Appearance of Half-Metallicity in the Quaternary Heusler Alloys

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I report systematic first-principle calculations of the quaternary Heusler alloys like Co$_2$[Cr$_{1-x}$Mn$_x$]Al, Co$_2$Mn[Al$_{1-x}$Sn$_x$] and [Fe$_{1-x}$Co$_x$]MnAl. I show that when the two limiting cases (x=0 or 1) correspond to a half-metallic compound, so do the intermediate cases. Moreover the total spin moment $M_t$ in $\mu_B$ scales linearly with the total number of valence electrons $Z_t$ (and thus with the concentration $x$) following the relation $M_t = Z_t - 24$, independently of the origin of the extra valence electrons, confirming the Slater-Pauling behavior of the normal Heusler alloys. Finally I discuss in all cases the trends in the atomic projected DOSs and in the atomic spin moments.

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I. INTRODUCTION

Heusler alloys consist a large family of intermetallic compounds which attract regularly considerable attention due to the variety of magnetic phenomena which they present. Lately the interest has focused on the ones being half-metals (HM) like NiMnSb or Co$_2$Mn[Sn]. These compounds are ferromagnets for which the minority spin-band presents a gap and the Fermi level falls within this gap. Thus the spin polarization at the Fermi level is 100% and these materials are of special interest for spintronic applications the spin of the electron and not the charge is used as the property to control the device. Contrary to other HM systems like the diluted magnetic semiconductors or the manganites and some oxides, the half- and full-Heusler alloys (e.g. NiMnSb and Co$_2$MnSn, respectively) and the zinc-blende compounds like Cr$_2$Mn present very high Curie temperatures making them attractive for industrial applications.

Lately I have devoted a lot of work on the latter compounds trying to address three main points i) the origin of the half-metallicity ii) whether the half-metallicity is preserved at the surfaces or films and iii) to predict new half-metallic materials which may present better growth on top of semiconductors. Using first principle calculations it was shown in the case of the ordered half-Heusler alloys like NiMnSb that the gap is formed between the occupied bonding $d$ states resulting from the interaction between the higher- and the lower-valent transition metal atoms and the corresponding antibonding states. For the full-Heusler alloys like Co$_2$MnSn the situation is more complicated since there are also states located only at the Co sites and the resulting gap is tiny. The total spin moment for the latter compounds is given by the relation $M_t = Z_t - 24$, where $M_t$ is the total spin moment in $\mu_B$ and $Z_t$ the total number of valence electrons. I will discuss this behavior in detail in a later paragraph.

In the present contribution I will conclude this study by examining the behavior of the so-called quaternary Heusler alloys. In the latter compounds, one of the four sites is occupied by two different kinds of neighboring elements like Co$_2$[Cr$_{1-x}$Mn$_x$]Al where the Y site is occupied by Cr or Mn atoms (see Fig. 1 in Ref. for the definition of the structure). To perform this study I used the Korringa-Kohn-Rostoker (KKR) method developed by Professor Akai, which has been already used with success to study the magnetic semiconductors. The atomic disorder at a specific site is implemented using the coherent potential approximation (CPA). The space is divided in non-overlapping muffin-tin spheres and the vanishing charge in the interstitial region is considered to be constant and charge neutrality is imposed. Such an approximation is reasonable to describe a close-packed structure like the one of the Heusler alloys. To check the validity of this description I compared the total spin moment with the full-potential calculations performed in Ref. For all the compounds with the exception of Co$_2$VAl both methods produced similar magnetic properties for the experimental lattice constants. V 3$d$ wavefunctions have a large extent and the muffin-tin approximation is not adequate to describe the V magnetism; thus I had to use a lattice constant 4% larger than the experimental one to get a half-metallic compound, as predicted by the full-potential KKR for the experimental lattice constant. I assumed that the lattice constant varies linearly with the concentration $x$ which has been verified for several ternary alloys. Finally I should mention that the total spin moment is not exactly an integer due to numerical inaccuracies. To decide whether an alloy is half-metallic or not I used the total DOS as a criterion, as was also the case in the previous studies. I will firstly focus my study on the behavior of the total spin moment for several cases and show that it follows the Slater-Pauling behavior when the limiting cases are half-metals. Afterwards I will study the case where the Y site (see Fig. 1 in Ref. is occupied by two different elements like Co$_2$[Cr$_{1-x}$Mn$_x$]Al, followed by the case when there are two different types of $sp$ atoms like Co$_2$Mn[Al$_{1-x}$Sn$_x$]. Final case is when the X sites are disordered like [Fe$_{1-x}$Co$_x$]MnAl. At the end I summarize and conclude.

