An investigation on the electronic Structure and Magnetic properties of $C0_2$CrAl Full Heusler Alloy

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ASTRACT

An electronic and magnetic properties of CO_2CrAl full heusler alloy was investigated in this paper Using the SPRKKR Greens function we investigated the detailed electronic structure of Cobalt based heusler alloys in CO_2CrAl , of both ordered and disordered state. Density functional theory was used within PBE-GGA Approximation. L21 Ordered CO_2CrAl shows 100% spin polarization within all the approximations, the half metallicity is also observed in YZ disordered state and experimentally obtained values of the magnetic moments are obtained by reducing the symetry. The exchange coupling between Co and Cr causes the variation in structural and magnetic properties. Obtained half metallic properties are mainly because of hybridizations between Co and Cr elements

Keywords: Spin Polarized Relativistic Korringa Kohn Rostoker , Generalized Gradient Approximation, Local Density Approximation, Half Metallicity , Spin Polarization.

INTRODUCTION

Heusler alloy is a ferromagnetic metal alloy that has face centered cubic crystal structure[Heusler 1963,Galanaski 2016].They have attracted enomous research attention in recent years due to their promising applications in spintronics

devices, shape memory devices, solar systems and many electronic devices [Webster and Ziebeck,1988;Hirohata et al.,2016,Takahashi et al 2016].The study of materials that exhibit such properties is of great importance due the rapid development of magneto electronic devices. Adding the spin degree of freedom to the conventional electronic devices, it has several advantages like non volatility, enhanced data processing, and decrease power consumption.[Galanaski, 2016].The Heusler alloys are categorized into two distinct groups by their crystalline structures; half Heusler alloys with the form ofXYZ in the C1 structure and full Heusler alloys with the form of X YZ inb2the L2 structure. Among proposed half-metallic ferromagnets (HMFs), the Heusler alloys holds the greatest potential to realize the half-metallicity at room temperature (RT) due to their lattice constant matching with the III-V semiconductors ,high Curie temperature above RT and large band gap at E in general. The half-metallicity was first predicted by de Groot and collaborators in 1983 when studying the band structure of a full heusler alloy NiMnSb Half metallic ferromagnets due to the enomous attention they have attracted in the last two decades because of their usefulness in spintronics/magneto-electronics[Groot et al.,1983].In half metallic materials the two spin bands shows a completely different behavior. The majority spin band shows the typical metallic behavior and the minority spin band exhibits a semi conducting behavior with a gap at the Fermi level[F Dahmane et al,.2015].The existence of the gap leads to 100% spin polarization at the Fermi level and finally a spin polarized current should be feasible in these compounds,

maximizing efficiency of magneto electronic devices. Half metals . In this research work, electronic structure and magnetic properties of Fe and Co based Heusler alloys were investigated theoretically within the Density Functional Theory (DFT) framework and spin polarized relativistic, Kohn Koringa Kohn Rostoker (SPRKKR)packages to investigate the properties like lattice parameter, total and partial density of states, band gap, converged energy, Fermi energy and exchange coupling constants using Full potential local density approximation (LDA) and generalized gradient approximation (GGA).The rest of the paper is arranged as follows; section 2 includes computational details and the method of calculation, section 3 is devoted to results and discussions and section 4 is summary of our conclusions.

Computational Method

The electronic structure and magnetic properties of Co2CrAl were calculated by 2 SPRKKR code [Ebert et al., 2011].The electronic structure calculation can be 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 can be treated, including non-collinear spin structures and arbitrary spin spirals. 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 l max= 3 and 2000 k-point has been used for all approximations.

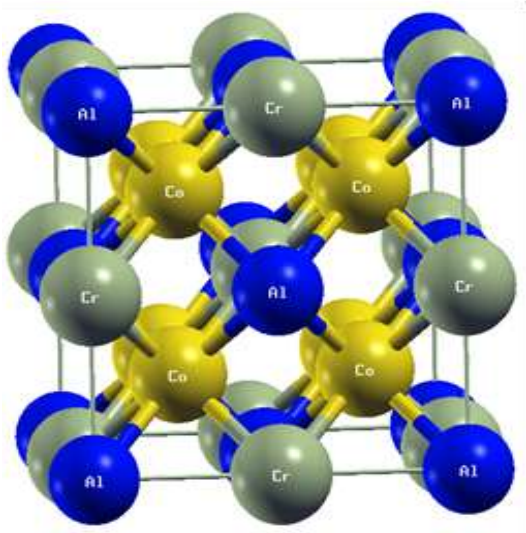

Fig. 2.0: Unit cell structure of Co2CrAl.

