

CALCULATION OF COULOMB REPULSION (U) FOR $3d$ TRANSITION ELEMENTS IN Co_2YAl TYPE HEUSLER ALLOYS

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Abstract—We performed the structure optimization of Co_2YAl ($Y = \text{Sc, Ti, V, Cr, Mn, Fe}$) Heusler alloys based on the generalized gradient approximation (GGA) within full potential linearized augmented plane wave (FP-LAPW) method. Based on the density functional theory we have calculated the Coulomb repulsion (U) for $3d$ transition elements like Sc, Ti, V, Cr, Mn, Co and Fe. The calculated results are compared with the previously reported values.

Keywords: GGA, Coulomb repulsion (U), constrained LDA

1. Introduction

The fact lies within the electronic and magnetic properties of correlated systems ($3d$ transition metals, actinides, and rare earths) which are largely dominated by a competition between a tendency towards delocalization due to band formation and a tendency towards localization due to Coulomb interaction between the electrons. Thus, any microscopic description of electronic structure of these systems involves the prediction of Coulomb interaction strengths between the electrons. Bandyopadhyay and Sarma calculated Coulomb interaction strengths (U_{dd} and U_{ff}) from Hartree–Fock–Slater atomic calculations for $3d$ transition and $5f$ actinide elements, respectively, and have reported a pronounced dependence of U_{dd} (or U_{ff}) on the number of electrons or the electronic configuration [1]. Till date there are very few experimental results for calculations of U_{dd} in the case of $3d$ transition elements [2,3]. Gunnarsson et al. have calculated U_{dd} specifically for Mn in CdTe [4]. The discovery of high-temperature superconductivity has developed more interest in a set of Hubbard-like model which is used to estimate the strongly correlated electronic structure of transition metal oxides, the parameters appearing in these models, hybridization, on-site and nearest neighbor Coulomb repulsion are taken to be effective parameters [5-8]. Accordingly the assumption in these models was that the long-range Coulomb interactions are effectively screened and the short-range on-site and nearest neighbour Coulomb interactions can be treated as effective parameters screened from their free ion values [9-10]. Gunnarsson et al. proposed that in order to calculate U one removes the transfer integrals between d orbitals and the rest of the system and

the occupancy of d orbitals is varied (δn_d), while the other electrons are allowed relax self-consistently, and it follows that $U = \delta^2 E_{tot} / \delta n_d^2$, where E_{tot} is the local density approximation (LDA) total energy [4]. Farkasovsky studied the ground state properties of the simplified Hubbard model and found that (i) a gap in the ground state energy always exists at the half-filled band, (ii) a preferred magnetic state and large U is a total spin singlet, (iii) U -dependence of the ground state energy has qualitatively the same form as one of the conventional Hubbard model [11]. The motive behind this work is to use Coulomb repulsion (U) in GGA or LDA which offers an efficient way to calculate the electronic and magnetic properties of complex transition metal oxides. It is well known that localized electrons LDA and GGA methods are not accurate enough for a proper description of some strongly correlated systems [12]. The idea behind the LSDA+ U method is to explicitly include the Coulomb interaction between strongly localized d or f electrons in the spirit of a mean-field Hubbard model, whereas the interactions between the less localized s and p electrons are treated within the standard local spin density approximation LSDA [13].

2. Crystal Structure

X_2YZ Heusler compounds crystallize in the cubic L_{21} structure (space group $Fm\bar{3}m$) [14].

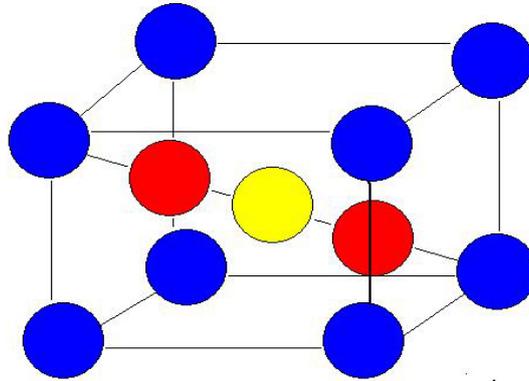


Fig. 1. Unit cell Structure of Co_2YAl : Co (red), Y (yellow) and Al (blue) atoms.

Structure of Co_2YAl : Co (red) atoms are at the $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$, Y (yellow) at $(1/2, 1/2, 1/2)$ and Al (blue) atoms at $(0, 0, 0)$. The cubic L_{21} structure consists of four inter-penetrating f.c.c. sub-lattices, two of which are equally occupied by Co. The two Co-site fcc sub-lattices combine to form a simple cubic sub-lattice as shown in Fig. 1.

