Tuning the magnetic properties of half-metallic semi-Heusler alloys by sp-electron substitution: the case of AuMnSn$_{1-x}$Sb$_x$ quaternary alloys

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Abstract

We study the electronic and magnetic properties of the quaternary AuMnSn$_{1-x}$Sb$_x$ Heusler alloys using first principles calculations. We determine their magnetic phase diagram and show that they present a phase transition from a ferromagnetic (FM) to an antiferromagnetic (AFM) state with increasing Sb concentration. For large Sb concentrations the AFM superexchange coupling dominates over the FM RKKY-like exchange mechanism. This behaviour is similar to that demonstrated by the isovalent Ni$_{1-x}$Cu$_x$MnSb alloy studied recently by the authors (Galanakis et al 2008 Phys. Rev. B 77 214417). Thus the variation of the concentration of the sp-electrons (Sn and Sb atoms) in the AuMnSn$_{1-x}$Sb$_x$ compound and the variation of the concentration of the non-magnetic 3d atoms (Cu) in Ni$_{1-x}$Cu$_x$MnSb lead to a similar tuning of the magnetic properties of the two Heusler alloys. We show that the inclusion of correlation effects does not alter the phase diagram of the AuMnSn$_{1-x}$Sb$_x$ compound. The calculated results are in good agreement with the available experimental data.

(Some figures in this article are in colour only in the electronic version)
to note here that CuMnSb is a well-known antiferromagnet and has been extensively studied both experimentally [9] and theoretically [10]. The exchange coupling mechanism in Mn-based Heusler alloys has been well understood [11] and for half-metallic systems it has been shown in [8] that the magnetic interactions depend strongly on the position of the Fermi level within the gap. As the concentration in Cu increases the Fermi level is shifted to a higher energy with respect to the minority-spin gap and at the transition point it crosses the minority-spin conduction band so that the AFM superexchange coupling of the Mn–Mn spin moments through the Cu atoms dominates over the FM RKKY-like interaction between the Mn atoms.

In the semi-Heusler alloys of the chemical type AuMnZ (Z = In, Sn, Sb), the magnetization is confined to the Mn sublattice and the Mn spin moments are well localized in space due to the large Mn–Mn distance, i.e. the 3d states belonging to different Mn atoms do not overlap considerably. Amft and Oppeneer calculated the largest zero-temperature polar Kerr rotation (−0.45◦) at about 1 eV photon energy) for AuMnSn [12]. The AuMnSn alloy is isovalent (same number of valence electrons in the primitive unit cell) to NiMnSb and AuMnSb is isovalent to CuMnSb. Thus the magnetic phase diagrams of AuMnSn1−xSbx and Ni1−xCu,MnSb compounds can be directly compared. In this paper we employ the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO) [13] within the local density approximation (LDA) [14] to study the phase diagram of the quaternary AuMnSn1−xSbx alloys and compare it with our published results on Ni1−xCu,MnSb compounds. We simulate the disorder within the coherent potential approximation (CPA) framework. Details of the calculations are similar to the ones presented in [8]. We have used the theoretical calculated equilibrium lattice constants: 5.83 Å for NiMnSb, 5.99 Å for CuMnSb, 6.333 Å for AuMnSn and 6.464 Å for AuMnSb. These are slightly different from the experimental ones: 5.93 Å for NiMnSb, 6.09 Å for CuMnSb, 6.341 Å for AuMnSn and 6.379 Å for AuMnSb [4, 15]. We should note here that we performed test calculations also for the experimental lattice constants and results on the electronic and magnetic properties were identical to the case of the theoretical lattice parameters leading to the same magnetic phase diagram. We have assumed that the lattice constant for the quaternary alloys varies linearly with the concentration x, since as shown in [4] this is the case for most of the quaternary Heusler compounds. We show that AuMnSn1−xSbx alloys present a similar magnetic phase diagram to the Ni1−xCu,MnSb compounds and the tuning of the magnetic properties is insensitive to the origin of the conduction electrons which mediate the Mn–Mn interactions.

