EPJ Web of Conferences **44**, 04002 (2013)
DOI: 10.1051/epjconf/20134404002
© Owned by the authors, published by EDP Sciences, 2013

FP-LMTO investigation of the structural, electronic and agneticproperties of Heusler compounds Ru2CrZ (Ge, Sn, Si)

Z. Aarizou, S. Bahlouli and M. Elchikh

Laboratoire de Physique des Mat´eriaux et des Fluides, D´epartement de Physique, Universit´e des Sciences et de la Technologie d'Oran-MB, BP 1505 Oran El Mnaouer, Algeria

Abstract. The electronic structure of the antiferomagnetic full Heusler alloys Ru_2CrZ (Ge, Sn, Si) have been studied by first principal calculations using Full-Potential linearized Muffin Tin Orbital (FP-LMTO) method based on the generalized Gradient Approximation (GGA). It was shown that obtained equilibrium lattice parameters agree well with available experimental data. The influence of Z-elements on the electronic structure and magnetic properties of these compounds is analysed.

1 introduction

During the last two decades, full-Heusler alloys have been investigated both theoretically and experimentally in a series of papers; see for instance the paper by C. Felser et al. [1]. They are suitable materials for spintronic applications since they can show 100 % spin-polarized carriers at the Fermi level. In fact, Half-Metallic Heusler Ferromagnets (HMF) have an energy-band gap for minority spin bands and the conduction electrons at the Fermi level (E_F) show 100 % spin polarization and can be used as spin-polarized electron sources along with metal oxides and IIIV group semiconductors.

Full Heusler compounds are ternary intermetallics with general formula X_2YZ, where X and Y denote the transition metals and Z may be any one of the large number of s-p elements belonging to the IIIB-VB group, element such as Al, Ga, Si, Ge, Sn, Sb, etc. These materials crystallize in L21 structure, which consists of four FCC sublatticeswith space group $Fm\bar{3}m$,with the followingWyckoff positions: X (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4), Y (0, 0, 0) and Z (1/2,1/2,1/2).

Some of the full Heusler alloys show other interesting properties like semiconducting or semimettalic and ferrimagnetic or antiferromagnetic behaviors. For instance, crystals of the type Ru_2MnZ, where Z stands for Si, Ge and Sn have been found to be antiferromagnets with Neel temperatures near room temperature [2]. Recently, Okada et al. succeeded in synthesizing Ru_2CrGe and Ru_2CrSn, and found that Ru_2CrGe is an antiferromagnet with Néel temperature T_N = 13 K and Ru_2CrSn shows a spin-glass-like behavior below T_g = 7 K [3]. Furthermore, the phase transition to ferromagnetic state of full-Heusler alloys $Ru_{2-x}Fe_xSi$ and $Ru_{2-x}Fe_xGe$ have been studied [4–6] where Fe are partially or totally substituted for Ru.

In this note, we recall the first-rinciple calculations method we used, then we show and discuss the results obtained on the structural optimization, the electronic properties and magnetic behavior of Ru_2CrSi, Ru_2CrGe and Ru_2CrSn. Finally we give a brief summary.

2 Computational details

As first-principle method we applied the FP-LMTO method [7, 8] as embedded in LmtART MStudio Mind-Lab 7 code developed by S.Y Savrasov [8,9]. We assumed the functional of exchange and correlation (GGA) as proposed by Perdew Wang (PW) [10]. We took the different muffin tin radius RMT as listed in Table 1:

Table 1. RMT(a.u.) of Ru, Cr and Z atoms for Ru2CrZ compounds.

Margin	Ru_2CrSi	Ru_2CrGe	Ru_2CrSn
Ru	2.477	2.509	2.535
Cr	2.38	2.413	2.535
Z	2.38	2.413	2.535

The basis set of our FP-LMTO calculations, are made of the $4d^7 5s^1$ and $3d^5 4s^1$ states for the transition elements Ru and Cr respectively. The valence states for the Z atoms are $3s^2 3p^2$ of Si, $4s^2 4p^2$ of Ge or $5s^2 5p^2$ of Sn. The filled