3. Calculation Details and Results

In this work, we have performed the full-potential linearized augmented plane wave (FP-LAPW) method accomplished by using the WIEN2K code [15] within GGA [16] scheme. We

have calculated onsite Coulomb repulsion (U) based on Hubbard model. The standard Hubbard Hamiltonian [17] is of the form

$$H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow}, \quad (1)$$

where $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ and $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (annihilates) an electron on site i with spin $\sigma = \uparrow$ or \downarrow . A nearest neighbor is denoted by $\langle i, j \rangle$. U is the onsite Coulomb repulsion between two electrons on the same site.

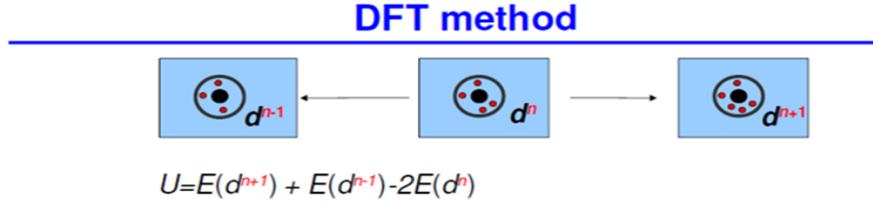


Fig. 2. DFT picture of U , (Anisimov et al., [13]).

The hybridization between nearest neighbor orbitals denoted by t , allowing the particles to hop to adjacent sites. The on-site energies are taken to be zero. Considering the atoms are embedded in a polarizable surrounding, U is the energy required to move an electron from one atom to another, far away, in that case. U is equal to the difference of ionization potential (E_I) and electron affinity (E_A) of the solid as shown in Fig. 2. Removing an electron from a site will polarize its surroundings thereby lowering the ground state energy of the $(N-1)$ electron system [18,19]. Thus

$$\begin{aligned} E_I &= E^{N-1} - E^N, \quad \text{and} \quad E_A = E^N - E^{N+1}, \\ U &= (E^{N-1} - E^N) - (E^N - E^{N+1}), \end{aligned} \quad (2)$$

where $E^{N(\pm 1)}$ are the ground state energy of $(N \pm 1)$ electron system.

Fig. 2 as proposed by Anisimov et al. [13] gives the simple picture of formation of Coulomb interaction U in $3d$ transition elements. For the calculation of the parameter U we used the method introduced by Gunnarsson et al. [4] as discussed in the Introduction. We have used 8-unit supercell and set the hopping integrals to the d shell of the central transition-metal ion equal to zero. The d occupancies of the other $3d$ ions were kept fixed at integral values by removing the hopping. The values of U barely depend on how one constrains the other $3d$ shells as long as the systems are rather localized. The occupancies of the d shell of the central atom at two values $(n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2)$ and $(n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2 - 1)$ and for these configurations the fully self-consistent potentials were determined, allowing all electrons to contribute to the screening. According to Slater's transition rule [20] one obtains

$$U = \varepsilon_{3d\uparrow}(n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2) - \varepsilon_{3d\downarrow}(n_{d\uparrow} = n/2 + 1/2, n_{d\downarrow} = n/2 - 1), \quad (3)$$

where $\varepsilon_{3d\uparrow}$ and $\varepsilon_{3d\downarrow}$ are the $3d$ eigenvalues at the central atom calculated at the fixed occupancies. In Table 1 we summarize our results of Coulomb repulsion (U) for the $3d$ -transition metal from equation (3) and compared with the results of Bandyopadhyay and Sarma. They have used Hartree–Fock–Slater atomic calculations to determine the Coulomb interaction strength U in presence of n_d electrons in the $3d$ level of transition elements [1] which is represented by Y' (Table 1).

Table 1. Lattice constants (a_0) and U (Ry).

Compounds	Lattice Constants, a_0 (Å)		Coulomb Repulsion, U (Ry)		
	Previous[21]	Our Calculation	Previous Y	Y'[1]	
		Our Calculation Co			
Co_2ScAl	5.960	6.320	0.298	0.032	0.077
Co_2TiAl	5.847	6.210	0.291	0.053	0.094
Co_2VAl	5.754	6.076	0.286	0.187	0.110
Co_2CrAl	5.727	5.727	0.293	0.257	0.132
Co_2MnAl	5.695	5.711	0.276	0.270	0.149
Co_2FeAl	5.692	5.748	0.286	0.281	0.171

The d states on the Co sites are more localized and one can expect a larger on-site Coulomb interaction than on the Y site, which is in agreement with $U_Y < U_{\text{Co}}$ [22]. With the increase of atomic number (Z) (in other words, the increase in valence electrons), the Coulomb repulsion (U) increases from Sc to Fe more or less linearly as shown in Fig. 3. The calculated values of U for Co and Fe are 0.286 Ry and 0.281 Ry, respectively, which are in good agreement with the previously calculated values using constrained LDA in FP-LAPW. $U_{\text{Co}} = 0.31$ Ry for Co, $U_{\text{Fe}} = 0.32$ Ry for Fe in the case of Co_2FeSi and $U_{\text{Mn}} = 0.39$ Ry for Co_2MnSi were reported by Balke et al. [23].

