Prediction of semiconducting behavior in minority spin of Co_2CrZ (Z = Ga, Ge, As): LSDA

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Abstract: Volume optimization was performed to obtain the theoretical lattice constants by using the generalized gradient approximation (GGA). The electronic and magnetic properties of Heusler alloys Co_2CrZ (Z = Ga, Ge, As) were investigated by using local spin density approximation (LSDA). Amongst the systems under investigation, Co_2CrGe and Co_2CrGa give 100% spin polarization at the Fermi level (E_F). Co_2CrGe and Co_2CrGa are the most stable half-metallic ferromagnets (HMFs); their E_F lie exactly at the gap of 0.24 eV and 0.38 eV, respectively, in the spin-down channel. Even though Co_2CrAs gives a distinct and bigger gap as compared to Co_2CrGa and Co_2CrGe, its E_F is not located at the middle of the gap in the spin-down channel. We have also found that the total magnetic moments increase as the Z goes from Ga to As. The calculated density of states and band structures show the HMF character for Co_2CrGe and Co_2CrGa.

Key words: GGA; half-metallicity; DOS; spin polarization and band structure
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1. Introduction

De Groot was the pioneer in discovering half-metallic ferromagnetism in semi-Heusler compound NiMnSb[1] by using first principles calculation based on the density functional theory. The discovery of half-metallicity has attracted much attention[2] because of its prospective applications in spintronics[3]. Recently, the rapid development of magnetoelectronics has intensified the search for ferromagnetic materials that are suitable for spin injection into a semiconductor[4]. One of the most promising classes of materials for this purpose is the half-metallic ferromagnets (HMFs), i.e., compounds for which only one spin channel presents a gap at the Fermi level (E_F), while the other has a metallic character, leading to 100% carrier spin polarization at the E_F[3, 5]. Ishida *et al.*[6] have also proposed that full-Heusler alloy compounds of the type Co_2MnZ (Z = Ge, Sn) are half-metals. Heusler alloys are particularly interesting systems because they exhibit a much higher ferromagnetic Curie temperature than other half-metallic materials[7]. Rai *et al.*[8, 9] investigated the ground states of Co_2MnAl and Co_2CrSi using LDA + U and LSDA methods, respectively. After the preparation and characterization of bulk Co_2MnZ (Z = Si, Ge, Ga, Sn), they are used as targets for pulsed laser deposition (PLD) of magnetic contacts for spintronic devices[10] due to their half-metallic nature. Theoretical studies on Mn_2VAl agree on its half-metallic character with a gap at the spin-up band instead of the spin-down band. As for the other half-metallic Heusler alloys[11], the generalized gradient approximation (GGA)[12] was used for the exchange–correlation potential. In our present work, we have studied the structural, electronic and magnetic properties of Co_2CrZ (Z = Ga, Ge, As) using the full potential linearized augmented plane wave (FP-LAPW) method.

2. Computation detail

A computational code (WIEN2K)[13] based on FP-LAPW method was applied for the structural calculations of Co_2CrZ. GGA was used for (the calculation of) the exchange correlation potential. The multipole expansion of the crystal potential and the electron density within muffin tin (MT) spheres was cut at $l = 10$. Nonspherical contributions to the charge density and potential within the MT spheres were considered up to $l_{max} = 6$. The cut-off parameter was $R_{mt}K_{max} = 7$. In the interstitial region, the charge density and the potential were expanded as a Fourier series with wave vectors up to $G_{max} = 12$ a.u.$^{-1}$. The number of k-points used in the irreducible part of the brillouin zone is 286. The MT radii (RMT) for each atom are tabulated in Table 1.

3. Crystal structure

Full-Heusler alloys[14] have the chemical formula X_2YZ (X = Co, Y = Cr and Z = Ge, Ga, As). The full Heusler structure consists of four penetrating fcc sublattices with atoms at 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 results in a L_{21} crystal structure having space group Fm-3-m, as shown in Fig. 1.

