

Effect of doping and disorder on the half metallicity of full Heusler alloys

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Heusler alloys containing Co and Mn are amongst the most heavily studied half metallic ferromagnets for future applications in spintronics. Using state-of-the-art electronic structure calculations, we investigate the effect of doping and disorder on their electronic and magnetic properties. Small degrees of doping by substituting Fe or Cr for Mn scarcely affect the half metallicity. A similar effect is also achieved by mixing the sublattices occupied by the Mn and *sp* atoms. Thus the half metallicity is a robust property of these alloys. © 2006 American Institute of Physics. [DOI: 10.1063/1.2235913]

The intensive development of electronics based on the combination of magnetic and semiconducting materials has brought in the center of scientific research new exotic materials. Half metallic ferromagnets, which were initially predicted by de Groot *et al.* in 1983,¹ have the peculiarity that the band structure of the minority-spin electrons is semiconducting while that of the majority-spin electrons is a normal metallic one. Such materials could maximize the efficiency of spintronic devices.² Several Heusler compounds such as NiMnSb and Co₂MnSi have been predicted to be half metals.³

Ishida *et al.* studied by means of *ab initio* calculations the full-Heusler compounds of the type Co₂MnZ, where Z stands for Si and Ge, and have shown that they are half metals.⁴ Later the origin of half metallicity in these compounds has been largely explained.³ Many experimental groups during the last years have worked on these compounds and have tried to synthesize them mainly in the form of thin films and incorporate them in spintronic devices. Westerholt and co-workers have extensively studied the properties of Co₂MnGe films and they have incorporated this alloy in the case of spin valves and multilayer structures.⁵ Reiss and co-workers managed to create magnetic tunnel junctions based on Co₂MnSi.⁶ A similar study of Sakuraba *et al.* resulted in the fabrication of magnetic tunnel junctions using Co₂MnSi as one magnetic electrode and Al–O as the barrier (Co₇₅Fe₂₅ is the other magnetic electrode) and their results are consistent with the presence of half metallicity for Co₂MnSi.⁷ Dong *et al.* recently managed to inject spin-polarized current from Co₂MnGe into a semiconducting structure.⁸ Finally, Kallmayer *et al.* studied the effect of substituting Fe for Mn in Co₂MnSi films and have shown that the experimental extracted magnetic spin moments are compatible with the half metallicity for small degrees of doping.⁹

It is obvious from the experimental results that the full-Heusler compounds containing Co and Mn are of particular

interest for spintronics. Not only they combine high Curie temperatures and coherent growth on top of semiconductors (they consist of four fcc sublattices with each one occupied by a single chemical element) but also in real experimental situations they can preserve a high degree of spin polarization at the Fermi level. In order to accurately control their properties it is imperative to investigate the effect of defects, doping, and disorder on their properties. Recently Picozzi *et al.* published a study on the effect of defects in Co₂MnSi and Co₂MnGe.¹⁰ Our work aims to further study the effect of doping and disorder on the electronic and magnetic properties of such compounds. Doping is simulated by substituting Fe or Cr for Mn while disorder occurs between the Mn and the *sp* atom. The electronic structure calculations are performed using the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO).¹¹ Details of similar type of calculations have been published elsewhere.¹² We assumed a ferromagnetic alignment for all studied compounds since the behavior of the experimental total spin moment of the perfect alloys is compatible with the Slater-Pauling behavior (see later discussion on the text and Ref. 9). Finally, we should note that we used the experimental lattice constants for all three compounds.

The first part of our investigation concerns the doping of Co₂MnSi, Co₂MnGe, and Co₂MnSn. To simulate the doping by electrons we substitute Fe for Mn, while to simulate the doping of the alloys with holes we substitute Cr for Mn. We study the cases of moderate doping substituting 5%, 10%, and 20% of the Mn atoms. The use of coherent potential approximation in our calculations ensures that the doping is performed in a random way. In Table I we have gathered the total spin moments for all cases under study and in Fig. 1 the total density of states (DOS) for the Co₂Mn_{1-x}Fe_xSi and Co₂Mn_{1-x}Cr_xSi compounds blowing up in the onsets of the region around the Fermi level where the gap exists.

