

## 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 compounds are identified to be half-metallic magnets. We show that the appearance of half-metallicity is associated in all cases with a Slater-Pauling behavior of the total spin-magnetic moment. There are three different variants of this rule for the inverse Heusler compounds 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 in these types of half-metallic Heusler compounds.

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### I. INTRODUCTION

The rise of nanotechnology and nanoscience during the last decade brought to the center of scientific research new phenomena and materials. Spintronics and magnetoelectronics compose one of the most rapidly expanding field in nanoscience.<sup>1</sup> Half-metallic magnetic compounds play a crucial role in this development.<sup>2</sup> 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.<sup>3,4</sup> The possibility of creating 100% spin-polarized current has triggered the interest on such compounds.<sup>5</sup> de Groot and collaborators in 1983 have initially suggested based on electronic structure calculations that NiMnSb, a semi-Heusler compound, is a half-metal<sup>6</sup> and since then several half-metallic compounds have been discovered.<sup>7</sup> Several aspects concerning the implementation of half-metallic compounds in realistic devices, like tunneling magnetic junctions or giant magnetoresistive junctions and spin-injectors, have been discussed in literature.<sup>8–10</sup>

The family of Heusler compounds incorporates more than 1000 members almost all crystalizing in a close-packed cubic structure similar to the binary semiconductors.<sup>11</sup> Most of them are metals exhibiting diverse magnetic phenomena. The lattice is a fcc with four equidistant sites as basis along the diagonal of the unit cell.<sup>3</sup> There are two families of Heusler compounds. 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 an  $sp$ -element and the structure is known as the  $C1_b$  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  $L2_1$  one with prototype  $\text{Cu}_2\text{MnAl}$ .<sup>12</sup> When the valence of the  $Y$  elements is the largest, the compounds crystallize in the so-called  $XA$  structure, where the sequence of the atoms is  $X$ - $X$ - $Y$ - $Z$  and the prototype is  $\text{Hg}_2\text{TiCu}$ .<sup>12</sup> The latter compounds are also known as inverse Heusler compounds. Several inverse Heuslers have been studied using first-principles electronic structure calculations

in literature.<sup>12–19</sup> In all cases the  $XA$  structure is energetically preferred to the  $L2_1$  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 Co-doped  $\text{Mn}_3\text{Ga}$  samples,<sup>20–23</sup> 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.<sup>24</sup> 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  $\text{Cr}_2\text{CoGa}$ .<sup>25</sup>

### II. MOTIVATION AND CALCULATIONAL DETAILS

Slater and Pauling showed in two pioneering papers that in the case of binary magnetic compounds, when we add one valence electron in the compound this occupies spin-down states only and the total spin magnetic moment decreases by about  $1\mu_B$ .<sup>26,27</sup> Interestingly, a similar behavior can also be found in half-metallic Heusler compounds, where the extra valence electron now occupies spin-up states increasing the total spin magnetic moment by about  $1\mu_B$ . It was shown that in the case of the semi-Heusler compounds such as 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  $M_t = Z_t - 18$ ,<sup>28</sup> while in the case of the  $L2_1$  full-Heuslers this relation becomes  $M_t = Z_t - 24$ .<sup>29</sup> These Slater-Pauling (SP) rules connect the electronic properties (the 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 quinary half-metallic Heusler compounds obey the SP rule,<sup>30–32</sup> and a generalized version exists when we pass from a half-metallic semi-Heusler to a half-metallic full-Heusler compound.<sup>33</sup> The aim of the present work is to exploit whether a generalized version of the SP rule can also be extracted for the inverse half-metallic full-Heusler compounds where all sites obey the tetrahedral symmetry. Such a relation would offer an extra strong tool in the study of half-metallic magnets.

