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Structural, electronic and magnetic properties of $Fe_{3-x}Mn_xZ$ (Z=Al, Ge, Sb) Heusler alloys

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ABSTRACT

Density functional theory based on full-potential linearized augmented plane-wave (FP-LAPW) method is used to investigate the structural, electronic and magnetic properties of $Fe_{3-x}Mn_xZ$ (Z=Al, Ge, Sb) Heusler alloys, where $0 \le x \le 3$. Alloys with $x \le 1$ are found to exhibit a ferromagnetic phase, whereas the rest have shown ferrimagnetic phase. The total spin magnetic moment shows a trend consistent with generalized Slater–Pauling type behavior. Alloys with $x > 0.75$ are found to be half metallic with indirect band gaps along $\Gamma - X$ symmetry line for stoichiometric and direct band gaps for nonstoichiometric alloys. We found that Mn rich composition of $Fe_{3-x}Mn_xZ$ alloys has high spin polarization.

1. Introduction

Recently, functional materials such as Heusler alloys [1] have attracted attention in fundamental and engineering science because of their new possible applications and phenomena. Heusler alloys have been the subject of experimental and theoretical interests due to three unique properties. Firstly, half-metallic behavior [2], where the majority spin band usually shows typical metallic behavior, whereas the other spin band (usually minority spin) is semiconducting or insulating, with fully spin polarization at Fermi level. Secondly, magnetic shape memory effect [3], where the magnetic shape memory alloys undergo structural transformations by changing the magnetic field. Thirdly, the inverse magnetocaloric effect [4], where some magnetic materials possess a reversible change in temperature caused by exposing the material to a changing magnetic field.

In addition to these three unique properties, Heusler alloys also provide fundamental aspects for magnetism in complex systems. Electronic structure calculations from first principles have been extensively used to predict new materials with predefined properties in order to maximize the efficiency of devices. Novel materials for spintronics applications have especially attracted considerable interest in the last decade [5]. Moreover, there has been an upsurge of interest in the ordered compound containing Fe. Furthermore, Heusler alloys of the type Fe_2MnZ [6] and Mn_2FeZ [7] have been proposed theoretically to show half-metallicity. Intermetallic Heusler alloys are amongst the most attractive half-metallic systems due to the high Curie temperatures, low coercivities, and the structural similarity to the binary semiconductors such as GaAs.

Concerning relevant theoretical studies, there is a substantial literature devoted to a variety of ordered Heusler-type phases and related systems where many previous studies are concerned to explain the effect of impurities concentration on the structural and magnetic properties of Heusler alloys. An extensive review of $Fe_{3-x}T_xSi$ alloys for various transition metals (T) has been carried out by Niculescu et al. [8]. Pugaczowa-Michalska et al. [9] examined the effect of local environment on the formation of local magnetic moments of $Fe_{3-x}Mn_xAl$ alloys in the concentration range $0 \le x \le 0.5$. In a recent work [10] we studied theoretically the electronic structure and spin polarization of $Fe_{3-x}Mn_xSi$ and $Fe_{3-y}MnSi_y$ alloys and found that the half-metallic behavior starts at $x = 0.75$ with a small direct band gap that increases for higher Mn concentrations. In addition, we investigated the electronic and magnetic properties of $Fe_{3-x}Cr_xSi$ alloys, by adopting two phases as the parent structures Fe_3Si and Fe_3Si have different phases, namely the $L2_1$ and A15, respectively [11]. We found that the alloys with Cr concentration of $x \le 0.75$ are more stable with the $L2_1$ than the A15 phase and vice versa for higher Cr concentrations.

The goal of this research work is to study, with ab initio accuracy over a wide concentration range, the effect of the main-group

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elements on the electronic and magnetic structures of bulk $Fe_{3-x}Mn_xZ$ (Z=Al, Ge, Sb) stoichiometric series alloys. Manganese concentration and the main-group elements (Z) play an important role in the electronic and magnetic structures of these alloys. The influence of Mn concentration and main-group elements on the electronic and magnetic structures is discussed in this work. Furthermore, the half-metallic behavior is investigated for some alloys in the series. We are thus able to delineate clearly how the majority and minority spin states and magnetic moments in Fe_3Ge develop when the Fe[B] site in the lattice is substituted by Mn atoms, and/or when Ge is replaced by a metalloid of a different valence.