We will start our discussion from the DOS presented in Fig. 1. As discussed in Ref. 3 the gap is created between states located exclusively at the Co sites. The states low in energy (around -6 eV) originate from the low-lying *p* states of the *sp* atoms (there is also an *s*-type state very low in

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TABLE I. Total spin magnetic moment in the unit cell for the case of Fe and Cr doping of the Mn site in μ_B .

Concentration (x)	0.00	0.05	0.10	0.20
$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Si}$	5.00	4.95	4.90	4.80
$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Ge}$	5.00	4.95	4.90	4.80
$\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Sn}$	5.02	4.98	4.92	4.82
$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$	5.00	5.05	5.09	5.14
$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Ge}$	5.00	5.05	5.10	5.19
$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Sn}$	5.02	5.06	5.11	5.20

energy which is not shown in the figure). The majority-spin occupied states form a common Mn–Co band while the occupied minority states are mainly located at the Co sites and the minority unoccupied states at the Mn sites. Doping the perfect ordered alloy with either Fe or Cr smoothens the valleys and peaks along the energy axis. This is a clear sign of the chemical disorder; Fe and Cr induce peaks at slightly different places than the Mn atoms resulting to this smoothing and as the doping increases this phenomenon becomes more intense. The important detail is what happens around the Fermi level and in what extent is the gap in the minority band affected by the doping. So now we will concentrate only at the enlarged regions around the Fermi level. The blue dashed lines represent the Cr doping, while the red dash-dotted lines are the Fe-doped alloys. Cr doping has only marginal effects to the gap. Its width is narrower with respect to the perfect compounds but overall the compounds retain their half metallicity. In the case of Fe doping the situation is more complex. Adding electrons to the system means that, in order to retain the perfect Half metallicity, these electrons should occupy high-energy lying antibonding majority states. This is energetically not very favorable and for these moderate degrees of doping a new shoulder appears in the unoccupied states which is close to the right edge of the gap, a sign of a large change in the competition between the exchange splitting of the Mn majority and minority states and of the Coulomb repulsion. In the case of the 20% Fe doping this new peak crosses the Fermi level and the Fermi level is no more exactly in the gap but slightly above it. Further substi-

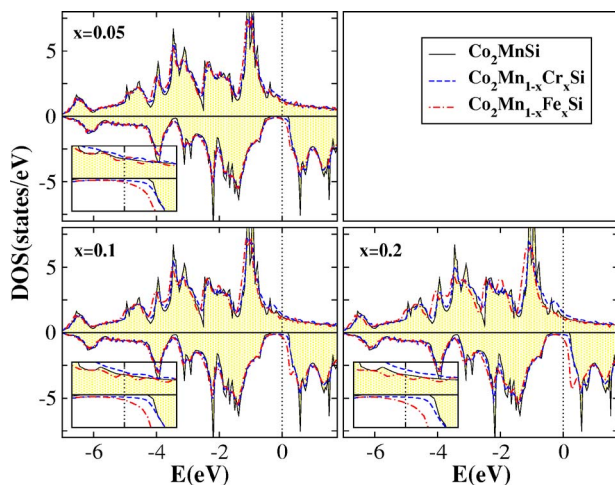


FIG. 1. (Color online) Spin-resolved total density of states (DOS) for the case of $\text{Co}_2\text{Mn}_{1-x}\text{Cr}_x\text{Si}$ and $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ for three different values of the doping concentration x . DOS's are compared to the one of the undoped Co_2MnSi alloy. In the onsets we have blown up the region around the Fermi level (which we have set as the zero of the energy axis). Note that positive values of DOS refer to the majority-spin electrons and negative values to the minority-spin electrons.

tion should lead to the complete destruction of the Half metallicity as in the quaternary Heusler alloys with a Mn–Fe disordered site.¹³ In the case of the corresponding Ge and Sn compounds the DOS is similar to the one of the Si-based compound and the gap has approximately the same width. The Fermi level is deeper in the gap for these compounds, at the middle of the gap for the Ge alloy and at the left edge for the Sn one. Doping the perfect compound now preserves completely the Half metallicity as reflected also on the total spin moments discussed in the next paragraph.

