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ORIGINAL PAPER

First-principles Study on Half-metallic Properties of the CoMnCrSb Quaternary Heusler Compound

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Abstract Within the framework of density functional theory, the electronic structure and magnetic properties have been studied for the CoMnCrSb quaternary Heusler compound. Features such as the lattice constant, the bulk modulus, and its pressure derivative are reported. The spin-up band of compound has metallic character, and spin-down band is semiconducting with an indirect gap of 0.50 eV at equilibrium lattice constant, resulting in stable half-metallic ferrimagnetic behavior with a magnetic moment of 3 μ_B. In addition, the ferromagnetic states are found to be energetically more favorable than paramagnetic states. Therefore, the CoMnCrSb compound is a candidate material for future spintronic application.

Keywords Quaternary Heusler compound · Magnetic materials · Ab initio calculations · Electronic structure

1 Introduction

Heusler compounds have been extensively studied, motivated by their gained importance due to advancements in spintronics [1–5].

Half-metallic ferromagnets (HMFs) meet all the requirements of spintronics, as a result of their exceptional electronic structure [1]. These materials behave like metals with respect to the electrons of one spin direction and like semiconductors (or insulator) with respect to the electrons of the other spin direction. In recent years, half-metallic ferromagnetism has been found in $La_{0.67}Sr_{0.33}MnO_3$ [6]; Co_2MnZ (Z = Ge, Sn) [7]; Ti_2CoAl [8]; NiCr (P, Se, Te, As) [9]; $Co_2Mn_{1-x}FexSi$ [10]; Co_2MnBi [11]; Mn_2CoAs [12]; ZrFeTiAl, ZrFeTiSi, ZrFeTiGe and ZrNiTiAl [13]; RbX (X = Sb,Te) [14]; $Sn_{1-x}MnxTe$ [15]; Ti_2VZ (Z=Al, Ga, and In) [16]; $Al_{1-x}Mn_xP$ [17]; Sr_2GdReO_6 [18]; CoFeMnSi [19]; NiMnSb [20]; Fe_3O_4 [21, 22]; Co_2MnSi [23]; ZrCoTiZ (Z = Si, Ge, Ga, and Al) [24]; Sr_2FeWO_6 [25]; Sr_2CoMoO_6 [26]; Sr_2CrWO_6 [27]; Sr_2FeReO_6 [28, 29]; Sr_2MnMoO_6 [30]; Sr_2CuOsO_6 [31]; Sr_2VOsO_6 [32]; Sr_2NiRuO_6 [33]; Sr_2FeTiO_6 [34]; Sr_2CrMoO_6 [35]; NiCoMnZ (Z = Al, Ge, and Sn) [36]; CoFeMnZ (Z = Al, Ga, Si, Ge) [37]; $Co_2Mn_{1-x}FexSi$ [38]; $Co_{16}Mn_7GdSi_8$ [39]; Co_2FeZ (Z = Al, Ga, Si, Ge) [40]; $Fe_{0.25}Co_{1.75}VSn$ [41]; CoFeMnSi, CoFeCrAl, CoMnCrSi, CoFeVSi and FeMnCrSb [42]; Cr_2MnAl [43]; Fe_2MnSi [44, 45]; NiCrP, NiCrSe, NiCrTe, and NiVAs [46]; Ti_2CoGa [47]; Mn_2VZ (Z = Al , Si) [48]; Mn_2ZnS [49]; Ti_2FeSi [50]; Mn_2CuMg [51]; and Mn_3Ge and Mn_2FeZ (Z = Al, Sb) [52, 53] and nearly 100 % high spin-polarization has been observed experimentally in the cases of CrO_2 and $La_{0.67}Sr_{0.33}MnO_3$ materials [54].

Generally, CoMnCrSb quaternary Heusler compound crystallize in the LiMgPdSn-type crystal structure [55, 56]. The resulting structure which has F-43m symmetry is generated The atomic coordinates for CoMnCrSb compound are listed in Table 1. It is known that CoMnCrSb crystallizes in the LiMgPdSn-type structure with three non-equivalent type structures (see Fig. 1).