As it was shown in Ref. the total spin moment in the case of the half-metallic full-Heusler alloys obeys the rule $M_t = Z_t - 24$, where $M_t$ is the total spin moment in $\mu_B$ and $Z_t$ the total number of valence electrons. The 24 arises from the fact that there are in total 12 occu-
I resume my results in Fig. 1. The first possible and assuming in all case a concentration increment of count several possible combinations of chemical elements moment for several quaternary alloys taking into ac-

From the binary alloys. In the latter compounds the tion metal d electrons. There are also five occupied bonding d bands created from the interaction between the Mn and the Co atoms. The Fermi level falls within the gap created by the occupied triple degenerated d states and the unoccupied double degenerated d states which are exclusively located at the Co sites and are permitted by the symmetry of the crystal. The moments behavior is the well-known Slater-Pauling behavior known from the binary alloys. In the latter compounds the spin moment decreases with \( Z_t \) since the spin-up states are completely occupied and the extra electrons occupy spin-down states reducing the total spin moment. In the case of the full Heusler alloys the Fermi level is fixed within the minority band gap and the extra electrons as we change the chemical elements occupy exclusively spin-up states and the total spin moment increases. Using the KKR-CPA method we calculated the total spin moment for several quaternary alloys taking into account several possible combinations of chemical elements and assuming in all case a concentration increment of 0.1. I resume my results in Fig. 1. The first possible case is when I have two different low-valent transition metal atoms at the Y site like \( \text{Co}_2[\text{Cr}_{1-x}\text{Mn}_x]\text{Al} \). The total spin moment varies linearly between the 3 \( \mu_B \) of \( \text{Co}_2\text{CrAl} \) and the 4 \( \mu_B \) of \( \text{Co}_2\text{MnAl} \). In the case of the \( \text{Co}_2[\text{Cr}_{1-x}\text{Fe}_x]\text{Al} \) and \( \text{Co}_2[\text{Mn}_{1-x}\text{Fe}_x]\text{Al} \) compounds and up to around \( x=0.6 \) the total spin moment shows the SP behavior but for larger concentrations it slightly deviates to account for the not integer value of \( \text{Co}_2\text{FeAl} \). This behavior on the figure is clearly seen when we compare the lines for the \( \text{Co}_2[\text{Mn}_{1-x}\text{Fe}_x]\text{Al} \) and \( \text{Co}_2\text{MnAl}_{1-x}\text{Sn}_x \) compounds; the latter family following the SP behavior. The second case is when I mix the sp elements, but as I just mentioned these compounds also obey the rule for the total spin moments. The third and final case is to mix the higher valent transition metal atoms like in \( \text{Fe}_{1-x}\text{Co}_x\text{Al} \) and \( \text{Rh}_{1-x}\text{Co}_x\text{MnAl} \) alloys. In the first case the total spin moment varies linearly between the 2 and 4 \( \mu_B \) of \( \text{Fe}_2\text{MnAl} \) and \( \text{Co}_2\text{MnAl} \) compounds, respectively. Rh is isoelectronic to Co and for the second family of compounds we find a constant integer value of 4 \( \mu_B \) for all the concentrations. A special case is \( \text{Mn}_2\text{VAI} \) which has less than 24 electrons and the total spin moment is -2 \( \mu_B \). If now I mix Mn and Co I get a family of compounds where the total spin moment varies linearly between the -2 \( \mu_B \) and the 2 \( \mu_B \) and for \( x=0.5 \) I get the case of a paramagnetic compound consisting of magnetic elements. Thus all the compounds obey the rule \( M_t=Z_t-24 \), showing the Slater-Pauling behavior regardless of the origin of the extra charge. In the next paragraphs I will analyze in detail every case.

