East European Journal of Physics
East Eur. J. Phys. **3**. 122-128 (2020) DOI:10.26565/2312-4334-2020-3-15

PACS: 71.15.Mb; 71.20.−b; 71.55.Ak

FIRST PRINCIPLES CALCULATION OF MANGANESE BASED HALF HEUSLER COMPOUNDS

Lalit Mohan[a], Sukhender[a], Sudesh Kumar[b], Deepak Sharma[c], Ajay Singh Verma*[,a]

[a]*Department of Physics, Banasthali Vidyapith, Banasthali 304022, India*
[b]*Department of Chemistry, Banasthali Vidyapith, Banasthali 304022, India*
[c]*Department of Physics, IIMT College of Engineering, Greater Noida, 201306, India*
**Corresponding Author: ajay_phy@rediffmail.com*
Received March 30, 2020; accepted May 27, 2020

The Half-Heusler compounds exhibit a diverse range of tuneable properties including half-metallic ferromagnetism topological insulator, solar cells and thermoelectric converters. We have studied four half-Heusler compounds MnFeIn, MnFeGa, MnNiAs and MnNiSb. The nature and properties of half-heusler compounds can be studied on the bases of their valance electron count. In this paper, Fe based compounds have 18 valence electrons; whereas 22 valence electrons in Ni based. The Density Functional Theory (DFT) has been performed with WIEN2k code. Ni based compounds with Mn located at octahedral sites are half-metals as revealed from the Density of States (DoS) and band structure calculations. In all of them, spin-up channels are conducting; whereas in MnNiAs and MnNiSb spin-down channels have the small band gaps. MnNiAs and MnNiSb exhibit half-metallic property with integer magnetic moments of 4 μ_B per formula unit and half-metallic gaps of 0.15 and 0.17 eV at their equilibrium volume respectively.
KEYWORDS: Half-heusler, Spin polarisation, Optimization, Half- metallic

INTRODUCTION

The Heusler compounds were named after its discoverer Fritz Heusler. Surprisingly, the compound is ferromagnetic although none of its constituent elements is magnetic by itself. Half-Heusler compound is an impressive group of unconventional semiconductors being comprised of metal and containing at least one transition metal. Based on their properties they can be used in many applications [1-5]. The structure of Manganese based Half-Heusler compounds is a combination of rock salt and Zinc blend type lattices. This class of compounds with a 1:1:1 stoichiometric composition and can be represented as XYZ type structure with space group F-43 m [6, 7]. The main group elements such as As, Ga, In and Sb represents Z in our study. These compounds can be viewed as Mn and Z form zinc blend sub lattice arranged in a primitive cell at Wyckoff positions (0,0,0) and $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$ whereas [8,9]. We can also mention the ordering by interchanging above said Wyckoff positions, but the preferred atomic arrangements have dependency on size of involved atoms and the inter-atomic interaction between them. But in our case the size dependency on arrangement of transition metal is dominating factor over inter-atomic interaction configured by electro negativity of atoms. So, Manganese is most electropositive atom in our series of interest occupies position (0,0,0) whereas p-block elements are most electronegative element arranged at (0.5,0.5,0.5) for such set of configuration the transition elements having intermediate electronegativity acts like a bridge to pass on valence electrons from electropositive to most electronegative atom. This bridge type consideration forwarded by electronegativity difference plays important role for determination of bonding nature of materials. Also, half Heusler compounds considered as ternary relatives of binary semiconductors with vacant tetrahedral structures [10, 11]. The properties of these compounds depend strongly on number of valance electron in the primitive cell which determine the band structure & physical properties of the compound. Generally, it has been observed that half Heusler compounds with 18 valence electron having closed shell configuration shows tuneable band gap apart from this phase compounds will show magnetic behaviour but manganese-based compounds show tuneable band gap with 22 valence electrons instead of 18 [12,13]. Such behaviour can also be seen in rare earth metal based half Heusler compounds [14, 15].