However, studies on CoMnCrSb compound is not explored well in the existing literature. This motivates us to investigate on the electronic, magnetic and mechanical properties of CoMnCrSb compound by performing the

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Table 1 Three non-equivalent structure type configurations

	4a(0,0,0)	4b(1/2,1/2,1/2)	4c(1/4,1/4,1/4)	4d(3/4,3/4,3/4)
Type I	Sb	Cr	Mn	Co
Type II	Sb	Mn	Cr	Co
Type III	Mn	Sb	Cr	Co

band structure calculations using the FP-LAPW method for PBE-GGA exchangecorrelation potentials.

2 Method of Calculations

The first-principles calculations were performed by employing FP-LAPW approach [57], based on the DFT [58] as implemented in WIEN2K code by Blaha et al. [59]. In its general form, the LAPW method expands the potential in the following form:

$$V(r) = \begin{cases} \sum_{\mathrm{LM}} V_{\mathrm{LM}}(r)\, Y_{\mathrm{LM}}(r) & \text{inside sphere} \\ \sum_{K} V_K e^{iK.r} & \text{outside sphere} \end{cases} \quad (1)$$

The Kohn-Sham equations are solved self-consistently using full-potential linearized augmented plane wave method. In the interstitial region, the plane wave cutoff value was imposed by the condition $R_{\mathrm{MT}}K_{\max} = 9$, where $K_{\max}$ is the plane wave cutoff and R_{MT} is the smallest of all atomic sphere radii. The radii R_{MT} of the muffin tins (MT) are chosen to be approximately proportional to the corresponding ionic radii. Exchange-correlation effects are treated using GGA as parameterized by Perdew et al. [60]. Self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4} Ry. The convergence criteria for total energy and force are taken as 10^{-5} and 10^{-4} eV/Å, respectively. The valence wave functions inside the spheres are expanded up to $l_{\max} = 10$, while the charge density was Fourier expanded up to $G_{\max} = 14$. The Monkorst-Pack special k-points were performed using 3000 special k-points in the Brillouin zone.

3 Results and Discussion

As the first step, total energy versus cell volume calculations were carried out for CoMnCrSb compound in both paramagnetic (PM) and ferromagnetic (FM) states (Fig. 2). The total energies versus the changed volumes are fitted to Murnaghan's equation of state [61] to determine the ground state properties, such as the equilibrium lattice constant a and the bulk modulus B and its pressure derivative B'. The calculated structural parameters of CoMnCrSb compound are reported in Table 1. Until now, an experimental or theoretical lattice parameters and the bulk modulus and its pressure derivative value have not been reported. It is also included in Table 1 the bulk modulus and its pressure derivative B' data for CoFeTiSb [62] and CoFeMnSi [63] for comparison purposes; one can see the ferromagnetic state is more favorable than nonmagnetic one in energy On the other hand, the type I (FM) structure is found to be energetically more favorable than type II (FM) and type III (FM) structure.

The calculated spin-polarized band structures of CoMnCrSb compound at the theoretical equilibrium lattice constant along high-symmetry directions of the first Brillouin zone are displayed in Fig. 3. The total and partial densities of states, in which the spin-up and spin-down sub-bands are plotted with black and red lines, respectively, are shown in Figs. 4 and 5. The Fermi level set as eV.

In Fig. 4 (type I), it is clear that the majority-spin band is metallic, while the minority-spin band shows a semiconducting gap around the Fermi level. In the minority-spin band, the valence band maximum (VBM) is located at 0.20 eV and the conduction band minimum (CBM) at 0.30 eV. The energy gap for spin-down electrons at around the Fermi level is 0.50 eV. It is evident that the compound exhibits a half-metallic ferromagnetic band structure; the minority channel shows a gap at the Fermi energy. Type I was also identified to exhibit a half-metallic ferromagnetic ground state. Types II and III in contrast to these findings