This is an Open Access article distributed under the terms of the Creative Commons Attribution License 2.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Article available at http://www.epj-conferences.org or http://dx.doi.org/10.1051/epjconf/20134404002

states $4d^{10}$ of Sn and $3d^{10}$ of Ge may also be considered as valence states, that are the default input in the code since the energy needed to separate semi-core and valence electrons was set to above -2Ry from the vacuum zero, which results in treating of Si, Ge and Sn semi-core electrons as valence electrons. The charge density and potential are expanded in spherical harmonics inside the spheres up to lmax = 6 and Fourier transformed in the interstitial region. The maximum value of angular momentum lmax = 6 is also taken for wave function expansion inside the atomic spheres. The lattice constants used in the present study, were obtained by minimizing the total energy Etot with respect to the experimental lattice parameters. The energy convergence criterion was set to 10^{-6} Ry. For k-space integration over the Brillion zone, we found that our calculations converge for a 10×10×10 tetrahedron mesh [11]. The energy cut-off and the number of plane waves used in our calculations are, respectively: (80.70 Ry; 9204) for Ru_2CrGe, (75.40Ry; 9204) for Ru_2CrSn and (84.09Ry; 9204) for Ru_2rSi. In our study the magnetic unit cell being twice that of the unit cell used in crystallography (defined above) if the AFM phase is considered. For this AFM phase, we adopt the so called FCC-AFM type II order. The magnetic moments on the atoms are ferromagnetically coupled on the (111) planes and antiferromagnetically coupled in adjacent planes. In fact, this arrangement (AFM type II) has been revealed experimentally for Ru2CrGe [6].

3. Results and descussion

3.1 Structural optimisation

We performed structural optimizations on our three Heusler compounds of interest, Ru_2CrSi, Ru_2CrGe and Ru_2CrSn, for the Nonmagnetic (NM), ferromagnetic (FM) and AFM phases. For the three Heusler compounds, the results of structural optimization are quite similar, so only the Ru_2CrSi structural optimization is shown in Fig. 1. The total energy differences $\Delta E = E_{AFM} - E_{FM}$ are negative, thus all our compounds Ru2CrZ are stable in the AFM phase which confirm the experimental results. We also computed the total energies for several lattice constants and fitted them with the empirical Murnaghan equation of state [12] the values of the optimized lattice constants for the three compounds are listed in Table 2. Our calculated lattice constants for Ru_2CrGe and Ru_2CrSn are in agreement with the experimental values, and to the best of our knowledge, no experimental data have been reported for Ru_2CrSi.

One can note that the theoretical lattice constant in Ru2CrZ (Z=Si,Ge and Sn) increases with the increasing atomic number of Si→Ge→Sn due to the increasing size of atomic radius while the absolute value of the energy differences ΔE decreases.

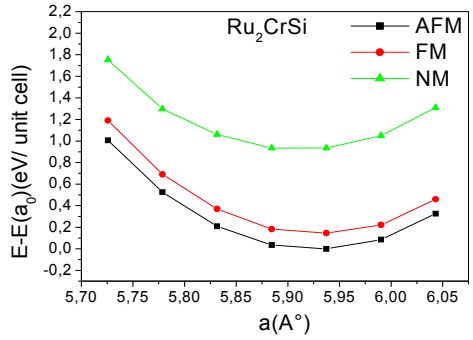

Fig. 1. Relative total energy (per unit cell) as a function of the lattice parameter for Ru_2CrSi, $E(a_0)$ being the ground state energy.

Table 2. Equilibrium lattice constants a0(°A) and total energy differences ΔE(eV/unit cell) for Ru_2CrSi, Ru_2CrGe and Ru2CrSn.

Compound	Calculation	a_0	ΔE
Ru_2CrSi	Our work Experimental Other [4]	5.93 5.94	-0.1414
Ru_2CrGe	Our work Experimental [3,6] Other [4]	6.05 5.97 6.02	-0.110
Ru_2crSn	Our work Experimental [3] Other [13]	6.26 6.19 6.233	-0.0984

3.2. Electronic and magnetic properties

The calculated band structures and the density of states of the AFM state of Ru_2CrSi, Ru_2CrGe and Ru_2CrSn, being quite similar, so only the Ru_2CrSi electronic structure will be presented here. Furethermore, our three compounds are all antiferromagnets, then the electronic properties of the two spin-channels are similar, consequently we reported only one spinchannel in Fig. 2.