Table 1. Muffin tin radius (RMT).

RMT (a.u.)	Compound		
	Co_2CrGa	Co_2CrGe	Co_2CrAs
Co	2.36	2.35	2.35
Cr	2.36	2.35	2.35
Z	2.20	2.21	2.21

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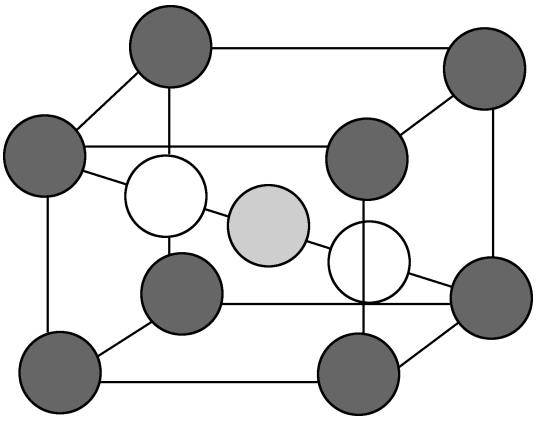

Fig. 1. Structure of Co_2CrZ: Co (white), Cr (gray) and Z (black) atoms.

3.1. Structural optimization for Co_2CrZ

Systematic calculations of the electronic and magnetic properties of the Heusler compounds Co_2CrZ are carried out in this work. The calculated results of the electronic properties are compared in order to study the effect of the valence electron concentration of different kinds of atoms on the magnetic properties and in particular the band gap in the minority states. The structural and electronic properties were calculated using GGA and LSDA, respectively. The optimized lattice constants, isothermal bulk moduli, and its pressure derivative were calculated by fitting the total energy to Murnaghan's equation of state[15]. The optimized lattice parameters were slightly higher than the experimental lattice parameters (see Table 2), in which the change in the lattice parameters are given by $\Delta(a_o)$. A series of calculated total energies as a function of volume can be fitted to an equation of states according to Murnaghan's equation (Eq. (1)).

$$E(V) = E_0 + \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1\right] - \frac{B_0 V_0}{B'_0 - 1}, \qquad (1)$$

where E_0 is the minimum energy at $T = 0$ K, B_0 is the bulk modulus at the equilibrium volume and B'_0 is the pressure derivative of the bulk modulus at the equilibrium volume.

Pressure, $P = -\frac{dE}{dV}$. Bulk modulus, $B_0 = -V\frac{dP}{dV} = V\frac{d^2E}{dV^2}$.

The results of the structural optimization are shown in Fig. 2. The detailed values of the optimized lattice parameters and bulk moduli are given in Table 2.

3.2. Spin polarization and half-metallic ferromagnets

The electron spin polarization (P) at the Fermi energy (E_F) of a material is defined by Eq. (2)[18].

$$P = \frac{\rho_\uparrow(E_F) - \rho_\downarrow(E_F)}{\rho_\uparrow(E_F) + \rho_\downarrow(E_F)}, \qquad (2)$$

where $\rho_\uparrow(E_F)$ and $\rho_\downarrow(E_F)$ are the spin-dependent density of states at the E_F. The $\uparrow$ and $\downarrow$ assigns the majority and the minority states, respectively. P vanishes for paramagnetic or anti-ferromagnetic materials even below the magnetic transition temperature. It has a finite value in ferromagnetic materials

