Generalized Slater-Pauling rule for the inverse Heusler compounds

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We present extensive first-principles calculations on the inverse full-Heusler compounds having the chemical formula \(X_2YZ\) where \((X = \text{Sc, Ti, V, Cr or Mn}), (Z = \text{Al, Si or As})\) and the \(Y\) ranges from Ti to Zn. Several of these alloys are identified to be half-metallic magnets. We show that the appearance of half-metallicity is associated in all cases to a Slater-Pauling behavior of the total spin-magnetic moment. There are three different variants of this rule for the inverse Heusler alloys depending on the chemical type of the constituent transition-metal atoms. Simple arguments regarding the hybridization of the \(d\)-orbitals of neighboring atoms can explain these rules. We expect our results to trigger further experimental interest on this type of half-metallic Heusler compounds.

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The rise of nanotechnology and nanoscience during the last decade brought to the center of scientific research new phenomena and materials. Spintronics and magneto-electronics comprise one of the most rapidly expanding fields in nanoscience.\textsuperscript{1} Half-metallic magnetic compounds play a crucial role in this development.\textsuperscript{2} These materials present usual metallic behavior for the one spin direction while an energy gap in the band structure is present in the other spin direction similarly to semiconductors.\textsuperscript{3} The possibility of creating 100\% spin-polarized current has triggered the interest on such compounds.\textsuperscript{4} De Groot and collaborators in 1983 have initially suggested based on electronic structure calculations that NiMnSb, a semi-Heusler alloy, is a half-metallic\textsuperscript{5} and since then several half-metallic compounds have been discovered.\textsuperscript{6} Several aspects concerning the implementation of half-metallic alloys in realistic devices, like tunnelling magnetic junctions or giant magnetoresistive junctions and spin-injectors, have been discussed in literature.\textsuperscript{7,8}

The family of Heusler alloys incorporates more than 1000 members almost all crystalizing in a close-packed cubic structure similar to the binary semiconductors.\textsuperscript{11} Most of them are metals exhibiting diverse magnetic phenomena. The lattice is a f.c.c. with four equidistant sites as basis along the diagonal of the unit cell.\textsuperscript{9} There are two families of Heusler alloys. The semi-(or half)-Heuslers have the chemical formula \(XYZ\) where the sequence of the sites is \(X\)-\(Y\)-\(void\)-\(Z\). The \(X\) and \(Y\) are transition-metal elements and \(Z\) is a \(sp\)-element and the structure is known as the \(C1\text{\textsubscript{3}}\) lattice. The second subfamily consists the full-Heusler compounds with the chemical formula \(X_2YZ\). When the valence of the \(X\) is larger than \(Y\), the atomic sequence is \(X\)-\(Y\)-\(X\)-\(Z\) and the structure is the well known \(L2\textsubscript{1}\) one with prototype \(\text{Cu}_2\text{MnAl}\).\textsuperscript{12} When the valence of the \(Y\) elements is the largest, the compounds crystallize in the so-called \(X4\) structure, where the sequence of the atoms is \(X\)-\(X\)-\(Y\)-\(Z\) and the prototype is \(\text{Hg}_2\text{TiCu}\).\textsuperscript{13} The latter alloys are also known as inverse Heusler compounds. Several inverse Heuslers have been studied using first-principles electronic structure calculations in literature.\textsuperscript{13–22} In all cases the \(X4\) structure is energetically preferred to the \(L2\textsubscript{1}\) structure. The latter has been also confirmed by experiments on \(\text{Mn}_2\text{CoGa}\) and \(\text{Mn}_2\text{CoSn}\) films as well as \(\text{Co}\) doped \(\text{Mn}_3\text{Ga}\) samples.\textsuperscript{21–23} but experiments on \(\text{Mn}_2\text{NiSb}\) revealed that the actual arrangement of the atoms at the various sites can be influenced by the preparing method.\textsuperscript{24} Inverse Heuslers are interesting for applications since they combine coherent growth on semiconductors with large Curie temperatures which can exceed the 1000 K as in the case of \(\text{Cr}_2\text{CoGa}\).\textsuperscript{25}

