Electronic structure of half-metallic magnets

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Abstract

We have analyzed the electronic structure of half-metallic magnets based on first principles electronic structure calculations of a series of semi-Heusler alloys. The characteristic feature of the electronic structure of semi-Heusler systems is a d-d gap in the density of states lying at/close to the Fermi level depending on the number of valence electrons. We have employed various indicators of chemical bonding to understand the origin of the gap in these systems, which is crucial for their half-metallic property. The density of states of other half-metallic magnets also supports a gap and it is a generic feature of these systems. We have discussed in some details the origin of magnetism, in particular, how the presence of the gap is crucial to stabilize half-metallic ferro and ferri magnetism in these systems. Finally, we have studied the role of magnetic impurities in semiconducting semi-Heusler systems. We show with the aid of model supercell calculations that these systems are not only ferromagnetic but also half-metallic with possibly high Curie temperature.

Key words: semi-Heusler, half-metals

1. Introduction

In the recent times, one of the most growing field of research interest is spin-electronics[1] (spintronics) where the spin of the electron over and above its charge is exploited to design new generation of electronic devices. The main ingredient for spintronics is a source of spin polarized charge carriers. The half-metallic ferromagnets where one spin direction behaves like a metal and the other is insulating results in 100% spin polarization. So during the spin injection process only electrons of either spin (up or down) can be injected into the system thereby providing an avenue for creation of perfect spin filter and spin dependent devices. The half-metallic ferromagnetism was first predicted by de Groot et. al.[2] by spin-polarized band structure calculations in the Mn-based semi Heusler alloy NiMnSb, which is now well established experimentally for single crystalline samples. In addition to Heusler and semi-Heusler alloys, the other known half-metallic ferromagnetic materials are oxides[3] (CrO$_2$ and Fe$_3$O$_4$), manganites La$_{0.7}$Sr$_{0.3}$MnO$_3$[4], the double perovskite compound Sr$_2$FeMoO$_6$[5], zinc-blende compounds like CrAs and CrSb[6]. Half-metallicity can also be induced in an otherwise semiconducting or insulating system by incorporation of transition metal impurities as demonstrated in the diluted magnetic semiconductors[7] like (In,Mn)As, (Ga,Mn)N, Co substituted TiO$_2$ and ZnO[8]. The current research in spintronics is directed toward...
an extensive search for new half-metallic materials with high Curie temperature. Also there are considerable effort to understand the physics responsible for the novel magnetic properties exhibited by these materials as improving this understanding, is likely to help in engineering these novel materials. In this communication, we shall address some of these issues by analyzing the electronic and magnetic structure of a series of Fe,Co and Ni based half-metallic semi-Heusler alloys.

![Crystal structure of semi-Heusler compounds](image)

**Fig. 1.** Crystal structure of semi-Heusler compounds.

The half-metallic semi-Heusler alloys with the general formula XMZ where X and M are transition metals and Z is a sp-valent element can be particularly attractive for spintronics applications due to their relatively high Curie temperature and the similarity of their crystal structure to the zinc-blende structure adopted by a large number of semiconductors like GaAs, ZnSe, InAs etc making them compatible with semiconductor technology. The key feature of the electronic structure of these materials is a gap close to the Fermi level and plays a crucial role to drive some of these systems to half-metallic ferromagnets. The gap in the electronic structure, seems to be a generic feature of half-metallic magnets[9] resulting from a unique combination of their novel crystal structure and chemical bonding. So it is crucial to understand the origin of the gap as well as to identify which factors (structural and chemical) that influences the gap. For the semi-Heusler systems, it has been found that the lattice parameter, the relative ordering of the atoms in the unit cell, reduced dimensionality(surfaces), chemical substitution(doping) and disorder have profound influence on the gap and hence the half metallic property [10]. So a proper coordination of all these factors is crucial for designing these materials for possible applications. In this respect, we have investigated the role of magnetic impurities in some semiconducting semi-Heusler systems. We find even for impurity concentration as low as 3 %, some semiconducting semi-Heusler systems can be transformed into half-metallic ferromagnets with possibly high Curie temperature. In this communication, we shall also discuss the electronic structure and origin of ferromagnetism in Mn doped semiconducting semi-Heusler alloy NiTiSn.