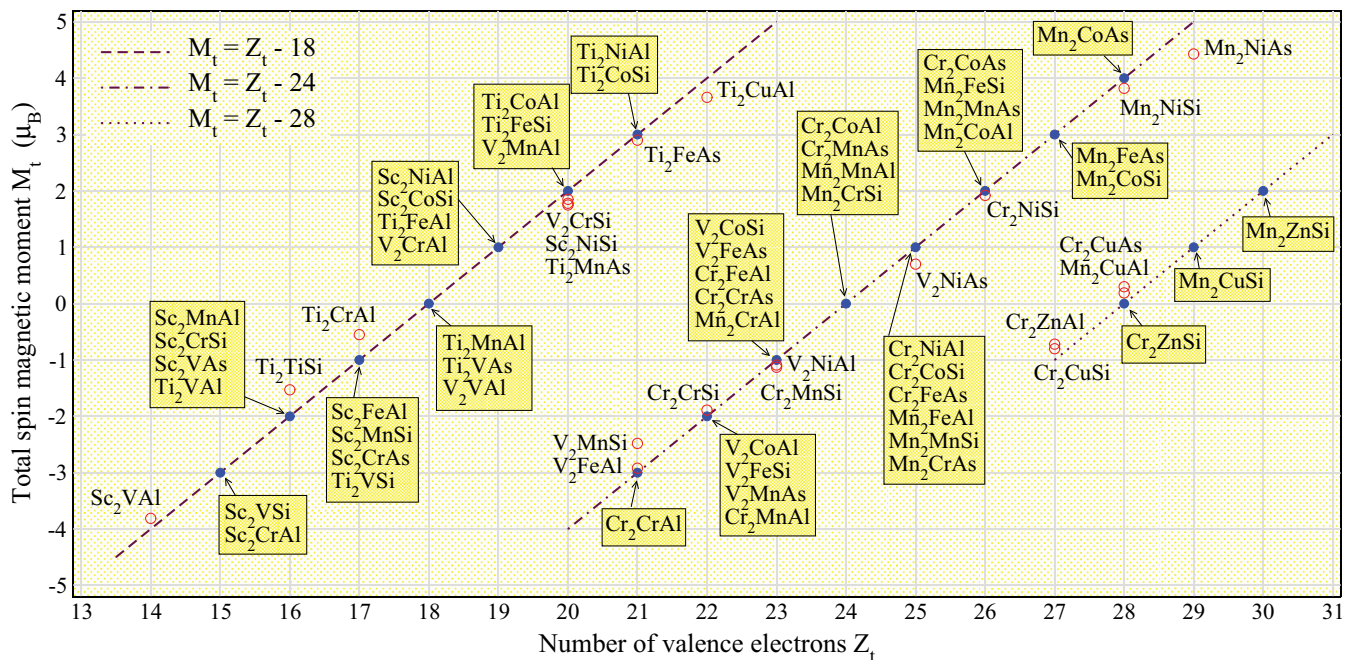


FIG. 1. (Color online) Total spin magnetic moments per unit cell (in  $\mu_B$ ) as a function of the total number of valence electrons in the unit cell for several compounds under study. The lines represent the three different forms of the Slater-Pauling rule. The compounds within the shaded frames (blue filled circles) follow one of these rules and are perfect half-metals; note that we have also included compounds with total spin magnetic moments only slightly deviating from the ideal integer values. The rest of the compounds in the figure (red hollow circles) still possess an energy gap in the spin-down band, but the Fermi level does not fall within or at the edges of the gap. Notice that the sign of the spin magnetic moments has been chosen so that the half-metallic gap is in the spin-down band.

For our calculations we used the full-potential nonorthogonal local-orbital minimum-basis band-structure scheme (FPLO)<sup>34</sup> within the generalized gradient approximation (GGA)<sup>35</sup> to study the electronic and magnetic properties of all the inverse  $X_2YZ$  compounds, where  $X = \text{Sc, Ti, V, Cr, or Mn}$ ;  $Y$  is a transition-metal atom ranging from Ti to Zn; and  $Z = \text{Al, Si, or As}$ . First, we determined the equilibrium lattice constants using total energy calculations and a dense  $20 \times 20 \times 20$   $\mathbf{k}$ -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  $X^A$  atom has the same local environment in the crystal as the  $Y$  atom.

### III. RESULTS AND DISCUSSION

In Fig. 1, we have plotted the total spin magnetic moment versus the total number of valence electrons in the unit cell considering in all cases that the half-metallic gap in the density of states (DOS) is located in the spin-down band. The compounds within the shaded frame (denoted with the blue filled circles) are either perfect half-metals or the Fermi level falls at the edge of the spin-down gap and the total spin magnetic moments deviate slightly from the ideal integer values. The latter compounds exhibit an almost 100% spin-polarization at the Fermi level, and a very small expansion or contraction of the lattice should shift the Fermi level within the energy gap.<sup>28</sup> When the

total spin magnetic moment is less than the ideal integer value, the Fermi level crosses the spin-down conduction band and a small expansion of the lattice would restore half-metallicity.<sup>28</sup> In contrast, when the total spin magnetic is slightly larger than the ideal integer value, the Fermi level crosses the spin-down valence band and a small contraction would shift the Fermi level in the spin-down energy gap.<sup>28</sup> The compounds in Fig. 1 with the red hollow circles also have a spin-down energy gap, but the Fermi level is well above or below the energy gap and their total spin magnetic moment per unit cell shows a sizable deviation from the ideal integer values, as shown in Tables I, II, and III. For these compounds, a large expansion or contraction is needed to restore half-metallicity, which is unlikely to occur.<sup>28</sup> Finally, there are several compounds which have been studied, as discussed in the preceding section, and which are not included in Fig. 1. These compounds are either semiconductors (case of the zero total spin magnetic moment) or usual metals in the rest of the cases (some of them are also magnetic metals). Since they are not relevant to the discussion of our article, we do not present them here. The reason for the various ground states of the inverse Heusler compounds is the minimization of the total energy as discussed in Ref. 36. When the Stoner theorem is fulfilled, they prefer to be magnetic and in most cases the half-metallicity stabilizes the magnetic behavior.<sup>37</sup>

In Fig. 1, for the cases of negative total spin magnetic moments, the spin-up are the minority and the spin-down the majority states, while in the case of positive total spin magnetic moments the opposite occurs. Our results can be grouped along three lines representing three variants of the SP rule.

