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.

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\textbf{TABLE I: Total and atom-resolved spin magnetic moments for the case of Fe and Cr doping of the Mn site in $\mu_B$. The total moment in the cell is the sum of the atomic ones multiplied by the concentration of this chemical element.}

| $x$ | Total Co Mn Cr Fe sp | Total Co Mn Fe sp |
|-----|-----------------------|------------------|
| 0.00 | Co$_{2}$Mn$_{1-x}$Cr$_{x}$Si | Co$_{2}$Mn$_{1-x}$Fe$_{x}$Si |
| 0.05 | 4.95 1.97 3.12 2.06 -0.09 | 5.05 2.02 3.13 2.87 -0.09 |
| 0.10 | 4.90 1.97 3.12 2.07 -0.09 | 5.04 2.06 3.17 2.85 -0.08 |
| 0.20 | 4.80 1.97 3.12 2.09 -0.08 | 5.14 2.13 3.16 2.82 -0.08 |
| $x$ | Co$_{2}$Mn$_{1-x}$Cr$_{x}$Ge | Co$_{2}$Mn$_{1-x}$Fe$_{x}$Ge |
| 0.00 | 5.00 1.87 3.20 -0.06 | 5.00 1.87 3.20 -0.06 |
| 0.05 | 4.95 1.86 3.21 2.05 -0.06 | 5.05 1.91 3.22 2.88 -0.06 |
| 0.10 | 4.90 1.86 3.22 2.07 -0.06 | 5.10 1.96 3.23 2.88 -0.06 |
| 0.20 | 4.80 1.86 3.22 2.10 -0.06 | 5.19 2.06 3.26 2.89 -0.05 |
| $x$ | Co$_{2}$Mn$_{1-x}$Cr$_{x}$Sn | Co$_{2}$Mn$_{1-x}$Fe$_{x}$Sn |
| 0.00 | 5.02 1.78 3.32 -0.08 | 5.02 1.78 3.32 -0.08 |
| 0.05 | 4.98 1.77 3.34 2.24 -0.08 | 5.06 1.82 3.35 2.89 -0.08 |
| 0.10 | 4.92 1.77 3.34 2.24 -0.08 | 5.11 1.87 3.36 2.90 -0.07 |
| 0.20 | 4.82 1.76 3.35 2.27 -0.08 | 5.20 1.98 3.38 2.91 -0.07 |

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 first predicted by de Groot and collaborators in 1983,\textsuperscript{1} have the peculiarity that the band-structure of the minority-spin electrons is semiconducting while of the majority-spin electrons is a normal metallic one. Such materials could maximize the efficiency of spintronic devices.\textsuperscript{2} Several Heusler compounds like NiMnSb and Co$_{2}$MnSi have been predicted to be half-metals.\textsuperscript{3}

Ishida and collaborators were, to the best of our knowledge, the first to study by means of ab-initio calculations the full-Heusler compounds of the type Co$_{2}$MnZ, where Z stands for Si and Ge, and have shown that they are half-metals.\textsuperscript{4} Later the origin of half-metallicity in these compounds has been largely explained.\textsuperscript{5} 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. The group of Westerholt has extensively studied the properties of Co$_{2}$MnGe films and they have incorporated this alloy in the case of spin-valves and multilayer structures.\textsuperscript{6} The group of Reiss managed to create magnetic tunnel junctions based on Co$_{2}$MnSi.\textsuperscript{7} A similar study of Sakuraba and collaborators resulted in the fabrication of magnetic tunnel junctions using Co$_{2}$MnSi as one magnetic electrode and AlO as the barrier (Co$_{25}$Fe$_{25}$ is the other magnetic electrode) and their results are consistent with the presence of half-metallicity for Co$_{2}$MnSi.\textsuperscript{8} Dong and collaborators recently managed to inject spin-polarized current from Co$_{2}$MnGe into a semiconducting structure.\textsuperscript{9} Finally Kallmayer \textit{et al.} studied the effect of substituting Fe for Mn in Co$_{2}$MnSi films and have shown that the experimental extracted magnetic spin moments are compatible with the half-metallicity for small degrees of doping.\textsuperscript{10}

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 sublattice with each one occupied by a single chemical element) but 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 \textit{et al.} published a study on the effect of defects in Co$_{2}$MnSi and Co$_{2}$MnGe.\textsuperscript{11} 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).\textsuperscript{12} Details of similar type of calculations have been published elsewhere.\textsuperscript{13}

The first part of our investigation concerns the doping of Co$_{2}$MnSi, Co$_{2}$MnGe and Co$_{2}$MnSn. 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 and atom-resolved spin moments for all cases under study and in Fig. 1 the total density of states (DOS) for the Co$_2$Mn$_{1-x}$Fe$_x$Si and Co$_2$Mn$_{1-x}$Cr$_x$Si compounds blowing up in the onsets 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 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 minority unoccupied at the Mn sites. Doping the perfect ordered alloy with either Fe or Cr first smoothens the valleys and picks along the energy axis. This is a clear sign of the chemical disorder; Fe and Cr induce picks at slightly different places than the Mn atoms resulting to this smoothening 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 substitution should lead to the complete destruction of the half-metallicity as in the Quaternary Heusler alloys with a Mn-Fe disordered site.

In Table I we have gathered the spin magnetic moments for all cases under study. The total spin moment $M_z$ of the perfect compounds follows the Slater Pauling behavior being the number of the valence electrons in the unit cell minus 24. 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.
TABLE II: Total and atom-resolved spin magnetic moments for the case of Mn-sp atom disorder in $\mu_B$. The total moment in the cell is the sum of the atomic ones multiplied by the concentration of this chemical element.

| $x$ | 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 -0.09 | 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 | 4.87 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 |

respectively. In most of the cases the total spin moments follow this behavior a clear sign of 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 $\mu_B$. In the case of the corresponding Ge and Sn compounds the Fermi level is more deep in the gap and for the Sn compound it does not cross any more the minority states. 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 $\text{Co}_2\text{MnSi}$ films.

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 atomic spin moments for all cases. Firstly note that the right column. In Table II we have gathered the total and atom-resolved DOS for both excess of the $sp$ atom changes in the table, no peculiarity and are little sensitive to the doping. 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.

We have studied the effect of doping and disorder on the magnetic properties of the $\text{Co}_2\text{MnSi}$, $\text{Co}_2\text{MnGe}$, $\text{Co}_2\text{MnSn}$ 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 $\text{Co}_2\text{MnSi}$ 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 like 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 $\text{Co}_2\text{MnGe}$ should be the most robust compound with respect to its half-metallic character for experimentalists and realistic applications.

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