Electronic Structure and Magnetic Properties of Co_2CrAl Full Heulser Alloy

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Abstract: With the help of first principle calculation we were presented the electronic structure properties of Co_2CrAl Full Heusler. The exchange and correlation effect were treated within VBH, VWN, PBE and MJW framework. Results suggest that Co_2CrAl is a half-metal where electrons at the Fermi level are 100% spin polarized. The half-metallicity is also visible for YZ disordered states. Experimentally reported magnetic moment values are obtained by reducing the symmetry. The exchange coupling in between Co and Cr causes to variation in structural and magnetic properties. Obtained half metallic and magnetic properties are mainly related to hybridizations in between Co and Cr elements.

IndexTerms **– Heusler alloys, Density Functional Theory, SPRKKR, Electronic Structure Properties, Magnetic Properties.**

I. INTRODUCTION

Heusler alloys were considered as a class of compounds known to display various appealing properties, such as high Curie temperature, magnetic anisotropy, semiconducting, half metallic and shape memory effects which are widely used in latest thin film based technologies (Zhu et al. 2016, Soni et al. 2016, Luo et al. 2015, Chandra et al. 2018, Jain et al. 2017). They are generally denoted by a formula X_2YZ and XYZ respectively full and half Heusler alloys, where X and Y represent a transition metal, while Z represents an s-p element. Among them Co-based Heusler alloys Co_2CrAl, Co_2FeAl, Co_2FeSi and $Co_2FeAl_{0.5}Si_{0.5}$ are very important because of structural, magnetic and electronic structure properties that were rapidly investigated by many researchers [Soni et al. 2016; Jain et al. 2014, Jain et al. 2015]. In this paper we used SPRKKR (spin polarized relativistic Korringa-Kohn-Rostoker) Green function method to detail investigation of electronic structure and magnetic properties of Co_2CrAl.

Co_2CrAl Heusler compounds are highly investigated by numerous researchers and exhibit half metallic behavior (Nehra et al. 2015, Ram et al. 2011). Among the all Heusler compounds only some alloys preserve half metallic behavior in disordered state.

The reported theoretical magnetic moment was found to be $3\mu_B$ and the band gap was 0.80ev. The experimental magnetic moment of Co_2CrAl alloy (1.55 μ_B is significantly smaller than the theoretical value of 3 μ_B for L21 ordered structure, which may be related to some kinds of defects that may occur in the system. Luo et al (2008) investigated the effect of doping Co_2CrAl on half metallicity and magnetism and reported that the compound is half metallic within the whole range of studies. They added that substituting Cr for Co leads to a high bonding peak above the Fermi level (EF) in the majority spin band while the energy in the minority spin band is retained.

Giant diamagnetism in half-metallic Co_2CrAl Heusler alloy was observed by Kim et al (2009). Motivated by importance of Co_2CrAl, in this work we investigated the electronic structure properties and exchange coupling behavior of Co_2CrAl by reduces symmetry, different disordering states.

II. COMPUTATIONAL

The electronic structure and magnetic properties of Co_2CrAl were obtained by SPRKKR code (Ebert et al, 2012). The electronic structure calculation has been done in a non-relativistic, scalar relativistic as well as fully relativistic mode. In the scalar-relativistic mode paramagnetic as well as spin-polarized systems were treated. In the fully relativistic mode, paramagnetic as well as spin-polarized systems with an arbitrary spin configuration can be dealt with. The exchange and correlation effect were treated within VBH, VWN, PBE and MJW framework (Perdew et al, 1992). The angular momentum expression up to lmax = 3 and 4000 k-point has been used for all approximations.

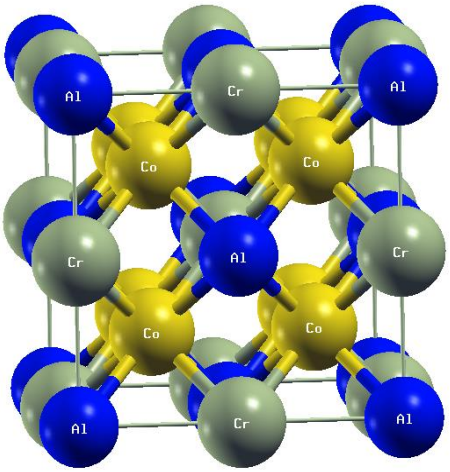

Fig. 1: Unit cell structure of Co_2CrAl

The energy conversion criterion tolerance has been set to 10^{-5}Ry. Fig. 1 shows the crystal structure of Co_2CrAl L21 order structure which used to perform calculations for ordered compound. The Co atom is placed at X Positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) and Cr atom placed at Y position (0.5, 0.5, 0.5) while Al at Z position (0, 0, 0). The effect on structural and magnetic properties of reduced symmetry also examined by using F43m space group, where Co occupied X (0, 0, 0) and Y (0.5, 0.5, 0.5) positions, Cr atoms occupied X (0.25, 0.25, 0.25) position and Al atom occupied Z (0.75, 0.75, 0.75) position. The density of states is calculated with the Greens function by adding a small imaginary part of 0.001 Ry to the energy for smaller value the band gaps becomes more visible. In our calculation spin-orbit interaction and noncollinear spin states are neglected.