TABLE I. For the compounds in Fig. 1 following the  $M_t = Z_t - 18$  rule, we present the calculated equilibrium lattice constant (second column), and the atomic and total spin magnetic moments (in  $\mu_B$ ) (third through seventh 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 and that  $Z_t$  is the total number of valence electrons in the unit cell. The ideal total spin magnetic moment associated with the perfect half-metals is just the total number of valence electrons,  $Z_t$ , minus 18. Notice that in some cases the atom-resolved spin magnetic moments do not sum to the total spin magnetic moment since we have used a two-digit accuracy after the decimal point.

$X_2YZ$	$a$ (Å)	$M_t = Z_t - 18$					$Z_t$
		$m^{X(A)}$	$m^{X(B)}$	$m^Y$	$m^Z$	$m^t$	
Sc <sub>2</sub> VAl	6.75	-0.22	-0.70	-3.07	0.19	-3.81	14
Sc <sub>2</sub> CrAl	6.68	0.38	-0.02	-3.57	0.21	-3.00	15
Sc <sub>2</sub> MnAl	6.58	0.59	0.34	-3.04	0.11	-2.00	16
Sc <sub>2</sub> FeAl	6.47	0.35	0.33	-1.64	0.03	-0.93	17
Sc <sub>2</sub> NiAl	6.50	0.58	0.29	0.09	0.01	+0.96	19
Sc <sub>2</sub> VSi	6.54	0.01	-0.59	-2.62	0.20	-3.00	15
Sc <sub>2</sub> CrSi	6.44	0.51	0.09	-2.74	0.15	-2.00	16
Sc <sub>2</sub> MnSi	6.36	0.64	0.61	-2.31	0.06	-1.00	17
Sc <sub>2</sub> CoSi	6.29	0.56	0.19	0.21	0.04	+1.00	19
Sc <sub>2</sub> NiSi	6.37	0.93	0.59	0.18	0.06	+1.77	20
Sc <sub>2</sub> VAs	6.55	0.33	-0.36	-2.16	0.13	-2.06	16
Sc <sub>2</sub> CrAs	6.49	0.84	0.67	-2.62	0.06	-1.06	17
Ti <sub>2</sub> VAl	6.34	0.40	-0.73	-1.72	0.09	-1.96	16
Ti <sub>2</sub> CrAl	6.33	-0.14	-0.42	0.00	0.01	-0.55	17
Ti <sub>2</sub> MnAl	6.24	1.44	1.30	-2.74	-0.01	0.00	18
Ti <sub>2</sub> FeAl	6.14	1.21	0.84	-1.02	-0.02	+1.00	19
Ti <sub>2</sub> CoAl	6.14	1.50	0.80	-0.23	-0.07	+2.00	20
Ti <sub>2</sub> NiAl	6.20	1.84	1.15	0.10	-0.08	+3.00	21
Ti <sub>2</sub> CuAl	6.32	1.96	1.70	0.05	-0.06	+3.66	22
Ti <sub>2</sub> TiSi	6.29	-0.25	-1.12	-0.25	0.08	-1.53	16
Ti <sub>2</sub> VSi	6.18	0.65	-0.03	-1.65	0.04	-1.00	17
Ti <sub>2</sub> FeSi	6.00	1.46	0.66	-0.10	-0.02	+2.00	20
Ti <sub>2</sub> CoSi	6.03	1.80	0.86	0.35	-0.02	+3.00	21
Ti <sub>2</sub> VAs	6.23	1.31	0.53	-1.86	0.01	0.00	18
Ti <sub>2</sub> MnAs	6.08	1.36	0.48	-0.03	-0.05	+1.76	20
Ti <sub>2</sub> FeAs	6.08	1.69	0.48	0.80	-0.06	+2.90	21
V <sub>2</sub> VAl	6.09	1.64	0.00	-1.64	0.00	0.00	18
V <sub>2</sub> CrAl	5.98	0.65	-0.37	0.77	-0.05	+1.00	19
V <sub>2</sub> MnAl	5.94	1.54	-0.41	0.94	-0.07	+2.00	20

Along the  $M_t = Z_t - 18$  line we find the Sc- and Ti-based compounds, along the  $M_t = Z_t - 24$  line the compounds with  $X = \text{Cr}$  or  $\text{Mn}$ , and finally along the  $M_t = Z_t - 28$  line the compounds where  $Y$  is  $\text{Cu}$  or  $\text{Zn}$ . The compounds with  $X = \text{V}$  are dispersed between the first two lines. A very interesting consequence of the SP rules are the Heusler compounds with a zero value of their total spin magnetic moment which are made of magnetic constituents and which 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).<sup>38-40</sup>

