

Study of Half-metallic Properties of Co_2YGe ($\text{Y} = \text{Sc, Ti, V, Cr, Mn, Fe}$): A Density Functional Theory

Dibya Prakash Rai,¹ Amit Shankar,¹ Sandeep,¹ Nirmala Devi,¹ Laishram Robindro Singh,² Brojen Indrajit Sharma,³ Madhav Prasad Ghimire⁴ and Ram Kumar Thapa^{1*}

¹Condensed Matter Theory Group, Department of Physics,
Mizoram University, 796004 Aizawl, India

²Department of Nanotechnology, North-Eastern Hill University, 793001, Shillong, India

³Department of Physics, Assam University, Silchar, 788001 Assam, India

⁴National Institute of Material Sciences, Tsukuba, Ibaraki 305-0047, Japan

*Corresponding author: dibyaprakashrai@gmail.com

Abstract: *Based on density functional theory (DFT) calculations, the electronic and magnetic properties of Co_2YGe Heusler compounds ($\text{Y} = \text{Sc, Ti, V, Cr, Mn}$ and Fe) were investigated. The density of states (DOS) and band structures were studied to understand their electronic properties. Of the investigated systems, Co_2CrGe and Co_2MnGe exhibited 100% spin polarisation at the E_F . Co_2CrGe was the most stable half-metallic ferromagnet (HMF) with a 0.24 eV energy gap at the Fermi level in the spin down channel. The total magnetic moment also increased as Y went from Sc to Fe , i.e., with increasing valence electrons. The calculated magnetic moments for Co_2CrGe and Co_2MnGe were $3.999 \mu_B$ and $5.00 \mu_B$, respectively. Based on the calculated results, the HMF character was predicted for Co_2CrGe and Co_2MnGe .*

Keywords: Half metallic properties, local spin density approximation, density of states, band structure, HMF, spin polarisation

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1. INTRODUCTION

Heusler alloys are ternary intermetallic compounds with an X_2YZ composition, where X and Y are transition elements ($\text{Ni, Co, Fe, Mn, Cr, Ti}$ and V , etc.) and Z is III, IV or V group elements ($\text{Al, Ga, Ge, As, Sn}$ and In , etc.). One promising class of materials is half-metallic ferromagnets (HMFs), i.e., compounds with only one spin channel presenting a gap at the Fermi level, while the other has a metallic character, which leads to 100% carrier spin polarisation at E_F .¹

Half-metallic materials have attracted much attention² due to their prospective applications in spintronics.³ The calculated electronic and magnetic properties of Co_2MnAl ⁴ and Co_2CrSi ⁵ based on local spin density approximation

(LSDA) indicates a half-metallic behaviour in the ground state. Miura et al.⁶ found some Co-based Heusler alloys exhibit over 70% spin polarisation. These materials include Co₂CrAl (99.9%), Co₂CrSi (100%), Co₂CrGa (93.2%), Co₂CrGe (99.8%), Co₂MnSi (100%) and Co₂FeAl (86.5%), etc.

In this paper, the ground state structural properties of Co₂YGe were studied via the full potential linearised augmented plane wave (FP-LAPW) method within the generalised gradient approximation (GGA).⁷ Numerous Co-based full Heusler compounds, such as Co₂TiAl,⁸ Co₂VAl,⁹ Co₂MnGe, Co₂MnSn,¹⁰ Co₂CrAl, Co₂CrGa,¹¹ Co₂MnSi,¹² Co₂CrSb¹³ and Co₂CrAs¹⁴, exhibit half metallic behaviour based on previous first principles calculations and are predicted to work well as spintronic devices. The electronic structure calculations play an important role in determining the HMF properties. The calculated density of states (DOS) and band structures indicate the electronic properties. The electronic calculations were based on the LSDA. An attempt was made to calculate the DOS and band structure for compounds similar to those discussed above, such as Co₂ScGe, Co₂TiGe, Co₂VGe and Co₂FeGe, with the expectation that they will exhibit half-metallic ferromagnetism and be applicable for spintronic devices.