III. RESULTS AND DISCUSSION

The equivalent lattice constants, converged energy and Fermi energy have been listed in Table 1 were obtained by Gaussian fitting total energy v/s lattice parameter values within the framework of different approximations as shown in Fig. 2. Observed values of lattice parameters for L21 ordered structure are quite underestimate from experimental values (5.74Å to 5.75Å) (Zhang et al., 2004, Hakimi et al., 2010). The GGA approximation gives minimum converged energy compared with other approximations. We have also mentioned previously theoretically reported values of lattice parameters.

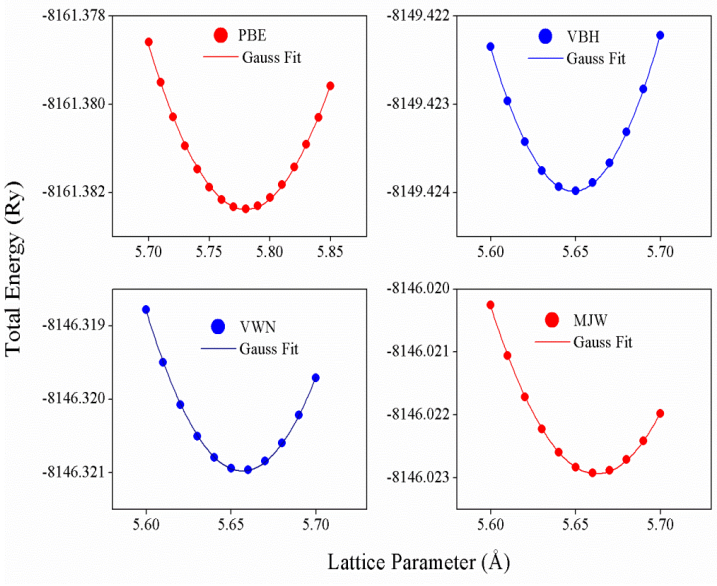

Fig. 2: Volume optimization curve

Table 1: Structural Parameters, Converged Energy and Fermi energy

Approx.	Obtained Lattice Parameters (Å)	Prev. Rep. Lattice Parameters (Å)	Converged energy (R_y)	Fermi Energy (R_y)
VBH-LDA	5.65	[a]5.66	-8149.4239	0.821
VWN	5.66	---	-8146.3210	0.815
MJW	5.66	---	-8146.0229	0.813
PBE-GGA	5.78	[b]5.73, [c]5.71	-8161.3824	0.769

[a](Chakraborty et al, 2007) [b](Alhaj and Hamad, 2012), [c](Hoshino et al., 2010)

Fig. 3 shows the total and individual density of states of Co_2CrAl, Co_2CrAl is a half-metallic ferromagnet, since the majority spin channel shows a metallic behavior, whereas the minority spin channel shows an insulating behavior within all approximations.

The spin polarization is defined as the imbalance of spin up and spin down electrons according to

$$sp = \frac{J^{\uparrow} - J^{\downarrow}}{J^{\uparrow} + J^{\downarrow}} \qquad (1)$$

With $J^{\uparrow}$ and $J^{\downarrow}$ denoting the separate spin-up and spin-down contributions to the total current density, respectively. This suggests that Co_2CrAl is a half-metal where electrons at the Fermi level are 100% spin polarized (Table 2). E(k) curve of Co_2CrAl, which is shown for down spin states with in different approximation in Fig. 4. The Fermi level shown by a broken horizontal line intersects the E(k) curves in the majority (up)-spin sate but is located at the energy gap in the minority (down)-spin state. That is, it is expected that the alloy shows typical semiconductor for the down-spin states. The energy band gap between the highest occupied valence state and the lowest unoccupied conduction state in the minority spin channel is varied from 0.567eV to 0.657eV within different approximations. Our result of the band gap is lower than previously reported values (Alhaj and Hamad, 2012) (Felser et al., 2005) and higher than that obtained by Block et al (2004), (0.18eV) which may be related to using a different approach to solve Kohn-Sham equations by using different approximation. However, we should mention here that DFT usually underestimates the band gap as compared to experiment, which is related to the weakness of the exchange correlation function. The gap originates from the strong hybridization between the d states of the higher valent Co and the lower valent Cr transition metal atoms.