Prior to the discussion of the SP rules in the inverse Heusler compounds, we should briefly discuss the origin of the rule in the half-metallic  $L2_1$  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-degenerate  $s$  and a triple-degenerate  $p$  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 compounds with respect to the semi-Heuslers, one has first to consider the interaction between the  $X$  elements. Although the symmetry of the  $L2_1$  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.<sup>29</sup> The  $d$  orbitals of the neighboring  $X$  atoms hybridize creating five bonding  $d$  states, which then hybridize with the  $d$  orbitals of the  $Y$  atoms creating five occupied and five unoccupied  $d$  hybrids, and five nonbonding  $d$  hybrids of octahedral symmetry (the triple-degenerate  $t_{1u}$  and double-degenerate  $e_u$  states). These nonbonding hybrids cannot couple with the orbitals of the neighboring atoms, since they do not obey the tetrahedral symmetry, and only the  $t_{1u}$  are occupied leading to a total of 12 occupied spin-down states.<sup>29</sup> In the case of semi-Heuslers, such as  $\text{NiMnSb}$ , the situation is simpler. The  $d$  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.<sup>28</sup> As a result, there are in total exactly nine occupied



TABLE II. Same as Table I for the compounds following the  $M_t = Z_t - 24$  relation.

$X_2YZ$	$M_t = Z_t - 24$						$Z_t$
	$a$ (Å)	$m^{X(A)}$	$m^{X(B)}$	$m^Y$	$m^Z$	$m^t$	
V <sub>2</sub> FeAl	5.93	-2.11	0.31	-1.20	0.09	-2.92	21
V <sub>2</sub> CoAl	5.92	-1.77	0.28	-0.54	0.03	-2.00	22
V <sub>2</sub> NiAl	5.95	-1.22	0.26	-0.11	-0.01	-1.09	23
V <sub>2</sub> MnSi	5.83	-1.73	0.50	-1.27	0.06	-2.48	21
V <sub>2</sub> FeSi	5.80	-1.55	0.45	-0.93	0.05	-1.99	22
V <sub>2</sub> CoSi	5.79	-0.86	0.24	-0.38	0.01	-1.00	23
V <sub>2</sub> MnAs	5.89	-1.41	0.73	-1.35	0.08	-1.95	22
V <sub>2</sub> FeAs	5.86	-0.76	0.40	-0.67	0.03	-1.00	23
V <sub>2</sub> NiAs	5.93	-0.35	0.76	0.27	0.01	+0.70	25
Cr <sub>2</sub> CrAl	5.92	-2.47	1.89	-2.47	0.12	-2.93	21
Cr <sub>2</sub> MnAl	5.82	-2.00	1.66	-1.75	0.09	-2.00	22
Cr <sub>2</sub> FeAl	5.77	-1.64	1.32	-0.73	0.04	-1.01	23
Cr <sub>2</sub> CoAl	5.80	-2.10	1.87	0.30	-0.05	+0.01	24
Cr <sub>2</sub> NiAl	5.78	-1.66	2.26	0.42	-0.03	+1.00	25
Cr <sub>2</sub> CrSi	5.74	-1.56	1.16	-1.56	0.07	-1.89	22
Cr <sub>2</sub> MnSi	5.65	-1.02	0.72	-0.88	0.04	-1.13	23
Cr <sub>2</sub> CoSi	5.67	-1.11	1.61	0.54	-0.04	+1.06	25
Cr <sub>2</sub> FeSi	5.75	-1.05	2.44	0.54	-0.00	+1.92	26
Cr <sub>2</sub> CrAs	5.86	-1.64	2.19	-1.64	0.11	-0.98	23
Cr <sub>2</sub> MnAs	5.79	-1.25	2.09	-0.89	0.06	+0.01	24
Cr <sub>2</sub> FeAs	5.77	-1.08	2.11	-0.04	0.02	+1.01	25
Cr <sub>2</sub> CoAs	5.80	-1.34	2.46	0.88	0.01	+2.01	26
Mn <sub>2</sub> CrAl	5.85	-1.68	2.81	-2.23	0.09	-1.00	23
Mn <sub>2</sub> MnAl	5.78	-1.41	2.75	-1.41	0.06	0.00	24
Mn <sub>2</sub> FeAl	5.74	-1.85	2.81	0.05	-0.01	+1.00	25
Mn <sub>2</sub> CoAl	5.73	-1.65	2.80	0.94	-0.08	+2.00	26
Mn <sub>2</sub> CrSi	5.72	-1.09	2.86	-1.85	0.10	+0.02	24
Mn <sub>2</sub> MnSi	5.64	-0.88	2.71	-0.88	0.06	+1.01	25
Mn <sub>2</sub> FeSi	5.60	-0.78	2.48	0.33	-0.02	+2.01	26
Mn <sub>2</sub> CoSi	5.62	-0.59	2.79	0.83	-0.02	+3.01	27
Mn <sub>2</sub> NiSi	5.66	0.46	2.94	0.44	-0.03	+3.82	28
Mn <sub>2</sub> CrAs	5.67	-0.60	2.73	-1.17	0.09	+1.05	25
Mn <sub>2</sub> MnAs	5.71	-0.35	2.68	-0.35	0.04	+2.01	26
Mn <sub>2</sub> FeAs	5.68	-0.66	2.84	0.81	0.01	+3.00	27
Mn <sub>2</sub> CoAs	5.74	-0.04	3.04	0.98	0.02	+4.00	28
Mn <sub>2</sub> NiAs	5.80	0.74	3.20	0.46	0.03	+4.43	29