2. COMPUTATIONAL

A computational code (WIEN2K)¹⁵ based on the FP-LAPW method was used to calculate the structure of Co₂YGe. Nonspherical contributions to the charge density and potential of up to $l_{max} = 10$ (the highest value of angular momentum functions) within the MT spheres were considered. The cut-off parameter was $R_{MT} \times K_{max} = 7$, where K_{max} is the maximum reciprocal lattice vector in the plane wave expansion, and R_{MT} is the smallest radius for all atomic spheres. $R_{MT} \times K_{max} = 7$ because the accuracy of the plane wave basis set was determined from K_{max} .

The product $R_{MT} \times K_{max} = 7$ is a better judge of the calculation accuracy. As R_{MT} increases, the closest a plane wave can come to a nucleus moves farther out. The part of the wave function no longer described by a plane wave displays a steep behaviour. Fewer plane waves are needed to describe the remaining, smoother parts of the wave function. The K_{max} can then be reduced, and a good rule is that $R_{MT} \times K_{max} = 7$ should be constant to maintain accuracy. Reducing K_{max} means reducing the matrix size because matrix diagonalisation is challenging, i.e., using a larger R_{MT} reduces the computation time. However, the R_{MT} cannot be too large, because the spherical harmonics are ill-suited to describe the wave functions in regions far from the nuclei.

Spherical harmonics can have $2l_{\max}$ nodes within the Muffin Tin sphere. To match these nodes, the shortest period for a plane wave should be $2\pi/K_{\max}$. The cut off for the plane waves (K_{\max}) and angular function (l_{\max}) are comparable in quality when they have an identical number of nodes per unit length. A finite value of l_{\max} means each plane wave matches at the sphere boundaries.¹⁶ The charge density and potential expand in the interstitial region as a Fourier series with wave vectors of up to $G_{\max} = 12 \text{ a.u.}^{-1}$. The irreducible part of the Brillouin zone used 286 k-points. The Muffin Tin sphere radii (R_{MT}) for each atom are tabulated in Table 1.

Table 1: Muffin Tin radius (R_{MT}).

RMT (a. u)	Compound					
	Co ₂ ScGe	Co ₂ TiGe	Co ₂ VGe	Co ₂ CrGe	Co ₂ MnGe	Co ₂ FeGe
Co	2.43	2.39	2.36	2.35	2.34	2.34
Y	2.43	2.39	2.36	2.35	2.34	2.34
Ge	2.29	2.24	2.21	2.21	2.20	2.20

2.1 Crystal Structure

Heusler alloys¹⁷ are intermetallic compounds with chemical formulas of X_2YZ ($X = \text{Co}$; $Y = \text{Sc, Ti, V, Cr, Mn}$ and Fe ; and $Z = \text{Ge}$). The full Heusler structure consists of four penetrating fcc sublattices with atoms at the $X1(1/4,1/4,1/4)$, $X2(3/4,3/4,3/4)$, $Y(1/2,1/2,1/2)$ and $Z(0,0,0)$ positions, which yields an L_{21} crystal structure with the Fm-3-m space group.

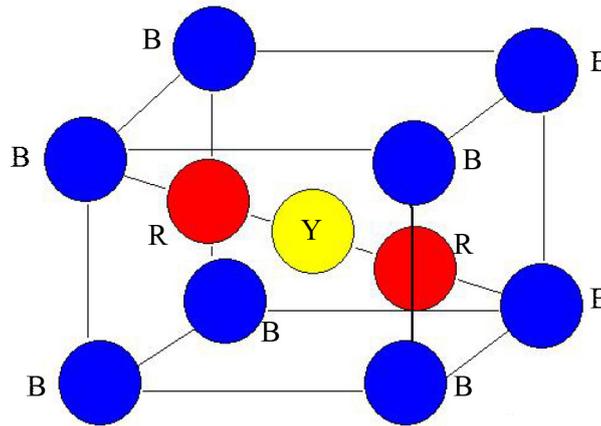


Figure 1: An outline of the Co_2YGe structure: Co (red - R), Y (yellow - Y) and Ge (blue - B) atoms.