The first large family of quaternary alloys which are susceptible to be HMs are the ones where there are two kinds, \( Y \) and \( Y^* \), of low-valent transition metal atoms: \( X_2(Y_{1-x}Y^*_x)Z \), where \( X \) stands for the high-valent transition metal atom and \( Z \) for the sp atom. I will concentrate my analysis on \( \text{Co}_2[\text{Cr}_{1-x}\text{Mn}_x]\text{Al} \). Already in Ref. 4 it was shown that both \( \text{Co}_2\text{CrAl} \) and \( \text{Co}_2\text{MnAl} \) are HMs with a total spin moment of 3 \( \mu_B \) and 4 \( \mu_B \), respectively.

### TABLE I: Atom-projected spin moments for \( \text{Co}_2[\text{Cr}_{1-x}\text{Mn}_x]\text{Al} \) with \( x=0,0.1,0.2, \ldots, 0.9,1 \).
The spin moments have been scaled to one atom. The total moment is given by the relation \( M_{\text{total}} = 2 \times m_{\text{Co}} + (1-x)m_{\text{Cr}} + x_m \text{Mn} + m_{\text{Al}} + m_{\text{int}} \), where \( \text{int} \) stands for the interstitial region.

| \( \text{Co}_2[\text{Cr}_{1-x}\text{Mn}_x]\text{Al} \) | \( m_{\text{Co}} \) | \( m_{\text{Cr}} \) | \( m_{\text{Mn}} \) | \( m_{\text{Al}} \) | \( m_{\text{Total}} \) |
|------------------|-------------|-------------|-------------|-------------|------------------|
| \( \text{Co}_2\text{CrAl} \)   | 0.698       | 1.686       | -0.060      | 3.007       |
| \( \text{Co}_2[\text{Cr}_{0.3}\text{Mn}_0.7]\text{Al} \) | 0.709       | 1.615       | 3.116       | -0.060      | 3.106            |
| \( \text{Co}_2[\text{Cr}_{0.5}\text{Mn}_0.5]\text{Al} \) | 0.718       | 1.547       | 3.068       | -0.061      | 3.206            |
| \( \text{Co}_2[\text{Cr}_{0.7}\text{Mn}_0.3]\text{Al} \) | 0.722       | 1.483       | 3.020       | -0.061      | 3.305            |
| \( \text{Co}_2[\text{Cr}_{0.8}\text{Mn}_0.2]\text{Al} \) | 0.726       | 1.416       | 2.971       | -0.061      | 3.405            |
| \( \text{Co}_2[\text{Cr}_{0.9}\text{Mn}_0.1]\text{Al} \) | 0.732       | 1.342       | 2.920       | -0.062      | 3.505            |
| \( \text{Co}_2[\text{Cr}_{1}\text{Mn}_0]\text{Al} \) | 0.729       | 1.317       | 2.864       | -0.063      | 3.605            |
| \( \text{Co}_2\text{MnAl} \) | 0.738       | 1.220       | 2.806       | -0.063      | 3.706            |
| \( \text{Co}_2[\text{Cr}_{2}\text{Mn}_0.8]\text{Al} \) | 0.746       | 1.093       | 2.744       | -0.064      | 3.806            |
| \( \text{Co}_2[\text{Cr}_{2.1}\text{Mn}_0.6]\text{Al} \) | 0.752       | 0.834       | 2.682       | -0.064      | 3.907            |
| \( \text{Co}_2\text{MnAl} \) | 0.755       | -2.603      | -0.064      | 4.020       |

