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Zr-Based Heusler Compounds for Biomedical Spintronic Applications

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Abstract

Current advances in microelectronics depend on novel approaches based on the synergistic use of charge and spin dynamics of electrons in multi-functional materials. Such new concepts have already found practical applications in magnetoelectronics or spintronics (e.g., spin valves or nonvolatile memory components). For efficient spintronic devices, it is desirable to have an enhanced spin polarization, that, to work with nearly 100% spin-polarized currents. Since half metallic materials have electrons of unique spin polarization around the Fermi level (finite density of states in only one spin channel), they are promising candidates for use as spin injectors in spintronic devices. Although the Heusler compounds reported in the literature presenting half-metallic ferro/ferrimagnetism are numerous, only a few contain elements with low toxicity, as for example zirconium, being also susceptible of convenient preparation and processing. Therefore, in future, zirconium-based compounds could become a much suitable alternative to the presently known cobalt, iron, chromium, titanium, manganese, or scandium-based half-metallic Heusler compounds, being of interest especially in biomedical spintronic related applications involved in corrosive/active environment.

Keywords: Heusler compounds, spintronics, half metallic, spin gapless semiconductors

1. Introduction

The recent developments in thin films and nanofabrication techniques of biosensors and related spintronic devices are the forefront of current research efforts, bridging material sciences, physics, chemistry, and engineering, to form a seamless integration of digital world into the soft or living systems. Magnetic functionalities may provide a sense of proximity, orientation, or displacement to this novel formulation of biomedical electronics.

High spin polarization is one of the requested and necessary properties of materials used as electrodes or spin pumping/spin analyzers elements in spintronics, including those used in medicine and this is by definition a characteristic of alloys with half-metallic properties [1, 2]. The property of half-metallic ferromagnetism initially discovered in Cu_2MnAl compound [2] consists in a metallic behavior of one spin channel of electronic structure and a semiconducting one in the other, thus creating a material with hybrid properties between metals and semiconductors. As

a direct consequence, there will be always a 100% net spin polarization at the Fermi level due to the unique spin polarization of electrons in only one channel.

In materials in which the unit cell consists of two distinct sublattices with antiferromagnetic coupling between them, an internal spin partial compensation occurs and this particular property was referred as half-metallic ferrimagnetism [3, 4], which comparing to half-metallic ferromagnetism exhibits lower magnetic moments per formula unit (f.u) and weaker stray fields. Moreover, if the magnetic moments of the constituent sublattices fully compensate each other (with a net spin = 0 μ_B /f.u.), an alloy with a completely compensated ferrimagnetism (CCF) [5] resulted and the compound was classified as half-metallic completely compensated ferrimagnet (HM-CCFs) [6]. However, such a complete spin polarization of carriers occurs in the case of zero temperature and only in the absence of the spin-orbit interactions. Apart from this, HM-CCFs are intensively studied to develop new stable spin-polarized electrodes for biomedical in-vivo applications, junctions or integrated spin-transfer torque nano-oscillators for telecommunication.

A particular class of half-metallic materials is Spin Gapless Semiconductors (SGS). These compounds exhibit around Fermi level, in one spin channel a typical semiconducting band gap, while in the other (where in usual half-metallic compounds a metallic character is present), the negligible density of states are equivalent to a very narrow almost zero band gap. The above described characteristic of electronic structure, places SGSs at the boundary between half-metallic compounds and semiconductors.

In this particular case of half-metallicity, the materials act like topological insulators, where in particular high Curie temperature may coexist with high resistance. A combination of spin gapless semiconducting properties with completely compensated ferrimagnetism (0 μ_B total magnetic moment per f.u.) leads to spin gapless completely compensated ferrimagnetism (SG-CCF) [7].