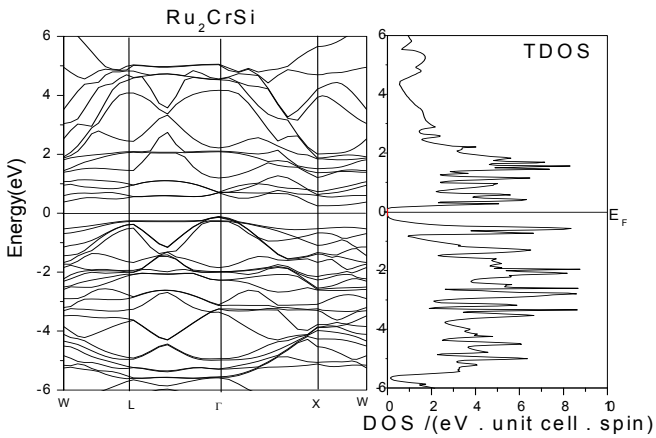

Fig. 2. Electronic structure of Ru_2CrSi: band structure (left side) and total density of states (right side).

The three Heusler compounds Ru_2CrZ present an indirect energy gap along Γ −X, i.e. in the (Δ) direction and the Fermi energy of these materials is just at the top of the valence band. We calculated the energy gaps (in eV) and found 0.35 for Ru_2CrSi, 0.14 for Ru_2CrGe and 0.02 for Ru_2CrSn. We note that our Heusler Z-atoms have an influence on the energy gap, therefore, the gap decreases as the number of valence Z increases. The partial density of states (PDOS) of Ru2CrSi as a function of energy is shown in Fig. 3, the PDOS of Ru2CrSi and Ru2CrSn being also almost the same. The high DOS around E_F is associated with hybridization of Ru(4d) and Cr(3d) electrons. We notice that the Cr compound exhibits a considerably larger gap compared with the Ru compound. In order to understand the influence of Z element on the gap width we plotted the PDOS of Z elements in Fig 4. The energy of (p) electrons is strongly dependent on the Z atom in Ru2CrZ, so the hybridization between (p) electrons with different energy and the (d) electrons affects the formation of the energy gap. We can see

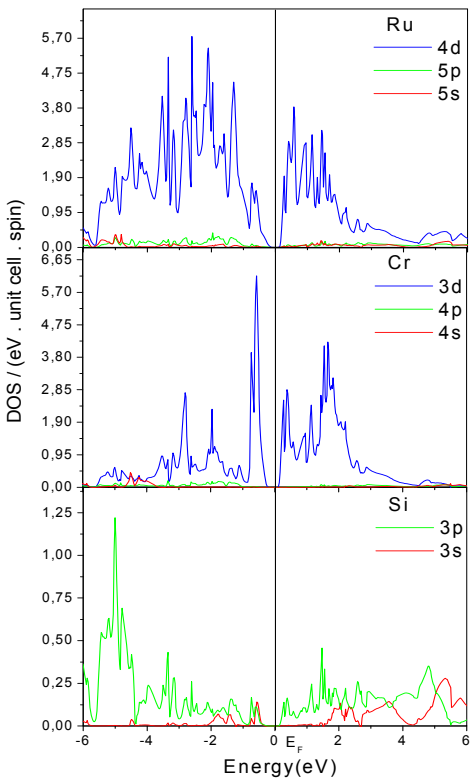

Fig. 3. Partial density of states of Ru2CrSi.

that the local magnetic moments of Cr become large with increasing the atomic number of the Z atoms but also the lattice constant has an influence on the magnetic properties, on the other hand the Ru atom carries negligible local moment as it was deduced from experiment [6]. However, the individual magnetic moment of Cr atoms found in our study, is about fifty

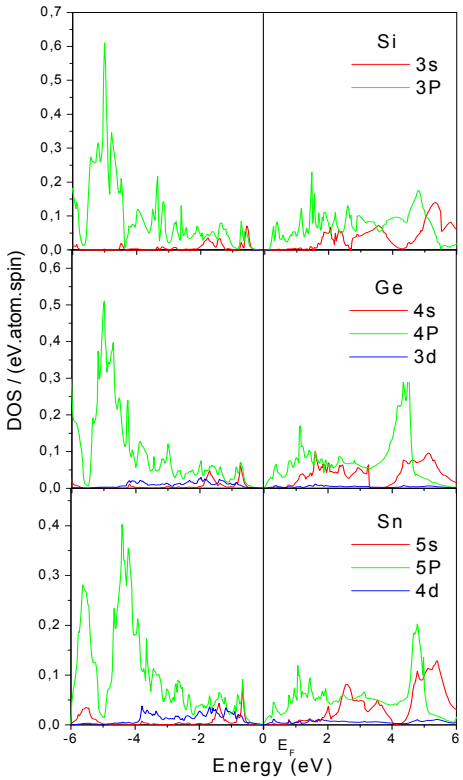

Fig. 4. Compared Partial density of states of Z elements.

percent greater than the value of 1.45 μ_B, estimated experimentally in the case of Ru2CrGe at 5 K [6], which indicates that itinerant exchange mechanism alone cannot explain this difference.

