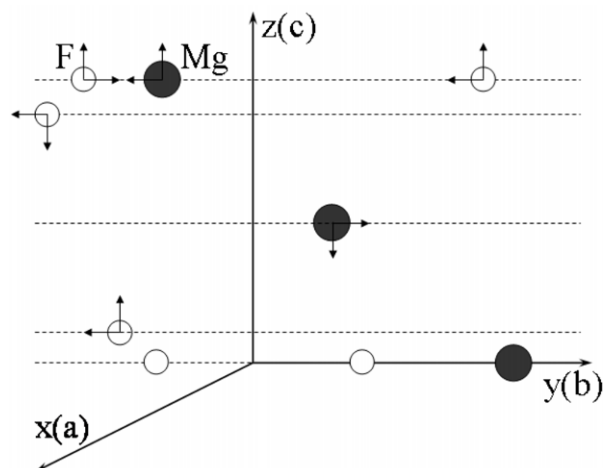


Figure 2. Schematic side view of the polar (111) surface.

chemical bonding and possible covalency effects, we used the standard Mulliken population analysis for the effective atomic charges Q and bond populations¹. The calculated effective charges are 1.756 e for the Mg ion and -0.878 e for the F ion. The bond population between Mg and F atoms is small, 0.042 e . The F-F bond population is negative -0.024 e , which indicates repulsion between F atoms. That is, MgF_2 is essentially ionic solid. The calculated forbidden gap is 9.48 eV (Table 1), in reasonable agreement with the experimental value (12.5 eV [1]).

¹ V.R. Saunders et al., CRYSTAL-2003 User Manual (University of Torino, Torino, Italy, 2003)

Table 1. The calculated bulk, (011) and (111) surface band gaps and surface energies (eV).

Surface/termination	Band gap	Surface energy (per cell)
(001) MgF ₂ /MgF ₂	9.5	2.07
(011) F ₂ /Mg ₂ /F ₂ [3]	8.9	1.60
(011) F ₂ /F ₂ /Mg ₂	8.8	1.38
(111) MgF ₂	8.2	1.13
Bulk	9.5 (expt 12.5 [1])	

3. Results

The calculated optical band gaps (Table 1) reveal the largest reduction for the polar (111) surface compared to the bulk (about 10%) whereas the effect for (011) surfaces with two terminations is twice smaller, 5% (and no effect is observed for the (001) surface). The predicted reduction of the optical band gap could be observed experimentally in thin MgF₂ films.

Following Ref. [8], the surface energies were also calculated and presented in Table 1. As one can conclude, the two types of the (011) terminations give similar results, and the general trend is the same as was observed earlier for BaF₂ surfaces [9, 10]: (111) < (011) < (001). That is, the (111) surface is energetically the most favourable.

For both (011) surface terminations we found that the upper layer with two fluorine atoms relaxes inwards. For F₂/Mg₂/F₂-terminated surface the F ion relaxation is 0.04 Å, or 1.27% of the lattice constant along the z direction [3], whereas for the F₂/F₂/Mg₂-termination (Fig. 1) the upper F layer moves even stronger inwards along the z axis, by 0.15 Å, or 4.78% (Table 2). The difference stems from the fact that in the latter, the surface is more polar than the former one (with the sequences of plane charges $-2e, -2e, +4e$ and $-2e, +4e, -2e$, respectively). In both cases, relaxations of ions and second and deeper planes are small. Such relatively small upper layer atomic displacements for polar surfaces are typical also for other fluorine crystals [8–11].

Analysis of the effective ionic charge changes caused by the (011) surface formation (Table 3) shows a small charge density redistribution between F and Mg ions in three top layers. In fact, the (011) surface remains very ionic, with the effective charges of F and Mg close to the formal charges of $-1e, +2e$.

Unlike the (011) surface, Mg atoms at the upper layer of the (111) surface move *upwards* along the z direction, by 0.08 Å or 2.55% (Table 4). The F atoms in the same plane move also up and even larger, by 0.13 Å or 4.14%. That is, F atoms sit above the Mg atoms. The surface rumpling is

Table 2. Atomic displacements in upper three layers on the F₂/F₂/Mg₂-terminated (011) surface along different axes (see directions in Fig. 1), values are given in Å and with respect to the lattice parameters.

Layer	Atom	Displacements					
		Δx (Å)	$\Delta x/a$	Δy (Å)	$\Delta y/b$	Δz (Å)	$\Delta z/c$
I	F	-0.04	-0.01	0.09	0.02	-0.15	-0.05
	F	0.04	0.01	0.09	0.02	-0.15	-0.05
II	F	0.01	0.00	-0.03	-0.01	0.00	0.00
	F	-0.02	0.00	0.03	0.01	0.00	0.00
III	Mg	0.00	0.00	0.00	0.00	0.00	0.00
	Mg	0.00	0.00	0.00	0.00	0.00	0.00

Table 3. The effective charges Q of ions near the F₂-F₂-Mg₂-terminated (011) surface and their deviation from the bulk charges, ΔQ .

Plane	Atom	Effective charge, Q(e)	$\Delta Q(e)$
I	F	-0.883	0.005
	F	-0.883	0.005
II	F	-0.887	0.009
	F	-0.887	0.009
III	Mg	1.761	-0.005
	Mg	1.761	-0.005

small, only 1.6%, which is unusual for the polar surfaces. The atomic relaxation is observed for the (111) surface up to 4th near surface layer.

Table 4. Atomic displacements in upper four layers on the MgF₂-terminated (111) surface along different axes (see directions in Fig. 2), values are given in Å and with respect to the lattice parameters.

Plane	Atom	Displacements					
		Δx (Å)	$\Delta x/a$	Δy (Å)	$\Delta y/b$	Δz (Å)	$\Delta z/c$
I	Mg	0.51	0.11	-0.36	-0.08	0.08	0.03
	F	0.50	0.11	-0.20	-0.04	0.13	0.04
	F	0.35	0.08	-0.47	-0.10	0.13	0.04
II	F	0.37	0.08	-0.26	-0.06	-0.12	-0.04
III	Mg	-0.16	-0.03	0.12	0.03	-0.04	-0.01
IV	F	0.03	0.01	-0.02	0.00	0.14	0.04
V	Mg	0.00	0.00	0.00	0.00	0.00	0.00
	F	0.00	0.00	0.00	0.00	0.00	0.00
	F	0.00	0.00	0.00	0.00	0.00	0.00

The perturbation of the effective ionic charges on the (111) surface (Table 5) is larger than at the (011) surface (Table 3), with the charge redistribution between Mg and F ions in the first plane. However, the effective charges

remain ionic and close to those in the bulk. Thus, both MgF₂ (011) and (111) polar surfaces demonstrate their ionic nature.

Table 5. The effective charges Q of ions near the MgF₂-terminated MgF₂ (111) surface and their deviation from the bulk charges ΔQ .

Plane	Atom	Effective charge, $Q(e)$	$\Delta Q(e)$
I	Mg	1.689	0.067
	F	-0.839	-0.039
	F	-0.839	-0.039
II	F	-0.833	-0.045
III	Mg	1.762	-0.006
IV	F	-0.900	0.022
V	Mg	1.688	0.068
	F	-0.884	0.006
	F	-0.884	0.006

4. Conclusions

Our *ab initio* calculations show that polar MgF₂ surfaces remain considerably ionic with relatively small surface relaxation and rumpling. We predict certain reduction of the optical band gap (largest for the (111) surface) which however does not affect considerably excellent optical properties of this material. The (111) terminated surface is expected to be energetically the most stable.

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