spin-down states and the SP relation is  $M_t = Z_t - 18$ .<sup>28</sup> For the half-metallic semi-Heuslers, the Fermi level is fixed within the spin-down energy gap. When the total spin magnetic moment is positive and there are more than 18 valence electrons in the unit cell, in the spin-up band structure all nine

bonding  $s$ ,  $p$ , and  $d$  states are occupied, as in the spin-down band, and the extra charge occupies the antibonding spin-up states.<sup>28</sup> When the number of valence electrons is less than 18, then the Fermi level crosses the spin-up bonding  $d$  states. In the case of full-Heusler compounds when  $Z_t > 24$ , the spin-up

TABLE III. Same as Table I for the compounds following the  $M_t = Z_t - 28$  relation.

$X_2YZ$	$M_t = Z_t - 28$						$Z_t$
	$a$ (Å)	$m^{X(A)}$	$m^{X(B)}$	$m^Y$	$m^Z$	$m^t$	
Cr <sub>2</sub> ZnAl	6.00	2.20	-2.89	-0.01	-0.02	-0.72	27
Cr <sub>2</sub> CuSi	5.79	1.58	-2.32	-0.05	-0.01	-0.80	27
Cr <sub>2</sub> ZnSi	5.85	1.89	-1.93	-0.01	0.05	0.00	28
Cr <sub>2</sub> CuAs	6.04	-3.05	3.32	0.03	0.00	+0.30	28
Mn <sub>2</sub> CuAl	5.87	-2.75	2.93	0.02	-0.05	+0.15	28
Mn <sub>2</sub> CuSi	5.75	-1.92	2.91	-0.01	0.01	+1.00	29
Mn <sub>2</sub> ZnSi	5.78	-0.80	2.77	0.01	0.02	+2.00	30

nonbonding  $e_u$  states are the first to be occupied followed by the antibonding states, while when  $Z_t < 24$  the Fermi level crosses either the spin-up nonbonding  $t_{1u}$  states or the spin-up bonding  $d$  states.<sup>29</sup>

All half-metallic Sc- and Ti-based compounds 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<sup>A</sup> (Ti<sup>A</sup>) 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 nonbonding ones. The five Sc<sup>A</sup>-Y (Ti<sup>A</sup>-Y) bonding  $d$  hybrids in their turn hybridize with the  $d$  orbitals of the Sc<sup>B</sup> (Ti<sup>B</sup>) atoms, creating again bonding and antibonding states. The difference with the  $L2_1$  full-Heuslers is that the Sc<sup>A</sup> (Ti<sup>A</sup>) and Y atoms have a large energy separation of their  $d$  orbitals, and as a result the five Sc<sup>A</sup>-Y (Ti<sup>A</sup>-Y) nonbonding  $d$  hybrids, the  $t_{1u}$  states, and the  $e_u$  states are very high in energy and they are empty, while in the usual  $L2_1$  full-Heuslers the triple-degenerate  $t_{1u}$  states were 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<sup>A</sup> (Mn<sup>A</sup>) and Y atoms is much closer and the nonbonding spin-down  $t_{1u}$  states are occupied like in the usual full-Heuslers (see the middle panel in Fig. 2), and the SP rule for them is the  $M_t = Z_t - 24$  one. The case in which 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  $V_2YZ$  compounds is material-specific, e.g.,  $V_2MnAl$  follows the  $M_t = Z_t - 18$  SP rule while  $V_2MnSi$  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 Tables I, II, and III we have gathered the calculated equilibrium lattice constant and the spin magnetic moments for all compounds presented in Fig. 1. In the case of the Sc- and Ti-based compounds, the theoretical lattice constants exceed 6 Å, as shown in Table I, due to the large extension of the Sc and Ti  $d$ -wave functions, 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  $Sc_2VAl$  up to almost  $4\mu_B$  for  $Ti_2CuAl$ , as shown in Fig. 1 for the Sc- and Ti-based compounds. 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. When we move to the Ti-based compounds, the Ti atoms contrary to the Sc ones can carry significant spin moment, which can even reach a value of almost  $2\mu_B$  as in  $Ti_2NiAl$ . This is due to the larger number of valence electrons of the Ti atoms. In the case of the V- (Cr- or Mn-) based compounds, 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

