Intermetallics 85 (2017) 197–205

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Structural, electronic and magnetic properties of $Ti_{1+x}FeSb$ Heusler alloys

Said M. Azar [a, *], Ahmad A. Mousa [b], Jamil M. Khalifeh [c]

[a] Department of Basic Sciences, Dar Al Uloom University, Riyadh, Saudi Arabia
[b] Department of Basic Sciences, Middle East University, Amman, 11831, Jordan
[c] Department of Physics, The University of Jordan, Amman, 11942, Jordan

ARTICLE INFO

Article history:
Received 31 May 2016
Received in revised form
6 January 2017
Accepted 17 February 2017
Available online 6 March 2017

Keywords:
Heusler alloys
Half-metal
First principles
DFT
FP-LAPW
TB-mBJ

ABSTRACT

Density functional theory calculations based on full potential linearized augmented plane-wave (FP-LAPW) plus local orbital method in the framework of GGA-PBE, as embodied in the WIEN2k code, is used to investigate the structural, electronic and magnetic properties of intermetallic $Ti_{1+x}FeSb$ Heusler compounds, where $(x = -0.75, -0.50, -0.25, 0.0, 0.25, 0.50, 0.75, 1.0)$. Moreover, the Tran-Blaha parameterized of the modified Becke-Johnson (TB-mBJ) exchange potential, as a semi-local method, is employed to predict the bandgap more precisely. The physical characteristic of these systems are found to be mostly determined by the crystal structure and the electron concentration or the number of valence electrons. We examined the site preference of the parent compound *TiFeSb* and varied the electron concentration by doping or removing a *Ti* atom and we found that the variation plays a crucial role in the physical properties of these material systems. Alloys with $x \leq 0$ are found to exhibit a ferrimagnetic phase, and the alloy with $x = 0.25$ exhibits non-magnetic properties, whereas the rest have shown ferromagnetic phase. The band-structure analysis of $Ti_{1.75}FeSb$ and Ti_2FeSb ($CuHg_2Ti$-type) alloys suggested that they could be ferromagnetic half-metallic candidates with bandgaps 0.350 and 0.468 eV, respectively. We found that *Ti* rich $Ti_{1+x}FeSb$ alloys have high spin polarization.

1. Introduction

The half-metallicity was first predicted in 1983 by de Groot *et al.* for the half-Heusler alloy *NiMnSb* [1] and Kücbler first realized their high magnetic moments and high spin polarization [2]. Heusler phases (X_2YZ and XYZ) are considered to be most attractive candidates for application in spintronic devices, since they exhibit extremely high Curie temperatures (905 K for Co_2MnGe), low coercivities and good lattice matching with conventional semiconductors such as GaAs. Used in MTJs with *MgO* tunnel barriers, TMR values as high as 750% at 2 K have been reached [3].

Ternary transition metal antimonid systems have recently attained more interest because of their possibility in technological applications such as spintronic as well as thermoelectric power generation. In addition, the lack of complete knowledge on phase formation and equilibria, crystal structure and homogeneity range as well as the diversity of the physical properties such as magnetic order, semiconducting-like behavior, half-metallicity and large Seebeck coefficient versus composition motivated the authors to investigate these systems. *FeTiSb* and other intermetallic semi-Heusler compounds and their solid solutions were investigated experimentally and theoretically. Their physical properties are influenced by the number of valence electrons. Some discrepancy was found between experimental and theoretical results [4]. In *TiFeSb* case, the compound is close to the magnetic-nonmagnetic boundary and its properties are very sensitive to any kind of atomic disorder [5]. Szytula *et al.*, by extensive experimental studies of *FeTiSb* alloy observed a Curie-Weiss like paramagnetism phase, with paramagnetic moment close to 2.8 μ_B, and its crystallographic structure is more complex than the normal semi-Huesler [6]. Experimental and theoretical study of the structural and transport properties of quaternary half-Heusler $Fe_{1-x}Ni_xTiSb$ alloys employed X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, resistivity, thermopower measurements, and KKR-CPA method. The presence of the energy gap at the nine bands allows us to consider *FeTiSb* compound as one hole system. Conversely, the KKR-CPA on a disordered $(Ti_{0.5}E_{0.5})_2FeSb$ (E denotes vacant site), in which *Ti* atoms are distributed randomly on two equivalent sites in the