FIG. 1: Calculated total spin moment \( M_t \) in \( \mu_B \) for a variety of compounds as a function of the concentration \( x \) \((x=0,0.1,0.2, \ldots, 0.9,1)\). I assumed that the lattice constant varies linearly with the concentration \( x \). With filled geometrical objects the cases obeying the rule \( M_t=Z_t-24 \) where \( Z_t \) is the total number of valence electrons; this is the so-called Slater-Pauling behavior.
In Fig. 2 I present the atom-projected DOS and in Table I the spin moments scaled to one atom for several concentrations. For all concentrations, one gets a HM system since the Fermi level falls within the minority gap. The width of the gap is the same for all compounds since the gap is formed between states located exclusively at the Co sites and which are little affected by the lower-valent transition metal atoms like Mn and Cr. This is clearly seen in Fig. 2 where the gap in the case of the Cr and Mn atoms is much larger than for the Co atoms. The total spin moment scales linearly between the two extremes reflecting the half-metallicity. For low Mn concentrations, the Mn atom acts like an impurity and the $t_{2g}$ electrons are well separated. This is clearly seen in the Mn DOS, where for small Mn concentration there is a double peak in the majority band just below the Fermi level. The lower peak is the $e_g$ electrons and the higher peak the $t_{2g}$ electrons of Mn. When the Mn concentration increases these states overlap and they can not be any more distinguished and Mn shows a more itinerant-like magnetism. The states lower in energy around -3 eV are $t_{2g}$-like states which couple to the $p$ states of Al and fill the bands created by the latter ones. In the case of Cr the behavior is the inverse. It is for the case of high Cr concentrations, where the $e_g$ and $t_{2g}$ are distinguished. For low Cr concentrations the population of the occupied minority states is larger and they are lower in energy than for high concentrations attracting also the unoccupied states lower in energy and resulting to a smaller spin moment. The differences in the Co DOS mainly arise from the different position of the Cr and Mn majority bands through the Coulomb interaction and the Co spin moment only slightly changes with the concentration. Finally in the case of Co$_2$[Cr$_{1-x}$Fe$_x$]Al and Co$_2$[Mn$_{1-x}$Fe$_x$]Al compounds the situation is similar but the Co moments show more important changes since Fe can not account only by itself for the extra electron and the Co moment has also to reach a higher value. This was discussed in detail in Ref. 4.

Now I will go on with the case of the X$_2$Y[Z$_{1-x}$Z$_x^*$] compounds, where I change the charge at the Z site. I studied both the Co$_2$Mn[Al$_{1-x}$Si$_x$] and Co$_2$Mn[Al$_{1-x}$Sn$_x$]. Si and Sn are isoelectronic and both families present the same behavior, thus I will restrict my presentation to the second family. The moment changes from 4 up to 5 $\mu_B$ linearly and thus all the intermediate cases are HMs. In Table II I have gathered the atom-resolved spin-moments. The $sp$ atoms show a practically constant moment and the extra charge is taken into account by the transition metal atoms. If I look carefully at the Mn majority spin band (not presented here), there are unoccupied states at the vicinity of the Fermi level which pass under the Fermi level and become occupied as the concentration of Sn increases. Thus the Mn spin moment increases practically linearly from 2.6 to 3.2 $\mu_B$. The higher polarization of the Mn $d$ states polarizes also the Co bands since they form a common majority band and the Co moment increases by 0.2 $\mu_B$.