The exchange correlation energy for a slowly varying density is given by

$$E^{XLDA} = \int \rho_{(r)E_{xe}(\rho)}\, dr$$

Where $exc(\rho)$ is the exchange correlation energy per particle of a Uniform electron gas density .The exchange correlation potential is given by

$$v_{xc}^{LDA} = [\rho(r)] = \frac{\delta Exc^{LDA}}{\delta\rho(r)} = Exc_{(\rho)} + \rho(r)\frac{\delta Exc(\rho)}{\delta\rho}$$

If the electron distribution is not Uniform .The Gradient of the density is taken in predicting bond length, binding energy of the molecules and crystal lattice constant[Mikel 2007]

$Exc^{GGA}[n\uparrow, n\downarrow] = \int Exc(n\uparrow, n\downarrow)\nabla n\uparrow, \nabla n\downarrow.$

Korringa Kohn Rostoker (KKR) introduced a multiple scattering method for the electronic structure of materials. This method involves use of multiple scattering theories for the solution of Schrödinger wave's equations and determination of electrons band structure [Pivos and Nikos, 2006]. The green function technique from the Schodinger wave equation can be represented by the equation

$$G^0(k\ k'E^0) = \frac{\delta kk'}{E^0 - Ek^0}$$

RESULTS AND DISCUSSION

The equivalent lattice constants, converged energy and Fermi energy have been listed in Table 4.1 are obtained by Gaussian fitting total energy v/s lattice parameter values within the framework of different approximations as shown in Fig. 4.2. Observed values of lattice parameters are quite underestimate from experimental values (5.74Å to 5.75Å) for L2 ordered structure [Zhang et al., 2004, Hakimi et al., 2010]. The GGA approximation gives minimum deviation compared with other approximations as the converged energy also minimum. We also mention previously theoretically reported values of lattice parameters.

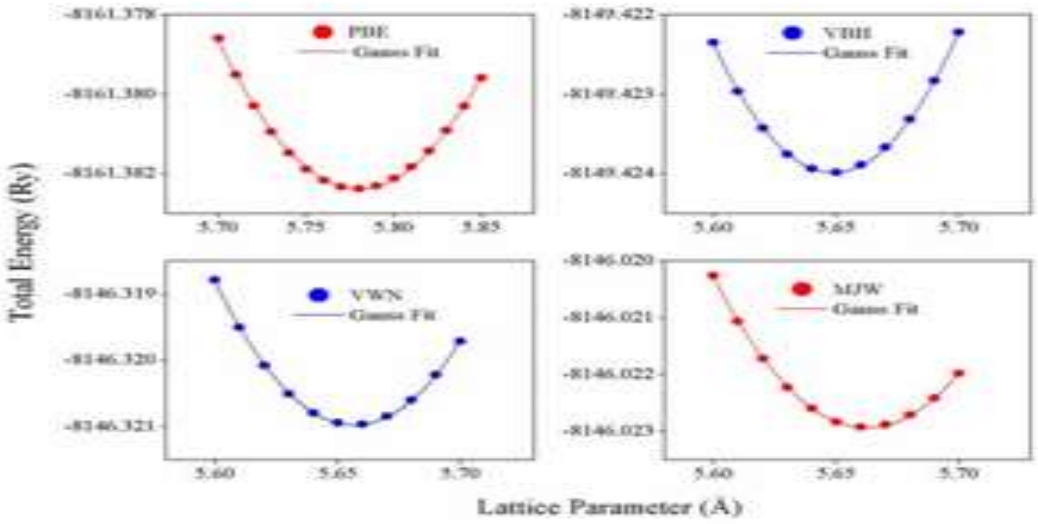

Fig 3.1 Volume Optimization Curves

Table 3. 1.Structural Parameters, Converged and Fermi Energy.