In Table I we have gathered the spin magnetic moments for all cases under study. The total spin moment M_t of the perfect compounds follows the Slater-Pauling behavior being the number of the valence electrons in the unit cell minus 24.³ In the case of the chemically disordered compounds, doping by 5%, 10%, or 20% of Cr (or Fe) atoms means that the mean value of the total number of valence electrons in the unit cell is decreased (or increased, respectively) by 0.05, 0.10, and 0.20 electrons, respectively. For most of the studied compounds the total spin moments follow this behavior reflecting the preservation of the Half metallicity, but in the case of $\text{Co}_2\text{Mn}_{0.8}\text{Fe}_{0.2}\text{Si}$ compound the total moment is $5.14\mu_B$ instead of the ideal value of $5.20\mu_B$. The atom-resolved moments present no peculiarity and are little sensitive to the doping. Our findings agree with the conclusions drawn by Kallmayer *et al.* for the Fe-doped Co_2MnSi films.⁹

In the second part of our study we study the effect of disorder between the Mn and the *sp* atoms. In Fig. 2 we present the atom-resolved DOS for both excess of the *sp* atom on the left column and excess of the Mn atoms on the right column. In Table II we have gathered the total and atomic spin moments for all cases. Firstly, note that the gap is much wider for the Mn and *sp* atoms than for the Co atoms since the states around the gap are of Co character

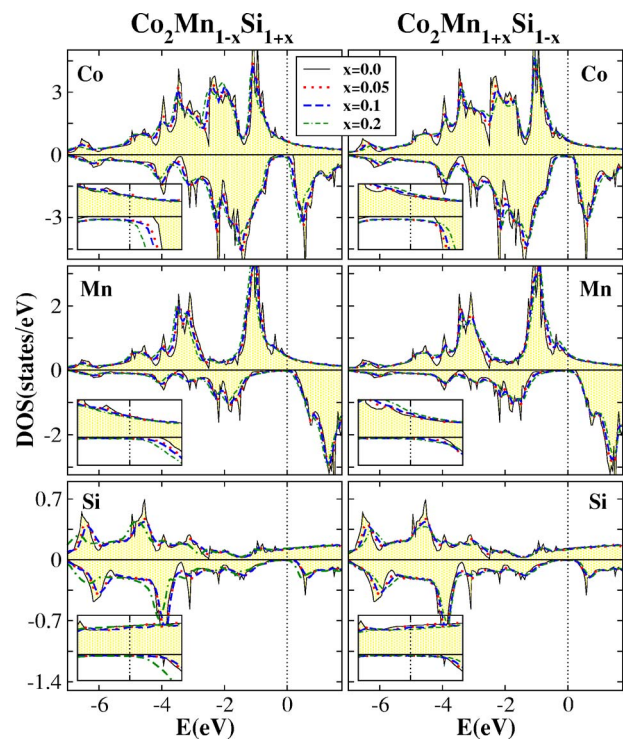


FIG. 2. (Color online) Atom-resolved DOS for the cases of Si (left panel) and Mn (right panel) excess in Co_2MnSi alloy with respect to the perfect one ($x=0$). In the onsets we have blown up the region around the Fermi level.