2. Crystal and paramagnetic electronic structure of semi-Heusler systems

The semi-Heusler compounds XMZ (X=Fe,Co,Ni; M=Ti,V,Cr,Mn,Mo; Z= Sn,Sb) studied in this work crystallize in the face centered cubic structure with one formula unit per unit cell as shown in Fig. 1. The space group is F4/3m (No 216). The M and Z atoms are located at 4a(0,0,0) and 4b(1/2,1/2,1/2) positions forming the rock salt structure arrangement. The X atom is located in the octahedral coordinated pocket, at one of the cube center positions 4c(1/4,1/4,1/4) leaving the other 4d(3/4,3/4,3/4) empty. When the Z-atomic positions are empty the structure is analogous to zinc blende structure which is common for large number of semiconductors. All the electronic structure calculations reported in this work have been done using the experimental lattice constant, except for FeMnSb, FeCrSb and CoMoSb where we have estimated theoretically the equilibrium lattice constant using full potential (FP) LMTO method as described in [11]. The analysis of the electronic structure and chemical bonding is carried out in the framework of the tight-binding linearized muffin tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [12] within LDA [13] as well as
GGA [14]. In Fig. 2, we have displayed the paramagnetic total density of states (DOS) for the compounds FeVSb, CoMoSb, NiTiSn, and NiMnSb with the valence electron count (VEC) ranging from 18 to 22 electrons. From Fig. 2, we gather that the characteristic feature of all semi-Heusler compounds considered here is a gap at/very close to the Fermi level. In addition, there is also a virtual gap far below the Fermi level. The former is a d-d gap resulting from the covalent hybridization of the higher valent transition element X with the lower valent transition element M while the latter is due to the X(Fe,Co,Ni)-d-Sb-p interactions [11], [15]. As we increase the number of valence electrons, the bands are progressively filled so that the 18 electron compounds are narrow gap semiconductors while the others with less or more than 18 valence electrons are metals in the paramagnetic phase. The states lying below the p-d gap are Sb p-sates. In fact, the Sb-s state is lying further below the chosen scale of the figure. The states lying below and above the d-d gap are the bonding and antibonding states resulting from the covalent hybridization of X with M. The bonding bands are predominantly of X-d character while the antibonding bands are predominantly M-d character. Hence below the d-d gap there are 9 bands (4 Sb s+p, 5 predominantly X-d) which in the paramagnetic state can accommodate 18 electrons. With 18 valence electrons all the bonding orbitals are occupied leading to saturation of otherwise highly unsaturated metallic bonds providing directionality and strong bonding. As a result, for the 18 electron compounds the Fermi level lies at the edge of the gap and make them semiconductors. However if there are more than 18 valence electrons the antibonding bands gets occupied and the paramagnetic state may no longer be stable. Such instabilities may be alleviated by the formation of magnetic phase to be discussed in the next section.

Fig. 2. Paramagnetic total DOS for semi-Heusler systems (see text). The number of valence electron is indicated in the figure. All energies are w.r.t the Fermi energy.

In order to understand the physical origin of the gap we have calculated the crystal orbital Hamiltonian population (COHP) [16] for various pairs of atoms, as it provides the information concerning the relative contributions to bonding arising from different interactions in the system. In COHP, we calculate the DOS weighted by the Hamiltonian matrix elements. The on-site COHP, corresponds to the atomic contribution and the off-site COHP covalent contribution to the bands. In Fig. 3, we have displayed the site projected DOS for a representative compound FeVSb and the off site