Approx	Obtained lattice Parameter(A)	Previously reported lattice Parameter(A)	Converged Energy(Ry)	Fermi Energy(Ry)
VBH-LDA	5.65	5.66	-8149.4239	0.82
VWN	5.66	------	-8146.3210	0.815
MJW	5.66	---	-8146.0229	0.81
PBE-GGA	5.78	5.73	-8161.3824	0.769

Fig. 4.3 shows the total and individual density of states of Co CrAl, as previously2reported Co2CrAl 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 of an electric current is defined as the imbalance of spin up and spin down electrons according to

$$Sp = \frac{J\uparrow - J\downarrow}{J\uparrow + J\downarrow}$$

denoting the separate spin-up and spin-down contributions to the total current density, respectively. This suggests that Co2CrAl is a half-metal where electrons at the Fermi level are 100% spin polarized (Table 4.2). E(k) curve of Co2CrAl, which is shown for down spin states with in different approximation in Ffig. 4.4. 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 F the down-spin states. The energy band gap between the highest occupied valence60 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, (0.18eV) [Block et al., 2004] 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 3.2 Obtained Magnetic Moments and Spin Polarization

Approximation	Magnetic Moments(μB)				Previouly Reported Magnetic Moment (μB)	Band Gap	Spin Polarization
	m(Co)	m(Cr)	m(Al)	m(Total)			
VBH-LDA	1.72	1.63	-0.06	3.29	2.96	0.567ev	100%
VWN	1.70	1.65	-0.07	3.28	-------	0.595ev	100%
MJW	1.69	1.66	-0.07	3.28	--------	0.571ev	100%
PBE-GGA	1.62	1.76	-0.11	3.28	3.00	0.657ev	100%

d

[Hoshino et al., 2010], e[Alhaj et al., 2013].

Experimentally it was reported that Co2CrAl is a ferrimagnetic with magnetic moment of 1.56 μB. theoretically no one obtained approximate values. According to the rule of "Z–24" a total magnetic moment of 3 μB since Co2CrAl has 27 electrons. Experimentally large deviation from this rule is observed. Theoretical reported value of magnetic moment is 3 μB. 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 nearest neighbor atoms of Co in Co2CrAl are Cr atoms. This suggests that d-states of Co in Co2CrAl 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 Co atoms. The first

of the up-spin state have some peaks in the same energy range, nd 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 Co2CrAl.

