First-principles investigations of electronic and magnetic properties of Fe$_2$V$_{1-x}$Cr$_x$Si Heusler alloys

P K Joshi*, K Kumar, G Arora, D Mali, P K Jangid and B L Ahuja

Department of Physics, University College of Science, Mohanlal Sukhadia University, Udaipur, 313001 Rajasthan, India.

E-mail: poojajoshi19@yahoo.com

Abstract. Full-Heusler alloys with chemical formula X$_2$YZ (X and Y being 3d and 4d transition metal elements and Z is p-block element) are interesting intermetallics because of their half metallic and spintronics applications. In this paper, the effect of doping of Cr atom at V-site of full-Heusler Fe$_2$V$_{1-x}$Cr$_x$Si (x=0, 0.5, 1.0) on their electronic and magnetic response is studied using full potential linearized augmented plane wave method. It is observed that Fe$_2$VSi and Fe$_2$V$_{0.5}$Cr$_{0.5}$Si does not show half-metallic character while Fe$_2$CrSi alloy shows half-metallicity. We observe increase in total magnetic moment with increasing Cr concentration in Fe$_2$V$_{1-x}$Cr$_x$Si. Further, density of states and energy bands are discussed to interpret the half-metallic character in Fe$_2$V$_{1-x}$Cr$_x$Si.

PACS No.: 71.15.-m, 71.15.Mb, 75.47.Np

Keywords: Electronic properties, Density functional theory, Metal and alloys

1. Introduction

Cubic $L2_1$ Heusler alloys are interesting because of their unusual transport and magnetic properties. Different materials like semiconductors, semimetals, normal Pauli metals, weak ferromagnets and half-metallic ferromagnets have been searched to exist in this class of materials [1-4]. In particularly, Fe$_2$VSi, belonging to this group, exhibits a structural transition along with anti-ferromagnetic (AFM) ordering with $T_N=123$ K [5-7]. Among earlier studies, Lue et al. [8] have reported the experimental properties such as electrical resistivity, thermal conductivity, Seebeck coefficient and heat capacity of Fe$_2$VSi$_{1-x}$Al$_x$ Heusler alloys along with first-principles calculations to investigate the structural and magnetic phase transitions. Elastic and magnetic response of Cr based full Heusler alloys using full-potential non-orthogonal local-orbital minimum basis method has been discussed by Aly et al. [9]. Temperature dependent thermodynamic properties of Fe$_2$VSi have been discussed by Ito et al. [10]. Lee [11] has reported the effect of mechanical alloying on the build-up of nano-crystalline phase of Fe$_2$CrSi.

In the present work, more systematic electronic and magnetic response of Fe$_2$V$_{1-x}$Cr$_x$Si (x=0, 0.5, 1.0) alloys using first-principles calculations is reported. We have investigated the spin-projected band structures, density of states (DOS) and magnetic moments of Fe$_2$V$_{1-x}$Cr$_x$Si (x=0, 0.5, 1.0) alloys within the framework of density functional theory (DFT).
2. First-principles calculations

In present investigations, a first-principles computations using full potential linearized augmented plane-wave (FP-LAPW) method as incarnated in WIEN2k code [12] are employed. Revised functional for solids as suggested by Perdew-Becke-Ernzerhof (namely PBEsol) for exchange and correlation potentials to derive the electronic and magnetic aspects of Fe2V1-xCrxSi (x=0, 0.5, 1.0) alloys is taken into account. It is worth noting that PBEsol approximation is designed to improve upon PBE for equilibrium properties of bulk solids and their surfaces. At room temperature, the crystal structure of Fe2VSi is reported to have cubic L21 symmetry (space group 225) with the lattice constant $a = 5.67 \, \text{Å}$ [10]. As per Wyckoff positions in Fe2VSi, two Fe atoms occupy the positions (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4), while the V and Si atoms occupy the positions (0, 0, 0) and (1/2, 1/2, 1/2), respectively [13]. We have considered a supercell of (1x1x2) for Cr doped alloy leadings to 8 atoms in supercell. Out of two V atoms in supercell, one V atom is replaced by Cr atom forming 50% doping of Cr at V-site (Fe2V0.5Cr0.5Si). Crystal structures of Fe2V1-xCrxSi (x=0, 0.5, 1.0) alloys are depicted in Figures. 1 (a-c). The radii for MT spheres were selected as 2.36, 2.25, 1.90 and 2.25 a.u. for Fe, V, Si and Cr atoms, respectively. Other parameter involved in FP-LAPW computation was $R_{MT} \times K_{max}=7$ (where $R_{MT}$ is the radius of smallest atomic sphere in the unit cell and $K_{max}$ is the magnitude of the largest $k$ vector). Further, maximum radial expansion was set to $l_{max}=10$, and cut-off for charge density was $G_{max}=12$ and the tolerance in total energies was kept to 10$^{-5}$ Ry.