Table 2: Obtained magnetic moment and spin polarization

Approx.	Magnetic moment				Prev. report magnetic moment (μ_B)	Band gap	Spin polarization
	m_{Co} (μ_B)	m_{Cr} (μ_B)	m_{Al} (μ_B)	m_{Total} (μ_B)			
VBH-LDA	1.72	1.63	-0.06	3.29	[d]2.96	0.567 eV	100%
VWN	1.70	1.65	-0.07	3.28	-----	0.595 eV	100%,
MJW	1.69	1.66	-0.07	3.28	------	0.571 eV	100%
PBE-GGA	1.62	1.76	-0.11	3.28	[e]3.00	0.657 eV	100%

[d](Hoshino et al., 2010), [e](Alhaj and Hamad 2013)

Experimentally it was reported that Co_2CrAl is a ferrimagnetic with magnetic moment of 1.56 μ_B. theoretically no one obtained approximate values. According to the rule of "Z–24" a total magnetic moment of 3μ_B since Co_2CrAl has 27 electrons. Experimentally large deviation from this rule is observed. Theoretical reported value of magnetic moment is 3 μ_B. The calculation performed with SPRKKR cannot reproduce the magnetic moment previously obtained by other code. Although the previously reported magnetic moment also very high compare to experimentally reported magnetic moment. Total magnetic moment remains stable against approximation only atoms resolved moment are varied. To examine the variation of magnetic moment, we pay attention to the neighbor atoms of Co atoms. The first nearest neighbor atoms of Co in Co_2CrAl are Cr atoms. This suggests that d-states of Co in Co_2CrAl hybridize with d-states of the first nearest neighbor atoms in lower energy range, because the potential around Cr is deeper than that of Co. Certainly, the DOS of Co and Cr of the up-spin state have some peaks in the same energy range, that is, the d-states of Co and Cr hybridize strongly. Therefore, the band tail (hole) of up-spin states above the Fermi level is small and the Co d-states of the up-spin state are mostly occupied. Thus, the magnetic moment of Cr atom is enhanced in Co_2CrAl.

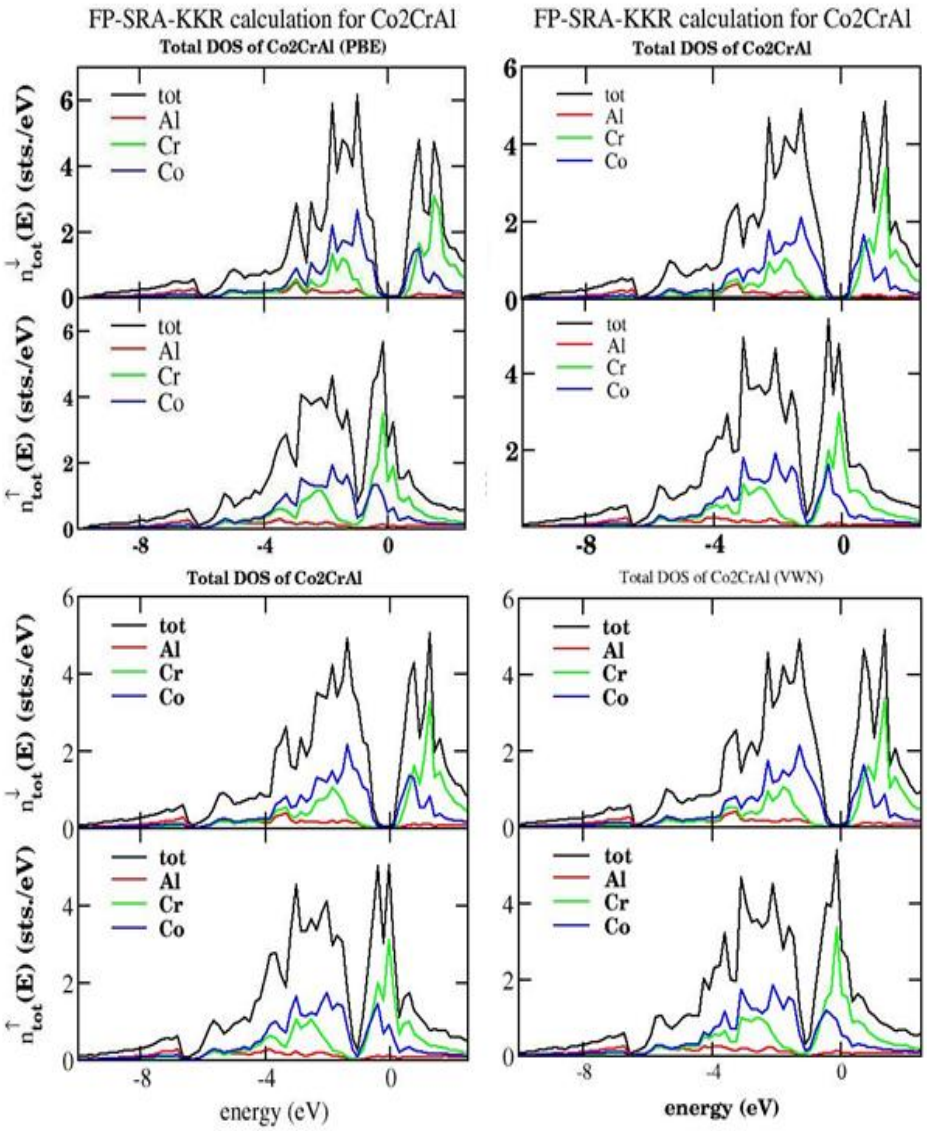

Fig.3: Partial and total DOS of $L2_1$ ordered Co_2CrAl

To obtain experimentally reported moment we were tried all possible relativistic or non relativistic calculations, full spin polarized relativistic and no collinear calculations. At last we reduced the symmetry from Fm3m to F43m, the obtained magnetic moment value is 0.56 μ_B.

