First-principles study of the (0001)-MgB₂ surface finished in Mg and B

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Abstract. We present a study based on Density Functional Theory (DFT) of the volume and two surfaces (0001) of MgB₂, one of them terminated in Mg and the other one terminated in B. Each one of the surface was relaxed and their electronic properties were determined. From calculation of the enthalpy of formation we found that the Mg-terminated surface is energetically favored. The bands seem to present a formation similar to the Dirac's cone as that are presented in graphene, but in MgB₂ is above of the Fermi level. In the three cases, volume and the two surfaces, the behaviour is boron-metallic, because there are strong presence of B orbital’s in the neighborhood of the Fermi level.

Keywords
MgB₂ surfaces, DFT, wien2k, superconductor, surface electronic states, apparent Dirac’s cones

1. Introduction
The main application of the MgB₂, from the discovery of its superconducting properties [1], is its facility to manufacture superconducting wires and tapes. In nanotechnology, is used to construct nanotubes, nanowires, and nanoparticles [2-9]. Additionally in its normal state, is a resistive electrical conductor, which is an important difference with superconducting ceramics and can be an important advantage for design of nano-devices. MgB₂ is also significantly cheaper than other superconducting materials. Josephson junctions based on MgB₂, are only reproducible if surfaces are smooth and high-quality. Experimentally, high-quality surfaces were obtained [10-13], and theoretically, calculations of the (0001) surfaces were carried out in [14, 15]. This work is devoted to present a comparison of the electronic properties in volume and surfaces.

2. Calculation details
Calculations were carried out by means or the code wien2k [16], which is based on DFT [17, 18]. We used the Generalized Gradient Approximation in the parametrization of PBE [19]. The muffin-tin radii were 2.15 and 1.52 u.a. for Mg and respectively. Energy separation between core and valence states was 6 Ry. Convergence of energy was 0.0001Ry. Rₘᵣₖ * Kₘₐₓ and lₘₐₓ were 7 and 10 respectively and
these parameters control the size of the basis-set to expand the solutions of the Kohn-Sham equations [18], according to LAPW method. The surfaces are simulated by means of the slab method, where each slab has 5 bilayers of MgB$_2$, with a vacuum space between slabs of ~12 Å, which guaranteeed that there are no-interactions between surfaces. The bulk cell parameters obtained are $a = 3.52$ Å and $c = 3.52$ Å, which are in a good agreement with other authors [14,15]. Figure 1a shows the hexagonal volumetric cell used.

3. Structural properties

Let us to cut a bulk of a material (Gibbs potential $G_0$) in two pieces ($G_1$ and $G_2$) and two surfaces ($G_{surf}$). Then $G_0 = G_1 + G_2 + G_{surf}$, with $G_{surf} = (U + PV - TS)_{surf} = U_{surf} - TS_{surf}$ ($V=0$ for a surface). By application the first law of thermodynamics to an open system at equilibrium:

$$U_{surf} = TS_{surf} - PV_{surf} + 2\gamma A + \sum \mu_i n_i$$  \hspace{1cm} (1)

where $2\gamma A$ is the energy of formation of the two surfaces ($2\gamma A = E_{surface}$, $A$ is the area of each surface), $\mu_i$ is the chemical potential of the atomic species $i$ and $n_i$ is the number of particles. Therefore, $G_{surf} = 2\gamma A + \sum n_i \mu_i$. At $P=0$ and $T=0$ we can approximate $G_{surf} \approx E_{DFT-slub}$ where $E_{DFT-slub}$ is the total energy of the slab calculated by wien2k.