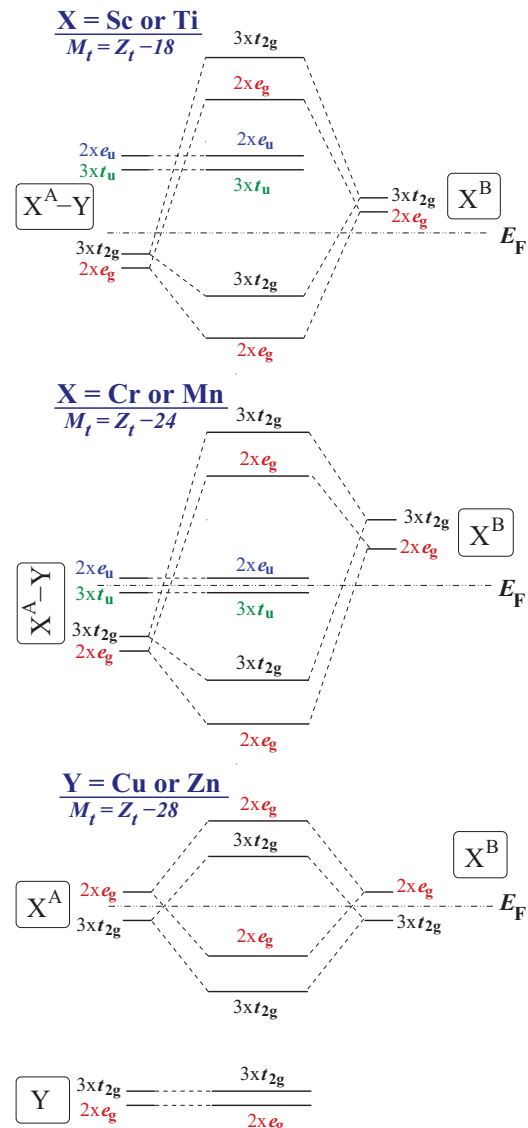


FIG. 2. (Color online) Possible hybridizations between spin-down  $d$  orbitals sitting at different sites in the case of the inverse  $X_2YZ$  Heusler compounds. The names of the orbitals and the superscripts follow the nomenclature discussed in the text; the coefficient represents the degeneracy of each orbital. Note that in the spin-down band structure, there are also deep in energy one  $s$  and three  $p$  occupied states due to the Z atom. With black we denote the  $3xt_{2g}$  orbitals, with red the  $2xe_g$ , with blue the  $2xe_u$  orbitals, and with green the  $3xt_{1u}$  orbitals.

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.<sup>41</sup>

Finally, we would like to dwell on the compounds in which the Y atom is Zn or Cu (see Table III). Similar compounds have been previously studied using first-principles calculations.<sup>42-46</sup> It has been suggested in Ref. 43 that there 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  $Ti_2CuAl$  showed a

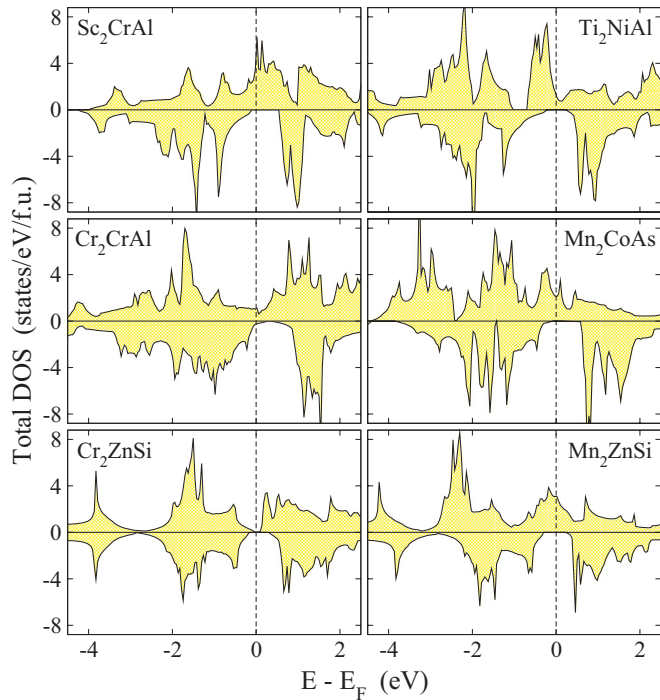


FIG. 3. (Color online) Total density of states (DOS) per formula unit, which coincides with the per unit cell value, for some selected compounds under study. Positive (negative) DOS values correspond to the spin-up (spin-down) states. We plot the DOS so that the half-metallic gap is located in the spin-down band structure. The zero of the energy axis corresponds to the Fermi level.