Slater and Pauling had shown in two pioneering papers that in the case of binary magnetic alloys when we add one valence electron in the compound this occupies spin-down states only and the total spin magnetic moment decreases by about 1 \(\mu_B\).\textsuperscript{26,27} Interestingly a similar behavior can be also found in half-metallic Heusler alloys.\textsuperscript{28} It was shown that in the case of the semi-Heusler compounds like \(\text{NiMnSb}\) the total spin magnetic in the unit cell, \(M_t\) scales, as a function of the total number of valence electrons, \(Z_t\), following the relation \(M_t = Z_t - 18\).\textsuperscript{29} while in the case of the \(L2\textsubscript{1}\) full-Heuslers this relation becomes \(M_t = Z_t - 24\).\textsuperscript{30,31} These Slater-Pauling (SP) rules connect the electronic properties (appearance of the half-metallic behavior) directly to the magnetic properties (total spin magnetic moments) and thus offer a powerful tool to the study of half-metallic Heusler compounds. It has been shown that also quaternary or quinternary half-metallic Heusler alloys obey the SP rule,\textsuperscript{32} and a generalized version exists when we pass from a half-metallic semi-Heusler to a half-metallic full-Heusler alloy.\textsuperscript{33} The aim of the present communication is to exploit whether a generalized version of the SP rule can be also extracted for the inverse half-metallic full-Heusler alloys where all sites obey the tetrahedral symmetry. Such a relation would offer an extra strong tool in the study of half-metals.

For our calculations we used the full-potential...
nonorthogonal local-orbital minimum-basis band structure scheme (FPLO) within the generalized gradient approximation (GGA) to study the electronic and magnetic properties of all the inverse XYZ alloys where X = Sc, Ti, V, Cr or Mn, Y is a transition-metal atom ranging from Ti to Zn, and Z = Al, Si or As. First, we determined the equilibrium lattice constants using total energy calculations and a dense 20 × 20 × 20 k-mesh grid to carry out the numerical integrations, and at the equilibrium constant we calculated the electronic and magnetic properties with more accuracy. In the following we use the superscripts A and B to distinguish the two X atoms sitting at the two inequivalent sites in the XA-structure (see Fig. 1 in Ref. 12 for a schematic representation of the structure). The XA3 atom has the same local environment in the crystal as the Y atom.

In Fig. 1 we have plotted the total spin magnetic moment versus the total number of valence electrons in the unit cell for all studied compounds which were found to be half-metals. We have considered in all cases that the half-metallic gap in the density of states (DOS) is located in the spin-down band. In the cases of negative total spin magnetic moments in the figure the spin-up are the minority and the spin-down the majority states. Our results can be grouped along three lines representing three variants of the SP rule. Along the $M_t = Z_t - 18$ line we find the Sc and Ti based alloys, along the $M_t = Z_t - 24$ line the alloys with X = Cr or Mn, and finally along the $M_t = Z_t - 28$ line the compounds where Y = Cu or Zn. The alloys with X = V are dispersed between the first two lines. A very interesting consequence of the SP rules are the Heuslers compounds with a zero value of their total spin magnetic moment which are made of magnetic constituents and which are belong to a special class of half-metallic antiferromagnets also known as fully-compensated ferrimagnets (we have not included the semiconducting or the simple-metallic systems in Fig. 1).36–38}