3. RESULTS AND DISCUSSIONS

3.1 Structural Optimisation for Co₂YGe

The structural and electronic properties of the Co₂YGe Heusler compounds were systemically calculated in this work. The electronic properties were studied to understand the effect different atoms and valence electron concentrations had on the magnetic properties and particularly the band gap in the minority states. The structural and electronic properties were calculated using GGA and LSDA, respectively. The optimised lattice constant, isothermal bulk modulus and its pressure derivative were calculated by fitting the total energy to the Murnaghan equation of state.¹⁸

The optimised lattice parameters were slightly higher than the experimental lattice parameters, with a change of $\Delta(a_o)$. This result confirmed the ferromagnetic configuration had less energy than the non-spin-polarised configuration for the Co₂YGe systems (Table 2). The structural optimisation results are shown in Figure 1. The optimised lattice parameters and bulk modulus are detailed in Table 2.

Table 2: Lattice parameters, bulk modulus and equilibrium energy.

Compound	Lattice Constants a_o (Å)			Bulk Modulus, B (GPa)	Equilibrium Energy (Ry)
	Previous	Calculated	$\Delta(a_o)$		
Co ₂ ScGe	5.953 ¹⁹	5.978	0.025	109.969	-11300.629
Co ₂ TiGe	5.842 ¹⁹	5.867	0.025	200.378	-11479.814
Co ₂ VGe	5.766 ¹⁹	5.792	0.026	202.158	-11670.736
Co ₂ CrGe	5.740 ¹⁹	5.770	0.030	250.438	-11873.835
Co ₂ MnGe	5.738 ¹⁹	5.749	0.011	219.479	-12089.405
Co ₂ FeGe	5.739 ¹⁹	5.758	0.019	162.677	-12317.674

3.2 Spin Polarisation and HMF

The electron spin polarisation (P) at Fermi energy (E_F) of a material is defined by the Equation 1:²⁰

$$P = \frac{\rho \uparrow (E_F) - \rho \downarrow (E_F)}{\rho \uparrow (E_F) + \rho \downarrow (E_F)} \quad (1)$$