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 full-Heusler discussed above. In the case of the Cr (Mn) -based compounds, half-metallicity was accompanied in all cases by an  $M_t = Z_t - 28$  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  $\text{Cr}_2\text{ZnSi}$  and  $\text{Mn}_2\text{ZnSi}$  compounds. As a result, also their atom-resolved spin magnetic moments in Table III 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-neighbor sites. The  $d$  orbitals  $\text{Cr}^A$  ( $\text{Mn}^A$ ) hybridize with the  $d$  orbitals of the  $\text{Cr}^B$  ( $\text{Mn}^B$ ) atoms forming five occupied  $d$  hybrids in the spin-down band and five unoccupied  $d$  hybrids

(see the bottom panel in Fig. 2 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 five  $d$  states of Cu (Zn), the one  $s$  and three  $p$  states created by the Z atom, and the five  $\text{Cr}^A$ - $\text{Cr}^B$  ( $\text{Mn}^A$ - $\text{Mn}^B$ ) 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  $\text{Cr}_2\text{ZnSi}$  in Fig. 3 that in the spin-up band we do have a metallic behavior as in usual half-metals, but the conduction and 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.<sup>47</sup> There is experimental evidence for such behavior in the inverse  $\text{Mn}_2\text{CoAl}$ .<sup>48</sup> Among our studied compounds 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 article.<sup>49</sup>

#### IV. CONCLUSIONS

We have presented 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 compounds were identified to be half-metallic magnets. We have shown that the appearance of half-metallicity is associated in all cases with a SP behavior of the total spin-magnetic moment. When  $X$  is 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  $X = \text{Cr or Mn}$ , the variant followed by  $M_t$  is  $M_t = Z_t - 24$ , and when  $X = \text{V}$ , 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  $X$  is Cr or Mn and  $Y$  is Cu or Zn, the half-metallic compounds follow an  $M_t = Z_t - 28$  rule due to the fully occupied Cu (Zn)  $d$  states. 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 in half-metallic magnets for spintronics and magnetoelectronics applications, offering experimentalists a more extended theoretical basis for the design of novel half-metallic compounds.

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<sup>1</sup>I. Žutić, J. Fabian, and S. Das Sarma, *Rev. Mod. Phys.* **76**, 323 (2004).

<sup>2</sup>M. I. Katsnelson, V. Yu. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, *Rev. Mod. Phys.* **80**, 315 (2008).

<sup>3</sup>I. Galanakis, Ph. Mavropoulos, and P. H. Dederichs, *J. Phys. D* **39**, 765 (2006).

<sup>4</sup>I. Galanakis and Ph. Mavropoulos, *J. Phys.: Condens. Matter* **19**, 315213 (2007).

<sup>5</sup>C. Felser, G. H. Fecher, and B. Balke, *Angew. Chem. Int. Ed.* **46**, 668 (2007).

<sup>6</sup>R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* **50**, 2024 (1983).

<sup>7</sup>W. E. Pickett and H. Eschrig, *J. Phys.: Condens. Matter* **19**, 315203 (2007).

<sup>8</sup>S. Chadov, T. Graf, K. Chadova, X. Dai, F. Casper, G. H. Fecher, and C. Felser, *Phys. Rev. Lett.* **107**, 047202 (2011).

