Ab initio design of half-metallic fully compensated ferrimagnets: The case of Cr_2MnZ (Z=P, As, Sb, and Bi)

I. Galanakis,[1,*] K. Özdoğan,[2,†] E. Şaşıoğlu,[3,4,‡] and B. Aktaş[2]
[1]*Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece*
[2]*Department of Physics, Gebze Institute of Technology, Gebze, 41400 Kocaeli, Turkey*
[3]*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[4]*Physics Department, Fatih University, 34500 Büyükçekmece, İstanbul, Turkey*
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Electronic structure calculations from first principles are employed to design half-metallic fully compensated ferrimagnets (or, as they are widely known, half-metallic antiferromagnets) susceptible of finding applications in spintronics. Cr_2MnZ (Z=P,As,Sb,Bi) compounds have 24 valence electrons per unit cell and calculations show that their total spin moment is approximately zero for a wide range of lattice constants, in agreement with the Slater-Pauling behavior for ideal half-metals. Simultaneously, the spin magnetic moments of Cr and Mn atoms are antiparallel and the compounds are ferrimagnets. Mean-field approximation is employed to estimate their Curie temperature, which exceeds room temperature for the alloy with Sb. Our findings suggest that Cr_2MnSb is the compound of choice for further experimental investigations.

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I. INTRODUCTION

In the last decade, a new field has evolved in solid-state physics focusing on the design of materials for spintronic applications.[1] First-principles electronic structure calculations have played a key role since several alloys for such applications have been initially predicted before their synthesis and their integration in realistic devices. Among these materials, the most promising ones are the so-called half-metals; magnetic materials which are normal metals for one spin direction and semiconductors for the other and thus electrons near the Fermi level are of a unique spin character.[2,3] The first predicted half-metal was the ferromagnetic Heusler alloy NiMnSb.[4]

The research on half-metallic ferromagnetic Heusler alloys is intense and several such alloys have been predicted.[5,6] An interesting case is also the half-metallic ferrimagnets; compounds where the different transition-metal atoms in the unit cell have antiparallel magnetic spin moments. Examples of such alloys are FeMnSb (Refs. 5 and 7) and Mn_2VAl.[8–11] All these half-metals exhibit the so-called Slater-Pauling behavior and the total spin moment in the unit cell is given as a simple function of the number of valence electrons. In the case of full-Heusler alloys having the chemical formula X_2YZ, this rule takes the form $M_t=Z_t-24$.[6] M_t is the total spin moment in the unit cell in μ_B and Z_t the total number of valence electrons. The number "24" comes from the fact that there are exactly 12 occupied electronic states in the semiconducting band. Thus, magnetic alloys with exactly 24 valence electrons should have exactly zero total spin moment. Such a compound would be perfectly suited for applications due to the negligible external magnetic field which it would create. The 24-valence electron compounds are known as half-metallic antiferromagnets, but their correct definition is "half-metallic (HM) fully compensated ferrimagnets (FCFs)"[12] and this is the reason why the characteristic temperature for these alloys is the Curie temperature and not the Néel temperature as in usual antiferromagnets. In the class of HM-FCFs, alloys belong to the hypothetical Heusler MnCrSb (Ref. 12) and Mn_3Ga (Ref. 13) compounds which have not yet been synthesized. Another root toward HM-FCF is the doping of diluted magnetic semiconductors[14] and inclusion of Co defects in Mn_2VAl and Mn_2VSi alloys; Co atoms substitute Mn ones having antiparallel moments between them.[15,16]