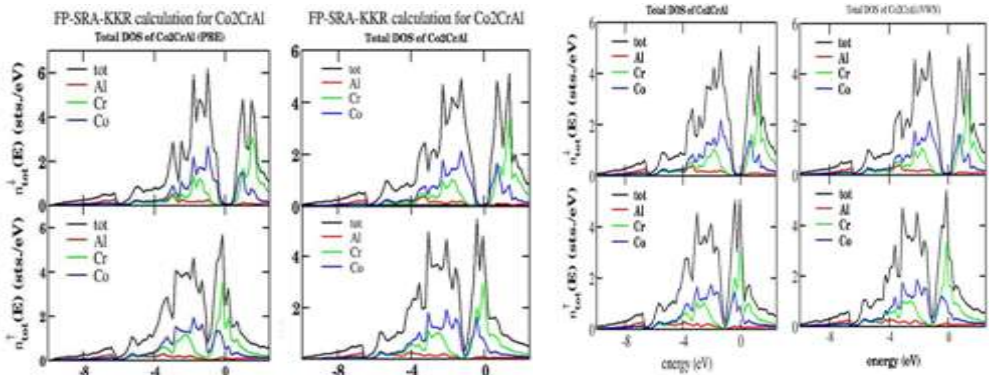

Fig.3.2: Partial and total Density of States of L21 Ordered Co2CrAl

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

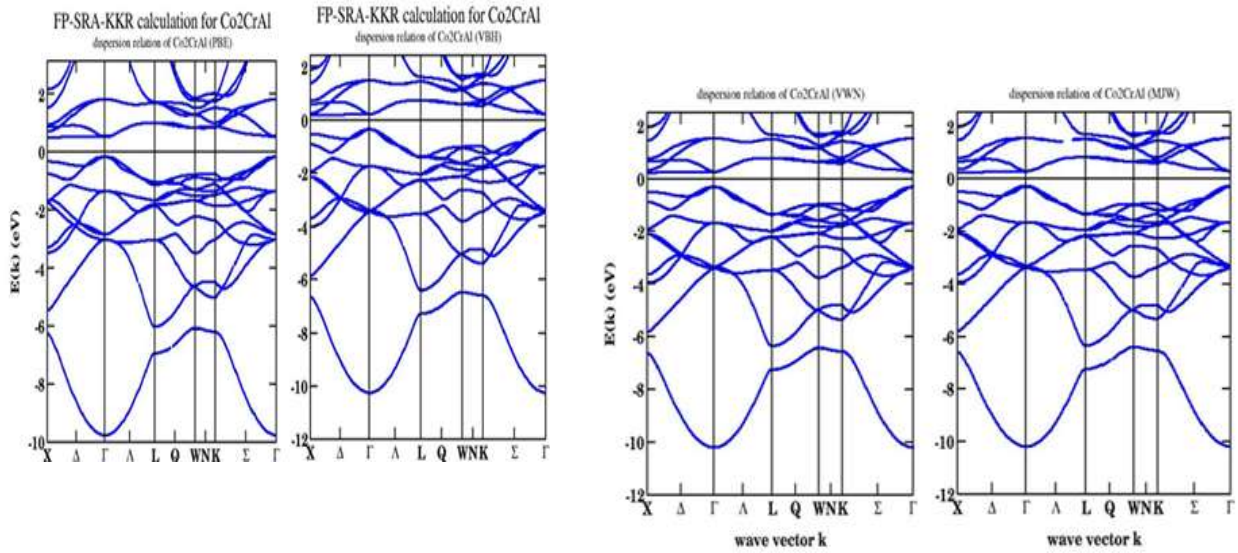

Fig. 3.3: Band structure of Co2CrAl

Results suggested that Co2CrAl not fully L21 ordered which leads to smallantisite 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 unit64 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 With the Heisenberg pair exchange coupling parameters and unit vectors 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 Jij within a real approach using an expression proposed by Liechtenstein et al. Exchange parameters for L21 symmetry were shown in Fig. 4.5(a). We

start with the discussion of the ordered Co2CrAl. It is notable that the exchange interactions are tightly confined to clusters of radius r ≤ a. In particular, the inter-sublattice interactions have significant contributions only for the nearest and second nearest neighbors, while the intra-sublattice contributions are significant up to r = a. An exponential damping of the exchange interactions is expected for half metals [Meinert et al., 2011]. 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 tonearest 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.