![Figure 1. Crystalline structure of (a) Fe2VSi, (b) Fe2V0.5Cr0.5Si and (c) Fe2CrSi alloys.](image)

3. Results and discussion

3.1 Electronic structure

To check the variation of electronic structure on doping of Cr in Fe2VSi at V-site, we have plotted spin projected energy bands along with total and partial DOS (3d states of Fe, V, and Cr with 3s and 3p states of Si) for Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi in Figure 2, computed using FP-LAPW-PBEsol scheme. A close observation of Figure 2(a) reveals that 3d states of Fe atom contribute in valence band (VB) region for both the spin-up and spin-down states and cross the Fermi level (EF) in spin-up DOS, which is in contrast to spin down DOS wherein no crossover of Fe-3d states at EF is seen. Above the EF (0 to 1 eV), it is observed that V-3d states in spin-down mode are more localized than the Fe-3d states. Small contribution of 3s and 3p states of Si are observed in both conduction band (CB) and VB region. Further, no energy gap is observed near EF in spin-up and spin-down states.

In Figure 2(b), it is observed that as we dope Cr at V-site, V-3d states get broadened in CB region of spin-down DOS. Due to Cr doping, new Cr-3d states are formed around the EF for spin-up states as seen in DOS while in spin-down states, Cr-3d states arise above the EF (0.18 – 4.5 eV). The doping of Cr at V-site does not significantly influence the 3d states of Fe, therefore we observed almost similar structure of DOS of Fe-3d states in Fe2V0.5Cr0.5Si and Fe2VSi (Figures 2a, b). As V atom is completely replaced by Cr atom, a small value of direct band gap of 0.508 eV is seen in spin-down states at $\Gamma$ point (Figure 2c).
Figure 2. Energy bands for spin-up (↑) and spin-down (↓) states along with total and partial (3d states of Fe, V and Cr along with 3s and 3p states of Si) density of states for (a) Fe$_2$VSi, (b) Fe$_2$V$_{1.5}$Cr$_{1.5}$Si and (c) Fe$_2$CrSi alloys computed using FP-LAPW-PBEsol scheme.
But in spin-up DOS, the 3d states of Cr and Fe atoms cross the E_F and have higher contribution at E_F. Therefore, we conclude that a complete replacement of V by Cr atom leads to half-metallic behaviour in Fe2CrSi Heusler alloy. Further, Fe-3d states have similar behaviour (Figure 2c) as found in Fe2VSi and Fe2V0.5Cr0.5Si alloys (Figures 2a, 2b).

3.2 Magnetic properties
The total magnetic moment in μB/f.u. is difference between the number of occupied spin-up and spin-down states. To check the role of Slater-Pauling rule in predicting the total magnetic moment M_T, we have used the standard prescription of Slater-Pauling rule which dictates that M_T = (Z_T - 24), where Z_T represents the number of valence electrons per unit cell. The total number of valence electrons in Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi are 25, 25.5 and 26, respectively. Accordingly, the calculated moments come to 1, 1.5 and 2 μB/f.u. for Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi alloys, respectively. Moreover, going beyond Slater-Pauling rule, we have investigated the magnetic moments of Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi alloys using FP-LAPW-PBEsol scheme.

