arXiv:cond-mat/0703078v1 [cond-mat.mtrl-sci] 2 Mar 2007

# Ab-initio design of half-metallic fully-compensated ferrimagnets: the case of $Cr_2MnZ$ (Z= P, As, Sb, Bi) compounds

I. Galanakis [a,*] K. Özdoğan [b] E. Şaşıoğlu [c,d] B. Aktaş [b]

[a] *Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece*
[b] *Department of Physics, Gebze Institute of Technology, Gebze, 41400, Kocaeli, Turkey*
[c] *Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*
[d] *Fatih University, Physics Department, 34500, Büyükçekmece, İstanbul, Turkey*

**Abstract**

Electronic structure calculations from first-principles are employed to design some new 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. Contrary to the alloys mentioned above half-metallic antiferromagnetism is unstable in the case of the $Cr_2FeZ$ (Z= Si, Ge, Sn) alloys.

*Key words:* Magnetically ordered materials, Ferrimagnetism, Electronic structure calculations, Half-metals
*PACS:* 75.47.Np, 75.50.Cc, 75.30.Et

## 1. Introduction

The last decade a new field has evolved in solid state physics focusing on the design of novel 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 alloys 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 [5,7] and $Mn_2VAl$ [8,9,10,11]. 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

* Corresponding author. Phone +30-2610-969925, Fax +30-2610-969368
*Email addresses:* galanakis@upatras.gr (I. Galanakis), kozdogan@gyte.edu.tr (K. Özdoğan), e.sasioglu@fz-juelich.de (E. Şaşıoğlu).

$X_2YZ$ this rule takes the form $M_t = Z_t - 24$ [6]. $M_t$ is the total spin moment in the unit cell in $\mu_B$ 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 compounds would be perfectly suited for applications due to the negligible external magnetic field which it would create. The 24-valence electrons compounds are known as half-metallic antiferromagnets, but their correct definition is "half-metallic (HM) fully-compensated ferrimagnets" (FCF)[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-FCF alloys belong the hypothetical Heusler MnCrSb [12] and $Mn_3Ga$ [13] compounds which have not been yet synthesized. Another root towards 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 communication 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. Contrary to these alloys the $Cr_2FeZ$ alloys (Z= Si, Ge or Sn) which have also 24 valence electrons are not suitable for realistic applications since they show a region of low density of states (DOS) for a very narrow range of lattice parameters and any deviation from these values completely destroys the low-DOS region. For the calculations we employed the full–potential nonorthogonal local–orbital minimum–basis band structure scheme (FPLO) 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 [18] where the image of the spin-down states in the spin-up band is not negligible as for the other lighter chemical elements.

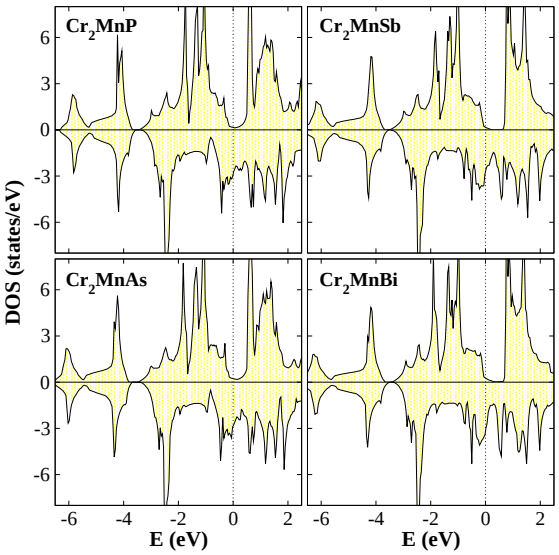



Fig. 1. (Color online) Total density of states (DOS) for the four compounds under study and for a lattice constant of 6.2 Å. All four alloys are almost half-metals. Positive values of DOS correspond to spin-up electrons and negative values to spin-down electrons. The energy scale is such that the zero 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.

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 more technological relevant $Cr_2MnZ$ compounds within the multi-sublattice mean field approximation already employed in the case of other Heusler alloys (see Refs. [11,21,22]).