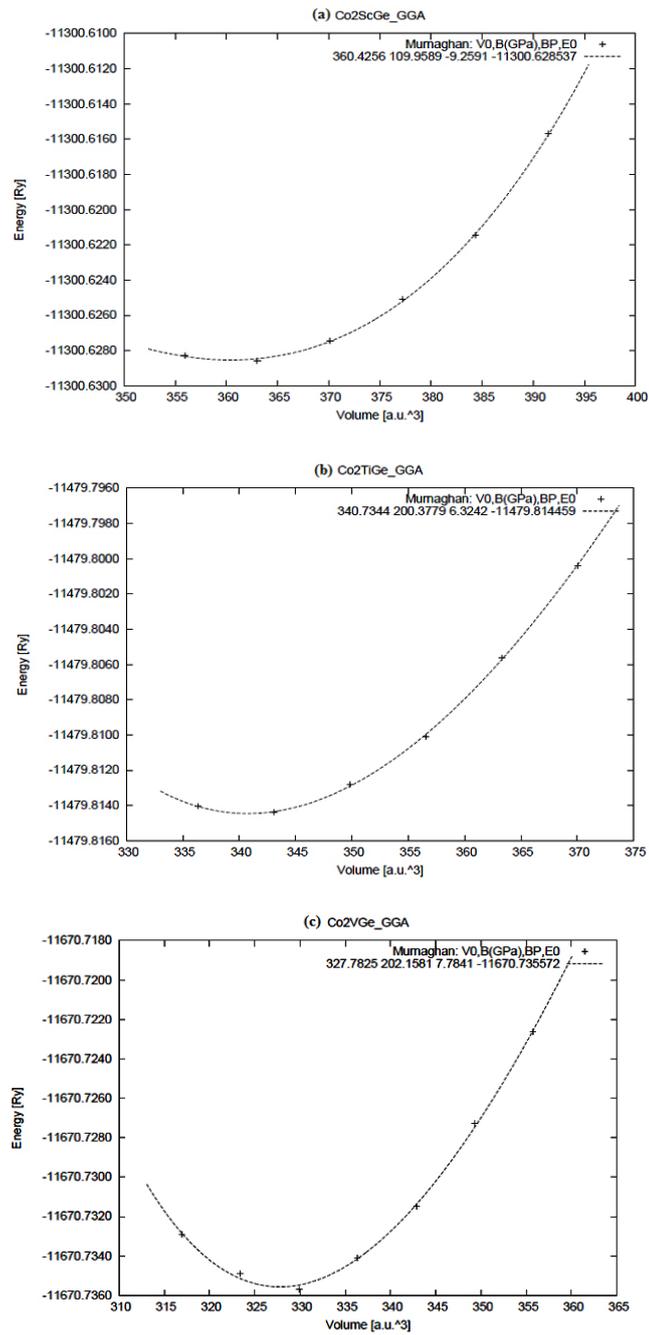


Figure 2: Optimisation of the lattice parameters. (continued on next page)

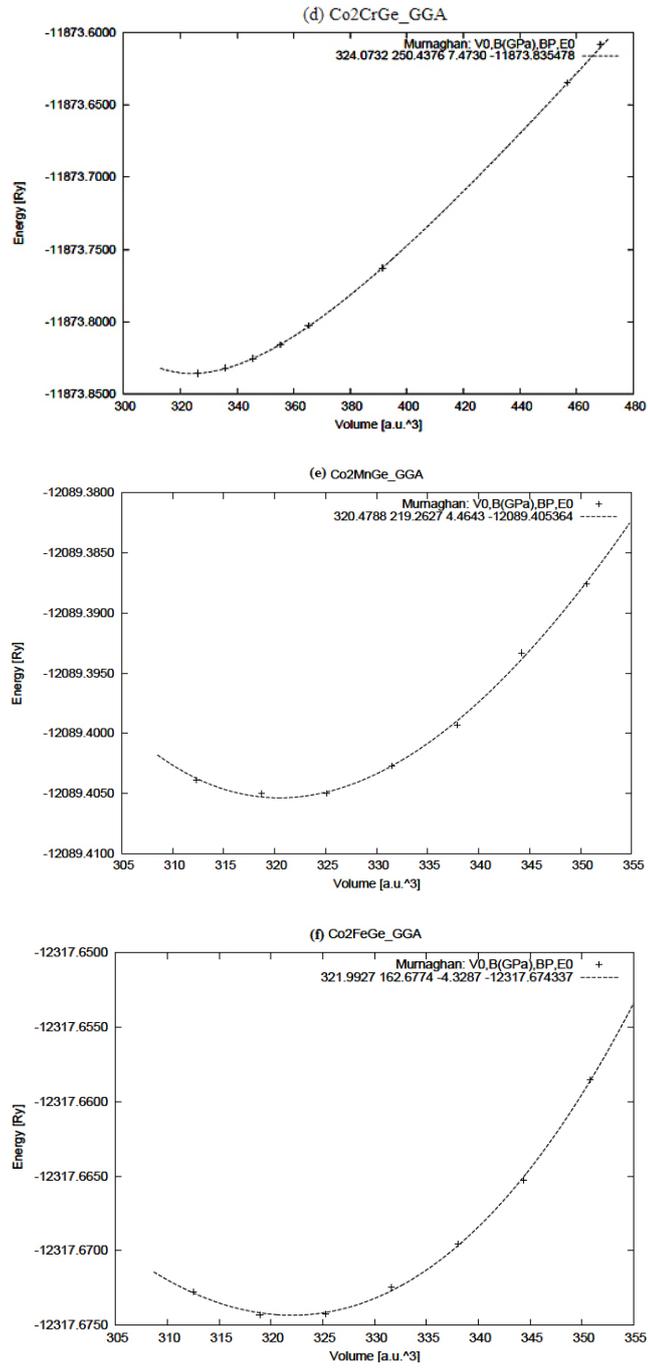


Figure 2: (continued).