If we take as area unit the area of and 1x1-cell, then

$$E_{surf} (1x1 \text{ cell}) = \frac{1}{2} (E_{DFT-slub} - \sum n_i \mu_i)_{1x1\text{cell}}$$ \hspace{1cm} (2)

Particularly,

$$E_{surface \, Mg-terminated \, (1x1\text{cell})} = \frac{1}{2} (E_{DFT-slub - Mg-terminated} - n_B \mu_B - n_{Mg} \mu_{Mg})_{1x1\text{cell}}$$ \hspace{1cm} (3)

and similarly for $E_{surface \, B-terminated \, (1x1\text{cell})}$. Using $\mu_{Mg} - \mu_{Mg-Bulk}$ as the independent variable, and after an algebraic job, we obtained

$$E_{(Mg/B)-terminated \, surface} = \frac{1}{2} \left( n_B - n_{Mg} \right) \left( \mu_{Mg} - \mu_{Mg-Bulk} \right) + \frac{1}{2} n_B \left( \mu_{Mg-Bulk} - \mu_{Bulk} \right) - n_{Mg} \mu_{Mg-Bulk}$$ \hspace{1cm} (4)

Figure 1. a) The cell used in calculations. The hexagonal symmetries are shown. The unit cell is marked with green lines. b) Energy of formation of the surfaces of MgB$_2$ as a function of the chemical potential of Mg.
where $\mu_{\text{Bulk}}$ is obtained from $E_{\text{DFT-bulk}}$ by each particle, and $-\Delta H_F$ is the enthalpy of formation of the MgB$_2$ [15]. We obtained, $\Delta H_F = 1.59$eV (discrepancy ~5.5% with [15]), and $\mu_{\text{Mg-Bulk}} = -5451.38$eV, $\mu_{\text{MgB}_2-\text{Bulk}} = -6804.15$eV, and for the surface Mg-terminated, we have $n_{\text{Mg}} = 6$ and $n_{\text{B}} = 10$ and for the surface B-terminated, $n_{\text{Mg}} = 5$ and $n_{\text{B}} = 12$. Additionally, $E_{\text{DFT-slab-Mg-terminated}}(1x1) = -39472.358$eV and $E_{\text{DFT-slab-B-terminated}}(1x1) = -35370.303$eV. Therefore,

$$E_{\text{surface}} = -\frac{1}{2}\left(\mu_{\text{Mg}} - \mu_{\text{Mg bulk}}\right) - 0.1\text{eV} \quad E_{\text{slab}} = \frac{1}{2}\left(\mu_{\text{Mg}} - \mu_{\text{Mg bulk}}\right) + 0.16\text{eV} \quad (5)$$

Figure 1b shows the plot of the formation energy for the two types of surfaces of MgB$_2$ as a function of the chemical potential using as reference the chemical potential of the Mg-bulk (Eq.5). We can conclude that the Mg-terminated surface is more favorable than the other one as have been informed by other authors [15], in all the range of the chemical potential of the Mg.

### 4. Electronic properties

Figure 2 shows the bands of the surfaces and the bulk. The material presents a conductor behavior. It is important to note that the bulk bands of this material at K-point, above the Fermi level, present a formation like as the Dirac's cones of graphene (highlighted with red circle in Figure 2 c). And these apparent Dirac's cones are also present in the surfaces bands for the two types of surface. Composition of bands, around the Fermi level, are due to the main contributions are due to B orbitals. p-B orbitals are situated in the region between -6.0eV up to Fermi level. There are orbitals of Mg in the conduction band and there also a bit at the bottom of the valence band. One can see that the surface band are similar to those volume, but the lines look parallel and repeated 5 times. Mg orbitals are mainly located above of the Fermi level. In the most stable surface, around the Fermi level, the presence of p-B orbitals is notorious and the Mg orbitals are majority above the Fermi level.

Figure 2  Band structures of MgB$_2$. (a) (0001) B-terminated. (b) (0001) Mg-terminated. (c) Bulk

### 5. Summary and Conclusions

We presented calculations about the volume and (0001) surfaces of the superconductor MgB$_2$. The results we obtained are in overall agreement with other authors. Taking in account the energy of formation, the Mg-terminated surface is more favorable than the other one. The material is a good electrical conductor in volume and any of the two surfaces, and the conduction of electricity is mainly...
carried out by p-B orbitals. Other observation is that the bands seem to present a formation very similar to the Dirac's cones as those are presented in graphene, but they are above of the Fermi level.

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7. References

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