Effect of surfaces and interfaces on the electronic, magnetic and gap-related properties of the half-metal Co₂MnSn

I. Galanakis
Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece
(Dated: February 1, 2008)

We present state-of-the-art electronic structure calculations for the Co₂MnSn full-Heusler alloy. We show that in its bulk form it is a half-metallic ferromagnet with the Fermi level being located within a tiny gap of the minority-spin density of states. Moreover the alloy shows the Slater-Pauling behavior with a total spin magnetic moment in the unit cell of 5 \( \mu_B \). In the case of the (001) surfaces, the broken bonds at the surface form a minority band pinned exactly at the Fermi level destroying the half-metallicity. Our calculations reveal that the interfaces with the non-magnetic metal V and the semiconductor InAs are no more half-metallic due to the different environment of the atoms of the half-metal at the interface. These interface states although localized only at the first few interface layers can become conducting when coupled to defect states and kill the spin-polarization of the current injected from the half-metal into the semiconductor or the non-magnetic metallic spacer.

PACS numbers: 75.47.Np, 75.50.Cc, 75.30.Et

I. INTRODUCTION

The last decade one of the most active research areas in solid state and materials science is the field of magnetoelectronics also known as spintronics. The aim is to replace conventional electronics by new devices where the spin of the electrons and not the charge transfer plays the key role. A central problem in this field is the injection of spin-polarized current from a metal into a semiconductor. In principle it is possible to achieve 100\% spin-polarized injected current if the magnetic lead is a half-metallic material. These alloys are hybrids between normal metals and semiconductors. The Fermi level crosses the majority spin-band as for a usual metal while it falls within an energy gap in the minority spin-band as in a semiconductor. The attention on the half-metals has been mainly concentrated on the intermetallic Heusler alloys like NiMnSb (semi-Heuslers) or Co₂MnSn (full-Heuslers) due to their very high Curie temperatures, which exceed considerably the room temperature reaching even values close to 1000 K, and their structural similarity to the widely used binary semiconductors like GaAs. In such compounds the behavior of the interface between the half-metal and the semiconductor is of great importance since interface states, although localized in space, couple with impurity or defect states killing the spin-polarization of the injected current.

In this communication we will concentrate on the properties of the (001) surfaces of the half-metallic Heusler alloy Co₂MnSn and its interfaces with the semiconductor InAs and the non-magnetic metal V. Its bulk properties are well-established (see for example) but only the MnSn terminated (001) surfaces have been theoretically studied using ab-initio electronic structure calculations. Theoretical investigations exist for the (001) surfaces of Co₂MnSi and Co₂MnGe compounds which are isovalence to Co₂MnSn (same number of valence electrons in the unit cell) and for the (001) surfaces of Co₂CrAl and their interfaces with the semiconductors GaAs and InP respectively. In all cases the half-metallicity was destroyed due to surfaces/interface states which were strongly localized near the surface/interface layers. Experimentally films of full-Heusler alloys have been grown by several groups (see for example articles in reference) and they are widely used for realistic applications like incorporated magnetic tunnel junctions and spin-valves.

We will start our study by presenting in section the bulk properties of Co₂MnSn and the (001) surfaces. There are two possible terminations: (i) a Co surface layer and a MnSn subsurface layer and (ii) a MnSn surface layer and a pure Co subsurface layers (for the exact structure see figure 1 in reference). In section we present our results on the (001) interfaces with the InAs semiconductor which has a lattice constant close to the one of Co₂MnSn and thus pseudomorphic growth could be in principle achieved and of the (001) interfaces with V since multilayers between Heusler alloys and V have been succesfully grown experimentally. InAs crystallizes in the zinc-blende structure which is similar to the \( L_2_1 \) structure of the full-Heusler alloys (see reference) and V crystallizes in a b.c.c. lattice. The \( L_2_1 \) structure of full-Heusler alloys, if one ignores the different chemical elements, is in reality a b.c.c. lattice and thus coherent growth of V on top of Co₂MnSn is possible. In section we summarize and conclude our results.

For the calculations we have used the the full-potential version of the screened Korringa-Kohn-Rostoker (KKR) Green’s function method in conjunction with the local spin-density approximation for the exchange-correlation potential. The details for the surface and interfaces calculations have been published elsewhere.

Dated: February 1, 2008
atom has a spin moment of around 0.93 $\mu_B$ which is analyzed in table I. Each Co atom has a large localized spin moment which is 3.20 $\mu_B$. The Sn atom has a small negative spin moment of -0.06 $\mu_B$ since the bonding majority $p$ states of Sn are spread over a wide energy range crossing the Fermi level while the bonding minority $p$ states are completely occupied.