## 2. $Cr_2MnZ$ (Z=P,As,Sb,Bi) alloys

We will start our discussion from the case of $Cr_2MnZ$ alloys. Since we want our compounds to have exactly 24 electrons, we choose Z to be one of the isovalent P, As, Sb or 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, e.g. the X atom has more valence electrons. In the compounds which we study, the opposite occurs. Moreover, state-of-the-art methods for synthesis of thin films like the Molecular Beam Epitaxy make possible to grow novel materials as multilayers or thin-films where the spacer or the substrate are

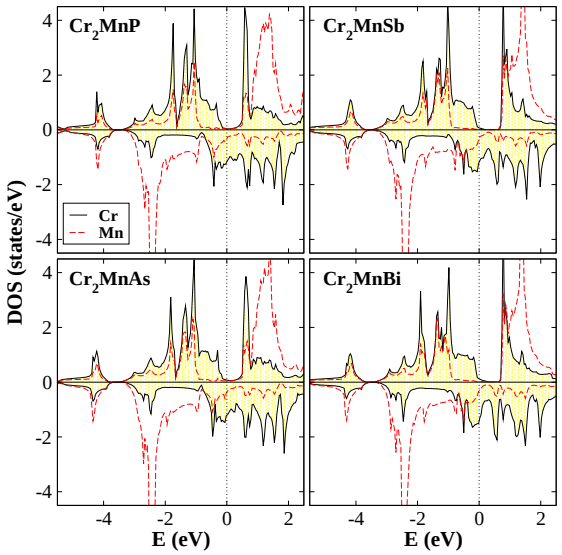



Fig. 2. (Color online) Cr and Mn resolved DOS for the four case presented in Fig. 1. Cr-DOS has been scaled to one atom.

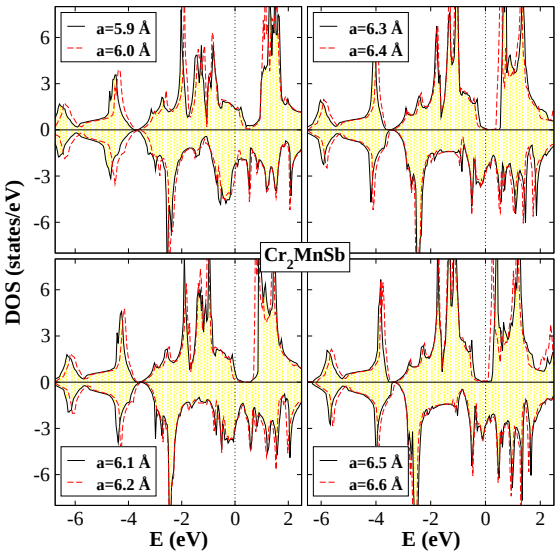



Fig. 3. (Color online) Total DOS for the $Cr_2MnSb$ alloy as a function of the lattice constant. As the lattice is expanded the Fermi level is shifted higher in energy similar to a rigid band model.

responsible for the lattice constant 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 with their lattice constant determined by an adjutant in a way that the desired electronic and magnetic properties appear. For this reason we have studied their properties as a function of the lattice constant. In Fig. 1 we present the total density of state (DOS) per unit cell for all four compounds and for a lattice constant a=6.2Å. 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 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=6.2Å. We do not present the DOS for the sp atoms since this is very small with respect to 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 the 6.2Å. The question which arises now is

if 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 8 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 persists 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 in a uniform way the lattice, 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 occur also 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 like $Co_2MnSi$ [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. Here 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 like $Cr_2MnBi$ 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.

We have not yet discussed the behavior of the magnetic spin moments in these alloys. We have gathered in Table 1 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 $\mu_B$. 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 to 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 atomic-like 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

Table 1
Total and atom-resolved spin magnetic moments in $\mu_B$ 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 between 6.2 and 6.6 Å. Note that the atomic moments have been scaled to one atom. Last column are the estimated Curie temperatures using the multi-sublattice mean-field approximation [21,11].

| $Cr_2MnP$ | | | | | |
|---|---|---|---|---|---|
| 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 | |

spintronics materials is a high Curie temperature which should exceed the 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 multi-sublattice mean field approximation [22]. Note that we do not present the exchange parameters here in order to keep the discussion short. The multi-sublattice mean field approximation has already been employed to other Heusler alloys and the results were in reasonable agreement with the experimental data [11,21,22]. 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 1. 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 the room temperature being 342 K close to the Curie temperature of $Co_2CrAl$ which is also under intense investigation [23].

