Ferrimagnetism and antiferromagnetism in half-metallic Heusler alloys

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Half-metallic Heusler alloys are among the most promising materials for future applications in spintronic devices. Although most Heusler alloys are ferromagnets, ferrimagnetic or antiferromagnetic (also called fully-compensated ferrimagnetic) alloys would be more desirable for applications due to the lower external fields. Ferrimagnetism can be either found in perfect Heusler compounds or achieved through the creation of defects in ferromagnetic Heusler alloys.

Introduction : The family of the ferromagnetic Heusler alloys, e.g. NiMnSb or Co_2MnSi, have been extensively studied during the last years due to their potential applications in magnetoelectronic devices [1]. Their main advantage with respect to other half-metallic systems is their structural similarity with the binary semiconductors and their high Curie temperatures. First principles calculations have been extensively employed to study their electronic and magnetic properties (see Refs. [2, 3, 4] and references therein). One of the most important features of these alloys is the Slater-Pauling behavior of their total spin magnetic moment which is given simply as a function of the number of valence electrons in the unit cell [5, 6]. Authors have studied in the recent years several aspects of these half-metallic alloys like the properties of surfaces [7, 8, 9] and interfaces with semiconductors [10, 11], the quaternary [12, 13], the orbital magnetism [14, 15], the effect of doping and disorder [16, 17], the exchange constants [18] and the magneto-optical properties [19].

Half-metallic ferrimagnetic Heusler alloys like Mn_2VAl, where Mn and V atoms have antiparallel spin moments, are of particular interest since they create smaller external magnetic fields and thus lead to smaller energy losses [20, 21]. In the extreme case like Cr_2MnSb (alloys with 24 valence electrons) Cr and Mn spin moments cancel each other and the compounds are named as fully-compensated half-metallic ferrimagnets or simply half-metallic antiferromagnets [22]. Defects in these alloys show a very interesting behavior. When we substitute Co atoms with Cr(Mn) in the $Co_2Cr(Mn)Al$ and $Co_2Cr(Mn)Si$ compounds, the impurity atoms couple antiferromagnetically with the other transition metal atoms lowering the total spin moment [23, 24]. Co and Fe impurities in Mn_2VAl and Mn_2VSi ferrimagnetic alloys have spin moments antiparallel to Mn and thus the total spin moment reaches closer to the zero value [25]. In this manuscript we will complete these studies presenting results for the Cr(Mn) impurites in ferromagnetic $Co_2Mn(Cr)Al$ and $Co_2Mn(Cr)Si$ alloys, the case of V and Cr impurities in ferrimagnetic Mn_2VAl and Mn_2VSi alloys and finally the 24-valence half-metallic antiferromagnetic alloys Cr_2FeZ (Z= Si, Ge, Sn) using the full–potential nonorthogonal local–orbital band structure scheme (FPLO) [26].

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Table 1 Total and atom-resolved spin magnetic moments in μ_B for the $[X_{1-x}X^*_x]_2YZ$ compounds. The atom-resolved spin moments have been scaled to one atom. We do not present the moments of the Z sp-atom since they are negligible with respect to the X and Y transition-metal atoms.

Compound	m^{Co}	m^{X^*}	m^{Y}	m^{Total}	Compound	m^{Mn}	m^{X^*}	m^{V}	m^{Total}
$[Co_{0.9}Cr_{0.1}]_2MnAl$	0.72	-2.57	2.79	3.43	$[Mn_{0.9}V_{0.1}]_2VAl$	-1.68	-1.00	1.03	-2.13
$[Co_{0.9}Cr_{0.1}]_2MnSi$	0.97	-1.55	3.03	4.40	$[Mn_{0.9}V_{0.1}]_2VSi$	-1.17	-1.10	0.92	-1.33
$[Co_{0.9}Mn_{0.1}]_2CrAl$	0.74	-1.75	1.70	2.60	$[Mn_{0.9}Cr_{0.1}]_2VAl$	-1.66	-1.8	1.12	-2.20
$[Co_{0.9}Mn_{0.1}]_2CrSi$	0.94	-0.95	2.14	3.60	$[Mn_{0.9}Cr_{0.1}]_2VSi$	-1.06	-1.58	0.96	-1.20