In table I we have also included the spin moments of the atoms at the surface and subsurface layers for both possible Co and MnSn terminations and in figure 2 we have included the DOS of these atoms with respect to the bulk. When we open the MnSn-terminated surface we break the bonds of the Mn and Sn atoms with their nearest neighboring Co atoms (each Mn or Sn atom has eight Co atoms as nearest neighbors and when we open the surface we break four such bonds). Due to the creation of these ligand states the Mn atoms regain some charge but since their majority states are almost completely occupied and it will cost a lot in Coulomb energy to occupy exclusively majority high-energy-lying antibonding states, they have to accommodate the extra charge also in minority-spin states. Thus although its spin moment only slightly increases reaching the 3.75 $\mu_B$ which is almost doubled reaching the 1.80 $\mu_B$. The unoccupied minority $d$ states are pushed lower in energy and the Fermi level is now within a very large broad peak and half-metallicity is completely destroyed. The altered Co DOS polarizes also the DOS of the Mn atoms at the subsurface layer which also shows an important minority DOS at the Fermi level. To conclude the (001) surfaces of Co$_2$MnSn show no more the half-metallic character of the perfect bulk compounds due to surfaces states created by the ligands.

### Table I: Mn and Co atom-resolved spin magnetic moments in $\mu_B$.

|                | $m^{Co}$ | $m^{Mn}$ |
|----------------|----------|----------|
| Bulk           | 0.93     | 3.20     |
| Surfaces       |          |          |
| (001) Co-term  | 1.80     | 3.35     |
| (001) MnSn-term| 0.91     | 3.75     |
| Interfaces     |          |          |
| Co/In          | 2.00     | 3.19     |
| Co/As          | 1.35     | 3.42     |
| Co/V           | 0.92     | 3.51     |
| MnSn/In        | 1.82     | 2.73     |
| MnSn/As        | 1.71     | 3.69     |
| MnSn/V         | 1.64     | 2.46     |

FIG. 1: (Color online) Total and atom-resolved density of states (DOS) in states/eV as a function of the energy for the bulk Co$_2$MnSn alloy. Positive values of DOS correspond to the majority-spin (spin-up) electrons and negative values to the minority (spin-down) electrons. We have chosen the zero energy to correspond to the Fermi level.

II. BULK AND SURFACE PROPERTIES

First we will discuss the case of the bulk Co$_2$MnSn. In figure 1 we have plotted the density of states (DOS) in units (number of states)/eV as a function of the energy in eV. The zero of the energy axis corresponds to the Fermi level, $E_F$. We have plotted both the total DOS and its projection on each atom. First, the compound is half metal since the Fermi level crosses the majority-spin (spin-up) electronic states while it is within a tiny gap of the minority-spin (spin-down) states. At around -9 eV are located the $s$ states provided by Sn. At around -6 eV start the $p$ bands of the Sn atom which accommodate also $d$ electrons of the transition metal atoms reducing the $d$-charge that should be accommodated by their $d$ bands. At -3 eV start the $d$ bands of the transition metal atoms. These states in the minority band are mainly of Co character. As explained extensively in reference 2 the gap is formed between states exclusively located at the Co sites which due to symmetry reasons do not hybridize with the $d$ orbitals of Mn. There are exactly 12 occupied minority states, one $s$ and three $p$ states of Sn, five bonding $d$ Co-Mn states and finally the triple degenerated $t_{2g}$ states which are exclusively located at Co sites as we discussed before.2 Since there are exactly 12 occupied minority spin states the total spin moment should follow the so-called Slater-Pauling behavior for the full-Heusler alloys being in $\mu_B$ the total number of valence electrons in the unit cell, which for Co$_2$MnSn is 29, minus two times the number of occupied minority-spin states. Thus the total spin moment in the unit cell should be 5 $\mu_B$. This value coincides with the calculated total spin moment which is analyzed in table I. Each Co atom has a spin moment of around 0.93 $\mu_B$ and the Mn atom has a spin moment only slightly increases reaching the 3.75 $\mu_B$ half-metallicity is completely destroyed since as can be seen in figure 2 there is a minority surface state pinned exactly at the Fermi level which persists also for the Co atom at the subsurface layer. The Co-terminated (001) surface presents even more strong deviations from the perfect half-metallicity. Each Co atom at the surface loses two out for its fours Mn neighbors and the symmetry of its environment completely changes. As a result its spin magnetic moment is almost doubled reaching the 1.80 $\mu_B$. The unoccupied minority $d$ states are pushed lower in energy and the Fermi level is now within a very large broad peak and half-metallicity is completely destroyed. The altered Co DOS polarizes also the DOS of the Mn atoms at the subsurface layer which also shows an important minority DOS at the Fermi level. To conclude the (001) surfaces of Co$_2$MnSn show no more the half-metallic character of the perfect bulk compounds due to surfaces states created by the ligands.
FIG. 2: (Color online) Upper panel : Atom-resolved DOS for the Mn atom at the surface layer and the Co atom at the subsurface layer in the case of the MnSn terminated Co$_2$MnSn(001) surface compared to the bulk case. Lower panel : same for the Co terminated Co$_2$MnSn(001) surface.