Particularly, attractive classes of alloys exhibiting half-metallic properties, based on which may be developed biosensors, the new electrode materials with high spin polarization include alloys like Heusler compounds [2]. This class of materials, used in present as electrodes for magnetic tunnel junctions were discovered by Fritz Heusler, in 1903, who reported that Cu_2MnAl alloy is ferromagnetic, even though, alone, none of constituent elements has magnetic properties [8]. These intermetallic alloys are described by two variants: the half-Heusler XYZ compounds, with C_{1b} crystal structure and the full-Heusler X_2YZ variants which typically crystallize in Cu_2MnAl (cubic L_{21})-type structure; where X is a transition metal, Y may be a rare-metal or a transition metal, and Z is a main group element. Recently, it has been shown that in case of a full-Heusler compounds X_2YZ , if the Y element is more electronegative than X, a structure with Hg_2CuTi -prototype is observed. This is the so called as inverse Heusler structure, crystallizing in $F43m$ space group [9], with X atoms placed in the $4a(0,0,0)$ and $4c(1/4,1/4,1/4)$ Wyckoff positions, Y in $4b(1/2,1/2,1/2)$ and Z in $4d(3/4,3/4,3/4)$, respectively. In this crystal structure, no octahedral symmetry O_h is adopted, and all atoms have tetrahedral symmetry T_d .

The Slater-Pauling curve gives the interrelation between the total magnetic moment and the valence electron concentration in ferromagnetic/ferrimagnetic alloys [10, 11]. The original Slater-Pauling approach suggests the existence of different laws, due to the average over all atoms of the total magnetic moment and the number of valence electrons. For compounds with different kinds of atoms and ordered crystalline structures, it is more appropriate to consider all atoms of the unit cell, to find the magnetic moment per unit cell.

In terms of two-orbital two-electron stabilizing interactions, within the framework of density functional theory, the states of each spin channel are occupied according to several aspects concerning ionic arguments, crystal structure of

primitive cell, lattice parameter, approximations made for the exchange and correlation interaction, energy threshold set between the core and valence states, and also Brillouin zone integration mesh. Based on ionic arguments, the most electropositive element transfers the valence electrons to the most electronegative element. The purpose is to obtain stable closed shell ions. In addition, strongly dependent by the atomic arrangement of atoms and environment, hybridization occurs whenever the sum of metallic radii (12-coordinated) of two first-neighbors exceeds the interatomic distance.

A particularly useful measure to describe the electronic properties of a material is the electron spin polarization P at Fermi level (ε_F), given by Eq. (1)

$$P = \frac{\rho_{\uparrow}(\varepsilon_F) - \rho_{\downarrow}(\varepsilon_F)}{\rho_{\uparrow}(\varepsilon_F) + \rho_{\downarrow}(\varepsilon_F)} \quad (1)$$

where $\rho_{\uparrow}(\varepsilon_F)$ and $\rho_{\downarrow}(\varepsilon_F)$ denote the spin projected density of states around Fermi energy. The states of opposite spin (majority and minority spin states or spin-up and spin-down states) are represented by arrows $\uparrow$ and $\downarrow$. Depending on the magnetic characteristic of the material, the electron spin polarization vanishes in case of antiferromagnetic and paramagnetic compounds or has a finite value for ferrimagnetic and ferromagnetic alloys, below the Curie temperature. When either $\rho_{\uparrow}(\varepsilon_F)$ or $\rho_{\downarrow}(\varepsilon_F)$ equals zero, the electrons around Fermi level are fully spin polarized.

For ternary 1:1:1 Heusler compounds, the Slater-Pauling rule was firstly reported by Kübler [12]. These compounds, with C_{1b} structure have three atoms per unit cell and follow the Slater-Pauling 18-electron-rule ($M_t = Z_t - 18$), where M_t is the total magnetic moment per the formula unit, Z_t is the total number of valence electrons, and 18 represents the number of occupied states in the spin bands. A Slater-Pauling 24-electron-rule ($M_t = Z_t - 24$) was found for the 2:1:1 family of full-Heusler compounds with L_{21} structure (Cu_2MnAl -prototype) [13]. The present work deals only with ternary 2:1:1 full-Heusler compounds with Hg_2CuTi type structure. Even though the origin of the band gap in the latter 2:1:1 full-Heusler compounds is different than that of the ternary 1:1:1 Heusler compounds, the corresponding Slater-Pauling rule is similar: 18-electron-rule ($M_t = Z_t - 18$). This Slater-Pauling 18-electron-rule was recently explained for Ti_2 -based full-Heusler compounds [4, 14].