$[Co_{1-x}Cr_x]_2MnZ$ and $[Co_{1-x}Mn_x]_2CrZ$ (Z= Al, Si) alloys : In the first part of our study we will concentrate on the case of defects in the strong ferromagnetic half-metallic Co_2CrZ and Co_2MnZ (Z= Al or Si) Heusler alloys. In Ref. [23] we have studied the case of Cr defects in Co_2CrAl and Co_2CrSi alloys; Cr atoms substitute Co atoms at the perfect X sites. We expanded this study in Ref. [24] studying the case of Mn impurities in Co_2MnAl and Co_2MnSi compounds. In all cases the impurity atoms had spin moments antiparallel to the other transition metal atoms lowering the total spin moment while keeping the half-metallic character of the parent compounds. We have expanded this study now considering Mn impurities in Co_2CrAl and Co_2CrSi and Cr impurities in Co_2MnAl and Co_2MnSi and present both the total and atom-resolved DOS's in Fig. 1. As was the case also in Refs. [23, 24] all compounds with defects present the half-metallic behavior and only in the case of $[Co_{0.9}Cr_{0.1}]_2MnSi$ alloy is the width of the gap slightly smaller with respect to the perfect Co_2MnSi alloy (not shown here). The total spin moments (see Table 1) are considerably smaller than the spin moments of the perfect compounds : 5 μ_B for Co_2MnSi, 4 μ_B for Co_2MnAl and Co_2CrSi, and 3 μ_B for Co_2CrAl. Thus these kind of defected alloys could be valuable for realistic applications. As for the compounds in the previous paragraph we have performed calculations for several concentrations but results are similar to the concentration which we present.

$[Mn_{1-x}V_x]_2VZ$ and $[Mn_{1-x}Cr_x]_2VZ$ (Z= Al, Si) alloys : In Ref. [25] we have shown that when we substitute Co or Fe for Mn in the ferrimagnetic hafl-metallic Mn_2VAl and Mn_2VSi alloys, the Co and Fe impurity atoms have spin moments parallel to the V atoms at the Y site and antiparallel to the Mn atoms. Thus the negative total spin moment of the alloys becomes smaller in magnitude and for specific concentration of defects we get a half-metallic antiferromagnet. We show now results when we use V and Cr as impurity atoms which have lower valence than Mn. As can be seen in Fig. 2, alloys with Cr impurities almost keep unaltered the gap in the spin-up band for both Al and Si-based compounds. Contrary to Cr atoms, the lighter vanadium shows a smaller exchange splitting and the Fermi level falls within a spin-up pick of the V DOS completely destroying the half-metallicity. We should also note that we present results only for a concentration of defects of x=0.1. We have performed calculations also for x=0.025,0.05 and 0.2 but the behavior of the compounds is similar to the case which we present.

Even more interesting is the behavior of the spin moments presented in Table 1. In the case of Co and Fe impurities, due to their positive spin moment, the total spin moment was approaching zero as we increased the concentration. Contrary to these chemical elements, V and Cr hybridize less with the neighboring Mn atoms which show a more atomic like behavior and thus increase the absolute value of their spin magnetic moment. V or Cr atoms have smaller spin moments than Mn atoms but they are in low concentration and as a result the total spin moment increases in magnitude from the -2 μ_B of the perfect Mn_2VAl and the -1 μ_B of the perfect Mn_2VSi (note that the total spin moments are negative since these alloys have less than 24 valence electrons according to the Slater-Pauling rule [6]). Thus such a doping with Cr and V would have no advantages over the perfect Mn_2VAl and Mn_2VSi compounds for realistic applications.

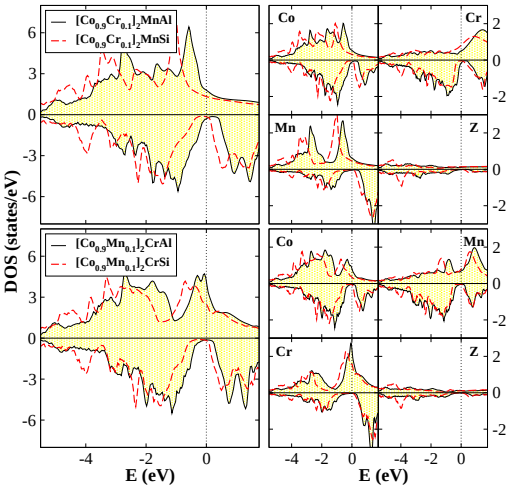

Fig. 1 (Color online) Total and atom-resolved DOS for Cr impurities in Co_2MnAl and Co_2MnSi alloys (upper panel) and Mn impurities in Co_2CrAl and Co_2CrSi compounds (lower panel).

