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Theoretical investigations of an influence of Ti on electronic structure and magnetic properties of half-metallic $Fe_2Mn_{1-x}Ti_xSi_{0.5}Al_{0.5}$ alloys

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ABSTRACT

Ab-initio electronic structure calculations are carried out for quinternary $Fe_2Mn_{1-x}Ti_xSi_{0.5}Al_{0.5}$ alloys basing on the density functional theory. When $x=0$, the alloy is a half-metallic ferromagnet with magnetic moment following the Slater–Pauling rule. Main carrier of magnetism of the alloy is manganese with the magnetic moment of about 2.5 μ_B. Replacement of Mn by Ti, changes its electronic and magnetic structure. Half-metallicity is present up to Ti concentration $x=0.375$. However, the further increase of Ti content leads to a strong decrease of electronic spin polarization. When the concentration of Ti increases, total magnetic moment strongly decreases. Fe magnetic moment, in the presence of titanium, changes its orientation into antiparallel in respect to the total magnetic moment and its absolute value increases with increasing Ti content. However, absolute value of Fe magnetic moment does not exceed 0.17 μ_B. Ti exhibits very weak spin polarization with magnetic moment not higher than 0.05 μ_B.

1. Introduction

For many years, Heusler type alloys [1] have drawn attention due to their interesting properties and new possible applications. Their ordering processes result in formation of large class of alloys, some of them having extreme characteristics [2], e.g. giant inverse magnetocaloric effect [3], magnetic shape memory effect [4], heavy-fermion behavior [5–7], and superconductivity [8] [9].

Very promising for application are half-metallic compounds. Since De Groot et al. reported that half-Heusler (XYZ) NiMnSb and PtMnSb alloys are half-metals (HMs) [10] many HMs were also predicted in the group of full-Heusler (X_2YZ) alloys [11,12]. In the HM the Fermi level crosses energy dispersion curves in one spin subband, while an energy gap at the Fermi level for the second subband appears. Thus electronic spin polarization, defined as [13]

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

where D_σ is density of states of σ spin at the Fermi level, for half-metal is equal to 100%. Evaluation of the spin polarization of ferromagnetic materials is a key factor while looking for materials potentially applicable in spintronics, because to realize high-performance devices, highly spin polarized ferromagnets are required. However, this feature is still difficult to measure [14]. In practice, the complete spin polarization of charge carriers can be only reached in the limiting case of zero temperature and vanishing spin–orbit interactions. Because most of the Heusler type compounds containing only 3d elements do not show any spin–orbit coupling, so they are good candidates to reveal half-metallic character [15]. In a group of Heusler alloys, the covalent hybridization between the lower energy d states of the high valent transition metal atoms X and the higher energy d states of the low-valent transition metal Y leads to the formation of the band gap for one spin direction at the Fermi level [15,16]. If the electrical current is perfectly spin polarized in the material, it makes possible to produce new devices controlled by magnetic field. It is quite different from traditional devices driven by electrical charge [17]. This exceptional property makes half-metallic ferromagnets ideal candidates for spin injection devices [15]. Spin transistor based on double tunnel junctions has been already constructed using half-metallic Co_2MnSi electrodes [18].

It is worth mentioning that although the family of X_2YZ Heusler alloys is large, there are still only a few examples of half-metallic ferromagnets which are not based on X=Co [15,19–21]. Fe-based Heusler half-metallic ferromagnets reveal some advantages in comparison with Co-based alloys, what draws much interest for further studies. In Fe-based alloys, saturation magnetization M_S is smaller when compared to conventional Co-based Heusler compounds (4–6 μ_B/f.u.) [22,23]. Since the critical current for spin transfer switching in magnetic tunnel junctions and the speed of domain wall motion are proportional to the M_S and M_S^{-1}, respectively, the small value of M_S will be an advantage for spin transfer-

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based switching [24]. It should be emphasized that the presence of Fe in Heusler alloys can lead to a significant increase in Curie temperature, like in $Co_2Mn_{1-x}Fe_xSi$, what is a key factor in spintronic materials [25]. On the other hand, still moderately high Curie temperature (e.g. 630 K in Fe_2CrSi [26]) provides both thermal stability at room temperature and potential applicability for thermally assisted switching devices [27]. Furthermore, large density of majority states at the Fermi level in Fe-based Heusler alloys ensures high stability of spin polarization against disorder and temperature effect [28]. For example, majority density of states in Fe_2CrSi equals to 7.0 states/eV what is about 5 times higher than in abovementioned Co_2MnSi [29].

According to band structure calculations, performed for half-Heusler NiMnSb and full-Heusler Co_2CrAl compounds, structural disorder has strong influence on the position and the width of the band gap [30,31]. Local strains and distortions can destroy half-metallicity [32–34]. However, half-metallic energy gap in Fe-based Heusler ferromagnets is insensitive to the atomic disorder [20] what makes them good candidates for spintronic applications.

Besides the stoichiometric Heusler compounds, quaternary, and quinternary Heusler alloys also exhibit interesting properties. There are some theoretical and experimental results for such alloys, however, still mainly for Co-based ones. By changing concentration of constituent chemical elements, one can continuously tune electronic and magnetic properties of the alloys. For example, Fe_2TiAl is a metal with pseudogap above the Fermi level [35]. In order to shift the Fermi level into higher energy region one needs to introduce more valence electrons at Y position in the crystal lattice [36]. Similarly, variation of the main group element in Heusler compound is a strong tool for tuning their physical properties [28]. For example electron spin polarization of full-Heusler alloy Fe_2MnAl equals 81%, but changing of Al into Ge, leads to an increase of polarization to 96% [28]. On the other hand, when the Y element is chromium (Fe_2CrZ), replacement of Al by Si leads to the almost total polarization, and the P values are 82% and 98% for Z=Al and Si, respectively [19]. Apart from abovementioned benefits of tuning of electronic properties, it is known that simultaneous doping with different transition metals and metalloids can improve mechanical properties of the alloy, what is also important factor while considering potential applications [37,38].