COMPUTATIONAL DETAILS

The first principles calculations are done by using full potential Linearized Aungumated Plane Wave method (FP-LAPW) implemented in WIEN2k simulation package to describe the interaction between atomic core and valence electrons [16]. Considering the valance electrons, the electronic wave function is expanded. Generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) is used to describe the exchange correlation energy [17]. For the geometry optimization of electronic structure; we have used the FP-LAPW method which lies within the framework of spin-polarized Density Functional Theory (SDFT). The cut-off energy separation between core and band states is kept -0.6 Ry for plane wave basis set in all studied materials. The energy convergence criterion was set to 0.00001 Ry and for charge to 0.001 e^-. Total numbers of K - point are kept 1000 for irreducible Brillouin zones in Wien2k.

RESULT AND DISCUSSION

In the first step, the lattice constants were determined. The total energies for mentioned compounds with half-Heusler structure as a function of the lattice constant are calculated. The equilibrium lattice constants were derived by minimizing the total energy.

Structural properties

For all compounds volume optimization was done based on the Murnaghan equation of state [18]. The volume vs. energy curves are shown in Fig. 1. The optimized volume, pressure, pressure derivative and the minimum ground state energy is calculated and tabulated in Table 1. The optimized value of the lattice constant was used for the DOS, band structures and magnetic moment calculations to predict the electronic and magnetic properties of compounds.

Table 1.

The calculated values of the equilibrium lattice constant a_o, equilibrium volume, the bulk modulus B (GPa), the pressure derivative of bulk modulus B_P and minimum energy during optimization.

Compound	Optimized Lattice Parameter (A^0)	Equilibrium Volume (V_0)	Bulk Modulus (GPa)	B_P	Energy
MnFeIn	5.7057	341.56	140.90	3.34	-16629.13
MnFeGa	5.7048	313.22	101.56	4.58	-5348.47
MnNiAs	5.7048	305.23	141.97	7.40	-9881.19
MnNiSb	5.9128	348.81	102.37	6.02	-18326.23