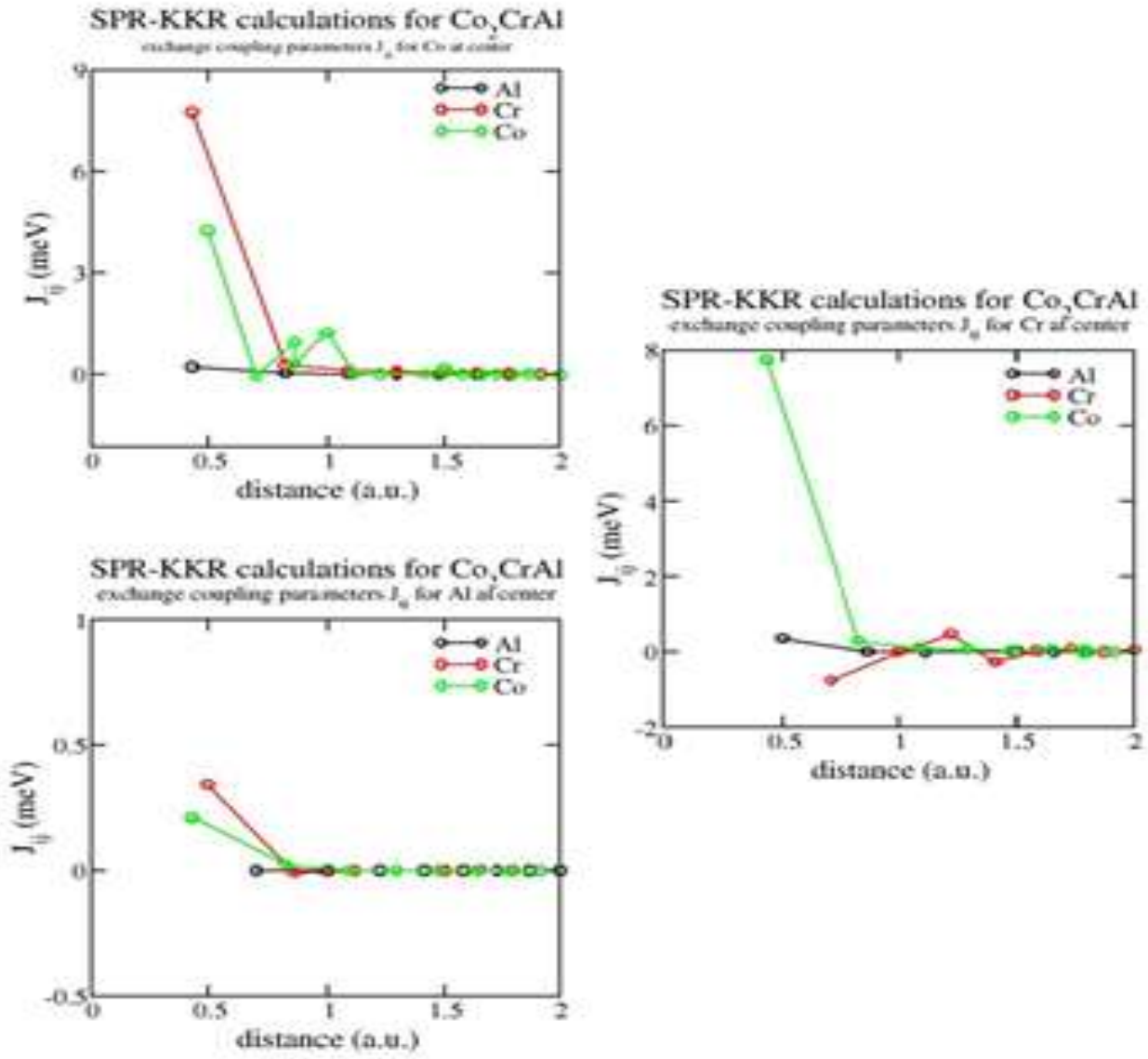

Fig 3.4 .Exchange Parameters for L21 CO_2CrAl

In the case of centre Al , interaction between Co and Cr, are effectively Zero, for all distances, Cr couple antiferromagnetically to Cr atoms, while Co and Cr coup; eferromagnetically. On the other hand, the intra sublattice interaction Cr-Cr are negative which leads to 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. 4.5 (b). We clearly have seen the dominating exchange interations in case of Co1 at center are Co1-Co2, Co1-Cr, where the Co1-Co2interaction is clearly the stronger one below 0.5 au after Co1-Cr dominated. The Co1-Al, Co1-Co1 neighbor interaction is much weaker in comparison. In case of Co2 at center the Co2-Cr interaction is clearly the stronger one and dominated. The Co1-Al and Co2-Co2 neighbor interaction is much weaker in comparison. In case of Cr interactions to nearest neighbor we observes that the dominating interactions in between Cr-Co1, Cr-Co2, where the Cr-Co2 interaction is clearly the stronger one. The Cr-Al, Co1-Al, Co2-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 Co1, Co2 and Cr couple ferromagnetically. On the other hand, the intrasublattice 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 Co1 and Co2 in case of reduced dimensions which also have rordered<rreduce 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.

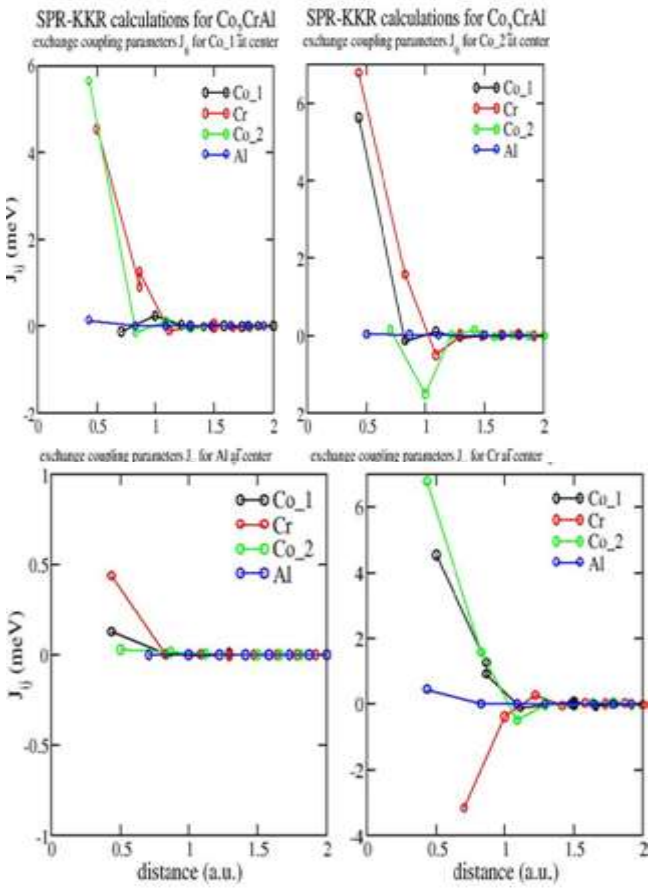

Fig 3.5. Exchange Parameters for Co_2CrAl with reduced Symetry

Fig 5 below shows total and partial DOS of reduced symmetry, it is observed that half metallic behavior was faded as the symmetry is reduced from L21,but the system still shows high spin polarization. The main contribution to magnetic moment arises from Co1 and Co2 atom.