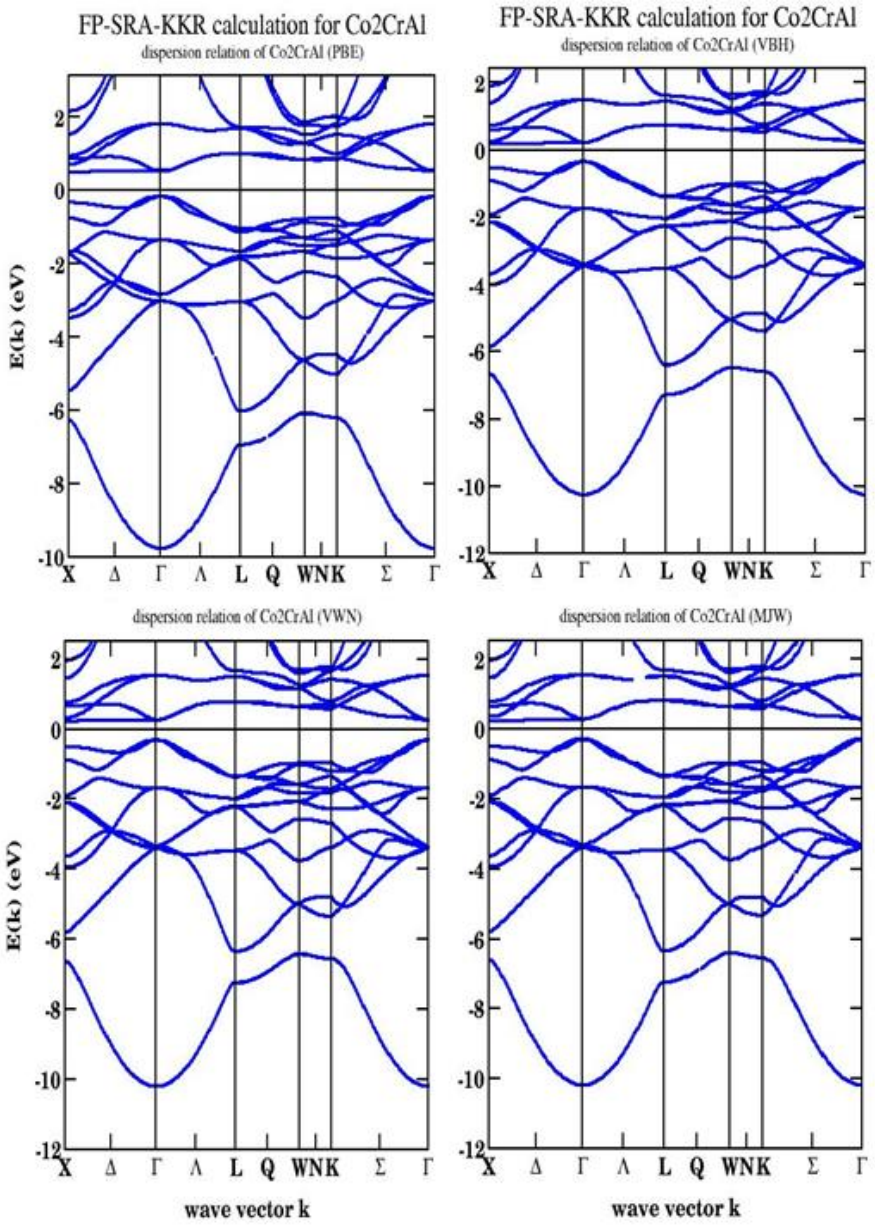

Fig. 4: Band structure of Co_2CrAl

Results suggested that Co_2CrAl not fully $L2_1$ ordered which leads to small antisite disorder that was very small and cause reduced in magnetic moment. Alloys with half-metallic properties should have an integer value of magnetic moment per unit cell. We can see that the value of magnetic moment per unit cell is not an integer within all approximation.