Many Co_2 , Mn_2 , Ti_2 , and Sc_2 – Heusler compounds reported in literature are ferromagnetic [15–18], ferrimagnetic half-metals [19], or spin gapless semiconductors [20]. Among them, Mn_2CoAl full-Heusler compound crystallizing in Hg_2CuTi -prototype was extensively studied: theoretically investigated, the structure was experimentally verified by XRD and the electron transport characteristics were obtained by a Physical Properties Measurement System (PPMS) on samples cut from ingots. The total magnetic moment was experimentally measured using a Magnetic Properties Measurement System (MPMS) [20]. Zirconium has a Pauling electronegativity value lower than those of all d-elements and hence Zr-based Heusler materials are supposed to crystallize in Hg_2CuTi type structure, similar to Mn_2CoAl .

Zirconium-based Heusler compounds were selected because they exhibit low toxicity and are corrosion resistant, being therefore susceptible of convenient preparation and processing in the field of electronic biomedical sensors ranging from healthcare and medical diagnosis, food safety, and environmental monitoring to life science research.

The information about the experimental preparation and electronic structure of Zr-based Heusler compounds with true half-metallic properties are still scarce. Therefore, to understand the properties of potential zirconium-based Heusler compounds, in the beginning, theoretical investigations can be performed via density functional theory (DFT). Self-consistent calculations using a “muffin-tin” model and various approximations to describe the exchange and correlation interactions can lead to valuable information about the energetically favorable crystalline structure, electronic configuration, or magnetic properties by means of the total energy minimization.

This chapter gives a comprehensive overview of the key electronic structures and magnetic properties usually found in half-metallic zirconium-based full-Heusler compounds.

2. Half-metallic ferrimagnetic materials

The cubic crystal structure of full-Heusler Zr_2YZ variants exhibits two magnetic sublattices, coupled to each other. Thus, the two Zr atoms are located in tetrahedral lattice sites and interact to each other. In addition, Zr and Y atoms form a second and more delocalized magnetic sublattice. Therefore, ferrimagnetic interaction between the Zr and Y atoms is frequently reported phenomena.

The total spin-polarized density of states of a typical half metallic ferrimagnetic material exhibits in the spin-up channel a semiconducting band gap while in the spin-down channel a metallic behavior. A relevant example is illustrated in **Figure 1** for Zr_2CrAl (unpublished results). The main contribution to the total density of states from spin-down channel comes from transition metal constituent elements, and these results are consistent with other published information [21].

Desirable candidates for magnetoelectronic devices, half-metallic ferrimagnetic compounds provide an unequivocal advantage over their ferromagnetic counterparts by reduction of the magnetic moment due to the ferrimagnetic interaction resulted from compensation of partial magnetic moments of the two different magnetic sublattices. This phenomenon is illustrated in **Figure 2** (unpublished results) for the Zr_2CrAl compound, where one can notice the magnetic moment of Cr atoms, partially compensated by magnetic moments of Zr located in the two different sublattices and having different neighborhoods. Similar DFT outcome were reported for Zr_2YZ ($Y = Cr, V, Z = Al, Ga, In, Pb, Sn, Tl$) [21–24].

Figure 3 (unpublished results) exhibits the position of the Fermi level and the width of the energy gap in spin-up channel as function of the lattice parameter. According to theoretical investigations, the Zr_2CrAl compound is a potential ideal candidate for spintronics, due to the presence of a steady energy gap in only one spin channel, for a large lattice parameter range.