In this Brief Report, we will study the appearance of stable half-metallic FCF in the case of the Cr_2MnZ alloys, where Z is P, As, Sb, or Bi, which all correspond to a total of 24 valence electrons. Cr and Mn atoms in these alloys have antiparallel spin moments and the compounds show a gap in the spin-up band (we have chosen it so that Cr atoms have positive spin moments and Mn atoms negative spin moments). These alloys keep the HM character for a wide range of lattice constants and the Fermi level behaves upon compression or expansion of the lattice similar to a rigid-band model. For the calculations, we employed the full-potential nonorthogonal local-orbital minimum-basis band-structure scheme within the local spin-density approximation to the density functional.[17] We should also note that we have used the scalar-relativistic formulation and thus the spin-orbit coupling was not taken into account. This is expected to play a crucial role only in the case of the compound containing Bi where the image of the spin-down states in the spin-up band is not negligible as for the other lighter chemical elements.[18]

Finally, we apply the augmented spherical wave (ASW) method[19] in conjunction with the frozen-magnon approach[20] to calculate the interatomic exchange interactions which are used to estimate the Curie temperature of the Cr_2MnZ compounds within the multisublattice mean-field approximation already employed in the case of other Heusler alloys (see Refs. 11 and 21).

II. RESULTS AND DISCUSSION

Since we want the Cr_2MnZ compounds to have exactly 24 electrons, we choose Z to be one of the isovalent P, As, Sb, or

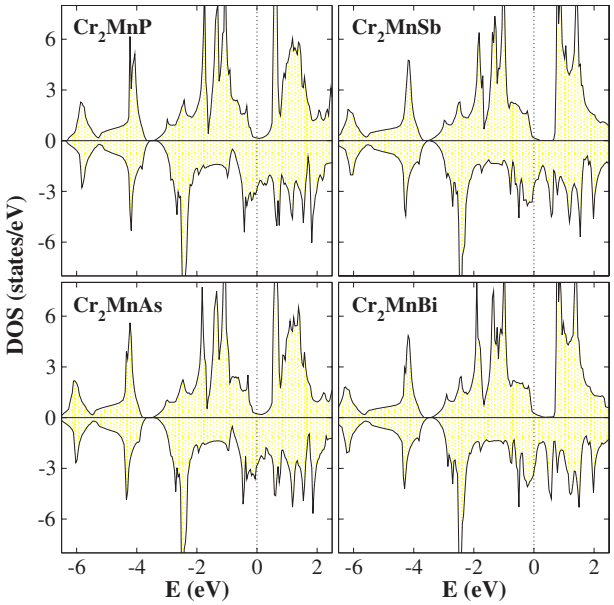

FIG. 1. (Color online) Total density of states (DOS) for the four compounds under study and for a lattice constant of 6.2 Å. All four alloys are almost half-metals. Positive values of DOS correspond to spin-up electrons and negative values to spin-down electrons. The energy scale is such that the zero energy corresponds to the energy of the Fermi level. We have chosen to present the gap in the spin-up band so that Cr atoms have positive spin moments and Mn atoms negative spin moments.

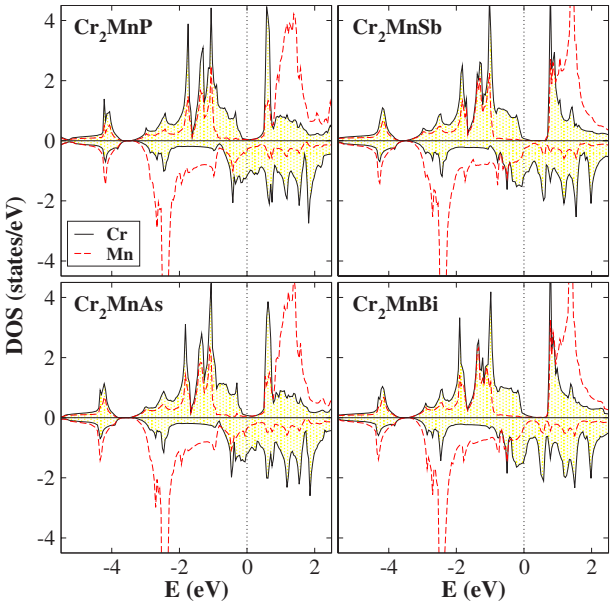

FIG. 2. (Color online) Cr and Mn resolved DOS for the four cases presented in Fig. 1. Cr DOS has been scaled to one atom.