where $\rho^\uparrow(E_F)$ and $\rho^\downarrow(E_F)$ are the spin dependent DOS at the E_F . The \uparrow and \downarrow symbols assign the majority and the minority states, respectively. P vanishes for paramagnetic or anti-ferromagnetic materials even below the magnetic transition temperature. Ferromagnetic materials below the Curie temperature have finite values.²¹ Electrons at the E_F are fully spin polarised ($P = 100\%$) when $\rho^\uparrow(E_F)$ or $\rho^\downarrow(E_F)$ equals zero.

The present work studies the properties of Co_2YGe compounds ($Y = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}$ and Fe). Of these compounds, only Co_2CrGe and Co_2MnGe exhibited 100% spin polarisation at the E_F (Table 3). According to the results, compounds containing Cr are interesting because they show large DOS at the E_F with $\rho^\uparrow(E_F) = 2.13$ states/eV (Table 3). This large value results from the E_F cutting through strongly localised states in Cr- d , whereas the contributions of the Co- d states to $\rho^\uparrow(E_F)$ are small as illustrated in Figure 3(d). However, $\rho^\downarrow(E_F) = 0.00$ states/eV for both Co and Cr atoms; therefore, Co_2CrGe is a half-metal with 100% spin polarisation at E_F . The same explanation applies to Co_2MnGe . Figure 3 summarises the DOS results calculated using the LSDA.

For the low magnetic moment compounds shown in Figure 3, the E_F is close to the minority conduction states. The gap size increases with movement from Sc to V, whereas the gap for the high magnetic moment compounds shown in Figure 4 decreases from Cr to Fe (Table 3). The Cr- d and Mn- d states exhibit some exchange splitting, which is responsible for creating high magnetic moments at the Cr and Mn sites [Figure 4 (d and e)]. The contribution from the majority states at the Fermi energy increases from Sc to Cr. However, from Cr to Fe the majority state contribution at the Fermi energy decreases (Figure 3 and 4).

Table 3: Energy gap and spin polarisation.

Compound	Energy gap E_g (eV)			Spin polarisation		
	$E_{\max}(\Gamma)$	$E_{\min}(X)$	ΔE	$\rho^\uparrow(E_F)$	$\rho^\downarrow(E_F)$	P%
Co_2ScGe	–	–	–	1.03	0.5	35.5
Co_2TiGe	–0.18	0.00	0.18	1.04	0.48	36.8
Co_2VGe	–0.25	–0.10	0.15	1.92	0.20	81.1
Co_2CrGe	0.00	0.24	0.24	2.13	0.00	100
Co_2MnGe	0.00	0.22	0.22	1.33	0.00	100
Co_2FeGe	–	–	–	1.25	3.5	47.4

For ($Y = \text{Cr}$ and Mn), the Fermi energy (E_F) lies in the middle of the gap for the minority-spin states, which provides the half-metallic character to the

investigated compounds [Figure 4 (d and e)]. According to Figure 5 (d and e), the indirect band gaps along the Γ -X symmetry for Co_2CrGe and Co_2MnGe were 0.24 eV and 0.22 eV, respectively. However, Co_2YGe Heusler alloys (Y = Sc, Ti, V and Fe) are not the perfect half-metals because the E_F falls into a rising peak in the minority-spin states.