Table 1 summarizes the published results regarding Zr_2CrZ ($Z = Al, Ga, In$) [21, 22]. As can be seen, the energy band gap (E_g) from spin-up channel increases as the atomic radii of Z elements increase. The ferrimagnetic interaction occurs between the zirconium atoms from both sublattice and the chromium ones, phenomena which are reflected by the opposite sign of the partial magnetic moments of Zr and Cr atoms. The total magnetic moment per f.u. for all compounds strictly follow the Slater Pauling rule described earlier.

In the ideal case of a fully compensated magnetic moment, a half-metallic ferromagnetic material would be obtained, useful to be applied in a junction device as a stable spin-polarized electrode based on spin-transfer effect.

Figure 1.
Partial and total density of states (PDOS and TDOS) of half-metallic ferrimagnetic Heusler compound, Zr_2CrAl at optimized lattice parameter.

Figure 2.
Partial and total magnetic moments in Zr_2CrAl Heusler compound.

The theoretical results from in literature for Zr_2VZ ($Z = Al, Ga, In, Si, Ge, Sn, Pb$) [23, 24] report that the most energetically favorable crystalline structure comparing with the Hg_2CuTi structure has the prototype Cu_2MnAl and in this configuration the materials do not present half-metallic properties. However, the Hg_2CuTi type structure can be synthesized experimentally due to the negative entropy of formation. In the inverse Heusler crystalline structure, the Zr_2VZ exhibits half metallic ferrimagnetic characteristics, the partial magnetic moment of Vanadium being opposite to the one of zirconium atoms.

Figure 3. The positions of the highest occupied states from the valence band (solid rhombs) and of the lowest unoccupied states from the conduction band (solid stars) of total DOSs (spin-up channel) for Zr_2CrAl as function of the lattice parameter.

Alloy	a (Å)	$\mu_{\text{Zr}(4a)} (\mu_{\text{B}}/\text{atom})$	$\mu_{\text{Zr}(4c)} (\mu_{\text{B}}/\text{atom})$	$\mu_{\text{Y}(4b)} (\mu_{\text{B}}/\text{atom})$	$\mu_{\text{Z}(4d)} (\mu_{\text{B}}/\text{atom})$	$\mu_{\text{t}} (\mu_{\text{B}}/\text{f.u.})$	$E_{\text{g}} (\text{eV})$
Zr_2CrAl	6.59 ^b	-0.955 ^b	-0.768 ^b	2.835 ^b	-0.110 ^b	1.000 ^b	0.452 ^b
Zr_2CrGa	6.635 ^a	0.849 ^a	0.702 ^a	-2.591 ^a	0.049 ^a	-1.000 ^a	0.629 ^a
	6.622 ^b	-1.011 ^b	-0.914 ^b	2.994 ^b	-0.068 ^b	1.000 ^b	0.512 ^b
Zr_2CrIn	6.875 ^a	1.016 ^a	0.859 ^a	-2.930 ^a	0.034 ^a	-1.000 ^a	0.673 ^a
	6.812 ^b	-1.213 ^b	-1.080 ^b	3.343 ^b	-0.049 ^b	1.000 ^b	0.615 ^b

^aRef. [22].
^bRef. [21].

Table 1. Calculated lattice parameters, partial, total magnetic moments, and energy band gap in Zr_2CrZ ($\text{Z} = \text{Al}, \text{Ga}, \text{In}$).

3. Spin gapless semiconductors

Particular cases of half-metallic ferromagnetic materials are the spin gapless semiconductors, where a semiconducting band gap is formed in one spin channel and a pseudo-band gap in the other one. Such a pseudo band gap is often called zero or closed band gap because the maximum energy of the valence band is very close to the minimum energy of the conduction band. The Zr_2MnAl compound presents a typical behavior of spin gapless semiconductors and may allow a tunable spin transport (see **Figure 4**). The Fermi level, located at 0.04 eV below the conduction band minimum, in case of Zr_2MnAl , falls into a typical spin gapless semiconducting band gap of 0.41 eV in spin-up channel, according to Ref [25]. In the spin-down channel, a zero band gap is reported around the Fermi level. In both spin channels, the significant contribution to density of states between -4.5 and -1.5 eV comes from the 3d electrons of Mn, while the 4d electrons from Zr atoms have contribution only above the Fermi level.