Table 3. The calculated absolute local magnetic moment (μ_B) of Cr and Ru atoms in Ru2CrZ compounds.

	$\lvert MCr \rvert$	$\lvert MRu \rvert$
Ru_2CrSi	2.477	2.509
Ru_2CrGe	2.38	2.413
Ru_2CrSn	2.38	2.413

It is interesting to note that when Ru is replaced by other elements like Co [14,15] or Mn [16], Heusler alloys exhibit half metallic ferromagnetic behavior. The conduction band minimum consists mostly of Ru(4d), Cr(3d) and smaller contribution of Z(p) orbitals; the valence band maximum is composed of Cr(3d), Ru(4d) and Z(p) electrons. Moreover, Z atoms create four fully occupied bands, comprising of one Z(s) and three Z(p) bands. This Z(s) is very low in energy and also well separated from other bands, on the other hand, Z(p) bands hybridize with p electron Ru and Cr, but they (Z(p) bands) are also low energy bands. The d- states of the transition metal atoms (Ru and Cr) extend from occupied

and unoccupied states and hybridize with each other. The widely spread d states are mainly due to the strong hybridization of the (3d) metals.

Let us note that the half metallic ferromagnetic behavior can be present in $Ru_{2-x}Fe_xCrSi$ for a particular range of Fe concentration x starting at x = 0.5 [4,5].

4 Sammary

We have performed first principles calculations on structural, electronic and magnetic properties of Ru_2CrSi, Ru_2CrGe and Ru_2CrSn using the Full-Potential Linear Muffin Tin Orbitals, these compounds are all Antiferromagnets, which is in agreement with the experimental results. The electronic properties show that these compounds have a semiconductor behavior with indirect gap along $\Gamma - X$. We found that the Z elements have an influence on the electronic properties as well as on the magnetic properties. Therefore the energy gap decreases as the number of valence Z increases also the theoretical values of the Cr local moments become larger with increasing of the Z atomic number. The high density of states around E_F is associated with hybridization of Cr(3d) and Ru(4d) electrons. Here we did not deal with the spin-glass behavior of Ru_2CrSn below T_g = 7K[3], which cannot be simply explained by our method of calculations.

References

1. T. Graf, C. Felser and S. S.P. Parkin, Progress in Solid State Chemistry **39**, (2011) 1.
2. M. Gotoh, M. Phashi, T. Kanomata, and Y. Yamaguchi, Physica B **306**, (1995) 213.
3. H.Okada et al., App. Phys.Lett. **92**, (2008) 062502.
   H.Okada et al., Journal of Physics: Conference Series **150**, (2009) 042153.
4. S. Mizutani, S. Ishida, S. Fujii, S. Asano, Mater. Trans. **47**, (2006) 25.
   S. Ishida, S. Mizutani, S. Fujii, S. Asano, Mater. Trans. **47**, (2006) 31.
5. M. Hiroi et al., Phys. Rev. B **79**, (2009) 224423.
   M. Hiroi et al., Journal of Physics: Conference Series **150**, (2009) 042058.
6. P.J Brown et al., J. Phys.: Condens.Matter **20**, (2008) 455201.
7. S.Y. Savrasov and D. Savrasov, Phys.Rev. B **46**, (1992) 12181.
8. S.Y. Savrasov, Phys. Rev. B **54**, (1996) 16470.
9. http://physics.ucdavis.edu/ mindlab
10. J. P. Perdew, S. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, (1996) 3865.
11. P.E. Blchl, O. Jepsen, O.K. Andersen, Phys. Rev. B **49**, (1994) 16223.
12. F.D Murnaghan, Proc. Nat. Acad. Sci. of U.S.A **30** (1944) 244.
    F. Birch, Phys. Rev. 71 (1947) 809.
13. M. Gillessen, R. Dronskowski, Journal Of Computational Chemistry, **30**, (2009) 1290.
14. H.C Kandpal, G. H Fecher and C. Felser; J. Phys. D: Appl. Phys **40** (2007) 1507.
15. Z. Aarizou, A. Akriche, S. Bahlouli and M. Elchikh, (Unplished work).
16. H. Luo et al, J. Magn. Magn. Mater. **320** (2008) 421.