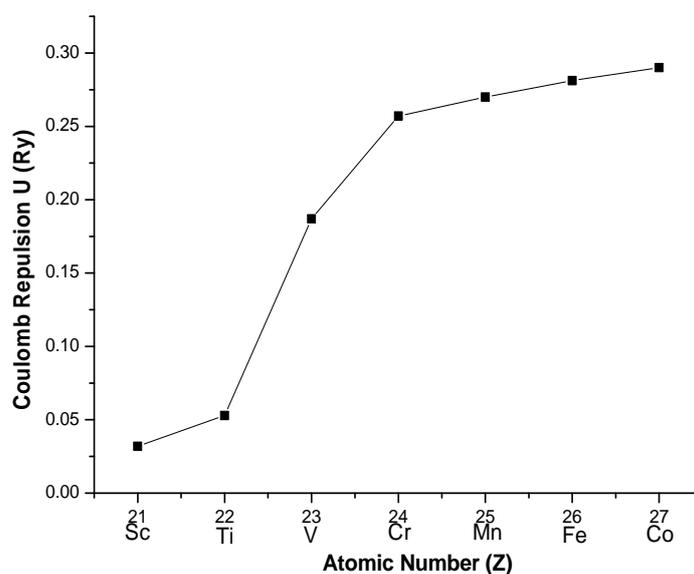


Fig. 3. Plot of U versus Z .

As reported by Kandpal [12] the calculated Coulomb repulsion (U) for $3d$ transition metals found in the constrained LDA calculations are considerably high to explain the metallic systems correctly and the same results we found in the case of Anisimov et al. [13] where they used constrained LDA for the calculations.

Table 2. Coulomb repulsion (U), exchange parameters (J) and the splitting between the d^{n-1} and d^{n+1} high-spin states (U^{eff}) [13].

Compounds	U	J	U^{eff}
CaCuO ₂	7.5 eV (0.550 Ry)	0.98 eV (0.072 Ry)	6.5 eV (0.478 Ry)
NiO	8.0 eV (0.590 Ry)	0.95 eV (0.070 Ry)	7.1 eV (0.522 Ry)
CoO	7.8 eV (0.574 Ry)	0.92 eV (0.068 Ry)	6.9 eV (0.507 Ry)
FeO	6.8 eV (0.500 Ry)	0.89 eV (0.065 Ry)	5.9 eV (0.434 Ry)
MnO	6.9 eV (0.507 Ry)	0.86 eV (0.063 Ry)	10.3 eV (0.757 Ry)
VO	6.7 eV (0.493 Ry)	0.81 eV (0.060 Ry)	5.9 eV (0.434 Ry)
TiO	6.6 eV (0.485 Ry)	0.78 eV (0.0574 Ry)	5.8 eV (0.426 Ry)

Kandpal et al. [21] set the values for $U_{Co} = 0.14$ Ry, $U_{Fe} = 0.132$ Ry and $U_{Mn} = 0.13$ Ry, independent of iron concentration. These values are closer to the values for the Coulomb repulsion (U) for $3d$ transition metals which are $U_{Co} = 0.193$ Ry, $U_{Fe} = 0.171$ Ry and $U_{Mn} = 0.149$ Ry reported by Bandyopadhyay and Sarma which were calculated by using Hartree–Fock–Slater atomic calculations [1]. The previously reported values of Coulomb repulsion (U) for transition metals like Cu in (CaCuO₂), Ni in (NiO), Co in (CoO), Fe in (FeO), Mn in (MnO), V in (VO) and Ti in (TiO) are tabulated in Table 2 [13]. These values of U reported by Anisimov et al. using the constrained density functional method are too high as compared to our results calculated using GGA.

4. Conclusions

We have performed the total-energy calculations to find the stable magnetic configuration and the optimized lattice constant. The on-site coulomb repulsion (U) was calculated for the transition elements like Sc, Ti, V, Cr, Mn, Co and Fe in Co₂Y(Sc, Ti, V, Cr, Mn and Fe)Al. The calculated values are in qualitative agreement with the previously calculated values. As reported by Kandpal [12] the calculated Coulomb repulsion (U) for $3d$ transition metals found in the constrained LDA calculations are considerably high to explain the metallic systems correctly and a similiar conclusions were drawn by Anisimov et al. [13]. Our results calculated using GGA in FP-LAPW method appeared to be small, as compared with the one calculated by using constrained LDA [13]. But the results of U for $3d$ transition elements obtained from Hartree–Fock–Slater atomic

calculations [1] are small as compared to our results. The motive behind this work is to use Coulomb repulsion (U) in GGA and LDA which offers an efficient way to calculate the electronic and magnetic properties of complex transition metal oxides. The idea behind the LSDA+ U method is to explicitly include the Coulomb interaction between strongly localized d or f electrons in the spirit of a mean-field Hubbard model, whereas the interactions between the less localized s and p electrons are treated within the standard local spin density approximation LSDA, LDA or GGA.

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