The gap formation in the half-metal Co_2MnSi compounds was discussed by Galanakis et al.²² and was due to the strong hybridisation between the Co- d and Y- d states combined with the large local magnetic moments and sizeable separation between the d -like band centres. A strong hybridisation feature (a small gap for Y = Ti and V with no gap for Y = Sc and Fe) was found to already occur in the DOS with the E_F cutting through a peak, which indicates an instability. For HMF Co_2YGe compounds (Y = Cr and Mn), the E_F is located in the gap of the minority-spin DOS as long as there are few states to fill and the gap is large.

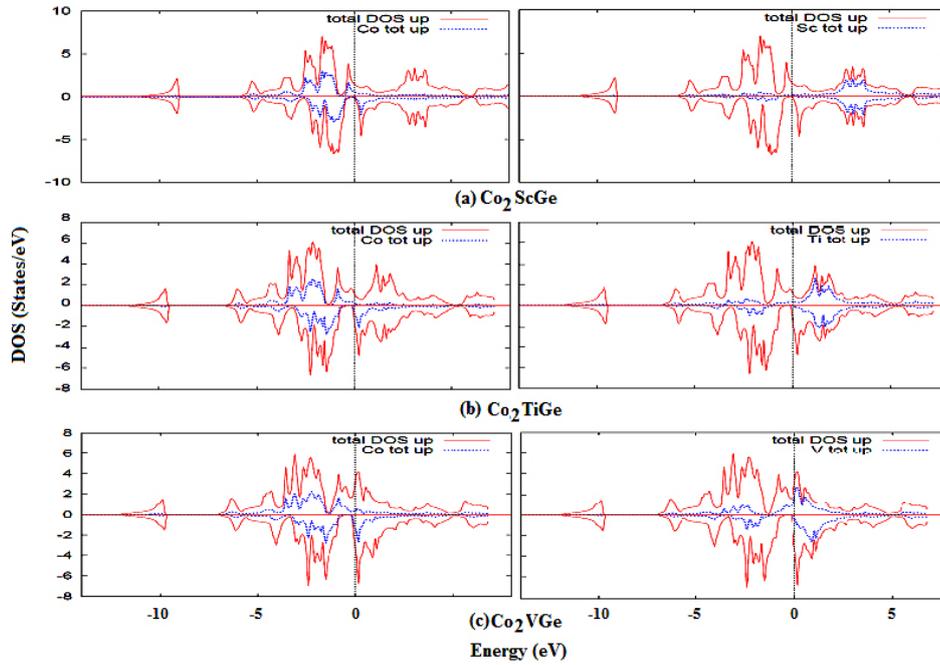


Figure 3: Total DOS for low magnetic moment compounds.

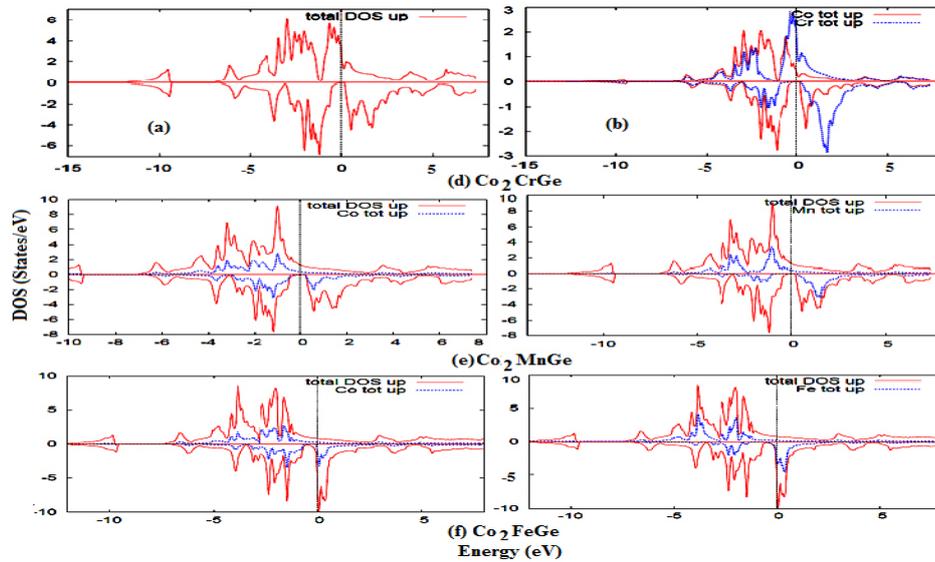


Figure 4: Total DOS for high magnetic moment compounds.

