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The energetic, electronic and magnetic structures of $Fe_{2-x}Co_xVSn$ alloys: Ab-initio calculations

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ABSTRACT

Density Functional Theory (DFT) calculations of a series of the nonstoichiometric $Fe_{2-x}Co_xVSn$ full Heusler alloy were carried out utilizing the full potential linearized augmented plane wave (FP-LAPW) method to investigate the electronic, energetic, and magnetic structures of the above systems. Unlike many concentration curves, increasing the cobalt concentration had a crucial effect on the spin polarization as it flattened at 100% at $x=1.50$, 1.75, and 2.00 where the half- metallic behavior was located with negative formation energy. Moreover, the total magnetic moment of the host material is found to increase with increasing Co concentration. Finally, the half metallic compounds found in some structures of this series might be useful in spintronic devices.

1. Introduction

Half-metallic ferromagnets (HMFs) form a unique class of materials that exhibit a metallic character for one spin sub-band and a semi-conducting or insulating character for the other band. This band structure configuration leads to 100% spin polarization at the Fermi level. Half-metallic ferromagnetism was first predicted through band structure calculation in the half-Heusler alloy NiMnSb by de Groot et al. [1]. Since then, there have been many reports on theoretical band structure calculations predicting the possible HMFs [2–4]. These HMFs can be used for perfect spin filters [5], and spin-injection devices [6].

There are two known types of Heusler systems that can exist with either the $L2_1$ or the $C1_b$ structures [7]. Alloys of the first type ($L2_1$) that are referred to as full Heusler alloys are ternary compounds with 2:1:1 stoichiometry and a chemical formula X_2YZ (space group 225:$Fm\bar{3}m$), where X and Y are represented by transition metals and Z by a main group element. The X atoms are usually located at both A and C sites at (0.25,0.25,0.25) and (0.5,0.5,0.5), respectively. Moreover, the Y and Z atoms are located at B(0.75,0.75,0.75) and D(0,0,0), respectively. The second type, the half Heusler alloys, is represented by the general chemical formula XYZ and the $C1_b$ structure with one of its four sublattices normally unoccupied (A site) [8].

The electronic and magnetic properties of the Heusler alloys are affected by several factors including the change of the constituents and the occurrence of defects. Li et al. [9], studied the effect of V doping on electronic structure and magnetic properties of $Co_2Fe_{1-x}V_xAl$ ($x=0$, 0.25, 0.5, 0.75, 1). They concluded that the spin polarization increases with increasing V content in the ordered $L2_1$ and disordered B_2 structures. The calculations showed that the stability of the $L2_1$ structure is enhanced with increasing V content. Nakataniet al [10], investigated the effect of substituting of Co with Fe on the magnetic property, electronic band structure, and spin polarization of $Co_{2-x}Fe_xCrGa$ Heusler alloys ($x=0$–0.3). The Fe addition in Co_2CrGa structure is noticed to improve the spin polarization of the full Heusler alloy regardless of its chemical disorder.

The electronic and magnetic properties of a series of Co-based full-Heusler alloys have been investigated using the first-principle calculations [11–13]. It is found that many of Co_2YZ are half metallic and follow the Slater–Pauling behavior where the total spin magnetic moment per unit cell (M_t) in μ_B scales with the total number of valence electrons(Z_t) following the rule:

$$M_t = Z_t - 24 \qquad (1)$$

Usually, some of the Heusler alloys exhibit a very interesting feature, which is the half-metallic ferromagnetism (HMF). HMF indicates that conduction electrons are 100% spin-polarized. This is typically explained based on the gap at the Fermi level, E_F, in the minority spin channel and the finite density of states at E_F for the majority spin channel. Hence, Half-metals are denoted as hybrids

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between semiconductors and normal metals and, therefore, considered as potential candidates for spintronic production.

Recently, we performed DFT calculations using full potential linearized augmented plane wave (FP-LAPW) method to investigate the perfect Co_2VSn full Heusler alloy [14]. This alloy was found to be a ferromagnetic half metal with a band gap of 0.56 eV and a total magnetic moment of 3.0 μ_B/f.u. We also investigated the effect of defects on the electronic and magnetic structures of this alloy. The formation energies were calculated for antisite, swap, and vacancy defects. We found that V_{sn} antisite, V, Co and Sn vacancies have relatively low formation energies with high probability to occur. The half metallicity is maintained in all structures with band gaps smaller than that of the perfect alloy except for Co_{Sn}, Sn_{Co} antisite and Co–Sn swap defected structures, which exhibit a metallic behavior [14].

In this work, we extend our previous investigation to report the effects of Co substitution, on the X-site of the nonstoichiometric $Fe_{2-x}Co_xVSn$ quaternary alloys ($x=0.25$–1.75) in steps of 0.25 aiming to explore potential HFM candidates within the investigated system. The rest of the paper is organized as follows: Section 2 focuses on the method of calculation; Section 3 is devoted on the results and discussion, and Section 4 presents the concluding remarks.