Figure 5 presents the contribution of double and triple degenerated states (d_{eg} and d_{t2g} , respectively) of Zr and Mn atoms, calculated around the Fermi level, at optimized lattice parameters. In Zr_2MnAl compound, the highest bonding states from valence band, below the E_{F} , belong to triple degenerated states of manganese

Figure 4.
Partial and total density of states (PDOS and TDOS) of spin gapless semiconductor Zr_2MnAl at equilibrium lattice parameter.

Figure 5.
The densities of states of double and triple degenerated states of Zr and Mn atoms, around the Fermi level, calculated at optimized lattice parameters for Zr_2MnAl . The Fermi level, d_{eg} and d_{t2g} , are illustrated with black dotted, red dashed, and blue solid line, respectively.

d_{t2g} , while the lowest anti-bonding states from conduction band come from the triple degenerated states d_{t2g} of Zr_1 , Zr_2 , and Mn. As a result, the energy gap from spin-up channel results due to Zr-Mn hybridization. The Zr_2MnAl alloy presents

an indirect band gap of 0.41 eV, in the spin up channel with the higher bonding states from valence band located in the Δ point and the lowest anti-bonding states from the conduction band, distributed in the Δ and W high symmetry points of Brillouin zone.

It is obvious that the change in the lattice parameter affects the presence of the zero band gap from spin channel and the width of the semiconducting band gap. In Zr_2MnAl alloy, the band gap increases initially by increasing the lattice parameter. The largest band gap is obtained for a lattice parameter of 6.6 Å, which corresponds to a volume increase of 2%. Above the lattice parameter of 6.6 Å, the spin gapless semiconducting properties of Zr_2MnAl compound disappear, due to the shifts of the Fermi level in to the conduction band. The width of the energy band gap from spin-up channel decreases as illustrated in **Figure 6**.

The spin gapless semiconductors may present a finite total magnetic moment; however in the particular case, when a perfectly compensated ferrimagnetism appears the total magnetic moment of compound equals zero and the alloy becomes a spin gapless completely compensated ferrimagnet, like Zr_2MnAl (see **Figure 7**).

Surprisingly, the zirconium element which does not exhibit natively magnetic properties shows magnetic behavior. A ferrimagnetic interaction occurs between the magnetic moments of Zr and Mn atoms, whereas the zirconium atoms, located in different Wyckoff positions, are coupled ferromagnetically. The magnetic moments of manganese increase with the lattice parameter, in all compounds. The magnetic moments of zirconium atoms coupled ferromagnetically decrease with the lattice parameter increase and compensate the magnetic moment of Mn atoms. The main element Al does not carry significant magnetic moments, but non-negligible contribution to the magnetic moment comes from conduction electrons.

Antiferromagnetic “ab initio” results were reported for Zr_2MnZ ($Z = \text{Al}, \text{Ga}$) [26–28] and were gathered in **Table 2**. For Zr_2MnAl , the band gap is slightly increased from 0.41 eV for ferromagnetic calculation to 0.48 eV to antiferromagnetic results. However, the semiconducting band gap from spin-down channel decreases when the atomic radius of the main element increases (when Ga replaces Al). Due to the different magnetic ordering structures, having the spin moments of manganese antiparallel (antiferromagnetic configuration) or parallel (ferromagnetic configuration) oriented, the sign of partial magnetic moments from **Table 2**, differs. However, the opposite spin orientation is clearly explaining the ferrimagnetic

Figure 6.

