

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 of 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 0.0001 Ry. R_{mt} , K_{max} and l_{max} 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 $\sim 12\text{\AA}$, which guaranteed that there are no-interactions between surfaces. The bulk cell parameters obtained are $a = 3.52\text{\AA}$ and $c = 3.52\text{\AA}$, 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 $G_0 = G_1 + G_2 + G_{\text{surf}}$, with $G_{\text{surf}} = (U + PV - TS)_{\text{surf}} = U_{\text{surf}} - TS_{\text{surf}}$ ($V=0$ for a surface). By application the first law of thermodynamics to an open system at equilibrium:

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

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

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

$$E_{\text{surface}} (1 \times 1 \text{ cell}) = \frac{1}{2} (E_{\text{DFT-slab}} - \sum n_i \mu_i)_{1 \times 1 \text{ cell}} \quad (2)$$

Particularly,

$$E_{\text{surface Mg-terminated}} (1 \times 1 \text{ cell}) = \frac{1}{2} (E_{\text{DFT-slab-Mg-terminated}} - n_B \mu_B - n_{\text{Mg}} \mu_{\text{Mg}})_{1 \times 1 \text{ cell}} \quad (3)$$

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

$$E_{\text{surface}}^{(\text{Mg/B})\text{-terminated}} = \frac{1}{2} \left[\left(\frac{1}{2} n_B - n_{\text{Mg}} \right) (\mu_{\text{Mg}} - \mu_{\text{Mg}}^{\text{Bulk}}) + E_{\text{slab}}^{(\text{Mg/B})\text{-terminated}} + \frac{1}{2} n_B (\mu_{\text{Mg}}^{\text{Bulk}} - \mu_{\text{MgB}_2}^{\text{Bulk}}) - n_{\text{Mg}} \mu_{\text{Mg}}^{\text{Bulk}} \right] \quad (4)$$

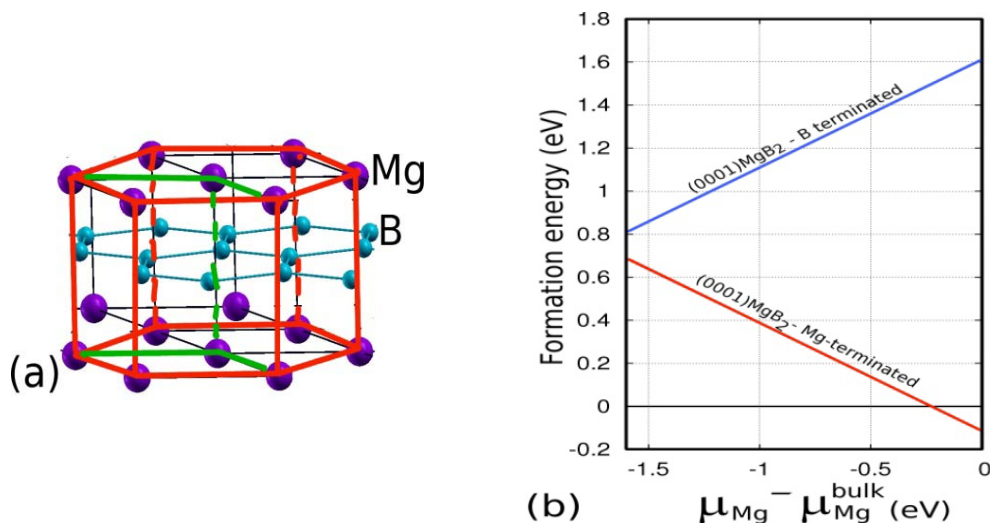


Figure 1. a) The cell used in calculations. The hexagonal symmetries are shown. The unit cell is marked with green lines. b) Energy of formation of the surfaces of MgB_2 as a function of the chemical potential of Mg.

where μ_{Bulk} is obtained from $E_{\text{DFT-bulk}}$ by each particle, and $-\Delta H_F \leq \mu_{\text{Mg}} - \mu_{\text{Mg}}^{\text{Bulk}} \leq 0$ and ΔH_F is the enthalpy of formation of the MgB_2 [15]. We obtained, $\Delta H_F = 1.59\text{eV}$ (discrepancy $\sim 5.5\%$ with [15]), and $\mu_{\text{Mg-Bulk}} = -5451.38\text{eV}$, $\mu_{\text{MgB}_2\text{-Bulk}} = -6804.15\text{eV}$, 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, $E_{\text{DFT-slab-Mg-terminated}}(1 \times 1) = -39472.358\text{eV}$ and $E_{\text{DFT-slab-B-terminated}}(1 \times 1) = -35370.303\text{eV}$. Therefore,

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

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.