2. Calculation method

The calculations are performed using DFT [15] based on the FP-LAPW method [16], as implemented in WIEN2K package [16]. The electronic exchange–correlation potential is described by the generalized gradient approximation (GGA) [17]. The ideal structure has close-packed L_{21} cubic structure with a space group $Fm\bar{3}m$ (255), which consists of four interpenetrated face-centered cubic (FCC) sublattices. The Fe atoms are placed at (0.25,0.25,0.25) and (0.75,0.75,0.75), whereas V and Sn atoms are located at (0,0,0) and (0.5,0.5,0.5), respectively. The calculations are performed using a $(1\times1\times1)$ cell with 16 atoms. The basis set parameters are a 16 Ryd cut off energy for the plane waves in the interstitial region between the muffin tins and 169 Ryd for the potential. The wave function expansion inside the muffin tins is taken up to $l_{max}=10$ and the potential expansion up to $l_{max}=4$, while the charge density Fourier is expanded to $G_{max}=12$. The core energy cutoff is taken as -6.0 Ryd. The Muffin tin radii (RMT) are displayed in Table 1 for all atoms. The k-point sampling in the irreducible part of the Brillouin Zone (BZ) is performed using $(12\times12\times12)$ Monkhorst-pack grid. All structures are fully relaxed until the forces on the atoms are less than 5 mRy/a.u. The convergence of the self consistent calculations are taken with respect to the total charge of the system with a tolerance of 0.0001 electron charge. The lattice constant is obtained by optimizing the structure using Murnaghan equation of state [18]. The calculated density of states (DOS) are performed using the tetrahedron method with Blöchl corrections [19].

Table 1
Structure, optimized lattice constant a(Å), bulk modulus B(GPa), and R_{MT} for nonstoichiometric $Fe_{2-x}Co_xVSn$ alloys.

Compound	Space group	a (Å)	B (GPa)	R_{MT}			
				Co	Fe	V	Sn
Fe_2VSn	$Fm\bar{3}m(2\ 5\ 5)$	5.9688	173.62	–	1.99	2.00	2.00
$Fe_{1.75}Co_{0.25}VSn$	$P\bar{4}3m(2\ 1\ 5)$	5.969	171.21	1.99	1.99	2.00	2.00
$Fe_{1.5}\ Co_{0.5}VSn$	$P\bar{4}m_2(1\ 1\ 5)$	6.027	175.99	1.99	1.99	2.00	2.00
$Fe_{1.25}Co_{0.75}VSn$	$P\bar{4}3m(2\ 1\ 5)$	6.029	166.28	2.26	2.26	2.20	2.12
FeCoVSn	$F\bar{4}3m(2\ 1\ 6)$	6.001	217.00	2.40	2.40	2.40	2.00
$Fe_{0.75}Co_{1.25}VSn$	$P\bar{4}3m(2\ 1\ 5)$	5.998	164.32	1.99	1.99	2.00	2.00
$Fe_{0.5}Co_{1.5}VSn$	$P\bar{4}m_2(1\ 1\ 5)$	5.995	180.95	2.43	2.43	2.33	2.28
$Fe_{0.25}Co_{1.75}VSn$	$P\bar{4}3m(2\ 1\ 5)$	5.981	188.21	2.30	2.30	2.30	2.30
Co_2VSn	$Fm\bar{3}m(2\ 5\ 5)$	6.022	178.03	2.30	–	2.30	2.30

3. Results and discussion

3.1. Structural properties

Properties of $Fe_{2-x}Co_xVSn$, with $x=0$–2 in step of 0.25, are listed in Table 1. The symmetry and space group of these systems as a function of Co concentration are given, where Fe atoms reside on A-sites for $x\le1$, and on both A and C sites, for $x>1$. As anticipated, increasing Co concentration resulted in increasing the lattice parameters' length. This was true as long as the Co atoms resided on the A site and $x<1.25$. As Co concentration increased and reached $x=1.25$, the lattice parameter began to contract. This contraction was explained based on changes of the first and second nearest neighbors of the Co and Fe atoms. Increasing the Co concentration on both the A and C sites are argued to create stronger bonds between the Co atoms and their immediate neighbors as evidenced by the decrease in the lattice parameter length as well as the unit cell volume. Hence, the structural and electronic properties of the stoichiometric and nonstoichiometric $Fe_{2-x}Co_xVSn$ alloys with $0\le x\le\ 2$ are summarized in Table 1, where all compounds are modeled using a cubic cell of 16 atoms. Also in the same Table 1, the R_{MT} for X, Y, and Z atoms of each structure is displayed.

3.2. Formation energy

The stability of $Fe_{2-x}Co_xVSn$ alloys can be deduced from the formation energy, E_f, which can take the form

$$E_f=E_{tot}-\sum n_i\mu_i \tag{2}$$

where, E_{tot}, is the total energy of the ideal Fe_2VSn and $Fe_{2-x}Co_xVSn$, n_i is the number of atoms for each constituent, and μ_i is the stable bulk phase chemical potential (Co, V, Sn, and Fe are in hcp, bcc, diamond, and bcc phases, respectively). The formation energy of the ideal Co_2VSn structure is taken as -0.225 eV from our previous work [14], where for the ideal Fe_2VSn structure the formation energy is found in this work to posses positive small value (0.019 eV) with an ability to be formed in agreement with Engen. et al. [21], see Table 2. The formation energy is surely influenced by the Co concentration as negative values of formation energies for $x>1$ was found. Such negative values imply possible higher degree of stability of these alloys in nature. However, at $x<1$, the alloys show positive formation energies suggesting that these kinds of structures are unstable in nature and thus energy must be supplied in order to synthesize them. The dependency of

Table 2
Formation energy, E_f (eV/f.u.), for perfect Fe_2VSn and nonstoichiometric $Fe_{2-x}Co_xVSn$ quaternary alloys.

Compound	E_f (eV)
Fe_2VSn	0.019
$Fe_{1.75}Co_{0.25}VSn$	1.120
$Fe_{1.5}Co_{0.5}VSn$	0.041
$Fe_{1.25}Co_{0.75}VSn$	0.033
FeCoVSn	0.070
$Fe_{0.75}Co_{1.25}VSn$	−0.367
$Fe_{0.\ 5}Co_{1.5}VSn$	−0.132
$Fe_{0.25}Co_{1.75}VSn$	−0.309
Co_2VSn	−0.225