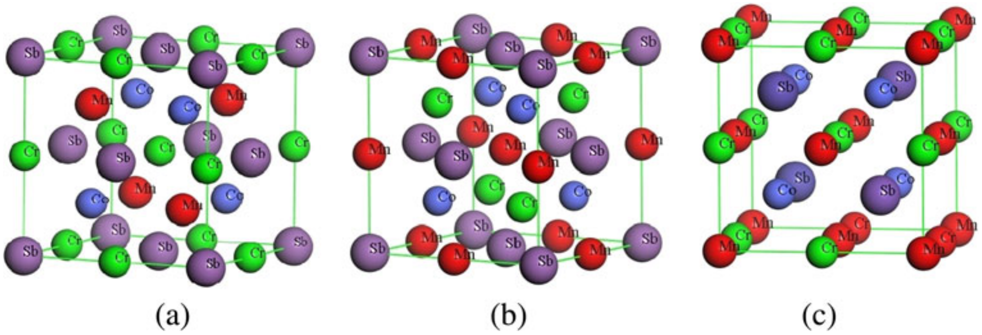
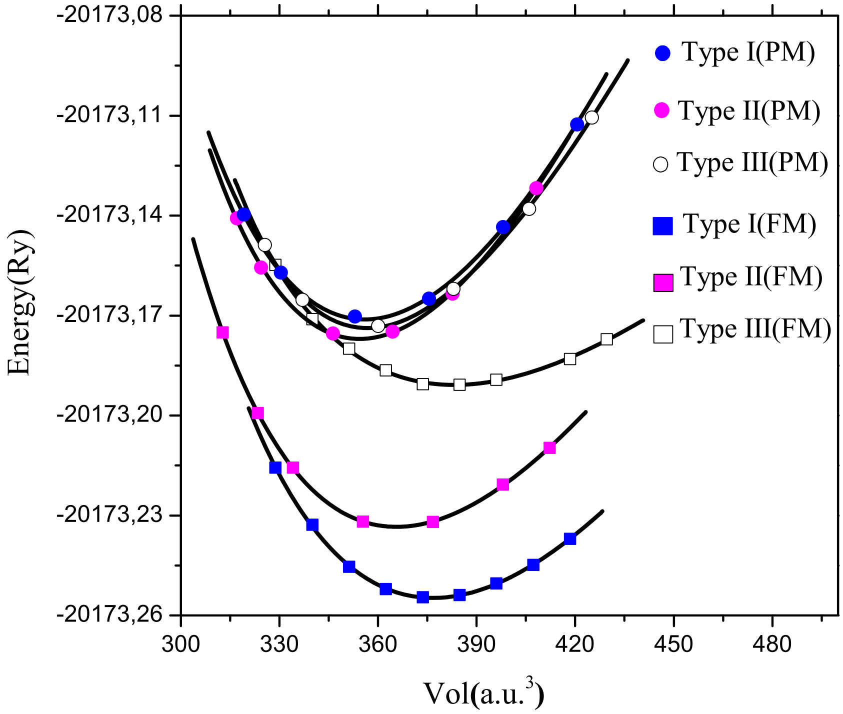


Fig. 1 Crystal structure of CoMnCrSb: **a** type I, **b** type II, and **c** type III

Fig. 2 Volume optimization for the CoMnCrSb quaternary Heusler compound



have states at the Fermi energy in both spin directions and are thus a normal metal.

Figure 5 shows the total density of states as a function of energy for the CoMnCrSb quaternary Heusler compound at its equilibrium lattice constant.