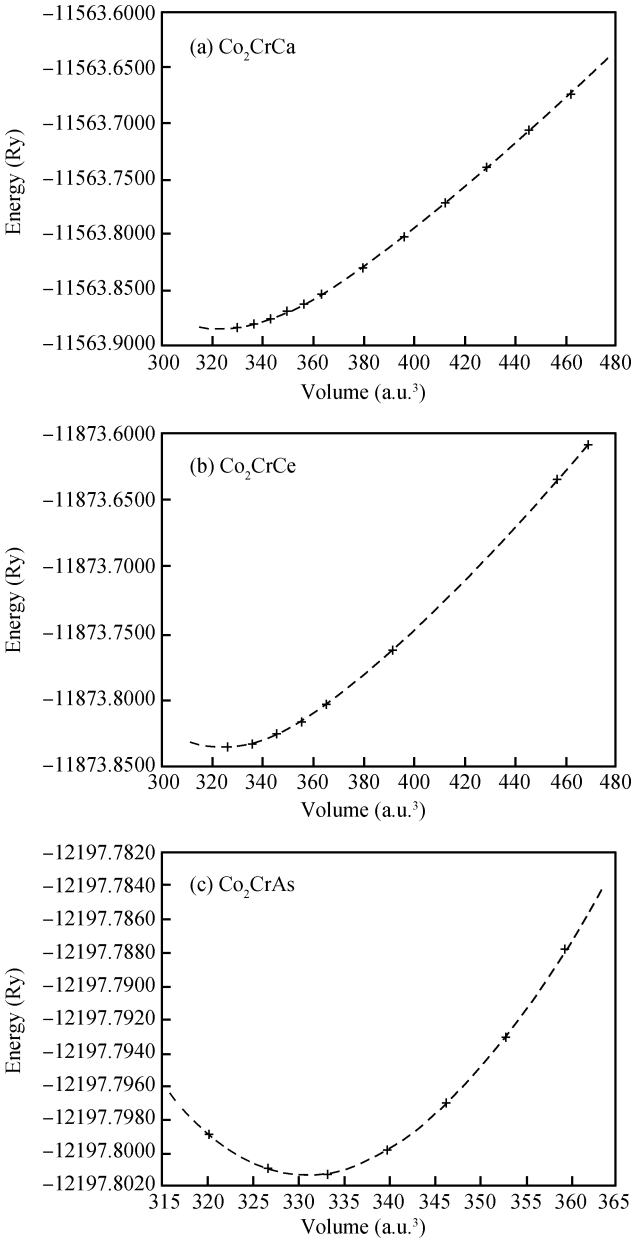

Fig. 2. Volume optimization of the lattice parameters.

below the Curie temperature[19]. The electrons at E_F are fully spin polarized ($P = 100\%$) when $\rho_\uparrow(E_F)$ or $\rho_\downarrow(E_F)$ equals zero. In the present work, we have studied systems like Co_2CrZ (Z = Ga, Ge, As). Among them, only Co_2CrGe and Co_2CrGa show 100% spin polarization at E_F (Table 3). According to our results, Co_2CrGe is an interesting compound as it shows a large DOS at the E_F of $\rho_\uparrow(E_F) = 3.00$ states/eV (Table 3). The reason for its large value is that E_F cuts through strongly localized states of Cr-d whereas the contribution of Co-d states to $\rho_\uparrow(E_F)$ at E_F is very small, as illustrated in Fig. 3(c). On the other hand $\rho_\downarrow(E_F) = 0.00$ states/eV for both Co and Cr atoms. As a result, the spin polarization is 100% at the Fermi level. The same explanation follows in the case of Co_2CrGa $\rho_\uparrow(E_F) = 4.200$ states/eV and $\rho_\downarrow(E_F) = 0.00$ states/eV, as shown in Fig. 3(a). According to this, Co_2CrGe and Co_2CrGa are half-metals which give 100% spin polarization at their E_F.

Figure 3 summarizes the results of the DOS which were

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

Compound	Lattice constant a_o (Å)			Bulk modulus	Equilibrium
	Previous	Calculated	$\Delta(a_o)$	B (GPa)	energy (Ry)
Co_2CrGa	5.805[16]	5.802	–0.003	262.6977	–11563.8846
Co_2CrGe	5.740[17]	5.770	0.030	250.4376	–11873.8355
Co_2CrAs	5.786[21]	5.810	0.014	192.3964	–12197.8013

Table 3. Energy gap and spin polarization.