The positions of the highest occupied states from the valence band (solid rhombs) and of the lowest unoccupied states from the conduction band (solid stars) of total DOSs (spin-down channel) for Zr_2MnAl as function of the lattice parameter.

Figure 7.
Total magnetic moments in spin gapless semiconductor Zr_2MnAl .

Alloy	a (Å)	$\mu_{Zr(4a)}$ ($\mu_B/atom$)	$\mu_{Zr(4c)}$ ($\mu_B/atom$)	$\mu_{Y(4b)}$ ($\mu_B/atom$)	$\mu_{Z(4d)}$ ($\mu_B/atom$)	μ_t ($\mu_B/f.u.$)	E_g (eV)
Zr_2MnAl	6.56 ^a	-0.77 ^a	-0.69 ^a	2.44 ^a	-0.04 ^a	0.00 ^a	0.41 ^a
	6.64 ^{b,*}	1.74 ^{b,*}	1.50 ^{b,*}	-3.26 ^{b,*}	0.02 ^{b,*}	0.00 ^{b,*}	
	6.968 ^{d,*}	1.47 ^{d,*}	1.35 ^{d,*}	-4.33 ^{d,*}	0.088 ^{d,*}	0.00 ^{d,*}	0.48 ^d
Zr_2MnGa	6.59 ^{c,*}	1.66 ^{c,*}	1.52 ^{c,*}	-3.08 ^{c,*}	-0.10 ^{c,*}	0.00 ^{c,*}	
	6.935 ^e	-1.48 ^e	-1.42 ^e	4.34 ^e	-0.030 ^e	0.00 ^e	0.31 ^e

^{*}Antiferromagnetic calculation was performed.

^aRef. [25].

^bRef. [26].

^cRef. [27].

^dRef. [28].

^eRef. [29].

Table 2.
Calculated lattice parameters, partial, total magnetic moments, and energy band gap in Zr_2MnZ ($Z = Al, Ga$).

interaction between the Mn and Zr atoms and the ferromagnetic coupling between the Zr atoms located in the two distinct sublattice. The total magnetic moment per f.u. calculated in both magnetic configurations is fully compensated by partial magnetic moments of constituents and follow the Slater Pauling curve for typical for half-metals.

4. Half-metallic ferromagnetic materials

Ferromagnetic zirconium-based half-metallic Heusler compounds represent another category of materials of specific interest in biomedical spintronic applications where a good response to an external magnetic moment is required and that is mainly related to their large total magnetic moment. From theoretical point of view, the materials which exhibit a metallic character in the majority density of states and a band gap in the minority one, around the Fermi level and the metallic total density of states resulted from summation of partial density of states of all elements are classified as half-metallic ferromagnets.

A typical example of density of states for a half-metallic ferromagnet is exemplified in case of Zr_2CoAl [30–34] (see **Figure 8**). In the majority channel, the significant contribution to density of states comes from the zirconium, located in the origin of unit cell and the cobalt atom. The band gap from minority channel (**Figure 9**) is formed between the 3d t_{2g} electrons of Co and the 4d t_{2g} unoccupied

electrons of Zr located in origin and 4d t_{2g} occupied Zr electrons locate in the 4c Wyckoff position of Hg_2CuTi prototype structure. This type of hybridization between the Y element and the two X atoms of a X_2YZ Heusler compounds is often reported for half-metallic ferromagnets.

In general, the half metallic ferromagnetic properties characterized by the presence of a semiconducting band gap in the minority spin channel of density of states continue to be maintained for a large enough range of lattice parameter in order to be stable from experimental point of view. This means that even if the unit cell volume increases or decreases the material would present a high spin polarization typical for half metallic materials. In case of Zr_2CoAl , the transition from metal behavior to half metallic characteristic occurs at a 6.43 Å lattice parameter, and it remains stable at experimentally achievable increases of unit cell volume (**Figure 10**) [30–34]. By definition, in the case of a ferromagnetic material, a net magnetization may be measurable because even if the majority and minority density of states is identical and equally occupied; these are shifted against each other. The total magnetic moment is obtained by adding the partial magnetic moments of constituent elements as presented in **Figure 11**.