TABLE II. Similar to Table I for the case of Mn-*sp* atom disorder in μ_B . Note that Mn, Si, Ge, and Sn spin moments are scaled to one atom. Note that for cobalt we give the sum of the moments of both Co atoms.

x	$\text{Co}_2\text{Mn}_{1+x}\text{Si}_{1-x}$				$\text{Co}_2\text{Mn}_{1+x}\text{Ge}_{1-x}$				$\text{Co}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$			
	Total	Co	Mn	Si	Total	Co	Mn	Ge	Total	Co	Mn	Sn
-0.20	4.40	1.92	3.19	-0.06	4.40	1.83	3.29	-0.05	4.41	1.78	3.41	-0.08
-0.10	4.70	1.95	3.15	-0.08	4.70	1.84	3.25	-0.06	4.73	1.75	3.41	-0.08
-0.05	4.85	1.96	3.14	-0.08	4.85	1.85	3.23	-0.06	4.88	1.76	3.37	-0.08
0.00	5.00	1.96	3.13	-0.09	5.00	1.87	3.20	-0.06	5.02	1.78	3.32	-0.08
0.05	5.15	1.99	3.10	-0.10	5.15	1.88	3.19	-0.07	5.17	1.80	3.28	-0.08
0.10	5.30	2.00	3.09	-0.10	5.30	1.90	3.16	-0.08	5.32	1.81	3.26	-0.09
0.20	5.60	2.03	3.05	-0.11	5.60	1.95	3.11	-0.10	5.62	1.82	3.24	-0.10

only. Mixing Mn and *sp* atoms changes the symmetry of the Co sites and in this way can induce new states in the gap and affect the Half metallicity. As shown in Fig. 2, substituting Si for Mn induces states just at the right edge of the gap while substituting Mn for Si pushes the unoccupied minority states even higher in energy and the gap becomes wider. Overall the DOS is smoothened by the disorder between the Mn and Si atoms but the main peaks do not change energy position.

In Table II we have gathered the total spin moments for all cases under study. Substituting 5%, 10%, or 20% of the Mn atoms by the Si, Ge, or Sn ones (which are all isoelectronic, e.g., same number of valence electrons) corresponding to the negative values of x in the table, results in a decrease of 0.15, 0.30, and 0.60 of the total number of valence electrons in the cell, while the inverse procedure results to a similar increase of the mean value of the number of valence electrons. The compounds containing Si and Ge show perfect Slater-Pauling behavior while the $\text{Co}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ deviate from the ideal values of the total spin moment although in this case the Fermi level is nearer the center of the gap. Sn is a much heavier element than both Si and Ge and its mixing with Mn alters considerably the Coulomb repulsions in the system having a more profound effect on the Half metallicity of the corresponding alloy. Thus disorder is more important for the heavy *sp* elements.

It is interesting also to look at the Mn spin moments. In the case of doping presented in the first part of our study doping scarcely changed the Mn spin moments. Mn atoms remained at the same sublattice with no immediate change to their close environment. In the case of disorder excess of Mn means that Mn atoms occupy also sites in the sublattice of the *sp* atoms while excess of the *sp* atoms means that *sp* atoms are found also in the sublattice occupied by Mn having a much larger effect on the Mn magnetic properties than in the case of doping where Cr and Fe atoms were found in the Mn-occupied sublattice. As a result the Mn spin moment can change by as much as $\sim 0.2\mu_B$ between the disordered and the perfect compound. The change in the total spin moment arises almost exclusively from the change in the Mn concentration.

We have studied the effect of doping and disorder on the magnetic properties of the Co_2MnSi , Co_2MnGe , and Co_2MnSn full-Heusler alloys. Doping simulated by the substitution of Cr and Fe for Mn overall keeps the Half metallicity. Its effect depends clearly on the position of the Fermi level, having the largest one in the case of Co_2MnSi where the Fermi level is near the edge of the minority-spin gap. On the other hand disorder between the Mn and the *sp* atom is more important for the heavy *sp* atoms such as Sn. Both disorder and doping have little effect on the Half metallic properties of the compounds which we study and they keep a high degree of spin polarization. It seems that half metallicity in Co_2MnGe is more stable with respect to the other two compounds.

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