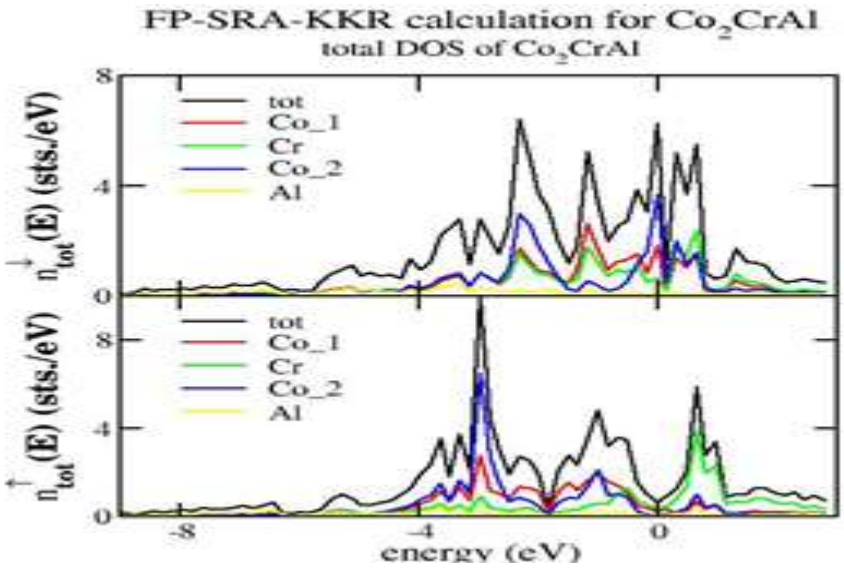

Fig. 3.6: Total and partial density of states of reduced symmetry Co2CrAl

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. 4.7 (a), 4.7(b), 4.74(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 ordered69 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 Co2CrAl 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 3.3: Magnetic properties of disordered Co2CrAl Heusler alloy
Type of disordering Converged
energy (Ry)

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

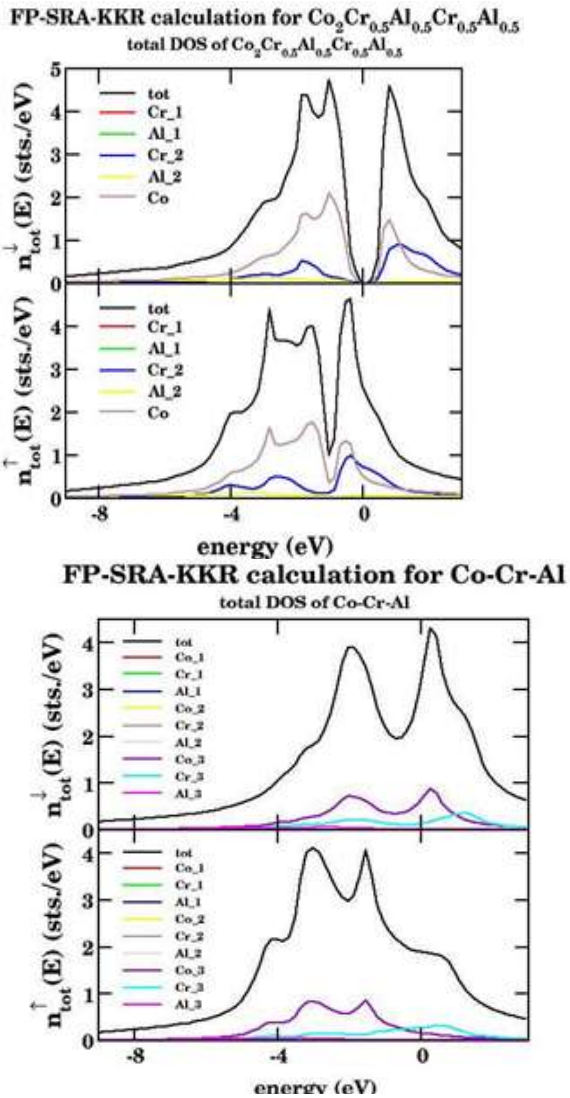

Fig 3.7(c): Total and partial DOS of X-Y-Z disordered Co2CrAl

CONCLUSION

The structural, electronic, and magnetic properties of ordered and disordered Co2CrAlwere studied by density functional calculations within PBE-GGA approximations. The half-metallicity is achieved for ordered Co2CrAl 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.

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