Bi. Usually, in the case of the full-Heusler alloys of the chemical type X_2YZ, X atoms have higher valence than the Y ones. In the compounds which we study, the opposite occurs. Moreover, state-of-the-art methods for the synthesis of thin films such as the molecular-beam epitaxy make possible the growth of materials as multilayers or thin films where the spacer or the substrate is responsible for the lattice adopted by the material which we want to grow. Thus, the Heusler alloys of the type Cr_2MnZ presented in this study could be eventually grown experimentally in the $L2_1$ structure with their lattice constant determined by an adjutant. For this reason, we have studied their properties as a function of the lattice constant. In Fig. 1, we present the total density of states (DOS) per unit cell for all four compounds and for a lattice constant $a=6.2$ Å. We have chosen the spin-up states such that Cr atoms have positive spin moments and Mn negative ones. For all four compounds under study and for this specific lattice constant, there is a real gap in the spin-up states for the alloys containing the heavier Sb and Bi atoms, while there is a region of tiny spin-up DOS for the compounds with P and As (note that since there is an equal number of states for both spin-directions, we do not employ the terms majority and minority to describe the spin bands). Since the spin polarization at this region for the two latter compounds is almost 100%, we can safely state that all four compounds present a real gap, the width of which is around 0.5–0.7 eV. In the case of the lighter P- and As-based compounds, the Fermi level falls within this gap and the Cr_2MnP and Cr_2MnAs are true half-metals, while for the Sb- and Bi-based alloys, the Fermi level is just below the left edge of the gap but the spin polarization is still almost 100%, partially thanks to the very large value of the spin-down DOS at this region.

The gap is created due to the large exchange splitting of both the Cr and Mn atoms as can be seen in Fig. 2, where we present the atom-resolved DOS for the same lattice constant $a=6.2$ Å. We do not present the DOS for the sp atoms since this is very small with respect to those of the transition-metal atoms. The occupied spin-up states are mainly of Cr character, while the occupied spin-down states are mainly located at the Mn atoms. Thus, the large exchange splitting between the occupied states of one spin direction and the unoccupied states of the opposite spin direction for both Mn and Cr atoms are added up to open the gap. We should also mention that just below the gap in the spin-up band, the states are made exclusively of Cr states. This can be understood in terms of the discussion in Ref. 6, where it was shown in the case of Co_2MnGe that the states just below the gap are the triple degenerated t_{1u} and just above the gap the double degenerated e_u. Both t_{1u} and e_u were located exclusively at Co sites and they did not hybridize with Mn states due to symmetry reasons. In the compounds under study, Cr plays the role of Co. Just below the gap, there are exclusively Cr t_{1u} states, while the larger exchange splitting of the Cr atoms with respect to the Co ones pushes the Cr e_u states higher in energy and they cannot be distinguished from the other states at the same energy region.

Our results up to now concern only one lattice constant, 6.2 Å. The questions which arise now are whether these four alloys present half-metallicity only for this specific lattice constant and how the gap behaves with the lattice parameter. In Fig. 3, we present the total DOS for Cr_2MnSb for an ensemble of eight different lattice constants ranging between 5.9 and 6.6 Å as an example since all four compounds present similar behavior. The spin-up band presents only marginal changes with the lattice constant and the gap per-