III. INTERFACES

We will start our discussion on the interfaces from the case of interfaces with vanadium. Vanadium in its bulk form is non magnetic but in proximity with strongly magnetic elements like Co or Mn its $d$ orbitals can be polarized through hybridization effects and it can obtain a spin magnetic moment. As in the case of surfaces, the interface can be either made up from a V and a Co interface layers or a V and a MnSn interface layers. In table I we have included the spin magnetic moments of the Co and Mn atoms at the interfaces since the Sn atoms present very small magnetic moments and in figure 3 we present the DOS’s of the atoms at the interface and subinterface layers for both possible structures at the interface.

When the interface is made up by Co and V, the Co atoms at the interface have now from one side two Mn atoms and two Sn atoms as nearest neighbors and from the other side four V atoms. Thus their symmetry is very close to the perfect $L2_1$ structure of the Heusler alloys and they have a spin moment almost identical to the bulk case. Also the spin moment of the Mn atoms at the subinterface layer is slightly larger than the bulk case. But although the spin moments for the Co/V case stay close to the bulk values, the DOS in figure 3 reveals that the half-metallicity is completely destroyed since now the states around the minority gap strongly overlap and the Fermi level falls within a deep of the DOS but not a gap anymore. The V atoms at the interface, $V^I$, are polarized by the Co atoms carrying a small spin magnetic moment while the V atoms at the subinterface layer, $V^{I-1}$, almost recover their bulk behavior and the DOS of the occupied states is similar for both spin directions. In the case of the MnSn/V interfaces the spin moments show larger deviations from the ideal bulk case and half-metallicity is completely destroyed.

We will complete our study by the case of interfaces with the InAs semiconductor. There are four different possible interfaces Co/In, Co/As, MnSn/In and MnSn/As. A close look at table I reveals that for all four interfaces Co at the interface layer or subinterface layers has a spin moment which is from 50% larger than the bulk value and reaches a value of 2 $\mu_B$ at the Co/In interface. In the case of the Co/As interface the spin moment is smaller than this maximum value (1.35 $\mu_B$) since the Co atoms at the interface have from the side of the half-metal two Mn and two Sn atoms as first neighbors and from the side of the semiconductor only two As atoms. Thus at the Co/As interface we have broken two out for the four Co-Mn bonds. Indium has a different number of valence electrons with respect to As and Sn and the environment of the Co atoms at the Co/In interface is considerably altered with respect to the bulk and this leads to this huge spin moment of 2 $\mu_B$ for the Co interface atoms. In the case of MnSn/In and MnSn/As interfaces the interface deviates even more from the bulk case since the Mn and Sn atoms at the interface have now from the side of the semiconductor two In or two As atoms as first neighbors, respectively, instead of the two Co atoms in the bulk. This is reflected on the large fluctuations of the Mn spin moments and the large spin magnetic moments of the Co atoms at the subinterface layers. As can be seen in figure 4 the half-metallicity is in...
all cases destroyed since even the In and As atoms of the semiconductor at the interface present DOS around the Fermi level due to the hybridization of their $p$ orbitals with the $p$ and $t_{2g}$ orbitals of the Co or Mn-Sn atoms at the interface layers of the Co$_2$MnSn alloy.

**IV. SUMMARY AND CONCLUSIONS**

We have performed state-of-the-art electronic structure calculations for the Co$_2$MnSn full-Heusler alloy. Our results for the bulk show that the alloy in form of single crystals is a half-metallic ferromagnet with the Fermi level being located within a tiny gap of the minority-spin DOS. The alloy shows the Slater-Pauling behavior with a total spin magnetic moment in the unit cell of 5 $\mu_B$. In the case of the MnSn terminated (001) surface, the broken bonds at the surface form a minority band pinned exactly at the Fermi level, while for the Co-terminated (001) surface the effect is even more pronounced. Our calculations reveal that both the interfaces with the non-magnetic metal V and the semiconductor InAs are no more half-metallic due to the different environment of the atoms of the half-metal at the interface. These interface states although localized only at the first few interface layers can become conducting when coupled to defect states and kill the spin-polarization of the current injected from the half-metal into the semiconductor.