The last case I will discuss is when I mix the high-valent transition metal atoms. The first family is the [Fe$_{1-x}$Co$_x$]$_2$MnAl, where the total spin moment increases from 2 to 4 $\mu_B$ with the concentration. The Al moment stays small and is negligible while the Mn moment is 2.6 $\mu_B$ for all concentrations. The Fe moment varies form -0.32 to -0.26 $\mu_B$ and the Co one from 0.63 to 0.75 $\mu_B$. Thus the atomic spin moments change little and the increase in the total spin moment arises exclusively from the substitution of Fe by Co. It is also interesting to compare [Fe$_{0.5}$Co$_{0.5}$]$_2$MnAl with FeCoMnAl. In the latter compound one of the sublattices is occupied exclusively by Fe atoms and the other by Co ones. Both systems are HMs as can be seen in Fig. 3 and the total spin moment is 3 $\mu_B$. Both compounds show similar atomic spin moments, thus the exact position of the Fe and Co atoms is not so relevant for the magnetic properties, which are

![FIG. 2: Atom-projected DOS of Co$_2$[Cr$_{1-x}$Mn$_x$]Al for three different values of $x$: 0.1,0.5,0.9. The DOS’s have been scaled to one atom.](image_url)
controlled mainly by the concentration of the chemical elements. If I compare the DOSs presented in Fig. 3 I see that the atom projected ones have the same characteristics although the ones for FeCoMnAl are more spiky. The main difference is a small majority gap just below the Fermi level in FeCoMnAl which is washed out for [Fe0.5Co0.5]2MnAl. This gap is the signature of the order.

The second family of compounds is the [Rh1−xCo2]2MnAl. Rh and Co are isoelectronic elements and the total spin moment is 4 µB for all concentrations. Also RhCoMnAl is a HM with magnetic properties similar to [Rh0.5Co0.5]2MnAl as it was the case for the compounds containing Fe. Since Rh moment is much smaller than the Co one, the Mn moment has to increase considerably, from 2.6 to 3.4 µB, with the increase of Rh concentration to keep the total spin moment constant.

A special case under study is the [Mn1−xCo2]2VAl family. For this compound the spin moment changes from −2 to 2 µB with the concentration x. As shown in Ref. 4 the Mn and V atoms in Mn2VAl are antiferromagnetically coupled and V carries a large spin moment, while in Co2VAl the Co and V atoms are ferromagnetically coupled and the moment is mainly carried by the Co atoms. For x=0.5 there is the case of a compound with zero total spin moment but with magnetic constituents; \( m^{\text{Mn}} = -0.47 \mu_B, m^{\text{Co}} = 0.20 \mu_B \) and \( m^V = 0.23 \mu_B \). The Mn spin moment decreases from −1.45 µB to -0.35 with the concentration x while the Co spin moment increases from 0.2 to 0.95 µB and the V one decreases from 0.8 to 0.16 µB.

In this contribution I expanded the study already performed for the ordered Heusler alloys to cover also the quaternary Heusler compounds like Co2[Cr1−xMnx]Al, Co2Mn[Al1−xSnx] and [Fe1−xCo2]2MnAl. Using the Korringa-Kohn-Rostoker method in the coherent potential approximation I have shown that independently from which site is disordered, all compounds are half-metals and the total spin moment \( M_t \) scales linearly with the total number of valence electrons \( Z_t \) following the rule \( M_t = Z_t - 24 \), thus \( M_t \) scales also linearly with the concentration x. Depending of the family under study the atomic spin moments change in a way that the above rule, known also as the Slater-Pauling behavior, is obeyed. Finally an interesting case is [Mn1−xCo2]2VAl where the moment scales linearly from −2 µB to 2 µB and for \( x = 0.5 \) the total spin moment is zero but the constituents are magnetic.

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12. I will use the abbreviation HM to denote both the “half-metal” and the “half-metallic”.

FIG. 3: Atom projected DOS in the case that both X sites are occupied by Co and Fe with 50% probability (system is denoted by [Fe0.5Co0.5]2MnAl) and when one sublattice is occupied exclusively by Fe and the other by Co atoms (system is denoted by FeCoMnAl). All compounds are half-metals. The numbers in the legends are the atomic spin moments in µB and the larger ones are the total spin moments.