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Density functional study of the half-metallic ferromagnetism in Co-based Heusler alloys Co_2MSn (M = Ti, Zr, Hf) using LSDA and GGA

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ABSTRACT

The half-metallic state in the Heusler alloys Co_2MSn (M = Ti, Zr, Hf) was studied by means of first principles calculation, using both, the Local Spin Density Approximation (LSDA) and the Generalized Gradient Approximation (GGA) to the exchange-correlation energy. While the GGA calculation shows that the three alloys are half-metallic ferromagnets, the LSDA results show that they are ferromagnetic but not half-metallic systems. The difference between the exchange-correlation functionals is analyzed through the electronic structure of the alloys. The origin of the gap in the minority spin channel for GGA calculations is discussed.

1. Introduction

The Heusler alloys show a wide variety of interesting magnetic properties such as Pauli paramagnetism, itinerant and local magnetism, helimagnetism, antiferromagnetism or heavy-fermion behavior. In recent years, it has been found that Heusler alloys exhibit a new magnetic phenomenon, half-metallic ferromagnetism. Groot et al. [1] were the first to predict half-metallic ferromagnetism through spin-polarized band structure calculation.

These alloys are thought to be metallic for one spin direction and showing semiconductive properties, at the same time, for the opposite spin direction, resulting in 100% spin polarization. This dual property has an important application in inter-metallic tunnel barriers or Schottky contacts, where they are not required to inject spins polarized current into the semiconductor at room temperature since in half-metallic ferromagnets (HMF) only electrons of either spin-up or spin-down can be injected into the system, creating a perfect spin filter. HMF has attracted much attention due to its possible application in spintronics [2].

Among the HMF full Heusler alloys, there is a Co-based group whose theoretical half-metallic ferromagnetism property is ambiguous. Electronic band structure calculations predict that Co_2MSn (M = Ti, Zr, Hf) is ferromagnetic, but the results about its semi-metallicity are not consistent. Within the framework of LSDA or GGA, some reports [3–7] have shown that the systems do not have a half-metallic ground state. However, Kandpal et al. [8,9] predict that the three systems are HMF. To contribute to solve this controversy, we carried out ferromagnetic band structure LSDA and GGA calculations in order to observe whether the systems showed a half-metallic ground state or not. In this work, we also analyze the magnetic moment, and the origin of the gap in the GGA density of states, in the minority spin channel in those systems.

2. Method

The calculations were performed using full potential linearized augmented plane wave method (FLAPW) [10], as implemented in the WIEN2k code [11] within the GGA of Perdew et al. [12] and LSDA with the exchange-correlation functional of Perdew and Wang with reparameterization of Ceperly–Alder data [13]. We chose muffin-tin radii (R_{MT}) of 2.4 a.u. for Co, 2.6 a.u. for Sn, 2.0 a.u. for Ti, and 2.4 a.u. for Zr and Hf. The self-consistent calculations were done with an LAPW basis set defined by the cutoff $R_{MT}K_{max} = 9$, plus local orbitals to relax linearization errors [14]. The Brillouin-zone samplings were done using the special **k**-point method, accurate convergence in the **k** point up to 413 inequivalent **k**, and for spin orbit calculations we used 641 **k** points. Inside the atomic spheres, the potential and charge density are expanded in crystal harmonics up to $l = 10$. The core levels are treated fully relativistically, whereas the valence electrons are calculated in two schemes: semi-relativistically, i.e., without spin–orbit coupling, and a fully relativistic scheme with spin–orbit coupling included in a second-variational treatment using the scalar-relativistic eigen-functions as basis.

3. Results and discussion

In Table 1, experimental, LSDA, and GGA computed lattice constant and, the bulk modulus for the three alloys are shown.

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The LSDA and the GGA total energy values, as a function of the volume, were fitted to the Murnaghan equation of state. The LSDA lattice constant is underestimated by about 2% in comparison to the experimental value. The GGA lattice constant is overestimated by less than 1%. The GGA bulk modulus is systematically smaller than the LSDA's values. These results follow the general trend when comparing these two approaches, GGA yields larger bond lengths and smaller bulk modulus than LSDA. However, both approximations are in good agreement with the experimental value.

Fig. 1 shows the LSDA and the GGA spin-polarized density of states (DOS) per spin for the three alloys. In the majority spin channel in both approximations the spin-polarized DOS shows a metallic character. In the minority spin channel there is a gap around the Fermi energy (ε_F) in both approximations, in the LSDA DOS the gap is smaller than the presented in the GGA calculation, and ε_F is placed after the minority gap while in GGA DOS, ε_F falls into the minority gap. Our calculations were made for different volumes in order to rule out lattice effects in the position of the gap with respect to ε_F. In the range from -10% to 10% of volume isotropic deformation, in the three alloys in both approximations, the position of the gap with respect to ε_F did not change. However, the size of the gap did present changes.