Compound	Energy gap E_g (eV)			Spin polarization		
	$E_{max}(\Gamma)$	$E_{min}(X)$	ΔE	$\rho_\uparrow(E_F)$	$\rho_\downarrow(E_F)$	$P(\%)$
Co_2CrGa	0.00	0.28	0.38	4.20	0.00	100
Co_2CrGe	0.00	0.24	0.24	3.00	0.00	100
Co_2CrAs	–0.50	–0.10	0.40	2.80	0.60	70

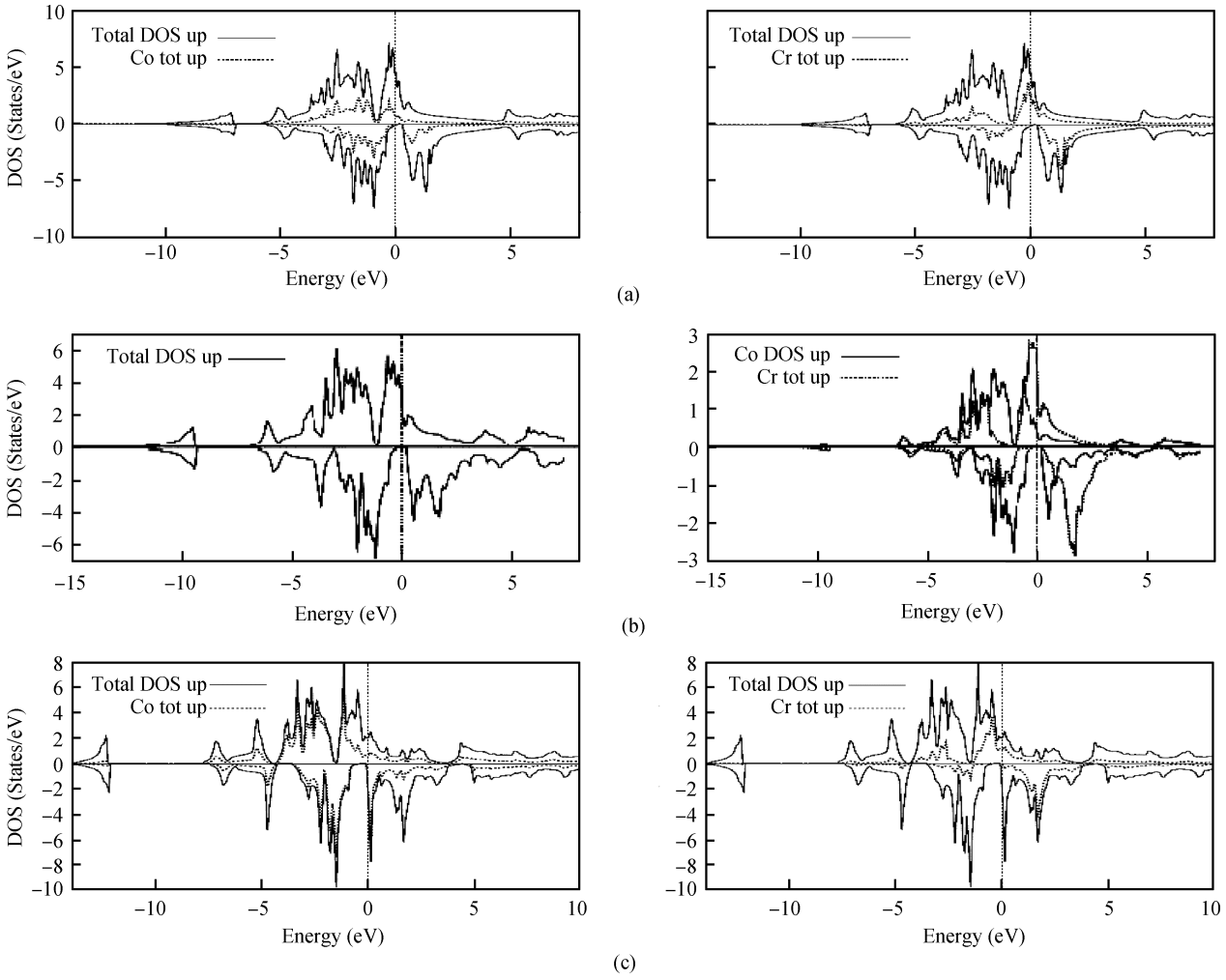

Fig. 3. (a) Total DOS of Co_2CrGa. (b) Total DOS of Co_2CrGe. (c) Total DOS of Co_2CrAs.

calculated using LSDA. For compounds with fewer electrons, the E_F is close to the minority valence states. The size of the gap increases as the Z moves from Ga to As. As compared to Co_2CrGa and Co_2CrGe, Co_2CrAs has a larger gap because the extra electrons in the latter case occupy majority states, leading to an increase of the exchange splitting between the occupied majority and the unoccupied minority states and thus to a larger gap for Co_2CrAs. A similar result was reported in the case of Co_2CrZ (Z = Al, Si) by Ozdogan *et al.*[20]. According to Figs. 4(a)–4(c), the indirect band gaps along the Γ–X symmetry directions are 0.28 eV for Co_2CrGa, 0.24 eV for Co_2CrGe and 0.40 eV for Co_2CrAs. For Co_2CrGa and Co_2CrGe, the E_Fs lie in the middle of the gap determining their semiconducting nature in the minority-spin channel, as shown in Figs. 3(a) and 3(b). The Heusler alloy Co_2CrAs is not a perfect half-metal even though there exists a gap of 0.40 eV because its E_F falls