## 3. $Cr_2FeZ$ (Z=Si,Ge,Sn) alloys

Motivated by our results on the $Cr_2MnZ$ alloys, we decided to study also another family of 24-valence electrons compounds containing Fe instead of Mn: the $Cr_2FeZ$ alloys where Z is Si, Ge or Sn. In the right lower panel of Fig. 4 we present the total and the Cr and Fe-resolved DOS for a lattice constant of 6.2 Å for the $Cr_2FeSn$ alloy (the other two compounds $Cr_2FeSi$ and $Cr_2FeGe$ present similar behavior). For this lattice constant all three compounds under study present a region of low DOS in the spin-up band and the Fermi level falls within this region. Contrary to the compounds containing Mn, where the spin-up occupied states are mainly of Cr character and the occupied spin-down states are of mainly Mn character, for the Fe-based alloys both the spin-up and spin-down occupied states exhibit a more mixed character. The electronic structure is more complicated than the Mn-based alloys and as a result when we slightly vary the lattice constant the band-structure changes in a way that the the region of low DOS is completely destroyed. This is illustrated again in Fig. 4 where we present also the DOS for $Cr_2FeSn$ and for lattice constants of 6.0 and 6.1 Å. Cr spin-up states below the Fermi level and the Cr spin-up states just above the Fermi level move one towards the other completely destroying the region of high spin-polarization. The reason is the different hybridization between the transition-metal atoms when we substitute Fe for Mn. The smaller exchange splitting of the Fe atoms closes the gap and this leads also to a different distribution of the Cr charge which no more shows a large band-gap as for the Mn-based alloys. To summarize our findings, the calculations suggest that the region of low spin-up DOS persists for $Cr_2FeSn$ between 6.2 and 6.3 Å and for $Cr_2FeSi$ and $Cr_2FeGe$ between 6.1 and 6.2 Å.

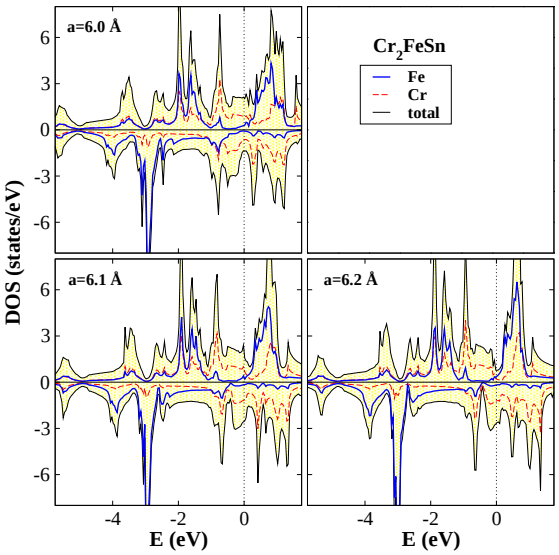



Fig. 4. (Color online) Total, Cr- and Fe-resolved DOS for the $Cr_2FeSn$ alloy and for three different values of the lattice constant. As the lattice is compressed, the region of low total spin-up DOS vanishes. $Cr_2FeSi$ and $Cr_2FeGe$ show similar DOS.

In Table 2 we present the spin-moments for the three compounds and for the lattice constant of 6.2 Å. Fe atoms can not surpass the barrier of 3 $\mu_B$ since the extra electron with respect to the Mn atom occupies mostly spin-up states reducing the Fe spin-moment with respect to the Mn atoms. As a result also the Cr spin moments are smaller. Overall the $Cr_2FeZ$ alloys with 24-valence electrons are not suitable for realistic application, contrary to their $Cr_2MnZ$ compounds since half-metallicity is very fragile in their case and thus we have not performed extra calculations for their Curie temperatures.

Table 2
Total and atom-resolved spin magnetic moments in $\mu_B$ for the $Cr_2MFeZ$ compounds where Z= Si, Ge, or Sn and for a lattice constant of 6.2 Å. The Si and Ge have a total spin moment very close to zero for lattice constants between 6.1 and 6.2 Å and the Sn alloy between 6.2 and 6.3 Å.

| Compound | $m^{Cr}$ | $m^{Fe}$ | $m^{Z}$ | $m^{Total}$ |
|---|---|---|---|---|
| $Cr_2FeSi$ | 1.527 | -2.856 | -0.106 | 0.092 |
| $Cr_2FeGe$ | 1.535 | -2.853 | -0.140 | 0.077 |
| $Cr_2FeSn$ | 1.447 | -2.789 | -0.111 | -0.007 |

## 4. Conclusion

We have employed ab-initio electronic structure calculations to design some new 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 the 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, large range of lattice constants where half-metallicity is present - and we expect it to be the alloy of choice for further experimental researches.