Prior to the discussion of the SP rules in the inverse Heusler alloys, we should shortly discuss the origin of the rule in the half-metallic L21 full-Heuslers (for more details see Ref. 29). In their case the corresponding SP rule is $M_t = Z_t - 24$. The role of the sp element is to provide in the spin-down electronic band structure a single s and a triple-degenerated p band deep in energy; they are located below the d-states and accommodate d-charge from the transition metal atoms. Due to the more complex d-d hybridizations in these alloys with respect to the semi-Heuslers one has first to consider the interaction between the X elements. Although the symmetry of the L21 lattice is the tetrahedral one, the X elements themselves, if we neglect the Y and Z atoms, form a simple cubic lattice and sit at sites of octahedral symmetry. The 11 orbitals of the neighboring X atoms hybridize creating five bonding d-states, which after hybridize with the 11 orbitals of the Y atoms creating five occupied and five unoccupied d-hybrids states. These non-bonding hybrids cannot couple with the orbitals of the neighboring atoms, since they do not obey the tetrahedral symmetry, and only the t1u orbitals are occupied leading to a total of 12 occupied spin-down states.39 In the case of semi-Heuslers, like NiMnSb, the situation is simpler. The 11 orbitals of...
the two transition metal atoms hybridize strongly creating five occupied bonding and five unoccupied antibonding $d$-states in the spin-down band structure. As a result there are in total exactly nine occupied spin-down states and the SP relation is $M_t = Z_t - 18$. All half-metallic Sc- and Ti-based alloys follow the $M_t = Z_t - 18$ rule as for the semi-Heusler compounds but its origin is different. A close look at the atom-resolved spin-moments, DOS and band structure can give more information on the origin of this rule. The Sc$^A$ (Ti$^A$) and the Y atoms sit at sites of the same symmetry and their $d$-orbitals hybridize as in the usual $L2_1$ full-Heuslers creating five bonding $d$-hybrids and five non-bonding. The five Sc$^A$-Y (Ti$^A$-Y) bonding $d$-hybrids in their turn hybridize with the $d$-orbitals of the Sc$^B$ (Ti$^B$) atoms creating again bonding and antibonding states. The difference with the $L2_1$ full-Heuslers is that the Sc$^A$ (Ti$^A$) and Y atoms have a large energy separation of their $d$-orbitals and as a result the five Sc$^A$-Y (Ti$^A$-Y) non-bonding $d$-hybrids, the $t_{1u}$ and $e_u$ states are very high in energy and they are empty while in the usual $L2_1$ full-Heuslers the triple-degenerated $t_{1u}$ states where occupied (see Fig. 2 for a schematic representation of the $d$-$d$ hybridizations in all cases under study). Thus now there are 9 and not 12 occupied states in the spin-down band and the SP rule is $M_t = Z_t - 18$ instead of $M_t = Z_t - 24$. When the X atom is Cr or Mn the energy position of the $d$-states of the Cr$^A$ (Mn$^A$) and Y atoms is much closer and the non-bonding spin-down $t_{1u}$ states are occupied like in usual full-Heuslers (see middle panel in Fig. 2), and the SP rule for them is the $M_t = Z_t - 24$ one. The case where X is V is more complex since the V is in between the Sc (Ti) and Cr (Mn) transition-metal elements. As a result no general rule can be deduced and the behavior of the total spin magnetic moment of the V$_2$YZ compounds is material specific, e.g. V$_2$MnAl follows the $M_t = Z_t - 18$ SP rule while V$_2$MnSi is close to the $M_t = Z_t - 24$ SP rule.

In Fig. 3 we present the total DOS for some selected cases and in Table I the calculated equilibrium lattice constant and the spin magnetic moments. In the case of the Sc- and Ti-based compounds the theoretical lattice constants exceed the 6 Å due to the large extension of the Sc and Ti $d$-wavefunctions while for the V-, Cr- and Mn-based compounds it is around 5.9 Å when Z = Al, around 5.8 Å when Z = As and around 5.7 Å when Z = Si. The total spin magnetic moment varies from almost $-4 \mu_B$ for Sc$_2$VAI up to almost $4 \mu_B$ for Ti$_2$CuAl as shown in Fig. 3 for the Sc- and Ti-based alloys. In the case of the Sc-based compounds the Sc atoms carry small spin magnetic moments of around 0.5 $\mu_B$ and mainly the Y atoms carry the spin magnetic moment as shown in Table I for two selected cases: Sc$_2$CrAl and Sc$_2$MnAl. When we move to the Ti-based compounds, the Ti atoms contrary

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**FIG. 2.** (color online). Possible hybridizations between spin-down $d$-orbitals sitting at different sites in the case of the inverse X$_2$YZ Heusler compounds. The names of the orbitals and the superscripts follow the nomenclature discussed in the text; the coefficient represents the degeneracy of each orbital. Note that in the spin-down band structure, there are also one $s$ and three $p$ occupied states due to the Z atom. With black color we denote the $3x_2g$ orbitals, red the $2x_e$, blue the $2x_e$ and green the $3x_e$ ones.