3.3 Magnetic Properties Calculated via the LSDA

For the compounds being investigated, all information on the partial, total and previously calculated magnetic moments is summarised in Table 4. This table shows the calculated total magnetic moments are exactly integer values for Co_2CrGe and Co_2MnGe as expected for half-metallic systems. For several compounds such as Co_2TiGe and Co_2VGe , the calculated total magnetic moments appear to be lower than the previous results. For small magnetic moment compounds, Co_2YGe ($Y = \text{Sc}, \text{Ti}, \text{V}$), the Co atoms contribute the most to the moment relative to compounds with higher magnetic moments, Co_2YGe ($Y = \text{Cr}, \text{Mn}, \text{Fe}$), (Table 4).

The local magnetic moment increased linearly from $Y = \text{Ti}$ to $Y = \text{Mn}$; however, the local magnetic moment was smaller for Fe than Mn, which destroyed the linear trend (Table 4). These results are consistent with the DFT study of Co_2FeSi by Wurmehl et al.²³ Additionally, the E_F was not in the gap of the minority-spin DOS when calculated with the LSDA. While the magnetic moment for the Co atoms in Co_2YGe remained nearly constant, i.e., approximately $1 \mu_B$, it diverges for ($Y = \text{Sc}$ and Fe) (Table 4).

The total magnetic moments were exact integers for the true half-metal compounds. As shown in Table 4, the Ge atoms carry a negligible magnetic moment and do not contribute much to the overall moment. Notably, the partial moment for the Ge atoms was anti-parallel to the Co and Y moments for the

HMF systems. The partial magnetic moments for the Ge atoms in the HMF compounds, Co₂CrGe and Co₂MnGe, were $-0.0296 \mu_B$ and $-0.0319 \mu_B$, respectively. These values emerged from the transition metal hybridisation and were caused by the electron wave functions overlapping as reported by Kandpal et al.²¹