---

* Corresponding author.
E-mail address: said@dau.edu.sa (S.M. Azar).

http://dx.doi.org/10.1016/j.intermet.2017.02.018
0966-9795/

$Fm\overline{3}m$ structure, gives a nonmagnetic ground state, in agreement with the experimental data. However, in this disordered case the energy gap is no longer seen [7]. Tremel *et al*., reported that $Ti_{1+x}FeSb$ ($-0.20 \leq x \leq 0.27$) transformation from defect AlLiSi-type to the partially filled $MnCu_2Al$-type [8]. A detailed theoretical analysis of the electronic structure of half-heusler alloys using various indicators of chemical bounding suggests that covalent hybridization of the high valent transition metal with the lower valent transition element is the key interaction responsible for the formation of the $d-d$ gap in these systems. Also, the *sp* metalloid plays a crucial role in the stability of these systems. The influence of the relative ordering of the atoms in the unit cell on the $d-d$ gap is also investigated [9]. Magnetic susceptibility measurements with a superconducting interference device (SQUID) magnetometer indicated Pauli paramagnetism for *TiFeSb* [10]. V. Raghavan investigated experimentally the $Fe-Sb-Ti$ alloys and he reported that the lattice parameter of $Ti_{1+x}FeSb$ varies from 0.59429 to 0.60182 nanometer when the concentration of *Ti* changed from 28.6% to 38.5%, and their space group are $F\overline{4}3m$ [11]. Also, R.V. Skolozdra *et al*. reported experimentally the crystal structure of $Ti_{0.80}FeSb$, *TiFeSb* and $Ti_{1.27}FeSb$ alloys [12]. Kurt R. A. Ziebeck group made precise magnetization measurements of weak itinerant electron ferromagnetic *CoVSb* by using SQUID and vibrating sample magnetometer [13]. The results were analyzed and interpreted using spin fluctuation theory. Laila Offernes *et al*. shown that the half-Heusler alloys exhibit an appreciable covalent contribution to the bonding independent of the electronic state at the Fermi energy [14]. Furthermore, they confirmed that the most of half-Heusler alloys with valence-electron content of 18 are semiconducting and more stable than those are metallic with valence-electron content not equal 18. Recently, Saadi Berri *et al*. concluded that the *CoFeTiSb* quaternary compound displays ferrimagnetic half -metallic behavior with a band gap of 0.53 eV and a spin magnetic moment of 2.00 μ_B [15].

The goal of this research work is to investigate the half-metallic characteristic as well as the crossover of the electronic and magnetic structures of bulk $Ti_{1+x}FeSb$ alloys when changing the concentration. We are thus able to delineate clearly how the majority and minority spin states and magnetic moments in *TiFeSb* develop when the [B] site in the lattice is filled by *Ti* atoms.

The rest of the paper is organized as follows: section 2 includes the details of the calculation methods, section 3 is devoted to results and discussion and section 4 is a summary of our conclusions.

2. Computational details

Density functional theory(DFT) [16], using the all-electron full-potential linearized augmented plane-wave (FP-LAPW) method [17–19] implemented in WIEN2k [20] package, is used to calculate the electronic and magnetic structures of a series of $Ti_{1+x}FeSb$ Heusler compounds. The electronic exchange-correlation energy is treated using the generalized gradient approximation parameterized by Perdew-Burke- Ernzerhof (GGA-PBE) [21,22]. Moreover, the Tran-Blaha parameterized of the modified Becke-Johnson (TB-mBJ) exchange potential approximation [23], as a semi-local method, is employed to predict the band gap more precisely. The total energy dependence on the cell volume is fitted to the modified Murnaghan equation of state (EOS) [24].