Table 1 summarizes the FP-LAPW based total and site-specific magnetic moments of Fe2V1-xCrxSi (x=0, 0.5, 1.0) alloys along with available experimental data [14, 15]. The present absolute spin moments of Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi are found to be 0.99, 1.56 and 1.96 μB/f.u., respectively, using FP-LAPW-PBEsol scheme. The present calculated total magnetic moments are close to those computed using Slater-Pauling rule which show reasonable applicability of Slater-Pauling-rule in such Heusler alloys.

| Sample       | Present work | Available expt. moment |
|--------------|--------------|------------------------|
|              | M_V         | M_Cr | M_Si | M_total | M_total (μB/ f.u.) |
| Fe2VSi       | 0.59        | 0.20 | 0.08 | 0.99    | 0.22 [14]          |
| Fe2V0.5Cr0.5Si | 0.99        | -0.20 | -0.02 | 0.99    | 1.56              |
| Fe2CrSi      | 0.17        | 1.60 | 0.04 | 1.96    | 2.05 [15]          |

Our calculated total magnetic moment for Fe2CrSi is in agreement with available experiment, although higher value of total magnetic moment is found for Fe2VSi than the corresponding experimental moment (Table 1). Site-specific magnetic moments of Fe2VSi, Fe2V0.5Cr0.5Si and Fe2CrSi alloys (Table 1) show that contribution of Si in forming total magnetic moment is negligible, while Fe site plays major role in formation of magnetic moment in all the three alloys. Further, in case of Fe2CrSi, the magnetic moment of Cr atom is aligned parallel to that of Fe. It is interesting to note that an increase in concentration of non-magnetic Cr atoms results in enhancement of total magnetic moment in the studied system.

4. Conclusions
We have employed FP-LAPW method with PBEsol approximation to investigate electronic and magnetic response of Fe2V1-xCrxSi (x=0, 0.5, 1.0) alloys. It is concluded that Fe2VSi and Fe2V0.5Cr0.5Si alloys do not show half-metallicity, while in Fe2CrSi a band gap of 0.508 eV in spin-down states leads to its half-metallic behaviour. An increase in total magnetic moment with increasing Cr concentration (at V-site) is witnessed in such system.

Acknowledgements
We thanks to Prof. Peter Blaha for providing WIEN2k code for FP-LAPW calculations. UGC-BSR Research Start-Up-Grant, University Grant Commission, New Delhi (No. F.30-476/2019(BSR) sanctioned to GA and financial supports of RUSA 2.0, MHRD, New Delhi are acknowledged.
References

[1] Buschow K H J and Van Engen P G 1981 J. Magn. Magn. Mater. 25 90
[2] Lue C S and Kuo Y K 2002 Phys. Rev. B 66 085121-1
[3] Kobayashi K, Umetsu R Y, Kainuma R, Ishida K, Oyamada T, Fujita A and Fukamichi K 2004 Appl. Phys. Lett. 85 4684
[4] Slebarski A, Deniszczyk J, Borgie W, Jezierski A, Swatek M, Winiarska A, Maple M B and Yuhasz W M 2004 Phys. Rev. B 69 155118
[5] Endo K, Matsuda H, Ooiwa K and Itoh K 1995 J. Phys. Soc. Jpn. 64 2329
[6] Kawakami M, Nishizaki S and Fujita T 1995 J. Phys. Soc. Jpn. 64 4081
[7] Kawakami M, Yamaguchi K and Shinohara T 1999 J. Phys. Soc. Jpn. 68 2128
[8] Lue C S, Kuo Y K, Horng S N, Peng S Y and Cheng C 2005 Physical Review B 71 064202
[9] Aly S H and Shabara R M 2014 J. Magn. Magn. Mater. 360 143
[10] Ito M, Kai K, Furuta T, Manaka H, Terada N, Hiroi M, A. Kondo and K. Kindo 2018 AIP Advances 8 055703
[11] Lee C H 2019 J. Nanosci. Nanotechnol 19 888
[12] Blaha P, Schwartz K, Madsen G, Kvasnicka D, Luitz J 2017 An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, User’s Guide, WIEN2k_17.1 (Vienna University of Technology, Vienna, Austria)
[13] Lundqvist S, March N H 1983 Theory of the inhomogeneous electron gas (Plenum, New York)
[14] Endo K, Tokiyama M, Matsuda H, Ooiwa K, Goto T and Arai J 2004 J. Phys. Soc. Jpn. 73 1944
[15] Hongzhi L, Zhiyong Z, Li M, Shifeng X, Heyan L, Jingping Q, Yangxian L and Guangheng W 2007 J. Phys. D: Appl. Phys. 40 7121