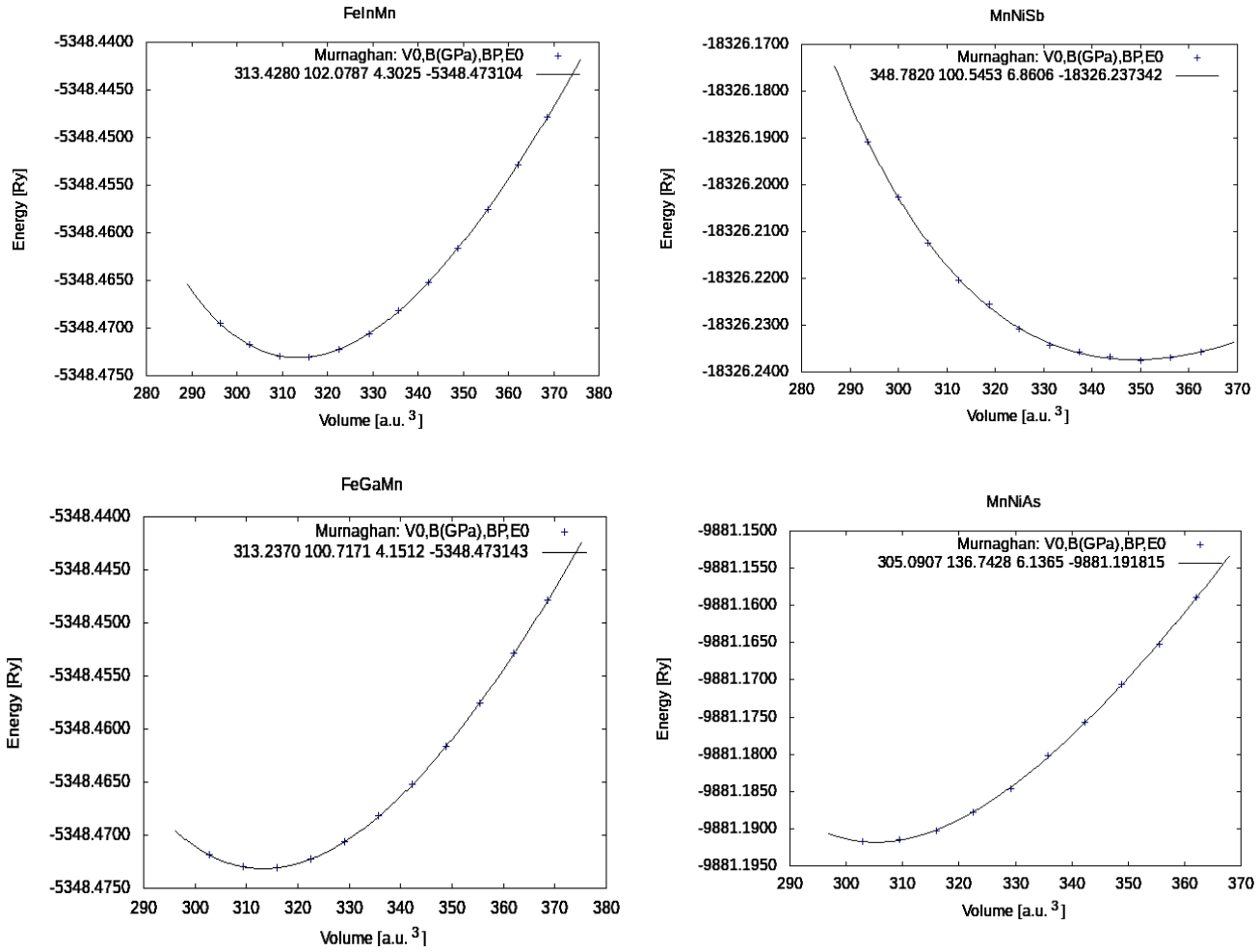

Figure 1. Total energy as a function of volume per formula unit corresponding to MnFeIn, MnFeGa, MnNiSb & MnNiAs alloys

Electronic and Magnetic Properties

The electronic structure plays an important role in determining the half-metallic properties of half-Heusler compounds, so in order to understand the electronic structure of compounds; we have calculated the total density of states (DOS) and shown in Fig. 2.