Table 3 overviews the state of the art ferromagnetic zirconium-based Heusler compounds. Most alloys incorporate cobalt, and the main elements carry an irrelevant partial magnetic moment. However, the influence of main elements over the energy band gap from spin-down channel is significant. The average width of band gap from spin-down channel is large enough to provide stable half-metallic characteristics for a large deformation of the unit cell. All results

Figure 8. Partial and total density of states (PDOS, TDOS) of half-metallic ferromagnetic Heusler compound, Zr_2CoAl , at optimized lattice parameter.

Figure 9.
The band structure of Zr_2CoAl for majority and minority spin channel, in the right and left panel, respectively, at equilibrium lattice parameter.

Figure 10.
The positions of highest bonding states from the valence band (solid purple rhombs) and of lowest anti-bonding states from conduction band (solid magenta stars) of total DOSs for Zr_2CoAl as function of lattice constants.

Figure 11.
The partial and total magnetic moments as a function of lattice constant for half-metallic ferromagnetic Zr_2CoAl Heusler compound.

gathered in **Table 3** are obtained based on density functional theory calculations, and these are influenced by the pseudo-potential used for electron-ionic core interaction. This is the reason for various reported band gaps of such compounds, as for example, the band gap reported by Ref [32] which is lower

Alloy	a (Å)	$\mu_{Zr(4a)}$ (μ_B / atom)	$\mu_{Zr(4c)}$ (μ_B / atom)	$\mu_{Y(4b)}$ (μ_B / atom)	$\mu_{Z(4d)}$ (μ_B / atom)	μ_t (μ_B / f.u.)	E_g (eV)
Zr ₂ CoAl	6.54	0.757 ^a		0.54 ^a		2.00 ^a	0.48 ^a
	6.575 ⁱ	1.211 ⁱ	0.303 ⁱ	0.538 ⁱ	-0.053 ⁱ	2.000 ⁱ	0.518 ⁱ
	6.59 ^c	1.34 ^c	0.36 ^c	0.4 ^c	-0.1 ^c	2.00 ^c	0.6046 ^c
	6.523 ^d	1.088 ^d	0.442 ^d	0.553 ^d	0.002 ^d	2.00 ^d	0.300 ^d
	6.575 ^e	1.21 ^e	0.3 ^e	0.54 ^e	-0.05 ^e	2.00 ^e	0.518 ^e
Zr ₂ CoGa	6.539 ^f	0.725 ^f	0.262 ^f	0.587 ^f	0.011 ^f	2.00 ^f	0.5905 ^f
	6.62 ^c	1.30 ^c	0.52 ^c	0.34 ^c	-0.16 ^c	2.00 ^c	0.6990 ^c
	6.593 ⁱ	1.162 ⁱ	0.402 ⁱ	0.505 ⁱ	-0.070 ⁱ	2.000 ⁱ	0.533 ⁱ
	6.509 ^d	1.074 ^d	0.526 ^d	0.522 ^d	0.013 ^d	2.00 ^d	0.353 ^d
	6.520 ^f	0.714 ^f	0.332 ^f	0.518 ^f	-0.001 ^f	2.00 ^f	0.6546 ^f
Zr ₂ CoIn	6.75 ^c	1.34 ^c	0.62 ^c	0.2 ^c	-0.16 ^c	2.00 ^c	0.7013 ^c
	6.627 ⁱ	1.215 ⁱ	0.455 ⁱ	0.417 ⁱ	-0.089 ⁱ	2.000 ⁱ	0.576 ⁱ
	6.714 ^d	1.085 ^d	0.581 ^d	0.427 ^d	0.011 ^d	2.00 ^d	0.268 ^d
	6.726 ^f	0.722 ^f	0.3630 ^f	0.429 ^f	-0.002 ^f	1.999 ^f	0.6580 ^f
Zr ₂ CoSi	6.68 ^c	1.59 ^c	0.58 ^c	1.0 ^c	-0.08 ^c	3.00 ^c	0.8419 ^c
Zr ₂ CoGe	6.70 ^c	1.65 ^c	0.65 ^c	0.86 ^c	-0.16 ^c	3.00 ^c	0.8365 ^c
Zr ₂ CoSn	6.76 ^b	0.946 ^b	0.446 ^b	0.8106 ^b	-0.013 ^b	3.00 ^b	0543 ^b
	6.790 ⁱ	1.625 ⁱ	0.605 ⁱ	0.829 ⁱ	-0.060 ⁱ	3.000 ⁱ	0.614 ⁱ
	6.81 ^c	1.70 ^c	0.68 ^c	0.78 ^c	-0.16 ^c	3.00 ^c	0.8537 ^c
	6.745 ^d	1.429 ^d	0.746 ^d	0.858 ^d	0.044 ^d	2.998 ^d	0.406 ^d
	6.745 ^g	1.429 ^g	0.746 ^g	0.858 ^g	0.044 ^g	3.000 ^g	0.65 ^g
Zr ₂ CoPb	6.86 ^c	1.72 ^c	0.76 ^c	-0.16 ^c	-0.24 ^c	3.00 ^c	0.58 ^c
Zr ₂ NiAl	6.60 ^h	1.02 ^h	0.98 ^h	0.61 ^h	0.15 ^h	2.87 ^h	0.44 ^h
Zr ₂ NiGa	6.58 ^h	1.06 ^h	0.81 ^h	0.58 ^h	0.21 ^h	2.86 ^h	0.50 ^h