- <sup>9</sup>M. Ležaić, Ph. Mavropoulos, J. Enkovaara, G. Bihlmayer, and S. Blügel, *Phys. Rev. Lett.* **97**, 026404 (2006).
- <sup>10</sup>P. Mavropoulos, M. Ležaić, and S. Blügel, *Phys. Rev. B* **72**, 174428 (2005).
- <sup>11</sup>T. Graf, C. Felser, and S. S. P. Parkin, *Prog. Solid State Chem.* **39**, 1 (2011).
- <sup>12</sup>K. Özdoğan and I. Galanakis, *J. Magn. Magn. Mater.* **321**, L34 (2009).
- <sup>13</sup>G. D. Liu, X. F. Dai, H. Y. Liu, J. L. Chen, Y. X. Li, G. Xiao, and G. H. Wu, *Phys. Rev. B* **77**, 014424 (2008).
- <sup>14</sup>M. Meinert, J.-M. Schmalhorst, and G. Reiss, *J. Phys.: Condens. Matter* **23**, 116005 (2011).
- <sup>15</sup>H. Luo, Z. Zhu, L. Ma, S. Xu, X. Zhu, C. Jiang, H. Xu, and G. Wu, *J. Phys. D* **41**, 055010 (2008).
- <sup>16</sup>J. Li, H. Chen, Y. Li, Y. Xiao, and Z. Li, *J. Appl. Phys.* **105**, 083717 (2009).
- <sup>17</sup>B. Xu, M. Zhang, and H. Yan, *Phys. Status Solidi B* **248**, 2870 (2011).
- <sup>18</sup>M. Pugaczowa-Michalska, *Intermetallics* **24**, 128 (2012).
- <sup>19</sup>N. Kervan and S. Kervan, *J. Phys. Chem. Solid* **72**, 1358 (2011); *Solid State Commun.* **151**, 1162 (2011); *J. Magn. Magn. Mater.* **324**, 645 (2012); E. Bayar, N. Kervan, and S. Kervan, *ibid.* **323**, 2945 (2011).
- <sup>20</sup>J. Winterlik, G. H. Fecher, B. Balke, T. Graf, V. Alijani, V. Ksenofontov, C. A. Jenkins, O. Meshcheriakova, C. Felser, G. Liu, S. Ueda, K. Kobayashi, T. Nakamura, and M. Wojcik, *Phys. Rev. B* **83**, 174448 (2011).
- <sup>21</sup>M. Meinert, J. M. Schmalhorst, C. Klewe, G. Reiss, E. Arenholz, T. Bohnert, and K. Nielsch, *Phys. Rev. B* **84**, 132405 (2011).
- <sup>22</sup>P. Klaer, C. A. Jenkins, V. Alijani, J. Winterlik, B. Balke, C. Felser, and H. J. Elmers, *Appl. Phys. Lett.* **98**, 212510 (2011).
- <sup>23</sup>V. Alijani, J. Winterlik, G. H. Fecher, and C. Felser, *Appl. Phys. Lett.* **99**, 222510 (2012).
- <sup>24</sup>H. Luo, W. Zhu, L. Ma, G. Liu, Y. Li, X. Zhu, C. Jiang, H. Xu, and G. Wu, *J. Phys. D* **42**, 095001 (2009).
- <sup>25</sup>I. Galanakis and E. Şaşıoğlu, *Appl. Phys. Lett.* **99**, 052509 (2011).
- <sup>26</sup>J. C. Slater, *Phys. Rev.* **49**, 931 (1936).
- <sup>27</sup>L. Pauling, *Phys. Rev.* **54**, 899 (1938).
- <sup>28</sup>I. Galanakis, P. H. Dederichs, and N. Papanikolaou, *Phys. Rev. B* **66**, 134428 (2002).
- <sup>29</sup>I. Galanakis, P. H. Dederichs, and N. Papanikolaou, *Phys. Rev. B* **66**, 174429 (2002).
- <sup>30</sup>I. Galanakis, *J. Phys.: Condens. Matter* **16**, 3089 (2004).
- <sup>31</sup>K. Özdoğan, B. Aktaş, I. Galanakis, and E. Şaşıoğlu, *J. Appl. Phys.* **101**, 073910 (2007).
- <sup>32</sup>K. Özdoğan, E. Şaşıoğlu, and I. Galanakis, *J. Appl. Phys.* **103**, 023503 (2008).
- <sup>33</sup>I. Galanakis, K. Özdoğan, and E. Şaşıoğlu, *Phys. Rev. B* **86**, 134427 (2012).
- <sup>34</sup>K. Koepernik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999).
- <sup>35</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>36</sup>E. Şaşıoğlu, L. M. Sandratskii, P. Bruno, and I. Galanakis, *Phys. Rev. B* **72**, 184415 (2005).
- <sup>37</sup>I. Galanakis and E. Şaşıoğlu, *J. Appl. Phys.* **109**, 113912 (2011).
- <sup>38</sup>H. van Leuken and R. A. de Groot, *Phys. Rev. Lett.* **74**, 1171 (1995).
- <sup>39</sup>S. Wurmehl, H. C. Kandpal, G. H. Fecher, and C. Felser, *J. Phys.: Condens. Matter* **18**, 6171 (2006).
- <sup>40</sup>I. Galanakis, K. Özdoğan, E. Şaşıoğlu, and B. Aktaş, *Phys. Rev. B* **75**, 172405 (2007); **75**, 092407 (2007).
- <sup>41</sup>D. Jiles, *Introduction to Magnetism and Magnetic Materials* (Chapman & Hall, London, 1998).
- <sup>42</sup>H. Luo, G. Liu, F. Meng, L. Wang, E. Liu, W. Wu, X. Zhu, and G. Jiang, *Comput. Mater. Sci.* **50**, 3119 (2011).
- <sup>43</sup>H. Luo, F. Meng, H. Liu, J. Li E. Liu, G. Wu, X. Zhu, and C. Jiang, *J. Magn. Magn. Mater.* **324**, 2127 (2012).
- <sup>44</sup>X.-P. Wei, S.-B. Chu, G.-Y. Mao, H. Deng, T. Lei, and X.-R. Hu, *J. Magn. Magn. Mater.* **323**, 2295 (2011).
- <sup>45</sup>X.-P. Wei, J.-B. Deng, S.-B. Chu, G.-Y. Mao, T. Lei, and X.-R. Hu, *J. Magn. Magn. Mater.* **323**, 185 (2011).
- <sup>46</sup>W.-Z. Wang and X.-P. Wei, *Comput. Mater. Sci.* **50**, 2253 (2011).
- <sup>47</sup>X. L. Wang, *Phys. Rev. Lett.* **100**, 156404 (2008).
- <sup>48</sup>S. Ouardi, G. H. Fecher, C. Felser, and J. Kübler, *arXiv:1210.0148*.
- <sup>49</sup>S. Skaftouros, K. Özdoğan, E. Şaşıoğlu, and I. Galanakis, *Appl. Phys. Lett.* **102**, 022402 (2013).