The rest of the paper is arranged as follows: Section 2 includes the structural details and the method of calculation, Section 3 is devoted to the results and discussion and Section 4 is a summary of our conclusions.

2. Computational details

Density functional theory (DFT) [12], using the all-electron full-potential linearized augmented plane-wave (FP-LAPW) method [13–15] implemented in WIEN2k [16] package, is used to calculate the electronic and magnetic structures of a series of $Fe_{3-x}Mn_xZ$ (Z=Al, Ge, Sb) compounds. The electronic exchange-correlation energy is treated using the generalized gradient approximation parameterized by Perdew–Burke–Ernzerhof (GGA-PBE) [17,18]. The total energy dependence on the cell volume is fitted to the Murnaghan equation of state (EOS) [19] by

$$E_{tot}(V)=\frac{B_0V}{\acute{B}_0(\acute{B}_0-1)}\left[\left(\frac{V_0}{V}\right)^{\acute{B}_0}+\acute{B}_0\left(1-\frac{V_0}{V}\right)-1\right]+E_0, \tag{1}$$

where B_0 is the bulk modulus, $\acute{B}_0$ is the bulk modulus derivative and V_0 is the equilibrium volume.

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 is Fourier expanded up to $G_{max}=14\,(\text{a.u.})^{-1}$. The plane-wave cut-off value $K_{max}\times R_{MT}=8$ is used for 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

Table 1

Comparison between the present work and tabulated experimental values as well as previous calculations. Optimized lattice constant a (Å), bulk modulus B (GPa), maximum valence electron band energy ($E_{V(max)}$), minimum conduction electron band energy ($E_{C(min)}$), band gap (E_g), half-metallic (HM) gap (E_S) and polarization (P).

Compound	Structure	Pa (Å)	B (GPa)	$E_{V(max)}$ (eV)	$E_{C(min)}$ (eV)	E_g (eV)	E_S (eV)	P (%)
Fe_3Al	DO_3	5.750 5.738[a] 5.820[b](*exp*)	169.9 169.3[a]					35
	$L1_2$	3.653 3.651[a]	169.4 174.9[a]					
Fe_2MnAl	$L2_1$ (Fm-3m)	5.683 5.670[c] 5.850[d](*exp*)	200.9	0.740	1.205	0.465		81
Mn_2FeAl	$L2_1$ (F-43m)	5.760 5.725[e]	150.2	0.674	1.218	0.544		99
Mn_3Al	DO_3	5.806 5.723[f]	143.9	0.555	1.098	0.543	0.116	100
Fe_3Ge	DO_3	5.736 5.760[g](*exp*)	167.7					20
	$L1_2$	3.642 3.667[g](*exp*)	179.6					
Fe_2MnGe	$L2_1$ (Fm-3m) DO_3	5.703 5.780[h](*exp*)	217.6	0.845	1.392	0.547		96
Mn_2FeGe	$L2_1$ (F-43m)	5.718 5.675[e]	214.4	0.893	1.376	0.482		87
Mn_3Ge	DO_3	5.765 5.749[f]	197.2	0.828	1.326	0.497		96
	$L1_2$	3.654 3.800[i](*exp*)	170.5					
Fe_3Sb	DO_3	5.996 5.90[b](*exp*)	159.5					23
Fe_2MnSb	$L2_1$ (Fm-3m)	5.955	192.6	0.979	1.668	0.689		82
Mn_2FeSb	$L2_1$ (F-43m)	5.999 5.925[e]	141.2	0.731	1.127	0.396	0.063	100
Mn_3Sb	DO_3	5.985 5.930[f]	174.4	0.768	1.375	0.607	0.043	100
	$L1_2$	3.811 4.000[j](*exp*)	177.1					

[a] Ref. [28].
[b] Ref. [29].
[c] Ref. [30].
[d] Ref. [31].
[e] Ref. [7].
[f] Ref. [32].
[g] Ref. [33].
[h] Ref. [34].
[i] Ref. [35].
[j] Ref. [36].