Self-consistent LSDA and GGA band structure at the calculated lattice parameter of Co_2TiSn in the minority and majority spin channels are shown in Fig. 2. To analyze how LSDA and GGA functionals acting on the orbitals in this alloy we will focus at the Γ point. The analysis is on the Co_2TiSn alloy but the results are qualitatively similar to the other two alloys. In the majority spin channel we can identify three zones where the approaches deal differently with the orbitals. The first zone, for energies below -2.0 eV, LSDA values are lower in energy than those of GGA. The second zone is around the doubly degenerate Γ_{12} state, mainly Co *e* orbitals, in this band the LSDA values are higher in energy than those of GGA. From these two zones we can see that the exchange-correlation potential experienced by the Co *d* orbitals are different. Focusing in the $\Gamma-\Delta-X$ direction, which is perpendicular to the Co_2 (1 0 0) planes, in the t_2 orbitals (Γ'_{25}), LSDA values are lower in energy than those of GGA, and the bands remain the same topology between approximations, while in the doubly degenerated Γ_{12} state (Co *e* orbitals), GGA values are lower in energy and the bands are topologically different among the approximations. The third zone is around ε_F, at the top of the valence band is Γ'_{25} state mainly Ti t_{2g} and above ε_F is Γ_{12} state mainly Ti e_g. These bands hybridize in X and **k** points with *d* states of Co. In this zone GGA and LSDA energy values have qualitatively similar results. The reason for these differences between the second and the third zones may be because in Co_2MSn, Co atoms are in the 8*c* site, they have four M atoms and four Sn atoms (T_d point symmetry). While the atom M is in the 4*a* site, surrounded by eight Co atoms in octahedral symmetry (O_h point symmetry). Therefore the local environment for the case of the atom M is more homogeneous than in the case of atoms Co. In full potential calculations LSDA and GGA have shown that homogeneity of the orbitals is relevant.

In the minority spin channel the *d* states from Co are now placed around ε_F. In this case the top of the valence band and the bottom of the conduction band have a weak interaction with the Ti atoms being the main interaction of a second nearest next neighbor. The Co atoms have four second next neighbors atoms all of them also Co. Below -1.5 eV, again LSDA values are lower in energy than those of GGA. At the top of the valence band at Γ'_{25} state are the Co t_2, GGA and LSDA have similar energy values. However, at the bottom of the conduction band at Γ_{12} state, the *e* orbitals from Co show the main difference between LSDA and GGA. While in GGA the states are empty, in LSDA the states are partially occupied therefore splitting of the Co *d* orbitals in LSDA is smaller than in GGA. This is a typical difference between GGA and LSDA functionals. GGA gives a larger exchange splitting, and a

Table 1
Experimental [15] and calculated lattice constant *a* (in Å) and bulk modulus B_0 (in GPa).

Alloy	Exp.	*a*		B_0	
		LSDA	GGA	LSDA	GGA
Co_2TiSn	6.076	5.948	6.092	205.16	171.42
Co_2ZrSn	6.242	6.135	6.283	188.32	158.31
Co_2HfSn	6.227	6.083	6.254	216.51	166.76

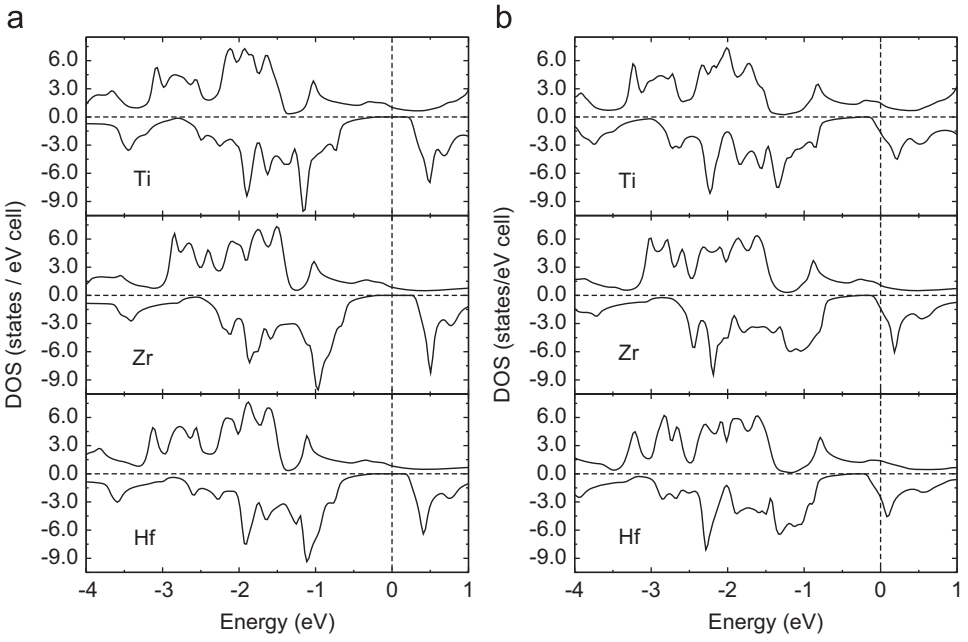

Fig. 1. Spin polarized (a) GGA and (b) LSDA density of states for Co_2MSn (M= Ti, Zr, Hf). The energy zero is set at the Fermi level.