Figure 6 illustrates the density of states (DOS) of Co eg and t2g, Mn eg and t2g, Cr eg and t2g, and Sb s and p electrons for the spin-up and spin-down sub-bands; in both spin channels, significant contribution to the total density of states in the energy range between −7.0 and −4.0 eV comes from p electrons of Sb elements; in the energy range between −4.0 and −1.0 eV, which represents the contribution of Mn eg and t2g spin-up hybridized with Cr t2g spin-down and Co eg and t2g orbital, one can see the exchange splitting in the Mn-d states, along with the fact that the Mn-eg (spin-up) states are occupied completely, while the Mn-t2g (spin-up) states are partially occupied. At the Fermi energy, the situation is markedly different. Such a band structure is the signature of a half-metallic material. The Mn (4b)-Co (4d) and Mn (4b)-Cr(4c) interaction involves primarily Co(4d)-Cr(4c) interaction, although direct hopping is also substantial (Co-Cr distances of a/2: not much longer than the Mn-(Co, Cr) distance is $a\sqrt{3/4}$). These values of polarization are similar to those already published for Ti_2FeSi full Heusler compound calculated with a full-potential linearized augmented plane wave

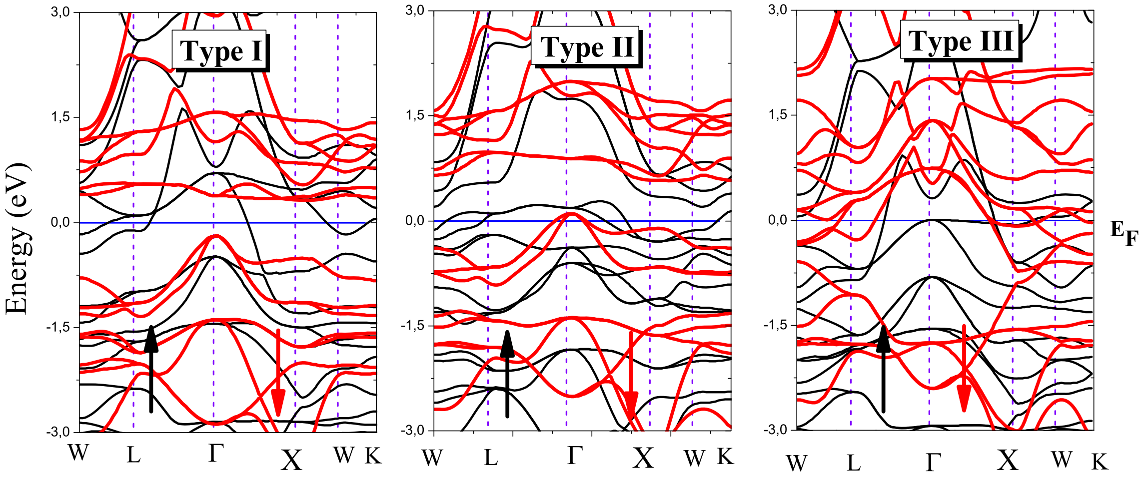


Fig. 3 The band structure of the CoMnCrSb quaternary Heusler compound for the spin-up and spin-down electrons