^aRef [30].
^bRef [35].
^cRef [31].
^dRef [32].
^eRef [33].
^fRef [34].
^gRef [36].
^hRef [37].
ⁱRef [21].

Table 3.
Calculated lattice parameters, partial, total magnetic moments, and energy band gap in Zr₂YZ (Y=Co, Ni; Z = Al, Ga, In, Si, Ge, Sn, Pb).

than the other published results. In all compounds, the ferromagnetic interaction between constituent atoms is represented by similar signs of the partial magnetic moments. The total magnetic moments, following Slater-Pauling curve, are higher than for ferromagnetic half-metallic compounds, and as consequence, the compounds may present a better response to an external magnetic field. Theoretical results regarding zirconium-based half-metallic compounds containing nickel provide information about electronic structures and magnetic properties in alloys with Al and Ga. These intermetallic compounds theoretically behave like half-metals from the electronic structure point of view; however their reported total magnetic moments do not follow the Slater Pauling curve.

In addition, the band gap from spin-down channel is significant lower than for compounds incorporating cobalt.

5. Conclusion

The individualized medicine and high precise diagnosis can benefit from the development of smart biosensors based on magnetic functionalities. Foreseeable applications of zirconium-based biosensors with half metallic character include the capability to measure, sense, or respond to magnetic stimuli desirable for in vivo sensitive detection of markers for diseases.

This chapter overviewed the recent advances of zirconium-based full-Heusler compounds from the point of view of electronic structure and magnetic properties. The representative materials described in this chapter obviously were selected to offer significant information to emphasis the certain differences in magnetic features: half-metallic ferrimagnetism, spin-gapless semiconducting, and half-metallic ferromagnetism. Based on this, the Y elements of Zr_2YZ were selected from the most commonly used transition metals (Cr, Mn, and Co), while the Z element was identical in all compounds (Al). The purpose was to underline the influence of d electrons of Y elements and hybridization interaction between the electrons of zirconium and Y atoms over the macroscopic magnetic properties.

Furthermore, the theoretical and experimental advances in designing and fabrication technology engage the construction of innovative materials to be integrated in biosensors with significant high throughput able to reform the biomedical field.

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