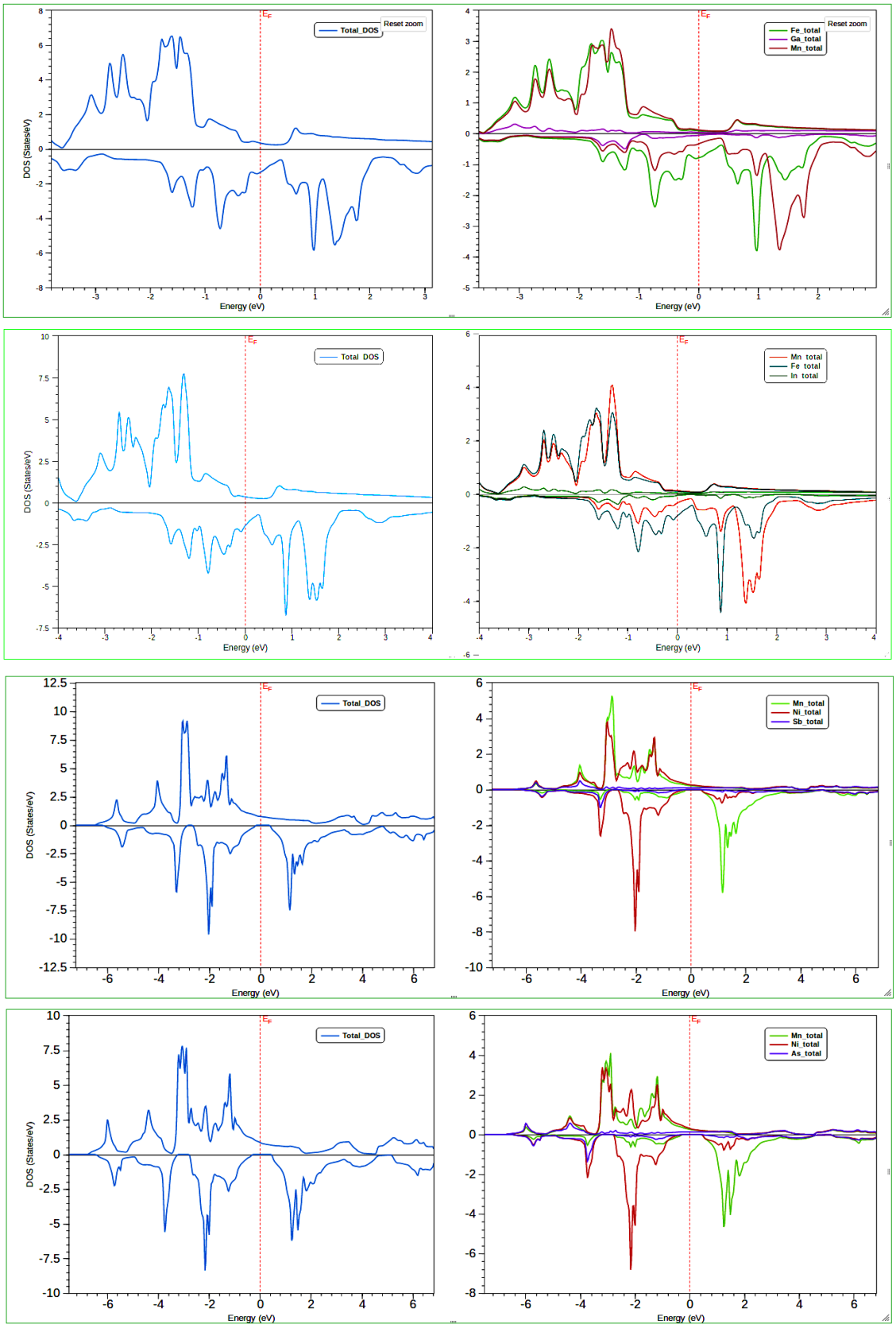

Figure 2. Total and atomic spin- density of states of all studied metallic (MnFeIn, MnFeGa) and half metallic ferromagnetic (MnNiSb, MnNiAs) compounds at their equilibrium lattice constant. Negative of DOS axis represents the minority spin

It is clear from the figure for both MnFeGa and MnFeIn both the majority and minority spin electrons exhibits metallic character. For MnNiAs and MnNiSb compounds, the electronic states in the majority-spin band are metallic and there is an energy gap at the Fermi level in minority-spin state confirms the half-metallic characteristics at their equilibrium lattice constants. We have focused on the calculations of MnNiAs and MnNiSb compounds, and the origin of half-metallic band gaps for these compounds has investigated. The partial DOS are also shown in the Fig. 2 for all the four compounds. Because the half-metallic band gap is an important factor in these materials, the atomic-projected DOSs of MnNiAs and MnNiSb compound. The states around -4.4 eV to -0.8 eV are essentially composed of Ni-d states with some admixture of As/Sb-p and Mn-d states. The states above 0.2 eV are mainly composed of Ni and Mn-d states. The Ni-d states are mainly located below the Fermi level, while the majority Mn-d states are mainly found around Fermi level. The ferromagnetism in MnNiAs and MnNiSb is attributed to the strong tendency of the d electrons of Mn^{3+} (d^4) to localize. The s and p states of Arsenic and Antimony are fully occupied and hybridize with unoccupied p and s state of Nickel, forming a set of low energy bonding a_1 and triple degenerated t_2 orbital, as well as a set of high energy anti-bonding and unoccupied orbital forming. The coupling of sublattices $[NiAs]^{3-}$ and $[NiSb]^{3-}$ with Mn^{3+} atom leads to the formation of bonding orbital doubly occupied and filled with 18 valance electrons. The anti-bonding hybrid orbital occupies four valance electrons. Mn^{3+} with d^4 configuration giving rise to a magnetic moment of approximately 4 μ_B.

To determine the band gap, we have also calculated the band structures of Half-Heusler compounds as shown in the Fig. 3. Both the panels for spin-up (black) channels and for the spin-down (blue) are given. Spin-down states have the band gaps and are, therefore, semiconducting. In the minority-spin band structure of MnNiSb and MnNiAs, the valence band maximum (VBM) is at the Γ-point and the conduction band minimum (CBM) at the X-point. Thus, the minority-spin band structure shows half-metallic behaviour with an indirect energy gap. The origin of the gap is mainly attributed to the covalent hybridization between the d-states of the Mn and Ni atoms, leading to the formation of bonding and anti-bonding bands with a gap in between [19]. The bonding hybrids are localized mainly at the Ni atoms whereas the anti-bonding states are mainly at the Mn sites.