Fig. 3. Site projected DOS (top) and COHP (bottom) for FeVSb. All energies are w.r.t. Fermi energy.
COHP for the nearest neighbor Fe-V, Fe-Sb and V-Sb interactions. The bonding contribution for which the system undergoes a lowering of energy is indicated by negative COHP and the antibonding contribution that raises the energy is represented by positive COHP. From the COHP plot in Fig. 3 we gather that the most dominant nearest neighbor interaction is between Fe and V. A comparison with the partial DOS reveals that the bonding and the antibonding states below and above the Fermi level is due to the the nearest neighbor Fe-V interaction and this is the key interaction to open up gap close to the Fermi level in these compounds. The occupied Sb states below the p-d gap are a result of Fe-Sb and V-Sb bonding interactions with a relatively dominant contribution from the Fe-Sb interactions. The presence of Sb atom which provides a channel to accommodate some transition metal d electrons in addition to its sp electrons is therefore crucial for the stability of these systems.

3. Spin polarized Calculations

The characteristic feature of the paramagnetic electronic structure of the semi-Heusler compounds discussed in the preceding section is a d-d gap close to the Fermi level. The paramagnetic electronic structure of other half metallic systems like CrO$_2$[17], Fe$_3$O$_4$[18], double perovskite Sr$_2$FeMoO$_6$[19], zinc blende compounds also sustains a gap close to the Fermi level and this seems to be a generic feature of half metallic systems. The presence of the gap [11], [20] has an interesting consequence for the magnetic properties of these systems. If the Fermi level lies in the antibonding complex and/or the density of states at the Fermi level is high then the paramagnetic state may no longer be stable. The stability can be achieved by developing magnetic order, this is due to the fact that upon spin polarization, the electrons arrange themselves so that the spontaneous magnetization makes the spin-up and spin-down electrons different. As a result, the overall bonding energy (gain in kinetic energy and reduction of Coulomb repulsion due to Hund exchange) is lowered to make the system stable. If the paramagnetic electronic structure supports a gap then in the process of spin polarization, depending on the position of the gap and the Fermi level, the rearrangement of the electrons, i.e. the depletion of the minority bands or the occupancy of the majority bands may happen in such way that it stabilizes half-metallic ferromagnetism. In figure 4(a) we have shown schematically the case relevant for semi-Heusler alloys. For semi-Heusler alloys(XMZ) with more than 18 VEC the Fermi level is at the antibonding complex of predominantly M character and the gap is below the Fermi level (figure 4(a), Z states are not shown). Now the depletion of the minority antibonding states above the gap may happen in such a way that none of the minority antibond-
ing states are occupied leading to complete spin polarization and we have a half-metallic ferromagnet. To stabilize the half-metallic ferromagnetic state by this mechanism the other important requirement is appreciable exchange splitting of the bands undergoing spin polarization. In Fig 5 we display, spin polarized DOS for FeCrSb, FeMnSb, CoMoSb and NiMnSb. We gather from the figure that the large exchange splitting of Mn and Cr are crucial to stabilize half metallic ferromagnetism, while CoMoSb is magnetic but not half metallic owing to the weak exchange splitting of the more extended Mo 4-d bands.

There is however, another possibility, to stabilize half-metallic magnetism. Such a mechanism for e.g. is realized in double perovskites Sr$_2$MM'$_4$O$_6$ (M=Fe, M'=Mo,Re) where the paramagnetic DOS is such that the states close to the Fermi level have both localized states (M) which are capable of sustaining large exchange splitting as well as delocalized states(M') with weak exchange splitting. It has been recently proposed [19], [21] that ferromagnetism in these systems can be stabilized by hybridization induced negative exchange splitting. In Fig. 4(b) we have schematically illustrated this mechanism relevant for half-metallic double perovskites like Sr$_2$FeMoO$_6$ where in the absence of any spin polarization Fe-d derived localized states (M) as well as Mo-O derived conducting states(M') are in close vicinity of the Fermi level (Fig. 4(b)). In the process of spin polarization, the localized M derived states will exchange split leaving the weakly exchange split M' derived states at the Fermi level if there is no hybridization between M and M' states. However, in the presence of hybridization which is rather strong in these systems, there is hybridization induced negative exchange splitting of M' (indicated by the arrows in Fig. 4(b)) leading to antiferromagnetic coupling between the localized M and the itinerant M' electron states. However, in order to support this large gain in energy by antiferromagnetic coupling the localized M states should remain ferromagnetically coupled. The presence of the gap coupled with the strong hybridization induced negative exchange splitting drives the system to be a half-metallic ferrimagnet.