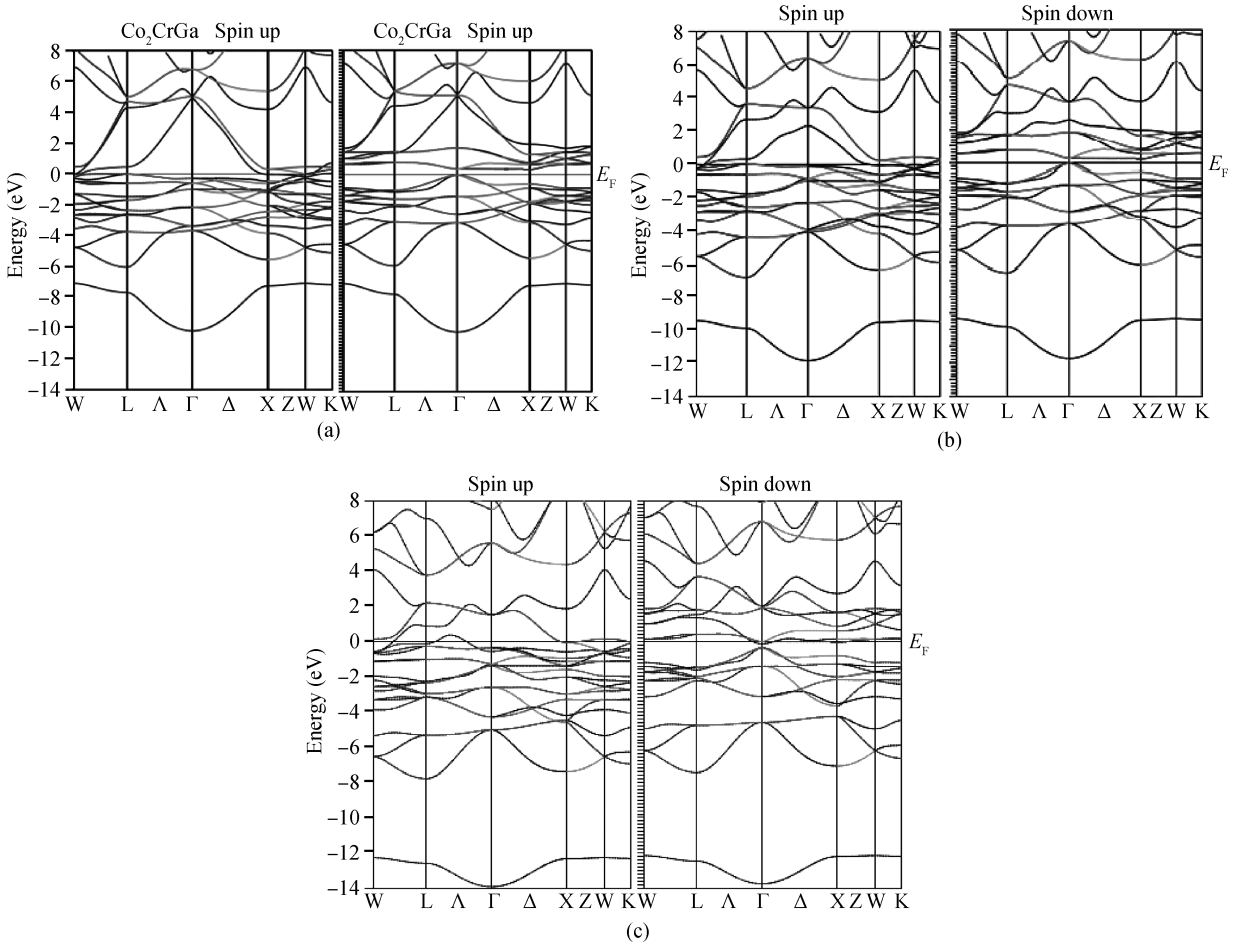

Fig. 4. (a) Band structure of Co_2CrGa. (b) Band structure of Co_2CrGe. (c) Band structure of Co_2CrAs.

Table 4. Total and partial magnetic moments.

Compound	Previous	Magnetic moment μ_B (LSDA) Calculated			
		Co	Cr	Z	Total
Co_2CrGa	3.05[16]	0.737	1.602	–0.064	3.030
Co_2CrGe	4.00[17]	0.932	2.122	–0.029	3.999
Co_2CrAs	5.00[21]	1.066	2.578	0.044	4.891

into an uprising peak of the minority-spin states. The same results have been reported by Kanbur and Gokoglu[21]. The formation of the gap for the half-metal compounds was discussed by Galanakis *et al.*[22] for Co_2MnSi, which was due to the strong hybridization between Co-d and Mn-d states, combined with large local magnetic moments and a sizeable separation of the *d*-like band centers.

3.3. Magnetic properties calculated in the LSDA

It is shown in Table 4 that the Cr sites have high magnetic moments in all of these compounds. The increase in the magnetic moments at the Cr sites is due the exchange splitting between the Cr-d states in the spin-up and spin-down channels, as shown in Figs. 3(a)–3(c). The calculated integer magnetic moments of the systems obey the Slater-Pauling rule[20], in which the total magnetic moment of the system scales with the number of valence electrons and is expressed as $M_t = Z_t - 24$, where Z_t is the number of valence electrons. Small deviations from this rule are also possible in several compounds, as already explained by Galanakis *et al.*[20]. Starting with the compounds under investigation, all the information regarding the partial, total and the previously calculated magnetic moments are summarized in Table 4. As is shown in Table 4, the calculated total magnetic moment is almost an integer value in the case of Co_2CrGe, as is expected for half-metallic systems. In most cases the calculated magnetic moments are in good agreement with the previous results. It is found that the partial as well as the total magnetic moment increase linearly, as shown in Table 4. We have found that the Co sites contribute much more to the magnetic moment in the As-based compound as compared with the Ga and Ge compounds. The same observation was also reported and explained by Kandpal *et al.*[16] because of the indirect connection between the specific magnetic moment at Co