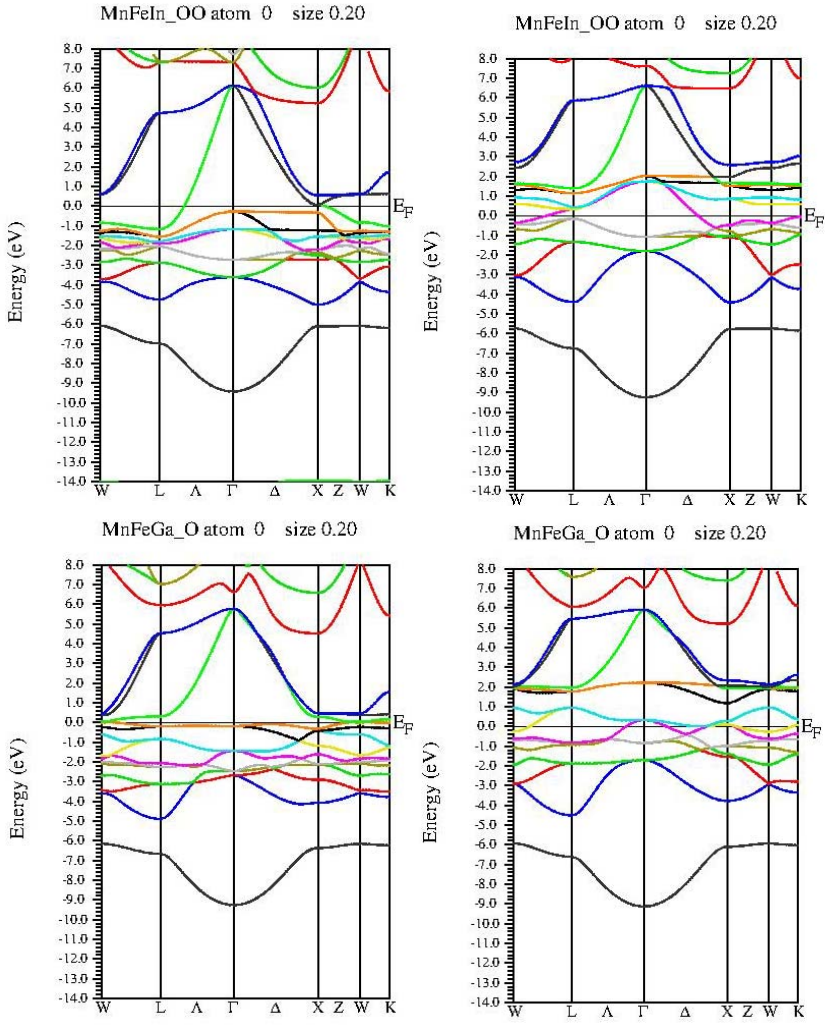

Figure 3. Spin resolved structure of compounds in majority spin channel (left) and minority spin channel (right), at the equilibrium lattice constant

(*Continued on next page*)