In the classical Heisenberg model the Hamiltonian of a spin system is given by (Meinert et al., 2011).

$$\mathcal{H} = -\sum_{ij} S_i S_j J_{ij} \qquad [2]$$

With the Heisenberg pair exchange coupling parameters J_{ij}, and unit vectors S_i, S_j pointing in the direction of the magnetic moment on site I and J site respectively. SPRKKR allows us to calculate the Heisenberg exchange coupling parameters J_{ij} within a real approach using an expression proposed by Liechtenstein et al. Exchange parameters for $L2_1$ symmetry were shown in Fig. 5(a). We start with the discussion of the ordered Co_2CrAl. One observes clearly the dominating Co-Cr, Co-Co nearest neighbor interactions with Co, where the Co-Cr interaction is clearly the stronger one. The Co-Al (second nearest neighbor interaction) is much weaker in comparison. In case of Cr interactions to nearest neighbor we observes that the dominating interactions in between Co-Cr, Co-Co, where the Co-Cr interaction is clearly the stronger same as in case of Co. The Cr-Al (second nearest neighbor interaction) is much weaker in comparison.

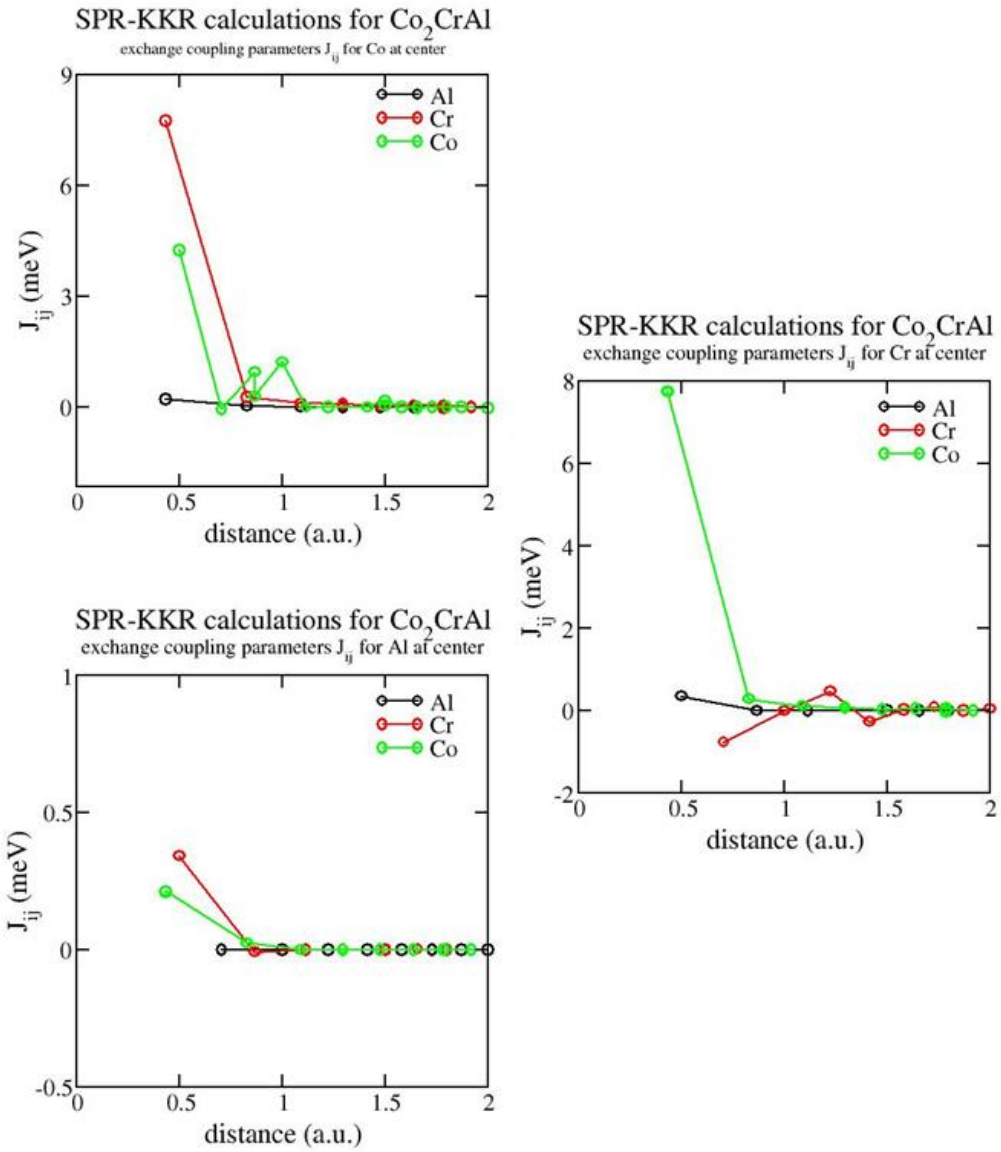

Fig. 5(a): Exchange parameters for $L2_1$ ordered Co_2CrAl

In the case of center Al, the interaction with Co and Cr are effectively zero for all distances. Cr couple antiferromagentically to Cr atoms while Co and Cr couple ferromagnetically. On the other hand, the intra-sublattice interactions (Cr-Cr interaction) are negative, which leads to a destabilization of the parallel alignment of the moments on one sublattice. In case of reduced symmetry systems the variation in exchange were shown in Fig. 5 (b). We clearly have seen the dominating exchange interactions in case of Co_1 at center are Co_1-Co_2, Co_1-Cr, where the Co_1-Co_2 interaction is clearly the stronger one below 0.5 au after Co_1-Cr dominated. The Co_1-Al, Co_1-Co_1 neighbor interaction is much weaker in comparison.