We will start our discussion from the calculated spin magnetic moments presented in figure 1. We have presented the total magnetic moments for the AuMnSn1−xSbx and Ni1−xCu,MnSb alloys as a function of the concentration for the FM state in figure 1. The solid black lines represent the Slater–Pauling (SP) behaviour obeyed by the perfect half-metallic ferromagnets (the total spin moment in µB is the number of valence electrons minus 18) [16]. We present the Mn magnetic moment corresponding to the AFM state for comparison. We should note that the spin magnetic moments of Au, Ni and Cu are zero in the AFM state for symmetry reasons while the Sb and Sn atoms have a very small magnetic moment value. For x = 0 the AuMnSn compound has a total spin moment slightly larger than the ideal 4 µB predicted by the SP rule for the perfect half-metallic ferromagnets since the Fermi level is slightly below the gap as can be seen in figure 2 where we have shown the total density of state (DOS) for both families of compounds. NiMnSb is an ideal half-metal and this is reflected in an integer value of the total spin magnetic moment which is 4 µB and the Fermi level is located in the middle of the gap. AuMnSn1−xSbx and Ni1−xCu,MnSb follow the SP rule up to x ≈ 0.5 and x ≈ 0.2, respectively, and at this point the half-metallicity is lost since the Fermi level is shifted and now crosses the minority-spin conduction band. This is clearly shown in figure 2. The shift of the Fermi

Figure 1. Calculated total spin moments (in µB) as a function of the concentration (x) for the studied AuMnSn1−xSbx and Ni1−xCu,MnSb in the FM configuration. We also present the Mn spin moment in the AFM configuration for comparison. The solid black lines represent the SP behaviour.

Figure 2. Spin-resolved DOSs in the case of AuMnSn1−xSbx (left panel) and Ni1−xCu,MnSb (right panel) around the Fermi level for selected values of x. We have set the Fermi level as zero of the energy axis. Positive values of DOS correspond to the majority-spin electrons and negative values to the minority-spin electrons.
level towards higher energies is easily understood. When we increase the concentration of Sb and Cu atoms, we dope the system with p charge. The corresponding majority-spin p states are extremely extended in energy and thus, when their occupation increases, they push the Fermi level to higher energy.

To reveal the mechanism for the loss of the half-metallic character we have to study the atom-resolved spin magnetic moments for the FM configuration presented in table 1. The spin magnetic moments of Au, Sn and Sb atoms change from $-0.022$, $-0.155$ and $-0.100$ to $0.118$, $-0.020$ and $0.044 \mu_B$, respectively, with increase in the Sb concentration in the AuMnSn$_{1-x}$Sb$_x$ compound. These atoms have almost filled electronic shells, since they provide electronic bands much lower in energy than the Mn ones [16], and they contribute marginally to the total spin moment. Thus the extra electron provided by the Sb atom has to be accommodated by the bands provided by the Mn atom. For AuMnSn, the spin magnetic moment of Mn is $4.192 \mu_B$ and thus most of the five majority-spin states are occupied. To further occupy the Mn majority states requires a lot of energy and the system prefers to also partially occupy the minority-spin states above the gap and the half-metallicity is lost. As a result the Mn spin moment is only around $0.32 \mu_B$ larger in AuMnSb reaching a value of $4.520 \mu_B$. The calculated magnetic moments are in good agreement with experimental values of AuMnSn [17] and AuMnSb [18] compounds. In the case of Ni$_{1-x}$Cu$_x$MnSb alloys the same phenomenon occurs: Ni, Cu and Sb atoms carry very small spin moments and Mn increases its spin moment by $0.31 \mu_B$ when all Ni atoms are substituted by Cu ones leading to the loss of half-metallicity.