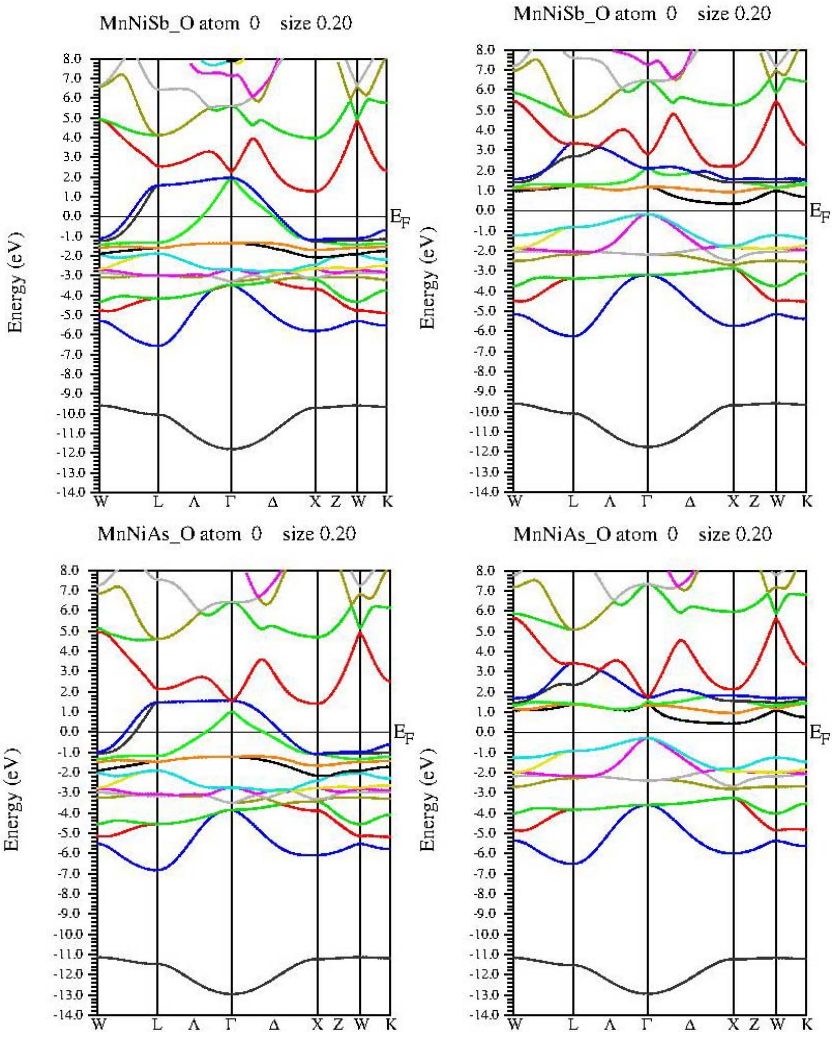

Figure 3. Spin resolved structure of compounds in majority spin channel (left) and minority spin channel (right), at the equilibrium lattice constant
(*Continuation*)

Here, we come to the magnetic properties of these Half-Heusler compounds. The Galanakis model describes the spin magnetic moment of half-Heusler compounds using the difference between spin-up and spin-down states [20,21]. The integral total magnetic moment, which is a typical characteristic of half metallic ferromagnetism, obeys the Slater-Pauling rule for the half-Heusler alloys $M_t = Z_t - 18$; where M_t is the total magnetic moment per formula unit and Z_t is the total number of valence electrons [22,23]. For example, Mn, Fe, Ni, In, Ga, Sb and As atoms have 7,8,10,3,3,5 and 5 valence electrons, respectively. The total magnetic moments per formula unit for these four compounds are integral and shown in table 2.

Table 2.

Calculated values of total magnetic moments of the compounds

μ_B	Mn	Fe/Ni	X(In, Ga, Sb, As)	Total
MnFeIn	3.291	2.367	-0.338	5.32
MnFeGa	3.21	2.342	-0.42	5.132
MnNiSb	3.883	0.298	-0.181	4
MnNiAs	3.812	0.332	-0.145	3.999

For example, Mn, Fe, Ni, In, Ga, Sb and As atoms have 7,8,10,3,3,5 and 5 valence electrons, respectively. Also, the spin polarization P is defined by the total number of valence electrons and total magnetic moment per formula unit is shown in Table 3. It is clear that the compounds with 22 valance electrons are 100% spin polarized. The calculated result has good agreement with theoretical value of magnetic moment.

Table 3.

Compound parameters

Compound	Z_t	M_t (μ_B)	Spin Polarization
MnFeIn	18	Zero	Unpolarized
MnFeGa	18	Zero	Unpolarized
MnNiAs	22	4	100%
MnNiSb	22	4	100%

SUMMARY AND CONCLUSIONS

Half-metallic behaviour of materials has been found and the applications in different aspects of the emerging field of spintronics, e.g. half-metallicity produces 100% spin polarization at the Fermi level; which generates a fully spin-polarized current. Furthermore, due to conduction of only one type of electrons, i.e. spin-up or down, they can be used as electrical switches. These properties make half-metals suitable for applications in Spintronics. We have been observed from theoretical calculations that Fe based half-Heusler compounds containing Mn at octahedral lattice have metallic behaviour inspite of they having 18 valance electron, whereas Ni based 22 valance electron alloys have band gap in their minority spin state.