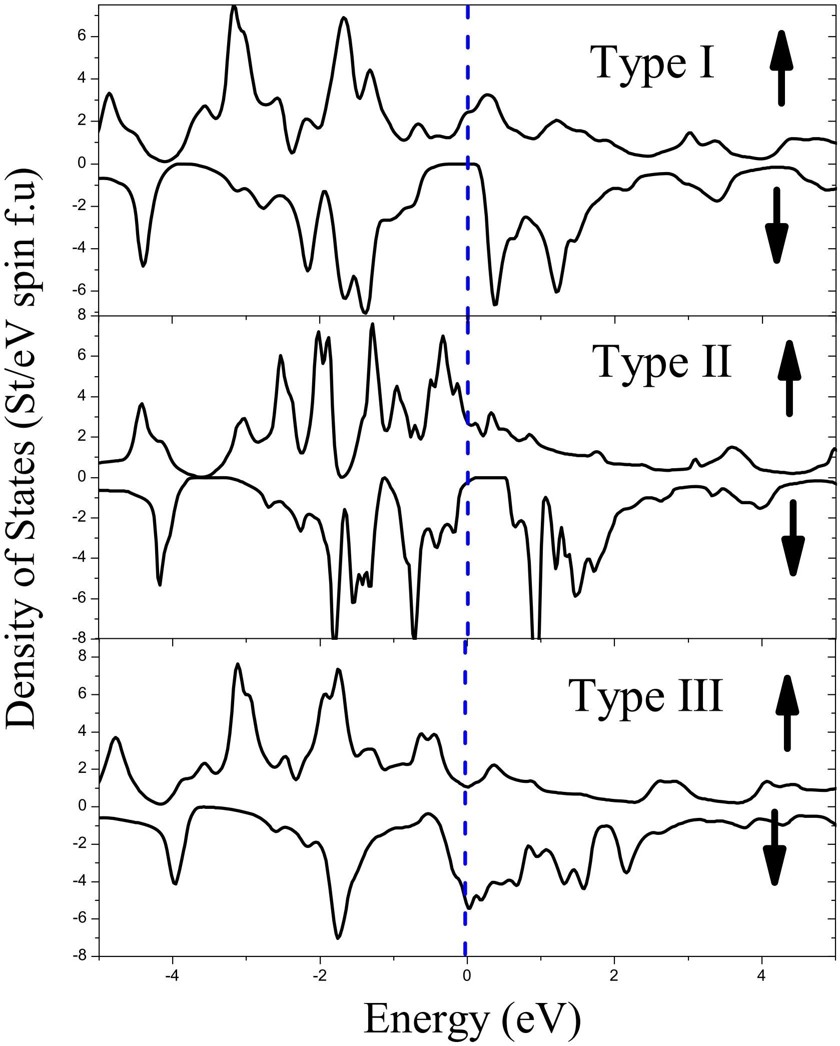


Fig. 4 Spin-polarized total densities of states (TDOS)

method [64]. In the energy range between 2.1 and 3.2 eV, the band of Sb s has no prominent effect on electronic structure of the system for both majority and minority states.

The calculated total and atom-resolved magnetic moments of CoMnCrSb compound is summarized in Table 2. For half-Heusler compounds with three atoms per formula unit, the Slater–Pauling rule is given by $m_{\text{tot}} = N\text{v} - 18$. In the case of X_2YZ Heusler material, there are four atoms per unit cell leading to the formula $m_{\text{tot}} = N\text{v} - 24$ rule. The total spin moment is 3 μ_B for the type II structure which have 27 valence electrons per unit cell Thus this compounds follow the Slater–Pauling behavior and the "rule of 24" [65] Alijani et al. [66] studied the electronic structure of CoFeMnZ (Z = Al, Ga, Si, Ge) alloys using first-principle calculations and found that the magnetic moment per manganese atom is ranging from −2.88 to 2.87 μ_B. However, for other Heusler alloys (e.g., Co_2YZ), the magnetic moment per Cobalt atom is known to have values ranging from 0.3 to 1.23 μ_B [67, 68], which is lower than that obtained for our Co_2MnSi films [69]. Our results for magnetic moment for chromium atoms are in agreement with previous studies [70], and the partial magnetic moments of the antimony atoms are very small.

Figure 6a illustrates the detailed information on the atomic and total magnetic moments as a function of lattice constant. The calculated total magnetic moment is 3 μ_B within all range of the lattice parameter. The calculated magnetic moments of the Cr atoms increase with increase in lattice constant, while the magnetic moment of the Mn atoms decreases and the magnetic moment of Co atoms slightly increases with lattice constant.

In Fig. 6b, the total density of states (TDOS) of CoMnCrSb compound at different lattice constants are presented. In minority spin, with lattice expanding, a clear change of the Fermi level position is observed. It is clearly seen in Fig. 6b that the CoMnCrSb Heusler compound has half-metallic nature above the lattice constant value of 6.067 Å. Therefore, the lattice constant variation does not affect the half-metallic behavior of the CoMnCrSb compound.