In the AFM state, Sb and Sn have very small magnetic moments while the magnetic moment of Au is zero in the AuMnSn$_{1-x}$Sb$_x$ compound for symmetry reasons. Similarly in the case of the Ni$_{1-x}$Cu$_x$MnSb alloys, Ni and Cu have zero spin moments, while Sb has a very small magnetic moment. The closeness in value between the Mn spin moments in the FM and AFM configurations shown in figure 1 can be understood if we examine the Mn-resolved DOS shown for all four CuMnSb, NiMnSb, AuMnSn and AuMnSb compounds in figure 3. Both in the FM and the AFM cases Mn atoms present a similar DOS and the small broadening of the bands in the AFM state occurs due to stronger hybridization with the other atoms in this case. The important point is that the similar DOS in the FM and AFM cases just above the Fermi level increases. This gives rise to the opposite behaviour in the relative contributions of the exchange mechanisms: a decrease in the RKKY-like coupling and an increase in the superexchange mechanism. At the transition

| $x$ | Total | Au | Mn | Sn | Sb |
|-----|-------|----|----|----|----|
| 0.0 | 4.015 | -0.022 | 4.192 | -0.155 | - |
| 0.2 | 4.199 | 0.023 | 4.286 | -0.117 | -0.078 |
| 0.4 | 4.399 | 0.064 | 4.392 | -0.073 | -0.033 |
| 0.6 | 4.541 | 0.094 | 4.459 | -0.038 | 0.004 |
| 0.8 | 4.582 | 0.103 | 4.470 | -0.026 | 0.018 |
| 1.0 | 4.682 | 0.118 | 4.520 | - | 0.044 |

| $x$ | Total | Ni | Cu | Mn | Sb |
|-----|-------|----|----|----|----|
| 0.0 | 4.000 | 0.255 | - | 3.847 | -0.102 |
| 0.2 | 4.175 | 0.310 | 0.072 | 3.982 | -0.070 |
| 0.4 | 4.216 | 0.324 | 0.078 | 4.042 | -0.052 |
| 0.6 | 4.224 | 0.327 | 0.080 | 4.083 | -0.038 |
| 0.8 | 4.220 | 0.327 | 0.083 | 4.113 | -0.025 |
| 1.0 | 4.244 | 0.096 | 4.158 | -0.010 |

As we have mentioned above, both AuMnSn$_{1-x}$Sb$_x$ and Ni$_{1-x}$Cu$_x$MnSb quaternary compounds lose their half metallic character at a concentration of $x \approx 0.5$ and $x \approx 0.2$, respectively. For these values of the concentration the Fermi level enters the minority-spin conduction band but the ferromagnetism is still favourable with respect to the AFM state. To study the phase transition, we have calculated the total energies for both the FM and the AFM configurations of the Mn spin magnetic moments. All energy calculations have been performed using a large AFM unit cell (which is double the FM unit cell). We determine the zero-temperature magnetic phase diagram as the difference in the corresponding total energies ($E_{AFM} - E_{FM}$) per AFM unit cell and we present our results in figure 4. AuMnSn$_{1-x}$Sb$_x$ shows a phase transition from FM to AFM coupling of the Mn spin moments for a critical concentration value $x \approx 0.7$. As seen in figures 2 and 3, when we substitute Sb for Sn, the Fermi level moves towards higher energies and the number of minority states just above the Fermi level increases. This gives rise to the opposite behaviour in the relative contributions of the exchange mechanisms: a decrease in the RKKY-like coupling and an increase in the superexchange mechanism. At the transition
properties of the quaternary AuMnSn$_{1-x}$Sb$_x$ ($0 \leq x \leq 1$) Heusler alloys using first principles calculations. We determine their magnetic phase diagram and we show that they present a phase transition from an FM to an AFM state with increasing Sb concentration. For large Sb concentrations the AFM superexchange coupling dominates over the FM RKKY-like exchange mechanism. Electronic correlation effects have a marginal effect on the magnetic phase diagram of these compounds. This is an alternative route for tuning the magnetic properties of the Heusler alloys with respect to the variation of the non-magnetic 3d atoms shown for Ni$_{1-x}$Cu$_x$MnSb alloys [8]. These findings can be used as a practical tool to design materials with given physical properties.

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Figure 4. Ground state magnetic phase diagram and total energy differences between AFM and FM configurations of the Mn magnetic moments in AuMnSn$_{1-x}$Sb$_x$ and Ni$_{1-x}$Cu$_x$MnSb as a function of the concentration ($x$). In the inset we show the total spin polarization of the conduction electrons of X (Au, Ni, Cu) and Z (Sn and Sb) atoms as a function of the concentration ($x$). Note that the energy differences are given for an AFM unit cell, while spin polarization of the conduction electrons is given for an FM unit cell.