In case of Co_2 at center the Co_2-Cr interaction is clearly the stronger one and dominated. The Co_1-Al and Co_2-Co_2 neighbor interaction is much weaker in comparison. In case of Cr interactions to nearest neighbor we observes that the dominating interactions in between Cr-Co_1, Cr-Co_2, where the Cr-Co_2 interaction is clearly the stronger one. The Cr-Al, Co_1-Al, Co_2-Al second nearest neighbor interaction and first nearest neighbor interations with respect to Al at center atom is much weaker and negligible in comparison. Cr couple antiferromagentically to Cr atoms while Co_1, Co_2 and Cr couple ferromagnetically. On the other hand, the intra-sublattice interactions (Cr-Cr interaction) are negative, which leads to a destabilization of the parallel alignment of the moments on one sub lattice. Co atoms at two site Co_1 and Co_2 in case of reduced dimensions which also have $r_{ordered} < r_{reduce\ sym}$ distance of radius. Over all compared with exchange interactions between full and reduced symmetry systems the exchange interactions in case of ordered structure are dominant which leads to high magnetic moment.

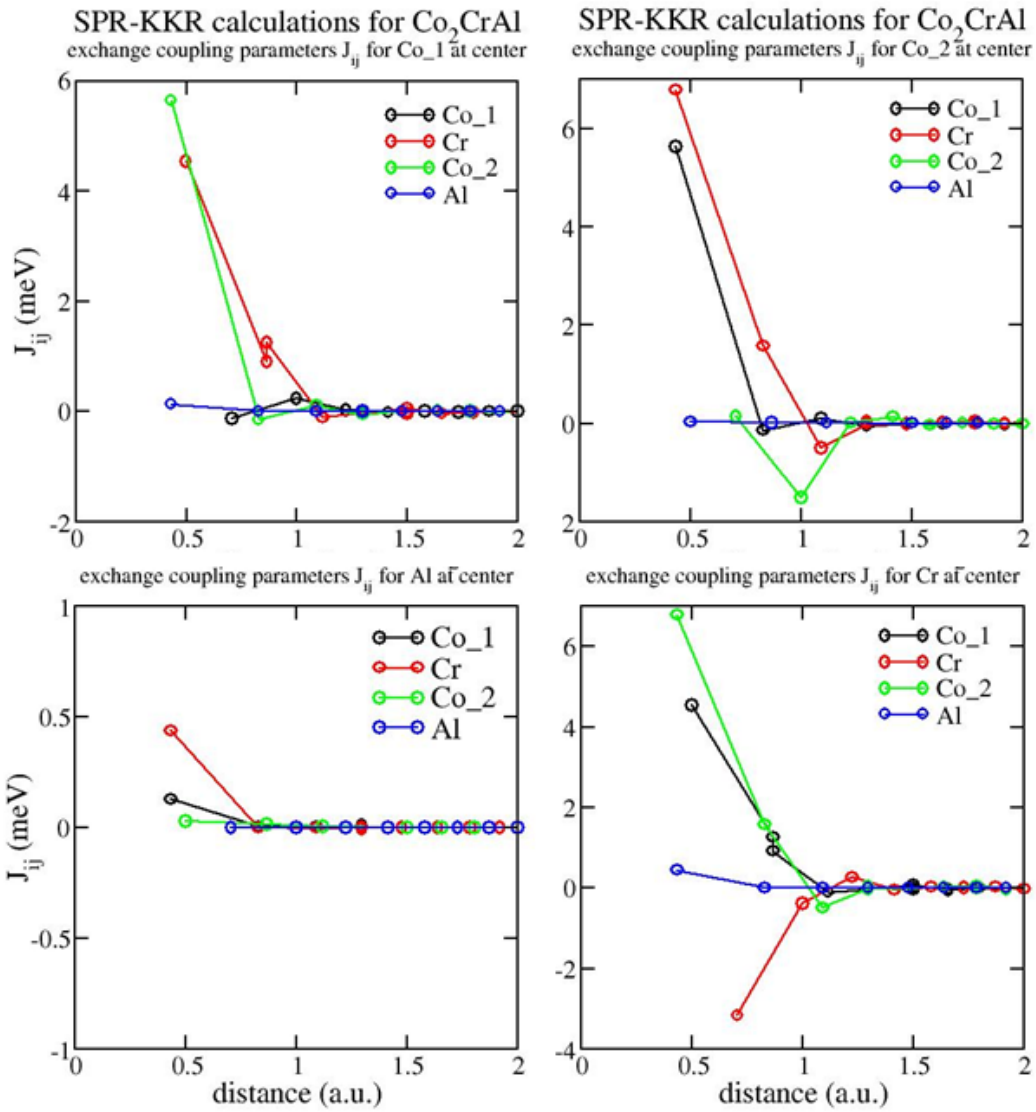

Fig. 5(b): Exchange parameters for Co_2CrAl with reduced symmetry

Fig. 6 shows total and partial DOS of reduced symmetry systems, it is observed that half metallic behavior was faded as symmetry reduced from $L2_1$ but still the systems shows high spin polarization. The main contribution to magnetic moment arises from Co_1 and Co_2 atoms.

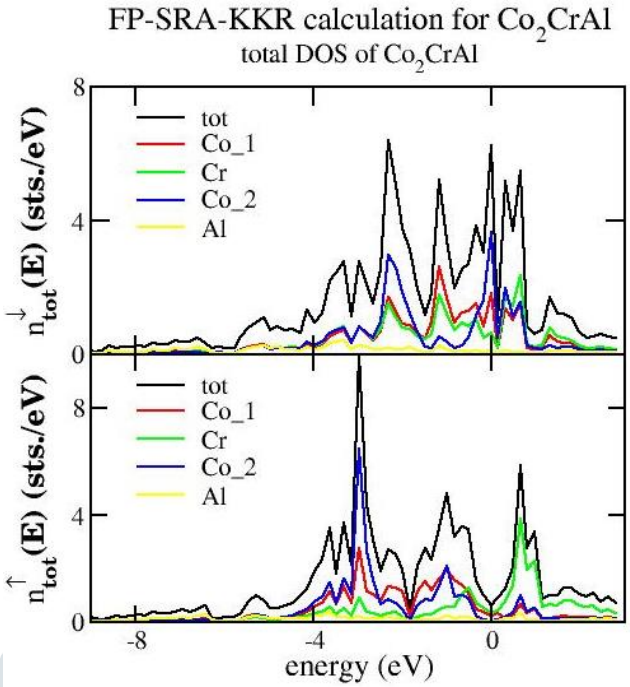

Fig. 6: Total and partial density of states of reduced symmetry Co_2CrAl