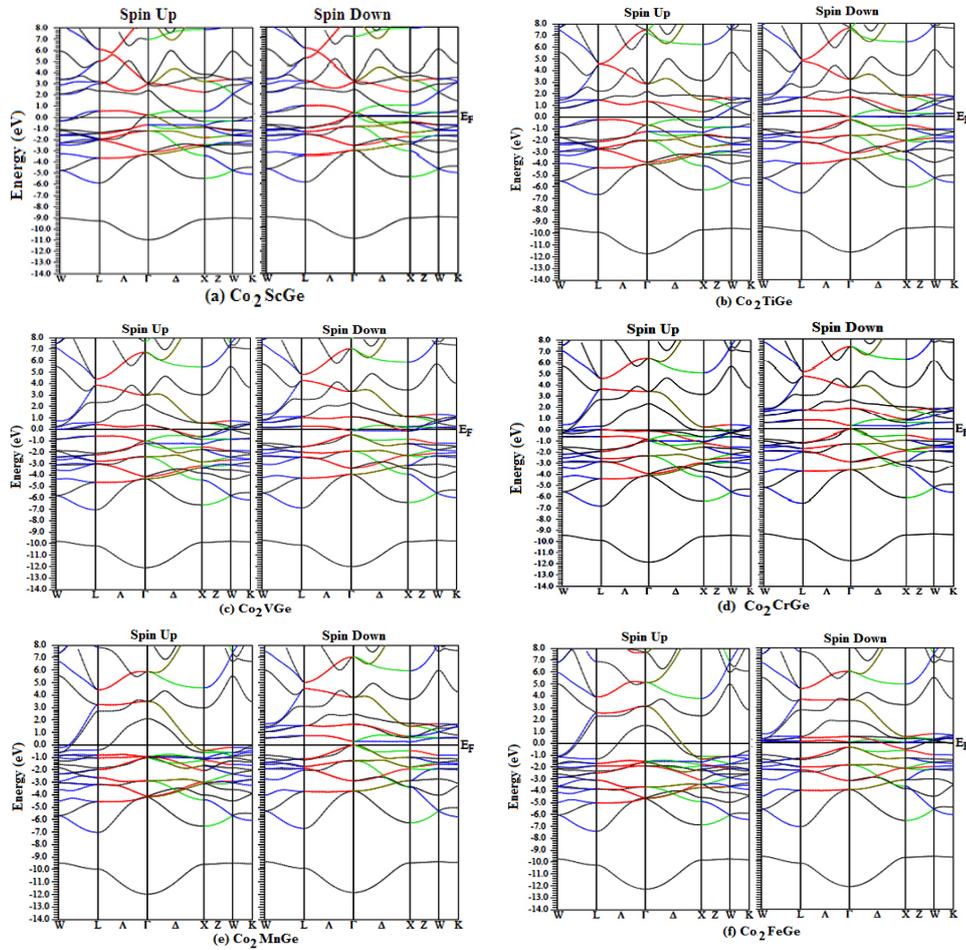


Figure 5: Band structure for Co₂YGe.

Table 4: Total and partial magnetic moments.

Compound	Magnetic moment, μ_B (LSDA)				
	Previous	Calculated			
		Co	Y	Ge	Total
Co ₂ ScGe	1.02 ¹⁹	0.572	-0.077	0.0009	1.012
Co ₂ TiGe	1.99 ¹⁹	0.951	-0.016	0.026	1.889
	1.97 ²¹				
Co ₂ VGe	2.82 ¹⁹	0.889	0.6324	0.007	2.437
Co ₂ CrGe	4.00 ¹⁹	0.932	2.122	-0.030	3.999
Co ₂ MnGe	5.00 ¹⁹	0.991	3.048	-0.032	5.000
Co ₂ FeGe	5.48 ¹⁹	1.320	2.777	0.004	5.391
	5.70 ²¹				

4. CONCLUSION

Total-energy calculations were used to find stable magnetic configurations and optimised the lattice constants. The DOS, magnetic moments and band structures for Co₂YGe (Y = Sc, Ti, V, Cr, Mn and Fe) compounds were calculated via the FP-LAPW method. The calculated results agreed well with previously calculated results. For high magnetic moment compounds, lighter transition elements, going from Fe to Cr, and fewer valence electrons yields wider gaps and more stable half-metallicities; therefore, Co₂CrGe was the most stable HMF.

For the HMF compounds (Co₂CrGe and Co₂MnGe), the partial moment of Ge is antiparallel to the Co and Y atoms. The possibility that half-metallicity appears in the full Heusler Co₂YGe (Y = Sc, Ti, V, Cr, Mn and Fe) compounds was investigated. Of these compounds, Co₂CrGe and Co₂MnGe exhibited half-metallic ferromagnetism with 100% spin polarisation at E_F. The existence of an energy gap in the minority spins (DOS and band structure) for both systems (Co₂CrGe and Co₂MnGe) indicates their potential as HMFs. The calculated magnetic moments for Co₂CrGe and Co₂MnGe being 3.999 μ_B and 5.00 μ_B , respectively, also evidenced this potential. The calculated results qualitatively agreed with an integral value, which supports the compounds being HMF.

The Fermi energy being located in the minority channel gap for the investigated system makes them half-metal ferromagnets. The Co-based Co₂YGe (Y is a transition element) Heusler alloys are the best candidates for spintronics applications.

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