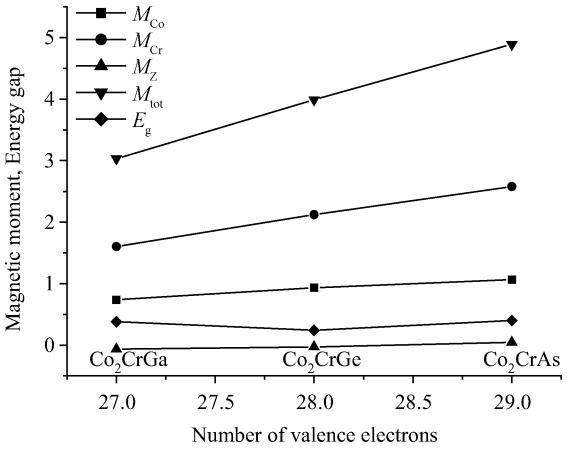

Fig. 5. Evaluation of the magnetic moments of Co_2CrZ (Z = Ga, Ge, As) and energy gaps with respect to the valence electrons.

the hybridization arising from the interaction between the electrons at the Co sites with the neighboring electrons in the Co t-$_{2g}$ states. As shown in Table 4, the Z atoms carry a negligible magnetic moment, which does not contribute much to the overall moment. We have also noticed that the partial moment of the Z atoms aligns anti-parallel to the Co and Cr moments of the systems. It emerges from the hybridization with the transition metals and is caused by the overlap of the electron wave functions. The small moments found at the Z sites are mainly due to the polarization of these atoms by the surroundings; magnetically active atoms as reported by Kandpal *et al.*[16].

Figure 5 is the plot of the total and partial magnetic moments of Co_2CrZ (Z = Ga, Ge, As) and the change in energy gaps against the valence electrons. It is clearly shown that the partial magnetic moments of Co, Cr and Z sites, as well as the total magnetic moments, are increasing with the valence electrons. In Fig. 5 the total and partial magnetic moments are represented as M_{tot}, M_{Co}, M_{Cr}, and M_Z. The energy gap is denoted as E_g. The moments of Ga and Ge are aligned anti-parallel to those of Co and Cr, which will reduce the total moments as shown in Table 4.

4. Conclusion

We have performed the total-energy calculations to find the stable magnetic configuration and the optimized lattice constant. The DOS, magnetic moments, and band structures of Co_2CrZ (Z = Ga, Ge, As) were calculated using the FP-LAPW method. The calculated results were in good agreement with the previously calculated results. For high *sp* elements, as the Z goes from Ga to As and the more valence electrons there are, the wider the gap is. As a result, a larger gap appears in the case of Co_2CrAs. For ferromagnetic compounds, the partial moment of Z is very small and the contribution is much smaller in the total magnetic moment. We have investigated the possibility of the appearance of half-metallicity in the case of the full Heusler compounds like Co_2CrGa and Co_2CrGe, which show 100% spin polarization at E_F. The existence of an energy gap at the E_F of Co_2CrGa and Co_2CrGe shows the semiconducting nature in the minority spin channel and the E_F cutting through the uprising peaks of the majority spin is an indication of being a potential HMF. The HMF characteristics are also supported by the integer value of the magnetic moments, i.e., 3.03μ_B for Co_2CrGa and 3.9999μ_B for Co_2CrGe. The calculated results are in qualitative agreement with the integral value, supporting the HMF. These characteristics make HMFs very important candidates for use in spintronics. The Co-based Heusler alloys Co_2YZ (Y is transition elements) are the most prospective candidates for applications in spintronics. This is due to a high Curie temperature beyond room temperature and the simple fabrication process such as dc-magnetron sputtering in Co_2YZ.

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