4. Electronic structure of doped semi-Heusler systems

In this section, we shall discuss the role of magnetic impurity Mn in the semiconducting semi-Heusler alloy NiTiSn having 18 valence electrons. In order to study the effect of the dilute Mn impurity in semi-Heusler systems (i.e., to simulate the effect of doping) we have constructed supercells with size dependent on the % of doping. In each supercell we have replaced two Ti atoms by two Mn atoms which also allowed us to study the interaction between Mn moments. The size of the supercell was chosen to ensure that the separation between the impurities is much smaller in comparison to the dimension of the supercell. Replacing a Ti atom with Mn atom puts three additional d-electron to the system per Mn atom, i.e. $\Delta Z = 3$. As a result, VEC > 18 and the system is not semiconducting and according to our previous discussion it is likely to stabilize in the ferromagnetic state. In Fig. 6(a) we show the total paramagnetic DOS for NiTi$_{1-x}$Mn$_x$Sn (x=6.25 %) system. The crucial feature of the DOS is the presence of a shallow donor level produced by the addition of Mn impurities and the Fermi level lies on this Mn
impurity driven state. In order to check whether the system sustains magnetic instability we have performed spin polarized density functional calculations in the framework of GGA with (i) two Mn spins parallel to each other, the ferromagnetic (FM) configuration and (ii) two Mn spins antiparallel to each other the antiferromagnetic (AFM) configuration. Our calculations within LMTO-ASA method shows that the ferromagnetic state is most stable for all concentrations, ranging from 25% Mn to 3.125% Mn. The doped systems are not only ferromagnetic but also half metallic sustaining a magnetic moment of 3 $\mu_B$ per Mn for all concentration ranges. In figure 6(b) we have shown the spin polarized DOS for the same system, indicating that the system is half-metallic. Here the defect states are screened metallically by the majority states so that the number of the minority states do not change and in this case the alloy moment is given by $m = \Delta Z$. The analysis of the DOS close to the Fermi level suggests that it is predominantly of Mn character. The Mn atoms substituting Ti are in tetrahedral arrangement with Ni, as a consequence Ni $t_{2g}$ - Mn $t_{2g}$ interactions are more favorable. The antibonding states near the Fermi level are of Mn $t_{2g}$ character, while the bonding states are Ni $t_{2g}$ like. However a bonding partner of Mn $t_{2g}$ like state is seen as a sharp peak at about -2 eV below the Fermi level. The $e_g$ like states are nonbonding. So out of the additional three electrons available, two are accommodated in the $e_g$ like sates keeping the $t_{2g}$ like state partially empty. This can be seen in Fig. 6(c). Such partially filled $t_{2g}$ states are favorable for ferromagnetism as the 3d electrons in the partially occupied 3d-orbitals is allowed to hop to the neighboring 3-d states provided the spin are parallel. The lowering of energy by hopping in the presence of parallel alignment of spin the so called double exchange mechanism stabilizes ferromagnetism. However if the band were empty such a lowering of energy is not possible and the AFM arrangement of impurity spin will be favored. Finally in Fig. 6(d) we show the energy difference $\Delta E = E_{AFM} - E_{FM}$ as a function of separation of the impurity. We see from the figure that $\Delta E$ decreases sharply with distance suggesting that the double exchange induced ferromagnetic interaction is short ranged. This indicates the formation of Mn clusters within a short radial distance and might lead to high values of $T_c$ in these systems. Based on this theoretical studies it will be interesting to investigate these systems experimentally.

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