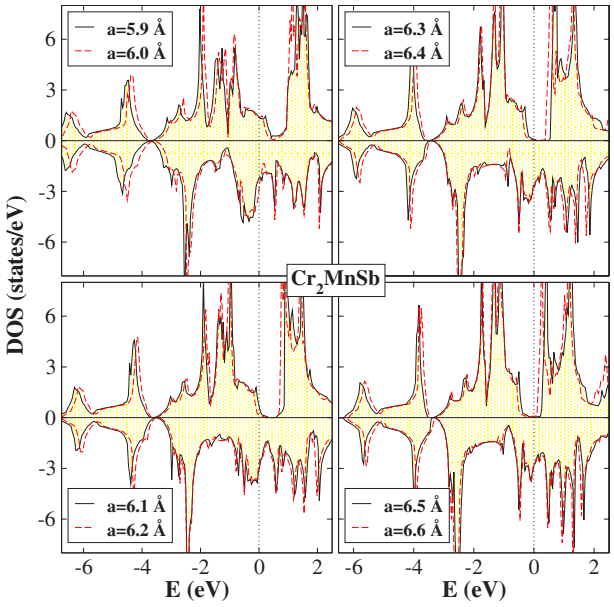

FIG. 3. (Color online) Total DOS for the Cr_2MnSb alloy as a function of the lattice constant. As the lattice is expanded, the Fermi level is shifted higher in energy similar to a rigid-band model.

sists for all the range of the lattice parameters which we studied. What differs is the position of the Fermi level, which behaves as in a rigid-band model. If we start from the 6.2 Å lattice parameter and we compress the lattice in a uniform way, the Fermi level is shifted lower in energy with respect to the gap, while the opposite occurs when we expand the lattice where the Fermi level is shifted higher in energy. Since the number of valence electrons is fixed to 24, when the Fermi level is out of the gap bounds small changes also occur in the spin-down band to take into account the extra charge in case that the Fermi level is below the gap or the missing charge when the Fermi level is above the gap. This behavior of the Fermi level is due to the *p* states of the *sp* atom and is opposite to the behavior of the full-Heusler alloys such as Co_2MnSi.[3] Thus, for all four compounds we can determine the range of lattice constants for which they are half-metallic. Our findings show that the Cr_2MnP and Cr_2MnAs alloys are half-metals between 6 and 6.2 Å, while Cr_2MnSn and Cr_2MnBi are half-metals between 6.2 and 6.6 Å. We should also note here that the calculated equilibrium lattice constants are 5.5, 5.7, 6.0 and 6.1 Å for *Z*=P, As, Sb, and Bi, respectively. Thus, Cr_2MnSb and Cr_2MnBi present half-metallicity close to their equilibrium lattice constant and it would be easier to grow half-metallic thin films of these compounds. Finally, we should note that, as mentioned in the introduction, we have used the scalar-relativistic approximation and we have not taken into account the spin-orbit coupling. As previous calculations on half-metals (see Ref. 18) have shown, this is important only for compounds containing Bi such as Cr_2MnBi and thus we expect the latter compound to be less likely to present half-metallicity. Moreover, the alloys containing P and As are probably difficult to be grown in such an expanded lattice constant demanded by the presence of half-metallicity. Thus, Cr_2MnSb is probably the ideal case for experimentalists to try to synthesize.

TABLE I. Total and atom-resolved spin magnetic moments in μ_B for the Cr_2MnZ compounds where *Z*=P, As, Sb or Bi and for different values of the lattice constant. The alloys containing P or As are half-metals between 6.0 and 6.2 Å, while the ones containing Sb or Bi are half-metals between 6.2 and 6.6 Å. Note that the atomic moments have been scaled to one atom. The last column are the estimated Curie temperatures using the multisublattice mean-field approximation (Refs. 11 and 21).

Cr_2MnP					
a (Å)	m^{Cr}	m^{Mn}	m^{P}	m^{Total}	T_C
6.0	1.528	−3.044	−0.071	−0.060	
6.2	1.796	−3.392	−0.098	0.102	240
Cr_2MnAs					
a (Å)	m^{Cr}	m^{Mn}	m^{As}	m^{Total}	T_C
6.0	1.515	−3.051	−0.124	−0.121	
6.2	1.805	−3.391	−0.099	0.096	250
Cr_2MnSb					
a (Å)	m^{Cr}	m^{Mn}	m^{Sb}	m^{Total}	T_C
6.2	1.670	−3.277	−0.100	−0.036	342
6.4	1.854	−3.589	−0.119	−0.001	
6.6	2.029	−3.874	−0.141	0.043	
Cr_2MnBi					
a (Å)	m^{Cr}	m^{Mn}	m^{Bi}	m^{Total}	T_C
6.2	1.608	−3.224	−0.096	−0.011	320
6.4	1.825	−3.543	−0.073	−0.083	
6.6	1.931	−3.687	−0.108	0.068	