To perform disorder calculations we have employed the coherent-potential approximation (CPA) developed by Blackman and collaborators in 1971 [Blackman et al., 1971]. Disordering effect was studied within GGA approximation with lattice parameter of 5.78Å for XY, YZ and XYZ disordered structures. In CPA each X-Y, Y-Z and X-Y-Z disordering will be studied by Y occupied ease site by appropriate equally distributed atoms at each site with a probability given by the respective concentration of each chemical type. Fig. 7 (a), 7(b), 7(c) shows the density of states for disordered structures respectively and obtained magnetic moment and converged energy values mention in Table 4.3. As disordered varies the value of structure and magnetic parameters also varies, the obtained value of converged energy value minimum for YZ disordered structure which is also more than ordered structure. The value of magnetic moment also changed. Compared to experimental values of magnetic moment the values well match with X-Y disordered structure and Y-Z disordered structure value well match with theoretically obtained magnetic moments values.

Half metallic properties of ordered Co_2CrAl is faded in case of XY and XYZ disordered structure but remains stable for YZ disordered states. XYZ and XY disordered compound shows metallic behavior. The band gap will reduced for Y-Z disordered structure to 0.26 eV due to variation in nearest neighbor configurations of Al atoms to Cr atoms.

Table 3: Magnetic properties of disordered Co_2CrAl Heusler alloy

Type of disordering	Converged energy (Ry)	Total magnetic moment m_{total} (μ_B)	Individual magnetic moment		
			m_{Co} (μ_B)	m_{Cr} (μ_B)	Al (μ_B)
XY	-8150.7254	1.47	0.69	0.81	-0.03
YZ	-8161.3755	3.28	1.67	1.71	-0.10
XYZ	-8161.2875	3.28	2.85	0.49	-0.06