**FIG. 3.** (color online). Total density of states (DOS) per formula unit, which coincides with the per unit cell value, for some selected compounds under study. Positive (negative) DOS values correspond to the spin-up (spin-down) states. We plot the DOS so that the half-metallic gap is located in the spin-down band structure. The zero of the energy axis corresponds to the Fermi level.
to the Sc ones can carry significant spin moment which can even reach a value of almost 2 \( \mu_B \) in Ti2NiAl. This is due to the larger number of valence electrons of the Ti atoms. In the case of the V-(Cr- or Mn-) based alloys all X transition metal atoms possess significant values of spin magnetic moments. Concerning the atoms at the Y sites: when \( Y = V \), Cr or Mn they carry spin moments with absolute values larger than 2 \( \mu_B \) when \( Y = Ni \) the Ni-spin moment is close to zero, and when \( Y = Fe \) or Co the absolute value of the Fe \((Co)\) spin magnetic moment can vary from 0 to \( \sim 1 \) depending on the material. The Z atoms carry negligible spin magnetic moments. The relative orientation of the spin magnetic moments is in most cases dictated by the Bethe-Slater curve which states that most transition metal atoms tend to have parallel spin magnetic moments with the exception of Mn and Cr which tend to have antiparallel spin magnetic moment with respect to their nearest neighbors.

Finally, we would like to dwell on the compounds where the Y atom is Zn or Cu. Similar compounds have been previously studied using first-principles calculations. It has been suggested in Ref. 47 that they should be a variant of the SP rule: \( M_t = Z_t - 28 \). Among the \((X = Sc, Ti \text{ or } V)\) studied compounds in this work, only Ti2CuAl showed a behavior close to half-metallicity. In this case the compound is close to the \( M_t = Z_t - 18 \) line, as shown in Fig. 1 and the same arguments stand as for the Sc- and Ti-based inverse Heuslers discussed above. In the case of the Cr \((Mn)\)-based alloys half-metallicity was accompanied in all cases by a \( M_t = Z_t - 28 \) SP behavior of the total spin magnetic moment. The Cu \((Zn)\) atoms have all their 3d-states occupied and they form a narrow band below the energy window shown in Fig. 3 for the Cr2ZnSi and Mn2ZnSi compounds. As a result also their atom-resolved spin magnetic moments in Table I are close to zero. Thus relevant for the discussion of the half-metallic gap shown in their DOS is only the interaction between the Cr \((Mn)\) atoms sitting at the A and B nearest neighboring sites. The d-orbitals Cr\(^{A}\) \((Mn^{A}\) hybridize with the d-orbitals of the Cr\(^{B}\) \((Mn^{B}\) atoms forming 5 occupied d-hybrids in the spin-down band and five unoccupied d-hybrids (see right panel in Fig. 3 for a schematic representation of the d-d hybridization scheme). This behavior is similar to the semi-Heuslers discussed above. Thus in total in the spin-down band we have 14 occupied states: the 5 d-states of Cu \((Zn)\), the one s- and three p-states created by the Z atom and the five Cr\(^A\)-Cr\(^B\) \((Mn^{A}\)-Mn\(^B\) bonding d-hybrids. This explains the \( M_t = Z_t - 28 \) SP rule for these compounds. Finally, we have to note in the DOS presented for Cr2ZnSi in Fig. 3 that in the spin-up band we do have a metallic behavior as in usual half-metals but the conduction and the valence bands touch each other creating a zero-width gap. Such compounds are known as spin gapless semiconductors and they form a special category of half-metals.

There is experimental evidence for such behavior in the inverse Mn2CoAl. Among our studied alloys we have identified six such compounds but the results will be presented in detail elsewhere since such a study exceeds the scope of the present Communication.