We have not yet discussed the behavior of the magnetic spin moments in these alloys. We have gathered in Table I both the total and atom-resolved spin moments for all four compounds and for the lattice constants where half-metallicity is present. This is verified by the calculated total spin moments which are very close to the ideal value of zero μ_B. The Cr and Mn spin moments are very close to the usual values which they adopt in intermetallic compounds. Each Cr atom has a spin moment around $1.5-2\mu_B$, while Mn have antiparallel spin moments which are approximately two times the Cr ones in order to achieve the zero total spin moment in the unit cell. The antiparallel coupling of the moments is expected. Each Cr atom has four Mn (and four *sp* atoms) as first neighbors and each Mn atom has eight Cr atoms as nearest neighbors, and as usually occurs for these specific transition-metal atoms, when they are very close in space, they couple antiferromagnetically. As we expand the lattice, we decrease the hybridization between neighboring atoms and we increase their atomiclike character and thus enhance their spin moments. The *sp* atoms have very small spin moments antiparallel to the Cr ones occupying the *X*

sites in the lattice. This behavior is well known in most Heusler alloys (see Ref. 2 for a discussion on this coupling).

Besides high spin polarization of the states at the Fermi level, an important further condition for spintronic materials is a high Curie temperature which should exceed room temperature for realistic applications. To estimate the Curie temperatures for the half-metallic Cr_2MnZ compounds, we first applied the ASW method in conjunction with the frozen-magnon approach to calculate the interatomic exchange interactions.[19,20] Then, the calculated exchange parameters are used to estimate the Curie temperature within multisublattice mean-field approximation.[11] Note that we do not present the exchange parameters here in order to keep the discussion short. The multisublattice mean-field approximation has already been employed to other Heusler alloys and the results were in reasonable agreement with the experimental data.[11,21] Thus, this approximation can be used for trustworthy estimations. We have calculated the Curie temperature for the lattice constant of 6.2 Å but it should vary only marginally for small changes of the lattice constants. We present our results at the last column of Table I. For the Cr_2MnP and Cr_2MnAs alloys, the Curie temperature was found to be 240–250 K and for Cr_2MnBi around 320 K which is not suitable for realistic applications. For the Sb alloy, it was found to exceed room temperature being 342 K close to the Curie temperature of Co_2CrAl, which is also under intense investigation.[22]

III. CONCLUSION

We have employed *ab initio* electronic structure calculations to design half-metallic fully compensated ferrimagnets (or, as they are widely known, half-metallic antiferromagnets) susceptible of finding applications in spintronics. Cr_2MnZ (Z=P, As, Sb, Bi) compounds have 24 valence electrons per unit cell and calculations show that their total spin moment is approximately zero for a wide range of lattice constants, in agreement with the Slater-Pauling behavior for ideal half-metals. Cr and Mn atoms have large antiparallel spin moments and these compounds are ferrimagnets. Upon expansion or compression of the lattice, the Fermi level is shifted as in a rigid-band model. Moreover, mean-field approximation was employed to estimate their Curie temperature, which exceeds room temperature for the alloy with Sb. Cr_2MnSb has significant advantages with respect to the other three compounds—larger Curie temperature, small influence of spin-orbit coupling, and large range of lattice constants where half-metallicity is present—and we expect it to be the alloy of choice for further experimental researches.

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*Electronic address: galanakis@upatras.gr
†Electronic address: kozdogan@gyte.edu.tr
‡Electronic address: e.sasioglu@fz-juelich.de

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