ORCID IDs

Lalit Mohan, https://orcid.org/0000-0003-3323-8296; **Sukhender**, https://orcid.org/0000-0002-2149-5669
Sudesh Kumar, https://orcid.org/0000-0002-7507-4712; **Deepak Sharma**, https://orcid.org/0000-0001-9163-9050
Ajay Singh Verma, https://orcid.org/0000-0001-8223-7658

REFERENCES

[1] K. Yang, W. Setyawan, S. Wang, M.B. Nardelli and S. Curtarolo, Nature Mater. **11**, 614–619 (2012), https://doi.org/10.1038/nmat3332.
[2] S. Wang, Z. Wang, W. Setyawan, N. Mingo and S. Curtarolo, Phys. Rev. X, **1**, 021012 (2011), https://doi.org/10.1103/PhysRevX.1.021012.
[3] T. Gruhn, Phys. Rev. B, **82**, 125210 (2010), https://doi.org/10.1103/PhysRevB.82.125210.
[4] A. Roy, J.M. Bennett, K.M. Rabe, and D. Vanderbilt, Phys. Rev. Lett. 109 037602 (2012), https://doi.org/10.1103/PhysRevLett.109.037602.
[5] Jiong Yang, Huanming Li, Ting Wu, Wenqing Zhang, Lidong Chen, and Jihui Yang, Adv. Funct. Mater. **18**, 2880–2888 (2008), https://doi.org/10.1002/adfm.200701369.
[6] B.R.K. Nanda, and I. Dasgupta, J. Physics: Condensed Matter, **15**, 7307 (2003), https://doi.org/10.1088/0953-8984/15/43/014.
[7] H.C. Kandpal, C. Felser, and R. Seshadri, J. Phys. D: Appl. Phys. **39**(5), 776 (2006), https://doi.org/10.1088/0022-3727/39/5/S02.
[8] R. Allmann, and R. Hinek, Acta Cryst. A, **63**, 412-417 (2007), https://doi.org/10.1107/S0108767307038081.
[9] P. Villars, and L.D. Calvert. *Pearson's handbook of crystallographic data for intermetallic phases*. (American Society for Metals, 1986).
[10] Zhang Xiuwen, Chinese Physics B, **27**(12), 127101 (2018), https://doi.org/10.1088/1674-1056/27/12/127101.
[11] Feng Yan, Xiuwen Zhang, Yonggang G. Yu, Liping Yu, Arpun Nagaraja, Thomas O. Mason, and Alex Zunger, Nat. Commun. **6**, 7308 (2015), https://doi.org/10.1038/ncomms8308.
[12] J. Tobola, and J. Pierre, J. All. Comp. **296**, 243-252 (2000), https://doi.org/10.1016/S0925-8388(99)00549-6.
[13] T. Graf, C. Felser, and S.S.P. Parkin, Progress in Solid State Chemistry. **39**(1), 1-50 (2011), https://doi.org/10.1016/j.progsolidstchem.2011.02.001.
[14] L. Zhang, X. Wang, and Z. Cheng, J. Alloys and Compounds, **7**, 16183 (2017), https://doi.org/10.1016/j.jallcom.2017.05.116.
[15] K. Gofryk, D. Kaczorowski, T. Plackowski, A. Leithe-Jasper, and Yu. Grin, Phys. Rev. B, **84**, 035208 (2011), https://doi.org/10.1103/PhysRevB.84.035208.
[16] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, R. Laskowski, F. Tran, and L.D. Marks, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (Technical Universitatwien, Austria, 2001), http://susi.theochem.tuwien.ac.at/reg_user/textbooks/usersguide.pdf.
[17] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996), https://doi.org/10.1103/PhysRevLett.77.3865.
[18] S. Ouardi, G.H. Fecher, B. Balke, X. Kozina, G. Stryganyuk, C. Felser, S. Lowitzer, D. Ködderitzsch, H. Ebert, and E. Ikenaga, Phys. Rev. B, **82**, 085108 (2010), https://doi.org/10.1103/PhysRevB.82.085108.
[19] I. Galanakis, P.H. Dederichs, and N. Papanikolaou, Phys. Rev. B, **66**, 134428 (2002), https://doi.org/10.1103/PhysRevB.66.134428.
[20] I. Galankis, and P.H. Dederiches, *Half-metallic Alloys: Fundamentals and Applications*, (Springer, Berlin, 2005), ISBN 10-3540277196.
[21] I. Galanakis, P.H. Dederichs, and N. Papanikolaou, Phys. Rev. B, **66**, 174429 (2002), https://doi.org/10.1103/PhysRevB.66.174429.
[22] I. Galanakis, P. Mavropoulos, and P.H. Dederichs, J. Physics D: Applied Physics, **39**, 765 (2006), https://doi.org/10.1088/0022-3727/39/5/S01.
[23] C. Felser, G.H. Fecher, and B. Balke, Angewandte Chemie International Edition, **46**, 668 (2007), https://doi.org/10.1002/anie.200601815.