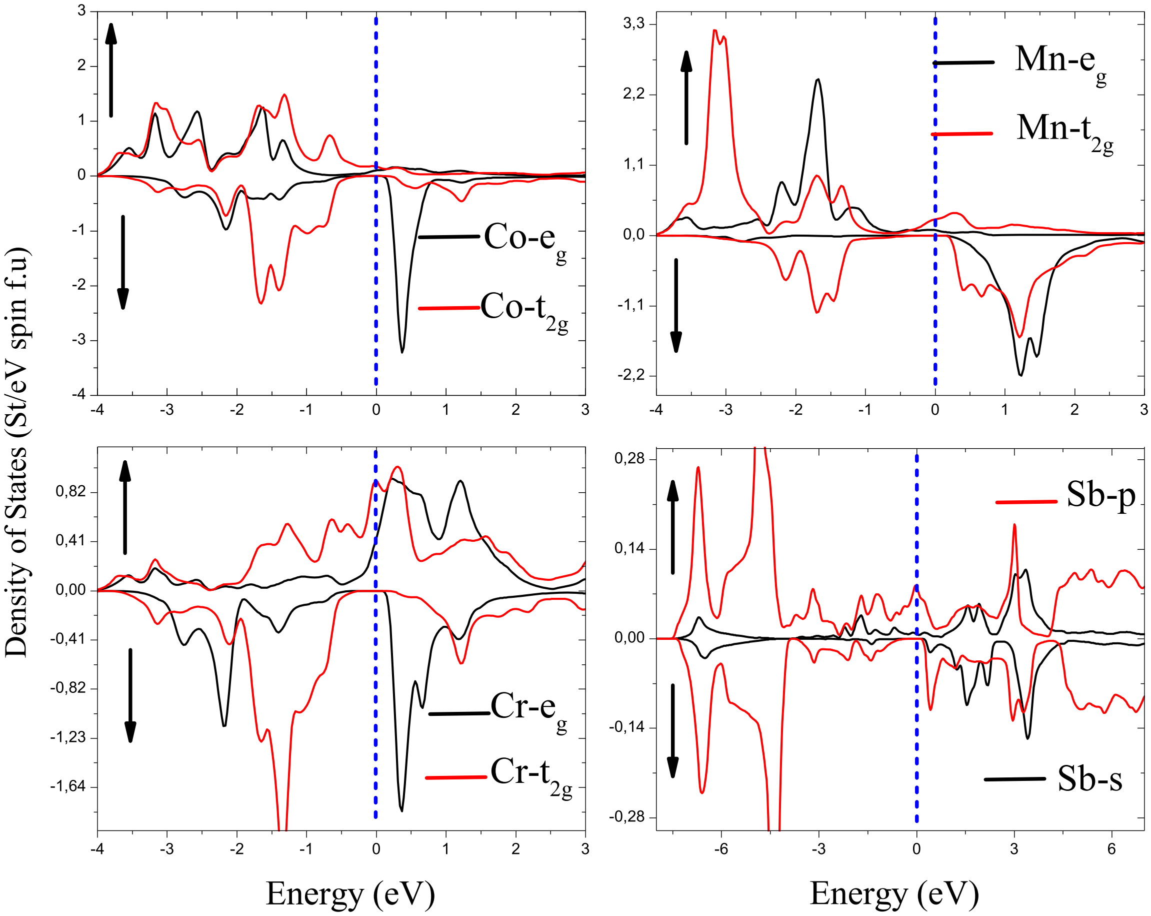


Fig. 5 Spin-polarized partial densities of states (DOS) of type I structure

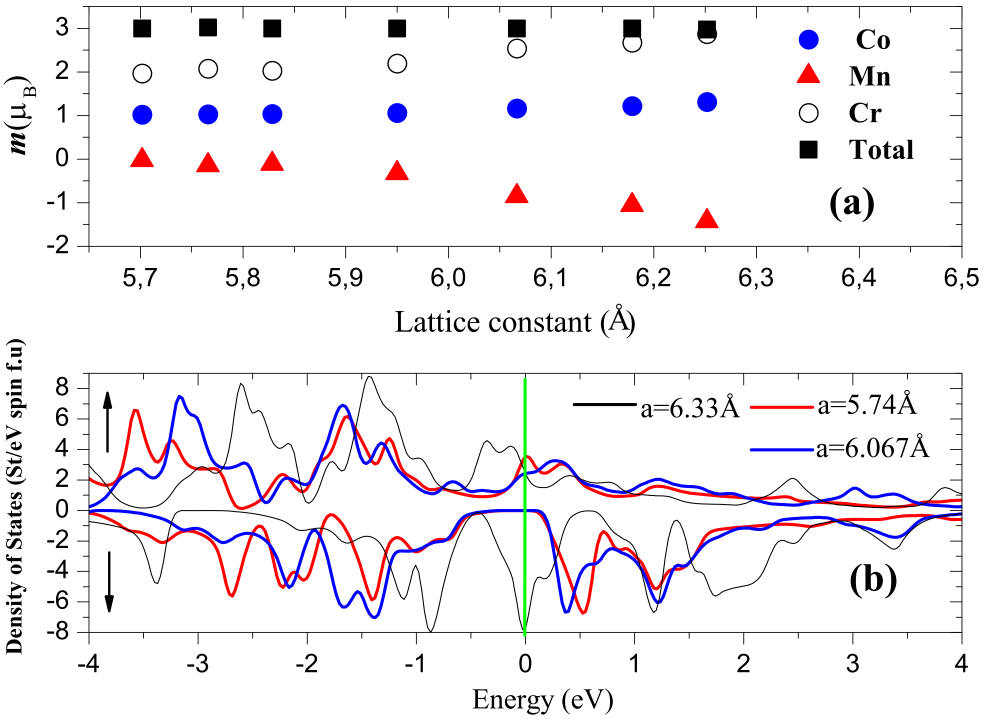


Fig. 6 Lattice constant dependencies of **a** magnetic moment and **b** total densities of states for type I structure

Table 2 Half-metallic lattice parameters, total and partial magnetic moment

Compound			a (Å)	B (GPa)	B'	E_{tot} (Ry)	ΔE (eV) = E(FM)− E(PM)
CoMnCrSb	Type I	FM	6.067	140.5112	5.251	−20, 173.254755	−1.141
		PM	5.953	196.253	4.4395	−20, 173.170848	–
	Type II	FM	6.007	153.878	5.895	−20, 173.233425	−0.767
		PM	5.944	213.69	5.001	−20, 173.177038	–
	Type III	FM	6.112	91.4726	6.410	−20, 173.190818	−0.232
		PM	5.957	211.9484	6.3757	−20, 173.173756	–
CoFeTiSb [62]	Type I	FM	6.08	175.18	4.52	–	–
		PM	6.11	127.82	4.29	–	–
CoFeMnSi [63]	Type I	FM	5.611	231	–	−8230.06630	–
	Type II	FM	5.613	–	–	−8230.04494	–
	Type III	FM	5. 649	–	–	−8230.01337	–
		m_{Co}	m_{Mn}	m_{Cr}	m_{Sb}	$m_{\text{interstitial}}$	m_{Total}
CoMnCrSb	Type I	1,14	3,17	−1.29	0.02	−0.069	3.00
	Type II	0.78	0.79	1.38	−0.12	−0.195	2.65
	Type III	1,21	2,23	−2.59	0.01	−0.190	0.68
CoFeMnSi [63]	Type I	1.05	–	–	−0.09	–	2.00
CoFeTiSb [62]	Type I	0.89	2.70	–	–	–	4.00
	Type II	0.95	0.58	–	–	–	3.98
	Type III	1.81	1.98	–	–	–	5.33

4 Conclusion

A novel Heusler compound, CoMnCrSb, has been studied by using first-principles FP-LAPW calculation method. At the equilibrium lattice constant, the spin-polarized calculations showed that the CoMnCrSb compound is half-metallic ferromagnetic. The total magnetic moments is 3 μ_B, which is consistent with the Slater–Pauling rule $m_{\text{tot}} = N_V - 24$ and a band gap in the minority-spin channel of 0.50 eV. Therefore, the CoMnCrSb compound is a good candidate material for future spintronic application.

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