Contrary to these alloys, half-metallic antiferromagnetism is unstable in the case of the $Cr_2FeZ$ (Z= Si, Ge, Sn) alloys which show a region of low density of states instead of a gap for a very narrow range of lattice constants.

Authors acknowledge the computer support of the "Leibniz Institute for Solid State and Materials Research Dresden".

References

[1] I. Žutić, J. Fabian, S. Das Sarma, Rev. Mod. Phys. 76 (2004) 323 .
[2] I. Galanakis, Ph. Mavropoulos, P.H. Dederichs, J. Phys. D: Appl. Phys. 39 (2006) 765.
[3] I. Galanakis and Ph. Mavropoulos, J. Phys.: Condens. Matter in press [preprint: cond-mat/0610827].
[4] R.A. de Groot. F.M. Mueller, P.G. van Engen, K.H.J. Buschow, Phys. Rev. Lett. 50 (1983) 2024.
[5] I. Galanakis, P.H. Dederichs, N. Papanikolaou, Phys. Rev. B 66 (2002) 134428.
[6] I. Galanakis, P.H. Dederichs, N. Papanikolaou, Phys. Rev. B 66 (2002) 174429
[7] R.A. de Groot, A.M. van der Kraan, and K.H.J. Buschow, J. Magn. Magn. Mater. 61 (1986) 330.
[8] S. Ishida, S. Asano, J. Ishida, J. Phys. Soc. Jpn. 53 (1984) 2718; R. Weht and W.E. Pickett, Phys. Rev. B 60 (1999) 13006.
[9] K. Özdoğan, I. Galanakis, E. Şaşıoğlu, B. Aktaş, J. Phys.: Condens. Matter 18 (2006) 2905.
[10] E. Şaşıoğlu, L.M. Sandratskii, P. Bruno, J. Phys.: Condens. Matter 17 (2005) 995.
[11] E. Şaşıoğlu, L.M. Sandratskii, P. Bruno, I. Galanakis, Phys. Rev. B 72 (2005) 184415.
[12] H. van Leuken and R.A. de Groot, Phys. Rev. Lett. 74 (1995) 1171.
[13] S. Wurmehl, H.C. Kandpal, G.H. Fecher, C. Felser, J. Phys.: Condens. Matter 18 (2006) 6171.
[14] H. Akai and M. Ogura, Phys. Rev. Lett. 97 (2006) 026401.
[15] I. Galanakis, J. Phys.: Condens. Matter 16 (2004) 3089.
[16] I. Galanakis, K. Özdoğan, E. Şaşıoğlu, B. Aktaş, unpublshed [preprint: cond-mat/0701611]
[17] K. Koepernik and H. Eschrig, Phys. Rev. B 59 (1999) 3174; K. Koepernik, B. Velicky, R. Hayn, H. Eschrig, Phys. Rev. B 58 (1998) 6944.
[18] P. Mavropoulos, K. Sato, R. Zeller, P.H. Dederichs, V. Popescu, H. Ebert, Phys. Rev. B 69 (2004) 054424.
[19] R. Williams, J. Kübler, C.D. Gelatt, Phys. Rev. B 19 (1979) 6094.
[20] V. Halilov, H. Eschrig, A.Y. Perlov, P.M. Oppeneer, Phys. Rev. B 58 (1998) 293.
[21] J. Kübler, J. Phys.: Condens. Matter 18 (2006) 9795.
[22] E. Şaşıoğlu, L.M. Sandratskii, P. Bruno, I.. Galanakis Phys. Rev. B 72 (2005) 184415.
[23] P.J. Webster and K.R.A. Ziebeck, in *Alloys and Compounds of d-Elements with Main Group Elements. Part 2.*, edited by H.R.J. Wijn, Landolt-Börnstein, New Series, Group III, Vol. 19,Pt.c (Springer-Verlag, Berlin 1988), pp. 75-184.