* Electronic address: galanakis@upatras.gr

1. I. Žutić, J. Fabian, and A. Das Sarma, Rev. Mod. Phys. 76, 323 (2004).
2. C. Felser, G. H. Fecher, and B. Balke, Angew. Chem. Int. Ed. 46, 668 (2007).
3. H. Zabel, Materials Today 9, 42 (2006).
4. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science 294, 1488 (2001).
5. I. Galanakis and P. H. Dederichs (eds): Half-metallic alloys: fundamentals and applications, Springer Lecture notes in Physics vol. 676, Springer (2005).
6. I. Galanakis, Ph. Mavropoulos, and P. H. Dederichs, J. Phys. D: Appl. Phys. 39, 765 (2006); I. Galanakis and
Ph. Mavropoulos, J. Phys.: Condens. Matter 19, 315213 (2007).

7 P. J. Webster and K. R. A. Ziebeck, in Alloys and Compounds of d-Elements with Main Group Elements. Part 2, edited by H. R. J. Wijn, Landolt-Boernstein, New Series, Group III, Vol. 19/c (Springer, Berlin), 1988, pp. 75-184.

8 K. R. A. Ziebeck and K.-U. Neumann, in Magnetic Properties of Metals, edited by H. R. J. Wijn, Landolt-Boernstein, New Series, Group III, Vol. 32/c (Springer, Berlin), 2001, pp. 64-141.

9 I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B 66, 174429 (2002).

10 G. Lee, L. G. Kim, J. I. Lee, and Y.-R. Jang, Phys. Stat. Sol. (b) 241, 1435 (2004).

11 I. Galanakis, J. Phys.: Condens. Matt. 14, 6329 (2002).

12 S. Picozzi, A. Continenza, and A. J. Freeman, J. Phys. D: Appl. Phys. 39, 851 (2006); S. Picozzi and A. J. Freeman, J. Phys.: Condens. Matter 19, 315215 (2007).

13 I. Galanakis, J. Phys.: Condens. Matter 16, 8007 (2004).

14 F. Y. Yang, C. H. Shang, C. L. Chien, T. Ambrose, J. J. Krebs, G. A. Prinz, V. I. Nikitenko, V. S. Gornakov, A. J. Shapiro, and R. D. Shull, Phys. Rev. B 65, 174410 (2002); T. Ambrose, J. J. Krebs, and G. A. Prinz, Appl. Phys. Lett. 76, 3280 (2000); M. F. Raphael, B. Ravel, A. M. Willard, S. F. Cheng, B. N. Das, R. M. Stroud, K. M. Bussmann, J. H. Claassen, and V. G. Harris, Appl. Phys. Lett. 70, 4396 (2001); Y. J. Chen, D. Basiaga, J. R. O’Brien, and D. Heiman Appl. Phys. Lett. 84, 4301 (2004); H. J. Elmers, G. H. Fecher, D. Valdaitsev, S. A. Nepijko, A. Gloskovskii, G. Jakob, G. Schönhense, S. Wurmehl, T. Block, C. Felser, P. C. Hsu, W. L. Tsai, and S. Cramm, Phys. Rev. B 67, 104412 (2003).

15 T. Marukame, T. Ishikawa, K. I. Matsuda, T. Uemura, and M. Yamamoto Appl. Phys. Lett. 88, 262503 (2006); T. Marukame, T. Kasahara, K. Matsuda, T. Uemura, and M. Yamamoto, Jpn. J. Appl. Phys. 44, L521 (2005).

16 R. Kelekar and B. Klemens, Appl. Phys. Lett. 86, 232501 (2005).

17 A. Bergmann, J. Grabis, B. P. Toperverg, V. Leiner, M. Wolff, H. Zabel, and K. Westerholt, Phys. Rev. B 72, 214403 (2005); J. Grabis, A. Bergmann, A. Nefedov, K. Westerholt, and H. Zabel, Phys. Rev. B 72, 024437 (2005); idem, Phys. Rev. B 72, 024438 (2005).

18 N. Papanikolaou, R. Zeller, and P. H. Dederichs, J. Phys.: Condens. Matter 14, 2799 (2002).

19 S. H. Vosko, L. Wilk, and N. Nusair, Can. J. Phys. 58, 1200 (1980).

20 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).