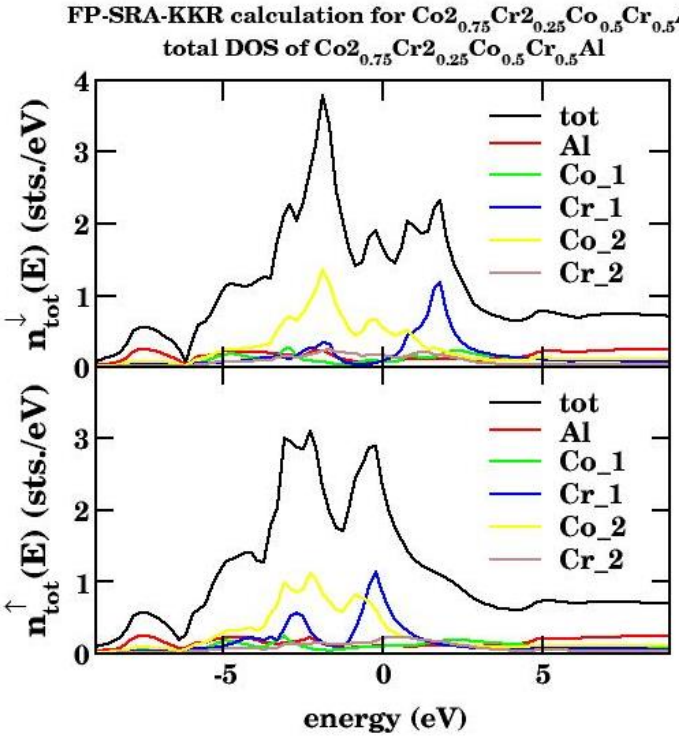

Fig. 7(a): Total and partial DOS of X-Y disordered Co_2CrAl

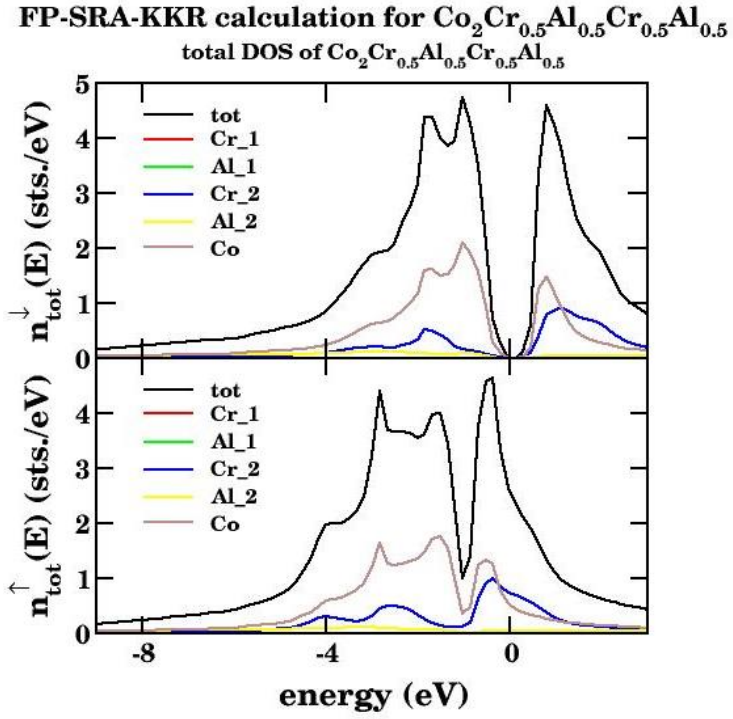

Fig. 7(b): Total and partial DOS of Y-Z disordered Co_2CrAl

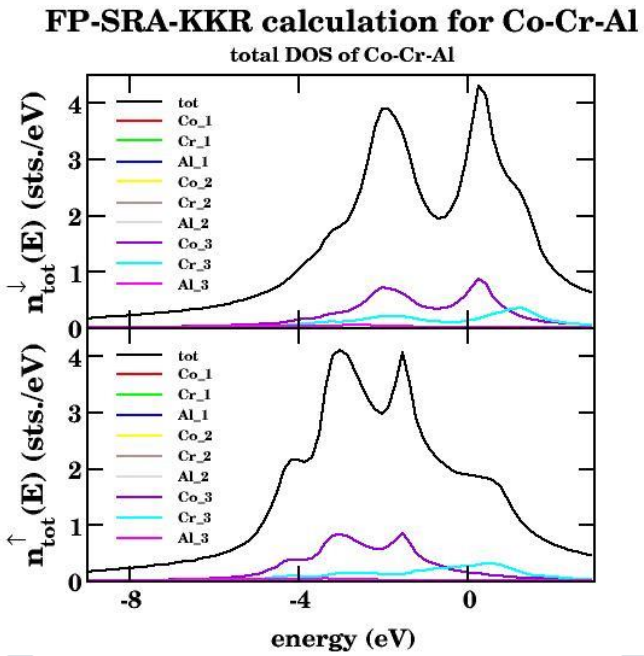

Fig. 7(c): Total and partial DOS of X-Y-Z disordered Co_2CrAl

IV. Conclusion

The structural, electronic, and magnetic properties of ordered and disordered Co_2CrAl were studied by density functional calculations within PBE-GGA approximations. The half-metallicity is achieved for ordered Co_2CrAl and YZ disordered states. Experimentally reported magnetic moment values are obtained by reducing the symmetry. The exchange coupling in between Co and Cr causes to variation in structural and magnetic properties. Obtained half metallic properties are mainly because of hybridizations in between Co and Cr elements.

V. Acknowledgment

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