By assuming the muffin-tin model for the crystal potential, the spherical harmonic expansion is used inside the muffin-tin sphere, and the plane wave basis set is chosen outside the sphere. The maximum value of angular momentum $l_{\max} = 10$ is taken for the valence wavefunction expansion inside the atomic spheres, while the charge density was Fourier expanded up to $G_{max} = 16(a.u.)^{-1}$. The plane wave cut-off value $K_{max} \times R_{MT} = 8$ is used in the plane wave expansion in the interstitial region of the unit cell, where R_{MT} denotes the smallest atomic sphere radius (muffin tin radius) and K_{max} gives the magnitude of the largest *K* vector in the plane-wave expansion. The values of R_{MT} are taken to be 2.3 $a.u.$ for Ti and Fe; 2.16 $a.u.$ for Sb. The energy cut-off specified in the generated free atomic density is about -95 eV to separate the core and the band states. The starting potential for the next cycle was typically obtained by roughly 10% mixing of the new potential. For *k*-space integration, a $16 \times 16 \times 16$ mesh is used in the irreducible wedge of the Brillouin zone(BZ). The BZ integrations are performed using the modified tetrahedron interpolation method [25] (with division of $1/48-th$ of the *BZ* into 192 small tetrahedrons).

For all calculations, the precision of the energy is 5.0×10^{-7} Ry. Furthermore, fully relativistic effects are taken into account for core electrons, whereas scalar relativistic approximation is used for valence electrons. Spin-orbit interaction is neglected in the calculations discussed here.

3. Results and discussion

3.1. Structural properties

In this section, we present and discuss the structural, electronic and magnetic properties of $Ti_{1+x}FeSb$ ($x = -0.75, -0.50, -0.25, 0.0, 0.25, 0.50, 0.75, 1.0$) Heusler alloys, where the conventional lattice cell of all $Ti_{1+x}FeSb$ compounds are presented in Fig. 1.

Firstly, we examined the crystallographic structures and the site preferences of the parent compound *TiFeSb*, because it has unclear structure. In Table 1 the atomic positions according to Wyckoff notation in six different structure phases are presented. In Fig. 2, the plots between energies with respect to lattice parameters for the six different structures are presented. The minimum total energy occurs for the α phase structure. The two phases γ and θ have the same energy - lattice parameter variation.

We have calculated the total energy as a function of lattice constant of $Ti_{1+x}FeSb$ Heusler alloys. The structures are fully relaxed until the forces on the atoms are less than 1 mRy. The plots of calculated total energy versus reduced volume of $Ti_{1+x}FeSb$ Heusler alloys, not presented here, give all the ground state properties, such as equilibrium lattice parameter *a*, bulk modulus *B* and its pressure derivative *BP*, in addition to the formation and the cohesive energies. Table 2 lists our calculated ground state properties, as well as the space group and atomic positions. The available experimental data and the result of previous theoretical calculations obtained by different models are presented as well. The calculated lattice parameters for the various alloys are in good agreement with previous experimental measurements [7–9,12], and also with the predictions of other computational methods [9].

The stability of $Ti_{1+x}FeSb$ solid solutions can be deduced from the formation and cohesive energies, where the formation energy, E_f, is given by

$$E_f = E_{tot} - \Sigma n_i \mu_i$$

Here, E_{tot} is the total band energy of the $Ti_{1+x}FeSb$ alloy, n_i is the number of atoms of each constituent, and μ_i is the stable bulk phase chemical potential of (*Ti*, *Fe* and *Sb* in the hcp, bcc and rehombic phase, respectively).

The cohesive energy is given by

$$E_{coh} = E_{tot} - \Sigma n_i E_{free,i}$$

where $E_{free,i}$ represents the total energy of the isolated free atom *i*.

Fig. 3 shows that the formation and the cohesive energies have