ПЕРШООСНОВИ РОЗРАХУНКІВ НАПІВХЕЙСЛЕРОВИХ СПОЛУК НА ОСНОВІ МАРГАНЦЮ

Лаліт Мохан[a], Сухендер[a], Судеш Кумар[b], Діпак Шарма[c], Аджай Сінгх Верма[a]
[a]Фізичний факультет, Банастхалі Від'япіт, Банастхалі, 304022, Індія
[b]Хімічний факультет, Банасталі Відяпіт, Банастхалі 304022, Індія
[c]Фізичний факультет, інженерний коледж ІІМТ, Велика Нойда, 201306, Індія

Напівхейслерові сполуки мають різноманітні властивості застосування включаючи напівферомагнітні топологічні ізолятори, сонячні елементи і термоелектричні перетворювачі. Ми досліджували чотири напівхейслерові сполуки: MnFeIn, MnFeGa, MnNiAs і MnNiSb. Природа і властивості напівхейслерових сполук може бути вивчена на основі розрахунку їх валентних електронів. У цій статті сполуки на основі Fe містять 18 валентних електронів; тоді як сполуки на основі Ni містять 22 валентних електрона. Функціональна теорія щільності (DFT) була розроблена з використанням коду WIEN2k. Сполуки на основі Ni з Mn, що розташовані в октаедричних зонах, є напівметалами, як це випливає з розрахунків густини станів і зонної структури. У всіх них канали з орієнтацією спіну вгору є такими, що проводять, тоді як в MnNiAs і MnNiSb канали з орієнтацією спіну вниз мають малу енергетичну щілину. MnNiAs і MnNiSb проявляють напівметалеві властивості з цілочисельними магнітними моментами в 4 μ_B на формульну одиницю і відповідно мають напівметалеві проміжки 0,15 і 0,17 еВ, при їх рівноважному об'ємі.

КЛЮЧОВІ СЛОВА: напівхейслерові сполуки, спінова поляризація, оптимізація, напівметалевий

ПЕРВООСНОВЫ РАСЧЕТА ПОЛУХЕЙСЛЕРОВЫХ СОЕДИНЕНИЙ НА ОСНОВЕ МАРГАНЦА

Лалит Мохан[a], Сухендер[a], Судеш Кумар[b], Дипак Шарма[c], Аджай Сингх Верма[a]
[a]Физический факультет, Банастхали Видьяпит, Банастхали, 304022, Индия
[b]Химический факультет, Банастали Видяпит, Банастхали 304022, Индия
[c]Физический факультет, инженерный колледж ИИМТ, Большая Нойда, 201306, Индия

Полухейслеровы соединения имеют различные свойства применения включая полуферомагнитные топологические изоляторы, солнечные элементы и термоэлектрические преобразователи. Мы исследовали четыре полухейслеровы соединения: MnFeIn, MnFeGa, MnNiAs и MnNiSb. Природа и свойства полухейслеровых соединений может быть изучена на основе расчета их валентных электронов. В этой статье соединения на основе Fe содержат 18 валентных электронов; тогда как соединения на основе Ni содержат 22 валентных электрона. Функциональная теория плотности (DFT) была разработана с использованием кода WIEN2k. Соединения на основе Ni с Mn, расположенных в октаэдрических зонах, являются полуметаллами, как это следует из расчетов плотности состояний и зонной структуры. Во всех них каналы с ориентацией спина вверх являются проводящими, тогда как в MnNiAs и MnNiSb каналы с ориентацией спина вниз имеют малую энергетическую щель. MnNiAs и MnNiSb проявляют полуметаллические свойства с целочисленными магнитными моментами в 4 μB на формульную единицу и соответственно имеют полуметаллические промежутки 0,15 и 0,17 эВ, при их равновесном объеме.

КЛЮЧЕВЫЕ СЛОВА: полухейслеровые соединения, спиновая поляризация, оптимизация, полуметаллический