In conclusion, we have presented extensive first-principles calculations on the inverse full-Heusler compounds having the chemical formula \( X_2YZ \) where \((X = Sc, Ti, V, Cr \text{ or } Mn), (Z = Al, Si \text{ or } As)\) and the Y ranges from Ti to Zn. Several of these alloys were identified to be half-metallic magnets. We have shown that the appearance of half-metallicity is associated in all cases to a SP behavior of the total spin-magnetic moment. When \( X = Sc \) or Ti, the total spin magnetic moment per formula unit (or unit cell) in \( \mu_B \) follows the rule \( M_t = Z_t - 18 \) where \( Z_t \) is the total number of valence electrons in the unit cell. When \( X = Cr \text{ or } Mn \), the variant followed by \( M_t \) is \( M_t = Z_t - 24 \), and when \( X = V \) the form of the SP rule is material specific. Both forms of the SP rule have been explained based on simple hybridization arguments of the transition metal d-orbitals. Finally we have shown that when \( X = Cr \text{ or } Mn \) and \( Y = Cu \text{ or } Zn \), the half-metallic compounds follow a \( M_t = Z_t - 28 \) rule due to the fully-occupied Cu \((Zn)\) d-orbitals. In the case of semi- and \( L2_1 \) full-Heusler compounds the formulation of the SP rules offered a theoretical basis on which the experimental design of novel materials took place. We expect that our study and the formulation of simple rules connecting the electronic and magnetic properties also in the case of the inverse full-Heusler compounds will strengthen the interest on half-metallic magnets for spintronics and magnetoelectronics applications offering to experimentalists a more extended theoretical basis for the design of novel half-metallic compounds.

### Table I

For selected compounds we present the calculated equilibrium lattice constant (2nd column), and the atomic and total spin magnetic moments (in \( \mu_B \)) (3rd-7th columns). We use the symbols A and B to denote the two early transition metal atoms sitting at different sites (see text for explanation). Note that the total spin magnetic moment is given per unit cell. \( Z_t \) is the total number of valence electrons in the unit cell and the last column presents the form of the SP rule obeyed by the compound.

| \( X_2YZ \) | \( a(\AA) \) | \( m^X(A) \) | \( m^X(B) \) | \( m^Y \) | \( m^Z \) | \( m^t \) | \( Z_t \) | SP |
|-----------------|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sc2CrAl        | 6.08     | 0.38            | -0.02           | -3.57           | 0.21            | -3              | 15              | Zr=18           |
| Sc2MnAl        | 5.58     | 0.59            | 0.34            | -3.04           | 0.11            | -2              | 16              | Zr=18           |
| Ti2FeAl        | 6.14     | 1.21            | 0.84            | -1.02           | -0.02           | +1              | 19              | Zr=18           |
| Ti2CoAl        | 6.14     | 1.50            | 0.80            | -0.23           | -0.07           | +2              | 20              | Zr=18           |
| Ti2NiAl        | 6.20     | 1.84            | 1.15            | 0.10            | -0.08           | +3              | 21              | Zr=18           |
| V2MnAl         | 5.94     | 1.54            | 0.80            | -0.23           | -0.07           | +2              | 20              | Zr=18           |
| V2CoAl         | 5.92     | -1.77           | 0.28            | -0.54           | 0.03            | -2              | 22              | Zr=24           |
| Cr2CrAl        | 5.92     | -2.47           | 1.89            | -2.47           | 1.89            | -2              | 22              | Zr=24           |
| Mn2CrAl        | 5.85     | -1.68           | 2.81            | -2.23           | 0.09            | -1              | 23              | Zr=24           |
| Mn2MnAl        | 5.78     | -1.51           | 2.70            | -1.51           | 0.06            | 0               | 24              | Zr=24           |
| Mn2FeAl        | 5.74     | -1.85           | 2.81            | -0.05           | -0.01           | +1              | 25              | Zr=24           |
| Mn2CoAs        | 5.74     | -0.04           | 3.04            | 0.98            | 0.02            | +4              | 28              | Zr=24           |
| Cr2ZnSi        | 5.85     | -1.89           | 1.93            | 0.01            | -0.05           | 0               | 28              | Zr=28           |
| Mn2CuSi        | 5.75     | -1.92           | 2.91            | -0.01           | 0.01            | +1              | 29              | Zr=28           |
| Mn2ZnSi        | 5.78     | -0.80           | 2.77            | 0.01            | 0.02            | +2              | 30              | Zr=28           |