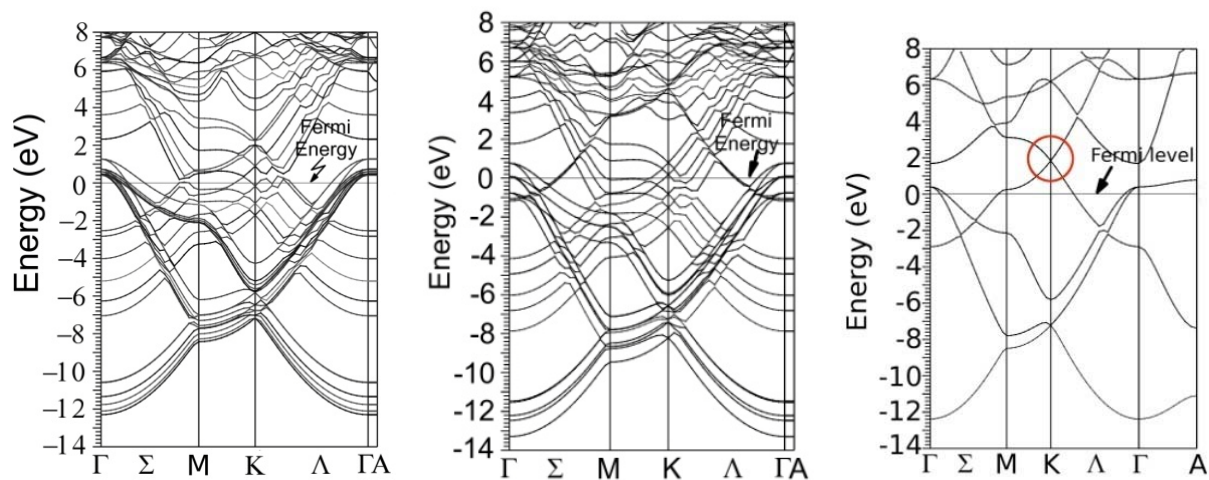


Figure 2 Band structures of MgB_2 . (a) (0001) B-terminated. (b) (0001) Mg-terminated. (c) Bulk

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

- [1] J Nagamatsu, N Nakagawa, T Muranaka, Y Zenitani, and J Akimitsu. 2001 *Superconductivity at 39K in magnesium diboride*. *Nature*, **410** 63
- [2] N Sano, O Kawanami, H Tamon. 2011 *Journal Applied Physics*, Vol **109** 034302 – 034302-6
- [3] X. Zhang, Y Ma, Z Gao, D Wang, L Wang, W Liu, and C Wang. 2008 *J. Appl. Phys.*, Vol. **103** 103915
- [4] E W Collings, M D Sumption, M Bhatia, M Susner, and S D Bohnenstiehl. 2008 *Supercond. Sci. Technol.* Vol **21** 103001
- [5] S Zhou, P Wang, B Zhang, H Gong, X Zhang. 2009 *Materials Letters*, **63**(20) 1680-1682
- [6] Shekhar C, Giri R, Malik SK, Siravastra ON. 2007 *J. Nanosciencie and Nanotechnology* **7**, (6) 1804-1809(6)
- [7] M Dias Lima, J Bykova, A. Howard, Ray, A Zakhidov. 2012 *American Physical Society*
- [8] R Ma, Y Bando, T Mori and D Golber. 2003 *National Institute for materials Science* **15** (16) 3194-3197
- [9] N Novosel, S Galić, D Pajić, Ž Skoko, I Lončarek, M Mustapić, K Sadro and E Babić. *Superconductor Science and Technology* **26**(6)
- [10] M Xu, Y Takano, T Hatano, T Kimura, D Fujita. 2003 *Applied Surface Science* **205**. 225-230
- [11] V Despoja, D J Mowbray and V M Silking. 2011 *Phys. Rev. B* **84** 104514
- [12] D R Lamborn, R H T Wilke, Q Li, X X Xi, D W Snyder, and J M Redwing. 2007 *Transactions on Applied Superconductivity* **17**(2) 2862-2866
- [13] P Orgiani, Y Cuil, J Chen, V Ferrando, A V Pogrebnjakov, J M Redwing, Q Li and X X Xi. 2006 *Advances in Science and Technology*, **47** 55-62
- [14] J Kortus, I I Mazin, K D Belashchenko, V P Antropov and L L Boyer. 2001 *Phys Rev B*. **86** (20)4656-4659
- [15] Z Li, J Yang, J G Hou, Q Zhu. 2002 *Phys Rev B*. **65** 100507-1
- [16] P Blaha, K Schwarz, G K H Madsen, D Kvasnicka and J Luitz. 2001 *WIEN2k, An Augmented Plane Wave + Local orbitals Program Oro Calculating Cristal Properties (Karlheinz Schwarz, Techn. Universität Wien, Austria)* ISBN 3-9501031-1-2
- [17] P Hohenberg and W Kohn. 1964 *Phys Rev*. **136** B864
- [18] W Khon and L J Sham. 1965 *Phys Rev* **140** A1133
- [19] J P Perdew, K Burke, M Ernzerhof, 1996 *Phys Rev* **77**(18) 3865-3868