Additionally to the unique properties, Heusler-type alloys provide very good insight into fundamental aspects of magnetism in complex systems. Due to the two different magnetic sublattices in full-Heusler compounds ferromagnetism, ferrimagnetism and half-metallic ferromagnetism can be found [15].

All these abovementioned properties are reflected in the electronic structure of the alloys. Thus, ab-initio electronic structure calculations can provide very useful tool for designing of new materials with desirable properties. Assuming particular concentrations of component chemical elements one can predict electronic and magnetic properties of the alloy. The aim of this study is systematic theoretical investigation of quinternary $Fe_2Mn_{1-x}Ti_xSi_{0.5}Al_{0.5}$ Heusler alloys. As it was mentioned before, by fractional concentrations of metalloids it is possible to tune electronic properties, For example, Fe_2MnSi is a ferromagnetic metal, but replacing 50% of Si by Al ($Fe_2MnSi_{0.5}Al_{0.5}$) leads to forming of half metallic band gap [39]. Additionally, equal concentrations of Al and Si were chosen in order to check a tendency, observed theoretically and experimentally, of lattice parameter's constancy in Fe-based intermetallic alloys with equal Al and Si concentrations. It was reported that equal concentrations of Al and Si in Fe-based intermetallic bcc compounds can keep constant lattice parameter while doping Fe with transition metals [39,40,41]. Furthermore, even for already investigated Fe-based Heusler alloys, there are still some discrepancies concerning electronic structure. Thus, description of the ground state requires further thorough studies.

2. Calculation details

2.1. Method of calculations

First principle spin-polarized calculations have been carried out using the Full Potential – Linearized Augmented Plane Waves with Local Orbitals (FP-LAPW+lo) method implemented in Wien2k code [42]. As it was already shown [15,43] in most cases the correct electronic ground state of Heusler-type alloys consisting of transition metals was obtained by the full-potential method in the generalized gradient approximation. Hence, the exchange correlation potential, in the generalized gradient approximation (GGA), was taken in the form given by J.P. Perdew, K. Burke and M. Ernzenhof [44].

In order to calculate electronic structure of quaternary $Fe_2MnSi_{0.5}Al_{0.5}$ and quinternary $Fe_2Mn_{1-x}Ti_xSi_{0.5}Al_{0.5}$ alloys the supercell structure with 8 and 32 atoms was used, respectively. It was obtained by the extension of the basic position of structure of cubic space group $Fm\bar{3}m$ into the three dimensional space. Two sets of Kohn–Sham single particle equations (for both spins) were solved self-consistently. Calculations were carried out for at least 120k-points in the irreducible wedge of the Brillouin zone. Further increasing of the k-grid did not significantly change the obtained results. The cutoff energy separating the valence from core states was set to -6.0 Ry. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps converged to values stable within 10^{-6} Ry. Furthermore, charge convergence was obtained on the level of 10^{-4} e. Radii of muffin-tin spheres for atoms were chosen to ensure nearly touching spheres and minimizing the interstitial space. The self-consistent procedure was carried out for the parameters $R_{MT}k_{max}=7$, where R_{MT} is the smallest atomic sphere radius in the unit cell and k_{max} is the interstitial plane-wave cutoff. The integration over the Brillouin zone was performed by the Blöchl tetrahedron method [45].

The results from the electronic structure calculations were compared to predictions based on the valence electron concentration, what is the main factor while considering magnetic properties and band gap in minority states for Heusler type alloys [46].

2.2. Crystal structure

The full-Heusler compound with a chemical formula X_2YZ (where X and Y are transition metals and Z is a main group element) crystallizes in $L2_1$ structure which can be thought as consisting of four interpenetrating *fcc* cubic Bravais lattices mutually shifted along the main diagonal, originated at (0,0,0), (¼, ¼, ¼), (½, ½, ½) and (¾, ¾, ¾) positions and abbreviated as A, B, C and D, respectively. In a perfectly ordered structure, X element is located in A and C sublattices, whereas B and D position are occupied by Y and Z atoms, respectively.

In $Fe_2Mn_{1-x}Ti_xSi_{0.5}Al_{0.5}$ alloys it was assumed during calculations that A and C position are totally occupied by iron, aluminium and silicon are placed in D position, whereas Mn and Ti atoms occupy B sites. While doping $Fe_2MnSi_{0.5}Al_{0.5}$ with Ti, lattice parameters were determined by total energy calculations.

3. Results

3.1. $Fe_2MnSi_{0.5}Al_{0.5}$

According to the total energy calculations equilibrium lattice parameter of $Fe_2MnSi_{0.5}Al_{0.5}$ equals to $a_0=0.5642$ nm. The alloy is a half-metallic ferromagnet with a total magnetic moment of 2.500 μ_B following the Slater–Pauling rule [47,48]. Total valence charge N_V of $Fe_2MnSi_{0.5}Al_{0.5}$ is equal to 26.5 e (the fractional number was obtained because of fractional concentrations of Al