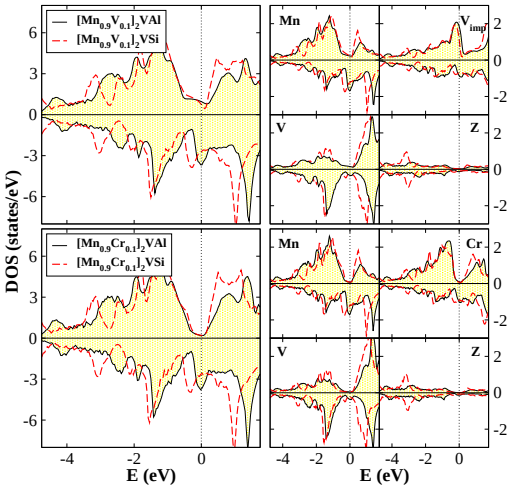

Fig. 2 (Color online) Total and atom-resolved DOS for V (upper panel) and Cr (lower panel) impurities in the case of Mn_2VAl and Mn_2VSi alloys. DOS's have been scaled to one atom.

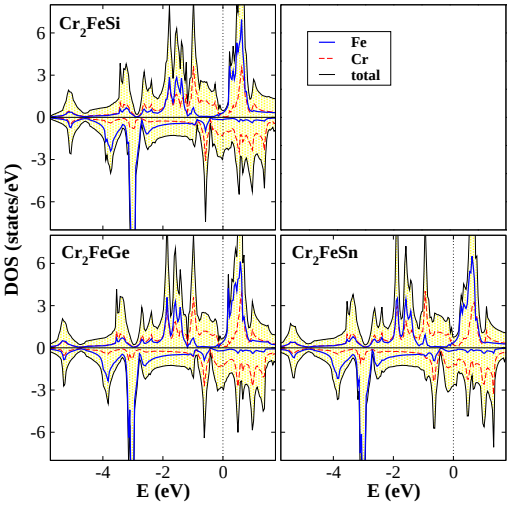

Fig. 3 Total, Cr- and Fe-resolved DOS for the Cr_2FeZ alloys where Z is Si, Ge or Sn and for a lattice constant of 6.2 Å.

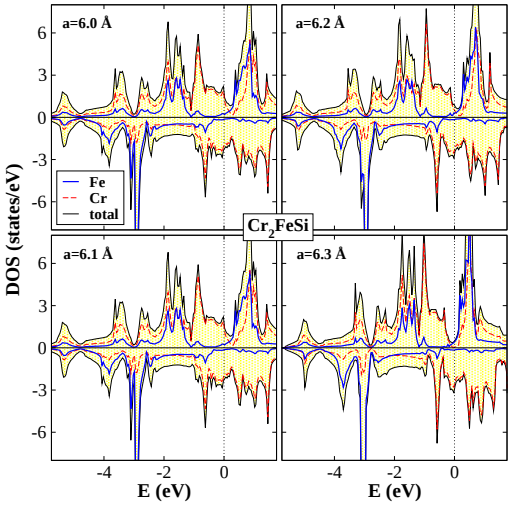

Fig. 4 (Color online) Total, Cr- and Fe-resolved DOS for the Cr_2FeSi alloy and for four different values of the lattice constant.

Cr_2FeZ (Z=Si,Ge,Sn) alloys : Motivated by our results on the Cr_2MnZ alloys [22], we decided to study also another family of 24-valence electrons compounds containing Fe instead of Mn: the Cr_2FeZ alloys where Z is Si, Ge or Sn. In Fig. 3 we present the total and the Cr and Fe-resolved density of states (DOS) for a lattice constant of 6.2 Å for all three alloys. For this lattice constant all the compounds under study present a region of low DOS in the spin-up band and the Fermi level falls within this region. Contrary to the compounds containing Mn, where the spin-up occupied states are mainly of Cr character and the occupied spin-down states are of mainly Mn character, for the Fe-based alloys both the spin-up and spin-down occupied states exhibit a more mixed character. The electronic structure is more complicated than the Mn-based alloys and as a result when we slightly vary the lattice constant the band-structure changes

in a way that the the region of low DOS is completely destroyed. This is illustrated in Fig. 4 where we present the DOS for Cr_2FeSi for four values of the lattice constant. Cr spin-up states below the Fermi level and the Cr spin-up states just above the Fermi level move one towards the other completely destroying the region of high spin-polarization upon compression. Lattice constants larger than 6.3 Å are unlikely to be achieved experimentally. The reason is the different hybridization between the transition-metal atoms when we substitute Fe for Mn. The smaller exchange splitting of the Fe atoms closes the gap and this leads also to a different distribution of the Cr charge which no more shows a large band-gap as for the Mn-based alloys. Finally we should also discuss the spin magnetic moments. Fe atoms for the lattice constant of 6.2 Å possess a moment slightly smaller than -3 μ_B and each Cr atom has a spin moment of around 1.5 μ_B resulting in the almost vanishing total spin moment requested by the Slater=Pauling behavior for the half-metals with 24 valence electrons [6]. Overall the Cr_2FeZ alloys with 24-valence electrons are not suitable for realistic application, contrary to the Cr_2MnZ compounds since half-metallicity is very fragile in their case (e.g. calculations suggest that the region of low spin-up DOS persists for Cr_2FeSi only between 6.2 and 6.3 Å).

Summary : We have presented first-principles calculations on several Heusler alloys. Cr(Mn) impurites occupying Co sites in $Co_2Mn(Cr)Al$ and $Co_2Mn(Cr)Si$ alloys couple antiferromagnetically to the other transition metal atoms resulting in ferrimagnetic compounds with lower total spin moments similarly to our previous studies on these alloys [23, 24]. V and Cr impurities occupying Mn sites in ferrimagnetic Mn_2VAl and Mn_2VSi alloys present spin moments parallel to the Mn atoms contrary to the behavior of the Fe and Co impurities in these alloys and they lead to larger absolute values of the total spin moments [25]. Finally, rhe 24-valence electron alloys Cr_2FeZ (Z= Si, Ge, Sn) show a region of low density of states instead of the real gap presented by the isovalent Cr_2MnZ (Z= P, As, Sb, Bi) [22] which persists only for a very narrow range of lattice constants.

References

[1] Half-metallic alloys: fundamentals and applications, Eds.: I. Galanakis and P. H. Dederichs, Lecture notes in Physics vol. 676 (Berlin Heidelberg: Springer 2005).
[2] I. Galanakis, Ph. Mavropoulos, and P. H. Dederichs, J. Phys. D: Appl. Phys. **39**, 765 (2006).
[3] I. Galanakis and Ph. Mavropoulos, J. Phys.: Condens. Matter in press [preprint: cond-mat/0610827].
[4] P. H. Dederichs, I. Galanakis, and Ph. Mavropoulos, J. Electron Microscopy **54**, i53 (2005).
[5] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 134428 (2002).
[6] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).
[7] I. Galanakis, J. Phys.: Condens. Matter **14**, 6329 (2002).
[8] I. Galanakis, J. Magn. Magn. Mater. **288**, 411 (2005).
[9] M. Ležaić, I. Galanakis, G. Bihlmayer, and S. Blügel, J. Phys.: Condens. Matter **17**, 3121 (2005).
[10] I. Galanakis, J. Phys.: Condens. Matter **16**, 8007 (2004).
[11] I. Galanakis, M. Ležaić, G. Bihlmayer, and S. Blügel, Phys. Rev. B **71**, 214431 (2005).
[12] I. Galanakis, J. Phys.: Condens. Matter **16**, 3089 (2004).
[13] K. Özdoğan, B. Aktaş, I. Galanakis, E. Şaşıoğlu, J. Appl. Phys. **101**, 073910 (2007).
[14] I. Galanakis, Phys. Rev. B **71**, 012413 (2005).
[15] Ph. Mavropoulos, I. Galanakis, V. Popescu, and P. H.Dederichs, J. Phys.: Condens. Matter **16**, S5759 (2004).
[16] I. Galanakis, K. Özdoğan, B. Aktaş, and E. Şaşıoğlu, Appl. Phys. Lett. **89**, 042502 (2006).
[17] K. Özdoğan, E. Şaşıoğlu, B. Aktaş, and I. Galanakis, Phys. Rev. B **74**, 172412 (2006).
[18] E. Şaşıoğlu, L. M. Sandratskii, P. Bruno, and I. Galanakis, Phys. Rev. B **72**, 184415 (2005).
[19] I. Galanakis, S. Ostanin, M. Alouani, H. Dreyssé, and J. M. Wills, Phys. Rev. B **61**, 599 (2000).
[20] K. Özdoğan, I. Galanakis, E. Şaşıoğlu, and B. Aktaş, J. Phys.: Condens. Matter **18**, 2905 (2006).
[21] E. Şaşıoğlu, L. M. Sandratskii, and P. Bruno, J. Phys.: Condens. Matter **17**, 995 (2005).
[22] I. Galanakis, K. Özdoğan, E. Şaşıoğlu, and B. Aktaş, Phys. Rev. B **75**, 172405 (2007).
[23] K. Özdoğan, I. Galanakis, E. Şaşıoğlu, and B. Aktaş, Phys. Stat. Sol. (RRL) **1**, 95 (2007).
[24] K. Özdoğan, I. Galanakis, E. Şaşıoğlu, and B. Aktaş, Sol. St. Commun. **142**, 492 (2007).
[25] I. Galanakis, K. Özdoğan, E. Şaşıoğlu, and B. Aktaş, Phys. Rev. B **75**, 092407 (2007).
[26] K. Koepernik and H. Eschrig, Phys. Rev. B **59**, 1743 (1999); K. Koepernik, B. Velicky, R. Hayn, and H. Eschrig, Phys. Rev. B **58**, 6944 (1998).